Precursor Routes to Selected Metal and Semiconductor Nanomaterials: Crystals, Composites, Colloids of Au, GaN, InN, CdSe and TiO$_2$

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2003
A Thesis submitted for the degree of
Dr. rer. nat.
(Doctor rerum naturalium)
in the Faculty of Chemistry
at Ruhr-University Bochum, GERMANY

By
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2003
Dissertation

Zur Erlangung des Grades eines
Doktors der Naturwissenschaften
(Doctor rerum naturalium)
der Fakultät für Chemie
der Ruhr-Universität Bochum, Deutschland

vorgelegt von
Harish Parala, M. Sc.
2003
To

Amma & Anna
In-laws
Munni & Anushka
This thesis is based on the experimental research work carried out during the period from January 1999 to December 2000 at the chair of Inorganic Chemistry II, Ruhr-University Bochum, Germany. Interpretation of the research data and the publication of the research work were carried out from January 2001 to August 2002. Majority of the research work has resulted into publications and are listed in chapter 9.

The Deutsche Forschungs Gemeinschaft (DFG) and Faculty of Chemistry, Ruhr-University Bochum, (RUB) Germany, supported the work described in this thesis.
"Es ist dafür gesorgt, daß die Bäume nicht in den Himmel wachsen."

J. W. von Goethe

(Dichtung und Wahrheit)
Acknowledgements

It gives me great pleasure to express my deep sense of gratitude to my mentor and research supervisor Prof. Dr. Roland A. Fischer for his inspiring guidance, constant encouragement, and advice over the years, and for the extent of freedom, and support that I have received from him ever since I joined his group.

I would like to express my sincere thanks to my colleagues Ursula Bossek, Jun. Prof. Dr. Anjana Devi, Ursula Fischer, Eliza Gemel, Julia Hambrock, Heike Kampschulte, Eva Maile, Sabine Masukowitz, Urmila Patil, Marie-Katrin Schroeter, Manuela Winter, Arne Baunemann, Ralf Becker, Raghunandan Bhakta, Mirza Cokoja, Rolf Deibert, Dr. Christian Gemel, Stephan Hermes, Frank Hipler, Jayaprakash Khanderi, Dr. Lianhai Lu, Rainer Schäfer, Dr. Rochus Schmid, Stephan Spöllmann, Tobias Steinke for their help and cooperation.

I also thank and cherish the support and help received from my former colleagues Sabine Bendix, Maria Diaz, Dr. Nicola Oberbeckmann, Dr. Ulrike Weckenmann, Dr. Barbara Wehner, Dr. Dana Weiss, Dr. Pia Wennek, Dr. Quingmin Cheng, Dr. Holger Fölsing, Dr. Holger Hoffmann, Dr. Thorsten Johann, Jürgen Klussmann, Dr. Andreas Manz, Prof. Dr. Jens Müller, Dr. Wolfram Rogge, Dr. Matthias Ruttert, Dr. Oliver Segnitz, Dr. Oliver Stark, Frank Stowasser, Dr. Jurij Weiβ, Andreas Westerwinter, Dr. Holger Winkler, Dr. Carl Winter, Dr. Andreas Wohlfart.

I gratefully acknowledge the following people for their help and assistance as noted: Dr. Alexander Birkner and Dr. Matthias Kolbe (TEM analysis), Dr. Roland Schmechel and Prof. Dr. Heinz von Seggern (Optical characterisations), Frank Stowasser and Dr. Andreas Wohlfart (XRD analysis), Dr. Ulrike Weckenmann and Frank Hipler (XPS analysis), Susanne Wiedemeyer (BET), Dr. Hans-Werner Becker (RBS), Dr. Rolf Neuser (SEM). Prof. Dr. Andreas Wieck and Andre Ebbers from the Experimental Physics IV are thanked for their help in PL measurements.

Warm and sincere thanks to Dr. Jurij Weiβ and Jun. Prof. Dr. Anjana Devi, for their assistance in the synthesis of precursors, guidance, suggestions and helpful discussions.
My special appreciation and thanks to Ursula Fischer, Heike Kampschulte and Sabine Masukowitz for all the help rendered on many occasions.

I acknowledge the help rendered by the workshop personnel of the Faculty of Chemistry.

I sincerely thank and cherish the support, understanding, and advice received from my parents, parents-in-law, and all the other family members.

I am very much indebted to my beloved wife, Anjana for her patience, understanding, help, and being a constant source of encouragement during the time it took to complete this work.

I am thankful to Sureshanna and Premaathige for their moral support.

I would like to specially thank many of my relatives and friends, Gudda, Bujji, Kukku, Puppy, Mina, Ralf, Sandra, Frank, Ramesh, Swati, Andre, Kerstin, and Wolfram, for all the help, support and being together with me in times of ups and down.

Finally, I wish to thank everyone who has contributed to the creation of a pleasant working environment in Anorganische Chemie II.
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<thead>
<tr>
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<tr>
<td>AAS</td>
<td>Atomic Absorption Spectroscopy</td>
</tr>
<tr>
<td>AFM</td>
<td>Atomic Force Microscopy</td>
</tr>
<tr>
<td>ALD</td>
<td>Atomic Layer Deposition</td>
</tr>
<tr>
<td>ALE</td>
<td>Atomic Layer Epitaxy</td>
</tr>
<tr>
<td>APD</td>
<td>Avalanche Photodetector</td>
</tr>
<tr>
<td>Azin</td>
<td>Azido bis-3-dimethylamino-propyl indium</td>
</tr>
<tr>
<td>Baziga</td>
<td>Bisazido dimethylaminopropyl gallium</td>
</tr>
<tr>
<td>BET</td>
<td>Brunauer-Emmett-Teller</td>
</tr>
<tr>
<td>CB</td>
<td>Conduction Band</td>
</tr>
<tr>
<td>CBE</td>
<td>Chemical Beam Epitaxy</td>
</tr>
<tr>
<td>CSD</td>
<td>Chemical Solution Deposition</td>
</tr>
<tr>
<td>CVD</td>
<td>Chemical Vapor Deposition</td>
</tr>
<tr>
<td>CVI</td>
<td>Chemical Vapor Infiltration</td>
</tr>
<tr>
<td>DLS</td>
<td>Dynamic Light Scattering</td>
</tr>
<tr>
<td>DRAM</td>
<td>Dynamic Random Access Memory</td>
</tr>
<tr>
<td>DTA</td>
<td>Differential Thermal Analysis</td>
</tr>
<tr>
<td>EA</td>
<td>Elemental Analysis</td>
</tr>
<tr>
<td>EDX</td>
<td>Energy Dispersive analysis of X-rays</td>
</tr>
<tr>
<td>FWHM</td>
<td>Full Width at Half Maximum</td>
</tr>
<tr>
<td>HDA</td>
<td>Hexadecylamine</td>
</tr>
<tr>
<td>HVPE</td>
<td>Hydride Vapor Phase Epitaxy</td>
</tr>
<tr>
<td>IC</td>
<td>Integrated Circuit</td>
</tr>
<tr>
<td>IR</td>
<td>Infra Red</td>
</tr>
<tr>
<td>IT</td>
<td>Information Technology</td>
</tr>
<tr>
<td>LCG</td>
<td>Laser assisted Catalytic Growth</td>
</tr>
<tr>
<td>LD</td>
<td>Laser Diode</td>
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<tr>
<td>LED</td>
<td>Light Emitting Diode</td>
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<tr>
<td>MCM-41</td>
<td>Mobil Composition of Matter</td>
</tr>
<tr>
<td>MBE</td>
<td>Molecular Beam Epitaxy</td>
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<tr>
<td>MOCVD</td>
<td>Metalorganic Chemical Vapor Deposition</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
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<tr>
<td>--------------</td>
<td>-------------</td>
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<tr>
<td>MOVPE</td>
<td>Metalorganic Vapor Phase Epitaxy</td>
</tr>
<tr>
<td>MS</td>
<td>Mass Spectrometry</td>
</tr>
<tr>
<td>NMR</td>
<td>Nuclear Magnetic Resonance</td>
</tr>
<tr>
<td>PCS</td>
<td>Photon Correlation Spectroscopy</td>
</tr>
<tr>
<td>PECVD</td>
<td>Plasma Enhanced Chemical Vapor Deposition</td>
</tr>
<tr>
<td>PL</td>
<td>Photoluminescence</td>
</tr>
<tr>
<td>PLD</td>
<td>Pulsed Laser Deposition</td>
</tr>
<tr>
<td>PVD</td>
<td>Physical Vapor Deposition</td>
</tr>
<tr>
<td>RBS</td>
<td>Rutherford backscattering Spectroscopy</td>
</tr>
<tr>
<td>SBA-15</td>
<td>Mesoporous silica</td>
</tr>
<tr>
<td>SAED</td>
<td>Selected Area Electron Diffraction</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscopy</td>
</tr>
<tr>
<td>SLS</td>
<td>Solution-Liquid-Solid</td>
</tr>
<tr>
<td>STM</td>
<td>Scanning Tunnelling Microscopy</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermogravimetry Analysis</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission Electron Microscopy</td>
</tr>
<tr>
<td>TOPO</td>
<td>Tri-n-octylphosphine oxide</td>
</tr>
<tr>
<td>UV-Vis</td>
<td>Ultra-Violet-Visible</td>
</tr>
<tr>
<td>VLS</td>
<td>Vapor-Liquid-Solid</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray Photoelectron Spectroscopy</td>
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<tr>
<td>XRD</td>
<td>X-ray Diffraction</td>
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Preface

Nano-scale materials have stimulated great interest due to their importance in basic scientific research and potential technological applications. These materials exhibit unique chemical and physical properties, differing substantially from those of the corresponding bulk solids because of their small size and extremely large surface-to-volume ratio. Nano-scale materials can be defined as systems in which at least one dimension is less than 100 nm, i.e. reducing 1, 2, or 3 dimensions (D) of a bulk material to the nanometre scale produces nanometre thick two-dimensional (2D) layers, one-dimensional (1D) nanowires or zero dimensional (0D) nanoclusters (nanoparticles/nanocrystals). The synthesis of nano-scale materials is critical and important work directed towards understanding the fundamental properties of small structures, creating nanostructured materials, and developing nanotechnologies.

Miniaturisation in electronics through improvements in established “top-down” fabrication techniques is approaching the point where fundamental issues are expected to limit the dramatic increases in computing seen over the past several decades. “Bottom-up” approaches to nanoelectronics where the functional electronic structures are assembled from well-defined nanoscale building blocks such as nanocrystals, nanowires/nanotubes and molecules have the potential to go far beyond the limits of top-down fabrication techniques.

The major part of this thesis deals with the synthesis and characterisation of a selection of very different nanoscale materials such as InN nanowhiskers, GaN, CdSe nanocrystals within the mesopores of silica templates (MCM-41, SBA-15) and ligand stabilised gold and TiO₂ nanocrystals. In the last part of the thesis, the growth and characterisation of nano-porous epitaxial GaN films by a simple chemical solution deposition technique is discussed.

The 1st chapter gives a brief historical overview and the development of a new interdisciplinary field of research: Nanoscience. The overview starts with the important developments in the field of nano-scale engineering predicted by the Nobel laureate physicist Richard Feynman and the trend in the miniaturisation of integrated circuits by Gordon Moore. Later, the general introduction and important applications of nanoscale materials such as nanocrystals, nanowires, carbon nanotubes, and other nano-scale materials are reviewed. In addition, the quantum size effects of semiconductor nanocrystals are briefly described in this chapter. The last part of this chapter highlights the importance of mesoporous materials such as MCM-41 and SBA-15 and their applications in template synthesis of semiconductor nanostructures.
Chapter 2 deals with the growth of InN nanowhiskers using single molecule precursor by chemical vapor deposition and their characterisation by different characterisation techniques such as X-ray diffraction (XRD), transmission electron microscopy (TEM), selected area electron diffraction (SAED), energy dispersive X-ray spectroscopy (EDS) and x-ray photoelectron spectroscopy (XPS). The approach described here is based on using a molecular precursor of Indium, \( \text{N}_3\text{In} [(\text{CH}_2)_3\text{N(CH}_3)_2]_2, [\text{Azido bis-3-dimethylamino-propyl indium, Azin}] \), where the compound delivers traces of indium metal besides InN upon thermal decomposition thus initiating an autocatalytic vapor-liquid-solid (VLS) growth mechanism. InN whiskers were grown on bare sapphire substrates in a cold wall CVD reactor. X-ray diffraction analysis and TEM analysis of InN whiskers confirmed the growth of hexagonal wurzite structure of InN. A detailed TEM analysis of InN whiskers revealed the presence of In droplet at the tip of each InN whisker.

In chapter 3, the growth of GaN nanostructures by vapor phase impregnation using mesoporous silica templates (MCM-41 and SBA-15) as host materials is described. The synthesis involves loading the organometallic precursor of gallium, \( \text{(N}_3)_2\text{Ga} [(\text{CH}_2)_3\text{N(CH}_3)_2]_2 \) [Bisazido dimethylaminopropyl gallium, Baziga] into a template matrix via chemical vapor infiltration (CVI) followed by thermal decomposition under flowing ammonia to generate GaN nanostructures. The GaN-encapsulated matrix systems with different pore diameters were characterised by XRD, \( \text{N}_2 \)-sorption analysis (BET surface area), TEM, SAED analysis, EDX analysis. In addition, the isolation of the freestanding GaN nanocrystals by removing the silicate templates is achieved and the resulting freestanding GaN nanocrystals were characterised by TEM and SAED analysis.

Chapter 4 deals with the synthesis and the characterisation of CdSe nanoparticles confined to the pores of porous host matrix MCM-41 (CdSe @ MCM-41). Unlike in the case of GaN nanoparticles, the growth of CdSe nanoparticles inside the host silica material was achieved by solution-phase impregnation method. The combination of wet impregnation technique and the pyrolysis of loaded organometallic precursors in a hot medium is a viable method for the synthesis of CdSe nanoparticles inside the pores of MCM-41. Nitrogen sorption measurements of CdSe loaded MCM-41 (CdSe @ MCM-41) revealed the reduction in BET surface area, and the pore volume, which indicates the decoration/coating of the inner surface of the silica walls. The broad reflections in the XRD pattern of CdSe @ MCM-41 confirmed the formation of CdSe nanoparticles. The combined results of TEM analysis and electron diffraction pattern analysis revealed that the mesoporous host structure was still intact after the growth of nanoparticles inside the pores of MCM-41. The composition was analysed by
XPS and EDX analysis. The optical characterisation of the composite CdSe @ MCM-41 showed the blue shifted absorption and broad photoluminescence, which indicates the quantum confinement of CdSe particles, which are formed inside the pores of MCM-41.

The 5th chapter presents the synthesis and characterisation of gold nanocrystals stabilised by organic capping ligands such as tri-n-octylphosphine oxide (TOPO) and hexadecylamine (HDA). Organically passivated gold nanocrystals were prepared by the reduction of gold ions by NaBH₄ in a simple one-phase route using TOPO, HDA, or a mixture of these two polar Lewis base solvents at elevated temperatures. The reduction of gold chloride (added as a solution in n-octylamine) in TOPO as well as in HDA at 160°C resulted in relatively uncontrolled growth of nanocrystals with a wide range of shapes. In contrast, growth in a mixture of TOPO and HDA under similar conditions resulted in the controlled growth of spherical gold nanocrystals. These nanocrystals were characterised by UV-Vis absorption spectroscopy (UV-Vis), TEM, SAED, and XRD analysis. The morphology and the structure of gold nanocrystals examined by TEM, and XRD confirmed the fcc structure of gold nanocrystals. Size distributions of gold nanocrystals were analysed by TEM and Photon correlation spectroscopy (PCS). The as-prepared TOPO/HDA capped gold nanocrystals were found to spontaneously self assemble when deposited on a copper grid, forming ordered hexagonal close packed two-dimensional (2D) lattices and these structures were analysed by TEM.

In the 6th chapter a non-hydrolytic synthetic approach for the growth of nano-scale TiO₂ particles and its characterisation is described. In contrast to established aqueous sol-gel techniques, the processing in hydrocarbon solvents at high temperatures allows the growth of very small freestanding TiO₂ nanocrystals. Intramolecularly adduct stabilised titanium alkoxide compound [Ti(OPrᵢ₃)(dmae)] was used as a precursor and organic passivating ligand TOPO was used as the reaction medium as well as a capping agent for the growth of nanocrystals. TiO₂ nanocrystals were characterised by XRD, TEM, and EDX. Particle size distribution analysis was carried out by TEM and PCS. Optical properties of TiO₂ nanocrystals were investigated by UV-Vis spectroscopy and PL measurements and these results confirmed the quantum confinement of TiO₂ nanocrystals.

Chapter 7 presents an efficient chemical solution deposition (CSD) approach to grow epitaxial nano-porous GaN layers at relatively low temperatures using single molecule precursors (SMPs). The SMPs \( (\text{N}_3)_2\text{Ga}[(\text{CH}_2)_3\text{N(C}_2\text{H}_5)\text{H}] \) Bisazido diethylaminopropyl gallium (compound 1) and \( (\text{N}_3)_2\text{Ga}[(\text{CH}_3)_2\text{N(CH}_3)_2\text{H}] \) Bisazido dimethylaminopropyl gallium (compound 2) were synthesised and characterised by standard methods. X-ray single crystal
structure analysis of compound 1 revealed that the precursor exists as a dimer in the solid state and is different compared to compound 2, which exists as a dimer of dimers. The thermal stability and the volatility of the precursors were analysed by thermogravimetric and differential thermal analysis (TG/DTA). The TG/DTA analysis revealed that compound 1 begins to vaporise significantly above 150°C and decomposes at relatively low temperatures. CSD experiments were carried out by spin coating the precursors on sapphire substrates in an inert atmosphere. The spin coated substrates were subsequently pyrolysed under ammonia ambient at different temperatures. Epitaxial GaN layers were grown on sapphire substrates and these layers were characterised for their morphology, microstructure, composition and optical properties by XRD, X-ray rocking curve (XRC) analysis, pole figure measurements, reciprocal space mappings, scanning electron microscopy (SEM), Rutherford back scattering (RBS), X-ray Photoelectron Spectroscopy (XPS), and room temperature Photoluminescence (PL) measurements.
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Chapter 1

1 Introduction

1.1 An Overview

The quest to realize Richard Feynman’s dream in his prophetic paper “There is Plenty of Room at the Bottom” is becoming increasingly challenging as electronic devices in a chip continue to decrease in size.¹ For the last few decades, electronic computers have grown more powerful as their basic sub-unit; the transistor has shrunk considerably in size. The drive towards miniaturisation and high-speed performance of integrated electronic circuits has stimulated considerable research efforts in every field of science around the world.² Since the discovery of the first transistor by Schockley, Brattain and Bardeen,³ nearly 50 years ago, the size of the transistor has shrunk incredibly and the number of transistors on an integrated circuit (IC) has doubled every 18 months. A trend first pointed out by Gordon Moore in 1960’s (Moore’s Law) and one that continues today⁴ (Fig. 1.1 and 1.2). However, the laws of quantum mechanics, plus the limitations of materials and fabrication techniques soon is likely to inhibit further reduction in the minimum size of today’s bulk-effect semiconductor transistors. Many researchers have projected that as the overall size of the bulk-effect, semiconductor transistor is aggressively miniaturised to approximately to 100 nm and beyond, the devices may no longer function as well. Thus, in order to continue the miniaturisation of IC in this century, it is likely that present day, micron-scale or microelectronic device designs will be replaced with new designs for devices that take advantage of the quantum mechanical effects that dominate on the much smaller nanometer scale.⁵

The Nobel laureate physicist Richard Feynman in 1959 delivered his now famous lecture and he stimulated his audience with the vision of exciting new discoveries if one could fabricate materials and devices at the atomic/molecular scale. He pointed out that, for this to happen, a new class of miniaturized instrumentation would be needed to manipulate and measure the properties of these small – nano-structures. As the 21st century unfolds the nanostructure science and technology (Nanoscience; Nanotechnology) is fundamentally changing the way that materials and the structures made from them will be manufactured in the future. Nanoscience/Nanotechnology is the popular term for the construction and utilisation of functional structures with at least one characteristic dimension measured in nanometres.⁶
Fig. 1.1 “Moore’s law” plot of transistor size vs. year. The trend line illustrates that the size of the transistor has decreased by a factor of 2 every 18 months since 1950.

Nanoscale science, engineering and technology are concerned with the manipulation of matter on the nanometre length scale, which is now generally taken as the 1 to 100 nm range. The synthesis of a material from nanoscale building blocks – building from the “bottom up” differs radically from the “top-down” lithographic approach conventionally used to fabricate sub micron devices. Feynman noted that nanoscale-engineering would require the development of complex instrumentation that could act as our eyes and fingers in the nanoworld. This vision was realised in the early 1980s by the invention of the scanning tunnelling microscope (STM)\(^7\) an instrument that exploits the quantum mechanical tunnel current flowing between a sharp metal tip and a conducting substrate to generate atomically resolved surface images.\(^8\) A family of related scanning probe microscopes (SPM) like atomic force microscope (AFM), magnetic force microscope (MFM) and scanning near-field optical microscope (SNOM) were subsequently developed. Thus, the emergence of relatively inexpensive analytical tools such as scanning probe microscopies, for interrogating and manipulating materials on the nanometre length scale heralded the emergence of nanoscience and nanotechnology.\(^9\)
During the past few decades, several previously unrelated fields of science have begun to focus on understanding and controlling physical and chemical phenomena on nano-meter length scale. The concept of molecular electronics using few molecules or a single molecule to perform the basic functions of digital electronics i.e., rectification, amplification and storage was first put forward in the mid 1970s. The concept is now realised for individual components, but the economic fabrication of complete circuits at the molecular level remains challenging because of the difficulty in connecting the molecules to one another and the possible solution is very much encouraging. Fabrication techniques to produce nano-scale objects have improved remarkably over the last few years. For example, using a combination of sophisticated metalorganic chemical vapor deposition (MOCVD) and molecular beam epitaxy (MBE) planar engineering (deposition) and scanned optical, X-ray, ion and electron beam engineering (nanolithographic) techniques, one can routinely produce nano-scale objects with essentially any desired architecture. In 1990, Eigler and Schweizer pioneered STM-based atomic-scale engineering and they constructed the IBM logo by positioning the
individual Xe atoms on a Ni surface at 4K. The STM-based atomic manipulation experiments were later exploited to the arrangement of a quantum coral formed by Fe atoms on a Cu (111) surface.\textsuperscript{14} The complementary metal oxide semiconductor (CMOS) based transistors have been fabricated with gate widths of 50 nm using lithographic techniques. The same lithographic techniques that defined the features of those transistors have been utilised to attach two electrodes to a single molecule.\textsuperscript{15} The use of biochemical molecular recognition principles (DNA technology) has been tested for the assembly or selective positioning of the nanomaterials,\textsuperscript{16, 17} and the realisation of the individual components has been achieved.\textsuperscript{18} The unique properties of the carbon nanotubes\textsuperscript{19} has opened up the exploration of new promising applications in energy storage and production,\textsuperscript{20} electron field emission sources,\textsuperscript{21} advanced scanning probes,\textsuperscript{22} and nano-electronic components,\textsuperscript{23} which can be integrated into the future nanoelectronic devices. The molecular self-assembly process that is the spontaneous assembly of molecules into structured, stable, non-covalently joined aggregates is now emerging as a new strategy in chemical synthesis, with the potential of generating non-biological structures with dimensions of 1-100 nm.\textsuperscript{24} Many clear applications of nanoscale materials in different fields of science and technology are already evident and are the targets of existing technology development programs. Applying the fundamental discoveries related to nanotechnologies has given birth to many start-up companies in the past few years. [\textit{Carbon nanotechnologies}, (carbon nanotubes), \textit{Nanophase technologies}, (oxide nanoparticles, ZnO), \textit{Quantum dot corporation}, (semiconductor quantum dots, labelling, and diagnostics, drug delivery), \textit{NanoSys Inc.}, (semiconductor nanowires, nanoelectronics, and sensor applications), \textit{Nanogen Inc.}, (DNA-directed nanofabrication of molecular/nanoscale devices)]. Over the years, several excellent review articles have appeared on nanotechnology,\textsuperscript{25} carbon nanotubes,\textsuperscript{26} nano-scale materials and its possible applications in different fields of science and technology.\textsuperscript{27}
Chapter 1

1.1.1 Semiconductor quantum dots

Nanostructures of semiconductor materials have been the subject of intense research in the last decade owing to the novel electronic, catalytic and optical properties. A crystalline semiconductor material, which is size restricted in three dimensions such that the electron wave functions are confined within its volume, is called a semiconductor quantum dot (QD). Semiconductor QDs refer to nanometre-sized, giant ($10^3$-$10^5$ atoms) molecules made from ordinary inorganic semiconductor materials such as Si, GaAs, and CdSe etc. They are larger than the traditional “molecular clusters” (~ 1 nm containing ≤ 100 atoms) common in chemistry, yet smaller than the structures of the order of a micron, manufactured by current electronic-industry lithographic techniques. The unusual properties of these quantum dots can be attributed to two main factors: the large surface to volume ratio of atoms and the confinement of charge carriers in a quantum mechanical box and this effect, now called quantum size effect. During the past two decades, chemists and physicists have extensively studied the size quantisation effects in semiconductor QDs. Nanocrystalline semiconductor QDs synthesised as colloids have generated great interest, since this quantum confined structures can be synthesised with a high degree of reproducibility and high quality. The group II-VI nanocrystals such as CdSe, which are often studied as a prototypical colloidal QD system, can be synthesised in macroscopic quantities with sizes that are tunable during the synthesis (1.5-10 nm) in a narrow size distribution. II-VI quantum dots have a band gap, which can be varied in a broad range (up to 4 eV) by changing either their size or chemical composition. The ability to control the size of the nanocrystallites and thereby colour of the nanocrystallites is a direct consequence of quantum confinement on the electronic states. Due to their small sizes and their interesting electronic properties, QDs are promising building blocks for the fabrication of electronic and optoelectronic solid-state devices. Quantum confined structures, which has great potential to develop as an important class of materials for the electronic industry of the 21st century and integrated circuits (ICs) might be further miniaturised.
1.1.2 Quantum size effects

The ability to tailor the properties of materials by constraining their physical dimensions has become an important tool in nanoscience and nanotechnology. When the size of the system is smaller than a characteristic length scale of interest, e.g., exciton radius, electron mean free path, or magnetic domain size, the properties deviate from those of the bulk material. Depending upon the particular system, the optical, electrical, and magnetic properties can be tailored by synthesising particles of specific size. In case of bulk semiconductors, the band gap is defined as the minimum energy required for exciting an electron from the valence band to the conduction band. The charge carriers (electron and hole) through Coulomb interaction may form a bound state; a so-called Wannier exciton, which has energy slightly lower than the bandgap. An (Wannier) exciton can be defined as the bound state of an electron–hole pair, which is due to a Coulomb interaction between the charge carriers. An exciton can be viewed as an electron orbiting a hole at a certain distance in a dielectric medium a situation very similar to a hydrogen atom. The distance between the electron and the hole is the Bohr radius of the exciton, \( a_{\text{exc}} \) and is given by

\[
a_{\text{exc}} = \frac{4 \pi \varepsilon_0 h^2}{m_e e^2} \varepsilon_{\infty} \left[ \frac{1}{m_e^*} + \frac{1}{m_h^*} \right] = a_0 \varepsilon_{\infty} \left[ \frac{1}{m_e^*} + \frac{1}{m_h^*} \right]
\]

In equation (1.1), \( a_0 \) is the Bohr radius of a hydrogen atom (0.529 Å), \( \varepsilon_{\infty} \) the high frequency relative dielectric constant of the medium, \( m_e^* \) and \( m_h^* \) the effective masses of the electron and hole respectively (both in units of \( m_0 \)). Usually, the effective masses of the charge carriers are only a small fraction of the electron rest mass. This in combination with the fact that the Coulomb interaction between the electron and hole is almost entirely screened (\( \varepsilon_{\infty} \sim 5 \)) results in a relatively large Bohr radius of the exciton. As the size of the semiconductor particle approaches the Bohr radius of the exciton (\( a_{\text{exc}} \)), the electron-hole pair gets spatially confined and assumes a state of higher kinetic energy. Therefore, when considering quantum size effects in semiconductor particles, the Bohr radius of the exciton gives an indication of the dimensions at which these effects become apparent. For common semiconductors, the Bohr exciton radius \( (a_{\text{exc}}) \) are in the range 10-100 Å and for CdSe, the bulk Bohr exciton radius is \( (a_{\text{exc}}) 56 \text{ Å}.^{34} \)

The first model calculations by Brus\(^35\) were based on the effective mass approximation and used a treatment of bulk states in the limit of small size. The effective mass approximation
had been developed for macrocrystalline materials but it had already been shown that it could also be used to quantitatively describe the motion of exciton in very thin semiconductor layers.\textsuperscript{36} Effects that could complicate the calculations, such as structural rearrangements as a function of size or the involvement of surface states, were not considered. The system was approximated by a spherical semiconductor particle with an infinitely high potential energy outside the sphere. For the energy of the lowest excited state (comparable to the value for the bandgap in the case of macrocrystalline semiconductor) as a function of the particle radius $R$, the following formula was derived.

$$E = E_g + \frac{\hbar^2}{8m_0R^2} \left[ \frac{1}{m_e^*} + \frac{1}{m_h^*} \right] - \frac{1.8e^2}{4\pi\varepsilon_0\varepsilon R}$$  \hspace{1cm} (1.2)$$

In equation (1.2) next to the bandgap of the macrocrystalline material ($E_g$), two terms are given, both dependent on the particle size. The first term is a confinement term, which increases as $R^{-2}$ and the second term is the Coulomb attraction, increasing with $R^{-1}$. In the limit of large $R$, the value for $E$ approaches that of $E_g$. Although the effective mass approximation is not valid for very small particle sizes, equation (1.2) has often been used to describe quantum size effects in nanocrystalline semiconductor particles. The dependency of $E$ on $R$ as given by equation (1.2) can be used to describe the results from size-dependent measurements of optical properties fairly well. Since the early calculations by Brus, several papers have appeared presenting models that are based on more realistic boundary conditions, such as a finite barrier height.\textsuperscript{37}  \textsuperscript{38}
Equation (1.2) implies that when the radius of a semiconductor particle decreases, the energy for the lowest excited state increases. In other words, this means that when a particle becomes smaller, its “bandgap” increases. As a consequence of the spatial confinement of charge carriers, the kinetic energy becomes quantised. Strictly speaking the word “bandgap” is inappropriate for very small particles. The quantisation of the kinetic energy manifests itself as a gradual transition of continuous energy bands to discrete energy levels. This transition starts at the edges of the energy bands, as these states are particularly sensitive to the particle
size. Fig. 1.3 schematically shows the change of the electronic properties of a semiconductor as its size decreases to values lower than the Bohr radius of the exciton ($a_{\text{exc}}$).

In addition to these effects, the increase of the relative surface area also results in major changes of the optical properties of semiconductor nanoparticles. As the number of atoms at the surface becomes comparable to the number of bulk (core) atoms, surface states will play an important role.\textsuperscript{39}

### 1.2 Applications of semiconductor nanostructures

The size dependent electronic and optical properties of semiconductor nanostructures have given a great opportunity for the construction of a new class of optical and electronic devices. A light emitting diode (LED) has been fabricated using a junction of n-type CdSe nanocrystals and a p-type semiconducting polymer (p-paraphenylene vinylene, PPV) layers. The emitting colours of the diode ranging from green to red can be fine–tuned by the sizes of the deposited nanocrystals and applied voltage.\textsuperscript{40} This successful example of employing size dependent characteristics of the nanocrystals into a useful device has opened a wide imagination of constructing other possible devices.\textsuperscript{41} Recently the group of Bawendi and Jensen (MIT) demonstrated a novel strategy to produce full colour emission using semiconductor QD-polymer composites.\textsuperscript{42} These composites were produced by stabilisation of the semiconductor QDs in long chain polylaurylmethacrylate (PLMA) matrices in the presence of tri-n-octylphosphineoxide (TOPO) ligands. These experiments demonstrated the potential application of QD-polymer composites in full colour displays. A critical parameter for the performance of a single electron transistor (SET), the principle of which is based on the Coulomb blockade effect, is the capacitance of the quantum dot, which is determined by its size. Employing the semiconductor QDs, single electron transistors were fabricated.\textsuperscript{43} QDs can be used as stable fluorescent biological labels in biological research. Core shell quantum structures of ZnS-CdSe or CdS-CdSe have a very high luminescence quantum yield (up to 100%). Since QDs can be easily attached to different biological molecules like DNA, and proteins, they find useful applications in biological tagging experiments as fluorescent labels.\textsuperscript{44,45} Recently, using core-shell InAs-ZnSe nanocrystals and conjugated polymers efficient near-infrared polymer nanocrystal light emitting diodes were fabricated. Semiconductor nanorods (CdSe) were successfully employed in the development of hybrid nanorod-polymer solar cells. At present, extensive research efforts are aimed at developing
new device concepts and fabrication approaches using well-defined nanoscale building blocks, such as molecules, quantum dots, nanowires, carbon nanotubes and a number of functional devices and device arrays including field effect transistors, p-n diodes, bipolar junction transistors and integrated logic circuits. The major important applications of nanoscale building blocks in different fields of science and technology are illustrated in Fig.1.4 and 1.5.

Fig. 1.4 Schematic illustration of main applications of semiconductor QDs: (i) Colloidal QDs can be made to emit a full spectrum of colours (for display applications) when excited with a single excitation source, (ii) Schematic illustration of a single electron transistor (SET) with one nanocrystal of CdSe as its active element, (iii) Schematic illustration of a photovoltaic based on an interpenetrating network of 5 nm diameter CdSe nanocrystals and the semiconducting polymer, (iv) Applications of core-shell (CdS-CdSe, or ZnS-CdSe) nanocrystals in biological labelling and fluorescence studies of biological cells.
Fig. 1.5 Approaches to nanoelectronics/molecular-scale electronics: (A) Diodes and transistors based on semiconductor nanowires (GaN, InP, GaP) are assembled with microfluidics to form logic circuits and logic functions (B) Carbon nanotube transistors are connected by gold interconnects to construct logic circuits (NOT, NOR) and random access memory cells (RAM) (C) Field effect transistors (FETs) based on self assembled monolayers of polyphenylene molecules are combined to create a logic circuit (NOT) (D) Porphyrin molecules store digital information as electrical charges like dynamic random access memory (DRAM) cells.46


1.3 Porous materials

Porous materials have attracted the attention of chemists and material scientists due to commercial interest in their application in chemical separation, heterogeneous catalysis and use as a host material to confine guest molecules, nanostructures, as well as scientific interest in the challenges posed by their synthesis, processing and characterisation. Porous materials are most frequently characterised in terms of pore sizes derived from gas sorption data and IUPAC conventions have been proposed for classifying pore sizes and gas sorption isotherms that reflect the relationship between porosity and sorption. Pores are classified according to pore diameter. Micropores have diameter less than 2 nm, mesopores have diameters between 2 and 50 nm and macropores have diameters greater than 50 nm.

1.3.1 Mesoporous materials

In 1992, researchers from Mobil Oil Corporation introduced a new concept in the synthesis of porous materials by using a self-assembled molecular array of surfactant molecules as structure directing template. In the case of silicates and aluminosilicates, the removal of these templates led to mesoporous molecular sieves with adjustable pore sizes ranging from 2-10 nm (MCM-41: Mobil Composition of Matter). An unusual mechanism for the formation of these materials, “liquid crystal templating” (LCT), in which supramolecular assemblies of cationic alkyltrimethylammonium surfactants serve as components of the template for the formation of these materials, was proposed to account for their formation. Recently, mesoporous silica SBA-15 with larger pore channels and higher thermal and hydrothermal stability than MCM-41 was synthesised by using triblock copolymer as template. The pore diameter of SBA-15 can be controlled uniformly over the range of 6-12 nm, which exceeds the typical pore size limit for well-ordered MCM-41. There are excellent reviews in the literature on synthesis, properties and applications of MCM-41 in different fields of research.

1.3.2 Template synthesis of nanostructures

Although nanomaterials are still predominantly prepared by physical methods such as sputtering and molecular beam epitaxy, currently there are significant efforts as well as desire
to prepare the materials by chemical techniques. Chemical routes are generally simpler and less expensive and have the advantages of improved stoichiometric control and intimate mixing. Numerous methods for the preparation of different nanomaterials have been reported, including reduction of metal salts and thermolysis or sonication of organometallic complexes. Ideally, the fabrication technique or the synthesis process of nanomaterial should exert control over the particle size, size distribution, shape and morphology. There are numerous chemical methods for the synthesis of nanomaterials, including the template synthesis route. Various templates like zeolites, micelles, block co-polymers, porous anodic alumina membranes (AAM), have been used for the synthesis of nanostructures with greater control over the particle size distribution. The schematic illustration of possible nanostructures like nanotubes, nanorods or nanowires and nanoparticles that can be fabricated inside a porous template is shown in Fig. 1.6.

![Fig. 1.6 Nanostructures that can be templated inside the porous templates.](image)

**1.3.3 Advanced applications of mesoporous materials**

MCM-41 is a mesoporous silica material possessing ordered channels arranged in a hexagonal lattice. In addition to its potential for large molecule separation and catalysis applications, these families of materials are attractive as a host template or framework for the preparation of nanomaterials with unique dimensions. Under appropriate synthesis conditions, the pore diameters of MCM-41 can be tuned with angstrom precision between 1.5 – 10 nm to generate
high aspect ratio solids. In addition to this, the nanopores of MCM-41 can be functionalised with monolayers, the composition of the pore walls can be varied, and metals and catalysts can be anchored. Fig. 1.7 shows the schematic illustration of these novel aspects of MCM-41.

Mesoporous and mesostructured materials (MCM-41, MCM-48, SBA-15 etc.) derived by a combination of surfactant/block copolymer templating sol-gel chemistry are attractive candidates for optical applications such as lasers, optical sensors, and photochromic materials. Moreover, mesoporous materials have been shown to be excellent hosts for synthesising quantum-confined structures. The ability to tailor the pore size and loading conditions offer the possibility to produce nanocrystals of both direct and indirect semiconductors. When the loading techniques are perfected, mesoporous materials will make it possible to produce highly ordered arrays of quantum dots, which could be useful for applications such as quantum dot lasers. Many excellent review articles on synthesis, characterisations and applications of mesoporous materials exist in the literature.
1.4 References

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Chapter 2

2 InN whisker growth by chemical vapor deposition

Abstract

Rationally controlled growth of nanoscale one-dimensional inorganic semiconductors is important for their applications in nanoscale electronics and photonics. Nanostructures of compound semiconductors of group-III nitrides are ideal building blocks for nanoscale optoelectronic devices. InN has a direct bandgap of 1.89 eV, and has a low decomposition temperature and the growth of nano-scale crystalline InN material at low temperatures is difficult to achieve. One of the approaches is to design and develop single molecule precursor (SMP) that decomposes at low temperatures, and use as a precursor for the growth of InN. In this chapter, the growth and characterisation of InN whiskers by chemical vapor deposition (CVD) using single molecule precursor is presented. Single molecule precursors of the type $\text{N}_3\text{In}[(\text{CH}_2)_3\text{N(\text{CH}_3)}_2]_2$ were developed and the growth of dense crystalline InN layers with preferred orientation was achieved using this compound. However, employing specific CVD process parameters InN whiskers were grown consistently by CVD using a cold wall CVD reactor on bare sapphire substrates at a growth temperature of 500°C. Detailed investigations on CVD grown InN whiskers by different characterisation techniques like X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive analysis of X-rays (EDX), X-ray photoelectron spectroscopy (XPS), Rutherford backscattering spectroscopy (RBS), transmission electron spectroscopy (TEM) and selected area electron diffraction (SAED) pattern are discussed in this chapter.
2.1 Introduction

2.1.1 Inorganic semiconductor nanowires

Nanoscale one-dimensional materials such as nanowires/nanowhiskers, nanorods, and nanotubes have stimulated great interest due to their importance in basic scientific research and potential technological applications. Many unique, interesting and fascinating properties have been proposed and demonstrated for this class of low dimensional materials such as metal-insulator transition, super mechanic toughness, higher luminescence efficiency, enhancement of thermoelectric figure of merit, and lowered lasing threshold. Nanostructures such as nanowires and nanotubes are attractive building blocks for nanoelectronics since their morphology, size, and electronic properties make them suitable for fabricating both nanoscale devices and interconnects. For example, a number of nanodevices such as FETs, bipolar transistors, inverters, light emitting diodes (LEDs) and even logic gates have been assembled from well-defined semiconductor nanowires.

Group-III nitrides, InN, GaN and AlN and their related alloys such as InGaN and AlGaN are a prominent topic of current research and attract considerable developmental efforts since their wide direct band gaps encompass a broad range of energies (1.9 eV to 6.4 eV). Applications such as blue light emitting diodes and laser diodes as well as high-speed field-effect transistors, ultraviolet photodetectors, and high temperature electronic devices have been demonstrated. Low dimensional nanostructures of compound semiconductors of group III-V are ideal building blocks for future nanoelectronic and optoelectronic devices. One-dimensional (1D) nanostructures of semiconductor materials have been synthesised using different techniques. Physical methods such as laser ablation, arc discharge, thermal evaporation and chemical methods such as chemical vapor transport and chemical vapor deposition can be used to generate the vapor species required during the nanowire nanowhisker growth.

Investigations on one-dimensional structures of group-III nitrides have been limited due to difficulties associated with their synthesis. However, semiconductor whiskers such as Si, Ge, GaP, GaAs, InP, and InAs have been widely studied over the last two decades because of their unique growth behaviour and crystal structure and these whiskers have been fabricated by
selective growth using conventional MOVPE process. Studies of whiskers have yielded much new information on growth processes fundamental to whiskers and on their crystal structure and optical properties. Recently, one-dimensional nanostructures of GaN like nanowires and nanorods were synthesised by different techniques.\(^\text{11}\) Han et al. synthesised GaN nanorods through a carbon nanotube confined reaction.\(^\text{12}\) Subsequently, Han et al. produced GaN-carbon composite nanotubes and nanorods by arc-discharge in nitrogen atmosphere.\(^\text{13}\) Duan and Lieber formed single-crystal GaN nanowires by laser assisted catalytic growth.\(^\text{14}\) Chen and Yen produced wire like structures using polycrystalline indium powder as a catalyst.\(^\text{15}\) Li et al. fabricated GaN nanorods by sublimation of GaN powder under an NH\(_3\) flow.\(^\text{16}\) In a parallel effort Cheng et al. formed GaN nanowires in anodic alumina membranes through gas-phase reaction of Ga\(_2\)O\(_3\) vapor with flowing NH\(_3\).\(^\text{17}\) Self-organised GaN nanocolumns were grown on Al\(_2\)O\(_3\) substrates by rf-radical-source molecular beam epitaxy.\(^\text{18}\) One-dimensional GaN structures were prepared by direct reaction of Ga vapor with flowing NH\(_3\) above 900°C.\(^\text{19}\)

### 2.1.2 Applications of nanowires/nanowhiskers

Recently, Duan et al. reported the general synthesis method of nanowires of compound semiconductors.\(^\text{20}\) They demonstrated the general and rational approach for hierarchical assembly of one-dimensional nanomaterials into well-defined functional networks that can bridge the nanometre through millimetre size regimes. They demonstrated how to build the smallest light emitting diodes using the p-doped and the n-doped InP nanowires.\(^\text{21}\) The schematic illustration of Nano-LED construction is as shown in Fig. 2.1. The p-doped and n-doped nanowires were assembled between two electrodes using an electric field gradient to form a nanoscale light emitting diode. When a current is passed between them, the electrons and holes are injected across the junction and recombine to emit light.\(^\text{22}\)
Chapter 2

Room temperature ultra-violet lasing in ZnO semiconductor nanowire arrays has been reported recently. The self-organised, well-oriented ZnO nanowires grown on sapphire substrates were synthesised with a simple vapor transport and condensation process. These wide band-gap semiconductor nanowires form natural laser cavities with diameters varying from 20 to 150 nm and lengths up to 10 µm. Under optical excitation, surface-emitting lasing action was observed at 385 nm, with an emission line-width less than 0.3 nm. The growth of designed one-dimensional nanowire superlattice heterostructures like GaP/GaAs, InAs/InP, and Si/Si-Ge placed within semiconductor nanowire/nanowhiskers by laser ablation and chemical beam epitaxy (CBE) and their electrical characterisation was reported. These new nanowire superlattice structures may find a diversity of possible applications, including thermoelectrics, nano-barcodes, injection lasers, and engineered one-dimensional waveguides.

2.1.3 Vapor-liquid-solid growth

Wagner and Ellis in 1964 proposed the original idea of vapor-liquid-solid (VLS) growth of semiconductor whiskers, when vapor growth techniques were developed to produce
crystalline semiconductors from hot gaseous reactants. In the first VLS experiments, a silicon precursor was degraded from the gas phase by chemical vapor deposition (CVD) over a surface containing liquid gold droplet to form an Au:Si alloy until saturation. Upon saturation, the semiconductor exits the droplet in the form of a whisker. Growth is sustained by continued Si absorption into the nucleating metal drop as the CVD reaction proceeds. The schematic illustration of the vapor-liquid-solid growth mechanism is as shown in Fig. 2.2.

**Fig. 2.2 Schematic illustration of vapor-liquid-solid nanowire growth mechanism including the three stages, (I) alloying, (II) nucleation, and (III) axial growth.**

In the first stage of whisker formation, a liquid eutectic alloy droplet composed of metal catalysts such as Au, Fe, etc., and nanowire/nanowhisker material such as Si, III-V, compounds etc., is formed first at certain growth temperature under the reaction conditions. These metal droplets act as liquid catalyst alloy clusters. These miscible liquid catalyst alloy clusters serves as a preferential site for absorption of gas phase reactants and when supersaturated they act as the nucleation site for crystallisation (II stage). Preferential one-dimensional (1D) growth of nanowire/whisker occurs in the presence of reactants as long as the catalyst (metal) remains as liquid (III stage). During the growth, the catalyst droplet alloy directs the nanowire/whisker growth direction and defines the diameter of the crystalline nanowire/whisker. Ultimately, the growth of nanowire/whisker terminates when the temperature is below the eutectic temperature of the catalyst alloy or the reactant is no longer available. Equilibrium thermodynamics can be used to define the minimum radius \( r_{\text{min}} \), of a liquid metal cluster as
Chapter 2

\[ r_{\text{min}} = \frac{2\sigma_{LV}}{RT \ln \sigma} V_L \]  

(2.1)

where, \( \sigma_{LV} \) is the liquid-vapor surface free energy, \( V_L \) is the molar volume of the liquid, \( R \) is the gas constant, \( T \) is the temperature, and \( \sigma \) is the vapor phase supersaturation. The existence of a minimum radius results from the free energy of liquid droplet being a balance of the energy gain of condensation and the energy cost in the interfacial energy. For most materials, the minimum critical radius is of the order of 0.1mm for \( \sigma = 1.02 \). Thus under equilibrium conditions, one should expect relatively large diameter clusters at the ends of the nanowires/whiskers as reported in the literature.\(^{29}\)

2.1.4 Solution-liquid-solid growth

In analogy to vapor-liquid-solid (VLS) growth mechanism observed at higher temperatures under chemical vapor deposition conditions, a solution-phase low temperature solution-liquid-solid (SLS) growth of nanowhiskers of group-III phosphides and arsenides has been demonstrated.\(^{30}\) Buhro et al. synthesised crystalline III-V materials such as InP, InAs\(^{31}\), GaAs and Al\(_x\)Ga\(_{1-x}\)As\(^{32}\) whiskers at low temperatures by SLS growth process. The size distributions of these whiskers obtained by SLS process are broad with whiskers having typical thickness of 20-200 nm and lengths up to 10 µm. The SLS mechanism is closely analogous to the well-known vapor-liquid-solid (VLS) mechanism in which crystals are grown from flux droplets that are fed from the vapor phase rather than a solution phase. The distinguishing features of solution-liquid-solid (SLS) growth process are (1) a solution dispersion of small liquid flux droplets, (2) a solution phase that feeds the elements of the crystal phase into the flux droplets, and (3) pseudo–one-dimensional growth of the crystal phase from the flux droplets after super saturation is achieved. Recently crystalline InN fibres were synthesised at relatively low temperature using Azido–Indium precursor by SLS growth process.\(^{33}\)

One-dimensional nanostructures like nanowires/whiskers of group-III nitrides have been synthesised by a variety of methods such as chemical vapor deposition, chemical vapor transport method, laser assisted catalytic growth, and oxide assisted catalytic growth (See Table 2.1). Most of them have reported the VLS mechanism as the possible growth process for such one-dimensional growth. Although many semiconductor nanowires/whiskers with different compositions have been successfully synthesised using the VLS growth technique, the mechanism of VLS growth is not clear. Only recently, the first real time observation of
semiconductor nanowire growth in an in-situ high temperature transmission electron microscopy (TEM) was reported which unambiguously demonstrates the validity of the VLS growth mechanism in nanometre scale.\textsuperscript{34}

Table 2.1 Important methods of synthesis of one-dimensional group-III nitride nanostructures.

<table>
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<td>Nanopillars</td>
<td>MOCVD with Single Molecule Precursor</td>
<td>45</td>
</tr>
<tr>
<td><strong>InN</strong></td>
<td>Nanowires</td>
<td>Vapor-Solid growth with In and In\textsubscript{2}O\textsubscript{3} powder</td>
<td>61</td>
</tr>
<tr>
<td></td>
<td>Nanowires</td>
<td>Thermal evaporation: In and NH\textsubscript{3}</td>
<td>62</td>
</tr>
<tr>
<td></td>
<td>Pillars</td>
<td>APHCVD with InCl\textsubscript{3} and NH\textsubscript{3}</td>
<td>42</td>
</tr>
<tr>
<td></td>
<td>Fibres</td>
<td>SLS method</td>
<td>33</td>
</tr>
</tbody>
</table>

Controlling the growth orientation is important for many of the proposed applications of nanowire/whiskers. By applying the conventional epitaxial crystal growth technique into the VLS process, it is possible to achieve precise orientation control during the growth of nanowire/whiskers. This technique, vapor-liquid-solid epitaxy (VLSE) is particularly
powerful in controlled synthesis of nanowire arrays. Epitaxial growth of Si and ZnO nanowires by VLSE growth process is reported recently. In a different approach, ZnO nanopillars have been electrodeposited epitaxially onto Au (111), Au (110) and Au (100) single-crystal substrates. Similarly, using a single molecule precursor \((\text{N}_3)_2\text{Ga}[(\text{CH}_2)_3\text{N}(\text{CH}_3)_2]\), controlled growth of oriented GaN nanopillars is accomplished by MOCVD process.

### 2.1.5 Single molecule precursor approach to nanostructures

One of the potential strategies for the synthesis of compound semiconductor nanostructures is the pyrolysis of single molecule precursor that incorporates the elements of a compound in a single molecule. Highly monodispersed quantum dots of CdS, CdSe, ZnS, and ZnSe with good optical properties were synthesised using novel air stable single molecule precursors. Nanoparticles of InS and InSe capped with TOPO (tri-n-octylphosphine oxide) were prepared by single source route. Single molecule precursors for group-III nitrides have been designed and developed by many research groups on the basis of volatile group-III amide, azide, and hydrazide compounds and have been investigated in MOCVD studies. Synthesis of nanocrystalline GaN was reported via the solid state pyrolysis of cyclotrigallazane, \([\text{H}_2\text{GaNH}_2]_3\), \([\text{Ga(NH)}_{3/2}]_x\), and the thermolysis of \([\text{Ga(NH)}_{3/2}]_x\), in trioctylamine. Controlled detonations of Lewis base adducts of Ga(N\(_3\))\(_3\) yielded quantum confined GaN particles. Thermal decompositions of \([\text{H}_2\text{GaN}_3]_n\) and \([\text{H(Cl)}\text{GaN}_3]_n\) yielded nanostructures of GaN. Using azide based precursors solution synthesis of colloidal GaN at low temperatures was reported.

However, in comparison with single molecule precursors of GaN, there exist very few reports on single molecule precursors of InN. One of the main reasons is that the In-N bond is weak compared to Ga-N, or Al-N bonds, and the equilibrium vapor pressure of N\(_2\) over InN is much higher than that over GaN and AlN. Intramolecularly adduct stabilised single molecule precursor organoindium azide, \(\text{N}_3\text{In}[(\text{CH}_2)_3\text{N}(\text{CH}_3)_2]_2\) (Azido[bis(3-dimethylamino) propyl]indium) and its application for the growth of InN films by MOCVD at low temperatures in a hot wall reactor was reported. These films were grown on different substrates like Si, GaAs, AlN, and GaN buffer layers. Apart from the recently published report on the solution phase synthesis of InN nanofibres at low temperature using an azido indium precursor, there hardly exists any literature on the chemical synthesis of InN nanostructures. Very recently synthesis of InN nanowires was achieved from a mixture of In
and In$_2$O$_3$ with a constant flowing NH$_3$ atmosphere.\textsuperscript{61} Selective area growth of InN nanowires on gold patterned Si(100) substrates was reported using a simple thermal evaporation method.\textsuperscript{62} Currently there are no important applications of pure InN. However, a significant amount of In must be incorporated into GaN layer to obtain blue light emission and it is quite clear today that InN quantum dots (QDs) in InGaN active layer is responsible for the high brightness of LEDs.\textsuperscript{63}
2.2 Experimental

2.2.1 Precursor synthesis and characterisation

Intramolecularly adduct stabilised single molecule precursor organoindium azide, $N_3\text{In}[(\text{CH}_2)_3\text{N(CH}_3)_2]_2$ (Azido[bis(3-dimethylamino)propyl]indium) (AZIN) used for the growth of InN whiskers was synthesised according to the procedure, which was reported earlier with slight modifications. The synthesis procedure is schematically shown in scheme 2.1.

\[
\begin{array}{c}
\text{2 Li} & + & \text{InBr}_3 & \xrightarrow{\text{Et}_2\text{O}} & \text{Br} & \xrightarrow{12 \text{ h, RT}} & \text{Me}_2\text{N} \\
& & & & & \xrightarrow{\text{1. Sublimation}} & \\
& & & & & & \overset{\text{2 + AgTfI, CH}_2\text{Cl}_2, \text{reflux} 48 \text{ h}}{\text{Me}_2\text{N}} \\
& & & & & & \overset{\text{3 + NaN}_3 (\text{excess}), \text{toluene, reflux} 48 \text{ h}}{\text{Me}_2\text{N}} \\
\end{array}
\]

Scheme 2.1 Synthesis scheme of $N_3\text{In}[(\text{CH}_2)_3\text{NMe}_2]_2$, after ref (54).

2.2.2 Thermal characterisation of the precursor

A detailed thermal analysis of the precursor $N_3\text{In}[(\text{CH}_2)_3\text{N(CH}_3)_2]_2$ was conducted to determine the volatility of the precursor and to optimise the vaporiser temperature during the growth of InN whiskers by CVD. Simultaneous thermogravimetric and differential thermal
analysis (TG/DTA) were carried out using a Seiko TG/DTA 6300S11 instrument in an argon atmosphere (100mL/min) under ambient pressure with a heating rate of 5°C/min using ≈10mg of the precursor.

2.2.3 CVD system employed for the growth of InN whiskers

A horizontal cold wall CVD reactor was employed for the growth of InN whiskers. A schematic diagram of the reactor is shown in Fig. 2.3.

![Fig. 2.3 Schematic diagram of the horizontal CVD reactor used for the growth of InN whiskers.](image)

The CVD reactor consisted of a quartz tube, at the centre of which the substrates are placed on a graphite susceptor. Substrate heating was accomplished by an inductive heating arrangement attached to a radiation pyrometer. The outer wall of the central zone of the quartz tube was cooled by water circulation. The quartz tube was attached to a glass vaporiser by means of O-ring joints, and the vaporiser was placed in an air bath that can be heated up to 150 °C. Single crystal sapphire c-plane Al$_2$O$_3$ substrates were used for the growth of InN whiskers. The rear end of the quartz tube was attached to a glass trap (which was cooled by liquid nitrogen) to collect the by-products of the process. A turbomolecular pump was used to conduct InN deposition at low pressures (8 mbar). The pressure of the reactor was regulated using a motor driven throttle valve, and mass flow controllers were used to monitor and control the different gases used for the process.
2.2.4 Whisker growth

The growth of InN whiskers was accomplished using a horizontal cold wall quartz tube reactor that was normally employed for the CVD of group-III nitrides. The c-plane sapphire \([\text{Al}_2\text{O}_3(0001)]\) substrates were used for the growth of InN whiskers. The substrates were degreased in trichloroethylene, etched in a mixture of \(\text{H}_2\text{SO}_4/\text{H}_3\text{PO}_4\) (3:1) and rinsed with distilled water and acetone before loading it into the reactor. CVD experiments were conducted under low pressures. The base pressure of the reactor was of the order of \(3 \times 10^{-6}\) mbar and the operating pressure for the growth of InN whiskers was maintained at 8.000 mbar. About 0.2 g of the precursor (AZIN) was taken in a precursor reservoir and high purity nitrogen (99.9999\%) was used as the carrier gas (flow rate of 50 sccm). The substrate temperature was varied in the temperature range 400 – 550°C. The growth of these whiskers was performed with ammonia (50 sccm, 99.998\%) as an additional reactive gas. The growth period normally lasted about 15 min, and the recovered substrates were characterised by a variety of techniques.

2.2.5 Characterisation of InN whiskers

The following characterisation techniques were used for the analysis of InN whiskers.

1. X-ray diffraction
2. Scanning electron microscopy
3. EDX analysis
4. Transmission electron microscopy
5. High resolution transmission electron microscopy
6. Selected area electron diffraction
7. X-ray photoelectron spectroscopy


2.3 Results and Discussion

2.3.1 Precursor characterisation

The precursor $\text{N}_3\text{In}[(\text{CH}_2)_3\text{N(CH}_3)_2]_2$ (Azido[bis(3-dimethylamino)propyl]indium) (AZIN) was obtained in the form of white crystalline needles and the precursor was relatively air stable compared to its Ga analogue. Precursor identification and characterisation were achieved by a number of different techniques such as single crystal x-ray diffraction (XRD), IR, NMR spectroscopy, mass spectrometry (MS), elemental analysis (EA), and atomic absorption spectroscopy (AAS).

2.3.2 Thermal characterisation of the precursor

The precursor $\text{N}_3\text{In}[(\text{CH}_2)_3\text{N(CH}_3)_2]_2$ is a white crystalline solid at room temperature. The volatility and thermal stability of the precursor were investigated using thermal analysis.

Fig. 2.4 Thermogravimetric and differential thermal analysis (TG/DTA) of $\text{N}_3\text{In}[(\text{CH}_2)_3\text{NMe}_2]_2$ under ambient pressure. (Ar flow rate = 100mL/min; heating rate 5°C/min).
Fig. 2.4 shows the TG/DTA analysis of the precursor under ambient pressure. From the TG curve, it is seen that the precursor begins to sublime at a temperature of about 80°C. There is a monotonic weight loss till about 250°C leaving a residue of about 19.6% in the sample pan. From the DTA curve, an endothermic dip at 74°C corresponds to the melting point of the precursor and the exothermic peak at about 250°C corresponds to the decomposition. From this it is clear that the precursor sublimes as well as decomposes at relatively low temperatures, and there is a sufficient temperature window between sublimation and decomposition of the precursor, which is an ideal requirement for CVD precursors.

### 2.3.3 InN whisker growth and characterisation

The growth of InN whiskers was achieved only when the CVD growth run was conducted on bare c-plane sapphire substrates [Al\textsubscript{2}O\textsubscript{3}(0001)] (Table 2.2). Normally growth of group-III nitrides is carried out by nitridating the sapphire surface with ammonia at high temperatures (900°C) so as to grow buffer layers (AlN) with thickness of the order of 20-50 nm to have a close lattice match with the group-III nitrides. When the deposition was conducted on nitridated substrates using the same precursor (AZIN) in the presence of ammonia, it was possible to achieve a complete coverage of the substrate leading to InN films which were dense, preferentially oriented and with a different surface morphology. The nucleation for such growth largely depends on the nature of the substrate surface, such as surface roughness, lattice mismatch etc. In the absence of ammonia as a reactive gas and on bare sapphire substrates, poorly crystalline InN whiskers (XRD analysis) with higher carbon content were obtained. Similar results were obtained for MOCVD of GaN thin films using single molecule precursor.

### 2.3.4 X-ray diffraction analysis

In general, the X-ray diffraction analysis of CVD grown InN whiskers showed the presence of In metal. In the case of InN whiskers grown at 500°C, the XRD analysis revealed that the intensity of the metallic In reflections is relatively weak compared to the intensity of InN reflections. Fig. 2.5 shows the XRD pattern of InN whiskers grown at 500°C by CVD. In the X-ray diffraction pattern, the (100), (002), (101), (102), (110), (103), (200), (112), (201), (004), (202) and (104) reflections correspond to the hexagonal wurtzite InN. The (006) reflection corresponds to the sapphire substrate.
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The broad (101) reflection of InN (2θ = 33.15°) compared to other reflections may be due to the overlapping with the (101) reflection of metallic In (2θ = 32.97°). Other reflections from metallic In (unmarked in Fig. 2.5) were also found, however it is seen that they have a weaker intensity than the InN reflections. In addition, the presence of metallic In at the upper end of each whisker was confirmed by SEM and TEM analysis.

![X-ray diffraction pattern of InN whiskers](image)

*Fig. 2.5 X-ray diffraction pattern of InN whiskers, which corresponds to wurtzite structure, grown by CVD at 500°C (8 mbar; N₂ 50 sccm; NH₃ 50 sccm) on c-plane Al₂O₃ substrates. Unmarked peaks from In metal droplets are also weakly visible at 2θ values of 36.4°, 39.2°, 54.5°, and 67.1°.*

Table 2.2 illustrates the different conditions employed for the growth InN whiskers. The comparison of measured d values of InN whiskers (Fig. 2.6) and reference d values of bulk InN is illustrated in Table 2.3.
Table 2.2 CVD process parameters employed for the growth of InN using $N_3In[(CH_2)_3NMe_2]_2$ as precursor.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Substrate temperature (°C)</th>
<th>Reactor pressure (mbar)</th>
<th>Carrier gas $N_2$ (sccm)</th>
<th>Ammonia flow rate (sccm)</th>
<th>InN layer obtained</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bare $Al_2O_3$</td>
<td>400</td>
<td>8</td>
<td>50</td>
<td>50</td>
<td>Poorly crystalline whiskers</td>
</tr>
<tr>
<td>Bare $Al_2O_3$</td>
<td>450</td>
<td>8</td>
<td>50</td>
<td>50</td>
<td>Poorly crystalline whiskers</td>
</tr>
<tr>
<td>Bare $Al_2O_3$</td>
<td>500</td>
<td>8</td>
<td>50</td>
<td>50</td>
<td>Highly crystalline whiskers</td>
</tr>
<tr>
<td>Bare $Al_2O_3$</td>
<td>550</td>
<td>8</td>
<td>50</td>
<td>50</td>
<td>Poorly crystalline whiskers (&gt;In)</td>
</tr>
<tr>
<td>Bare $Al_2O_3$</td>
<td>600</td>
<td>8</td>
<td>50</td>
<td>50</td>
<td>Poorly crystalline whiskers (&gt;In)</td>
</tr>
<tr>
<td>Bare $Al_2O_3$</td>
<td>500</td>
<td>8</td>
<td>50</td>
<td>nil</td>
<td>Poorly crystalline whiskers with higher carbon content</td>
</tr>
<tr>
<td>Nitridated $Al_2O_3$</td>
<td>500</td>
<td>8</td>
<td>50</td>
<td>50</td>
<td>Dense and preferentially oriented thin film</td>
</tr>
</tbody>
</table>
Table 2.3 Comparison of measured $d$ values of InN whiskers (Fig. 2.5) and reference $d$ values of bulk InN.

<table>
<thead>
<tr>
<th>Reflection ($hkl$)</th>
<th>$2\theta$ (degrees)</th>
<th>Measured $d$ values (Å)</th>
<th>Reference $d$ values (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>28.966</td>
<td>3.075</td>
<td>3.080</td>
</tr>
<tr>
<td>002</td>
<td>31.361</td>
<td>2.845</td>
<td>2.850</td>
</tr>
<tr>
<td>101</td>
<td>33.152</td>
<td>2.695</td>
<td>2.700</td>
</tr>
<tr>
<td>102</td>
<td>43.253</td>
<td>2.084</td>
<td>2.090</td>
</tr>
<tr>
<td>110</td>
<td>51.594</td>
<td>1.764</td>
<td>1.770</td>
</tr>
<tr>
<td>103</td>
<td>57.012</td>
<td>1.612</td>
<td>1.614</td>
</tr>
<tr>
<td>200</td>
<td>60.414</td>
<td>1.530</td>
<td>1.531</td>
</tr>
<tr>
<td>112</td>
<td>61.615</td>
<td>1.502</td>
<td>1.504</td>
</tr>
<tr>
<td>201</td>
<td>62.821</td>
<td>1.476</td>
<td>1.478</td>
</tr>
<tr>
<td>004</td>
<td>65.390</td>
<td>1.425</td>
<td>1.426</td>
</tr>
<tr>
<td>202</td>
<td>69.581</td>
<td>1.348</td>
<td>1.350</td>
</tr>
<tr>
<td>104</td>
<td>73.261</td>
<td>1.291</td>
<td>1.291</td>
</tr>
</tbody>
</table>

2.3.5 Scanning electron microscopy

The surface morphology of the InN whiskers grown by CVD were analysed by scanning electron microscopy (SEM). A typical SEM image of the InN whiskers is shown in Fig. 2.6. It is observed that the InN whiskers with diameters 10-200 nm and lengths up to few micrometres (10-100 µm) cross each other and are randomly distributed on the surface of the sapphire substrate (Fig. 2.6). A high magnification SEM image of InN whiskers is shown in Fig. 2.7. It is evident from the image that InN whiskers grow randomly on the $\text{Al}_2\text{O}_3$ surface.
Fig. 2.6 SEM image (low magnification) of InN whiskers grown on c-plane $\text{Al}_2\text{O}_3$ substrates by CVD at 500°C (8 mbar; $\text{N}_2$ 50 sccm; $\text{NH}_3$ 50 sccm).

Fig. 2.7 SEM image (higher magnification) of InN whiskers grown on c-plane $\text{Al}_2\text{O}_3$ substrates by CVD at 500°C (8 mbar; $\text{N}_2$ 50 sccm; $\text{NH}_3$ 50 sccm).
SEM images of the single InN whisker [Fig. 2.8(e) and Fig. 2.8(f)] showed that the InN whiskers grow out of the In droplets as confirmed by EDX analysis and which is in agreement with the XRD results.

*Fig. 2.8 SEM images of InN whiskers (a-d) and (e-f) showing the presence of In droplet at the tip of the whisker.*
2.3.6 EDX analysis

EDX analysis (Fig. 2.9) of InN whiskers revealed that the whiskers contain mainly In and N along the whisker length, while only In was detected in the droplet attached to the tip of the whisker. The presence of In metal droplets at the ends of the whiskers provides strong evidence for a vapor-liquid-solid growth mechanism.

![EDX analysis of InN whiskers grown at 500°C showing the presence of In and N. The signals from Al, O and Au are due to substrate and evaporation of metallic Au during the sample preparation.](image)

2.3.7 Transmission electron microscopy

Fig. 2.10 (a) shows the representative TEM image of a single InN whisker. As previously observed by SEM, the whiskers were straight and long. In addition, TEM images also showed the In metal droplets at the tip of the each whisker. A typical TEM image of single InN whisker is displayed in Fig. 2.10 (b) to illustrate the details of the whisker growth where the whisker was terminated with In metal droplet.
2.3.8 High-resolution transmission electron microscopy

The high-resolution transmission electron microscopy (HRTEM) images recorded on the individual InN whiskers provided further insight into their structures. HRTEM images of majority of the InN whiskers exhibited good crystalline quality with clear lattice fringes. A typical example of HRTEM image of InN whisker showing the lattice resolution is presented in the Fig. 2.11. The image showed clear lattice planes as indicated in the figure. The spaces between lattice planes are close to those obtained from bulk InN. The space of ~ 0.3 nm between the arrowheads corresponds to the distance between two (100) planes [inset of Fig. 2.11], which agrees very well with the reported value of bulk InN.
Fig. 2.11 HRTEM image of an InN whisker with the lattice resolution. The space of \( \approx 0.3 \) nm between the arrowheads corresponds to the distance between two (100) planes.

2.3.9 Selected area electron diffraction

The representative selected area electron diffraction (SAED) patterns of InN whiskers are as shown in Fig. 2.12(a) and Fig. 2.12(b). These SAED patterns taken along [11\( \overline{2} \)0] and [0001] zone axis confirm that the whiskers are hexagonal InN.

Fig. 2.12 Selected area electron diffraction (SAED) patterns of InN whiskers taken along (a) [11\( \overline{2} \)0] and (b) [0001] zone axis.
2.3.10 X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) has been used to investigate the elemental composition of InN whiskers. The survey spectrum of InN whiskers showed the presence of In, and N from the whiskers and Al, O, and C from the substrate as well as from the absorbed gaseous molecules. Higher resolution spectra were taken of the In 3d region, Fig. 2.13 (a) and N 1s [Fig. 2.13 (b)]. The In core is spin – orbit split to the 3d_{5/2} peak at 444.3 eV and 3d_{3/2} peak at 451.9 eV. The peak at around 397.6 eV corresponds to N 1s of InN. These results are close to the reported values for bulk InN films.\textsuperscript{65}

![In 3d and N 1s XPS spectra](image)

Fig. 2.13 High resolution XPS scan of In 3d cores and N 1s core for InN whiskers grown at 500°C. The In 3d core is spin-orbit split into 3d_{5/2} and 3d_{3/2} peaks.

2.3.11 Proposed growth mechanism for InN whiskers

The combined results clearly demonstrate the growth of InN whiskers by CVD from a tailored molecular precursor. However, there are a few important questions like, what are the underlying chemical processes involved in the formation of InN whiskers and what the growth mechanism for InN whiskers is. As reported, metal droplets catalyse whisker and fibre growth under high-temperature CVD conditions in a process known as vapor-liquid-solid (VLS) growth, which was first described, by Wagner and Ellis in 1964. In VLS growth, the liquid metal cluster or catalytic metal droplets acts not only as the energetically favoured site
for absorption of gas-phase reactants, but also promote both precursor decomposition and crystal lattice construction.

![Diagram](image)

**Fig. 2.14 Schematic illustration of proposed vapor-liquid-solid (VLS) growth mechanism for InN whisker growth by CVD.**

From the growth process conditions and the presence of In metal droplets at the end of each nanowhisker, we believe that the growth mechanism is very similar to the VLS growth described by Wagner and Ellis. Moreover these whiskers were grown on bare sapphire substrates and may act as a kind of catalytic site, promoting thermal decomposition of precursor molecules for the nanowhisker growth (Fig. 2.14). Previously, using a molecular beam sampling technique and quadrupole mass spectrometry the fragmentation of the precursor was studied as a function of substrate temperature. It was shown that fragments like \( \text{H}_y\text{N}_x\text{In} \) as well as In atoms appear in the boundary layer of the substrate.\(^{66}\) These fragments are expected to contribute to the formation of InN whiskers and a detailed investigation is required in this regard. It was found that the amount of \( \text{H}_y\text{N}_x\text{In} \) species increases with substrate temperature, while the amount of In-C fragments decreases. The relative abundance of In atoms rises rapidly with the substrate temperature. At temperatures above 450°C, no In-N bonded species were detected and this may lead to In-rich depositions. Therefore the substrate temperature can control the concentrations of those species relevant to the growth of InN. Thus it is possible to design organometallic precursors to produce \( \text{H}_y\text{N}_x\text{In} \) as the growth species, which can play a major role in the growth of InN layers. From these data we conclude that the observed whisker growth at low temperatures (400 - 500°C), is an intrinsic feature of this particular precursor. Even though nanowhiskers / nanostructures of Si, GaAs, GaN, InAs, InP were grown by employing the VLS growth mechanism, to our knowledge this is the first report of autocatalytic VLS growth of InN whiskers by CVD using a molecular precursor.
2.4 Summary and Conclusions

The growth of InN whiskers was achieved by chemical vapor deposition using a single molecule precursor. XRD analysis revealed that InN whiskers have hexagonal wurtzite structure. SEM investigations of the whiskers indicated the random distribution of the whiskers and they are few micrometers in length. EDX analysis showed the presence of both In and N signals from the whiskers, while from the tip of these whiskers only In was detected. TEM and SAED analysis confirmed the hexagonal InN whisker growth by CVD. The combined results of InN whisker analysis taken together, it is proposed that the autocatalytic vapor-liquid-solid (VLS) growth process may be a reasonable explanation for the InN whisker formation by CVD.
2.5 References


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Chapter 3

3 Synthesis of GaN nanostructures using mesoporous silica as template via chemical vapor infiltration of single molecule precursor

Abstract

GaN is one of the most promising semiconducting materials suitable for designing and fabricating optoelectronic devices. A vapor phase based synthesis route was developed to produce GaN nanoparticles using porous host templates such as MCM-41 and SBA-15. This was achieved by infiltrating single molecule precursors (containing Ga and N in one molecule) in the vapor phase and then a subsequent heat treatment for the pyrolysis of these precursors inside the host matrices resulted in the formation of nanosized GaN particles. The synthesis of GaN nanoparticles and their characterisation by X-ray diffraction analysis (XRD), N\textsubscript{2} sorption studies (BET), transmission electron microscopy (TEM), energy dispersive analysis of X-rays (EDX), selected area electron diffraction (SAED) analysis, \textsuperscript{71}Ga NMR, and elemental analysis are presented in this chapter.
3.1 Introduction

Wide band gap III-V nitrides are the most prominent materials of current research and attracts considerable attention due to its potential applications in the field of light emitting diodes (LEDs), laser diodes, UV photodetectors, high speed field effect transistors (FETs) and high temperature electronic devices. Other applications include read-write laser sources for high-density information storage for magnetic and optical media, laser printers, and full colour electroluminescent displays. The successful achievement in developing the GaN based electronic devices has attracted the highest scientific attention of physics, chemistry, materials science community and synthesis and development of GaN in thin film form is very well developed. In contrast to this, nanometre-scale low-dimensional structures of GaN (nanoparticles or quantum dots, nanowires or nanorods) have received less attention. With increasing miniaturisation of electronic components, nano-scale low dimensional structures are expected to play a vital role as materials for both interconnects and emerging future technologies important for the development of nanoelectronics and nanodevices while they represent an exciting and intellectually challenging area of current research.

The large pore size, high surface area, and thermally stable mesoporous materials such as MCM and SBA family have created great interest in using these materials in catalysis and catalytic support applications. More recently, mesostructured materials have attracted interest for electronic and optical applications. It has been recognised that mesoporous systems are promising candidates for the next generation low-\(k\) dielectric materials for integrated circuits.

Ordered mesoporous materials like MCM-41 and SBA-15 hosts allow the inclusion and ordered growth of semiconductor nanostructures with regular dimensions as well as uniform size distribution. The meso size range of 2-50 nm is attractive for producing size-confined structures such as quantum dots or nanowires. Some of the early examples involved metal-organic chemical vapor deposition to grow GaAs and InP nanocrystals by Srdanov et al. and Agger et al. respectively. Both groups synthesized siliceous MCM-41 structures, which were then loaded into MOCVD reactors for growth. For GaAs nanocrystals, optical investigations showed a luminescence shift of 0.1 eV attributed to quantum confinement. In case of InP nanocrystals, NMR, XRD, TEM and optical measurements were used to show quantum confinement. CdS nanoclusters have been absorbed into the channels of MCM-41 by functionalisation of thiol groups. In\(\text{}_2\text{O}_3\) nanoparticles were formed in the irregular
mesoporous silica material and novel photoluminescence properties were observed.\(^8\) ZnO nanoparticles were confined to the pores of MCM-41 by functionalising the pores of MCM-41 with ethylenediamine groups and using it as an absorbent for \(\text{Zn}^{2+}\) and subsequent calcinations of MCM-41 in air.\(^9\) ZnS nanoparticles were confined to the pores of MCM-41\(^10\) and SiGe QDs were prepared in an ordered mesoporous silica film coated on Si substrate.\(^11\) The pores of various mesoporous materials like MCM-41, MCM-48, SBA-15 have been filled with polymers,\(^12\) metal nanoparticles like Au,\(^13\) Ag,\(^14\) Pt,\(^15\) Pd,\(^16\) Co,\(^17\) metal oxides like \(\text{TiO}_2,\)\(^18\) \(\text{Fe}_2\text{O}_3,\)\(^19\) and semiconductors like PbS,\(^20\) by either simple solution impregnation or vapor infiltration processes. Leon et al. developed a slight modification of the MOCVD method to make germanium nanocrystals.\(^21\) They used an elimination reaction of digermane (\(\text{Ge}_6\text{H}_6\)) with the hydroxyls of siliceous mesoporous materials to synthesise quantum-confined germanium. A detailed transmission electron microscopy (TEM) analysis found that the germanium nanocrystals were inside the mesopores. Later, Ozin and co-workers improved upon this scheme to produce size confined silicon nanocrystals.\(^22\) More recently, Holmes et al. reported the use of a novel supercritical fluid solution–phase approach to produce silicon nanowires within the pores of mesoporous silica.\(^23\) The synthesis of nanocrystalline GaN in the pores of an aerogel matrix is reported by Goodwin et al.\(^24\) GaN nanoparticles with diameters of 10-40 nm were synthesised in a silica aerogel host matrix by pyrolysis of dimeric dimethylgallium-diphenylamide (\(\text{Me}_2\text{GaNPh}_2\))\(^2\). The microscopic structure and nanometre scale pore sizes of the aerogel matrix limited the growth of GaN material and led to the development of nanocrystalline GaN in the aerogel. Similarly, controlled oxidation of bulk GaN powders inside xerogel cavities led to the formation of composites of GaN nanoparticles embedded in a silicate matrix.\(^25\) It is generally difficult to grow GaN nanostructures inside MCM-41 employing the conventional CVD process, since the formation of GaN requires temperatures above 1000°C using the classical precursors such as trimethylgallium and a very large excess of ammonia.\(^26\) However, tailored single molecule precursors\(^27\) have been reported in the literature, allowing the growth of crystalline GaN at reasonably low temperatures. Utilising the concept of colloidal chemistry and using a single molecule precursor approach Manz et al.\(^28\) and Micic et al. synthesized the colloidal GaN quantum dots.\(^29\) Winkler et al. used a slightly different approach to produce quantum confined GaN in MCM-41.\(^30\) Instead of reacting calcined MCM-41 powders with gas-phase molecules at high temperatures, in this approach pores of MCM-41 were loaded with an inorganic single molecule precursor triazido(trimethylamine)gallium. The sample was then heated to 500°C under ammonia to
decompose the complex and form GaN. By controlling loading concentrations and washing procedures, it was possible to control the amount of GaN deposited on the surface relative to that in the mesopores. While all samples showed a blue shifted excitation onset along with a bulk excitation, extensive washing reduced the signal of bulk GaN. Estimates of the band gap in reference to the 2.7 nm pore size gave good agreement with experimental evidence, suggesting that the final composites had GaN inside the pores of MCM-41.\textsuperscript{31} Recently, using the single molecule organometallic azide precursor, (N\textsubscript{3})\textsubscript{2}Ga[(CH\textsubscript{2})\textsubscript{3}N(CH\textsubscript{3})\textsubscript{2}]
Bisazedo(dimethylaminopropyl)gallium (Baziga) controlled growth of GaN nanopillars by MOCVD was reported.\textsuperscript{32} The synthesis of nanosized GaN particles by chemical vapour infiltration method has some advantages compared to the typical solution-phase method. The influence of solvent can be completely avoided in the gas phase route and an advantage of using organometallic molecular precursors is that they tend to cleanly generate the desired material with a controlled growth rate at relatively low growth temperatures, which are the superior characteristics of MOCVD precursors.

In this chapter, the single molecule precursor approach (using (N\textsubscript{3})\textsubscript{2}Ga[(CH\textsubscript{2})\textsubscript{3}N(CH\textsubscript{3})\textsubscript{2}]
Bisazedo(dimethylaminopropyl)gallium (Baziga) as precursor) for the synthesis of GaN particles using MCM-41 and SBA-15 as host templates by chemical vapor infiltration (CVI) are presented.
3.2 Experimental

3.2.1 Synthesis and characterisation of mesoporous solids (MCM-41 and SBA-15)

Chemicals
All the chemicals used for the synthesis were of analytical grade. The following chemicals were used for the synthesis of mesoporous host material MCM-41. (a) Hexadecyltrimethylammonium bromide, (HDTAB; Aldrich) \( \text{C}_{16}\text{H}_{33}[\text{N(CH}_3\text{)}_3]\text{Br} \) (b) Tetramethoxysilane, (TMOS; Fluka) \( \text{Si(OCH}_3\text{)}_4 \), (c) 1,2-Diamineethane, (E-Merck) \( \text{NH}_2\text{CH}_2\text{CH}_2(\text{NH}_2) \), (d) Boric acid, (J. T. Baker), \( \text{B(OH)}_3 \), (e) Pure distilled \( \text{H}_2\text{O} \) (Millipore)

Procedure
The mesoporous silica host MCM-41 was synthesised according to the procedure reported in the literature, using \( \text{C}_{16}\text{H}_{33}[\text{N(CH}_3\text{)}_3]\text{Br} \) (Hexadecyltrimethylammonium bromide) (HDTAB) as template and \( \text{Si(OCH}_3\text{)}_4 \) (Tetramethoxysilane) (TMOS) as the silica source. A typical synthesis method is as follows. HDTAB, (10.98 g, 0.03 mol) was added to a clear solution (under magnetic stirring) containing 30 ml of 2 molar 1, 2-Diamineethane \( [\text{EN} = \text{NH}_2\text{CH}_2\text{CH}_2(\text{NH}_2)] \) (ethylenediamine) and distilled \( \text{H}_2\text{O} \). Tetramethoxysilane (4.45 ml, 0.03 mol) was then slowly added drop wise using a syringe under Ar atmosphere and the reaction mixture became like a viscous gel. Stirring was continued for 10 min after the addition of TMOS and finally 20 ml of \( \text{B(OH)}_3 \) (boric acid) solution was added. The reaction mixture gel was stirred for 30 min at room temperature. The final ratio was 1.0 (HDTAB) : 2 (EN) : 1 (TMOS) : 0.043 (B (OH)_3) : 74 (H_2O) (molar ratio). The homogeneous silica mixture was filled in a polypropylene (Nalgene) bottle and kept in an oven at 95°C without stirring for 14 days. The host material MCM-41 was obtained by removing the mother liquid and intensively washing with distilled \( \text{H}_2\text{O} \) and ethanol. The resulting MCM-41 (as-synthesised MCM-41) sample was subjected to heat treatment (calcinations) in an oven under air.

The mesoporous silica materials SBA-15 were synthesised as reported in the literature at the Department of Chemistry, Korea Advanced Institute of Science and Technology (KAIST) Taejon, Korea. Calcinations and characterisation of SBA-15 was carried out at Lehrstuhl für Anorganische Chemie II, Ruhr-Universität-Bochum, Germany. The calcined SBA-15 was characterised by X-ray diffractometry analysis (XRD), Transmission electron microscopy (TEM),
and N₂ sorption measurements (BET). The fully characterised SBA-15 was used for the CVI experiments.

### 3.2.2 Calcinations of MCM-41

The as-synthesised MCM-41 was subjected to calcinations under air in a programmable furnace in order to expel the templating species from the mesoporous material. The calcinations were performed under mild temperature conditions (slow heating process) to avoid alteration of the silica framework. The temperature program used for the calcinations of as synthesised MCM-41 is shown in Table 3.1.

**Table 3.1 Temperature program used for the calcinations of as-synthesised MCM-41.**

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Room temperature (20°C) - 125</td>
<td>180</td>
</tr>
<tr>
<td>125</td>
<td>180</td>
</tr>
<tr>
<td>125 - 200</td>
<td>180</td>
</tr>
<tr>
<td>200</td>
<td>360</td>
</tr>
<tr>
<td>200 - 600</td>
<td>600</td>
</tr>
<tr>
<td>600</td>
<td>900</td>
</tr>
<tr>
<td>600 - 125</td>
<td>600</td>
</tr>
<tr>
<td>125 – Room temperature (20°C)</td>
<td>300</td>
</tr>
</tbody>
</table>

### 3.2.3 CVI reactor set-up

Fig.3.1 shows the schematic diagram of the horizontal hot-wall CVD reactor used for CVI experiments. It consists of (a) turbomolecular pump, (b) rotary pump, (c) throttle valve to control the pressure (d) shut off valve, (e) and (g) pressure gauge heads, (f) liquid nitrogen cooled trap, (h) horizontal quartz tube reactor with two shallow quartz boats, (i) thermostated air bath to heat the precursors, (j) precursor vaporiser with an inlet and outlet, and (k) mass flow controllers.
Chapter 3

3.2.4 CVI experiments

Chemical vapor infiltration experiments were carried out using a horizontal CVD reactor (Fig. 3.1). A typical CVI experiment is as follows. About 0.5 g of calcined mesoporous host materials (MCM-41 or SBA-15) were placed inside the reactor in a quartz boat and dried at 300°C for 2 hours under dynamic vacuum ($10^{-3}$ Torr) in order to remove physically absorbed water on the silica surface. The temperature of the precursor vaporiser was raised to 90°C. Vapor infiltration of the precursor onto the mesoporous hosts were carried out at different temperatures (see table 3.2) under reduced pressure. After the infiltration, the vaporiser was closed and the temperature of the reactor was raised slowly at 10°C/min. Subsequently, the mesoporous host materials were pyrolysed under flowing NH$_3$ (50 sccm) for 2 hours at
different temperatures. The reactor temperature was reduced to room temperature and the mesoporous host materials were recovered from the reactor and characterised by various characterisation techniques.

### Table 3.2 CVI experimental conditions.

<table>
<thead>
<tr>
<th>Host material (Samples)</th>
<th>Vaporiser temperature °C</th>
<th>Infiltration temperature °C</th>
<th>Growth temperature °C</th>
<th>Time (min)</th>
<th>NH₃ flow (sccm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GaN@ MCM-41</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>90</td>
<td>750</td>
<td>750</td>
<td>120</td>
<td>50</td>
</tr>
<tr>
<td>B</td>
<td>90</td>
<td>650</td>
<td>700</td>
<td>120</td>
<td>50</td>
</tr>
<tr>
<td>C</td>
<td>90</td>
<td>550</td>
<td>700</td>
<td>120</td>
<td>50</td>
</tr>
<tr>
<td>D</td>
<td>90</td>
<td>500</td>
<td>700</td>
<td>120</td>
<td>50</td>
</tr>
<tr>
<td>E</td>
<td>90</td>
<td>200</td>
<td>700</td>
<td>120</td>
<td>50</td>
</tr>
<tr>
<td>GaN@ SBA-15</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>F</td>
<td>90</td>
<td>200</td>
<td>700</td>
<td>120</td>
<td>50</td>
</tr>
</tbody>
</table>

### 3.2.5 Characterisation of empty and loaded mesoporous solids

The as-synthesised, calcined, and loaded (GaN @ MCM-41 and GaN @ SBA-15) mesoporous solids were characterised by various characterisation techniques such as low angle X-ray diffraction (XRD) analysis ($2\theta = 1 \text{ – } 10^\circ$), high angle x-ray diffraction analysis ($2\theta = 20 \text{ – } 70^\circ$), thermogravimetric and differential thermal analysis (TG/DTA), transmission electron microscopy (TEM), high resolution transmission electron microscopy (HRTEM), selected area electron diffraction (SAED) analysis, N₂-sorption analysis (BET surface area and pore size distribution analysis, BJH), and elemental analysis.
3.3 Results and Discussion

3.3.1 X-ray diffraction analysis

3.3.1.1 X-ray diffraction analysis of empty MCM-41 and empty SBA-15

High quality MCM-41 material has unidirectional pore channels, which are arranged in a regular hexagonal pattern (Fig.3.2) in contrast to other mesoporous materials, which generally have irregular spaced pores. The silicate wall however, has no long-range order, in the sense of a crystalline material, and can be considered as amorphous. Nevertheless, the low angle x-ray diffraction pattern of MCM-41 shows up to 5 peaks depending on the regularity of the material. These reflections, which have been indexed on the basis of a hexagonal symmetry results from the hexagonal periodic arrangement of the pore channels in MCM-41.

\[ a_0 = 2 \frac{d_{(100)}}{\sqrt{3}} \]

Fig. 3.2 Schematic drawing of the pore structure of MCM-41 including the 2-dimensional unit cell.

Glinka et al.,\textsuperscript{35} performed small angle neutron scattering experiments on calcined MCM-41 and these results confirmed that the low angle x-ray diffraction peaks of MCM-41 originate from the periodic arrangement of pore channels and are not due to any periodicity in the silicate framework of MCM-41. Gies et al. reported that in case of MCM-41 type materials, the increase or decrease in the X-ray peak intensity is not necessary an indication of a change in the regularity of the pore channel arrangement.\textsuperscript{36} The generation of X-ray diffraction peaks results from the difference in the scattering power (or scattering contrast) between the two building blocks (silicate wall and pore channel) of the MCM-41 material.
As-synthesised and calcined MCM-41 were characterised by low angle x-ray diffraction (Fig. 3.3 and Fig. 3.4). X-ray powder diffraction diagrams showed five peaks and can be indexed based on the hexagonal symmetry. This symmetry is due to the pore channels of uniform size arranged in a regular hexagonal pattern. The $d$ values in the diffraction pattern therefore are related to the pore diameter. The hexagonal cell parameter $a_0$ has been calculated based on the indexed powder diffraction pattern and $a_0$ value equals to the sum of the pore diameter and thickness of the silicate wall. It was demonstrated that the alkyl chain length of the surfactant forming the micelle determines the pore diameter of the mesopores of MCM-41.\textsuperscript{37} In case of MCM-41 materials where HDTAB was used as a surfactant, the normal $d$ value is around 4 nm.\textsuperscript{38}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig3_3.png}
\caption{Low angle XRD analysis of as-synthesised MCM-41 with hexagonal indices. The inset shows the clear (210) and (300) reflections.}
\end{figure}

XRD patterns of as-synthesised and calcined MCM-41 showed 5 peaks indicative of high quality material with channel like pores which are arranged in a hexagonal honey comb pattern with a high degree of regularity. The $d$ value of the (100) reflection of as synthesised MCM-41 is 4.18 nm leading to a lattice constant $a_0$ (as synth) = 4.83 nm.

In case of calcined MCM-41, the $d$ value of (100) reflection is 4.11 nm and the corresponding lattice constant $a_0 = 4.74$ nm. Due to slow calcinations process the XRD peaks (100) reflections are identical in both as synthesised and calcined MCM-41.
Fig. 3.4 Low angle XRD analysis of calcined MCM-41 with hexagonal indices. The inset shows the clear (210) and (300) reflections.

Table 3.3 Structural parameters of as synthesised and calcined MCM-41.

<table>
<thead>
<tr>
<th>As synthesised MCM-41</th>
<th>Calcined MCM-41</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>hkl</strong></td>
<td><strong>d (nm)</strong></td>
</tr>
<tr>
<td>100</td>
<td>4.18</td>
</tr>
<tr>
<td>110</td>
<td>2.40</td>
</tr>
<tr>
<td>200</td>
<td>2.08</td>
</tr>
<tr>
<td>210</td>
<td>1.57</td>
</tr>
<tr>
<td>300</td>
<td>1.38</td>
</tr>
<tr>
<td>100</td>
<td>4.11</td>
</tr>
<tr>
<td>110</td>
<td>2.36</td>
</tr>
<tr>
<td>200</td>
<td>2.04</td>
</tr>
<tr>
<td>210</td>
<td>1.54</td>
</tr>
<tr>
<td>300</td>
<td>1.36</td>
</tr>
</tbody>
</table>

However, the XRD peaks of the calcined MCM-41 have changed with respect to two parameters. The *d* values are smaller due to slightly reduced lattice parameters. The most
significant change is the increase in the XRD peak intensity in case of calcined MCM-41 compared to as-synthesised MCM-41.

X-ray diffraction pattern (low angle) of SBA-15 showed a well-resolved pattern with a prominent peak at 0.8° and two weak peaks at 1.6 and 1.8° 2 theta are observed that match very well with pattern reported in the literature (Fig. 3.5). The XRD peaks can be indexed to a hexagonal lattice with a \( d \) (100) spacing of 98.48 Å, corresponding to a large unit cell parameter \( a_0 = 113.71 \) Å.

![SBA-15 XRD pattern](image)

*Fig. 3.5 Low angle X-ray diffraction analysis of SBA-15 showing the characteristic peaks.*

<table>
<thead>
<tr>
<th>( hkl )</th>
<th>( d ) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>9.848</td>
</tr>
<tr>
<td>110</td>
<td>5.604</td>
</tr>
<tr>
<td>200</td>
<td>4.811</td>
</tr>
</tbody>
</table>

*Table 3.4 Structural parameters of calcined SBA-15.*

3.3.1.2 X-ray diffraction analysis of GaN @ MCM-41 and GaN @ SBA-15
As a representative example, the low angle XRD pattern for the empty MCM-41 and GaN filled MCM-41 (sample E) is compared in Fig. 3.6. It is observed that the highly ordered hexagonal pore structure of MCM–41 is till intact although the intensities of the characteristic XRD reflections of MCM–41 are reduced for sample E, i.e., only one predominant peak in the low angle 2θ region was observed and the other two were diminished as compared to the empty MCM-41. This can be attributed to the pore filling which reduces the scattering contrast between the pores and the wall of the mesoporous material (i.e., the material is incorporated into the pores).

![Fig. 3.6 Low angle X-ray diffraction analysis of empty MCM-41 and GaN @ MCM-41 (sample E).](image-url)
Fig. 3.7 High angle X-ray diffraction analysis of GaN @ MCM-41 (Sample E).

Additionally, the peaks of GaN @ MCM-41 (sample A - D) are shifted to higher angles (Fig. 3.8 and table 3.5) and this may be attributed to contraction of framework during the treatment of the host material. In Fig.3.7, the amorphous nature of the host silicate material give rise to very broad reflections centred around $2\theta = 22-28^\circ$. The broad diffraction peaks in the XRD pattern corresponds to hexagonal GaN structure, which are marked by their indices in Fig.3.7. Using Debye-Scherer formula the particle diameter was determined and it was found to be around 25 nm. This indicates that GaN particles were also grown outside the MCM-41, which was confirmed by TEM/EDX analysis.
Fig. 3.8 Low angle X-ray diffraction analyses of GaN @ MCM-41 prepared at different conditions.

Fig. 3.9 shows the high angle XRD patterns of GaN @ MCM-41 prepared by different conditions. In Fig. 3.9 a very broad XRD reflection peak around 26° arises from the diffraction of the amorphous wall of MCM-41. GaN loaded MCM-41 (sample A and B) show sharp peaks that can be indexed as hexagonal phase of GaN with lattice constants comparable to the values of bulk GaN. The XRD peaks are relatively broad due to the small size of the particles. But in case of samples (C and D) the XRD peaks are relatively broad compared to the samples A and B indicating that very small particles of GaN are formed which cannot be detected by XRD. TEM/EDX investigations of samples C and D confirmed these results.
Fig. 3.9 High angle X-ray diffraction analyses of GaN @ MCM-41 annealed at different temperatures.

In case of GaN @ SBA-15 (Fig. 3.10), in the small angle region the characteristic reflections (three) of SBA-15 are detected with decreased intensity (compared to empty SBA-15, Fig. 3.5). This shows that, the ordered pore structure of host silica material SBA-15 is maintained during the infiltration of the precursor and the formation of GaN particles.

Fig. 3.10 Low angle X-ray diffraction analysis of GaN @ SBA-15.
Similar to GaN @ MCM-41 samples relatively weak visible XRD reflections of GaN were observed in the wide-angle XRD pattern of GaN @ SBA-15 (Fig. 3.11). These results confirm the formation of GaN particles and are most probably located outside the pore system of the host structure SBA-15. TEM/EDX investigations of GaN @ SBA-15 supported these results.

![Fig. 3.11 High angle X-ray diffraction analysis of GaN @ SBA-15.](image)

**Table 3.5 Structural parameters of GaN @ MCM-41 and GaN @ SBA-15.**

<table>
<thead>
<tr>
<th>hkl</th>
<th>Sample A</th>
<th>Sample B</th>
<th>Sample C</th>
<th>Sample D</th>
<th>Sample E</th>
<th>Sample F</th>
</tr>
</thead>
<tbody>
<tr>
<td>110</td>
<td>2.221</td>
<td>2.189</td>
<td>2.193</td>
<td>2.193</td>
<td>2.203</td>
<td>5.334</td>
</tr>
<tr>
<td>200</td>
<td>1.928</td>
<td>1.919</td>
<td>1.930</td>
<td>1.908</td>
<td>1.928</td>
<td>4.572</td>
</tr>
</tbody>
</table>
3.3.2 Thermogravimetric analysis

Thermogravimetric analysis (TG/DTA) of the as-synthesised MCM-41 material was performed in an atmosphere of air. After the sample was dried in air, the weight loss observed was around 1.0%. Three distinct stages were observed in the thermogram of the as-synthesised sample. In the first stage, molecular water desorbs at 25-150°C. The second stage is related to the decomposition and combustion of surfactant species at 150-400°C. During the third stage, from 400 up to 600 °C, silanol group condensate to form siloxane bonds and water molecules are desorbed. The overall weight loss of the as-synthesised MCM-41 material was 31.1%. The TGA curve as well as the information from the thermogravimetric analysis coincides very well with the reported results.

3.3.3 Nitrogen sorption analysis

Nitrogen sorption experiment on mesoporous materials like MCM-41 is an efficient tool for providing information about the surface area (BET surface area), pore volume and pore size distribution. The BET (Brunauer-Emmett-Teller) surface area, of the empty MCM-41 was calculated using the standard BET method. The pore size distribution was calculated from BJH (Barrett-Joyner-Halender) theory on the basis of desorption data from the N$_2$ sorption studies. The pore size was estimated as the value corresponding to the maximum of the BJH pore-size distribution. The parameters that are calculated form the N$_2$ sorption studies of empty MCM-41 are listed in Table 3.6. MCM-41 was obtained as white high quality host material characterized by a very narrow pore-size distribution of 2.7 nm obtained from BJH theory, a large BET surface area of 983 m$^2$/g. The nitrogen sorption isotherms for calcined empty MCM-41 is shown in Fig. 3.12. The isotherms are of type IV classification, which is typical of adsorption of mesoporous materials. The decrease in BET surface area of GaN @MCM-41 (Sample E) (632 m$^2$/g) in comparison with that of empty MCM-41 (983 m$^2$/g), as well as the decrease in pore volume (26 %) of GaN @ MCM-41 (Sample E) with respect to empty MCM-41, are consistent with pore filling of the MCM-41 matrix with GaN. Similarly, in case of GaN @ SBA-15 (Sample F) the BET surface area was reduced to 540m$^2$/g compared to empty SBA-15 (730m$^2$/g). These results suggest that majority of the nanometre scaled pore space /void space of the host material (MCM-41 or SBA-15) is open and a small portion of the channels may be blocked by the growth of GaN nanostructures. This was confirmed by TEM investigations.
Table 3.6 Nitrogen sorption analysis of empty MCM-41 and empty SBA-15.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Empty MCM-41</th>
<th>Empty SBA-15</th>
</tr>
</thead>
<tbody>
<tr>
<td>BET surface area</td>
<td>983 m$^2$/g</td>
<td>730 m$^2$/g</td>
</tr>
<tr>
<td>Pore volume</td>
<td>0.87 cm$^3$/g</td>
<td>0.81 cm$^3$/g</td>
</tr>
<tr>
<td>Pore size distribution (BJH)</td>
<td>2.7 nm</td>
<td>6.2 nm</td>
</tr>
</tbody>
</table>

### 3.3.4 Elemental analysis

The loading of MCM-41 and SBA-15 by GaN was confirmed by elemental analysis such as inductively coupled plasma (ICP) analysis, atomic absorption spectroscopy (AAS) and C, H, N analysis, revealing 9.45 wt. % of Ga for GaN @ MCM-41 (sample E). The molar ratio Ga:N was 0.8:1. From C, H, N and AAS analysis, the following elemental composition (in wt %) was obtained. Si 29, Ga 9.45, B 0.59, N 2.57, H 3, C 0.69 ($\Sigma = 45.3\%$). In case of GaN @ SBA-15 the following elemental composition was obtained. Si 27.2, Ga 8.3, N 1.6, C 0.5, H 1.66 ($\Sigma = 39.26\%$). The remainder of the material could be attributed to oxygen.
3.3.5 NMR spectroscopy

The solid-state $^{71}$Ga-NMR spectra of GaN @ MCM-41 was recorded and compared with a standard bulk sample of GaN. A typical quadrupolar resonance of crystalline bulk was absent for GaN @ MCM-41. However, two broad resonances at 145 ppm and 170 ppm were observed which could be attributed to small GaN particles formed without an extended crystalline order as compared with the bulk phase.

3.3.6 Transmission electron microscopy

3.3.6.1 Transmission electron microscopy of empty MCM-41 and empty SBA-15

Transmission electron microscopy (TEM) and selected area electron diffraction (SAED) pattern analysis are two important and key methods for the characterisation of the composites and porous materials and it is helpful in identification of the phase obtained (hexagonal MCM-41). A detailed TEM investigation on MCM-41 type material was reported in the literature. Fig. 3.12 shows high-resolution transmission electron microscopy (HRTEM) images of calcined MCM-41. In Fig. 3.13, the TEM images (a) and (b) show the pore channels of MCM-41 with the incident electron beam perpendicular to the pore channels. Fig. 3.13 (c and (d) provide another view of MCM-41, which show the characteristic hexagonal pore channels of MCM-41 and these TEM images were taken with the incident electron beam parallel to the direction of the pore channels of MCM-41.

Transmission electron microscopy (TEM) analysis (Fig. 3.14) of empty SBA-15 showed well-ordered hexagonal arrays of mesopores (ID channels) and confirm that SBA-15 has a 2D hexagonal structure. The distance between the mesopores is estimated to be 6.2 nm, which is in good agreement with that determined from the XRD data. Figures 3.14 (a), (b), (c), and (d) show TEM images with the incident electron beam perpendicular to the direction of main channels of calcined SBA-15. Fig. 3.14 (e) shows the TEM image with the incident electron beam parallel to the direction of the channels and these channels exhibit well ordered hexagonal structures similar to that of MCM-41. However, the pore diameter is about 6.2 nm, which is much larger than those of MCM-41 (2.7 nm).
Fig. 3.13 Representative TEM images of empty MCM-41. Images (a) and (b) were taken perpendicular to the pore channels of MCM-41, and images (c) and (d) were taken parallel to the pore channels of MCM-41.
Fig. 3.14 Representative TEM images of empty SBA-15. The image was taken parallel to the pore channels.
3.3.6.2 Transmission electron microscopy of GaN @ MCM-41 and GaN @ SBA-15

Fig. 3.15 (a), (b), and (c) show the TEM images of GaN @ MCM-41 and Fig. 3.16 (a) to (d) show the TEM images of GaN @ SBA-15 respectively. A typical honeycomb structure of MCM-41 was observed in the TEM analysis [Fig 3.15 (c)]. The ordered hexagonal mesopore structure of MCM-41 was evidently maintained at 700°C [Fig. 3.15 (a)]. The walls appeared slightly thicker and showed greater electron contrast than the empty MCM-41. It reveals that the hexagonally ordered mesostructure of the host material MCM-41 was unaffected by loading GaN onto it. This indicates that the grafting technique by chemical vapor infiltration does not cause significant deterioration of the MCM-41 framework.

Fig. 3.15 TEM images of GaN @ MCM-41. (a) TEM image with clean surface; (b) and (c) TEM images showing the presence of GaN particles on the outer surface; Inset: SAED patterns.
Fig. 3.15 (b) shows the TEM image of GaN @ MCM-41 (sample E) and the inset shows the SAED pattern. The SAED pattern indicates a weak diffraction rings combined with a broad diffuse background of host MCM-41. Calculation of $d$-spacings and the analysis of electron diffraction rings indicate the hexagonal phase of GaN, which is in agreement with the XRD data. Fig. 3.15 (c) shows TEM image of a representative region where GaN particles were grown outside the MCM-41 surface, causing broad reflections in the XRD pattern (Fig. 3.7).

Fig. 3.16 shows the TEM images of GaN @ SBA-15. The highly ordered pore structure of SBA-15 is preserved during the formation of GaN nanostructures [Fig. 3.16 (a) and (b)]. As shown in TEM image 3.16 (c) GaN particles appear as dark objects and are homogeneously distributed in the host silica material. As in the case of GaN @ MCM-41, GaN particles were grown outside the pore surface of host material SBA-15 [Fig. 3.16 (d)]. EDX analyses were performed to investigate the composition of the composites and mainly Ga, N, Si, O, C peaks are obtained along with Cu (from the grid). Fig. 3.17 (a) and (b) show the EDX analysis of GaN @ MCM-41 and GaN @ SBA-15 respectively.
3.3.6.3 EDX analysis

Fig. 3.17 EDX analyses of (a) GaN @ MCM-41 and (b) GaN @ SBA-15.
3.3.6.4 Transmission electron microscopy of freestanding GaN nanocrystals

In an attempt to isolate GaN nanocrystals from the host silicate matrices, the product (GaN @ MCM-41) was treated carefully with 20% HF acid, which dissolved the host silicate matrix and gave rise to a dark grey colored powder, which was washed repeatedly with ethanol. The resulting powder suspension was centrifuged to obtain the nanocrystals in the powder form. TEM images of unsupported GaN nanocrystals are shown in Fig. 3.18. It is found that the diameter of the nanocrystals varies from 5 nm to 20 nm. In general, freestanding nanocrystals obtained tend to partially aggregate possibly to reduce the surface free energy which is observed for the nanocrystals.

![TEM images of freestanding GaN nanocrystals.](image)

Fig. 3.18 TEM images of freestanding GaN nanocrystals.
3.3.6.5 Selected area electron diffraction

Selected area electron diffraction (SAED) analysis of freestanding GaN nanocrystals showed (100), (101), (102), (110), and (112) diffraction rings (Fig. 3.19). The diffuse nature of the rings is a simple manifestation of the crystal shape effect due to the small size of the particles. Analysis of the diffraction pattern and the calculation of the $d$-spacings confirmed the hexagonal phase of GaN nanocrystals.

![Selected area electron diffraction (SAED) pattern of freestanding GaN nanocrystals.](image)

*Fig. 3.19 Selected area electron diffraction (SAED) pattern of freestanding GaN nanocrystals.*
3.4 Summary and Conclusions

Mesoporous silica host materials MCM-41 and SBA-15 were synthesised and characterised by different characterisation techniques such as X-ray diffraction, N$_2$-sorption analysis, and transmission electron spectroscopy. These host materials were subsequently used for the synthesis of GaN nanoparticles by chemical vapor infiltration technique. Organometallic azide based compound $(\text{N}_3)_2\text{Ga}[\text{(CH}_2\text{)_2N(CH}_3\text{)_2}] \quad \text{Bisazido(dimethylaminopropyl)gallium (BAZIGA)}$ was used as a precursor for the growth of GaN nanoparticles. The ordered hexagonal structures of the host silica materials MCM-41 and SBA-15 were maintained even after loading of the precursor and subsequent heat treatment and the growth of GaN nanostructures, which was verified by TEM and XRD. A combined result of X-ray diffraction analysis, N2-sorption analysis, transmission electron microscopy, selected area electron diffraction analysis, and energy dispersive analysis of X-rays show the growth of GaN nanoparticles inside/outside the silicate host materials and does not affect the mesoporous silica framework. The combined matrix assisted and chemical vapour infiltration process can be extended to other materials as well as to other multidimensional structures by using the appropriate host architectures.
3.5 References

Chapter 4

4 Confinement of CdSe nanoparticles inside MCM-41

Abstract

In this chapter, the synthesis and the characterisation of CdSe nanoparticles confined to the pores of MCM-41 (CdSe @ MCM-41) are presented. The combination of wet impregnation technique and the pyrolysis of organometallic precursors in a hot medium is a viable method for the synthesis of CdSe nanoparticles inside the pores of MCM-41. Nitrogen sorption measurements of CdSe loaded MCM-41 (CdSe @ MCM-41) revealed the reduction in BET surface area, and the pore volume, which indicates the decoration/coating of the inner surface of the silica walls. The broad reflections in the XRD pattern of CdSe @ MCM-41 confirmed the formation of CdSe nanoparticles. The combined results of TEM analysis and electron diffraction pattern analysis showed that the mesoporous host structure remained intact after the growth of nanoparticles inside the pores of MCM-41. The composition was analysed by XPS and EDX analysis. The optical characterisation of the composite CdSe @ MCM-41 showed the blue shifted absorption and broad photoluminescence, which indicates the quantum confinement of CdSe particles, which are formed inside the pores of MCM-41.
4.1 Introduction

4.1.1 CdSe nanostructures

The controlled organisation of inorganic materials into multidimensional arrays is the foundation for both logic and memory devices, as well as nonlinear optical and sensing devices. Many of these devices are currently fabricated using lithographic patterning processes that have progressively developed towards greater integration densities and small sizes. At scales below 100 nm, ion and electron beam lithography becomes prohibitively expensive and time consuming, and more importantly, at these scales quantum effects fundamentally change the properties of devices. Currently there are strong desire and requirement to develop nanoscale architectures and these developments will require alternative fabrication methods. Arrays of nanoparticles formed by non-conventional methods are being explored for use as viable alternatives to standard lithography patterned devices. The function of these devices will be based on phenomena such as coulomb charging, inter-dot quantum tunnelling and other coherent properties derived from the quantum size effects.

Nanoscale templates for constrained synthesis, in-situ deposition, or direct patterning of nanometre scale inorganic arrays are being developed using both artificial and natural materials. Mesoporous materials such as MCM-41, SBA-15, and microphase separated block co-polymers and hexagonally close packed spheres have been used for nanoscale fabrication. Natural materials such as DNA, proteins, and some other biological molecules have been used as templates for the fabrication of nanoscale structures.

Colloidal inorganic nanocrystals are of great interest for both fundamental research and technical applications, due to their strong size and shape dependent properties and excellent chemical processibility. Among the semiconductor nano scale systems, colloidal CdSe nanocrystals are probably the most extensively investigated nanoscale systems. This is largely due to the well-established, very successful preparation methods for good quality, highly efficient monodisperse CdSe nanocrystals. Control of nanocrystal shape is important in various applications such as solar cells, light emitting diodes and biological labelling. Recently, many research groups have demonstrated the systematic variation of the size and
shape of the CdSe nanocrystals leading to different size/shape controlled growth\textsuperscript{12} like rod, arrow, teardrop, tetrapod, and rice shaped CdSe nanocrystals.\textsuperscript{13} Organisation of nanoscale systems is an important objective and control over the spatial arrangement often leads to new materials with chemical, mechanical, optical and electronic properties distinctly different from those of their bulk component parts. Moreover, chemically directed assembly of nanoscale materials is often an attractive alternative compare to the conventional techniques such as vapour deposition or photo and electron beam lithographies. A few excellent examples of chemical routes to nanostructured materials and thin films are zeolite synthesis,\textsuperscript{14} porous membrane template synthesis,\textsuperscript{15} layer-by-layer inorganic,\textsuperscript{16} colloidal particle, and polymer polyelectrolyte assembly\textsuperscript{17} and microcontact printing.\textsuperscript{18} There are numerous chemical methods for synthesizing nanomaterials, including the templated synthesis of the desired material inside porous media. Many templates have emerged, such as micelles, block copolymers, porous alumina, polycarbonate membranes, zeolites, and mesoporous materials. MCM-41 is a mesoporous silica material possessing ordered channels arranged in a hexagonal lattice. In addition to its potential for large molecule separation and catalysis applications, this family of materials is attractive as host framework for the preparation of nanomaterials with unique dimensions. Under appropriate conditions, the pore diameters can be tuned with angstrom precision between 2 nm and 10 nm. As described in the previous chapter, many metal and semiconductor nanostructures have been incorporated inside the channels of MCM-41.

In this chapter, confinement of CdSe nanoparticles inside the channels of MCM-41 and its characterisation by different characterisation techniques is presented.
4.2 Experimental

4.2.1 Synthesis of CdSe @ MCM-41

Chemicals

All the chemicals used for the synthesis were of analytical grade. Following chemicals were used for the synthesis of CdSe @ MCM-41. (a) \((\text{CH}_3)_2\text{Cd}\) [(Synthesised and characterised in the laboratory using methyl magnesium iodide (~ 3M in diethyl ether)] (Fluka), and \(\text{CdCl}_2\) (Acros), (b) Selenium powder (Merck), (c) Tri-n-octylphosphineoxide (TOPO; Aldrich), (d) Tributylphosphine (TBP; Fluka), (e) Methanol (Fluka), (f) Toluene (Fluka).

Synthesis of the starting compound \((\text{CH}_3)_2\text{Cd}\)

The synthesis of \((\text{CH}_3)_2\text{Cd}\), which is one of the starting materials for the synthesis of CdSe nanoparticles, was taken up in the laboratory itself. The synthesis procedure reported by Anderson et al was slightly modified. All manipulations were conducted using a dry box under argon \((\text{O}_2, \text{H}_2\text{O} < 1\text{ppm})\), carefully dried solvents, a good ventilated hood and inert gas \((\text{Ar})\) techniques (schlenk-line).

About 88 ml (0.26mol) of methyl magnesium iodide solution (~ 3M in diethyl ether) was taken in 250 ml flask and cooled under ice and 20.165 g (0.11mol) of \(\text{CdCl}_2\) was added under flushing argon with vigorous stirring. The whole mixture was stirred for 30 minutes. The ether solution of \((\text{CH}_3)_2\text{Cd}\) was filtered to a distillation flask and was subjected to fractionation. The first fraction coming over at 35°C was ether. Distillation was further continued at 110°C and a colourless liquid thus collected was distilled further for two more times to remove the excess of ether left behind. The product was then characterised by NMR and it was observed that traces of ether were still present in the product \((\text{CH}_3)_2\text{Cd}\). The NMR integral showed 10.52% of ether in ~8g of \((\text{CH}_3)_2\text{Cd}\) obtained. The product was stored in a refrigerator in the glove box after being vacuum transferred.

Procedure

About 500mg of calcinated and characterised empty MCM-41 was dried in vacuum at 300°C for 24 hours and transferred to the glove box. Precursor solutions of Cd and Se were prepared according to the literature in the glove box by dissolving 0.8 g Se in 8 g of tributylphosphine (TBP). To this about 2 g of \((\text{CH}_3)_2\text{Cd}\) was added and the solution was diluted by 4:1 with TBP. About 1 ml of this stock solution was then diluted by 5 ml of TBP and the resulting
solution was mixed with 500mg of MCM-41 and stirred under vacuum for 3 days. About 24 g of tri-n-octylphosphineoxide (TOPO) was heated to 200 °C, dried and degassed for 30 min. The temperature was then raised to 325°C under approximately 1 atm. of Ar. When the temperature had stabilised, the heterogeneous suspension of precursor filled MCM-41 was injected into the reaction flask (TOPO) using a large bore size syringe. The temperature of the reaction flask was reduced to 300°C and the heating was continued for another 15 min. The solution was cooled to room temperature under Ar. Adding 50 ml of dry methanol then precipitated the solid solution. The precipitate was washed with methanol (20 ml) three to four times to remove the TOPO. The composite was separated from the solution by filtration and washed repeatedly with 20 ml of toluene and filtered and vacuum dried for an hour. The toluene solution obtained after washing the composite was characterised by UV-Vis absorption spectroscopy. A portion of the dried composite before washing with toluene was characterised by XRD. The washed CdSe @ MCM-41 composite was vacuum dried for an hour and was subjected to various characterisation techniques. The schematic illustration of this procedure is shown in Fig. 4.1.

![Schematic illustration of synthesis route for CdSe @ MCM-41](image)

*Fig. 4.1 Schematic illustration of synthesis route for CdSe @ MCM-41.*
4.2.2 Characterisation of CdSe @ MCM-41

There are two sets of composites. (a) CdSe/MCM-41 (sample 1, before the washing cycles) and CdSe @ MCM-41 (sample 2, after the washing cycles). The following characterisation techniques were used for the analysis of the samples.

1. Low angle x-ray diffraction analysis (2θ = 1 – 10°)
2. High angle x-ray diffraction analysis (2θ = 20 – 70°)
3. UV-Vis absorption spectroscopy
4. Nitrogen adsorption-desorption measurements (BET surface area)
5. Transmission electron microscopy (TEM)
6. EDX analysis
7. X-ray photoelectron spectroscopy (XPS)
8. Chemical analysis (AAS + ICP analysis)
9. UV-diffuse reflectance spectroscopy
10. Photoluminescence spectroscopy
4.3 Results and Discussion

4.3.1 X-ray diffraction analysis

To confirm the formation of CdSe nanoparticles, a portion of the precipitate CdSe/MCM-41 composite mixture (before the washing cycles) was characterised by XRD (Fig. 4.2). A small portion of the toluene solution used for the removal of TOPO capped CdSe particles formed on the outer surface of MCM-41 [see Fig. 4.5 (a) & (b)] was characterised by UV-Vis absorption spectroscopy [Fig. 4.2(b)]. The UV-Vis absorption spectrum not only confirms the formation of CdSe nanoparticles but also indicates an exciton peak position at 2.2eV, which corresponds with the average particle size of about 4 nm on the basis of a comparison with the spectra and calculations of reported results.20 This shows that these nanoparticles are likely to be formed outside the pore surface. The broad reflections in the XRD pattern [Fig. 4.2(a)] confirm the formation of hexagonal CdSe nanoparticles outside the MCM-41.

![Figure 4.2](image-url)

Fig. 4.2 (a) XRD pattern of CdSe/MCM-41 composites (before washing cycles) confirming the formation of hexagonal CdSe nanoparticles (b) Room temperature UV-Vis absorption spectrum of toluene solution obtained after washing with the CdSe/MCM-41 composites indicating the presence of CdSe nanoparticles.
However, from XRD analysis alone, it is not possible to confirm the formation of CdSe nanoparticles inside the pores of MCM-41 or on the outer surface. Fig. 4.3 and 4.4 show the comparison of XRD patterns of empty MCM-41 and CdSe @ MCM-41 (sample 2, after washing cycles) composites for the low-angle region ($2\theta = 1-10^\circ$) and the high angle region ($2\theta = 20-70^\circ$) respectively. It is observed that the highly ordered hexagonal pore structure of MCM-41 is still intact while the intensities of the characteristic XRD reflections of MCM-41 are reduced for CdSe @ MCM-41. This can be attributed to the pore filling of the host material, which reduces the scattering contrast between the pores and the walls of the molecular sieve. (Fig. 4.3) (Particles are confined to the pores of MCM-41). The reduced reflections (broadening of the XRD peaks) of CdSe in the XRD pattern of CdSe @ MCM-41 (Fig. 4.4) indicate that very small particles are formed inside the pores of MCM-41.

*Fig. 4.3 Low angle ($2\theta = 1-10^\circ$) X-ray diffraction pattern of empty MCM-41 and loaded CdSe @ MCM-41.*
Fig. 4.4 High angle ($2\theta = 20 - 70^\circ$) X-ray diffraction pattern of empty MCM-41 and loaded CdSe @ MCM-41.

4.3.2 Transmission electron microscopy

4.3.2.1 CdSe/MCM-41 composite (sample 1)

TEM investigation of unwashed CdSe/MCM-41 composite is as shown in Fig. 4.5 (a) and (b). TEM images showed that the highly ordered host material pore structure has been preserved during the semiconductor growth process. These TEM images were taken with the beam direction parallel to the pore direction and the ordered pore structure can be seen [Fig. 4.5(b)] despite many dark areas [Fig. 4.5(a)], which are surface deposits of CdSe particles that were grown outside the pore surface of MCM-41. These results support the X-ray diffraction data [Fig. 4.2(a)], which suggests existence of CdSe nanoparticles outside the pore surface of MCM-41.
4.3.2.2 CdSe @ MCM-41 (sample 2)

The TEM image of CdSe @ MCM-41 composite is shown in Fig. 4.6. It reveals that the hexagonally ordered mesostructure (Fig. 4.7 at higher magnification) of the host material MCM-41 was unaffected by the presence of CdSe inside the pores. This indicates that the grafting technique does not cause significant deterioration of the MCM-41 framework. The CdSe @ MCM-41 composite exhibits two types of electron diffraction pattern. The electron diffraction pattern shown in Fig. 4.8 is obtained by viewing the CdSe @ MCM-41 composite along the axis of hexagonal pores. This gives the [0001] pattern with a six-fold symmetry. When viewed normal to the hexagonal pore axis, a one dimensional diffraction pattern was obtained (Fig. 4.8). These electron diffraction patterns are in good agreement with the reported results and confirm that the ordered network of MCM-41 material was unaffected by the growth of CdSe particles inside the pores of MCM-41. In addition, CdSe @ MCM-41 composite exhibits stronger electron contrast than the empty MCM-41 and moreover the semiconductor-filled composite was much more stable under the electron beam than the empty MCM-41. These observations indicate that the walls of the silica host material have been coated with CdSe particles, and similar observations were reported for Fe clusters confined to the mesopores of MCM-41.21
Fig. 4.6 TEM image of a single CdSe @ MCM-41 composite particle.

Fig. 4.7 HRTEM image of a single CdSe @ MCM-41 particle showing the hexagonal network.
4.3.3 EDX analysis

We have attempted, but failed to directly observe the particles of CdSe in the channels of MCM-41 by TEM analysis. This is probably due to the fact that the contrast between the silica frame works of MCM-41 and CdSe particles is too weak, as in the case of Fe$_2$O$_3$ inside the mesoporous host. To confirm the presence of CdSe in the channels of MCM-41, EDX analysis was performed on the mesoporous region (where no CdSe particles are externally visible, Fig. 4.7). EDX analysis (Fig. 4.9) on these areas was carried out and produces strong Cd and Se signals indicating the confinement of CdSe nanoparticles inside the pores of MCM-41. In the EDX analysis, in addition to Cd and Se peaks, Si and O peaks (MCM-41) as well as Cu and C peaks (support grid) were detected. However, it is interesting to note that there are no detectable P peaks in the EDX spectrum. This result provides evidence that most of the TBP and TOPO have been removed from the CdSe @ MCM-41 composites by repeated washing cycles. From the EDX spectrum an approximate ratio of 1.1: 1.0 for Cd: Se, 16.5: 1.0 for Si: Cd and 26.4: 1.0 for Si: Se was determined, which are comparable with the results obtained from the chemical elemental analysis.

Fig. 4.8 Electron diffraction patterns of CdSe @ MCM-41 composite particle viewing along the axis of hexagonal pores and one-dimensional electron diffraction pattern of CdSe @ MCM-41 obtained by viewing normal to the hexagonal pore axis.
Fig. 4.9 EDX spectrum of CdSe @ MCM-41 composite (Fig. 4.7 where no CdSe particles are externally visible) showing the strong peaks of Cd and Se. The peaks from Si and O are from MCM-41 while Cu and C arise from the support grid.

### 4.3.4 Nitrogen sorption analysis

Nitrogen sorption experiments of CdSe @ MCM-41 provide the information on the pore characteristics of these materials. The parameters calculated from these data for the empty MCM-41 and loaded CdSe @ MCM-41 are listed in the Table 4.1. The decrease in BET surface areas, pore diameters and pore volumes indicate that CdSe clusters should be confined to the pores of MCM-41.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>CdSe @ MCM-41</th>
</tr>
</thead>
<tbody>
<tr>
<td>BET Surface area</td>
<td>240 m$^2$/g</td>
</tr>
<tr>
<td>Pore volume</td>
<td>0.275 cm$^3$/g</td>
</tr>
<tr>
<td>Decrease in pore volume (%)</td>
<td>32</td>
</tr>
</tbody>
</table>

Table 4.1 Nitrogen sorption analysis of CdSe @ MCM-41.
4.3.5 Chemical analysis

The loading of MCM-41 was confirmed by inductively coupled plasma (ICP) and atomic absorption spectroscopy (AAS) analysis, revealing 3.5 wt. % for Cd and 2.3 wt. % for Se. The molar ratio for Cd: Se was 1.07: 1.0. The presence of small trace of impurities like hydrocarbons in CdSe @ MCM-41 was confirmed by IR spectroscopy and elemental analysis by comparing the results with that of empty MCM-41 (Table 4.2).

Table 4.2 Chemical analysis of CdSe @ MCM-41.

<table>
<thead>
<tr>
<th>AAS + ICP analysis</th>
<th>Empty MCM-41</th>
<th>CdSe @ MCM-41</th>
</tr>
</thead>
<tbody>
<tr>
<td>Composition (wt %)</td>
<td>Si 62.3, C 0.3, H 0.5</td>
<td>Si 62.1, Cd 3.5, Se 2.3, C 2.1, H 2.0</td>
</tr>
</tbody>
</table>

4.3.6 X-ray photoelectron spectroscopy

XPS measurements have been carried out on CdSe @ MCM-41 composites to confirm the loading of the semiconductor material inside MCM-41. The survey spectra showed the presence of Cd and Se apart from Si, O from MCM-41 and C, O from absorbed gaseous molecules. Higher resolution spectra of Cd and Se region were recorded [Fig. 4.10 (a) and (b)]. Fig. 4.10 (a) shows the XPS spectrum in the Cd 3d_{5/2}, Cd 3d_{3/2} binding energy region with a spin orbit separation of 6.6 eV. The Cd 3d 5/2 peak is centred at 404.3 eV and Cd 3d_{3/2} peak is centred at 410.9 eV. Fig. 4.10 (b) shows the XPS spectrum in the Se 3d binding energy region and the peak is centred at 53.4 eV. The difference between the Cd and Se peak positions is 350.9 eV and this matches well with the bulk value of 350.97 eV. Both the scans of Cd and Se showed asymmetric and broad peaks indicating the presence of more than one chemical environment for both Cd and Se atoms. These observations may lead to the probable conclusions that either Cd atoms or Se atoms or both will react with the silanol groups of MCM-41 to form Si-O-Cd or Si-O-Se bonds. However, more detailed studies of XPS are necessary to provide the direct evidence for these conclusions. No detectable P peaks were recorded in the XPS survey scans and this supports the conclusions that the TBP and TOPO have been removed by the washing cycles.
Chapter 4

4.3.7 UV-Vis diffuse reflectance spectroscopy

UV-Vis diffuse reflectance spectroscopy was employed for the characterisation of the CdSe @ MCM-41 composite. The UV-Vis absorption spectrum of the CdSe @ MCM-41 composite (Fig. 4.11) was obtained by applying the Kubelka-Munk function to the diffuse reflectance spectrum. The spectrum shows the characteristic absorption of quantised CdSe particles. The significant blue shift in the absorption spectrum clearly indicates quantum confinement of CdSe particles inside the pores of MCM-41. The host matrix MCM-41 is optically transparent as observed in Fig. 4.11.

Fig. 4.11 UV-Vis absorption spectrum of CdSe @ MCM-41 composite obtained by applying the Kubelka-Munk function to diffuse reflectance spectrum of CdSe @ MCM-41.
4.3.8 Photoluminescence spectroscopy

The room temperature photoluminescence (PL) spectrum of CdSe @ MCM-41 is shown in Fig. 4.12. The emission maximum of the PL spectrum of CdSe @ MCM-41, excited with excitation energy of 5 eV, is around 1.8 eV. The shift in the PL maximum to higher energies relative to the bulk value (1.74 eV) correlate well with the quantum confinement of CdSe particles inside the pores of MCM-41. In general for SC QDs, the optical properties largely depend on the distribution of particle size, shape, and the nature of the QD surface. The broad PL spectrum of CdSe @ MCM-41 is possibly due to both the deep trap sites at the particle surface and the defects within the confined nanoparticles. Also, the particle-size distribution may contribute to the inhomogeneous broadening of the PL spectrum.

![Fig. 4.12 Room temperature photoluminescence spectrum of CdSe @ MCM-41 composite excited with photon energy of 5 eV.](image)

4.3.9 Proposed mechanism

Rapid injection of organometallic reagents in a coordinating solvent to grow mono-disperse CdSe nanoparticles is a well-developed method. Wet impregnation of the organometallic precursors inside the pores of MCM-41 optimises the delivery of the precursors inside the pores for the nucleation and growth of nanoparticles. Combining these two strategies, we propose the following mechanism for the formation of CdSe nanocrystals inside the pores of
MCM-41 (Fig. 4.1). We used tributylphosphine (TBP) as a solvent for Se as well as a medium for the wet impregnation of the precursors inside the pores of MCM-41. (CH$_3$)$_2$Cd precursor which is readily available inside the pores after the wet impregnation, will react with the silanol groups of MCM-41 and the Se atoms that are initially bound to TBP are freely available inside the pores for the formation of CdSe, once the precursor composite mixture is injected into a hot medium (325°C, TOPO). Since the boiling point of TBP (240°C) is well below the growth temperature of CdSe, it can be removed readily from the pores of MCM-41 during the high temperature treatment. The hot liquid medium (TOPO) used for the growth of CdSe can be easily washed by methanol and the CdSe particles (capped with TOPO) that are formed at the outer surface of MCM-41 are readily washed with toluene and will not be adsorbed strongly to the MCM-41 surface because of the TOPO capping acting as a surfactant.
4.4 Summary and Conclusions

Although the confinement of CdSe nanoparticles inside porous silicon material was reported earlier,\textsuperscript{23} to the best of our knowledge this success in filling the pores of MCM-41 with CdSe nanoparticles is achieved for the first time. This study demonstrated that the combination of wet impregnation technique and the pyrolysis of loaded organometallic precursors in a hot medium is a viable method for the synthesis of CdSe confined in MCM-41. Combined results of XRD, TEM, EDS, XPS and optical characterisation proved that CdSe nanoparticles are confined to the pores of MCM-41 and the hexagonally ordered mesostructure of MCM-41 is remained intact after the growth of CdSe nanoparticles inside the mesopores. Further investigations on the process of confinement of nanocrystals inside the pores of MCM-41 is required for the development of high quality nanocomposites, since the quality of the nanocrystals (crystallinity/particle surface/polydispersity) incorporated inside the porous matrix determines both the devices in which the nanocrystals can be used and the size and surface-dependent properties that can be studied.
4.5 References

1. V. V. Zhirmov, D. J. Herr, *Computer*, 2001, 34, 34.
Chapter 5

5 Synthesis and characterisation of organically capped gold nanocrystals

Abstract

In this chapter, the synthesis and characterisation of gold nanocrystals stabilised by organic capping ligands such as tri-n-octylphosphine oxide (TOPO) and hexadecylamine (HDA) are presented. Organically passivated gold nanocrystals were prepared by NaBH₄ reduction of gold ions in a simple one-phase, non-aqueous route using TOPO or HDA or a mixture of these two polar Lewis base solvents at elevated temperatures. The reduction of gold chloride (added as a solution in n-octylamine) in TOPO as well as in HDA at 160°C resulted in relatively uncontrolled growth of nanocrystals with a wide range of shapes. In contrast, growth in a mixture of TOPO and HDA at similar conditions resulted in the controlled growth of spherical gold nanocrystals. Gold nanocrystals were characterised by UV-Vis absorption spectroscopy, transmission electron microscopy, selected area electron diffraction and X-ray diffraction analysis. The morphology and the structure of gold nanocrystals were examined by TEM and XRD and confirm the fcc structure of gold nanocrystals. Size distributions of gold nanocrystals were analysed by TEM and Photon correlation spectroscopy (PCS). The as-prepared TOPO/HDA capped gold nanocrystals were found to spontaneously self assemble when deposited on a copper grid, forming ordered hexagonal close packed two dimensional lattices and these structures were analysed by TEM.
5.1 Introduction

5.1.1 Historical background: The past

Nanocrystals of noble metals (mainly gold) in the form of colloids and sols had been used for different purposes and colloidal metals are of ancient lineage. Selmi, Faraday and Graham evolved several methods for preparation of colloidal metals well over a hundred years ago. Colloidal metals were the subject of extensive studies by these and other pioneers including Tyndall, Rayleigh, Ostwald, Mie, and Bredig. Rideal, was among the first to probe their catalytic properties for selective conversions such as the hydrogenation of organic molecules. In numerous other respects, colloidal metals have played a prominent part in man’s broader cultural activities. They figure eminently in stained glass windows and other decorative-artistic features as well as in medicinal contexts.¹

Faraday prepared colloidal dispersions of gold by reducing an aqueous solution of a gold salt such as sodium chloroaurate (NaAuCl₄) with a solution of phosphorous in carbon disulphide. Faraday believed that the particles of his colloidal gold were of dimensions smaller than the wavelength of visible light. Rinde concluded, on the basis of ultra centrifugation technique, that colloidal gold prepared according to Faraday’s recipe possessed an average diameter of 19 Å. Faraday investigated the stability of colloidal gold, while Mie developed his theory of light scattering from colloidal suspensions to describe the colour changes observed in colloidal gold suspensions as the average particle size changes. Mie explained the reasons for the intense color of the colloidal gold by solving Maxwell’s equations for the absorption and scattering of electromagnetic radiation by spherical particles.² Using high resolution electron microscopy, Thomas et al. showed that colloidal dispersions of gold prepared according to Faraday’s method, contain a wide distribution of particle sizes, some being as small as 30 Å others as large as 300 Å in diameter and many of the particles occur as rather flat plates with some evidence of crystallographic twinning.³ Over the past few decades, many scientists developed several synthetic approaches to produce gold nanocrystals⁴ and there exist excellent books⁵ and review articles in the literature.⁶
5.1.2 Current research: The present

In the last two decades, there has been growing interest in the metal nanoparticle research due to the interest in their unique physical properties, chemical reactivity and possible applications as bio-/chemosensors, nanoelectronics components, biological taggants and catalysts/catalyst supports. Metal particles in the nanometre size regime show characteristic size dependent properties different from bulk metals with the most significant size effects occurring at 1-10 nm range. The electronic properties of metal particles have been investigated within the context of decreasing electronic device size features to the nanoscopic level. Moreover, in addition to the unusual electronic properties, nanoparticles of noble metals (Au, Ag, and Pt) exhibit increased photochemical and catalytic properties due to their high surface to volume ratio. Several approaches have been considered to synthesise gold nanoparticles in aqueous as well as non-aqueous media by adopting chemical, sonolytic, radiolytic, and photolytic approaches.

There are many synthetic methods to make gold nanoparticles, however; only a few methods produce particles of uniform size. The most common approach involves citrate reduction of a gold salt to produce 12-20 nm size gold particles with a relatively narrow size distribution (standard deviation 10-16 %). The most popular method for producing smaller gold particles was developed by Brust et al. This method utilises borohydride reduction of gold salt in the presence of an alkanethiol-capping agent to produce 2-5 nm particles. By varying the thiol concentration, sizes can be controlled between 2-5 nm. Schmid et al. reported the preparation of uniform and stable Au$_{55}$(PPh$_3$)$_{12}$Cl$_6$ clusters stabilised by bulky triphenylphosphine ligands (1.5 nm diameter 2 shells ) and these phosphine-stabilised gold clusters with sizes 1.4 (± 0.4) nm have also been further converted to thiol capped clusters by ligand exchange in order to improve their stability and recently phosphine stabilised monodispersed gold particles 1.5 (± 0.4) nm were prepared using a similar protocol to the Brust method. Most of the methods to make small gold clusters take advantage of the strong capping action of thiols, disulfides, polymers, with mercapto and cyano functional groups and dendrimers. Organic ligands has been utilised as capping agents for the synthesis of Ag, Cu, Pb, Cr, Ni, Pt and Fe/Pt alloy nanocrystals. The method of preparing metal nanocrystals in organic solvents is useful for suspending metal nanoparticles in a wide variety of solvents without allowing aggregation and assembling them as two- and three-dimensional arrays.
5.1.3 Applications of gold nanocrystals

A burst of research activity is seen in recent years in the area of synthesis and organic functionalisation of different size and shape of gold nanoparticles. The size and shape dependent optical and electronic properties make an interesting case for many applications. By varying the shape of the metal nanoparticle, a variety of optical properties such as peaks in absorption, significant enhancement in Raman scattering intensity, and nonlinear properties has been reported. In case of silver, studies on the plasmon resonance of individual colloidal nanoparticles show that triangular, pentagonal, and spherical particles can display red, green, and blue colour respectively under optical microscopy. Binding a photoactive molecule (e.g. pyrene) to metal nanoparticle enhances the photochemical activity and renders the organic-inorganic hybrid nanoassemblies suitable for light harvesting and optoelectronic applications. The schematic illustration of potential applications of gold nanocrystals in different fields is illustrated in Fig. 5.1.

![Diagram showing potential applications of gold nanocrystals in different fields.]

**Fig. 5.1 Potential applications of gold nanocrystals in different fields.**

5.1.4 Dynamic light scattering

The determination of particle size and size distribution is important in nano-scale systems, since the properties of the nanocrystals depend strongly on size and its precise and fast determination is essential for the interpretation of the physical properties. In most cases, the
particle size distribution analysis is carried out by electron microscopy analysis and x-ray diffraction analysis of the system. Electron microscopy image analysis of nanocrystal systems is straightforward and independent of particle size distribution. However, inferring the ensemble average properties such as average diameter or shape based on the limited regions examined by typical TEM investigations are akin to determining the street layout of a big city by just examining a square centimetre of sidewalk— which is not statistically significant. This statistical uncertainty occurs partly due to human subjectivity when deciding which areas of the grid to image and photograph and also is due to size segregation effects during the drying process. In addition, drying the nanoclusters out on a TEM grid can cause size changes to the clusters, induce aggregation or lead to chemical changes like oxidation of the clusters. Moreover, one can neither see the organic groups used to passivate a cluster surface using electrons nor determine the size of this organic shell. In case of powder X-ray diffraction analysis it is difficult to measure and interpret the sizes of very small nanocrystals. In this regard, the use of Dynamic Light Scattering (DLS) technique, which enables the determination of the particle sizes including the ligand shells, could provide significant additional information on the size distributions of the nano-scale systems. Recent progress in the development of light scattering instruments and the usage of novel detectors (the use of avalanche photodiodes (APD) as detectors instead of photomultiplier tubes (PMT)) has made it possible to perform DLS experiments of small particles in the few nanometre range with lower power lasers. The schematic illustration of the typical DLS experimental set-up is as shown in Fig. 5.2.

Dynamic light scattering (DLS) also known as photon correlation spectroscopy (PCS) is the most versatile and useful technique for measuring in-situ the sizes the size distributions and (in some cases) the shapes of nanoparticles in liquids. DLS techniques are hydrodynamic techniques, in that they directly measure hydrodynamic quantities, usually the translational and rotational diffusion coefficients, which are then related to sizes and shapes via theoretical relations. PCS is now a standard technique that is widely used in many areas of research like biophysics, colloidal particle research and polymer laboratories. It can be used for routine particle characterisation as well as for studies of the nature of interactions of molecules and particles in liquid dispersions.
Photon correlation spectroscopy (PCS) is based on the fact that the intensity of light scattered from a dispersion of particles into a given scattering angle is the result of interference on the surface of a square-law detector between lights scattered from different particles in the medium. The phases at the detector of the light scattered from different particles depend on the relative positions of the particles relative to the direction of the incoming and scattered light beams. Thus at a given instance, the total scattered intensity at a given scattering angle depends on the positions of the particles (structures). The particles, however, are constantly executing Brownian motion so that their positions fluctuate. Thereby the scattered intensity also fluctuates. These scattered intensity fluctuations occur on the time scale that it takes a particle to move a significant fraction of the wavelength of light. The scattered intensity itself is a stochastic signal, since it reflects the thermal (Brownian) motion of the particles. To extract useful information from the signal, its time correlation function is computed. This is usually done using an autocorrelator – a computer equipped with special boards to allow rapid real-time calculation of the scattered intensity time correlation function.

In a typical PCS or DLS set-up, there is a monochromatic laser beam with vertical polarization and wavelength $\lambda_0$ (in vacuum) irradiating a suspension of colloidal particles.
Chapter 5

The incident laser light causes the particles to behave as oscillating electric dipoles radiating light of the same frequency (elastic scattering) in all directions. Interaction of the electric fields (interference) scattered by the different particles in the suspension causes the formation of a complex speckle pattern ruled by the position and the orientation of the different scatterers. Because of the Brownian motion of the colloidal particles, this speckled pattern is subjected to fast intensity fluctuations in time. Because of the time scale of motion of the scatterers, these intensity fluctuations contain some valuable information about the dynamic behaviour of the system. If we consider the scattered light intensities $I(t)$ in a certain scattering direction $\vartheta$ as function of time $t$, we can obtain the intensity autocorrelation function

$$G_2(\tau) = \lim_{T \to \infty} \frac{1}{T} \int_{-T/2}^{T/2} I(t)I(t + \tau)dt$$ .............................................. (5.1)

This function can be experimentally constructed in real time by a digital correlator. In the case of a pure homodyne set-up (no unscattered light reaches the detector) and a sufficiently dilute suspension, the relation can be rewritten in the form

$$G_2(\tau) = A \left[ 1 + f \left| g^{(1)}(\tau) \right|^2 \right]$$ ......................................................... (5.2)

which is called the Siegert relation, where $A$ denotes the baseline value of the autocorrelation function, which equals the square of the mean scattered intensity $\langle I(t) \rangle^2$ and $f \leq 1$ is the spatial coherence factor. The spatial coherence factor $f$ is determined by the angular resolution of the experimental light receiver.

If the scattering suspension contains only one kind of particles (monodisperse), all with the same spherical shape and electrical isotrope, then the normalised first-order autocorrelation function $g^{(1)}$ has the form of a single-exponential decaying function

$$g^{(1)}(\tau) = e^{-\Gamma \tau}$$ ................................................................. (5.3)

where

$$\Gamma = D q^2$$ ................................................................. (5.4)

$D$ is the translational diffusion coefficient of the particles in suspension and

$$q = (4\pi n / \lambda_0) \sin(\theta / 2)$$ ................................................................. (5.5)

is the modulus of the scattering vector ($n$ is the refractive index of the suspension). Once we know the translational diffusion coefficient of the particles, it is easy to find the radius $r$ of
the particles by using the Stokes-Einstein equation (for spherical particles in a dilute dispersion)

\[ D = \frac{kT}{6\pi\eta r} \]  

(5.6)

where \( k \) is the Boltzmann constant, \( \eta \) the viscosity of the suspending liquid, and \( T \) the absolute temperature. Thus, for spherical nanoparticles, the particle radius (including any solvation layer or capping ligand) may be derived from the PCS experiment.

In the more general case in which the particles are non-spherical or flexible, the radius derived from the self-diffusion coefficient and the Stokes-Einstein relation is called the “hydrodynamic radius”. The hydrodynamic radius of non-spherical particles is of course, not equal to a geometrical particle radius. The relation between the translational diffusion coefficient or hydrodynamic radius and the actual dimensions of non-spherical particles depends on the particle shape.

Dynamic light scattering technique has certain limitations, the most critical being the relatively low information content inherent in the measured signal (low signal-to-noise S/N). In DLS technique one cannot separate out the contribution of each size cluster in the population to the total correlation function, and thus a separate fractionation method is still required for a satisfactory analysis. The particle size distribution determined at any single angle can at best be only a measure of those cluster populations, which contribute significantly to the measured signal at that angle. This is a physical limit and applies regardless of the inversion technique used to analyse the data. One can combat this limitation by performing a series of single angle measurements at several angles, and if they all give similar results, then the results is probably representative.

In this chapter, DLS technique has been applied to investigate the particle size analysis of organically capped gold nanoparticles, in addition to TEM analysis.
5.2 Experimental

5.2.1 Synthesis of organically capped gold nanoparticles

Chemicals:
The following chemicals of analytical grade were used for the synthesis of organically capped gold nanoparticles.
(a) tri-n-octylphosphine oxide (TOPO), (C_{24}H_{51}OP), (Fluka), (b) Hexadecylamine, (HDA), (C_{16}H_{35}N), (Acros) (c) n-Octylamine, (C_{8}H_{19}N), (Acros) (d) Tetraaurochloric acid (HAuCl_{4}.3H_{2}O), (E-Merck) (e) Sodium borohydride, (NaBH_{4}), (J.T.Baker) (f) Methanol, (Fluka), (g) Toluene, (Fluka).

A typical synthesis of organically capped gold nanoparticles was as follows. About 0.02 g of AuCl_{4} was dissolved in 2 ml of n-octylamine. The solution was injected into a reaction flask containing a mixture of 7.5 g of TOPO, 2.5 g of HDA (or 10 g of TOPO or 10 g HDA) and 0.0325 g of NaBH_{4} at 160 °C. The reaction flask was maintained at 160°C for 30 min and the solution was cooled to room temperature under flowing argon. Precipitating the reaction mixture with methanol isolated gold nanocrystals. The isolated gold nanocrystals were washed several times with methanol to remove excess capping ligands before analysis. The resulting gold nanoparticles can be readily dispersed in toluene or hexane. The schematic illustration of the synthesis procedure is shown in Fig. 5.3.

Fig. 5.3 Schematic illustration of synthesis of gold nanocrystals.
5.2.2 Characterisation

Organically capped gold nanocrystals were characterised by UV-Vis absorption spectroscopy, X-ray diffraction analysis, transmission electron microscopy, and selected area electron diffraction analysis. The size distribution analysis of gold nanoparticles was obtained from TEM and PCS measurements. Evidence for the presence of the capping ligands was obtained using mass spectrometry, NMR and XPS analysis.

Preparation of sample for XPS analysis

Preparations of self assembled monolayers (SAMs) of 4,4’-biphenyldithiol (BDT) on Ag substrates and assembly of TOPO/HDA capped gold nanocrystals on SAMs.

Ag substrates for XPS measurements were prepared by evaporation of 100 nm of metal silver wire (99.9999%; from Heraeus) onto polished silicon wafers (100) with a 5 nm titanium layer using a commercial evaporator (UNIVAC 300, Leybold) at a base pressure of 10^{-6} mbar. The wafers were cut into 10x13 mm pieces prior to the self-assembly process.

SAMs were prepared by immersion of silver substrate in a 1 mM ethanolic solution of biphenyldithiol for 24 hours washed thoroughly with ethanol and dried in a stream of Argon. The thiol modified Ag substrate was immersed in toluene solution containing gold nanoparticles overnight, washed thoroughly with toluene and dried in a stream of Argon.

Photon correlation spectroscopy

PCS experiments were performed using a commercial ALV photon correlation spectrometer (ALV Laser-vertriebsgesellschaft, Lagen, Germany). The schematic representation of the PCS experimental set-up is as shown in Fig. 5.2. The ALV/DLS/SLS/-5000 compact goniometer system is a laser light scattering measurement system for simultaneous angular dependent determination of dynamic (measurement of time dependent intensity fluctuations) and static light scattering (measurement of the total integrated light intensity). This system allows measurements of auto-correlation function of the scattered light detected by Avalanche photodetector (APD) and automatically executes the on-line data analysis by an ALV-5000E /WIN Multiple Tau Digital Correlator. The data analysis results in the calculation of apparent diffusion constants (translational and rotational) and hydrodynamic size or size distributions if Stokes-Einstein relation is applicable. All measurements were performed at room temperature using quartz cuvettes sealed with a septum to avoid decontamination of the samples with oxygen and water.
5.3 Results and Discussion

5.3.1 Optical characterisation

Metal nanocrystals like gold, silver, and copper show distinct and characteristic well-defined plasmon absorption in the visible region. The surface plasmon absorption in the metal nanoparticles arises from the collective oscillations of the free conduction band electrons that are induced by the incident electromagnetic radiation. The optical absorption properties of gold nanocrystals in the visible range are very much dictated by the effect of the boundary conditions of the coherent electron oscillations and also due to the interband $d$ to $sp$ electronic transitions. The surface plasmon absorption spectra of gold nanoparticles is characterised by a strong absorption band in the visible region at 520-540 nm.

![UV-Vis absorption spectra of TOPO/HDA, TOPO, and HDA capped gold nanocrystals.](image)

Very small gold particles (< 2 nm) as well as bulk gold do not show this absorption. UV-Vis absorption spectroscopy of TOPO, HDA, and TOPO/HDA capped gold nanoparticles dispersed in toluene showed the characteristic plasmon resonance associated with the
spherical colloidal gold nanocrystals at 520-540 nm. Fig. 5.4 shows the UV-Vis absorption spectra of TOPO, HDA and TOPO/HDA capped gold nanocrystals.

5.3.2 X-ray diffraction analysis

Samples for X-ray diffraction analyses were prepared by removing the toluene and dispersing the sample in methanol. The dispersion was centrifuged, methanol was removed, and the resulting powder was dried. The powder was then spread on a single crystal Si sample holder for analysis. X-ray diffraction patterns of TOPO, HDA and TOPO/HDA capped gold nanocrystals are shown in Fig. 5.5 to 5.7. XRD analyses of TOPO, HDA and TOPO/HDA capped gold nanocrystals showed the broad peaks at 2θ values of 38.184°, 44.392° and 64.576° corresponding respectively to the 111, 220, and 200 planes of fcc gold. The analysis of diffraction line widths indicated that the nanocrystalline domains were less than 10 nm in size. The average sizes of the gold nanoparticles were determined by X-ray diffraction peak line width broadening using the Debye-Scherer equation,

\[ D = \frac{K\lambda}{\beta \cos \theta} \]

where, D is the average nanocrystals diameter in Å, \( \beta \) is the corrected band broadening (FWHM), \( K \) is a constant related to the crystallite shape and the way in which \( D \) and \( \beta \) are defined, \( \lambda \) is the wavelength of the X-ray source, and \( \theta \) is the diffraction angle.
Transmission electron microscopy analysis of gold nanocrystals capped with different capping ligands such as TOPO, HDA, and TOPO/HDA was carried out to obtain information about the structure, morphology, shape, and size distribution of nanocrystals. Transmission
electron microscopy of gold nanocrystals passivated with different capping ligands showed a distinct relationship between morphology and the capping ligands. Synthesis of gold nanocrystals with TOPO or HDA as capping ligand resulted in relatively uncontrolled growth of nanocrystals of different sizes and shapes. Fig. 5.8 (a) and (b) show the typical TEM images of TOPO capped gold nanocrystals in which spherical, oval, and elongated nanocrystals ranging in size from 4 to 20 nm in diameter can be seen. Similarly, uncontrolled growth of gold nanocrystals was observed when HDA was used as a capping ligand. Fig. 5.9 (a) and (b) show the typical TEM images of HDA capped gold nanocrystals in which rectangular, spherical and bean shaped nanocrystals ranging in size from 6 to 25 nm in diameter can be seen. The isolated re-suspended gold nanocrystals (both TOPO and HDA capped) were stable in toluene only for few days.

Figure 5.8 TEM images of TOPO capped gold nanocrystals.

Figure 5.9 TEM images of HDA capped gold nanocrystals.
In contrast, growth of gold nanocrystals in a mixture of TOPO and HDA resulted in the more controlled growth of spherical nanocrystals ranging in size from 6 to 12 nm and nanocrystals were stable in toluene for months. Fig. 5.10 (a) and (b) show the typical TEM images of TOPO/HDA capped gold nanocrystals. The morphology of the gold nanocrystals is controlled by various properties of the capping ligands. The Lewis basicity must be sufficient for significant interaction to occur and the bond formed has to be sufficiently labile to allow controlled growth of nanocrystals. A balance must be achieved between the growth rate and ligand stability to facilitate the growth of nanocrystals of a uniform size. Longer chain ligands tend to favor slower growth and hence the formation of, relatively smaller nanocrystals. The role of organic capping ligands in controlling the particle sizes and shapes has been reported recently for the growth of organically passivated cadmium chalcogenides and Co nanocrystals. Some in-depth investigations into capping agents and their effect on particle sizes etc, were reported by Sun and Murray on long chain acid/phosphine oxide capped cobalt and more recently by Alivisatos and Co-workers.

### 5.3.4 High resolution transmission electron microscopy and selected area electron diffraction analysis

High-resolution transmission electron microscopy images (Fig. 5.11) were obtained at an operating voltage of 200 keV. A typical phase-contrast image obtained from the material; along with the corresponding selected area electron diffraction (SAED) pattern is shown in
Fig. 5.12. The characteristic rings in the polycrystalline diffraction pattern are shown in Fig. 5.12. The characteristic rings in the polycrystalline diffraction pattern can be indexed to the (111), (200), (220), (311), (222) and (400) allowed reflecting planes expected from fcc Au. The diffuse nature of the rings is a simple manifestation of the crystal shape effect due to the nanoscale size of the particles. Discrete gold nanoparticles were observed in electron micrographs, some of which exhibit characteristic (111) and (200) lattice fringes. A significant number of particles exhibit multiple twinning and preferential (111) surface facet planes are clearly visible in some instances.

Fig. 5.11 HRTEM image of TOPO/HDA capped gold nanocrystals

Fig. 5.12 Representative images of SAED pattern of gold nanocrystals (a) TOPO/HDA capped gold nanocrystals (b) HDA capped gold nanocrystals
Spontaneous self-assembly has been reported before for highly monodispersed TOPO capped CdSe nanocrystals and thiol capped gold nanocrystals. The as prepared TOPO/HDA capped gold nanocrystals were found to spontaneously self assemble when deposited on a copper grid, forming ordered hexagonal close packed two dimensional lattices (Fig. 5.13). Similar observation was reported for silver and gold nanocrystals capped with TOPO/Ocatdecylamine ligands.

FAB mass spectrometry of gold nanocrystals prepared in the mixed solvent system revealed the presence of not only TOPO (m/z 387) and hexadecylamine (m/z 242), but also n-octylamine (m/z 129.25). Solution $^1$H NMR of TOPO/HDA capped gold nanoparticles displayed typical broad resonances between 0.5 and 2.0 ppm, which makes assignment to either ligand difficult. Solution $^{31}$P NMR displays a strong resonance at ca 50 ppm, similar to the resonance observed in uncoordinated TOPO. This indicates that TOPO is only weakly coordinated to the gold surface as TOPO strongly bound to a CdSe quantum dot surface exhibits a shift in the $^{31}$P resonance.

5.3.5 X-ray photoelectron spectroscopy

Figure 5.14 shows the survey spectrum of TOPO/HDA capped gold nanocrystals. The presence of C and O comes mainly from atmospheric contamination due to the exposure of the samples to air. The positions of both C and O lines correspond to standard values for adsorbed species, showing the absence of significant charging. As expected, we detect XPS
lines from Au, N and S in addition to the Ag lines (substrate). However, no P lines were detected by XPS. These results support that TOPO is only weakly bound to the surface, and is much more labile than TOPO bound to a semiconductor surface such as CdSe. Similar results were reported for silver nanoparticles capped with TOPO/Octadecylamine ligands. The inset in figure 5.14 shows the high resolution XPS spectrum of gold nanoparticles. The binding energies of the doublet for Au 4f\(_{7/2}\) (83.8 eV) and Au 4f\(_{5/2}\) (87.5 eV) shown in the figure are characteristics of Au\(^0\). However, the band around 84.9 eV indicates the presence of Au\(^1\), which was found in the gold octanethiol complex.

Fig. 5.14 XPS spectrum of TOPO/HDA capped gold nanocrystals. Inset: High resolution XPS spectrum of Au showing the doublet, Au 4f\(_{7/2}\) and Au 4f\(_{5/2}\).

### 5.3.6 Photon correlation spectroscopy

Fig. 5.15 shows a representative DLS correlation function of TOPO/HDA capped gold nanocrystals obtained at a scattering angle 90°. The corresponding intensity distribution is shown in Fig. 5.16 (average intensity 60.607 kHz). The correlation function showed a single decay corresponding to average radius of 4.789 nm. Table 5.1 shows the particle size distribution analysis determined from different scattering angles. These results suggest that TOPO/HDA capped gold nanocrystals are relatively monodisperse in nature. Size distribution
analyses obtained from PCS experiments can be compared with the size analysis obtained from TEM.

Fig. 5.15 Representative correlation function measured by DLS on gold nanocrystals capped with TOPO/HDA.

Fig. 5.16 Intensity distribution measured by DLS on gold nanocrystals capped with TOPO/HDA.
The evaluation of the obtained DLS correlation function yields a larger hydrodynamic radius than the radius determined by TEM analysis (Average diameter; 8 ± 0.5 nm). This is caused by the organic passivating ligand shell and can be interpreted as a monolayer of the capping ligands. PCS experiments carried out in tetrahydrofuran (THF) instead of toluene as solvent show no significant effect on the observed hydrodynamic radius and confirm low influence of the solvent on the hydrodynamic radius for gold nanocrystals.

Table 5.1 Size distribution analysis of TOPO/HDA capped gold nanocrystals measured by PCS.

<table>
<thead>
<tr>
<th>Scattering angle</th>
<th>Average scattering Intensity (kHz)</th>
<th>1st order Cumulant analysis Radius (nm)</th>
<th>2nd order Cumulant analysis Radius (nm)</th>
<th>3rd order Cumulant analysis Radius (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>90</td>
<td>60.607</td>
<td>5.25</td>
<td>4.79</td>
<td>4.76</td>
</tr>
<tr>
<td>75</td>
<td>64.523</td>
<td>5.30</td>
<td>4.89</td>
<td>4.75</td>
</tr>
<tr>
<td>60</td>
<td>75.161</td>
<td>5.52</td>
<td>5.08</td>
<td>4.94</td>
</tr>
<tr>
<td>45</td>
<td>100.299</td>
<td>6.87</td>
<td>5.63</td>
<td>5.59</td>
</tr>
</tbody>
</table>

Table 5.2 shows the particle size distribution analysis of TOPO and HDA capped gold nanocrystals. In case of TOPO as capping ligand, the average radius of gold nanocrystals was 3.97 nm and for HDA capped gold nanocrystals the average radius was 7.00 nm.

Table 5.2 PCS size distribution analysis of TOPO and HDA capped gold nanocrystals.

<table>
<thead>
<tr>
<th>Capping Ligand</th>
<th>Scattering angle</th>
<th>Average scattering Intensity (kHz)</th>
<th>1st order Cumulant analysis Radius (nm)</th>
<th>2nd order Cumulant analysis Radius (nm)</th>
<th>3rd order Cumulant analysis Radius (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TOPO</td>
<td>90</td>
<td>35.620</td>
<td>4.57</td>
<td>3.97</td>
<td>3.81</td>
</tr>
<tr>
<td>HDA</td>
<td>90</td>
<td>68.354</td>
<td>7.23</td>
<td>7.00</td>
<td>6.84</td>
</tr>
</tbody>
</table>
5.4 Summary and Conclusions

In summary, colloidal gold nanocrystals capped with different organic passivating ligands such as TOPO, HDA and mixture of TOPO/HDA have been prepared in a non-aqueous route. Organically passivated gold nanocrystals were prepared by NaBH₄ reduction of gold ions in a simple one-phase, non-aqueous route using TOPO or HDA or a mixture of these two polar Lewis base solvents at elevated temperatures. The reduction of gold chloride (added as a solution in n-octylamine) in TOPO as well as in HDA at 160°C resulted in relatively uncontrolled growth of nanocrystals with a wide range of shapes. In contrast, growth in a mixture of TOPO and HDA at similar conditions resulted in the controlled growth of spherical gold nanocrystals. Gold nanocrystals were characterised by UV-Vis absorption spectroscopy, transmission electron microscopy, selected area electron diffraction and X-ray diffraction analysis. The morphology and the structure of gold nanocrystals were examined by TEM and XRD and confirm the fcc structure of gold nanocrystals. Size distributions of gold nanocrystals were analysed by TEM and Photon correlation spectroscopy (PCS). The as-prepared TOPO/HDA capped gold nanocrystals were found to spontaneously self assemble when deposited on a copper grid, forming ordered hexagonal close packed two dimensional lattices and these structures were analysed by TEM.
5.5 References

Chapter 6

6 Colloidal nanocrystals of TiO$_2$: Synthesis and characterisation

Abstract

In this chapter the synthesis of nano-scale TiO$_2$ particles exhibiting the quantum confinement effect by a nonhydrolytic approach is presented. Thermal decomposition of a modified titanium alkoxide precursor, [Ti(OPr$_1$)$_3$(dmae)] in a co-ordinating solvent, tri-n-octylphosphine oxide (TOPO) at high temperature yielded good quality, quantum confined TiO$_2$ nanocrystals. In contrast to established aqueous sol-gel techniques, the processing in hydrocarbon solvents at high temperatures allows access to very small free standing crystallites, and opens up new possibilities for control over size distribution, surface chemistry and particle agglomeration. TiO$_2$ nanocrystals were characterised by UV-Vis absorption spectroscopy, Photoluminescence spectroscopy, X-ray diffraction analysis, transmission electron microscopy and EDX analysis. Optical characterisations of TiO$_2$ nanocrystals reveal a strong and a broad blue light emission around 370 nm. Transmission electron microscopy analysis showed that TiO$_2$ nanocrystals were relatively spherical in shape with a size distribution of 3-5 nm. Photon correlation spectroscopy analysis of TiO$_2$ nanocrystals dispersed in toluene gave the average diameter as 3.3 nm. The slow evaporation of the solvent toluene leads to the formation of monolayers/bilayers of ordered spherical structures of TiO$_2$ nanocrystals.
6.1 Introduction

Nanocrystalline TiO$_2$ particles have been intensively studied because of their outstanding chemical and physical properties, which are of interest for many applications. Depending on the application TiO$_2$ particles must fulfil a wide variety of requirements in terms of particle size, size distribution, morphology, crystallinity and phase. For many applications particle size might be considered the most important parameter because it has a tremendous effect on the mechanical, electronic, magnetic, and optical properties.\(^1\) Ultra small TiO$_2$ particles with diameters between 1 and 10 nm have been reported to fall into the transition state of molecular and bulk material properties exhibiting quantisation effects\(^2\) and unusual luminescence properties.\(^3\) Size quantisation effects for anatase have been reported for particles as large as 22 nm.\(^4\) However, typical quantum size properties such as increasing band gap energies with decreasing particle size and blue shifts in the UV-Vis spectrum upon charge injection occurred only for particles smaller than 3 nm.\(^5\) This coincides well with Stucky et al.,\(^6\) who found recently a shift in the band edges for anatase nanocrystallitites with radii between 0.5 and 2.5 nm.

Until now, photovoltaics, the conversion of solar energy to electric power has been dominated by solid-state junction devices often made of silicon. But this dominance is now being challenged by the emergence of a new generation of photovoltaic cells, based on nanocrystalline oxide materials such as TiO$_2$ and conducting polymer films.\(^7\) In addition, nanocrystalline metal oxides such as TiO$_2$ have potential and demonstrated applications in modern technologies including microelectronics, gas sensors, catalysis, and photocatalysis.\(^8\) Due to this, in recent years, there has been increased interest in studying nano-scale TiO$_2$ materials as nanoparticles,\(^9\) nanowires,\(^10\) whiskers,\(^11\) and nanotubes.\(^12\) There are many synthetic routes for the creation of TiO$_2$ and the controlled hydrolysis of metal alkoxide or halide precursor and subsequent condensation to the inorganic framework is the most generalised sol-gel process.\(^13\) Major problems associated with the sol-gel process are fast hydrolysis and condensation rates of early transition metal alkoxides as well as particle agglomeration at low temperatures. TiO$_2$ nanocrystals prepared by sol-gel method have fully hydroxylated surfaces and these hydroxyl groups have strong influence on the catalytic and photocatalytic properties such as electron-transfer rates and reducing properties.\(^14\) To prevent particle agglomeration reverse micelle\(^15\) or microemulsion techniques\(^16\) have been used for the synthesis of oxide materials. Increased photocatalytic activity was reported recently for TiO$_2$.
prepared by ultrasonic irradiation and glycothermal methods. Since, the structural, catalytic and photo catalytic properties of nano-scale TiO\textsubscript{2} in general depend on the crystallinity and the nature of the nanocrystal surface, there would be a great scientific as well as technological value in the development of synthetic strategies to create nano-scale TiO\textsubscript{2}. Rapid thermal decomposition of molecular precursors in the presence of strong co-ordinating ligands such as tri-n-octylphosphine oxide (TOPO) at high temperatures yielded good quality metal\textsuperscript{18} and highly crystalline semiconductor nanocrystals.\textsuperscript{19} However, there are very few reports on successful synthesis of oxide nanocrystals employing similar non aqueous/nonhydrolytic strategies.\textsuperscript{20, 21} Surface stabilisation of TiO\textsubscript{2} nanocrystals with capping ligands such as TOPO allows the possibility of ready exchange of capping ligands as well as manipulation of nanocrystal surface. In addition, organically capped nanocrystals are highly dispersible in hydrocarbon solvents and should provide better control over size, surface and prevent the aggregation of nanocrystals. Recently, the synthesis of TOPO capped TiO\textsubscript{2} nanocrystals were demonstrated, but this system does not exhibit quantum confinement.\textsuperscript{22} Alkoxides of titanium [Ti(OR)\textsubscript{4}, (R = Et, Pr\textsubscript{i}, Bu\textsubscript{t})] have been used as titanium precursors in metalorganic chemical vapor deposition (MOCVD) process to fabricate thin films of TiO\textsubscript{2} and ferroelectric oxides such as BaTiO\textsubscript{3}, Pb(Zr, Ti)O\textsubscript{3}, (Ba, Sr)TiO\textsubscript{3} and these materials have several important applications in microelectronic industry.\textsuperscript{23} Replacing one or more isopropoxide groups in Ti(OPr\textsubscript{i})\textsubscript{4} with donor functionalised alkoxide ligands such as dimethylaminoethoxide (OCH\textsubscript{2}CH\textsubscript{2}NMe\textsubscript{2}) (dmae) or diethylaminoethoxide (OCH\textsubscript{2}CH\textsubscript{2}NEt\textsubscript{2}) (deae) leads to the formation of more fully saturated compounds such as [Ti(OPr\textsubscript{i})\textsubscript{3}(dmae)],\textsuperscript{24} Ti(OPr\textsubscript{i})\textsubscript{3}(deae)], or Ti(OPr\textsubscript{i})\textsubscript{2}(deae)\textsubscript{2}. The conventional titanium alkoxide precursors are highly reactive towards air and water, but modified titanium alkoxide precursors have reduced air/moisture sensitivity compared to parent alkoxides and used as alternative precursors in liquid injection MOCVD.\textsuperscript{26} In this chapter, a nonhydrolytic method to synthesise nanosized TiO\textsubscript{2} particles is described. Rapid thermal decomposition of modified alkoxide precursor of titanium in a co-ordinating solvent TOPO yielded nanosized TiO\textsubscript{2} particles. Nanosized TiO\textsubscript{2} particles were characterised by different characterisation techniques.
6.2 Experimental

6.2.1 Synthesis of $\text{[Ti(OPr)}_3\text{(dmae)}]$  

Chemicals  
All the chemicals used for the synthesis were of analytical grade and were handled with rigorous exclusion of air and moisture using glove box and standard schlenk vacuum line technique. The following chemicals were used for the synthesis of titanium alkoxide precursor $\text{[Ti(OPr)}_3\text{(dmae)}]$ and the synthesis of $\text{TiO}_2$ nanocrystals (a) Titanium tetraisopropoxide $\text{[Ti(OPr)}_4\text{]}$ (Aldrich), (b) Dimethylaminoethanol (Hdme) (Aldrich), n-hexane (J.T.Baker), tri-n-octylphosphine oxide (TOPO) (Aldrich), methanol (Fluka), toluene (Fluka).

Procedure  
Modified titanium alkoxide precursor $\text{[Ti(OPr)}_3\text{(dmae)}]$ was synthesised according to the procedure reported in the literature. A typical synthesis is as follows: $\text{[Ti(OPr)}_4\text{]}$ (19.9g, 0.07mol) was dissolved in n-hexane (120 ml) and Hdme (6.7g, 0.075 mol) was added. The resulting solution was refluxed with stirring for 1 h and was then allowed to cool. All volatilities were removed under vacuum and product was obtained as colourless oil. The compound was then purified by vacuum distillation.

6.2.2 Synthesis of $\text{TiO}_2$ nanocrystals  
In a typical synthesis of $\text{TiO}_2$ nanocrystals, 10 g of TOPO was heated to 200°C degassed periodically and flushed with argon. The temperature of the reaction flask was raised and stabilised at 325°C and 0.35g of the modified alkoxide precursor $\text{[Ti(OPr)}_3\text{(dmae)}]$ was injected rapidly into the reaction flask under Ar atmosphere. Immediately after the injection, the colourless solution rapidly changes to yellow-green and the temperature of the reaction was maintained at 300°C for 15 min. The solution was cooled to 50 °C and treated with methanol to generate yellow-green flocculates, which were separated by centrifugation. The resulting nanocrystals could be readily dispersed in polar solvents like toluene or hexane.

6.2.3 Characterisation  
The compound $\text{[Ti(OPr)}_3\text{(dmae)}]$ was characterised by $^1\text{H}$ and $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopy, elemental analysis and mass spectroscopy which confirmed the stoichiometry.
Thermal properties of $\text{[Ti(OPr)}_i\text{)}_3(\text{dmae})]$ was analysed by TG/DTA and compared with $\text{[Ti(OPr)}_i\text{)}_4]$.

Nanosized TiO$_2$ particles were characterised by different techniques, which are listed below. Particle size distribution analysis was carried out by Photon correlation spectroscopy and size distributions were compared with transmission electron microscopy.

1. UV-Vis absorption spectroscopy
2. Photoluminescence spectroscopy
3. X-ray diffraction analysis
4. Transmission electron microscopy
5. Energy dispersive analysis of X-rays (EDX)
6. Photon correlation spectroscopy
6.3 Results and Discussion

6.3.1 Thermal characterisation

Thermogravimetric and differential thermal analysis (TG/DTA) of the precursor [Ti(OPr\textsuperscript{i})\textsubscript{3}(dmae)] was carried out and compared with [Ti(OPr\textsuperscript{i})\textsubscript{4}] which is shown in Fig. 6.1. Both the precursors begin to vaporise at room temperature. However, as we can observe from the TG curve, the parent alkoxide [Ti(OPr\textsuperscript{i})\textsubscript{4}] begins decompose at lower temperature compared to [Ti(OPr\textsuperscript{i})\textsubscript{3}(dmae)].

![Thermogravimetric analysis](image)

*Fig.6.1 Thermogravimetric analysis of the precursor [Ti(OPr\textsuperscript{i})\textsubscript{3}(dmae)] compared with [Ti(OPr\textsuperscript{i})\textsubscript{4}].*

6.3.2 Optical characterisation

6.3.2.1 UV-Vis absorption spectroscopy

UV-Vis spectroscopy is used to characterise the optical absorption of TiO\textsubscript{2} nanocrystals dispersed in toluene as shown in Fig. 6.2. The spectrum indicates that the onset of absorption appears at 370 nm. The blue shift in the onset of optical absorption of TiO\textsubscript{2} particle relative to the bulk anatase TiO\textsubscript{2} (E\textsubscript{g} = 382 nm) implies the quantum confinement of TiO\textsubscript{2} nanocrystals. With decreasing particle size, an increase of the band gap energy and therefore a blue shift in
the absorption edge was accounted in many studies as quantum size effects for very small (d < 4 nm) TiO$_2$ particles.

![Absorption spectrum of TiO$_2$ nanocrystals](image)

*Fig. 6.2 UV-Vis absorption spectrum of TiO$_2$ nanocrystals dispersed in toluene.*

### 6.3.2.2 Photoluminescence spectroscopy

The emission from the TiO$_2$ nanocrystals dispersed in toluene at room temperature was obtained by excitation of the sample. A Fluoro Max-2 instrument with a continuous ozone-free xenon lamp (150W) and a R928P photo multiplier tube as a detector was used for the analysis. A broad emission spectrum was obtained and a sharp increase in the emission intensity at 320 nm is observed, reaching a maximum around 370 nm (Fig. 6.3). This type of blue light emission (band-to-band transition) was reported earlier for specially synthesised aqueous TiO$_2$ colloids (d = 3 nm).$^{27}$ Emission spectra were recorded using different excitation wavelengths (275 - 295 nm) to confirm that the broad band (300 – 550 nm) is due to very small TiO$_2$ particles. These results suggest that the TiO$_2$ particles show the effect of quantum confinement.
6.3.3 X-ray diffraction analysis

To characterise the crystal structure of TiO$_2$ nanocrystals, XRD analysis was carried out on a sample prepared by placing the TiO$_2$ nanocrystals (dispersed in toluene) on a glass substrate and slowly heating the substrate to 350°C. The XRD pattern of TiO$_2$ nanocrystals placed on the glass substrate is as shown in Fig. 6.4. The broad shoulder around 20-30° is due to the glass substrate and a small sharp overlapping peak at 2θ value at 25.6° was observed. Due to the overlapping of the peaks of glass substrate and the prominent peak of anatase TiO$_2$ at 25.6°, it is difficult to clearly observe the peaks due to TiO$_2$ nanocrystals.
6.3.4 Transmission electron microscopy

Morphology and the size of the nanocrystals were examined by transmission electron microscopy. TiO$_2$ nanocrystals dispersed in toluene were deposited onto the porous carbon film on a Cu grid for TEM analysis. The typical TEM images, Fig.6.5 (a) and (b) revealed that the nanocrystals have a relatively spherical shape with a size distribution of 3 - 5 nm. Highly monodispersed TOPO capped semiconductor nanocrystals as well as thiol capped metal nanocrystals exhibited spontaneous self-assembly to form well ordered two-dimensional lattices. Previously, Fritzmaurice et al.$^{28}$ suggested that the polarity of the liquid medium affects the wetting properties and subsequently influences the aggregation of nanocrystals. The mechanism of solvent dewetting in annular ring structures formed by drying a metal colloid on a substrate was examined by Ohara et al.$^{29}$ and Gelbart et al.$^{30}$ Slow evaporation of a dispersion of TiO$_2$ nanocrystals in toluene (minimum amount) on a TEM grid leads to the formation of monolayers/bilayers of ordered spherical structures [Fig. 6.6 (a)-(d)]. These spherical aggregates of nanocrystals are well ordered and we believe that the formation of these self assembled structures and the degree of ordering depends on the polarity of the solvents, rate of solvent evaporation, concentration of the nanocrystals.
Fig. 6.5 (a) TEM images of TiO$_2$ nanocrystals, (b) at higher magnification.

Fig. 6.6 TEM images of spontaneously self-assembled spherical aggregates of primary TiO$_2$ nanocrystals.
6.3.5 EDX analysis

EDX analysis (fig. 6.7) was performed in order to determine the composition of nanocrystals and mainly Ti and O peaks were obtained along with Cu and C peaks (from the TEM grid) and P peaks from the capping ligand TOPO.

![EDX analysis](image)

*Fig. 6.7 EDX analysis of TiO$_2$ nanocrystals*

6.3.6 Particle size distribution analysis by photon correlation spectroscopy

In addition to TEM analysis, the particle size distribution analysis of TiO$_2$ nanocrystals was studied by photon correlation spectroscopy. TOPO capped TiO$_2$ nanocrystals were dispersed in spectroscopic grade toluene and filtered through a 0.2 µm filter (Millipore). Experiments were carried out at room temperature by placing the sample filled quartz cuvette in the centre of the scattering cell surrounded by the index matching liquid (toluene). The scattering intensity autocorrelation functions were obtained at a scattering angle of 90° using a APD detector (HIGH QE). Results were analysed using an ALV-5000/E Multiple Tau digital correlator. CONTIN method was used for the data analysis.
Fig. 6.8 shows the particle size distribution of TOPO capped TiO$_2$ nanocrystals obtained by PCS at a scattering angle of 90°, which gave the average diameter of the TiO$_2$ nanocrystals as 3.3 nm ± 0.8 nm. These results are in good agreement with the TEM size distribution analysis of TiO$_2$ nanocrystals.

![Graph showing particle size distribution of TiO$_2$ nanocrystals](image)

Fig. 6.8 Particle size distribution analysis of TiO$_2$ nanocrystals by PCS.
6.4 Summary and Conclusions

In summary, thermal decomposition of a modified titanium alkoxide precursor, [Ti(OPr′)₃(dmae)] in a co-ordinating solvent, tri-n-octylphosphine oxide (TOPO) at high temperature yielded good quality, quantum confined TiO₂ nanocrystals. TiO₂ nanocrystals were characterised by UV-Vis absorption spectroscopy, Photoluminescence spectroscopy, X-ray diffraction analysis, transmission electron microscopy and EDX analysis. Optical characterisations of TiO₂ nanocrystals reveal a strong and a broad blue light emission around 370 nm. Transmission electron microscopy analysis showed that TiO₂ nanocrystals were relatively spherical in shape with a size distribution of 3-5 nm. Photon correlation spectroscopy analysis of TiO₂ nanocrystals dispersed in toluene gave the average diameter as 3.3 nm. The slow evaporation of the solvent toluene leads to the formation of monolayers/bilayers of ordered spherical structures of TiO₂ nanocrystals.
6.5 References


Chapter 7

7 An efficient chemical solution deposition method for epitaxial GaN layers using single molecule precursors

Abstract

This chapter presents an efficient chemical solution deposition (CSD) method to grow epitaxial GaN layers at relatively low temperatures using single molecule precursors (SMPs). The SMPs \((\text{N}_3)_2\text{Ga}[(\text{CH}_2)_3\text{N}](\text{C}_2\text{H}_3)_2\) Bisazido diethylaminopropyl gallium (compound 1) and \((\text{N}_3)_2\text{Ga}[(\text{CH}_2)_3\text{N}](\text{CH}_3)_2\) Bisazido dimethylaminopropyl gallium (compound 2) were synthesised and characterised by standard methods. X-ray single crystal structure analysis of compound 1 revealed that the precursor exists as a dimer in the solid state and is different compared to compound 2, which exists as a dimer of dimers. The thermal stability and the volatility of the precursors were analysed by thermogravimetry and differential thermal analysis (TG/DTA). Chemical solution deposition experiments were carried out by spin coating the precursor solution on sapphire substrates in an inert atmosphere. The spin-coated substrates were annealed under ammonia ambient at different temperatures. Epitaxial GaN layers were grown on sapphire substrates and these layers were characterised for their morphology, microstructure, composition and optical properties by X-ray diffraction (XRD), X-ray rocking curve (XRC) analysis, pole figure measurements, reciprocal space mappings, scanning electron microscopy (SEM), Rutherford back scattering (RBS), X-ray photoelectron spectroscopy (XPS) and room temperature photoluminescence (PL) measurements.
7.1 Introduction

7.1.1 An overview

The evolution of lighting technology has been characterised by the invention of increasingly brighter and more efficient light sources since the discovery of incandescent light bulb by Thomas Edison in 1879.\(^1\) During the first part of the 20\(^{th}\) century, more powerful and efficient light sources such as neon lamps and fluorescent lamp tubes were developed and these light sources were used for different applications like filament and fluorescent lamps for interiors, neon lamps for exterior advertising and sign boards, and sodium discharge lamps for street lighting applications. The second part of the 20\(^{th}\) century, witnessed emergence of electronic lighting technology due to the development of high-efficiency electroluminescence semiconductor devices which led to the light-emitting diode (LED) technology.\(^2\) The discovery of light amplification by stimulated emission of radiation (LASER action) in 1962 allowed the production of semiconductor diodes with highly coherent bright light emission which soon found applications in telecommunications (optical fibre network), data storage devices (compact-disc technology), documentation and printing applications (laser printers).\(^3\) Light emitting diodes operating in the red–to-yellow region of the electromagnetic spectrum, with light emitting efficiencies superior to those of incandescent lamps became available in the early 1990’s.\(^4\)

The history of group-III nitrides dates effectively from about 1970 when a number of researchers began applying heteroepitaxial growth to produce reasonably high quality GaN films on sapphire substrates. The quality of the material was more than adequate for the measurement of quite a large range of parameters which established the basic semiconducting properties such as lattice constants, band gap, refractive index, phonon energies.\(^5\) However, group-III nitride based devices were not developed due to lack of suitable substrates, poor crystal quality of the layers grown on sapphire substrates, a high n-type background carrier concentration and the inability to p-dope the material efficiently.\(^6\) Further, the development in modern thin film growth techniques of molecular beam epitaxy (MBE) and metal-organic chemical vapour deposition (MOCVD) in 1990’s led to the growth of high quality group-III nitride materials by different groups.\(^7\) Strenuous efforts were made to optimise the growth conditions by introducing suitable buffer layers (between the sapphire substrate and active GaN) of AlN or GaN\(^8\) and the development of two flow MOCVD reactors led to the
development of high quality GaN layers in 1990’s and subsequently the commercial production of GaN based electronic and optoelectronic devices.\textsuperscript{9}

In this current century, the handling, distribution, display, and storage of large quantities of information is becoming increasingly important due to the tremendous developments that are expected in the area of information technology (IT) for everybody. The interface or the interaction of human/machine has one of the highest priorities in IT and due to the fact that information transfer into the human brain is mainly based on visual sensing by the eyes (reading, capturing entire picture, etc.), for which display technology plays a crucial and decisive role in the future. The future generation displays should be flat, bright coloured, lightweight and energy efficient. So the high brightness LEDs are finding an increasing range of applications and many companies such as Nichia, Toyoda Goasei, Cree, Osram Opto-semiconductors, Lumileds Lighting and GELcore are producing the nitride based LEDs for various applications.\textsuperscript{10}

\subsection*{7.1.2 Light emitting diode}

The basic component of electronic lighting technology is the light emitting diode. It is a simple semiconductor device that emits light when an electric current is passed through it. It consists of a back-to-back sandwich of p-type and n-type semiconductor material (p-n junction) characterised by a bandgap $E_g$. When a current is passed through the diode, electrons in the conduction band flow across the junction from the n-doped side, and the holes in the valence band flow from the p-doped side. (Fig.7.1) The result is that a significant number of electrons and holes recombine at the p-n junction, emitting light with an energy $h\nu = E_g$. In an LED, the energy of the photon is determined primarily by the energy bandgap, where recombination of electrons and holes occur. Since the human eye is only sensitive to light with photon energies from 3.1 eV to 1.6 eV corresponding to wavelengths of 400 to 780 nm, mainly compound semiconductors are used for the fabrication of LEDs.\textsuperscript{11} The main compound semiconductor materials used for the fabrication of LEDs and their corresponding photon energies; wavelengths and their relative response to the human eye are shown in Fig. 7.2. The application of various semiconductors in lighting technology with respect to the performance of the electroluminescence devices is shown in Fig. 7.3.
Fig. 7.1 Schematic diagram of a light emitting diode. The characteristics of the emitted light are related to the energy gap $E_g$ between the conduction and valence band in the semiconductor and $E_F$ is the Fermi energy.

Fig. 7.2 Examples of compound semiconductors and their corresponding photon energies, wavelengths and relative response to the human eye.
Fig. 7.3 The rate of development in electroluminescence devices since the discovery of Thomas Edison’s first bulb.

### 7.1.3 Applications of group-III nitrides

The group-III nitrides (InN, GaN and AlN) represent an important trio of semiconductors because of their direct bandgap ranging from 1.9 eV (InN) through 3.4 eV (GaN) to 6.2 eV (AlN). In addition, they form a complete series of ternary alloys, which spans whole range of the visible spectrum and extends well into the ultraviolet (UV) region. These unique properties make them ideal candidates for carefully tailored optoelectronic devices. Few important applications have been realised and these devices are commercially available in the market. Prominent among them are short wavelength laser diodes (LDs) (blue, UV) for optical disk readout applications and high efficiency light emitting diodes (LEDs) for various lighting and illumination applications like traffic light signals, full colour displays, displays in mobile phones and in automobile industry as interior automotive lighting. The light emitting diodes (LEDs) could be considered the ultimate general source of continuous light due to their high luminescence efficiency, quick response time and long lifetime. The major drawback which previously prevented the widespread application of coloured LEDs has been the lack of high intensity blue and green LEDs. As blue is one of the
three primary colours (RGB: red, green, blue), blue LEDs are required to reproduce the full colour spectrum and achieve pure white light. The multi coloured (white) systems have many wide spread applications as information boards for roads, railway stations, airports and large scale street displays.\textsuperscript{15}

Short wavelength laser diodes like blue laser diodes of GaN have potential applications in read/write on compact disks (CDs), while CD players now use 780 nm (near infrared) lasers to read the data. Using shorter wavelength blue lasers it is possible to decrease the spot size on the disk, creating a four-fold increase in data storage capacity on conventional disks like CDs and digital video disks (DVDs).\textsuperscript{16}

7.1.4 Important properties of group-III nitrides

Group-III nitrides exist mainly in two crystallographic structures, hexagonal wurzite and cubic zinc blend, which is thermodynamically unstable. Table 7.1 summarises the important properties of group-III nitrides.\textsuperscript{17}

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<th>AlN</th>
<th>GaN</th>
<th>InN</th>
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<td>(a_0 = 3.1892 \pm 0.0009)</td>
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<td>(Hexagonal)</td>
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</table>
Chapter 7

7.1.5 Commonly used techniques to grow GaN

7.1.5.1 Halide vapor phase epitaxy

In contrast to the manner in which silicon devices and integrated circuits were developed, III-V semiconductor devices have always depended on the epitaxial growth of high quality thin films on modest substrate material. Because of the elemental nature of Si, it proved possible to grow bulk crystals of device quality, whereas III-V compounds suffered from problems with stoichiometry which made it impossible to grow bulk material of comparable quality. The establishment of GaAs technology in the 1960’s was based largely on the growth of epitaxial films on bulk GaAs substrates, which were grown by halide vapour phase epitaxy (HVPE) method. However, in case of GaN, the inability to p-dope the GaN layers led to rapid decline in interest in HVPE methods, once MOCVD came into the scene. However, recently GaN growth by HVPE method has renewed interest on account of its potential to yield nearly strain free films of up to 200 μm thickness which could be used as substrates for homoepitaxial growth of GaN by MOCVD or MBE techniques.

7.1.5.2 Molecular beam epitaxy

Molecular beam epitaxy (MBE) was developed during the 1970’s for the growth of GaAs and its alloys such as AlGaAs, GaInAsP, AlGaInAs etc. Its success depends on the fact that thin film growth takes place in an all-stainless-steel ultrahigh vacuum vessel in the pressure range $10^{-10}$-$10^{-11}$ Torr, thus ensuring high purity conditions. The main advantage of MBE process are the precise control of composition inherent in the use of molecular beams of atoms which are switched on and off almost instantaneously by mechanical shutters, and the ability to change composition within the space of a single monolayer of material with the possibility of ideal in-situ monitoring techniques. High quality GaN thin films of both hexagonal and cubic phase were grown by molecular beam epitaxy technique and there is an excellent review on GaN thin film growth by MBE.

7.1.5.3 Metalorganic chemical vapour deposition

Metalorganic chemical vapor deposition (MOCVD) is a non-equilibrium growth process, which relies on vapor transport and subsequent reactions of group-III alkyls and group-V hydrides in a heated zone. The growth of bulk single crystal GaN is difficult due to the large equilibrium dissociation pressure of nitrogen over the nitrides at necessary growth
temperatures unlike Si and other III-V semiconductors like GaAs. All commercially available GaN based nitride semiconductor devices are fabricated by growing thin films via MOCVD typically on sapphire substrates employing the buffer layers of AlN or GaN using the chemical reaction of group-III alkyls, \( \text{MR}_3 (M = \text{Al, Ga, In and } R = \text{CH}_3, \text{C}_2\text{H}_5, \text{tBu}) \) and \( \text{NH}_3 \) with \( \text{H}_2 \) and \( \text{N}_2 \) as carrier gases at atmospheric or reduced pressure of about 100 hPa. The basic MOCVD reaction describing the GaN deposition is described in eqn (7.1)

\[
(\text{CH}_3)_3\text{Ga} + \text{NH}_3 \rightarrow \text{GaN} + 3\text{CH}_4
\]

7.1.6 Precursors for growth of group-III nitrides

The commonly employed precursors trimethylgallium, trimethylaluminium, trimethylindium and ammonia used for the growth of group-III nitrides have sufficient volatility and appropriate reactivity to decompose thermally into the desired material. But the trialkyl compounds are pyrophoric and extremely sensitive to \( \text{H}_2\text{O} \) and \( \text{O}_2 \) sensitive and ammonia is extremely corrosive and toxic. The major difficulties associated with these precursors include the predeposition reactions between the trialkyls and ammonia as well as the need for huge overpressures of ammonia (> 10^3) to minimise nitrogen dissociation from the growing film and to compensate for poor ammonia cracking efficiency. Alternative chemical sources like, alkylamines, hydrazine, and its derivatives have been used as nitrogen precursors to substitute the conventionally used ammonia and to reduce the growth temperature.

7.1.6.1 Single molecule precursor concept

Single molecule precursors offer an excellent way of transporting desired stoichiometric composition of multiple elements with different volatilities to the growth surface. An ideal or successful single molecule precursor should preserve the desired element ratio, possess easily removable terminal ligands and should exhibit sufficient volatility. The main advantage of the single molecule precursor is that, it can simplify the process control and allow the growth of the desired material even with rather inexpensive equipment (no-gas mixing system and precise control units) and offers the possibility of lowering the growth temperature. The apparent activation energy of the over-all process is lowered due to the presence of preformed bonds, which are relevant for the growth of the material. However, there are some general drawbacks in using single molecule precursors for MOCVD and related applications. The vapor pressures of single source precursors at ambient conditions are usually lower (< 1 Torr)
compared to the conventional precursors (> 10 Torr) due to the increased molecular weight of the compound and they often exhibit a more complex molecular structure compared to the conventional precursors. This eventually gives rise to unselective fragmentation of the ligand sphere and the organic residues attached to the atoms of interest, leading to incorporation of impurities into the growing material. Due to the fixed element ratio it may be difficult to precisely control the stoichiometry in case of single molecule precursors of semiconductors, where the properties of the resulting thin films are dependent on the ppm range. Thus, with SMP one parameter is lost i.e. the control of stoichiometry by adjusting the molar fractions of individual source in the gas phase.

7.1.6.2 Single molecule precursor approach to GaN layers:

The major limitation associated with the classical process for growing GaN films using conventional precursor by MOCVD is the co-pyrolysis of the precursors with a large excess of NH$_3$ at very high temperatures (> 1000°C) which leads to a large, background n-type carrier concentration due to nitrogen deficiency in the GaN layers. This is due to the high stability of the N-H bond in NH$_3$ and the cracking efficiency of NH$_3$ is as low as 5% at 700°C. Moreover, the group-III alkyls are pyrophoric in nature while NH$_3$ is highly toxic. An alternative route to this problem may be the use of single molecule precursors (SMPs) containing both the constituents that incorporate a direct Ga-N bond and that do not contain any strong N-H bonds or even organic groups which can offer potential for significant improvement in the growth process and film quality and thereby avoiding the use of ammonia as the nitrogen source. Considerable effort is currently being directed to the development of alternative molecular routes for the synthesis of group-III nitrides. Novel volatile single molecule precursors for group-III nitrides have been increasingly studied as precursors for MOCVD. Preformed M-N bonds in the precursor molecule lower the activation energies for the chemical vapor deposition growth process.

The most significant drawback of SMPs however is the following. Chemical gas phase epitaxy is typically achieved at conditions close to the transition between kinetic and mass transport controlled growth at temperatures high enough to allow good surface mobility of the growth species. The adjustment of the molar fractions of the individual precursor for the components of the material in the gas phase above the substrate is crucial to get to this regime. In the case of group-III nitrides, it is the N effusion from the nitrides at high temperatures necessary for epitaxial growth and the complex chemistry involved when
standard precursors are employed that necessitate the free adjustment of V/III ratios, as a very important parameter for optimising the whole system. This option appears to be lost when SMPs are used, as these precursors exhibit a fixed ratio of the components of the material, typically close to 1:1. Exactly, this problem arose along the work on SMPs for GaAs and InP. A special precursor design is needed, based on detailed knowledge of the fragmentation, to circumvent this problem. Nevertheless, SMPs containing the nitrogen component in a chemically activated form directly attached to the group-III metal, thus circumventing the problem of the inefficient activation of ammonia, are attractive candidates as SMPs for group-III nitrides especially for low temperature growth where ammonia cannot be used. An ideal single molecule precursor for the group-III nitrides would be a non pyrophoric, non explosive, non toxic, air stable liquid compound with high vapor pressure, exhibiting molecular structure with strong covalent M-N bond and less M-C, N-H bonds.

7.1.6.3 Azide based single molecule precursors for GaN

About a decade ago, azide based single molecule precursors were developed for MOCVD experiments for AlN and GaN thin films. The trimeric precursors \([\text{Et}_2\text{M}(\text{N}_3)]_3\) (M = Al, Ga) were used for the MOCVD of AlN and GaN films grown in the temperature range 450-900°C. The fragmentation of the azide group into dinitrogen and a reactive nitrene intermediate is a well-known decomposition pathway of covalent azides. Most of the recent work on single molecule precursor (SMP) for group-III nitrides has concentrated on azide derivatives. Intramolecularly Lewis base-stabilised organometallic azide compounds of the type \((\text{N}_3)_a\text{M}[(\text{CH}_2)_3\text{NMe}_2]_{3-a}\) (M= Al, Ga, In and a= 1, 2) were found to be sufficiently volatile due to their monomeric, or only very weakly associated structure in the solid state. In addition, these compounds were proved to be non–pyrophoric, non-explosive (if moisture is completely excluded) and some compounds even air stable (in the case of In compound). Their general suitability for the deposition of respective nitride materials has been demonstrated. In the case of a Ga compound, the SMP Bisacido dimethylaminopropyl gallium, \((\text{N}_3)_2\text{Ga}[(\text{CH}_2)_3\text{N(CH}_3)_2]\) Baziga, yielded high quality GaN films superior to any other reported MOCVD of SMPs. To study the effect of small variations in the ligand system on the volatility of these types of compounds, the ethyl congener of Baziga was synthesised and its application to grow GaN layers by MOCVD was also demonstrated.
7.1.7 Overview of techniques to deposit thin films

The deposition of thin film layers on different substrates is an essential step in many fields of modern technology, and applications range from large area optical coatings on windows and layers to improve friction and wear to applications in microelectronics. Considering this broad range of applications, it is obvious that there cannot be one perfect deposition method, which can be applied to all fields and materials. Thin films can be deposited by a wide variety of deposition techniques that can be classified according to the phase from which they are deposited. The relationship between different film deposition techniques is shown in Fig. 7.4. The important liquid deposition processes are spin coating, dip coating and spray pyrolysis. Chemical vapor deposition involves, vapor phase epitaxy (VPE), atomic layer epitaxy (ALE), plasma enhanced CVD (PECVD), while the main physical vapor deposition processes are sputtering, evaporation, pulsed laser deposition (PLD) and molecular beam epitaxy (MBE).

![Film Deposition Diagram]

Fig. 7.4 Relationship of different film deposition methods.

7.1.8 Chemical solution deposition

Chemical solution deposition (CSD) method for producing films involves the dissolution of a soluble precursor for the desired film in a suitable solvent and deposition on a substrate...
surface by spin coating or dip coating to obtain a uniform film followed by a thermal treatment. The schematic illustration of CSD by spin coating is shown in Fig. 7.5.

Fig. 7.5 Schematic illustration of CSD by spin coating.

Spin coating has been widely used in microelectronic industries for preparing thin films such as photoresists, interlayer dielectrics and buffer coatings. Fabrication of thin films by chemical solution deposition (spin coating) generally involves four basic steps:

1. Synthesis of the precursor or precursor solution
2. Deposition by spin-casting or dip coating
3. Temperature treatment (drying and pyrolysis of the precursor)
4. High temperature treatment for the crystallisation of the coating into desired material.

The nature of the thin films (thickness) obtained by spin coating is generally dependent on following factors: (a) spin speed, (b) spin time, (c) radius of spinning disk, (d) viscosity of the precursor/solvent used, (e) density of the precursor, (f) precursor concentration, (g) precursor volatility, (h) surface material of wafer, and (i) wafer radius.

CSD process was extensively used and investigated for the deposition of metal oxide perovskite thin films. The typical flow diagram for chemical solution synthesis and film deposition is illustrated in Fig. 7.6.
Coating a single-crystal substrate with a suitable crystal structure and lattice match can generally produce epitaxial films. Research investigations have shown that if the thickness of the film is less than a critical value, the shrinkage associated with drying and converting the precursor into an inorganic solid will not cause cracking because the film strain energy released by crack extension would be less than the energy required to form the new free surface associated with the crack. Polycrystalline films are generally produced when the inorganic amorphous film crystallises at temperatures above the pyrolysis temperature. There are several different mechanisms responsible for the conversion of a polycrystalline film into a single crystalline film. These mechanisms depend on factors that include substrate-film lattice mismatch and interfacial energies.
7.1.9 Advantages and disadvantages of the CSD method

CSD method has been used extensively in electroceramic research fields to develop thin films of ferrite, high temperature superconductors, dielectrics, ferroelectrics and antireflection coatings. Specific applications for which CSD is commercially viable include decoupling capacitors, pyroelectric infrared detectors, piezoelectric micromotors and chemical microsensors based on surface acoustic wave technology.\textsuperscript{50}

CSD method facilitates the stoichiometric control of complex materials (oxides) better than other techniques such as sputter deposition and metalorganic chemical vapor deposition. The main advantage of CSD process is that it is a simple, fast and cost efficient method to survey extensive ranges of film composition. Moreover, composition uniformity, molecular scale mixing (including dopants) and control of film thickness are possible with this method. A wide variety of precursors are available compared to CVD since the solubility in a particular solvent is the principal requirement. Further it is a process compatible with many semiconductor fabrication technologies and it may be the deposition method of choice for applications that do not require conformal depositions and that have device dimensions of 2 \( \mu \)m or greater. The apparatus required to deposit the films in case of CSD is much simpler than that often required for a CVD process. However, CSD processes have the disadvantages that conformal coverage and selective deposition is hard to achieve and the contamination of the films by the reaction by-product is a very serious limitation. The apparent disadvantages of the CSD route are the lack of understanding of film processing, film quality and properties. The use of CSD technique for the fabrication of perovskite thin films and more fundamental aspects of CSD process are reviewed in the literature.\textsuperscript{51}

7.1.10 Application of single molecule precursors for CSD of group-III nitrides

There are very few reports in the literature on CSD of GaN\textsuperscript{52} unlike in the case of oxides (e.g. dielectrics, ferroelectrics, and superconductors). Using polymeric precursor compounds, GaN and BN layers were obtained by CSD. GaN layers were obtained by CSD on r-plane \( \alpha \)-\( \text{Al}_2\text{O}_3 \) as well as on c-plane \( \text{Al}_2\text{O}_3 \) using a solution prepared by the reaction of GaCl\textsubscript{3} with excess bis (trimethylsilyl) carbodiimide and an annealing program in ammonia ambient. The structure and composition of the actual precursor in solution was not reported. But the composition \( \text{Ga(NCN)}_{1.05}(\text{SiMe}_3)_{0.20}\text{Cl}_{1.05} \) was noted, based on the chemical analysis of the obtained solid
after removing all volatile compounds from the above reaction and vacuum drying of the residue at 210°C. While evidence was given for the growth of GaN crystallites from the liquid precursor, the films were much thinner (low XRD intensity) and the morphology was extremely inhomogeneous with strongly faceted regions (r-plane). An unexpected bimodal size distribution of the grains (c-plane, high density of 10 nm grains and a few 150 nm grains) was observed. Recently, synthesis of wurtzite GaN films with a nitrogen-based precursor molecule, gallium dimethyl amide and a oxygen-based precursor molecule, gallium isopropoxide was reported. Boron rich BN films with a thickness of up to 2 µm have been prepared on Si/SiO\textsubscript{2}/Si substrates by vacuum or inert atmosphere pyrolysis at 900-1100°C of spin coated polyborazine precursor.

SMPS of the type \((\text{N}_3)_a\text{M}[\text{(CH}_2)_3\text{NMe}_2]_{3-a}\) (M= Al, Ga, In and a = 1, 2 ) are ideal precursors for the growth of nitride layers by CSD since, using nitrogen rich molecular precursors and pyrolysis under an ammonia ambient is viewed as analogous to aqueous sol-gel type CSD process. Thus, low boiling, very soluble, viscous gallium precursors are ideal compounds to grow high quality GaN layers by CSD. It is expected that these types of precursors efficiently react with ammonia to yield the nitride material of higher quality in a sol-gel type process.

In case of MOCVD, the homogeneous gas-phase pyrolysis or cracking of the individual source molecules is important, for example in the case of GaN, the growth active species are most likely Ga atoms and NH\textsubscript{x} radicals. CSD rather relies on the condensation of the precursors to form a polymer network directly on the substrate surface, which is transformed into the desired product by solid-state epitaxy upon annealing. So, SMPS that are nitrogen rich and that are as free of heteroatoms as possible appear to be very attractive candidates for CSD of GaN.

In this chapter, the synthesis and characterisation of SMPS \((\text{N}_3)_2\text{Ga}[(\text{CH}_2)_3\text{NR}_2]\) where R = CH\textsubscript{3}, C\textsubscript{2}H\textsubscript{5}, their application as precursors for the CSD experiment to grow GaN layers and the characterisation of GaN layers obtained will be discussed. The successful approach in growing high quality GaN layers using the SMPS compounds by MOCVD encouraged us to attempt these compounds as precursors for CSD experiments.
7.2 Experimental

7.2.1 Precursor synthesis and characterisation

The single molecule precursors Bisazido[3-(diethylamino)propylgallium, (N₃)₂Ga[(CH₂)₃NEt₂]], compound 1 and Bisazido dimethylaminopropyl gallium (N₃)₂Ga[(CH₂)₃NMe₂]], compound 2 were synthesised from GaCl₃, NaN₃, Li [(CH₂)₃NEt₂] and Li [(CH₂)₃NMe₂] ligand according to scheme 7.1.

![Scheme 7.1 Synthesis scheme of (N₃)₂Ga[(CH₂)₃NR₂]: R = CH₃, C₂H₅. (Ref. 33)](image)

Compound 1 was synthesised as follows:
About 8.79 g (72.7 mmol) of Li[(CH₂)₃NEt₂] dissolved in 150 ml of dry ether was slowly added (dropwise) to a suspension of 12.8 g (72.7 mmol) of GaCl₃ in 400 ml ether (cooled to –78°C). After complete addition of the ligand, the reaction mixture was allowed to warm up to room temperature and was further stirred for 10 hrs. After removing the solvent, the product was either sublimed (at 100°C) or distilled (short path flask to flask distillation) which resulted in a white solid with a yield of 17.9 g (96.5%). The product [3-(diethylamino)propyl]
gallium dichloride [Et₂N(CH₂)₃]GaCl₂ was analysed. ¹H-NMR: (C₆D₆, 25°C): δ = 0,682ppm (t, 6H, J = 7,87Hz, CH₃CH₂-); 0,733 (t, 2H, J = 7,18Hz, CH₂-CH₂-Ga); 1,256 (quint, 2H, J = 6,87Hz, -CH₂CH₂CH₂-); 1,869 (t, 2H, J = 6,115Hz, -CH₂CH₂N), 2,146 (sextup, 2H, J = 6,99Hz, CH₃CH₂H₂-); 2,809 (sextup, 2H, J=7,08Hz, CH₃CH₂-).

¹³C-NMR: (C₆D₆, 25°C): δ=7,726 ppm (2C, CH₃CH₂-); 9,00 (1C, GaCH₂-); 20,572 (1C, -CH₂CH₂CH₂-); 43,989 (2C, CH₂CH₂N-); 54,721 (1C, -CH₂CH₂N-). Anal. calcd.: N:5,49; C:33,01; H:6,33, found (%): N:5,57; C:32,71; H:6,22. MS (SI, 70eV) m/z (%) = 254.71.

To about 5g (19.63 mmol) of freshly sublimed Cl₂Ga[(CH₂)₃NEt₂] in 30 ml dry toluene, 5.104g (78.52 mmol, excess) of NaN₃ was added. The reaction mixture was refluxed at 111°C for two days. After filtration of the product from the white residue (NaCl), the solvent was removed. The end product was in the form of a white wax. It was distilled from flask to flask and this resulted in transparent crystals. The yield was about 4g (14.92 mmol) 76%.

¹H-NMR: (C₆D₆, 25°C) δ= 0,469ppm (t, 2H, J=7,56Hz, GaCH₂-); 0,623 (t, 6H, J=7,18Hz, CH₃CH₂-); 1,187 (quint, 2H, J=6,95Hz, -CH₂CH₂CH₂-); 1,755 (t, 2H, J=6,08Hz, -CH₂CH₂N), 2,273 (quartet, 4H, J=7,16Hz, CH₂CH₂-) ¹³C-NMR: (C₆D₆, 25°C) δ=2,50ppm (GaCH₂-); 7,61 (CH₃CH₂-); 20,55 (-CH₂CH₂CH₂-); 43,85 (CH₂CH₂N-); 55,32 (-CH₂CH₂N-). (m/z) (%) (M⁺)-N₃: 225; (M⁺)-2(N₃): 182. IR (toluene): ν(N₃) = 2099.3 cm⁻¹.

The details of the synthesis and characterisation of single molecule precursor (N₃)₂Ga[(CH₂)₃N(CH₃)₂], bis azido dimethylamino propylgallium, (Baziga) (compound 2) and its single crystal structure analysis is described in detail in reference 33.

The synthesis of the single molecule precursor compounds 1 and 2 yielded transparent crystalline material upon purification by repeated distillation. The synthesis was scaled up to larger batches (10–20g) and precursor identification and characterisation were achieved by a number of different techniques such as IR, NMR, mass spectrometry (MS), elemental analysis (EA) and atomic absorption spectroscopy (AAS) and single crystal X-ray diffraction analysis.

7.2.1.1 Thermal characterisation of the precursors

Thermogravimetric and differential thermal analysis (TG/DTA) of compound 1 and 2 were carried out to evaluate the thermal stability of these precursor compounds. The thermal characteristics of the precursor compounds was analysed using a Seiko TG/DTA 6300S11 instrument in an argon atmosphere (100mL/min) under ambient pressure with a heating rate of 5°C/min using ≈10mg of the precursor.
7.2.2 Chemical solution deposition experiments

7.2.2.1 Substrates

All the CSD experiments were carried out using c-plane Al₂O₃ substrates (Crystec GmbH, Germany). Polished electronic device grade Al₂O₃ (0001) substrates were cut into small square pieces measuring 1cm X 1cm and used for CSD experiments.

7.2.2.2 Substrate cleaning

The following procedure was used to clean the substrates. Each substrate was thoroughly cleaned using hot, analytical grade organic solvents. Every substrate was first suspended for a few minutes in boiling trichloroethylene (approximately 50 ml). It was then etched in a mixture of H₂SO₄/H₃PO₄ (3:1), for 2 minutes and rinsed with distilled water and acetone before mounting it on the spin coater.

7.2.2.3 Spin coater

As the single molecule precursors compounds 1 and 2 are moisture sensitive, the CSD experiments were carried out inside the glove box (Lab master 130, MBraun GmbH, Munich, Germany, O₂ <1ppm, H₂O <1 ppm). For this, the spin coater (KW-4A, Chemat Technology Inc., Northridge, USA) was installed inside the glove box for spin coating the precursor, and the spin coater was externally connected to the vacuum pump (outside the glove box).

7.2.2.4 Film deposition

Few drops (2-3) of compound 1 and 2 [diluted with toluene ~ 0.38 mol/L] were dropped on the substrate surface and the disc was rotated at a high speed (1000/2000 rpm) for one minute. The spin-coated substrates were then transferred into a quartz tube and placed inside a programmable furnace (outside the glove box). The pyrolysis temperatures were programmed and a constant flow of ammonia (50 sccm, 99.998%, Messer Griesheim GmbH, Germany) was introduced when the temperature of the furnace attained 200°C. The substrate temperature was varied in the temperature range 600-800°C. The pyrolysis and the deposition conditions are illustrated in Table 7.2

| Temperature program employed for GaN growth on c-plane Al₂O₃ by CSD. | 150 |
### 7.2.3 Film characterisation

Chemical solution deposited GaN films were investigated employing the following characterisation techniques. (For details see chapter 8)

1. X-ray diffraction analysis.
2. High-resolution X-ray diffraction analysis; X-ray rocking curve analysis.
3. Pole figure measurements and Reciprocal space mappings.
4. X-ray photoelectron spectroscopy
5. Rutherford backscattering spectroscopy
7. Photoluminescence spectroscopy.
7.3 Results and Discussion

7.3.1 Precursor characterisation

Compound 1 \((N_3)_2Ga[(CH_2)_3N(C_2H_5)_2]\) represents an ethyl congener of compound 2 \((N_3)_2Ga[(CH_2)_3N(CH_3)_2]\), Bis azido dimethylamino propylgallium (Baziga). Compound 1 crystallizes at room temperature (20°C) (mp. 48°C) as transparent crystals and in the monoclinic space group C2/c. The crystal structure of compound 1 is shown in Fig. 7.7.

![Crystal structure of compound 1, \((N_3)_2Ga[(CH_2)_3N(C_2H_5)_2]\). Selected bond distances (Å) and angles (°): Ga(1)-N(31) 1.906(3), Ga(1)-N(21) 1.915, Ga(1)-N(1) 2.073, N(31)-Ga(1)-N(21) 106.88(15), N(31)-Ga(1)-N(1) 101.46(13), N(21)-Ga(1)-N(1) 102.89 (13).]

Compound 1 can be described as a dimer and its molecular packing in the crystal is interestingly different from compound 2 (where it was described as a dimer of dimer, Fig. 7.8). Two molecules with the gallium centres Ga(1) and Ga(1A) are linked together by one single head-to-tail azide bridge (Fig. 7.7) \([Ga(1)-N(33A) = 3.027Å, Ga(1A)-N(33) = 3.027Å]\) which is significantly larger than in the case of compound 2 \([2.814 (5) Å]\). So, small variations in the ligand system can contribute to the changes in the crystal packing.
Fig. 7.8 Crystal structure of Compound 2, \((\text{N}_3)_2\text{Ga}[(\text{CH}_2)_3\text{N(CH}_3)_2]\) Bis azido(dimethylaminopropyl) gallium (Baziga) (after ref 33).

7.3.2 Thermal characterisation of the precursors

Thermogravimetric and differential thermal analysis (TG/DTA) can be used as a powerful tool in analysing the volatility and thermal stability of the precursor compounds. By examining the precursor compounds by TG/DTA, it is possible to follow the changes in the volatility of the precursor due to substitution of various chemical groups in the ligand. Moreover, TG/DTA is very helpful in comparing the thermal behaviours of almost identical precursor molecules like compound 1 and 2.

Thermal stability and the volatilisation of compound 1 and 2 was analysed by TGA/DTA. Fig. 7.9 shows the TG/DTA pattern of compound 1 with a heating rate of 5°C/min. It is seen from the TG curve that the precursor begins to volatilise at about 150 °C and there is a progressive weight loss till 260°C followed by a step at 260°C. Above 350°C there is no significant weight loss observed and a residue of about 31.95% is left behind in the crucible. The expected residue that should be left behind assuming the precursor to cleanly decompose to form GaN is about 31.25% and this matches very closely to the obtained value. From DTA curve, an endothermic dip around 48°C corresponds to the melting point of the precursor.
compound 1. At higher temperature (260°C) a sharp exothermic peak indicates the precursor decomposition.

TG/DTA analysis of compound 2 gave similar results except for the changes in the melting point of the precursor (35°C) as well as in the exothermic peak at 275°C (precursor decomposition).

Fig. 7.9 TG/DTA of (N$_3$)$_2$Ga[(CH$_2$)$_3$N(C$_2$H$_5$)$_2$] under ambient pressure (argon flow rate = 100 mL/min) and heating rate of 5°C/min.

7.3.3 MOCVD of GaN using compound 1 and 2

The precursor compounds 1 and 2 were used as single molecule precursors for the growth of GaN layers for MOCVD experiments. High quality epitaxial GaN layers were grown on Al$_2$O$_3$ substrates from compound 2 in a home built horizontal cold wall reactor. Compound 2 yielded high quality thin films of GaN superior to any other GaN films reported for MOCVD of GaN using single molecule precursors. MOCVD studies using compound 1 gave as good results as compared with compound 2.$^{56}$ The azide groups in the precursor molecules of compounds 1 and 2 serve as the main source of nitrogen for GaN growth (in the absence of additional ammonia) by MOCVD.
7.3.4 GaN film growth by chemical solution deposition

It was possible to grow GaN films by CSD using the molecular precursor compounds 1 and 2 on bare sapphire substrates without any additional source of ammonia. However, films with poor crystallinity were obtained from pyrolysis of compounds 1 and 2 without ammonia. Most of the films were polycrystalline in nature with lower intensities of the characteristic X-ray reflections. In order to improve the crystalline quality of the films as well as the purity, additional ammonia was employed. Thus, the CSD process using nitrogen rich molecular precursors and ammonia can be viewed as analogous to aqueous sol-gel type CSD processes. Ammonia could be an important reagent and it is definitely likely that some N comes from ammonia at temperatures as high as 800°C (where ammonia is known to thermally crack to release nitrogen atoms). However, in earlier studies by MOCVD, precursors such as compound 2 yielded stoichiometric GaN without any additional nitrogen source. Nevertheless, when ammonia was additionally employed, the C content in the films was significantly reduced. Thus for CSD of GaN layers low boiling, very soluble, viscous liquid gallium precursors are necessary which efficiently react with ammonia to yield the nitride material of higher quality in a sol-gel type process.

GaN films obtained using compound 1 and 2 have been grown on bare sapphire substrates in the presence of ammonia and post annealed with ammonia at different temperatures (600 - 800°C) (Table 7.2).

7.3.5 X-ray diffraction analysis

X-ray diffraction (XRD) analysis of GaN films grown by CSD is performed to investigate the crystalline quality of the films. XRD analysis of GaN films obtained below 700°C showed low intensity and they were polycrystalline. Fig. 7.10 shows the representative example of XRD pattern of GaN film obtained at 700°C, using compound 1 which is polycrystalline in nature with higher intensity. Similar results were obtained when compound 2 was employed in CSD experiments. These XRD results are in good agreement with the GaN films grown by MOCVD below 700°C using compounds 1 and 2 (polycrystalline films were obtained below 700°C). Well-oriented films were obtained above 750 °C, as indicated by only one single GaN reflection at 34.6° of the α-GaN (002) lattice plane in the 0 - 2θ scan. Fig. 7.11 and 7.12 show the XRD pattern of GaN film grown on c-plane Al₂O₃ by CSD at 800°C using compound 1 and 2 with NH₃ respectively.
Fig. 7.10 XRD pattern of a GaN film grown on c-plane Al$_2$O$_3$ by CSD at 700°C using $(N_3)_2Ga[(CH_2)_3N(C_2H_5)_2]$ (I) and NH$_3$ (polycrystalline film).

Fig. 7.11 XRD pattern of a GaN film grown on c-plane Al$_2$O$_3$ by CSD at 800°C using $(N_3)_2Ga[(CH_2)_3N(C_2H_5)_2]$ (I) and NH$_3$. 
7.3.5.1 X-ray rocking curve analysis

X-ray rocking curve (XRC) analysis of the (002) GaN reflection (compound 1, Fig. 7.11) were conducted using a high resolution X-ray diffractometer which indicate the presence of two types of crystallites of different orientations (superposition of the individual XRCs) resulting in pairs of values for the full-width at half maximum (FWHM) of 0.023° and 0.883° for films obtained at 750 °C as well as 0.034° and 0.641° for films obtained at 800 °C respectively. When compound 1 was spin coated as such without dilution, thicker films were obtained and the crystallinity of the material was reduced (FWHM = 1.156°). The high quality epitaxial GaN layers grown from compound 2 by MOCVD gave a single XRC with a FWHM of 0.04°. The XRC analysis of (002) GaN reflections of compound 2 (Fig. 7.12) gave FWHM values as 0.042° and 0.071°. Fig. 7.13 shows the XRC analysis of (002) GaN reflections of compound 1 and 2 (800°C).

Fig. 7.12 XRD pattern of a GaN film grown on c-plane Al₂O₃ by CSD at 800°C using \( (N₃)₂Ga[CH₂N(CH₃)₂] \) (2) and NH₃.
7.3.5.2 High resolution XRD analysis, pole figure measurements and reciprocal space mappings

Further investigations on the crystalline quality of the GaN films were carried out by pole figure measurements and reciprocal space mappings, to characterise more precisely the structural relation of the layers relative to the substrate. Pole figure measurements were employed to analyse the in-plane orientation and to determine the epitaxial growth as well as the orientation of the $\alpha$-GaN films relative to the c-plane sapphire substrate. This was set up with fixed values of $2\theta = 36.9^\circ$ and $\omega = 18.45^\circ$ to collect the X-rays diffracted ($\psi = 0 - 70^\circ$, $\phi = 0 – 360^\circ$). The 2D plot (Fig. 7.14) shows the reflections from GaN 0002 and 1011 at different $\psi$ and $\phi$ angles. The orientation of the sapphire substrate is illustrated by three 1014 reflections and the orientation of the $\alpha$-GaN is illustrated by six 1011 reflections. From the arrangement of these reflections, the hexagonal symmetry and the epitaxial growth was confirmed and the in-plane orientation of the $\alpha$-GaN films deposited on c-plane sapphire substrate was 30°, which is a well recognised value.

Fig. 7.15 shows the two-dimensional (2D) plot of the XRD reciprocal space mapping for an epitaxial GaN layer grown at 800°C using compound 1. The vertical and horizontal axis corresponds to $2\theta$ and $\omega$ scans respectively ($2\theta$ values in steps of 0.02°). Based on this plot, a columnar growth of the $\alpha$-GaN in the [0001] direction has been determined and compared with a commercially grown $\alpha$-GaN film (by CVD), which showed a similar feature.

Similarly, Fig. 7.16 and 7.17 show the pole figure measurement and the two-dimensional (2D) plot of the XRD reciprocal space mapping respectively for an epitaxial GaN layer grown at 800°C using compound 2.
Fig. 7.14 Pole figure measurement of a GaN film grown on c-plane Al₂O₃ by CSD at 800°C (compound 1) and the inset shows a schematic illustration of the orientation of the GaN film relative to the sapphire substrate.

Fig. 7.15 A 2D-plot of the XRD reciprocal space mapping for an epitaxial GaN film grown on c-plane Al₂O₃ by CSD at 800°C using compound 1.
Fig. 7.16 Pole figure measurement of a GaN film grown on c-plane Al₂O₃ by CSD at 800°C using compound 2. The inset shows a schematic illustration of the orientation of the GaN film relative to the sapphire substrate.

Fig. 7.17 A 2D-plot of the XRD reciprocal space mapping for an epitaxial GaN film grown on c-plane Al₂O₃ by CSD at 800°C using compound 2.
7.3.6 X-ray photoelectron spectroscopy

The composition of the GaN layers were analysed by X-ray photoelectron spectroscopy (XPS) and examination of the GaN films revealed (Fig. 7.18 and 7.19) the presence of both Ga and N peaks as well as Al and O peaks (substrate). In contrast to MOCVD results using compound 1 and 2, small traces of C impurities (XPS) were detected. This is probably due to the incomplete fragmentation and desorption of both, the solvent toluene as well as the ligand propylamine.

![Graph showing XPS analysis of a GaN film grown on c-plane Al$_2$O$_3$ by CSD at 800°C using compound 1.](image)

**Fig. 7.18** XPS analysis of a GaN film grown on c-plane Al$_2$O$_3$ by CSD at 800°C using compound 1.

![Graph showing high resolution XPS scans of Ga$2p$ cores and N$1s$ cores of GaN film grown on c-plane Al$_2$O$_3$ by CSD at 800°C using compound 1.](image)

**Fig. 7.19** High resolution XPS scans of Ga$2p$ cores and N$1s$ cores of GaN film grown on c-plane Al$_2$O$_3$ by CSD at 800°C using compound 1.
7.3.7 Rutherford backscattering spectroscopy

Rutherford backscattering spectroscopy (RBS) was used to obtain the gallium and nitrogen contents and to estimate the film thickness. Due to discontinuity in the film, the exact composition of Ga and N in the film could not be calculated, however the Ga and N signals were identified. The film thickness was estimated to be approximately in the range 6 to 8 µm. Fig. 7.20 shows the RBS spectrum of a GaN layer grown on c-plane Al$_2$O$_3$ by CSD at 800°C using compound 1.

![RBS spectrum](image)

Fig. 7.20 Rutherford backscattering spectrum (RBS) of a GaN layer grown on c-plane Al$_2$O$_3$ by CSD at 800°C using compound 1.

7.3.8 Scanning electron microscopy

The surface morphology of GaN films obtained by CSD using compounds 1 and 2 was characterised by scanning electron microscopy (SEM) and compared with the GaN layers grown in a home built cold wall MOCVD reactor. GaN films grown by CSD using compound 1 were discontinuous (due to cracking) and porous in nature (Fig. 7.21). The films were composed of rather uniform hexagonal and columnar crystal domains, which are fused together. The film was too thick which produced mud cracks due to constrained shrinkage during pyrolysis, and showed low-density network of crystallites with an average grain size of 20-30 nm (Fig. 7.21 d). The nucleation and growth of the films are similar to the island growth mode (columnar growth) where small droplets or clusters initially nucleate directly on
the surface and these clusters grow into islands of the film material, which eventually coalesce to form a continuous film. This growth mode takes place when the ad-atoms adhere strongly to each other than to the substrate.

![Fig. 7.21 SEM images of (a) GaN film grown on c-plane Al<sub>2</sub>O<sub>3</sub> by CSD at 800°C using compound 1, and (b-d) at higher magnifications.](image)

![Fig. 7.22 SEM images of (a) GaN film grown on c-plane Al<sub>2</sub>O<sub>3</sub> by CSD at 800°C using compound 2, and (b) at higher magnification.](image)
The observed shrinkage and the cracking of the film may be due to lattice mismatch between the epitaxial layer and the substrate and various other parameters like different thermal expansion coefficients of the film and substrate, film thickness, reactivity of the precursor etc. Similar surface morphology was obtained when compound 2 was used as precursor for CSD experiments (Fig. 7.22).

When the film and substrate have similar structures and a small lattice mismatch, but different chemistries, it has been shown that epitaxial nanometre sized grains are formed at the substrate/film interface during the crystallization of the amorphous film produced during the pyrolysis. Upon heating to the higher temperatures these epitaxial grains grow across the substrate by consuming the other grains and grow to the surface of the film to eventually convert the polycrystalline film into a single crystal.\(^{57}\) If the film and substrate have different structures, then epitaxial grain growth is delayed until a columnar, polycrystalline microstructure is produced by normal grain growth. Once the polycrystalline film has a columnar microstructure, grains with specific orientations that have lower surface and / or interfacial energies will tend to grow abnormally to consume all other grains. Concurrently, films with columnar microstructure undergo an instability in which the free energy is lowered by uncovering the substrate, leaving behind separated grains or seeds of preferred orientations produced during abnormal grain growth.\(^{58}\)

However, when compounds 1 and 2 were used as precursors for MOCVD experiments the surface morphology of the GaN films were different, [Fig. 7.23 (a) and (b)] and hexagonal growth with island like morphology was observed and these structures coalesce together forming continuous and relatively dense GaN layers. In contrast to CSD grown layers, these layers were grown on nitridated substrates.

![Fig. 7.23 SEM images of GaN film grown on c-plane Al\(_2\)O\(_3\) by MOCVD at 800°C using (a) compound 1 and (b) compound 2 at higher magnification [after ref (34)].]
7.3.9 EDX analyses

The EDX analyses of the GaN films are shown in Fig. 7.24. In addition to Al and O peaks (from the substrate) Ga, N, and C peaks were detected. Au peak is due to the sputtering of the film by Au.

Fig. 7.24 EDX analyses of GaN layers grown on c-plane $\text{Al}_2\text{O}_3$ by CSD at 800°C using (a) compound 1 (Fig. 7.21) and (b) compound 2 (Fig. 2.22).

7.3.10 Optical characterisation

It is important to analyse the optical properties of GaN layers obtained by CSD experiments to evaluate its luminescence behaviour. The optical properties of the films were analysed by room temperature photoluminescence spectroscopy (Fig. 7.25). The PL spectrum exhibited a broad yellow luminescence band at 2.25 eV. Despite intense use of GaN in LED and other optoelectronic device applications, the origin of the defect related luminescence band at about 2.2–2.3 eV, commonly referred to as yellow luminescence (YL) in undoped (unintentionally doped) GaN is not yet clearly established.\(^5^9\) Recently a detailed study of yellow and green luminescence in a high purity freestanding GaN layer was reported.\(^6^0\) The origin and the behaviour of the broad luminescence band around 2.2–2.3 eV were attributed to the surface oriented deep defects and structural imperfections.
The room temperature PL spectrum of GaN layers grown by CSD experiments showed similar features and broad luminescence band around 2.25 eV, which may be attributed to the deep levels caused by the lattice defects. A very weak band edge emission at 3.45 eV was observed in the PL spectrum. It is reasonable to expect that by further refinement in the processing conditions and using nucleation layers as substrates (buffer layers of GaN or AlN) it may be possible to obtain better quality GaN layers by CSD with improved optical properties.
7.4 Summary and Conclusions

A simple approach of chemical solution deposition (CSD) method to grow epitaxial GaN layers using single molecule precursors (SMPs) was demonstrated. The thermal behaviour of SMPs was analysed by TG/DTA. SMPs, which are suitable for the growth of GaN layers by MOCVD, are also useful as precursors for the growth of GaN layers by CSD. Highly crystalline and epitaxial films of GaN were obtained by pyrolysing the spin-coated precursor above 800°C. Polycrystalline films of GaN were obtained at pyrolysis temperature below 800°C. The crystalline quality of GaN layers were analysed by XRD and the combined results with pole figure measurements, and reciprocal space mappings confirmed the epitaxial growth of GaN layers. The microstructure and morphology of the CSD grown GaN layers are compared with the MOCVD grown GaN films. These results show that there are more choices for precursors, and their selection as well as processing conditions has a significant impact on resulting films in terms of film morphology and crystallisation behaviour. The precursors, which are nitrogen rich and as free of heteroatoms as possible, are ideally suited for CSD. The SMPs which are suitable for nitride MOCVD are also interesting candidates for CSD and these layers may be useful for the growth of nucleation layers as well as thick (> 200 µm) large area crystalline films.
7.5 References

10 *Compound Semiconductor* 2001 (April).


8 General characterisation techniques

8.1 X-ray diffraction analysis

X-ray diffraction analyses were carried out employing a D8-Advance Bruker axs diffractometer using CuK$_\alpha$ radiation ($\lambda = 1.5418$ Å). XRD instrument consists of CuK$_\alpha$ as X-ray source with Nickel filter, and a Goebel mirror with a parallel plate collimator and OED detector. High angle XRD measurements were carried out with $\theta$ - 2$\theta$ geometry in the range 20 - 80° using a position sensitive detector. The low angle XRD analyses were carried out using Cu K$_\alpha$ radiation ($\lambda = 1.5418$ Å) with $\theta$ - 2$\theta$ geometry in the range 1 - 10° using a scintillation counter.

8.2 HRXRD analysis, pole figure measurements and reciprocal space mappings

A high resolution X-ray diffractometer (D8-Discover-Bruker AXS) was employed to perform high-resolution rocking curve analysis of the epitaxial GaN films (Chapter 7) as well as to generate reciprocal space mappings and pole figures. For the rocking curve analysis, a pinhole configuration was used with Cu K$_\alpha$ radiation, and a Goebel mirror with a parallel plate collimator combined with 0.1 mm divergence slits were placed in front of the detector. This arrangement permits high intensity with good resolution. The X-ray reciprocal space mappings were obtained by performing the $\omega$-scans by inclining the sample continuously along the 20 axes, and the pole figures were obtained by rotating the sample along the $\psi$ axes at different $\phi$ positions.

8.3 Chemical analysis

The chemical analyses of the samples were carried out using an ICP-instrument from Philips, (Philips-Unicom PU 7000) in the Mineralogy department at the Ruhr-University Bochum. Atomic absorption spectroscopy analysis and the elemental analysis were performed in the Spectroscopy and Chromatography department at the Ruhr-University Bochum using AAS Vario 6 and Elementar Vario EL instruments.
8.4 UV-Vis absorption spectroscopy

UV-Vis absorption spectra were recorded using an instrument from Perkin-Elmer Lambda 9N-1062 spectrometer.

8.5 IR-spectroscopy

Infrared spectroscopy analysis was carried out either using NaCl window or pressed KBr discs on a Perkin-Elmer FT-IR spectrometer 1720X.

8.6 UV-diffuse reflectance spectroscopy

UV-diffuse reflectance measurements were carried out using PE Lambda 900 occupied with integrating sphere. The UV-Vis absorption spectrum was obtained by applying the Kubelka-Munk function to the reflectance spectrum. These experiments were carried out at the Materials Science Department of Technical University Darmstadt, Germany.

8.7 Photoluminescence spectroscopy

Photoluminescence measurements of the composite CdSe @ MCM-41 (Chapter 4) were performed at room temperature. A chopper-modulated D_2 lamp (lock-in technique) was used as an excitation source. The luminescence signals were collected by quartz lenses using a cut-off filter (280 nm) and a monochromator (ISA HR 640) and detected by a photomultiplier (Hamamatsu R 4220). These experiments were carried out at the Materials Science Department of Technical University Darmstadt, Germany.

The optical characterisation of the GaN layers grown by CSD method (Chapter 7) was investigated by room temperature photoluminescence spectroscopy (PL). Room temperature PL measurements were conducted using a He-Cd laser (Kimmon, 38mW, \( \lambda = 325\text{nm} \)). The set up consists of SPEX 500 M spectrometer (JobinYvon) and Si-Photodiode DSS-S025A. The signal was chopped and detected using lock-in-technology with a SR 850 DSP Lock-in Amplifier. PL experiments were carried out at the Physics Department (Prof Dr. A. D. Wieck) of Ruhr-University Bochum, Germany.
Chapter 8

Luminescence properties of TiO$_2$ nanocrystals (Chapter 6) were investigated using a Fluoro Max-2 instrument with a continuous ozone-free xenon lamp (150W) and a R928P photomultiplier tube.

8.8 Nitrogen sorption experiments

Nitrogen adsorption-desorption measurements were carried out using Autosorb –1 instrument from Quantachrome Corporation, Boynton Beach /FL, USA with nitrogen as adsorbate at 77K. The samples were degassed for 12 hours at 300°C in vacuum before the measurements. For the determination of the surface area the BET method was used. Barrett-Joyner-Halenda (BJH) calculations were made for the pore volume and pore size distribution for the adsorption portion of the isotherm. The calculations of the measurements were analysed by the software programme provided by Quantachrome Corporation (Autosorb –1 for Windows; Version 1.19). These experiments were carried out at the Technical Chemistry Department (Prof. Dr. M. Muhler) of Ruhr-University Bochum, Germany.

8.9 Thermal analysis

The thermal analyses of the compounds were carried out using a Seiko TG/DTA 6300S11 instrument in argon atmosphere (100 mL /min$^{-1}$) under ambient pressure. The furnace was heated to 600°C at heating rate of 5°C/min. About 10 mg of the sample was used for the each analysis.

8.10 Transmission electron microscopy

Transmission electron microscopy (TEM) images were acquired with a Hitachi H-8100 TEM instrument, operated at 200 kV with tungsten filament.

Sample preparations

The InN whiskers (Chapter 2) grown on bare sapphire substrates did not adhere well to the substrate, and could be easily removed from the substrate. This made sample preparation easier for TEM analysis and was carried out as follows. A small piece of the substrate was taken and ultrasonically dispersed in ethanol for 15min. The ethanolic solution was then dropped on a holey carbon coated grid for observation by TEM. Selected area electron diffraction (SAED) analysis was performed to characterise the phase of the InN whiskers.
TEM analyses of empty MCM-41, empty SBA-15, GaN @ MCM-41, GaN @ SBA-15, and CdSe @ MCM-41 were carried out as follows. TEM samples were prepared by suspending the desired samples in ethanol followed by sonication for 15 min in an ultrasonic bath. The suspension was then dripped onto a copper grid (Ted Pella Inc.) and allowed to dry overnight. The dried copper grid was then loaded to the TEM instrument for further analysis.

Similarly, TEM analysis of gold and TiO$_2$ nanocrystals were carried out using Hitachi H-8100 TEM operated at 200 kV with a tungsten filament. TEM grids were prepared by suspending the nanocrystals in toluene followed by sonication for 15 min in an ultrasonic bath. The suspension was then dripped onto a copper grid and allowed to dry for overnight. The dried copper grid was then loaded to the TEM instrument for the analysis.

**X-ray energy dispersive analysis**

X-ray energy dispersive analysis was performed using an EDX analysis system attached to the TEM instrument. X-ray energy dispersive spectra (EDS) were recorded using Oxford Link with Si (Li) crystal with ultrathin window ATW 2.

### 8.11 Scanning electron microscopy

Scanning electron microscopy (SEM) analyses were carried out using LEO-1530 Gemini SEM, instrument equipped with an energy dispersive x-ray analysis unit, Oxford ISIS EDX system. Before the SEM analysis, metallic Au was evaporated on the surface of the specimen to form a conducting layer to avoid electrostatic charging. These analyses were conducted at the central microscope facilities of Ruhr-University Bochum.

### 8.12 X-ray photoelectron spectroscopy

XPS experiments were carried out with a modified Fisons X-ray photoelectron spectrometer equipped with an Al K$_\alpha$ X-ray source and a CLAM3 electron energy analyser. The pass energy was set to 50 eV. The typical operating pressure was less than $10^{-8}$ mbar. All binding energies were referenced to the substrate signal. Survey X-ray photoelectron spectra and high resolution XPS spectra were collected for desired elements.
9 Publications


9.1 Poster presentations


4. Indium Nitride Whisker Growth by Chemical Vapor Deposition, Anjana Devi, Harish Parala and Roland A. Fischer, 199\textsuperscript{th} meeting of the Electrochemical Society, March 2001, Washington DC, USA.

5. Nanosized GaN Particles by Chemical Vapor Infiltration, Harish Parala, Anjana Devi and Roland A Fischer, 199\textsuperscript{th} meeting of the Electrochemical Society, March 2001, Washington DC, USA.


**Curriculum Vitae**

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  - Course: German Language Course (Intensive)
- 04/1998: Registered as a student at Ruhr-University Bochum, Germany
- 06/ 1998 – 12/1998: Research Project at the Inorganic Chemistry II, Faculty of Chemistry, Ruhr-University Bochum, Germany
  - Project: Synthesis and Characterisation of Metal and Semiconductor Nanoparticles
  - Project Guide: Prof. Dr. Roland A. Fischer
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