Surface-enhanced Raman Spectroscopy Investigation of Surfaces and Interfaces in Thin Films on Metals

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Abstract

The fabrication and characterization of novel surface-enhanced Raman spectroscopy (SERS)-active substrates as well as their applications are presented in this dissertation. The SERS-active substrates were prepared by combining plasma enhanced chemical vapor deposition and physical vapor deposition. The obtained film coated substrates are proved to be SERS-active and the enhancement factor is determined to be up to $10^5$-$10^7$. In comparison to other methods reported in the literature, this method is easy, reproducible and applicable to many different substrates. The applications of the prepared SERS-active substrates in various research fields are reported in detail as well. SERS was used to study the growth of an ultra-thin organosilicon plasma polymer film and the results elucidated the relation between the enhancement factor and the thickness of the plasma polymer film. The enhancement factor decreased sharply in the first 20 nm thickness range, which agrees with the proposed “first layer enhancement mechanism”. Moreover, the phase transition of TiO$_2$ thin films was successfully investigated by using a TiO$_2$/SERS-substrate model system. The Raman signal of the TiO$_2$/SERS-active substrate was enhanced at least two orders of magnitude compared to that of the Si-supported TiO$_2$ film and 20 times relative to that of the TiO$_2$/Ag/Si system. The enhanced signal could be attributed to the localized electromagnetic field from the surface plasmon excitation of metal Ag decoration. The results indicate the potential applications of SERS in analysis of metal/metal oxide in materials science in the future. In addition, SERS was also intensively applied to in-situ characterize the modification effects of different plasmas on thin metal films, carbon nanotubes and polystyrene films. The described back-scattering experimental set-up for the in-situ SERS measurements is shown to be a promising technique for in-situ plasma modifications and characterization of different surfaces. In particular, the kinetic adsorption process of 2-mercaptobenzothiazole (MBT) on silver surface was in-situ monitored by combining SERS and the quartz crystal microbalance (QCM) technique. The results demonstrated that the adsorption of MBT molecules was achieved by a chemical bond between the exocyclic sulfur atoms in MBT molecules and silver atoms on the surface. The orientation of MBT molecules on the silver surface is likely to be either perpendicular or tilted relative to the silver surface. The combined SERS and QCM techniques are shown to be able to facilitate more profound insight into the nature of the adsorption of organic molecules on metal surfaces.
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Chapter 1: Preface

1.1 Motivation

We are looking for a technique that allows chemical understanding of the processes at metal/gas, metal/polymer and metal/electrolyte interfaces in various environments. Raman could be an appropriate one because it can provide information on chemical structures and physical forms, identify substances from the characteristic spectra, and determine quantitatively or semi-quantitatively the amount of substances. Moreover, the good applicability makes it possible for Raman to measure a whole range of physical states of the samples, for example, as gases, liquids or solids, in hot/cold states, in bulk or as surface layers. But the natural weak signal confined the applications of Raman in practice.

The discovery of surface-enhanced Raman scattering (SERS) made the weak Raman intensity not a fatal limitation anymore. SERS refers to the phenomenon that the Raman signal from adsorbates on roughened metal surfaces is enhanced by a factor of $10^4$-$10^6$ due to the excitation of surface plasmon resonance on roughened metals and/or the ‘first layer’ enhancement including charge transfer interactions between adsorbates and metals. SERS has exhibited an extremely high sensitivity in the detection of single molecule and received wide applications in fields including surface and interface science, electrochemistry, analytical chemistry, biological and biomedical science and materials science.

However, three obstacles blocked the development of this sensitive technique. First, the giant enhancement effect was only found on coinage metals, Au, Ag and Cu, which limited the applications of SERS in widely used transition metals in industry. Second, it is still a big challenge to prepare the appropriate SERS-active substrates to meet the requirements whether in research or in practice. The last one is the unclear enhancement mechanisms, although electromagnetic enhancement and chemical enhancement have been accepted as the main enhancement mechanisms, none of them can explain all the observed phenomena.

Thus, the aim was to develop versatile SERS-active substrates which could meet the following requirements, such as large enhancement factor, good stability, reproducibility, and the process of fabrication should be easy, fast and applicable to different substrates. To satisfy all these requirements, plasma enhanced chemical vapor deposition (PECVD) combined with physical vapor deposition (PVD) was used to prepare the SERS-active...
substrates.

Moreover, the relation between SERS intensity and the film thickness, and the enhancement factor as a function of the film thickness are seldom mentioned in the literature because of the poor reproducibility of the film and the SERS-active substrates. Organosilicon plasma polymer films have shown an excellent reproducibility on various substrates, concerning the film morphology and the chemical composition. Therefore, the model system organosilicon plasma polymer/SERS-active substrate is an ideal system to be studied in order to reveal the above-mentioned scientific questions.

Normal Raman spectroscopy has been applied in studying the phases of the metal/metal oxide films and identifying the chemical composition in materials science for a long time. However, the application of SERS technique in this field is relatively new, especially in the characterization of the thin films (< 100 nm). SERS could be a relative easy, fast, sensitive alternative tool in analysis of thin films. The investigation of the phase transition of TiO₂ thin films by SERS would show the possible applications of SERS in analysis of other important metal/metal oxide in industry in the future.

Plasma modification plays a very important role in surface science and interface engineering. It is an interesting topic to characterize the products, evaluate the modification effects and deduce the detailed mechanisms of different plasma modifications, especially in in-situ conditions. Besides the traditional analytical techniques, SERS could be another alternative to perform in-situ analysis and characterization of the plasma modifications.

Quartz crystal microbalance (QCM) is a very sensitive and extensively used technique to control the film thickness and SERS is very sensitive in detecting the information of the adsorbed molecules on the surface. 2-mercaptobenzothiazole (MBT) has various and widespread industrial applications. It is well known to be an effective corrosion inhibitor and is recommended for the protection of lead, copper and its alloys. The adsorption mechanisms of MBT on metals are of great importance for the applications of MBT in industry. The combination of QCM and in-situ SERS measurements during the adsorption process of MBT would be of great benefit to better understand its adsorption mechanisms on metals.
1.2 Scope of the Thesis

The primary aim of this work is focused on the development of novel SERS-active substrates and their applications in various research fields. The basic principle is borrowing the rough feature from the supported underlayer to produce the rough noble meal surface and achieve the surface enhancement effect. The prepared substrates meet the following requirements, such as stable, reproducible, possessing large enhancement factor and easiness for preparation. The obtained SERS-active substrates were successfully applied in various research projects, including investigation of the growth of the thin organosilicon plasma polymer films, studying the phase transition of the sputtered TiO$_2$ thin films with annealing treatment, in-situ characterization of the plasma modification effects on metal and polymer surfaces, and in-situ monitoring of the adsorption process of organic molecules on metals combining QCM and SERS techniques.

The thesis is divided into 8 chapters. The motivation of this work and the scope of the thesis are described in chapter 1. A general introduction to the background and the advancements about Raman and surface-enhanced Raman scattering is presented in chapter 2. It contains the background of Raman scattering, SERS features, the widely accepted enhancement mechanisms, the advancements of SERS in extending the applications to transition metals, new methods to fabricate SERS substrates, the proposed new enhancement mechanisms and special applications of SERS in adhesion science. In chapter 3, the fabrication of novel SERS-active substrates achieved by combining PECVD and PVD techniques is shown. The surface characterization of the prepared SERS-substrate was carried out by means of atomic force microscope (AFM), scanning electron microscope (SEM), ultraviolet-visible spectroscopy and electrochemical impedance spectroscopy. The enhancement factor of the prepared SERS-substrates was probed with trans-1, 2-bis (4-pyridyl) ethylene molecule and calculated according to the method reported in the literature. As one of the applications of the prepared SERS-active substrates, the growth of ultra-thin organosilicon plasma polymer film is investigated by surface-enhanced Raman spectroscopy in chapter 4. The relation between SERS intensity and the film thickness, and the enhancement factor as a function of the film thickness are presented. The phase transition of the sputtered TiO$_2$ thin films on SERS substrates with annealing treatment is discussed in detail in chapter 5 by using SERS, AFM, SEM, grazing incidence X-ray diffraction and X-ray photoelectron spectroscopy (XPS) techniques. In chapter 6, the glass-based SERS-active substrates are extensively used
to in-situ explore the surface modification effects of different plasmas. The modification of Cu surface by a plasma cycle, modification of carbon nanotubes by N\textsubscript{2} plasma, as well as the modification of thin polystyrene films by O\textsubscript{2}, (Ar + H\textsubscript{2}) and (N\textsubscript{2} + H\textsubscript{2}) plasmas are reported. In chapter 7, the adsorption process of MBT molecule is in-situ investigated by combining SERS and QCM techniques. The experimental set-up was introduced in detail and various techniques such as AFM, SEM, infrared reflection absorption spectroscopy, XPS, in-situ SERS and QCM were combined to study the adsorption of MBT molecules on metals. The possible orientation of MBT on silver surface was proposed by comparing the SERS spectra of MBT adsorbed on gold surface and on silver surface as well as the data in the literature. The whole thesis is concluded in chapter 8 and the further work in the future is also indicated.
Chapter 2: General Introduction

2.1 Background of Raman Scattering

The phenomenon of inelastic scattering of light was first postulated by Smekal in 1923 [1-a] and first experimentally observed in 1928 by Indian physicists C. V. Raman and K. S. Krishnan [1-b]. When a monochromatic light (at frequency $\nu_0$) illuminates molecules with internal modes of vibration (at frequency $\Delta\nu$), a very small portion of the incident light is scattered off from the molecules with its color either red or blue shifted (from $\nu_0$ to $\nu_0'$. The frequency difference between the incident light and the scattered light equals to the molecular vibrational frequency,

$$\nu_0 - \nu_0' = \pm \Delta\nu$$  \hspace{1cm} (2-1)

Since then, this phenomenon is referred to as Raman effect.

2.1.1 Raman Effect

As well known, photons interact with molecules and induce transitions between energy states. Most photons are elastically scattered in a process called Rayleigh scattering. In Rayleigh scattering, the scattered photons have the same frequency as the incident photons ($\nu_0$). Raman spectroscopy is based on Raman effect, which is based on the inelastic scattered photons by molecules. In Raman scattering, the energies of the incident and scattered photons are different. A simplified energy diagram that illustrates these concepts is given in Fig. 2-1 (a). The energy of incident photon is $h\nu_0$ and the difference between the two energy states ($V = 0$ and $V = 1$) is $h\Delta\nu$.

The Raman scattering process is called Stokes scattering when it occurs from the ground vibrational state ($V = 0$) to a higher energy excited vibrational state ($V = 1$) due to the energy absorption by the molecules ($h\Delta\nu$). However, due to thermal energy, some molecules may be present in an excited state ($V = 1$) as shown in Fig. 2-1 (a). Scattering from the excited states ($V = 1$) to the ground state ($V = 0$) is called anti-Stokes scattering, which involves a transfer of energy to the scattered photons ($h\Delta\nu$). All these concepts can be found in Fig. 2-1 (b). The relative intensities of these two processes depend on the population of the various states of the molecules.

In the scheme of Raman and Rayleigh spectra shown in Fig. 2-1, notice that the Stokes and
anti-Stokes lines are symmetrically displaced from the Rayleigh line. This occurs because in either case one vibrational quantum of energy is gained or lost. Furthermore, the anti-Stokes line is much less intense than the Stokes line. This is because more molecules in the ground state than those in the excited state which can give the anti-Stokes line (Maxwell-Boltzmann distribution law). Hence, in Raman spectroscopy, the more intense Stokes scattering is measured in most cases.

\[
\begin{align*}
E_1 + h\nu_0 & \quad \text{Virtual states} \\
E_0 + h\nu_0 & \\
h(\nu_0 - \Delta\nu) & \\
h\nu_0 & \\
E_1 & \quad h\Delta\nu \\
E_0 & \quad V = 0 \\
V = 1 & \\
\end{align*}
\]

(a)

2.1.2 Raman Selection Rules and Raman Intensities

2.1.2.1 Raman Selection Rules

Raman spectroscopy and infrared (IR) adsorption spectroscopy are two main spectroscopic tools to detect the vibrations in the molecules. A general question is that when the vibrations of molecules can be detected by Raman or IR spectroscopy, namely, vibrational modes are Raman-active or IR-active, which is concerning the so-called selection rules. As well known, the selection rules of IR spectroscopy is that there must be a net change in permanent dipole moment during the vibrations. As shown in Fig. 2-2, the symmetric stretch in carbon dioxide is not IR-active because no net change occurs in the dipole
moment. The asymmetric stretch is IR-active due to a change in dipole moment.

\[
\alpha \propto \alpha_0 \cos 2\pi v_0 t
\]

The Raman selection rule is analogous to that for an IR-active vibration. For a vibration to be Raman-active, the polarizability of the molecule must change with the vibrational motion. The concept of polarizability will be explained in the next section. As shown in Fig. 2-3, the symmetric stretch in carbon dioxide is Raman-active because the polarizability of the molecule changes. The shape of electron cloud at the equilibrium state is different from that when it is in the extended and compressed symmetric motions.

\[
\mu \propto E_0 \cos 2\pi v_0 t
\]

It can be induced that symmetric vibrations can cause the intense Raman intensity which is contrasted to the IR where the asymmetric vibrations cause more intense according to the above mentioned selection rules. Thus, Raman spectroscopy and IR spectroscopy complement each other.

### 2.1.2.2 Raman Intensities

A simple, classical electromagnetic field description of Raman spectroscopy can be used to explain many of the important features of Raman band intensities [2-4]. The dipole moment, \( \mu \), induced in a molecule by an external electric field, \( E = E_0 \cos 2\pi v_0 t \) \((E_0\) is the amplitude and \( t \) is the time), is proportional to the field as shown in equation 2-2.

\[
\mu = \alpha E = \alpha E_0 \cos 2\pi v_0 t
\]  

The proportionality constant \( \alpha \) is the polarizability of the molecule. The polarizability,
which is a tensor quantity, can be qualitatively described as the ease with which molecular orbitals are distorted by the presence of an external field. If the molecule itself is vibrating at frequency $\nu$ corresponding to its normal mode and the nuclear displacement (normal coordinate) is written as $Q = Q_0 \cos 2\pi \nu t$, where $Q_0$ is the vibrational amplitude, then for small amplitudes of vibration, $\alpha$ is a linear function of $Q_0$,

$$\alpha = \alpha_0 + (\partial \alpha / \partial Q)_0 Q$$

(2-3).

Here $\alpha_0$ is the polarizability at the equilibrium position, and $(\partial \alpha / \partial Q)_0$ is the rate of change of $\alpha$ with respect to the change in a normal coordinate $Q$, evaluated at equilibrium position.

The characteristic vibrational frequency $\nu$, can mix with exciting light $\nu_0$, to form sum and difference frequencies in the scattered radiation. By combining the above equations, one can obtain the following equation:

$$\mu = \alpha E_0 \cos 2\pi \nu_0 t$$

$$= \alpha_0 E_0 \cos 2\pi \nu_0 t + (\partial \alpha / \partial Q)_0 Q_0 E_0 \cos 2\pi \nu_0 t \cdot \cos 2\pi \nu t$$

(2-4)

$$= \alpha_0 E_0 \cos 2\pi \nu_0 t + \frac{1}{2} (\partial \alpha / \partial Q)_0 Q_0 E_0 \times \left\{ \cos [2\pi (\nu_0 + \nu) t] + \cos [2\pi (\nu_0 - \nu) t] \right\}$$

Here the first term describes Rayleigh scattering (elastic scattering) of frequency $\nu_0$ and the second term gives the Raman scattering (inelastic scattering) of frequencies $(\nu_0 - \nu)$ (Stokes) and $(\nu_0 + \nu)$ (anti-Stokes) which may be detected as shifts from the Rayleigh frequency although they are very weak. The magnitude of these shifts reflects the characteristic vibration of the molecule. Some discussions based on the equation (2-4) are listed as below:

(1) If $(\partial \alpha / \partial Q)_0 = 0$, the second term vanishes. Thus, the vibration is not Raman active according to the Raman selection rule because the molecular polarizability doesn’t change during the vibration.

(2) If a vibration does not greatly change the polarizability, then the polarizability derivative will be near zero, and the intensity of the Raman band will be low. Scattering intensity is proportional to the square of the induced dipole moment $\mu$, which is proportional to the square of the polarizability derivative, $(\partial \alpha / \partial Q)^2$ [2-b].

(3) The equation also shows the two possibilities to achieve an intense Raman intensity. One is from the molecules with larger polarizability and the other one is the stronger electric field experienced by the molecules.

Based on equation (2-4), it can be deduced that the vibrations of a highly polar moiety, such
as the O-H bond, are usually weak, because the external electric field can not induce a large change in the dipole moment and stretching or bending of the bond does not change this as well. However, the vibrations of the moieties with distributed electron clouds, such as $C = C$, can be detected easily in Raman spectrum, because the $\pi$-electron cloud of the double bond is easily distorted in an external electric field. Bending or stretching of the bond changes the distribution of electron density substantially, and also causes a large change in induced dipole moment.

Actually, two impediments made Raman as a non-popular analysis tool in the first several decades. One is that Raman scattering is a very weak effect compared to the IR absorption. Raman scattering is a second-order process and the differential Raman cross sections $(d\sigma/d\Omega)$ are less than $10^{-29}$ cm$^2$·sr$^{-1}$ in the absence of resonance effect. The scattering therefore tends to take place, via a virtual state, where typically only 1 in every $10^6$-$10^8$ photons is actually Raman scattered [1-b]. The other one is because of the competitive effect, namely, fluorescence. The weak Raman signal normally is overlapped by the much stronger fluorescence signal. However, the advances in instrument technology have simplified the equipment and reduced the problems substantially. Especially, the discovery of enhanced Raman effect further speeded up the applications of Raman spectroscopy in various fields.

### 2.2 Surface-enhanced Raman Scattering (SERS)

#### 2.2.1 Discovery of Surface-enhanced Raman Scattering

First surface-enhanced Raman scattering (SERS) observation was made by Fleischmann et al. on the pyridine molecules adsorbed from aqueous solution onto a silver electrode roughened by means of successive oxidation-reduction cycles in 1974 [5]. The original idea was to generate a high surface area on the roughened metal. Although those authors obtained Raman spectra as good as the following researchers, they apparently attributed the effect to an increase in the electrode surface area caused by the roughening process, which enables more pyridine molecules adsorbed on the surface.

Gradually people realized that the surface area was not the key point in this phenomenon. After a period of search in the dark, Van Duyne et al. [6] and independently Creighton et al.
[7] were the first ones who recognized that the large intensity could not be attributed to the increase in surface area alone. They noted that likely the increase in Raman intensity from the roughened surface would be less than a factor 10, whereas the enhancement obtained was of an order of $10^6$. This enormously strong surface Raman signal must be caused by a true enhancement of Raman scattering efficiency itself, and now it has been dubbed surface-enhanced Raman scattering.

### 2.2.2 Key Features of Surface-enhanced Raman Scattering

The pioneers summarized the key features of SERS and listed briefly as below [1-b, 2, 8]:

- The largest enhancement (with enhancement factor (EF) > $10^6$ and EF ~ $10^{14}$ for single molecule measurements) is observed from the coinage metals, namely, Ag, Au and Cu. Many transition metals have relatively weak surface enhancement. Their EF values depend on the nature of the metal, for example, $10^3$ ~ $10^4$ for Pt, Rh, Ni, Co, and Fe, and $10^1$ for Pd. Few work has been reported on other "free electron" metals, such as alkali metals.

- Surface roughness in the scale from 10 to 200 nm with appropriate preparation is crucial to produce a strong SERS signal. The roughness at atomic scale, such as certain ad-atoms, ad-clusters, steps, kinks or vacancies can assist further enhancement.

- SERS has been observed at solid/liquid, solid/gas, and solid/solid interfaces as an interface-sensitive technique. Molecules adsorbed in the first layer on the surface show the largest enhancement. However, the enhancement also has some long-range aspect with molecules separated from the surface by tens of nanometers showing some enhancement depending on the substrate morphology and physical environment.

- The Raman bands from SERS-active surfaces with various roughness are completely depolarized unless single nanoparticle are employed, in contrast to spectra taken from molecules adsorbed on atomically smooth surfaces. Overtone and combination bands are not prevalent. Selection rules are relaxed, resulting in the appearance of normally forbidden Raman modes in the surface-enhanced Raman spectra.

- A very large number of molecules adsorbed on or near the surfaces of metals exhibit SERS, but their EF values could be very different. It depends on the bond type between metal and molecules.
2.2.3 Enhancement Mechanisms

A number of SERS mechanisms have been proposed to explain the above-mentioned SERS characteristics. However, no one mechanism can explain all of the observed phenomena. Electromagnetic enhancement (EM) and chemical enhancement (CE) are two widely accepted mechanisms contributing to the SERS effect in recent years [2, 9-11]. The former is associated with large local fields caused by electromagnetic resonance and the latter is a resonance-like Raman process associated with the electronic structure (state) of the metal and the adsorbates.

2.2.3.1 Electromagnetic Enhancement (EM)

The electromagnetic mechanism has been the fundamental theory for the computational approach to calculate the Raman enhancement and it has been thoroughly reviewed in the literature [2, 9-12]. Some concepts of the theory are being revised in the literature and further evolved specific theories, in particular involving ‘hot spots’, are still being developed [9-b]. Several electromagnetic models for interpreting the SERS phenomenon have been summarized and described in detail by Moskovits [10] and Vo-Dinh [2-b] in their reviews, including the models for flat or rough surfaces, spheroidal particles, metallic nanospheres, concentric spheres, prolate spheroids and ellipsoids.

A simplified schematic diagram for understanding the concept of electromagnetic SERS enhancement is shown in Fig. 2-4. The metallic ‘nanostructure’ is a small sphere with the complex dielectric constant \( \varepsilon(\nu) \) in a surrounding medium with a dielectric constant \( \varepsilon_0 \). The diameter of the sphere \( 2r \) is small compared with the wavelength of light (Rayleigh limit).

\[
\epsilon = \epsilon' + i\epsilon''
\]

\[
E_{\text{M}} = E_0 + E_{\text{SP}}
\]

\[
E_{\text{SP}} = \frac{r^3 \left( \epsilon - \epsilon_0 \right) E_0}{\epsilon + 2\epsilon_0 \left( r + d \right)^2}
\]

Fig. 2-4: Simple schematic diagram for understanding the concept of electromagnetic SERS enhancement (for an explanation see the text) [9-a].
A molecule in the vicinity of the sphere (distance \(d\)) is exposed to a field \(E_M\), which is the superposition of the incoming field \(E_o\) and the field of a dipole \(E_s\) induced in the metal sphere. The field enhancement factor \(A(\nu)\) is the ratio of the field at the position of the molecule and the incoming field,

\[
A(\nu) = \frac{E_M(\nu)}{E_o(\nu)} \approx \frac{\varepsilon(\nu) - \varepsilon_0}{\varepsilon(\nu) + 2\varepsilon_0} \left( \frac{r}{r + d} \right)^3
\]

(2-5)

\(A(\nu)\) is particularly strong when the real part of \(\varepsilon(\nu)\) is equal to \((-2\varepsilon_0)\). Additionally, for a strong electromagnetic enhancement, the imaginary part of the dielectric constant needs to be small. This condition describes the resonant excitation of surface plasmons of a metal sphere.

In an analogous fashion to the laser field, the scattered Stokes or anti-Stokes field will be enhanced if it is in resonance with the surface plasmons of the metal sphere. Taking into account enhancing effects for the laser and the Stokes field, the electromagnetic enhancement factor for the Stokes signal power \(G_{S}(\nu_s)\) can be written as:

\[
G_{em}(\nu_s) = |A(\nu_L)|^2 |A(\nu_s)|^2 \left( \frac{\varepsilon(\nu_L) - \varepsilon_0}{\varepsilon(\nu_L) + 2\varepsilon_0} \right)^2 \left( \frac{\varepsilon(\nu_s) - \varepsilon_0}{\varepsilon(\nu_s) + 2\varepsilon_0} \right)^2 \left( \frac{r}{r + d} \right)^{12}
\]

(2-6)

\(A(\nu_L)\) and \(A(\nu_s)\) are the enhancement factors of laser field and the scattered Stokes field, respectively. The equation (2-6) based on a very simple model already describes the important properties and peculiarities of the electromagnetic SERS enhancement. It shows that the enhancement scales as the fourth power of the local field of the metallic nanostructure and that it is particularly strong when the excitation and scattered fields are in resonance with the surface plasmons.

The equation (2-6) also shows that electromagnetic SERS enhancement is a long range effect, which means the molecules do not require direct contact with the SERS-active substrate, but it strongly decreases with growing distance described by the decay of the field of a dipole over the distance \([1/d]^3\) (see equation (2-5)) to the fourth power, which results in \([1/d]^{12}\) just like shown in equation (2-6).

In summary, EM enhancement models have the following features [9, 12]:

- The excitation of a plasmon resonance can occur in an isolated nanoparticle, void, and aggregate of nanoparticles or a rough surface. The plasmon resonance is determined by
the optical properties of the material, the size and shape of the nanostructure, surface roughness and other variables as in bimetallic structures, nanoshells and nanowires.

• The local field enhancement reaches a maximum for a molecule directly attached to the surface (first layer effect) and it also has a long range-component that extends its effect up to about 10 nm away from the interface.

• EM effects are generally independent of the adsorbed molecules.

As shown in Fig. 2-5, EM enhancement mechanism involves the creation of a surface plasmon on the substrate surface, which transfers energy through an electric field to the target molecules allowing otherwise inaccessible vibrational structure to be determined.

![EM enhancement mechanism of surface enhanced Raman scattering](image)

\[ h\nu_{inc} = h\nu_{inc} \pm h\nu_{vib} \]

**Fig. 2-5: EM enhancement mechanism of surface enhanced Raman scattering [13-a].**

### 2.2.3.2 Chemical Enhancement (CE)

Chemical enhancement is also referred as charge transfer (CT) and short-range effect. In comparison to EM enhancement, aspects of chemical enhancement contribution are less known [11, 13-b]. Actually, it has been proved to be very difficult to study the chemical enhancement mechanism selectively for two reasons. First, it is generally thought the contribution has only a factor of $10^{-1}$ compared to a factor of $10^4$–$10^7$ for EM enhancement. Second, almost any experimental parameters which can be varied to probe a system will have an influence via both mechanisms, making the separation of two effects very difficult. It is extremely important, however, to understand the chemical mechanism for both fundamental reasons and for its relevance to analytical applications, because the observed SERS spectra contain the information about the adsorbate and its environment, in particular its interactions with the enhancing nanoparticles, its spatial orientation as well as the polarization properties of the local electric filed. Since the effects are multiplicative, unexpected chemical enhancement could lead to analytical conclusions, which are not only
quantitatively wrong but even qualitatively wrong [12, 13-b].

The early evidence for the existence of chemical enhancement was mostly inferential. Scientists found that SERS intensities of the molecules CO and N₂ adsorbed on the surface differ by a factor of 200 under the same experimental conditions. This result is very hard to explain using only electromagnetic enhancement because the polarizabilities of the molecules are nearly identical and even the most radical differences in orientation upon adsorption could not produce such a large difference. The second evidence comes from potential-dependent electrochemical experiments. When the molecule adsorbed on the ‘flat’ surface in the nanometer scale, the enhancement factor is dependent on the electrode potential [2-a, 13].

Chemical enhancement can be explained by a resonance-like Raman mechanism. Fig. 2-6 depicts the operative charge transfer mechanism for a molecule adsorbed on an electrode. The resonance Raman process is very unlikely because of the large energy gap between the highest occupied molecular orbitals (HOMO) and the lowest unoccupied molecular orbitals (LUMO) in spite of the perturbed redistribution of the energy level for a molecule adsorbed on a rough surface. However, the resonance Raman scattering can occur through photon-driven charge-transfer processes between the metal and adsorbates. It is assumed that transitions from states near the Fermi level are preferred because of favorable matrix elements involving wave function overlap of localized electron density of states. The whole process can be identified by the following four steps [2, 13]:

Step 1: An electron-hole pair of the metal is created by the incident photon with energy ℏν₀, and the electron is excited as a "hot electron";
Step 2: The so-called "hot electron" tunnels into the accessible vacant levels, such as the LUMO of the adsorbate, generating a charge-transfer excited state;
Step 3: A negative ion (adsorbate molecule-electron) created in step 2 has an equilibrium geometry differing from that of the original adsorbate molecule and the electron will return to the metal and the nuclear in the adsorbate will get relaxed during this charge-transfer process;
Step 4: The electron will recombine with the hole created in step 1, which leads to a vibrationally excited neutral molecule and to emission of a Raman-shifted photon with energy ℏν. 
In general, chemical effects contribute to SERS in a short range, on the molecular scale. This mechanism depends on the adsorption site, the geometry of bonding and the energy levels of the adsorbate molecules. Although the CE mechanism is not a general mechanism and is restricted by its chemical specificity, it can provide useful information uniquely on chemisorptive interactions between metals and adsorbates.

![Fig. 2-6: Schematic diagram of the four-step process of the photon-driven charge transfer model for a molecule adsorbed on an electrode [2].](image)

The above discussions described the chemical enhancement mechanism qualitatively, but some vague interpretations still exist about this mechanism. For example, what is the magnitude of the chemical enhancement and whether it is in fact present? The general opinion is that the enhancement factor of chemical enhancement is from 10 to $10^3$ [14]. However, in any case, it is generally agreed that the electromagnetic enhancement effect is significantly larger in magnitude.

### 2.3 Advancements in Surface-enhanced Raman Scattering

The discovery of SERS made a strong impact on surface science because of its extremely high surface sensitivity, both in fundamental and applied research. It not only provided a stimulus for the study of enhanced optical scattering from the surfaces and interfaces, but also opened up a new field of surface-enhanced spectroscopy that includes surface enhanced second-harmonic generation (SE-SHG) [15-18], surface enhanced infrared
SERS did not develop to be as powerful a surface technique as many people had hoped because three obstacles blocked its practice and theory. First, the huge enhancement can be obtained only on coinage metals, namely, Ag, Au and Cu, on which the surface plasmon resonance can be easily excited in the visible to the near-infrared light region [10-11]. This limited the applications of this ultra-sensitive surface technique to the transition metals, which have wide applications in industry. Second, it is still a challenge to fabricate an appropriate SERS-active substrates to satisfy the requirements in the process of research and industry. The last one is the unclear enhancement mechanisms. Although a number of enhancement mechanisms were proposed to explain the observations during the past thirty years, no one can explain all the observed phenomena [33].

In brief, the advancements of SERS are the solutions to solve the above-mentioned three main obstacles, namely, to fabricate the appropriate SERS-active substrates to meet the requirements for practice and research, to extend the applications of SERS technique and to clarify the exact mechanisms of SERS. In the following parts, the latest achievements focused on these three branches will be reviewed.

### 2.3.1 Extension of SERS to Transition Metals

Transition metals were considered for a long time that they had no enhancement effects because it is difficult to excite the surface plasmon resonance in the visible region. It is a big challenge for the experts to get the enhancement from transitional metals. The scientists developed a new strategy based on the ‘borrowing SERS’ in the 1980’s [34-35], either by depositing SERS-active metals onto the non-SERS-active substrates including semiconductors, or by depositing non-SERS-active materials over SERS-active substrates. The purpose is to take advantages of the long-range electromagnetic effect. It is noted that the strong electromagnetic field generated on SERS-active substrates is damped...
significantly by the coated films, which should be ultra-thin, namely, 3-10 atomic layers. However, it is very difficult to use such a thin film to cover the rough substrates completely, which results in the difficulty to entirely eliminate the contribution from the SERS-active substrates because of the pinhole in the overlayer. Weaver et al. reported a series of work on pinhole-free transitional metal over the SERS-active Au surface by electrochemical atomic layer epitaxy using constant-current deposition at a low current density or by redox replacement of under potential-deposited metals on Au [36]. It has been shown that this method is very promising if one can prepare the pinhole-free ultra-thin film for different materials with good stability in a wide range of potential and temperature. With this strategy, the adsorption of phthalic acid on anatase TiO\textsubscript{2} and Anthrax Biomarker on the Al\textsubscript{2}O\textsubscript{3} overlayer were successfully investigated by SERS [37].

An alternative strategy is to generate the SERS directly from transition metals. Tian et.al found that the transition metals can still show a small enhancement effect with proper methods of preparation [33]. For example, electrochemical oxidation-reduction cycle (ORC) and current controlled ORC were used to obtain the rough transition metal surfaces and the enhancement from the Fe, Pt, Pd, Zn, Ni, Ru and Co was achieved [33, 38-40]. However, the enhancement effect is smaller compared with the noble metals. It ranges from one to four orders of magnitude depending on the nature of the metals and the surface morphology. The adsorption/desorption of pyridine and other molecules dependent on the potential have been successfully investigated by SERS [33, 38-40].

2.3.2 Fabrications of Versatile SERS-active Substrates

To further promote SERS technique, the prepared SERS-active substrates should meet several requirements, which are supposed to have a large enhancement factor, good reproducibility from one sample to another; stable SERS signal with time, simple preparation process and easiness to be applied to many substrates in parallel [41]. Moreover, if template structures are used, they should be inert, mechanically stable and not lead to additional peaks in the Raman spectrum.

Tens of methods to fabricate the SERS-active substrates were developed in the past three decades, from the initial electrochemical roughening cycles to the latest nanofabrication technique. For transition metals, electrochemical oxidation-reduction cycles (ORC), current controlled ORC, templates synthesis of metal nanowire arrays [33] and chemical etching
were developed. For the traditional coinage metals, the new methods to produce the SERS-active substrates appeared in the past twenty years besides the most popular ORC method. For example, sol-gel produced Au nanoparticles [43], sandwich structure [44-45], electro-deposition of silver island-like films at high potential [41], Ag/SiO$_2$ bilayer substrates produced by PECVD and PVD [46]; photochemical deposition of SERS-active silver nanoparticles [47], self-assembled metal colloid monolayers [48], 2-dimensional Ag-films [49], deposition of silver on the porous silicon by immersion plating [50] and layer by layer techniques [51-52] have been preformed as useful processes to generate SERS-active substrates. Recently, plasma oxidation-reduction cycles have been successfully applied to roughen silver films and thereby to generate SERS-active substrates [53].

Nanotechnology shows its powerful ability and wide applications in fabricating the new SERS-active substrates because it can form different, ordered and reproducible nanostructures, which are very important both in practice and theoretical research. In principle, nanofabrication solves two problems: one is the creation of well-defined structures that are optimally tuned to SERS, i.e., that give extraordinary enhancement factors; the other one is the opportunity to create reproducible structures that will give rise to reproducible SERS measurements, ideally on large numbers of substrates.

Up to know, the well known substrates with metallic nanostructures include roughened metal electrodes, metal colloids, metal island-like films, silver coated nanospheres, metal-coated alumina nanoparticles, silver-coated titanium dioxide nanoparticles, silver-coated silica nanoparticles, lithographic and grafting structures, silver-coated cellulose, and silver membranes [12]. Except the ordered, well-defined nanostructures, one of the most significant developments in SERS has been an exponential increase in synthetic capabilities for anisotropic metal nanoparticles [54-56]. Reliable synthesis of core-shell particles, rods, triangular prisms, dumbbells, nanocrescents [57], nanobars, nanorices and nanocubes [58] and even more obscure shapes have been described. Each of these nanostructures may offer advantages with respect to SERS, both by the ability to tune the plasmon band into the interested spectral regions (i.e, the near-IR range), and by the shape-based control of EM enhancements. Van Dynue et al. used novel atomic layer deposition to deposit the dielectric spacers to study the SERS distance dependence and control the nanoscale dielectric environment. The results testified the EM enhancement decayed in the range of several nanometers [59].
Although nanofabrication can create well-defined structures that can contribute to extraordinary enhancement factors, and the reproducible structures may give rise to reproducible SERS measurements, it may not provide any advantages for improving the reproducibility of SERS measurements. The critical parameters are the beam size in the experiments and the required spatial resolution [14].

2.3.3 New Theories of SERS Enhancement Mechanisms

The enhancement mechanisms of SERS were always hot topics for scientists since it was discovered in 1974 by Fleishman [5]. Several excellent reviews have been contributed by Otto [11, 60], Moskovits [10], Birke and Lombardi [61-62], Creighton [63], Pettinger [64], Campion and Kambhampati [13], as well as Kneipp [9, 65]. Different models were proposed to explain the SERS enhancement mechanisms, but no one can explain all the observed phenomena. Some new derivative theories based on the EM enhancement mechanism and charge transfer theory were developed to further interpret the SERS enhancement mechanisms in the past 30 years and they will be discussed in the following.

2.3.3.1 Derivative Theory Based on the Electromagnetic Enhancement Mechanism

The properties of the surface itself undoubtedly play very important roles in SERS. These properties include the shapes and sizes of the particle, the interparticle distance and the frequency-dependent dielectric function of the surface material in electromagnetic enhancement model [10]. To exactly describe the properties of the surface is a primary target to establish the model used in theory. In recent years, the discrete dipole approximation (DDA) has made it possible to evaluate the optical response of nanoparticles with various shapes and sizes of an arbitrary rough surface. The results from the calculation are in agreement with the experimental data in some cases [66-69], but the shortcomings in describing the actual shapes of the particles and the difficulty to calculate the large assemblies make DDA model have to combine with the other methods.

Shalaev et al developed a new theoretical approach to predict the extremely large electromagnetic field enhancement on fractal surfaces [70-73]. Combining the DDA method and the features of fractal from the aggregated colloids or rough surfaces, they found the strongly enhanced effect in the special regions, i.e., hot areas or hot spots and confirmed them in experiments [74]. It is in these special regions that the resonance of the electromagnetic radiation is concentrated. The locations of the hot areas depend strongly on
the geometry of the fractal, the excitation wavelength and the polarization of the incident laser. In addition, it has been demonstrated that the same area could be a hot spot or a cold zone depending on the excitation wavelength used.

2.3.3.2 Derivative Theories Based on the Chemical Enhancement Mechanism

A general introduction to the chemical enhancement mechanism has been presented in the section 2.2.3.2. In brief, chemical enhancement is a charge transfer process. Every factor influencing the charge transfer process will lead to a significant change of the Raman intensity. These factors include the excitation frequency, the vibrational mode, the adsorbing site, the coverage of the surface and the concentration of the electrolyte. Normally, the Franck-Condon and Herzberg-Teller coupling mechanisms were used to explain the contributions to the SERS intensity when the excited states are involved [75-77], but they can only be applied in limited fields.

Recently, the wave packet method from Heller’s time dependent theory [78-79] has been used by Kambhampati et al. to describe the chemical enhancement of pyromellitic dianhydride on the Cu (100) and Cu (111) single crystal surfaces and the simulation results have been proved by the experiments in UHV [13, 80]. In this method, the polarizability is represented in the time domain as a half Fourier transformation of the auto-correction function and the description of this function can be found in the literature [81]. It should be pointed out that this model is simplified without considering the Duschinsky mixing and anharmonic effect [82].

Some other advanced theories, such as single molecule SERS and quantum mechanical model, will be briefly introduced in the following. Kneipp et al. successfully detected the SERS spectrum of single molecule on the silver nanoparticles and found that the enhancement factor can be up to $10^{14}$ [83-86]. Some possible interpretations are listed here:

(1) For single molecular SERS, enhancement factor (~$10^6$) from the contribution of resonance Raman effects has to be considered if the target molecule has electronic transitions in the wavelength range close to the excitation laser with the electromagnetic enhancement.

(2) The fractal structure of the silver colloidal cluster is responsible to the $10^{14}$ times enhancement factor in the near-IR experiments, where no resonant SERS exists [83].

(3) Chemical enhancement mechanism is thought to be the reason that high SERS effect
was observed on single nanoparticle without fractal structures.

Pettinger suggested a quantum mechanical model to describe the SERS enhancement based on the surface plasmon polariton model under the interaction of the surface with the light. He presented an expression and tried to use it to evaluate the total surface enhancement including the electromagnetic and charge transfer contributions [87]. However, the expression has to be simplified because of its complexity, until now it can only be applied in very limited systems.

Finally, the understanding about the SERS from the transition metals was also developed in the past 30 years. Now the widely accepted theories are the charge transfer mechanism confirmed by Tian’s group [32, 36-40, 88] and the lightning rod effect proposed by Gersten and Nitzan [89]. However, more systematic investigations both experimental and theoretical are still required to completely understand the SERS effect from transition metal.

2.3.4 Proposed Scientific Standards for SERS-active Substrates

It is commonly observed that SERS data differ from one laboratory to another one because of the absence of the standards with respect to the reproducibility and stability, which are essential for technology adoption by other than those reporting the data. In 2006, M. J. Natan proposed some standards to be applied to new (or existing) SERS architectures that are of interest [14]:

1. The spot-to-spot reproducibility should be less than 20% over 10 mm²;
2. The substrate-to-substrate reproducibility should be less than 20% over 10 substrates;
3. Three non-resonant analytes are recommended to be used for the enhancement determination and the enhancement factors should be calculated and compared;
4. The stability of SERS substrates should be satisfied with a signal less than 20% variation measured weekly over one month;
5. The enhancement factors should be measured over regions corresponding to the size of the laser beam or larger.

In addition, some other remarkable advancements were also achieved in the past 30 years, for example, surface-enhanced hyper-Raman spectroscopy (SEHRS) [90-92], surface-enhanced resonance Raman spectroscopy (SERRS) [93-95], tip-enhanced Raman spectroscopy (TERS) [96-98] and ultraviolet excited SERS [99-100], as well as in-situ
SERS used to investigate the orientation, adsorption/desorption of the molecules or self-assembled monolayer and the reaction on the electrode surfaces [101-104]. The introductions concerning these achievements will not be addressed due to the space limitations.

2.4 Applications of SERS in Adhesion Science

The applications of SERS have been extended to many fields including industry [105-108] and research fields in the past thirty years, especially in materials science, medicine and biology [109-115]. It can even be applied to the art identification, archeology and relative research fields [116-118]. In this section, the applications of SERS in adhesion science are reviewed due to the importance to this present work.

High adhesion strength at polymer/metal interfaces, even in hostile environments, is a key requirement in many technical applications. To understand the interactions between polymers and metals, as well as to clarify how polymer/metal interfaces degrade over long exposure time in corrosive environments, various in-situ techniques have been developed in spectroscopy, electrochemistry and microscopy [120]. SERS is one of the new techniques developed in recent years, which can provide more profound insight into adhesion science.

2.4.1 Applications of SERS at Solid/Liquid Interfaces

The aqueous solution is most prominent electrolyte whether in the nature or in the laboratory environment. It has a strong adsorption in traditional IR spectroscopy, while it is a weak scattering in Raman spectroscopy. This advantage determines Raman spectroscopy to be a suitable tool to study the adsorption of molecules on metal surfaces in aqueous media as reported in the literature [2, 29-40]. Moreover, the structure and orientation of water molecules at solid/liquid interfaces are of fundamental interest in various fields of science, particularly in electrochemistry [120].

Actually, SERS from water was not reported until 1981 [121]. Most of SERS spectra from water were observed in the water/Ag, water/Cu, water/Au systems or in UHV environment [122-126]. The results indicate that the SERS spectra of water arose from a special complex involving "silver adatoms (cluster), halide ions, cations and water" rather than "free" water molecules [124]. Pemberton et al. used SERS to investigate the interfacial H2O and electrolyte behavior of LiCl, LiBr, LiI and LiClO4 on Ag electrodes in several isomers of
butanol. Six (O-H) bands were observed in the surface spectra under the controlling of electrode potential. They deduced that the possible configurations of water can be:

1. H₂O hydrogen-bonded to specifically adsorbed anions at the electrode surface at potentials positive of the potential of zero charge (pzc) (at ca. 3500 cm⁻¹);
2. H₂O in the primary solvation shell of the Li⁺ at potentials negative of the pzc (at ca. 3570 cm⁻¹);
3. “Free” H₂O not associated with specific ions, perhaps weakly held in the secondary solvation shell of Li⁺ (between 3600 and 3650 cm⁻¹);
4. OH⁻ weakly involved with Li⁺, perhaps in a solvent-separated ion pair (at 3600 cm⁻¹);
5. OH⁻ species adsorbed through the oxygen atom to the Ag electrode surface (at ca. 3630 cm⁻¹);
6. Crystalline LiOH species which form owing to the poor solubility of this salt in the isomers of butanol (at ca. 3660 cm⁻¹).

When the OH⁻ formed on the electrode during the reduction of H₂O at negative potentials, three bands were observed which can be assigned to the configurations (4)-(6) [127]. Chang and Chen investigated the influence of methanol, ethanol, 1-propanol, and acetone on the SERS intensity of water molecules on Ag electrodes in 0.1 M KBr electrolyte. They found that the SERS intensity of water increased when the studied solvents were added during the potential hold after the reduction was completed. It is because that the solvents are efficient in disrupting the hydrogen bonding between the adsorbed water and the bulk water network [128]. Cao and Tian also studied the interfacial water at a silver electrode in acetonitrile solutions by means of SERS under the controlling of the electrode potential. They observed two SERS bands at 3487 and 3586 cm⁻¹ and assigned them to the interfacial H₂O molecules. The former band is favored at relatively positive potentials and assigned to H₂O molecules interacting with the electrode surface via the oxygen atoms. The latter one can be observed in a wider potential region and assigned to the H₂O molecules with one or both of the hydrogen atoms facing the electrode [129].

### 2.4.2 Applications of SERS for the Study of Self-assembled Monolayers

Bifunctional organic molecules are often used as adhesion promoting self-assembled monolayers (SAMs). Such kind of molecules have special properties, one end of the organic molecule is a functional group that can bond to the metal surface; the other end consisting of hydroxyl, epoxy, amino, or carboxyl groups, can react with the reactive
groups in the polymer [119]. Therefore, the polymer can be adhered to metal surface via this promoting layer. The most popular functional SAMs systems are organothiols, organosilanes and organophosphonates. Thiol groups can bind only to oxide-free surfaces such as Au, Ag, or Cu [130-132], whereas organosilanes and organophosphonates can strongly bond to oxide-covered and hydroxide-covered metals thus are applicable for engineering metals [133-134].

For the study of the monolayer adsorption, scanning tunneling microscopy (STM) has been applied extensively. However, STM is disabled in the case of engineering materials because of the dielectric native oxides on the metal surface. SERS can also be applied in the field of SAMs as an excellent spectroscopic tool in the future although most of the investigations are concentrated on the noble metals now. Gold and silver colloid particles were bound to the substrate through multiple bonds between the colloidal metal and the functional groups in the polymer such as cyanide (CN), amine (NH₂), and thiol (SH) groups [135]. The geometry of molecules adsorbed on the gold surface, the structure of monolayer and the orientation of the molecules can be investigated by SERS [132, 136-137]. Moreover, Tian et al. tried to clarify the mechanism of DNA immobilization by using SERS to examine the ordered ds-DNA monolayer on gold electrode [138]. Liao et al. investigated the adsorption kinetics of 4-mercaptobiphenyls on gold and found that the molecular dipole and the electron density on the S-atom affect the adsorption process of thiols on gold [139].

2.4.3 Applications of SERS at Adhesive/Primer Interfaces

SERS has also been extensively applied in adhesive/primer systems in recent years. M. Suzuki et al. successfully applied SERS to clarify the role of a primer, 6-(N-(4-vinylbenzyl)-propylamino)-1, 3, 5-triazine-2, 4-dithion, on the adhesion between dental precious metals and resin [140-141]. He et al. used SERS to study the controlled interface between carbon fibers and the epoxy resin and the results showed that thiols chemisorbed on Ag/carbon fibers in the form of thiolate species via the strong S–Ag coordinative bonds [142]. Webster investigated the role, including concentration, conformation, and bioactivity, of adsorbed vitronectin in enhancing osteoblast adhesion to nanophase alumina by means of SERS [143]. In addition, Vogel et al. studied organically modified titanium substrates with SERS and revealed a selective enhancement of some vibrational modes of the sol-gel layer on the modified substrates [144]. K. Fraoua combined SERS and XPS techniques and proved that the iron nitride species are responsible for the strong adhesion of polypyrrole to
iron or steel surfaces treated with nitric acid [145].

In this chapter, a short introduction to Raman scattering was given at the beginning of this chapter. The two main SERS mechanisms and the key features of SERS effect were discussed. In addition, the advancement of SERS technique and its applications in adhesion science were reviewed.

2.5 References

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Chapter 3: Fabrication and Characterization of Novel SERS-active Substrates

3.1 Introduction

As mentioned in section 2.3, three main obstacles impeded the potential applications of the SERS technique since it was discovered in the mid-1970s [1-3]. One of them is that it is difficult to fabricate an appropriate SERS-active substrate to meet the requirements whether in practice or in research. The as-prepared SERS-active substrate should have a large enhancement factor, good reproducibility from one sample to another, high stability even stored over a long time, quick fabrication in a large scale and the easiness of preparation applicable to many substrates in parallel [4]. Moreover, when the template was used, it should be inert, mechanically stable and not introduce additional bands in Raman spectra.

Tens of methods have been developed to prepare SERS-active substrates in the past thirty years and some of them have been reviewed in section 2.3.2 [5-16]. Depending on the type of application, each of these surfaces has its special advantages and disadvantages. For example, electrochemically roughened metal electrodes are suitable for the in-situ monitoring the adsorption/desorption of molecules as a function of potential [5-6], while the shortcoming encountered in the process of preparation is the need to polish the surface mechanically prior to SERS-activation to ensure reproducible starting conditions. It can cause the introduction of surface irregularities, which result in a broad distribution of enhancement factor across the surface [17], or lead to contamination with polishing paste or/and previously adsorbed analyte molecules [18] and this method is also time-consuming.

For the noble metal colloid fabricated by sol-gel technique, the natural properties of colloid determined that the stability of the obtained substrates is always a big problem and the reaction conditions are rigorous [11-13]. The similar drawbacks exhibit in nanofabrication technology to fabricate SERS-active substrates.

In this chapter, a method to prepare the SERS-active substrates by combining plasma enhanced chemical deposition (PECVD) and physical vapor deposition (PVD) was introduced, which is substrate-independent, well reproducible on a large scale. The principle of the preparation is that thin noble metal layer borrows the rough features from the supporting plasma polymer film and the whole model system will produce large
enhancement effect. The SiO$_2$-like plasma polymer film was chosen as the supporting film, because it is stable and will not lead to additional Raman peaks in practical measurements. The surface structure and the optical properties of the prepared substrates were characterized by atomic force microscope (AFM), field emission scanning electron microscope (FE-SEM), ultraviolet-visible (UV-Vis) spectroscopy, Raman spectroscopy and electrochemical impedance spectroscopy (EIS) in detail, respectively.

### 3.2 Experimental Details

#### 3.2.1 Materials and Chemicals

The used solid, supporting substrates were polished silicon wafers (Si-Mat, Germany) and normal microscope slides for different experiments. Hexamethyldisilane (HMDS, (CH$_3$)$_6$Si$_2$, 98%, Merck, Germany) was used as the monomer for plasma polymer film deposition as received without further purification. Trans-1, 2-bis (4-pyridyl) ethylene (BPE) powder (97%, Sigma-Aldrich, Germany) was dissolved into dilute aqueous solutions and used as a probe molecule to determine the enhancement factor of the prepared substrates. The molecular formula of HMDS and BPE are shown in Fig. 3-1.

![Molecular formula of HMDS and BPE](image)

An aqueous solution of BPE at a concentration of 5 × 10$^{-5}$ M was prepared with deionized water according to the literature [19]. To accelerate the dissolution, the solution was placed in the ultrasonic bath for 5 minutes. For the adsorption of BPE, the prepared substrates were immersed in the BPE solution for 1 hour, rinsed with a great of deionized water and dried in a nitrogen stream. After that, the samples were measured with Raman spectrometer immediately.
3.2.2 Preparation of SERS-active Substrates

The used silicon substrate was cut into 2 × 2 cm² pieces and cleaned ultrasonically in ethanol for 5 minutes and dried in a stream of nitrogen. The deposition of HMDS plasma polymer films were preformed using PECVD technique in a vacuum reaction chamber with a linear microwave source (Roth und Rau, Wuestenbrand) at a power of 300 W and a frequency of 2.46 GHz (see Fig. 3-2). The width of the plasma zone was 150 mm and little plasma can be observed outside of this zone.

The whole deposition process is described as following: the samples were firstly exposed to an oxygen plasma at the pressure of 20 Pa passing through the plasma zone at a constant speed of 1 mm/s to remove the organic contaminations and to introduce some free radicals on the silicon surfaces. The HMDS plasma polymer films were deposited subsequently while the substrates were moved over the plasma zone at a constant speed of 5 mm/s. The ratio of partial pressures between HMDS monomer and argon was 1:4 and the total pressure was 20 Pa. The obtained HMDS plasma polymer films were exposed to O₂ plasma again in the final step for 300 seconds to generate nanoporous SiO₂-like plasma polymers and to remove the residual CH groups produced during the plasma deposition [20-21]. The thickness of final cauliflower-like plasma polymer films were approximately 120 nm thick as measured and determined by spectroscopic ellipsometry.

Silver layers with different thicknesses were deposited on the as-prepared nanoporous, cauliflower-like HMDS plasma polymer films by means of PVD technique. The deposition

Fig. 3-2: Schematic representation of a microwave plasma chamber set-up [21].
process was performed by electron beam evaporation in a vacuum chamber under the base pressure of $10^{-6}$ mbar (Univex 450, Leybold Technologies, INC, USA) The thickness of the silver layer was controlled by a quartz crystal microbalance (QCM) during the evaporation process and the final silver layer thickness values were 17 and 100 nm for different experiments, respectively. The prepared substrate is schematically presented in Fig. 3-3.

![Schematic representation of a SERS-active substrate prepared by combining PECVD and PVD techniques](image)

**Fig. 3-3: Schematic representation of a SERS-active substrate prepared by combining PECVD and PVD techniques [22].**

### 3.2.3 Surface Characterization and Analysis

**Atomic force microscope (AFM)**

The topography of the prepared surfaces was characterized by AFM measurements, which were carried out using a Dimension 3100 (Digital Instruments, USA) in tapping mode with a rectangular silicon cantilever with a spring constant 34-54 N/m and a 300-400 KHz resonance frequency. The tip length is 124 μm and the opening angle is about 34°. The roughness calculations were performed using the Digital Instruments (DI) software.

**Field emission scanning electron microscope (FE-SEM)**

The morphology of the films was additionally investigated by means of a field emission scanning electron microscope (Zeiss 1550VP, Germany). The applied accelerating voltage is adjusted to 8 or 15 KV according to the surface conditions of the samples.

**Surface-enhanced Raman spectroscopy (SERS)**

Surface-enhanced Raman spectroscopy measurements were performed using a modular system (Dilor, LabRAM, ISA Instruments. SA, INC, France). It consists of a red He-Ne laser (632.8 nm) with 20 mW power and a green Ar+ laser (514.5 nm) with adjustable output power, $100 \times 0.9$ microscope objective, an Olympus BX40 confocal microscope,
charge couple devices camera (cooled down to -70 °C by liquid nitrogen), 600/1800 grooves/mm gratings and a holographic notch filter. The experimental parameters were adjusted as following: the laser power was set at 2 mw to avoid the possible degradation of the BPE molecules, the pinhole was 1000 μm and the size of slit was set to 100 μm with 10 seconds spectra acquisition time for a good S/N ratio.

**Fourier transformation infrared (FT-IR) spectroscopy**

Fourier transformation infrared spectrometer (Nicolet Nexus 870, Thermo Electron Corporation, USA) was used to characterize the final products of HMDS plasma polymer films with post-oxidation in transmission mode. The used detector is DTGS detector (Deuterated-Triglycine-Sulfate) and the samples were normally subjected to 512 scans at a resolution of 4 cm⁻¹.

**Ultraviolet-visible (UV-Vis) absorption spectroscopy**

UV-Vis absorption spectra measurements were carried out by using a Lambda 800 spectrometer (PerkinElmer™ Instruments GmbH, Germany). A cleaned microscope glass was always used as a reference to obtain absorption spectra of both 17 and 100 nm silver films deposited on the bare glass covered with nanoporous SiO₂-like films. The UV-Vis spectra data were treated with the software from the same company.

**Electrochemical impedance spectroscopy (EIS)**

EIS measurements were used to determine the real microscopic surface area of silver films supported by the rough SiO₂-like plasma polymer films. The impedance measurements were performed using a commercial FAS2™ potentiostat (Inc. Gamry Instruments) with the data acquisition and subsequent analysis carried out using EIS300/Echem Analyst software. A standard three-electrode electrochemical cell was used for the EIS measurements: the working electrode with a reproducible exposed area of 0.785 cm², a silver wire as a pseudo-reference electrode and a platinum counter electrode. The electrochemical tests were carried out in a quiescent aerated borate buffer solution (pH = 9.1: 0.2 M H₃BO₃ (Merck, p.a.), 0.05 M Na₂SO₄ (Merck, p.a.), 0.05 M Na₂B₄O₇·10H₂O (Merck, p.a.)) prepared from distilled water at room temperature. Impedance spectra were measured at open circuit potential after 300 seconds equilibration in the electrolyte.
Ultraviolet-visible (UV-Vis) spectroscopic ellipsometry

The thickness of the HMDS plasma polymer films on the polished Si-wafer was measured by means of UV-Vis spectroscopic ellipsometry (SE800, SENTECH Instruments GmbH, Germany) in the wavelength range between 300 to 800 nm at three different incident angles of 50°, 60° and 70°. The evaluation of the ellipsometric measurements was carried out with the SENTECH software. The fitted values of thicknesses and reflection indices were in good agreement with the data in the literature.

3.3 Results and Discussion

3.3.1 Chemical Composition of the HMDS Plasma Polymer Films

Previous investigations showed that plasma polymerization of an organosilane at high partial pressure yielded cauliflower-like organosilicon plasma polymers, which can be chemically converted into SiO₂-like plasma polymer products by using post-oxygen plasma calcinations [21-23]. It was shown that the nanoroughness of the films can be preserved during the oxygen plasma calcination process. The FT-IR spectrum of the obtained HMDS plasma polymer film is shown in Fig. 3-4.

![Fig. 3-4: FT-IR transmission adsorption spectrum of an about 120 nm thick nanoporous HMDS plasma polymer film.](image)

The IR band at 1071 cm⁻¹ dominates the spectrum and it can be assigned to the asymmetric stretching of Si-O-Si groups and there is almost no information from carbon in the film [21-23]. The organic components of the HMDS plasma polymer films were entirely oxidized...
during the post-oxidation, as no -CH$_3$ or -CH$_2$ bands appear in the FT-IR spectrum (see missing deformation band of -CH$_x$ groups between 1300 and 1500 cm$^{-1}$). The peak at about 931 cm$^{-1}$ indicates the existence of hydroxyl groups in the film and the peak at 804 cm$^{-1}$ can be assigned to the Si-O-Si bending vibration. Thus, it can be concluded that the obtained HMDS plasma polymer films are SiO$_2$-like films with additional silanol groups.

3.3.2 Morphology of the Prepared SERS Substrates

AFM is a powerful tool to characterize the film topography. Fig. 3-5 (a)-(f) present the surfaces of different films prepared on different substrates, including the cleaned Si-wafer, Si-wafer coated by HMDS plasma polymer film, silver layers with different thicknesses deposited on Si-wafer and on Si-wafer coated by the HMDS plasma polymer film.

A cleaned, smooth, polished Si-wafer surface with small roughness served as a reference (see Fig. 3-5 (a), the root-mean-square (RMS) value is less than 1 nm). As shown in Fig. 3-5 (b) the nanoporous SiO$_2$-like HMDS plasma polymer film is full of nanopores with sizes in the range between 50 and 250 nm. The distribution of roughness is statistical and characterized by a RMS value of 40 nm. To estimate the inherent roughness of a thin silver layer (thickness is 17 nm), silver was deposited directly on top of a cleaned Si-wafer.

It can be observed from the AFM image in Fig. 3-5 (c) that the obtained thin silver film is not perfectly smooth but displays islands with a diameter ranging from 30 to 100 nm and a height of less than 10 nm. After the deposition of the thin silver film on top of the nanoporous SiO$_2$-like HMDS plasma polymer film, it can be observed in Fig. 3-5 (d) that the silver film clearly imitates the topography of the SiO$_2$-like HMDS plasma polymer film. The roughness remains high and the RMS value is 30.6 nm.

The AFM images of 100 nm silver deposited on the smooth Si-wafer and on the plasma polymer film are also shown in Fig. 3-5 (e)-(f). The roughness of 100 nm silver film on Si-wafer is slightly larger than that of 17 nm silver film deposited on the same substrates. However, the topography of 100 nm silver film deposited on the HMDS plasma polymer film is similar to that of 17 nm silver film deposited on the same substrate, which preserved the rough feature from the HMDS plasma polymer under layer. According to the electromagnetic enhancement mechanism [24-28], such a rough, richly defective silver surface is particularly suitable to promote the surface enhancement effect.
Chapter 3: Fabrication and Characterization of Novel SERS-active Substrates

Fig. 3-5: AFM images of different surfaces (scan size $1 \times 1 \, \mu \text{m}$): (a) polished Si-wafer; (b) SiO$_2$-like HMDS plasma polymer film deposited (a); (c) 17 nm silver film deposited on (a); (d) 17 nm silver film deposited on (b); (e) 100 nm silver film deposited on (a); (f) 100 nm silver film deposited on (b).

Since the sharp features of the HMDS plasma polymer films are difficult to be detected by the AFM technique due to the limited radius of the AFM tip, FE-SEM investigations were additionally performed to illustrate the nanostructure of the SiO$_2$-like HMDS plasma polymer films and the silver film deposited on SiO$_2$-like HMDS plasma polymer films with different thicknesses (see Fig. 3-6).
Fig. 3-6: FE-SEM images of the different surfaces: (a) nanoporous SiO$_2$-like plasma polymer film; (b) 17 nm silver film deposited on (a); (c) 100 nm silver deposited on polished Si-wafer; (d) 100 nm silver film deposited on (a).

The FE-SEM image of the HMDS plasma polymer film in Fig. 3-6 (a) confirms the cauliflower-like structure of the SiO$_2$-like HMDS plasma polymer film and a large surface area is generated by the plasma polymerization process. The cauliflower-like structure is similar to the one recently shown by Tian et al., who produced rough Zn surfaces by oxidation-reduction cycles and observed enhanced Raman scattering. Furthermore, they also evaluated the local electromagnetic field generated by this structure with three-dimensional finite difference time domain (3D-FDTD) method [29]. Fig. 3-6 (b) shows the FE-SEM image of 17 nm silver layer deposited on the rough SiO$_2$-like HMDS plasma polymer film. The silver layer covers the small features from the SiO$_2$-like plasma polymer film and basically inherits the rough features from the SiO$_2$-like plasma polymer film. The particle size in Fig. 3-6 (b) is not uniform and it is in the range from 50 to 150 nm. Many
kinds of surface features can be clearly observed, such as small crevices, pores, clusters and aggregated particles.

The surface of 100 nm silver film deposited on the smooth Si-wafer exhibits as a compact layer and some ridge-like structures are present in Fig. 3-6 (c). The whole surface is smooth, but it has some small protrusions which produce small roughness. The morphology of 100 nm silver film deposited on the rough HMDS plasma polymer film is similar to that of the 17 nm silver layer on HMDS plasma polymer, which is rich of surface defects. The main differences between two surfaces in Fig. 3-6 (b) and (d) are: 100 nm silver film in Fig. 3-6 (d) behaves as a continuous film and more aggregated silver particles are on the surface. This fractal structure may act as so called “hot spots” to generate the strong enhancement effect with the excitation [25].

3.3.3 Determination of the Enhancement Effect

To determine the enhancement effect of the prepared substrates, the normal Raman spectrum of BPE powder and surface-enhanced Raman spectrum of BPE adsorbed on the as-prepared substrate from aqueous BPE solution (5 × 10^{-5} M) are compared (see Fig. 3-7). It should be noted that the Raman signal of BPE adsorbed on a polished Si-wafer from the above-mentioned aqueous solution cannot be detected in our experiments.

As well known, frequency shifts, line widths and relative intensities of the Raman lines characterize the Raman spectrum of a molecule [26]. Fig. 3-7 shows the SERS spectrum of BPE and the normal Raman spectrum of BPE powder. The spectra were shifted vertically for clarity. The information of BPE adsorbed from the aqueous solution at such a low concentration can be even detected, so the obtained Raman spectrum must be enhanced. Both the Raman spectra of BPE powder and BPE adsorbed on the silver surface are similar except small shifts occur on the silver surface. The shifted Raman lines in frequency or in line width is due to the interaction between molecule and metals [26]. The biggest differences between the normal Raman spectrum and the SERS spectrum are in the width of the peaks (all broader in SERS spectrum) and the relative intensity of ‘doublet’ at 1193 and 1229 cm^{-1}, 1594 and 1631 cm^{-1}. The observed SERS spectra of the adsorbed BPE are in perfect agreement with the reported spectra in the literature [19, 30-33]. The characteristic peaks of BPE, namely, benzene ring breathing (1010 cm^{-1}), ring vibration (1198 cm^{-1}), in-plane CH bending of ethylene (1312 cm^{-1}), benzene ring stretching (1603 cm^{-1}) and C=C
stretching mode (1636 cm\(^{-1}\)) clearly appear in the SERS spectrum. Comparing our results with those reported in the literature, the favorite orientation of adsorbed BPE is assumed to be perpendicular to the silver surface [34]. The results demonstrate that the prepared substrates are SERS-active and the enhancement factor can reach values up to \(10^5 \sim 10^7\) according to proposed calculation method [35].

![Graph showing Raman intensity vs. wavenumber for BPE powder and SERS spectrum of BPE adsorbed on the prepared substrate.](image)

**Fig. 3-7:** Normal Raman spectra of BPE powder and SERS spectrum of BPE adsorbed on the prepared substrate (17 nm Ag-film deposited on 120 nm SiO\(_2\)-like HMDS plasma polymer film) from aqueous BPE solution (5 \(\times\) \(10^{-5}\) M).

### 3.3.4 Influence of the Silver Film Thickness on the Enhancement Effect

In order to evaluate the effect of the silver film thickness on the Raman intensity, the spectra of BPE adsorbed on the rough silver films with different thicknesses were measured and the results are presented in Fig. 3-8.

The results show that the Raman intensity increases with increasing silver film thickness to a certain extent. The lower enhancement effect of 17 nm silver layer compared to that of 100 nm silver layer could probably be attributed to the incomplete surface coverage of 17 nm silver layer over the rough HMDS plasma polymer film. The plot of Raman intensity of Si-peak vs. thickness of silver top layer also proved the incomplete coverage of thinner silver film (see Fig. 3-9). As shown in Fig. 3-9, the peak at 520 cm\(^{-1}\) assigned to Si-wafer can be always detected until the silver film thickness is up to 100 nm. The Raman intensity of this peak decreased with the increasing thickness of the top silver layer because the laser cannot penetrate the thicker silver layer. The distribution of silver particles in the thinner
silver film (17 nm) is in the form of single particle, clusters or islands formed by aggregated particles (see Fig. 3-6 (b)), whereas the 100 nm silver film shows a continuous film rich of defects (see Fig. 3-6 (d)). The following EIS experiment also proved this point because the 17 nm silver film deposited on the rough nanoporous SiO$_2$-like plasma polymer film didn’t show any conductivity in the electrochemical environment. Thus there are still some areas of the surface that are SERS-inactive in the case of 17 nm silver film deposited on the rough nanoporous SiO$_2$-like plasma polymer film.

![Fig. 3-8: SERS spectra of BPE adsorbed on 17 and 100 nm silver films deposited on 120 nm Si-supported nanoporous SiO$_2$-like plasma polymer film.](image)

**Fig. 3-8:** SERS spectra of BPE adsorbed on 17 and 100 nm silver films deposited on 120 nm Si-supported nanoporous SiO$_2$-like plasma polymer film.

![Fig. 3-9: Evolvement of Raman intensity of Si-peak with increasing thickness of silver films.](image)

**Fig. 3-9:** Evolvement of Raman intensity of Si-peak with increasing thickness of silver films.

### 3.3.5 Optical Properties of the SERS-active Substrates

The surface enhancement effect has a strong dependence on the optical properties of the substrates. It is believed that the localized surface plasmon resonance (SPR) is responsible
for the electromagnetic enhancement that leads to surface-enhanced Raman scattering and other surface-enhanced spectroscopic processes [36]. UV-Vis spectroscopy was applied to study the optical properties of the silver films with 17 and 100 nm thicknesses. To avoid the baseline effect, the second derivative UV-Vis absorption spectra were used to present the difference of optical properties between two silver films. Second-derivative spectra display sharp minimum values where maximum values are located in the original spectra, hence the minimum values can be used to identify the positions of SPR peaks. Fig. 3-10 shows UV-Vis spectra of silver films with different thickness deposited on the nanoporous SiO$_2$-like plasma polymer films.

**Fig. 3-10:** Second-derivative of UV-Vis spectra of PVD silver films with different thicknesses deposited on the nanoporous SiO$_2$-like films (the substrate is glass).

The shapes of the obtained spectra with different silver thicknesses are similar, but the second derivative absorbance intensities are significantly different. Both of them have obvious absorption peaks at about 360 nm. This broad band is caused by the surface plasmon resonance of the silver nano-islands according to the literature [37-40]. The absorption of 100 nm silver film is much stronger than that of 17 nm silver film and the SPR peak of 100 nm silver film is much sharper than that of 17 nm silver film. This is likely why the Raman signal of the adsorbed BPE on 100 nm silver film is stronger than that on 17 nm silver film. In addition, the SPR peak of 100 nm silver has a small blue shift compared to that of 17 nm silver. The blue shift of the SPR peak may be explained by the corresponding morphological change, from isolated islands in 17 nm silver film deposited on the SiO$_2$-like film to the continuous structure in 100 nm silver film on the SiO$_2$-like film.
Meanwhile, the UV-Vis spectra also proved that the obtained SERS spectra are not resonance SERS spectra, because the wavelength of used He-Ne laser in our experiments is far away from 363 nm.

### 3.3.6 Effect of Rough SiO$_2$-like Film on the Enhancement Effect

The question arises if the pure silver film deposited on smooth substrates can lead to a similar enhancement effect. To reveal the difference caused by the nanoporous SiO$_2$-like plasma polymer film, SERS spectra of adsorbed BPE from aqueous solution on 100 nm silver films deposited on a smooth, polished Si-wafer and on the nanoporous SiO$_2$-like plasma polymer surface are presented in Fig. 3-11.

![Fig. 3-11: SERS spectra of BPE adsorbed on 100 nm silver films deposited on a smooth Si-wafer and on the Si-supported nanoporous SiO$_2$-like plasma polymer film.](image)

The spectrum of BPE adsorbed on the 100 nm silver film deposited on smooth polished Si-wafer was magnified by a factor of 100 for improving clarity. In both cases, a SERS effect is observed, but the enhancement factor is quite different. The spectrum from the 100 nm silver deposited on the rough SiO$_2$-like plasma polymer film exhibits more detailed information about the adsorbed molecules and the obtained signal is significantly more intense than that from the 100 nm island-like silver film deposited on the smooth Si-wafer substrate. The enhancement factor of the 100 nm silver film deposited on Si-supported rough plasma polymer film increases at least by two to three orders of magnitude compared with the 100 nm silver film deposited on the smooth Si-wafer.

The difference of enhancement factor between two kinds of surfaces can be explained by
the presented different morphology. As described in above section 3.3.2 (see Fig. 3-6 (c) and (d)), the 100 nm silver layer deposited on Si-wafer is a compact layer with small roughness, while it exhibits a very rough surface when the same silver layer was deposited on the rough, nanoporous SiO$_2$-like plasma polymer films. The silver film deposited on rough nanoporous SiO$_2$-like plasma polymer film is easy to produce surface lasmonmon resonance to enhance the electromagnetic field as been proved by UV-Vis measurements in section 3.3.5.

### 3.3.7 Effect of the Surface Area on the Enhancement Effect

To further evaluate the effect of the rough SiO$_2$-like plasma polymer film on the enhancement mechanism, the real microscopic surface area was measured by means of electrochemical impedance spectroscopy (EIS) (see Fig. 3-12). Because of the insufficient conductivity of the 17 nm island-like silver film deposited on the nanoporous SiO$_2$-like plasma polymer film, the characterization of this film by means of EIS was not possible. However, EIS data of the 100 nm silver film deposited on the nanoporous SiO$_2$-like plasma polymer film were obtained and thereby confirmed the UV-Vis spectroscopic data. The real surface area could be obtained from EIS spectra by comparing the double layer capacitance $C_{DL}$ of the silver film deposited on the nanoporous SiO$_2$-like plasma polymer film with that of the silver film deposited on Si-wafer. The surface area $A$ has been derived from fitted impedance data according to a serial connection of the electrolyte resistance and the constant phase element $Q$:

$$\frac{Q^{Ag/Si}}{Q^{Ag/SiO_2/Si}} = \frac{A^{Ag/Si}}{A^{Ag/SiO_2/Si}}$$

(3-1)

where $A^{Ag/Si}$ and $A^{Ag/SiO_2/Si}$ are the surface area of silver deposited on the Si-wafer and that of silver deposited on the rough nanoporous SiO$_2$-like plasma polymer films, respectively.

According to the equation 3-1, the real microscopic surface area of silver increased by about a factor of eight when the silver film was deposited on the nanoporous SiO$_2$-like plasma polymer film, which is in agreement with the results reported by Albrecht and Creighten [3]. Therefore, the enhancement of Raman intensity can only partly attributed to the increased surface area contribution and the corresponding enhancement factor caused by the increased surface area is only about one order. The main contribution should be assigned to the electromagnetic enhancement effect.
Fig. 3-12: Electrochemical impedance spectra of 100 nm silver films deposited on the smooth Si-wafer and on the nanoporous SiO$_2$-like plasma polymer film (electrolyte: Borate buffer, pH 9.1) ($A_{Ag/Si}^{Ag} / A_{Ag/SiO_2/Si}^{Ag} \approx 1:8$).

The surface enhancement factor of the synthesized silver film on the nanoporous substrate can be explained by the generation of an increased number of hot spots within the silver film and the increased surface area in combination with the possibility of multiple reflection of the incident radiation.

### 3.3.8 Stability of the SERS-active Substrates

The stability of the SERS-active substrates is also a very important criterion when it is evaluated in practical applications. Therefore, the Raman intensities of BPE adsorbed on the fresh prepared SERS-active substrate and on the SERS-active substrate stored under ambient condition over two months were compared in Fig. 3-13.

Fig. 3-13: Stability evaluation of the prepared SERS-active substrates.
The results clearly showed that both of the SERS spectra are totally identical except the difference of Raman intensity. It proved that the prepared SERS-active substrates with this method are very stable. The surface enhancement effect still remains and the enhancement factor doesn’t change much, even when the SERS-active substrates were stored over a long time, which is very promising in the practical applications.

3.4 Conclusions

The reported synthesis of SERS-active substrates, based on the combination of plasma polymerization, plasma calcination and silver deposition by PVD, leads to a large surface enhancement factor as could be proven by the adsorbed BPE probe molecules.

By plasma polymerization of HMDS, cauliflower-like HMDS plasma polymer films can be deposited. An oxygen plasma treatment converts these films into rough SiO$_2$-like plasma polymer films (plasma calcinations) while preserving the nanoporosity. On these rough nanoporous SiO$_2$-like plasma polymer films silver with various film thicknesses can be deposited by means of PVD. Thin PVD silver films imitate the nanoporous structure of the SiO$_2$-like plasma polymer films, thus silver surfaces with high microscopic surface area and probably high densities of hot spots can be generated. At lower silver film thickness, silver islands formed on the rough SiO$_2$-like plasma polymer films as confirmed by UV-Vis spectroscopy. Silver film with 100 nm thickness becomes continuous but an SPR peak at about 360 nm can still be observed. The difference of enhancement factor between thin and thicker, smooth and rough silver layers can be explained by the different optical properties induced by various surface morphologies.

The capacitance measurements by means of electrochemical impedance spectroscopy showed that the microscopic surface area of the 100 nm silver film deposited on the rough SiO$_2$-like plasma polymer film is increased by about one order of magnitude in comparison to that of the silver film deposited on smooth Si-wafer. This result further confirmed that the increased surface area is not the main contribution for the enhancement effect in SERS.

This way of SERS surface preparation leads to stable, reproducible surface structures and large surface enhancement factors. Moreover, it provides the possibility to coat a number of substrates in the same way during one deposition cycle, which will be shown in the following chapters.
3.5 References

4.1 Introduction

Raman spectroscopy has been used as a quantitative analysis tool for a long time to analyze different kinds of samples, such as the trace pollution of chemical compounds in water treatments, the impurities in glass in industry, the degree of crystallinity of model compound in pharmaceutical research, the carbon nanotubes in catalysis field, the content of oils and fats in food industry, and proteins in biology [1-6]. Pelletier presented the basis of using Raman to calculate the quantity of detected samples in his review [7], but he only considered spontaneous Raman scattering and excluded the SERS.

Only a few publications considered the correlation between the concentration of adsorbate on the SERS-active substrate and the resulting Raman intensity of the adsorbate peaks [8-11]. Most of the investigations were focused on the molecular structure or the orientation of the adsorbed molecules on the SERS-active substrates. This is due to the several problems related to the SERS experiments. The primary problems are the reproducibility of the SERS-active substrates and the determination of enhancement factor because of the non-uniform scientific criteria [12]. Actually, it is difficult to reproduce SERS amplification processes, which can be explained by the extreme sensitivity of the enhancement on the metal structures. Only slight variations of parameters such as cluster size and shape of the particles can produce changes in the enhancement factor by several orders of magnitude. Additionally, the co-action of different enhancement mechanisms can result in different enhancement factors for different molecules or molecular vibrations [13].

As well known, the first layer effect will generate the maximum enhancement according to the electromagnetic enhancement mechanism [14]. How to separate and determine the adsorbed first monolayer and the adjacent multilayer is still a problem in SERS field. In our case study, the growth of ultra-thin organosilicon plasma polymer films was probed as a model system to study the first layer effect. Organosilicon plasma polymer film was chosen because the thickness of these films can be reproducibly adjusted with nanometer accuracy and these plasma polymers form continuous and almost defect-free films even at nanometer thickness [15]. Moreover, Organosilicon plasma polymer films grow similarly on different
substrate materials and show excellent reproducibility concerning their chemical composition and thickness.

The enhanced Raman activity of as-prepared SERS-active substrates was proved and the reproducibility and stability were also verified in chapter 3. The prepared substrates in chapter 3 will be used as the SERS-active substrates in this chapter.

4.2 Experiment Details

4.2.1 Materials and Chemicals

Argon (~99.998%), oxygen (~99.995%) and nitrogen (~99.99%) (Messer Griesheim GmbH, Germany) were used as gases for the plasma processes. Hexamethyldisiloxane (HMDSO, (CH₃)₆Si₂O, purity > 98%, Fluka, Germany) was used as liquid monomer without further purification for the deposition of HMDSO plasma polymer films and the molecular formula is shown in Fig. 4-1. The polished Si (100) wafers (Si-Mat, Germany) and gold coated quartz crystals were used as substrates. The preparation of SERS-active substrates and the parameters of different apparatus are the same as the ones mentioned in the experimental section 3.2.

![Molecular formula of hexamethyldisiloxane (HMDSO)](image)

4.2.2 Deposition of Thin HMDSO Plasma Polymer Films

One custom made bell-jar type reactor with parallel capacitive electrodes was used to perform plasma deposition to achieve extremely smooth thin HMDSO plasma polymer films as shown in Fig. 4-2.

The substrates and a gold coated quartz crystal of 20 mm diameter used for in-situ quartz crystal microbalance measurements (QCM) were fixed in the grounded electrode during the plasma deposition process. HMDSO plasma polymer films with different thickness values
were deposited on the SERS-active substrates with a 100 nm silver film. The same HMDSO plasma polymer films were deposited on cleaned, polished Si-wafers simultaneously for the determination of film thickness by spectroscopic ellipsometry. The thickness of thin HMDSO plasma polymer films was controlled in-situ by QCM during the deposition process and calibrated by spectroscopic ellipsometry after deposition. A piezoelectric quartz crystal with a resonance frequency of 10 MHz coated with a 200 nm PVD gold film served as a substrate for the QCM measurements.

Prior to the plasma deposition process, the reactor was evacuated down to $5 \times 10^{-4}$ mbar by means of a turbo pump (Pfeiffer Vacuum). A liquid nitrogen trap was installed between the vacuum pump and the reactor to avoid the diffusion of oil from the pump into the vacuum chamber. The process pressure was adjusted by a down stream by-pass system and
controlled by means of a gas independent capacitive pressure gauge (MKS). A mass flow controller (MKS) was used to adjust the overall flow rate by means of a pure argon flow, and the partial pressures of the monomers and oxygen were adjusted by needle valves.

An audio-frequency voltage source supplying about 400 V to the electrodes was used to initiate the plasma. The overall flow rate was adjusted to 1.5 sccm and the final gas partial pressures of Ar, O₂ and HMDSO monomer for the plasma polymerization were 0.2, 0.05 and 0.05 mbar, respectively. Films prepared using the same conditions on different dates showed good reproducibility in all of the tests used [15]. The final thickness values of deposited HMDSO plasma polymer films were 3.9, 4.5, 9.6, 23.0, 35.6, 95.9 and 184.1 nm, respectively, which were determined by spectroscopic ellipsometry on polished silicon substrates.

The parameters for the AFM, SEM, FT-IR and SERS spectroscopy measurements of the HMDSO plasma polymer films are the same as shown in section 3.2.3.

4.3 Results and Discussion

4.3.1 Topography of the HMDSO Plasma Polymer Films

To investigate the topography of the HMDSO plasma polymer films, AFM measurements were performed on Si-supported and SERS-substrate-supported HMDSO plasma polymer films and the results are shown in Fig. 4-3 (a)-(h) and Fig. 4-4 (a)-(h), respectively.

Fig. 4-3 (a) presents the topography of cleaned Si-wafer surface as the reference. Fig. 4-3 (b), (e) and (f) show the topography evolution of HMDSO plasma polymer films with increasing film thickness. The corresponding curves of step height are also shown in Fig. 4-3 (c), (d), (g) and (h). The HMDSO film thicknesses in Fig. 4-3 (b), (e) and (f) are 9.6, 95.9 and 184.1 nm, respectively.

The AFM results showed that the HMDSO plasma polymer films are very smooth, defect-free and the change of their roughness values can be neglected in a large range of film thickness (from 4.0 to 184.1 nm in our case study). When the film thickness changed from about 9.6 to 184.1 nm, the roughness of the film increased slightly, but the RMS value was still less than 1 nm (the step height of the AFM images in Fig. 4-3 is smaller than 0.25 nm), which is in agreement with the results reported in literature [15]. Therefore, it can be
concluded that this kind of thin and smooth HMDSO plasma polymer film will not change the morphology of the SERS-active substrate and it will just imitate the features of the supporting SERS-active substrates.

Fig. 4-3: AFM images of HMDSO plasma polymer films with different thicknesses: (a) Si-wafer; (b) 9.6 (c) 95.9 and (f) 184.1 nm HMDSO film on Si-wafers; (c), (d), (g) and (h) the step heights of the AFM images in (a), (b), (e) and (f), respectively.
The topography evolution of SERS-active substrates covered by HMDSO plasma polymer films with increasing film thickness is shown in Fig. 4-4 (a), (b), (e) and (f). Fig. 4-4 (a) presents the AFM image of the as-prepared SERS-active substrate as the reference as done in Fig. 4-3 (a). The HMDSO film thicknesses in Fig. 4-4 (b), (e) and (f) are the same as those in Fig. 4-3 (b), (e) and (f).

Fig. 4-4: Topography of different surfaces: (a) SERS-active substrates, (b), (e) and (f) 9.6, 95.9 and 184.1 nm HMDSO plasma polymer films deposited on (a); (c), (d), (g) and (h) step heights of the AFM images in (a), (b), (e) and (f), respectively.
As discussed in chapter 3, the topography of SERS-active substrates is very rough and the distributions of silver particles are significantly different, including single silver particles, aggregated silver particles formed by 2 or 3 single silver particles. After the SERS substrates were covered by HMDSO plasma polymer films with different thicknesses, the AFM results in Fig. 4-4 showed that topography of the SERS-active substrates didn’t change or only slightly changed.

The RMS values of SERS-active substrates coated with HMDSO plasma polymer films of different thicknesses calculated by DI software are 36.8, 36.6 and 36.3 nm, respectively (see Fig. 4-4 (d), (g) and (h)), which is similar to that of the SERS-active substrate shown in Fig. 4-4 (c) (37.0 nm). This is because the HMDSO plasma polymer films are very smooth, defect-free and the roughness changes only slightly in a large film thickness range, which has been proved previously. This tiny change can be neglected in the experiment, because the RMS value is a statistical value calculated by the software. Therefore, thin, smooth and homogeneous HMDSO plasma polymer films just imitate and inherit the rough features of the SERS-active substrates. It is an ideal probe system for uncovering the relation between film thickness and SERS intensity and the enhancement factor as a function of film thickness.

In addition, FE-SEM measurements were performed on the SERS-subs trates covered with the HMDSO plasma polymer films of different film thicknesses and the results are shown in Fig. 4-5 (a)-(d).

As can be seen from Fig. 4-5 (a) to (d) the surface morphology of the SERS-substrate was only gradually changed by the deposition of the thin HMDSO plasma polymer films. When the film thickness was very small, for example, 4.5 nm, the HMDSO plasma polymer film could not cover the whole rough silver surface (see Fig. 4-5 (b)). The film is presented in the form of fractal. The defects on the rough silver surface can still be clearly observed. With an increase in the thickness of HMDSO plasma polymer films, the boundaries of silver particles smeared out and the crevices or the pores between particles were more and more filled with the HMDSO plasma polymer films (see Fig. 4-5 (c) and (d)). The shape of silver particles and the island-like structure were smoothened by the thicker HMDSO plasma polymer films, but the deposited HMDSO plasma polymer films still exactly imitated the topography of the silver layer on SERS-active substrates.
Fig. 4-5: FE-SEM images of the HMDSO plasma polymer films on SERS-active substrates as a function of the film thickness: (a) SERS-active substrate, (b)-(d) 4.5, 35.6 and 184.1 nm HMDSO plasma polymer film on SERS-active substrates, respectively.

4.3.2 Chemical Composition of the HMDSO Plasma Polymer Films

To determine the chemical composition of the HMDSO plasma polymer films, FT-IR and Raman spectroscopic measurements of Si-supported and SERS-substrate-supported HMDSO plasma polymer films were carried out. Fig. 4-6 (a) and (b) present the FT-IR transmission spectra of an HMDSO plasma polymer film (thickness is 184 nm) deposited on a cleaned Si-wafer substrate.

According to data in the literature [16-17], the peaks at 798, 845, 1034, 1267, 2910 and 2965 cm⁻¹ can be assigned to the rocking of methyl and stretching of SiC in Si-Me₂; rocking of methyl and stretching of SiC in in Si-Me₃; symmetric stretching of SiO in Si-O-Si; symmetric bending of CH₂ in Si-Me₅; asymmetric stretching of C-H in Si-Me₂ and asymmetric stretching of C-H in Si-Me₃, respectively.
The SERS spectrum of 184 nm HMDSO plasma polymer film deposited on the SERS-active substrate is presented in Fig. 4-7. The two peaks at 2910 and 2971 cm\(^{-1}\) dominated the SERS spectrum and they can be assigned to the asymmetric stretching vibrations of the methylene and methyl groups of the organosiloxane-like structure [17, 18], which agrees with the FT-IR results. Both of the two Raman peaks can be observed in all of the Raman spectra, thus they were chosen as the criterion to interpret the relation between Raman intensity and HMDSO plasma polymer film thickness. The peaks at 1340 and 1590 cm\(^{-1}\) are from the laser-induced carbonization of the surface adsorbates or thin film [8].
films deposited on the cleaned Si-wafer and the SERS spectrum of 35.6 nm HMDSO plasma polymer film in the wave number range between 2500 and 3100 cm\(^{-1}\). The comparison of the Raman intensity in Fig. 4-8 (a) and (b) demonstrates again that the Raman intensity of the HMDSO plasma polymer film deposited on SERS-active substrate in Fig. 4-8 (b) even with lower thickness (35.6 nm) is much more intense than that of the HMDSO plasma polymer film deposited on Si-wafer substrate in Fig. 4-8 (a) with higher film thickness (184 nm).

4.3.3 Growth of the HMDSO Plasma Polymer Films on SERS-active Substrate

To investigate the relation between the Raman intensity and the film thickness during the growth of the HMDSO plasma polymer films, the respective SERS spectra of HMDSO plasma polymer films deposited on SERS-active substrates are shown as a function of the film thickness in Fig. 4-9. The measured thicknesses of HMDSO plasma polymer films are 3.9, 4.5, 9.7, 23.0, 35.6, and 95.9 nm, respectively. The Raman spectra were shifted vertically for clarity. The stretching vibration of the C-H in methyl and methylene groups was identified as the most suitable peak for the evaluation of the thickness dependence of the peak intensity.

The results show that the information of C-H in Si-Me\(_2\) can be detected in the SERS spectrum even at a film thickness of about 3.9 nm, which again demonstrates the advantage of the presented SERS-active substrates. Moreover, it is apparent that the Raman intensity
of the HMDSO plasma polymer film increases with the increasing HMDSO film thickness as shown in Fig. 4-9.

![Fig. 4-9: SERS spectra of thin HMDSO plasma polymer films with different thickness values (The film thicknesses are 3.9, 4.5, 9.7, 23.0, 35.6, and 95.9 nm from bottom to top, respectively. All the spectra were vertically shifted by 200 arb. units for clarity).](image)

To evaluate the SERS effect of these prepared substrates further, the Raman signal obtained from the HMDSO plasma polymer films deposited on the different substrates were compared as shown in Fig. 4-10. Fig. 4-10 shows the Raman intensities of HMDSO plasma polymer films resulting from three substrates, namely, 53.9 nm HMDSO film on cleaned Si-wafer (Fig. 4-10 (a)), 53.9 nm HMDSO film on 100 nm smooth silver layer (Fig. 4-10 (b)) and 9.7 nm HMDSO film deposited on prepared SERS-active substrate (Fig. 4-10 (c)).

![Fig. 4-10: Comparison of the Raman intensity of 53.9 nm thick HMDSO film deposited on (a) Si-wafer, (b) PVD-Ag-film deposited on Si-wafer; (c) 9.7 nm HMDSO film on the prepared SERS-active substrate.](image)
As seen in Fig. 4-10 (a), the information of HMDSO film can’t be detected by normal Raman when it was deposited on the cleaned, smooth Si-wafer even the thickness was up to 53.9 nm. Actually, it wasn’t detected until the thickness of film was up to about 100 nm in our case study. Compared to the polished Si-wafer substrate, the smooth PVD-Ag film on Si already showed a small enhancement effect as discussed in chapter 3. However, the rough SERS-active substrate leads to a strong additional enhancement effect compared to the above mentioned substrates (Si-wafer and Ag film). Not only the Raman intensity, but also the resolution of the spectrum is much higher than those of the other two substrates under the same measurement conditions.

### 4.3.4 Determination of the Enhancement Factor

To calculate the enhancement factor for the SERS spectra of thin HMDSO plasma polymer films, the integral of the CH-stretching peak in the normal Raman spectrum of a relatively thick film (184 nm HMDSO plasma polymer film) deposited on a Si-wafer surface was measured. The integral Raman peak intensity of this film was divided by its thickness leading to Raman integral intensity per nanometer film thickness. This value was then compared with the measured SERS integral intensity per nanometer film thickness of HMDSO plasma polymer films with varying thicknesses on the rough SERS-active substrates according to:

\[
SEF = \frac{\frac{I_{SERS}}{d_{film \ in \ nm}}}{\frac{I_{RS}}{d_{film \ in \ nm}}}
\]

where \( I_{SERS} \) and \( I_{RS} \) is the SERS intensity and normal Raman intensity of the HMDSO plasma polymer films respectively, \( d_{film} \) represents the thickness of HMDSO plasma polymer film and \( SEF \) is the surface enhancement factor.

The observed changes of Raman intensity and surface enhancement factor (SEF) as a function of the HMDSO plasma polymer film thickness are displayed in Fig. 4-11. As may be seen in Fig. 4-11, the SERS integral intensity of HMDSO plasma polymer films deposited on the SERS-active substrates increases with the increasing HMDSO film thickness. However, the surface enhancement factor drops very sharply in the thickness range between 0 and 20 nm. Most likely there are two contributions for the increasing SERS integral intensity. One is from the increasing HMDSO plasma polymer film
thickness, which means the Raman intensity is proportion to the film thickness, because the Raman intensity is proportional to the illuminated molecules by the laser beam. The other one is from enhanced electromagnetic field produced by SERS-active substrates. In our case study, the latter is the main contribution.

According to the first layer enhancement theory [14], SERS intensity of deposited thin HMDSO plasma polymer film is dependent on the distance between the HMDSO plasma polymer film and the top silver layer. Larger distance induces weaker Raman intensity. The research has dedicated that the field of a dipole decrease as \((1/d)^3\) with increasing distance [19]. Only within several nanometers contacted to the metal surface an extremely high enhancement factor can be observed. When the layer thickness is larger than about 10 nm, the enhancement factor will decrease sharply. This result is clearly confirmed by the reported results for thin HMDSO plasma polymer films and is in agreement with the conclusion from Murray and Allara [20].

For a few nanometers thin HMDSO plasma polymer films an enhancement factor of up to \(2 \times 10^3\) could be achieved, which decreased by more than one order of magnitude at a distance of more than 20 nm to the rough silver surface. It is not surprising that the measured large enhancement factor of BPE (see chapter 3) could not be achieved for the organosilicon plasma polymer films because the plasma polymer films have the structure quite different from those of the starting monomers as a result of fragmentation of the monomers during the plasma deposition. Normally, the films are highly cross-linked and this results in the small polarizability of siloxane-like networks, which is not chemically
bonded to the silver surface [21]. However, the enhancement factor is sufficient to allow
the application of SERS to the very important class of untra thin siloxane plasma polymer
films.

4.4 Conclusions

The as-prepared SERS-active substrates were used to investigate the growth of thin
HMDSO plasma polymer films. The advantages of the prepared HMDSO plasma polymer
film/SERS-active substrates model system were presented in detail in this chapter.
Obviously, the surface enhancement effect allows the investigation of the thin HMDSO
plasma polymer films in a thickness range of a few nanometers.

It seems that the resultant increase in the Raman intensity of thin SERS-substrate-supported
HMDSO plasma polymer films originates from a combination of the electromagnetic
enhancement mechanism and the increase in the actual number of detected molecules in the
thicker film. The achieved enhancement factors for these HMDSO plasma polymer films
are not so high as those of BPE or other Raman-sensitive molecules, which act as probe
molecules in SERS research. It is likely that due to the small polarizability of the siloxane
network in case of the organosilicon plasma polymer films the overall enhancement factor
is smaller in comparison to BPE molecules. The enhancement factor drops sharply within
the first 20 nm thickness range of HMDSO plasma polymer film, because the enhanced
electromagnetic field is strongly dependent on the distance between HMDSO thin film and
silver top layer.

4.5 References

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Chapter 5: SERS Investigation of the Phase Transition in Thin TiO₂ Films

5.1 Introduction

Surface-enhanced Raman scattering (SERS) is a phenomenon involving a large increase in the Raman scattering cross section of molecules adsorbed at surfaces of metallic nanoparticles [1]. Since it was discovered in the mid-1970s [2-4], SERS had a significant impact on surface and interface science because of its high spatial resolution (up to 1 μm), extremely high sensitivity (up to the detection of single molecule) and rich information content for the adsorbed layers at metal/electrolyte, metal/polymer interfaces, especially in the aqueous solution [5-10].

In comparison to the research related to the phenomena of molecules, however, the applications of SERS in materials science are relative new and not been fully considered so far. Not like the vibrations created in organic molecule, where the electron cloud is polarized by the incident radiation; the vibrations created in solid material samples are from the interactions between radiation and the lattice, where no definable molecules in which the atoms are linked by covalent bonds can be found [11]. When the materials are in amorphous phase, broad Raman peaks or only fluorescence background but no information of the materials can be acquired; while when the materials are in crystalline phase, the vibrations created by radiation interacting with lattice become strong and can be detected by Raman spectroscopy. It is easy to understand: the more crystalline phase in materials, the stronger the Raman intensity. Normal Raman spectroscopy has wide applications in characterization of bulk materials or thick (>1 μm) films, for example, to identify the different phases of iron oxide [12-14], to in-situ detect the corrosion products of iron in electrolyte [15-16], to interpret the properties of diamond-like film [17-18] and to evaluate the doping effects in semiconductor industry [19-20]. As for the thin (10-100 nm) films, normal Raman spectroscopy has its natural disadvantage, namely, very weak signal. In this chapter, the phase transition of thin titanium dioxide (TiO₂) films sputtered on the SERS-active substrates presented in chapter 3 was investigated to extend the applications of SERS. The thin TiO₂ film/SERS-active substrate was selected as a model system, because TiO₂ is probably one of the most extensively studied oxide system and it is easy to get the well
ordered, nearly perfect surfaces [21].

Since the nano-TiO$_2$ appeared in the 1980s, it has attracted very much attention because of its catalytic properties, as used in photoelectric and photochemical reactions [22]. Nano-TiO$_2$ is a polymorphic substance and is present in three crystalline phases: anatase, rutile, and brookite with different properties and structures [23]. However, only rutile and anatase play important roles in the applications of thin TiO$_2$ films, thus are of interest here to be studied with various surface techniques. The anatase phase of TiO$_2$ generally has a higher activity in oxidative photocatalysis. It can be used as a photocatalyst in heterogeneous catalysis to degrade the environmental pollutants in waste water and gas [24], or as an optical coating in optics [25] and as gas sensors and varistor in electric device [26].

The phase transition of TiO$_2$ films studied by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and normal Raman spectroscopy has been reported in some published papers [27-34]. However, in our case study, the TiO$_2$ film thickness is in the nanometer range, whereas most TiO$_2$ film thicknesses in the reported papers are in the micrometer range or even much thicker. As will be presented in this chapter, the SERS-active substrates following the preparation process described in chapter 3 are applied to investigate the phase transition of thin TiO$_2$ film. The results show that SERS is an excellent and sensitive tool in studying the phase transition of thin TiO$_2$ films. It is also shown that the prepared SERS-active substrates can be applied not only to the study of adsorbed organic molecules or organic thin films, but also to the analysis of thin metal oxide films.

5.2 Experimental Procedures

The whole process and detailed information about the preparation of the SERS-active substrates can be found in chapter 3 and the SERS-active substrates with 100 nm silver layer were used in this chapter [35].

5.2.1 Deposition of Thin TiO$_2$ Films by means of Magnetron Sputtering

The used deposition system in this chapter is a laboratory radio frequency (RF)-magnetron sputtering system as shown in Fig. 5-1. The used target was TiO$_2$ with a high purity (99.9%, Matech, Germany). The sputtering process was started when the base pressure in the sputtering chamber was achieved down to $7.0 \times 10^{-7}$ mbar. The sputtering process was performed in pure argon gas atmosphere at the pressure $7.0 \times 10^{-3}$ mbar with an 8 sccm gas
flow rate. The used RF power and the DC bias voltage were set at 100 W and 339 V, respectively. The sputtering process lasted for 12 minutes and the temperature of the substrate was kept constant at 25 °C during the whole process. With the above-mentioned deposition parameters, the final thickness of the deposited TiO₂ layer was determined to be about 12 nm by means of spectroscopic ellipsometry. The obtained samples were annealed at 500 °C afterwards in a pure nitrogen protective atmosphere for 1 hour and cooled down to the room temperature in the nitrogen. All the obtained samples were measured immediately before and after annealing treatments.

5.2.2 Surface Characterization and Analysis

The parameters and the detailed information about the apparatus of atomic force microscope (AFM) and field emission scanning electron microscope (FE-SEM) can be found in section 3.2.3.

Grazing Incidence X-ray Diffraction (GIXRD)

GIXRD analysis was performed on the Bruker AXS Advance D8 system (Baltic Scientific Instruments). The measurements were performed using Cu Kα radiation at 40 KV, 40 mA. The angle of incidence is 0.7 ° and the step between measurements is 0.08 ° in the range from 20 to 70 °. The experimental set-up is presented in Fig. 5-2.
Surface-enhanced Raman Spectroscopy (SERS)

Surface-enhanced Raman spectroscopy measurements were performed using a modular system (Dilor LabRAM, ISA Instruments. SA, INC, France) that consists of a green Ar⁺ laser (514.5 nm) with 20 mW output power, 100 × 0.9 microscope objective, an Olympus BX40 confocal microscope, charge couple devices camera (cooled down to -70 °C), 600/1800 grooves/mm gratings and a holographic notch filter. The experimental parameters were adjusted as follows: the pinhole was 1000 μm and the size of slit was set to 100 μm and the spectra acquisition time was 10 seconds for every measurement. To avoid the extra transition of TiO₂ film induced by the heating from the incident laser radiation, the power of laser was set to 0.2 mW.

X-ray Photoelectron Spectroscopy (XPS)

The chemical compositions of the thin TiO₂ films were investigated by means of X-ray photoelectron spectroscopy (Quantum 2000, Physical Electronics, USA). The spectra were measured using a spectrometer equipped with a concentric hemispherical analyzer and a monochromated Al Kα X-ray source at a 45° take-off angle with respect to the sample surface. The samples were measured under UHV conditions: from 10⁻⁹ to 10⁻⁸ mbar. A sample area was analyzed with a pass energy of 93.9 eV for survey spectra and 23.5 eV for detailed elemental spectra. The spectra were calibrated by using C 1s peak (Binding Energy, BE = 285 eV for -C-C- groups) as an internal reference. During the fitting procedure, the line width (full width at half-maximum, FWHM) of the peaks was kept constant for all respective element spectrum components in a particular spectrum.
5.3 Results and Discussion

5.3.1 Grazing Incidence X-ray Diffraction (GIXRD) Measurement

As well known, XRD is a powerful tool in studying the structure of bulk crystalline materials for decades. However, it can also play an important role for probing the internal interfaces and the vertical and lateral correlation of mono- and multilayer structures near the sample surfaces. Since the refractive index of matter at air-sample interface for X-rays is smaller than that of matter at unity, the X-ray penetration depth can be drastically reduced to several nanometers if the beam strikes the sample surface at a very shallow grazing angle. Thus the vertical density profile can be probed by X-ray specular reflectometry. The detection of information from the near-surface can be realized by choosing a grazing incidence geometry, which combines the depth sensitivity of X-ray reflection and the strain sensitivity of the wide-angle X-ray diffraction [37].

Fig. 5-3: GIXRD spectra of 12 nm thin TiO₂ film sputtered on SERS-active substrates: (a) before annealing treatment; (b) after annealing treatment.

GIXRD technique was applied to study the structure of as-prepared thin TiO₂ thin films in our experiment and the characteristic XRD spectra of the TiO₂ samples before and after annealing are shown in Fig. 5-3. As can be seen from the curve (a) in Fig. 5-3, no feature peaks of anatase TiO₂ appear and the strongest signal is from the top silver layer of the SERS-active substrate. There is no anatase or other crystalline phases involved in the as-prepared thin TiO₂ film before annealing. It can be concluded that the thin TiO₂ film without annealing treatment is almost amorphous or a little crystalline under the detection limitation of GIXRD technique. This is attributed to the sputtering of the thin TiO₂ films at
a relative low substrate temperature. When the TiO$_2$/SERS-substrate system was annealed at 500 °C for 1 hour, the phase transition occurred and the crystalline content in the thin TiO$_2$ film increased. The characteristic peaks of TiO$_2$ anatase phase are marked in Fig. 5-3 (b), which agrees with the data in the database of the software [38-39]. Moreover, no rutile structure is observed from the GIXRD analysis.

5.3.2 Topography of Thin TiO$_2$ Films on Different Substrates before and after Annealing Treatment

AFM and FE-SEM were used to characterize the topography and morphology of thin TiO$_2$ films sputtered on different substrates before and after annealing treatment, namely, on smooth Si-wafers, on silver layer deposited on Si-wafers and on the SERS-active substrates. The corresponding results are presented in Fig. 5-4 and Fig. 5-5. The topography of above mentioned three substrates without TiO$_2$ films has been discussed previously in chapter 3. In Fig. 5-4 the topography of 12 nm TiO$_2$ films sputtered on the different substrates before and after annealing treatment and the curves of step height of the corresponding surfaces are presented.
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Fig. 5-4: Topography of the surfaces of 12 nm TiO$_2$ films deposited on different substrates before (left side) and after annealing treatment at 500 °C for 1h (right side): (a) and (b) on Si-wafers; (e) and (f) on 100 nm Si-supported silver films; (i) and (j) on SERS-active substrates; (c), (d), (g), (h), (k) and (l): step height of the surfaces in (a), (b), (e), (f), (i) and (j), respectively.

As shown in Fig. 5-4 (a), the pure thin TiO$_2$ films deposited on Si-wafers are very smooth and almost defects free as described in literature [21]. The root-mean-square (RMS) value of thin TiO$_2$ film on Si-wafer in Fig. 5-4 (a) is less than 1 nm and the roughness doesn’t
change even with annealing treatment (Fig. 5-4 (b)). The step height of the surfaces in Fig. 5-4 (a) and (b) is also very low (< 0.2 nm see Fig. 5-4 (c) and (d)). The behavior of thin TiO$_2$ films is similar to the thin HMDSO films reported before (see chapter 4, Fig 4-3) and it will not change the surface conditions of the supporting substrates significantly.

The AFM images of thin TiO$_2$ films on Si-supported 100 nm silver films before and after annealing are shown in Fig. 5-4 (e) and (f). The thin TiO$_2$ films on Si-supported silver films show island-like structures with different sizes. The RMS values are 1.8 and 1.9 nm for TiO$_2$ on Si-supported silver films before and after annealing treatments. The presented surface topography mainly inherits from the supported silver film. Fig 5-4 (g) and (h) show that the step height of the thin TiO$_2$ films on Si-supported silver films increases slightly in comparison to that of thin TiO$_2$ films on Si-wafers, but it remains very low (< 1 nm).

The AFM images of thin TiO$_2$ films deposited on SERS-active substrates before and after annealing are shown in Fig. 5-4 (i) and (j). As can be seen, the surface conditions remain almost same before and after annealing, the RMS values are 37.5 and 39.0 nm, respectively. The thin TiO$_2$ films on the SERS-substrates show much rougher, island-like structures, because this kind of sharp surface features is inherited from the supporting SERS-substrates as mentioned in chapter 3. The step height of the thin TiO$_2$ films deposited on SERS-active substrates shown in Fig. 5-4 (k) and (l) is much larger than that of the thin TiO$_2$ films on silver film or Si-wafer (< 30 nm). This confirms the thin TiO$_2$ films on SERS-active substrates borrowed the rough features from the SERS-active substrates.

The AFM images and the curves of step height in Fig. 5-4 clearly show that the surface topographies of the investigated model systems (TiO$_2$/Si, TiO$_2$/Ag/Si and TiO$_2$/SERS-active substrates) after annealing are very similar to those before annealing, i.e. the surfaces still remain the respective characters after annealing treatment.

Because AFM images can’t show the sharp features of the obtained rough surfaces perfectly, FE-SEM was used to characterize the sharp features of the TiO$_2$ surfaces complementarily. Fig. 5-5 (a)-(c) show the surface morphology of Si-supported silver films, thin TiO$_2$ films deposited on the Si-supported silver film before and after annealing. In Fig. 5-5 (d)-(f) the surface morphology of SERS-active substrates, thin TiO$_2$ films deposited simultaneously with the samples in Fig. 5-5 (b) on SERS-substrates before and after annealing.
As presented in Fig. 5-5 (a) the surface of the 100 nm pure silver films deposited on the Si-wafers shows some randomly oriented coalesced islands and some cracks can be observed.
between the island-like structures. The formation of such kind of structure could be attributed to the uneven distributed stress due to the island coalescence or contiguity during the film growth process [40]. When the thin TiO$_2$ films were sputtered on top of the 100 nm Si-supported silver films, the cracks on the surface disappear and the surfaces seem smoother than those of the Si-supported silver films, because the thin TiO$_2$ films will cover the defective surfaces completely and fill in the cracks. Moreover, the shape of the island-like particles becomes more spherical (see Fig. 5-5 (b)). After the thin TiO$_2$ films were annealed at 500 °C for 1 hour, the surfaces remained quite smooth (see Fig. 5-5 (c)), but the size of the island-like structures increased slightly due to the annealing treatment.

Fig. 5-5 (d) shows the surface morphology of the prepared SERS-active substrates with a higher magnification (500 kX). It can be seen that the surface of SERS-active substrate is very rough and rich of defects. Many kinds of defects can be observed on the surface of the SERS-active substrate, for example, aggregated Ag particles, cracks, caves, holes or islands as described in chapter 3. Fig. 5-5 (e) presents the morphology of the thin TiO$_2$ films deposited on the SERS-active substrates. The thin TiO$_2$ film doesn’t exist as a continuous film on such kind of rough substrate, but many very fine TiO$_2$ nanoparticles are dispersed homogeneously on the rough SERS-active substrate surface. The size of TiO$_2$ nanoparticles is about several nanometers and the distribution of the nanoparticles is very uniform on the surface of the SERS substrate. The morphology of SERS-active substrate remains almost same after the deposition of the thin TiO$_2$ film, because the amount of the deposited TiO$_2$ is not so much, so that the fluctuant feature of the SERS-active substrate can be preserved. This agrees with the above-shown AFM results. In Fig. 5-5 (f) the morphology of the fine TiO$_2$ nanoparticles deposited on the SERS-active substrates after annealing is shown. It can be clearly observed that the number of fine TiO$_2$ particles on the surface of the SERS-active substrates decreased significantly, whereas the size of the TiO$_2$ particles increased. It may be interpreted that the uniformly distributed fine TiO$_2$ nanoparticles grew into bigger nanoparticles due to Ostwald ripening during the annealing treatment, because the surface energy of the nanoparticles decreases with the increasing particle size [41-42].

5.3.3 XPS Measurements

The XPS measurements were performed on the thin TiO$_2$ films deposited on the SERS-active substrates with annealing treatments to reveal their chemical composition. The corresponding results are shown in Fig. 5-6.
The three peaks of C 1s spectrum at 285.0, 286.7 and 288.9 eV in Fig. 5-6 (a) can be assigned to the carbon contaminants, C=O groups and carbonates, respectively [43]. Two major peaks in Ag 3d spectrum at 374.1 and 368.1 eV are the typical peaks from Ag 3d 3/2 and Ag 3d 5/2 (see Fig. 5-6 (b)). Fig. 5-6 (c) shows two reasonably symmetric Ti 2p peaks of the deposited TiO₂ thin films, as did the nearly defect-free TiO₂ films reported in the literature [28, 44-45]. After curve fitting using Gaussian distribution functions, the spin-orbit components (2p 3/2 and 2p 1/2) of the Ti 2p peak are well shown by two major peaks at 459.2 and 465.0 eV corresponding to the Ti⁴⁺ in a tetragonal structure. The binding energy of the Ti 2p 3/2 component is consistent with a surface region in which titanium is primarily in the Ti⁴⁺ oxidation state in the form of TiO₂ [46-47]. No other species such as Ti³⁺, Ti²⁺, Ti¹⁺ or Ti⁰⁺ can be rationally deconvoluted from the XPS spectra of the samples [48]. The O 1s spectrum in Fig. 5-6 (d) was fitted into three components. The one at 532.9 eV can be attributed to the carbonates, the one at 532.0 eV may arise from the hydroxyl
(OH) groups chemisorbed on the surface of samples and the one at 530.5 eV should be from the Ti-O bond in TiO$_2$ film [49-50]. The binding energies of Ti 2p and O 1s peaks indicated that titanium oxide is formed on the surface of the SERS-active substrates.

### 5.3.4 Raman and SERS Measurements

In the above sections, the phase transition of the thin TiO$_2$ films during the process of annealing treatment was detected by GIXRD measurements, and AFM and SEM measurements exhibited the morphological changes of the thin TiO$_2$ films during the annealing treatment. In addition, XPS results confirmed the formation of TiO$_2$ film after annealing on the SERS-active substrates. In this section, the phase transition of TiO$_2$ thin films before and after annealing treatments is studied by means of surface-enhanced Raman spectroscopy. As both the anatase and rutile phases are sensitive to Raman scattering, this may provide valuable information on the phase composition, crystallinity, crystallite size and defect (oxygen vacancy) concentrations during the annealing treatment [21]. Fig. 5-7 (1)-(3) show the Raman spectra of thin TiO$_2$ films deposited on the different substrates, namely, on Si-wafers, on 100 nm Si-supported silver films and on SERS-active substrates. All the spectra were acquired with the identical measurement parameters and the spectra were shifted vertically for clarity.

As can be seen, no information of thin TiO$_2$ films can be detected when they were deposited on the above-mentioned three different substrates before annealing treatments (spectra (a) in Fig. 5-7 (1)-(3)) except the dominating fluorescent background from the supporting substrates. As mentioned at the beginning of this chapter, Raman can’t detect the information of TiO$_2$ when it is in amorphous phase or has small amount of crystalline phase under the detection limitation. Therefore, the deposited thin TiO$_2$ films before annealing treatment are mainly amorphous, and this is in agreement with the GIXRD results shown previously.

When the thin TiO$_2$ film was annealed at 500 °C for 1 hour, the amorphous TiO$_2$ was totally converted into anatase phase, which can be identified from Raman spectra. For the thin TiO$_2$ film deposited on the Si-wafer, the only obtained information about anatase phase is the peak at 147 cm$^{-1}$ with a weak signal. The signal from the background is very strong, which is characterized by the peak at 304 cm$^{-1}$ attributed to the Si-wafer substrates (see Fig. 5-7 (1) spectrum (b)). While for the thin TiO$_2$ film deposited on Si-supported silver film, all
the characteristic peaks of anatase phase appear in the spectrum (b) in Fig. 5-7 (2). Furthermore, for the thin TiO$_2$ film deposited on the SERS-active substrates, not only all the peaks of anatase TiO$_2$ appear, but also the Raman intensity of anatase phase in spectrum (b) in Fig. 5-7 (3) is much stronger than the former in Fig. 5-7 (2). The enhancement factor for the thin TiO$_2$ films deposited on the SERS-substrates is about two orders of magnitude larger than that on Si-wafers and one order larger than that on Si-supported silver films (see Fig. 5-7 (4)).

Fig. 5-7: Raman spectra of thin TiO$_2$ films on different substrates: (1) TiO$_2$ (18 nm)/Si; (2) TiO$_2$ (12 nm)/Ag/Si; (3) TiO$_2$ (12 nm)/SERS-substrates (Curve (a) and (b) denote before and after annealing, respectively); (4) Comparison of Raman intensity of (a) TiO$_2$/Ag/Si and (b) TiO$_2$/SERS–active substrates after annealing treatments (the spectra were vertically shifted for clarity).

Anatase is tetragonal with four formula units per unit cell and six Raman active modes ($A_{1g}+2B_{1g}+3E_g$) [51]. As can be seen in Fig. 5-7 (3), except for the weak peak at 199 cm$^{-1}$, which is assigned to the $E_g$ mode from the pure anatase crystal, all the characteristic peaks
of the anatase phase can be well distinguished in the surface-enhanced Raman spectrum. Those peaks appearing at 151 and 642 cm$^{-1}$ are from E$_g$ phonon modes with the band at 151 cm$^{-1}$ being most prominent in the spectrum. The fundamental B$_{1g}$ mode occurs at 401 cm$^{-1}$, while the band at 520 cm$^{-1}$ can be assigned to both an A$_{1g}$ and a B$_{1g}$ mode because of the small separation of these phonons. No distinct peak that corresponded to rutile phase (~440 cm$^{-1}$) appears in the spectra shown in Fig. 5-7 [30-34]. The Raman peaks of anatase phase slightly blue shifted in comparison to the data in the literature, which is probably attributed to the quantum size effect induced by the very fine TiO$_2$ nanoparticles obtained by the sputtering [52-53] or some impurity of brookite in the obtained films (~150 cm$^{-1}$) [30-34]. In general, the phase transition happens at the temperature over 350 °C, which is not exact in our case study. Actually, the transition didn’t happen until the temperature was over 500 °C. The possible reason of the delayed crystallization of antase phase is that the presence of silver atoms seemed to increase the activation barrier for the crystallization. Similar phenomena have been reported for an incorporation of Fe in TiO$_2$ films and for sol-gel-prepared Ag-TiO$_2$ films [38-39, 54].

5.4 Conclusions

In this chapter, the phase transition of thin TiO$_2$ films prepared by magnetron sputtering on different substrates was investigated by means of different methods, such as GIXRD, AFM, FE-SEM, XPS and Raman spectroscopy. The results showed that the phase transition of thin TiO$_2$ film with annealing treatment was successfully studied by Raman spectroscopy combining other techniques. Especially the anatase phase of the TiO$_2$ can be very easily distinguished by using the TiO$_2$/Ag system and the Raman signal of the TiO$_2$/SERS-active substrate is enhanced at least two orders of magnitude compared to that of the Si-supported TiO$_2$ films and 20 times than that of the TiO$_2$/Ag/Si system. The enhanced signal can be attributed to the localized electromagnetic field from the surface plasmon excitation of metal Ag decoration.

The investigation of the phase transition of the TiO$_2$ thin films by SERS shows the possible applications of SERS in analysis of other important metal/metal oxides in industry in the future.
5.5 References

Chapter5: SERS Investigation of the Phase Transition in Thin TiO2 Films


Chapter 6: In-situ SERS Study of Plasma Surface Modification Effects

6.1 Introduction

Plasma has been a very useful technique for depositions and surface modifications of different materials in the past several decades, both in industry and in research [1-19]. Plasma modifications have been widely performed on various surfaces of metals [1-3], polymers [4-6], biomaterials [7-9], semiconductors [10-13], composites [14-15] or even ceramics [16-17]. The plasma surface modification is so attractive because the key feature of this modification is confined to the outermost layers of the surfaces (several hundreds of angstroms) without altering the bulk properties of the materials [4]. It is a rapid, clean and nonsolvent process, which can alter the physical or chemical properties of the surfaces such as chemical composition, wettability, crystallinity, conductivity, lubricity or topography.

The plasma modification processes can be roughly classified into four categories, namely, contaminant removal; surface activation; etching and cross-linking [4, 12]. Unique surface properties required by various applications can be realized by selecting a suitable reaction gas and proper process parameters. The normally used gases for plasma surface modifications include argon, oxygen, nitrogen, hydrogen, water vapor or the mixture of these pure components. Concerning the effect of different plasmas, it is widely accepted that the oxygen plasma treatment can increase the surface energy and remove the contaminants, whereas hydrogen plasma can reduce the metal oxide and inert gas plasma can cause the cross-linking at a polymer surface [3, 8-9].

To better understand the plasma surface modifications, it is necessary to design in-situ experiments and analysis. Due to the ageing effect, the results obtained in ex-situ conditions will deviate from the truth happening on the surface. The ageing effect is a phenomenon that the concentration of functional groups introduced on a solid surface by plasma modification may change as a function of time depending on the environment and temperature [4]. Various in-situ surface analytical techniques have been applied to monitor the plasma modification processes and analyze the products of plasma, such as in-situ fourier-transformation infrared spectroscopy [20-22], in-situ Raman spectroscopy [23], in-
situ X-ray photoelectron spectroscopy (XPS) [24-25], whereas in-situ SERS investigation is seldom mentioned in the literature.

In this chapter, the prepared glass-based SERS-active substrates were applied to in-situ investigate the plasma modifications of metals, polymers and carbon nanotubes. The experimental set-up and procedures of modifications were introduced in detail and the effects of various plasma modifications on different surfaces were discussed as well.

6.2 Experimental Details

6.2.1 Sample Preparations

The normal microscope glass slides were cut into 1.8 × 1.8 cm² slices, cleaned ultrasonically in ethanol for 5 minutes and dried in a flowing nitrogen stream. The preparation process of the SERS-active substrates can be found in chapter 3 [26].

Three kinds of samples were prepared and used for different experiments:

(1) For the plasma modifications of thin metal films, the cleaned glass slices were first covered by rough, nanoporous SiO₂-like plasma polymer films and then coated by a 20 nm silver layer deposited by means of PVD. Finally, another 10 nm top copper layer was deposited on silver film in the same PVD chamber;

(2) The second kind of plasma modification was performed on multi-wall carbon nanotubes (CNTs) supplied by Applied Science Inc (Ohio, USA), which have an inner diameter of from 20 to 50 nm and an outer diameter of from 70 to 200 nm. The as-received CNTs were first thermally treated at 800 °C under helium atmosphere for 1 hour to remove all the impurities from the surface. Then the CNTs were ultrasonically dispersed into pure ethanol for 30 minutes. Several droplets of the ethanol solution containing CNTs were dropped on the glass-based SERS-active substrates (with 20 nm silver film) and dried in air. The CNTs adsorbed on the surface of SERS-active substrates were placed into the plasma chamber immediately for the nitrogen-plasma modification.

(3) A glass slice with 10 nm silver film having island-like structure and thin top layer of polystyrene (PS) film was the third kind of samples, which were used to evaluate the modification effects of different plasmas. The thin polystyrene coating (PS, number average molecular weight (Mn) = 2.1 × 10⁶ g·mol⁻¹, polydispersity index (PDI) = 1.15,
Polymer Source Inc, Canada) was obtained by means of dip-coating technique from the PS solution with a concentration of 5 mg/ml (in tetrahydrofuran). The final thickness of PS film is about 20 nm determined by spectroscopic ellipsometry. The schematic representations of all the above-mentioned samples are shown in Fig. 6-1.

![Fig. 6-1: Schematic representations of the prepared samples for the plasma modifications: (a) metal films and carbon nanotubes on glass-based SERS-active substrates; (b) PS film on glass-supported silver islands.](image)

### 6.2.2 Experimental Set-up and Procedures

The schematic representation of the experimental set-up for the in-situ plasma modifications in combination with Raman measurements is shown in Fig. 6-2. The principle is to take advantage of the confocal ability of Raman spectrometer. In this experimental set-up, the laser can focus on the thin metal or polymer film coated on the glass-based SERS-active substrate from its backside because of the transparency of the used glass substrate. The Raman spectra of the samples during the different plasma modification processes can be obtained simultaneously.

The whole system consists of a glass chamber with two wing tubes for gas flow in and out. A rotary vane pump was used to evacuate the plasma chamber. Prior to any processing of
samples, the chamber was evacuated to a base pressure of \(~10^{-3}\) mbar. A commercial high voltage power supply was used to apply an alternating, pulsed and adjustable voltage with a frequency of 30.7 kHz to one of the two electrodes and one of the electrodes was earthed for generating plasma. The sample was placed facing to the plasma zone and fixed on the hatch of the glass chamber by a cover.

The process pressure was adjusted by a down stream by-pass system and controlled by means of a gas independent capacitive pressure gauge (MKS). A mass flow controller (MKS) was used to adjust the overall flow rate by means of a pure argon flow, and the partial pressures of the hydrogen, nitrogen and oxygen were adjusted by needle valves. All the plasma treatments were performed at a pressure of 0.4 mbar. The overall flow rate and the partial pressure used for plasma treatments are listed in the Table 6-1.

The experimental procedures were listed as follows:

1. For the plasma modifications of copper surfaces, the copper film was first treated in a reducing plasma, which was activated by an argon and hydrogen mixture (Ar/H\(_2\) = 1:2) for 2 minutes to at least partially remove its native oxide layer and the contaminants on the surface. Subsequently, the copper surface was exposed to an oxygen plasma for 1, 2 and 3 minutes, respectively. In the final step, the copper sample was exposed to a plasma of argon and hydrogen mixture again to reduce the oxide products.

2. For the plasma modifications of carbon nanotubes, CNTs were exposed to a pure nitrogen plasma (0.4 mbar) for 1, 2 and 4 minutes, respectively.
For the plasma modifications of polystyrene films, the prepared samples were exposed to argon plus hydrogen (Ar/H₂ = 1:2), nitrogen plus hydrogen (N₂/H₂ = 1:3) and pure oxygen plasma for some time until the films were completely removed. A Raman spectrum was recorded after every step of these plasma treatments. The laser was refocused every time before collecting the Raman spectrum because the vibrations from the ambient pump could make the laser defocus in Z direction.

Table 6-1: Flow rate and partial pressures of different plasma modification processes

<table>
<thead>
<tr>
<th>Plasma gas</th>
<th>Overall flow rate and overall pressure (10 sccm, 0.4 mbar)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PAr (mbar)</td>
</tr>
<tr>
<td>(Ar + H₂) plasma</td>
<td>(~1:2)</td>
</tr>
<tr>
<td></td>
<td>0.13</td>
</tr>
<tr>
<td>O₂ plasma</td>
<td></td>
</tr>
<tr>
<td>N₂ plasma</td>
<td></td>
</tr>
<tr>
<td>(N₂ + H₂) plasma</td>
<td>(~1:3)</td>
</tr>
<tr>
<td></td>
<td>-</td>
</tr>
</tbody>
</table>

The 5 × 10⁻⁵ M aqueous BPE solution was used again as a probe molecule to check the confocal ability of Raman spectrometer as done in chapter 3. Glass-based SERS-active substrates were immersed into the BPE solution for 1 hour, rinsed by plenty of deionized water and blown in a dry nitrogen stream. The used objectives of Raman spectrometer for front and backside were 100 X and 10 X, respectively. The spectra acquisition time was 10 seconds for the measurements of BPE adsorption and 100 seconds for the in-situ Raman measurements. The laser power was set at 10 mW in all the in-situ measurements.

The parameters for the field emission scanning electron microscopy (FE-SEM), Raman and UV-Vis spectroscopy measurements are the same as shown in section 3.2.3.

The parameters and the detailed information about the apparatus of XPS spectrometer can be found in section 5.2.2.
6.3 Results and Discussion

6.3.1 Feasibility of the Back-scattering In-situ Raman Measurements

To compare the difference in the SERS spectra collected from the front and backside of the glass-based SERS-active substrate, the corresponding SERS spectra of the adsorbed BPE molecules on glass-based SERS-active substrate are shown in Fig. 6-3.

![Fig. 6-3: SERS spectra of BPE molecules adsorbed on glass-based SERS-active substrate measured from front and backside.](image)

It is obvious that the Raman spectra of the adsorbed BPE from front and backside are similar except for the Raman intensity. The Raman intensity from backside decayed to about half of that from front side. This can be attributed to the attenuated laser power by the transparent glass slide and the defocused laser beam because of the rough SiO₂-like interlayer film between silver film and the glass substrate. However, the result proved that the design of the back-scattering geometry of the SERS-active substrate worked well and it could be used in the following plasma modifications in combination with the in-situ plasma reaction chamber.

6.3.2 Plasma Modifications of Thin Cu Films on SERS substrates

6.3.2.1 Optical Properties of Thin Cu Films before and after Plasma Modifications

To investigate the change in the optical properties of the thin copper film during the plasma modifications, UV-Vis spectra of a copper film deposited on a glass-based SERS-active
substrate before and after plasma modifications in comparison to that of a glass-based SERS-active substrate are shown in Fig. 6-4.

![UV-Vis spectra of different samples](image)

*Fig. 6-4: UV-Vis spectra of different samples: (a) 10 nm copper film deposited on glass-based SERS-active substrate; (b) (a) modified with a plasma cycle ((Ar + H₂) plasma – O₂ plasma – (Ar + H₂) plasma) mentioned in section 6.2.2; (c) a glass-based SERS-active substrate.*

The as-prepared glass-based SERS-active substrate shows a typical surface plasmon resonance (SPR) peak of silver at 390 nm (see Fig. 6-4 (c)). According to the literature [27-31] the absorption band with $\lambda > 350$ nm is associated with the surface plasma resonance of silver particles in the size range larger than 10 nm, which can be proved by our SEM images (see Fig. 6-5). When another 10 nm copper layer covered on top of the glass-based SERS-active substrate, two broad SPR peaks appeared (see Fig. 6-4 (a)). One of them is in the wavelength range from 320 to 550 nm, which is very likely from silver in the SERS-substrate considering the more pronounced surface plasmon resonances of silver. However, it became broad compared to the SPR peak of silver in SERS-substrate (Fig. 6-4 (c)). The other one is located between 560 and 680 nm and centered at ~600 nm, which could be attributed to the SPR peak of copper nanoparticles [31-32]. The contributions from some copper oxide products formed under the ambient condition could not be excluded, because the SPR peak induced by d-d electron transitions of Cu$^{2+}$ in distorted octahedral surrounding by oxygen in CuO particles is also in this wavelength range [32-34].

The broad SPR peak between 560 and 680 nm disappeared after the copper film supported
by the glass-based SERS-active substrate was exposed to the mentioned plasma treatments cycle ((Ar + H₂) plasma– O₂ plasma– (Ar + H₂) plasma). It may be due to the reduction of the copper oxide products in the strong reductive reaction atmosphere. The SPR peak located at 422 nm mainly induced by the silver film had a big red-shift (see Fig. 6-4 (b)), which could result from the morphological change of the silver surface during the plasma modifications. It will be discussed in the following section in detail.

6.3.2.2 Morphological Change of Thin Cu Films before and after Plasma Modifications

FE-SEM was used to reveal the surface morphology of copper films supported by glass-based SERS-active substrates before and after cyclic plasma modifications. As shown in Fig. 6-5 (a), the prepared SERS-active substrate presents a defect-rich surface, which mainly inherited the rough features of the nanoporous SiO₂-like plasma polymer film on glass substrates. As discussed in chapter 3, silver layer formed an island-like structure at a lower thickness and followed the fluctuation of the rough SiO₂-like plasma polymer film. The silver particles on the surface of SERS-active substrates show different appearances, such as single particle, aggregated clusters, cracks and crevices. Furthermore, the morphology of the as-prepared SERS-active substrate didn’t change much when another thin Cu layer of 10 nm was deposited on top. The thin Cu film just followed the morphology of the SERS-active substrate (see Fig. 6-5 (b)). Fig. 6-5 (c) shows that the morphology of the thin copper film on SERS-active substrate changed a lot after the cyclic plasma modifications. Some deep cracks, bigger clusters are present on the surface and the surface seems smoother compared to that before plasma modifications. The original defects of the copper film on SERS-active substrates diminished significantly. It is obvious that the cyclic plasma modifications had a very strong surface modification effect on the copper top layers.

As well known, the SPR peaks are very sensitive to the shape, size of the nanoparticles and the interparticle distance. It is also reported that the SPR peaks red shifted when the size of metal particles increased [35-36]. Therefore, the FE-SEM results explained very well why the SPR peak of (Ag + Cu) layer in the UV-Vis spectra in Fig. 6-4 red shifted after the plasma modifications.
Considering the obvious morphological change of the thin copper film on SERS-active substrates during the plasma modifications, the evolution of the copper-covered silver nanoparticles during the plasma modification processes should be clarified. We assume that the disappearance of the small metal particles resulted from the atomic diffusion of metal (silver and copper) along the plasma polymer surface, which is described as Oswald ripening. Oswald ripening (also referred as Oswald coarsening) is a process, in which smaller particles are essentially consumed by larger particles during the growth process as a consequence of the smaller particles have higher surface energies [37-39].

In the process of plasma modifications the charged ions and electrons produced by plasma bombarded on the metal surface and transferred the charges and energy to the metal atoms simultaneously. It led to the increased mobility of the silver or copper atoms on the surface of the samples. Therefore, Ostwald ripening process was accelerated, i.e. the smaller particles dissolved and the size of some larger particles increased as shown in Fig. 6-5 (c).

Fig. 6-5: FE-SEM images of different samples: (a) a SERS-active substrate; (b) 10 nm copper film on SERS-active substrate; (c) (b) modified by a cyclic plasma treatments ((Ar + H2) plasma – O2 plasma – (Ar + H2) plasma, see the details in section 6.2.2).
6.3.2.3 In-situ Raman spectra of Thin Cu Films in the Process of Plasma Modifications

Surface-enhanced Raman spectroscopy has been successfully applied to some in-situ experiments, such as monitoring the adsorption/desorption of molecules dependent on the applied potential on electrode surface [40-42]. In our case study, in-situ SERS was applied to monitor the modification effects of different plasmas on thin copper film. The SERS spectra of the thin copper layer modified with different plasmas are displayed in Fig. 6-6.

For the as-prepared copper film on glass-based SERS-active substrate, some inevitable contaminations from the laboratory environment can be observed, as is characterized by a Raman peak at 2915 cm\(^{-1}\), which can be assigned to the (-CH\(_2\)) groups due to the ambient contaminations (see Fig. 6-6 (b) curve 1)). The peak at 1596 cm\(^{-1}\) can be assigned to the carbon-relevant contaminant in the process of PVD deposition or the organic molecules [43-45]. The glass substrate was characterized by three Raman peaks at 560, 786 and 1093 cm\(^{-1}\), which correspond to the deformation modes of the decoupled SiO\(_4\) tetrahedra, symmetric vibrations of Si-O-Si and tectosilicates [46]. As can be seen, these three Raman peaks stayed invariable during the whole plasma modification processes.

![Fig. 6-6: In-situ SER spectra of a thin copper film exposed to cyclic plasma modifications: curve1: prepared sample; curve 2: with 2 minutes (Ar + H\(_2\)) plasma; curve 3 - 5: with further 1, 2 and 4 minutes O\(_2\) plasma; curve 6: with another 2 minutes (Ar + H\(_2\)) plasma. (The spectra were vertically shifted for clarity).](image)

After the sample was treated in (Ar + H\(_2\)) plasma for 2 minutes, the contaminant on the surface were removed which can be indicated by the disappearance of the Raman peak at
2915 cm\(^{-1}\) (see Fig. 6-6 (b) curve 2). The remove of the contaminations were attributed to the strong cleaning effect of (Ar + H\(_2\)) plasma. Two kinds of cleaning effects could have happened during this plasma modification process as described in literature [4]. One is the physical modification from the bombardment of the inert argon plasma and the other one is the chemical reaction between reductive H\(_2\) plasma and the contaminantants on the sample surface. In our case study, the physical cleaning effect was relative weak because the kinetic energy of the Ar\(^+\) was low at such a low pressure. The main cleaning effect may come from the chemical cleaning effect of the hydrogen plasma. The mechanism behind hydrogen plasma cleaning is that the active hydrogen atoms produced in the plasma will react with the materials placed in the plasma to form the volatile hydride compounds [10-11]. As can be seen from the Raman spectrum in Fig. 6-6 (b) curve 2, some contaminants from the lab atmosphere was eliminated from the surface, but the carbon-relevant contaminants characterized at 1596 cm\(^{-1}\) were not removed in this step. A surface occupied by a number of active hydrogen atoms could also be achieved, so that it is easier for the sample to react with the active species produced in the following oxygen plasma modification processes.

Two processes occurred simultaneously in oxygen-plasma modifications: one is the etching of the contaminations through reactions between atomic oxygen and carbon atoms on the metal surface, giving volatile reaction products; the other one is a formation of oxygen functional groups on the metal surface through reactions between some active species from the oxygen plasma and the surface atoms [4]. As can be seen in Fig. 6-6 (b) curve 3, it is noticed that the peak at 1596 cm\(^{-1}\) from the carbon-relevant contaminants totally vanished after the sample was treated in the oxygen plasma. It is mainly due to the etching effect of the oxygen plasma. The formation of oxygen functional groups can be indicated by the increasing intensity of a Raman peaks at 810 cm\(^{-1}\) after the sample was treated with the O\(_2\) plasma for 1 minute. This new Raman peak can be assigned to the bending modes or a vibration combined Cu-OH and Ag-OH [32-34, 47-48]. The possible sources of (-OH) groups could be from the reactions between the active hydrogen atoms produced in the mixture of (Ar + H\(_2\)) plasma and the active oxygen atoms generated by the O\(_2\) plasma; or from the (-OH) groups produced by H\(_2\)O plasma, which could be from the trace H\(_2\)O mixed in the reaction O\(_2\) gas flow or the H\(_2\)O adsorbed on the walls of the plasma chamber and on the sample surface [49].
When the copper sample was treated further by the oxygen plasma, the Raman intensity of the peak at 810 cm\(^{-1}\) increased with the increasing plasma treatment time (see Fig. 6-6 (a) curve 3, 4 and 5). As well known, Raman intensity is directly proportional to the number of scattering centers present in the volume illuminated by the laser beam. Thus, it can be concluded that more Cu-OH (or Ag-OH) products were gained with longer oxygen-plasma treatment time. After the sample was treated in O\(_2\) plasma for 3 minutes, the Raman intensity of (Cu-OH) (or combination of Cu-OH and Ag-OH) didn’t change any more even with further oxygen-plasma treatment. It may give some hints that the active hydrogen atoms were totally consumed after the oxygen-plasma treatment for 3 minutes or the whole thin mixed metal layer was completely converted into the metal hydroxyl products.

The sample recovered to the original status again when it was modified in the following (Ar + H\(_2\)) plasma for additional 2 minutes. The Raman intensity of the peak at 810 cm\(^{-1}\) decreased to the similar level as that before any oxygen-plasma treatment (see Fig. 6-6 (a) curve 6), which is due to the reduction of the metal hydroxide layer achieved by the hydrogen plasma via the reactions between the hydrogen radicals and the metal hydroxide. The following reactions could have occurred: Ag-OH + H\(^{\bullet}\) \(\rightarrow\) Ag + H\(_2\)O or Cu-OH + H\(^{\bullet}\) \(\rightarrow\) Cu + H\(_2\)O \[12\], so that the products of (M-OH) were totally reduced by the (Ar + H\(_2\)) plasma.

### 6.3.3 Plasma Modifications of Carbon Nanotubes Supported by SERS-active Substrates

Carbon nanotubes (CNTs) have attracted considerable attention because of their extraordinary properties such as high strength and flexibility, high thermal and electrical conductivity, low density as well as high surface area. Moreover, the surface modifications of CNTs are very important issues to introduce more exciting properties to CNTs, for example, to introduce more defects on the surface of CNTs, which is very important in catalyst industry \[50-52\].

In this section, the carbon nanotubes exposed to the nitrogen plasma was in-situ investigated by our experimental set-up. Fig. 6-7 shows the in-situ SERS spectra of carbon nanotubes before and after nitrogen plasma treatments.
Chapter 6: In-situ SERS Study of Plasma Surface Modification Effects

For the as-received carbon nanotubes on SERS-active substrate, two Raman peaks at 1569 and 1373 cm$^{-1}$ are clearly shown, which can be assigned to G-band and D-band of carbon nanotubes (see Fig. 6-7 (1)) [53-55]. In detail, the peaks at 1569 and 1373 cm$^{-1}$ are attributed to the Raman-active E$_{2g}$ in-plane vibration mode and the Raman-inactive A$_{1g}$ in-plane breathing vibration mode, named G (graphite) and D (disorder)-bands, respectively. G band is the characteristics of graphitic phase which indicates the presence of crystalline graphitic carbon in CNTs. The G-band at 1569 cm$^{-1}$ corresponding to the graphitic carbon is very broad, indicating that some carbon in the tube walls is disordered and the CNTs contain some amorphous carbon. The origin of D band has been attributed to the disordering-induced features such as defects generated in the graphitic planes of CNTs due to curvature and presence of amorphous carbon as well as small domain size effect [55]. The intensity ratio of these two bands (I$_D$/I$_G$) is considered as a parameter to characterize the quality of CNTs. Higher intensity ratio means higher degree of disordering in CNTs. As shown in Fig. 6-7, intensity ratio of (I$_D$/I$_G$) changed from the initial value of 0.6 for the as-received CNTs to 0.94 after treated in nitrogen plasma for 4 minutes. That indicates that more defects were introduced in the carbon nanotubes during the process of nitrogen plasma modification.

![Raman Spectra](image)

Fig. 6-7: SERS spectra of carbon nanotubes before and after nitrogen-plasma treatments: (1) as-received carbon nanotubes supported by SERS-substrate; (2)-(3) modified by nitrogen plasma for 2 and 4 minutes, respectively.

In addition, XPS measurements were performed to understand the modification effect of N$_2$ plasma on CNTs in more detail. Fig. 6-8 shows C 1s, N 1s and O 1s photoelectron spectra from the CNTs with nitrogen plasma modification and the assignations of XPS peaks are
listed in Table 6-2 according to the data reported in the literature [56-60]. XPS results indicate the presence of nitrogen function groups on the surface of CNTs.

In the C 1s spectrum, five peak components are resolved. The peak centered at around 284.5 eV is corresponding to C–C bonds, as expected from the graphitic structure or amorphous carbon in the CNTs. The peaks at 285.7 and 286.9 eV can be associated to C-OH, C-O-C and/or C=N sp² species. Since the presence of C=O and/or O-C=O functional groups usually appear at higher binding energy, the peaks at 287.9 and 289.2 eV could be assigned to these groups [56-58]. The exact position and intensity of those peaks, however, are somewhat uncertain, because they depend very much on the exact background fitting [56]. The N 1s spectra of the same samples exhibit more pronounced spectral features as shown in Fig. 6-8 (c) and Table 6-2. Four peak components can clearly be observed for the spectrum, which are at 398.4, 400.2, 405.0 and 407.2 eV, respectively. The peak at 400.2
eV can be attributed to a type of species named N-5 (see Table 6-2) from pyrrolic, pyridones or nitroso (–NO) groups [57-58]. Other peaks with binding energy higher than 405 eV can be attributed to oxidized species of nitrogen (i.e., nitrite and nitrate) and the O 1s spectra also proved this point. Besides the already mentioned band attributed to the N-5 species, it is possible to observe one species named N-6 that is typically attributed to pyridine groups of nitrogen (see Table 6-2) [57-58]. Moreover, the XPS results also showed the concentration of nitrogen increased from 0.20 to 0.33 after the nitrogen plasma modification, which confirmed the nitrogen-containing groups were introduced to the surface of CNTs by the N$_2$ plasma.

**Table 6-2:** XPS peaks assignations detected on CNTs surface after N$_2$ plasma treatments [56-58]

<table>
<thead>
<tr>
<th>Zones</th>
<th>BE (eV)</th>
<th>Assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>284.5</td>
<td>C-C in CNT</td>
</tr>
<tr>
<td></td>
<td>285.7</td>
<td>C-O</td>
</tr>
<tr>
<td>C 1s species</td>
<td>286.9</td>
<td>C=N or C-N</td>
</tr>
<tr>
<td></td>
<td>287.9</td>
<td>C=O</td>
</tr>
<tr>
<td></td>
<td>289.2</td>
<td>O=C=O</td>
</tr>
<tr>
<td></td>
<td>398.4</td>
<td>N-6</td>
</tr>
<tr>
<td>N 1s species</td>
<td>400.2</td>
<td>N-5</td>
</tr>
<tr>
<td></td>
<td>405.0</td>
<td>-NO$_2$</td>
</tr>
<tr>
<td></td>
<td>407.2</td>
<td>-NO$_3$</td>
</tr>
<tr>
<td>O 1s</td>
<td>531.2</td>
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<tr>
<td></td>
<td>533.6</td>
<td>nitrates</td>
</tr>
</tbody>
</table>

### 6.3.4 Plasma Modifications of Thin Polystyrene Films

In this experiment, three kinds of plasmas were used to modify thin polystyrene (PS) films coated on the glass-supported island-like silver films. The used plasmas include oxygen plasma, argon plus hydrogen mixture plasma and nitrogen plus hydrogen mixture plasma. The aim of these experiments is to monitor the products of different plasma treatments by means of in-situ SERS technique. As mentioned in previous section 6.3.2.3, physical and chemical modifications were supposed to occur during the plasma modification processes.
and Raman spectroscopy was used to in-situ investigate those corresponding effects. The physical effect is principally the plasma etching effect, which can be realized by almost all used plasmas. The chemical effects involve the introduction of new functional groups, such as C-O, C=O, O-C=O and CO$_3$ related to the O$_2$ plasma, C-N, C=N and C≡N produced by the nitrogen plus hydrogen mixed plasma [4].

All of the obtained Raman spectra of thin PS films before and after different plasma treatments are shown from Fig. 6-8 to Fig. 6-10 and the assignments of the characteristic Raman peaks in original polystyrene are listed in Table 6-3 [61].

**Table 6-3**: Assignments of the characteristic Raman peaks in polystyrene [61]

<table>
<thead>
<tr>
<th>Peak position (cm$^{-1}$)</th>
<th>Assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td>1004</td>
<td>Ring breathing</td>
</tr>
<tr>
<td>1032</td>
<td>In-plane CH deformation</td>
</tr>
<tr>
<td>1205</td>
<td>C$_6$H$_5$-C vibration</td>
</tr>
<tr>
<td>1310</td>
<td>CH$_2$ in-phase twist</td>
</tr>
<tr>
<td>1352</td>
<td>CH deformation</td>
</tr>
<tr>
<td>1410</td>
<td>Ring stretch</td>
</tr>
<tr>
<td>1452</td>
<td>CH$_2$ deformation</td>
</tr>
<tr>
<td>1527</td>
<td>Ring stretches</td>
</tr>
<tr>
<td>1604</td>
<td>Ring stretches</td>
</tr>
<tr>
<td>2915</td>
<td>Anti-symmetric CH$_2$ stretch</td>
</tr>
<tr>
<td>3060</td>
<td>Aromatic CH stretch</td>
</tr>
</tbody>
</table>

The results of Raman measurements after the different plasma treatments are summarized and listed in the following:

(1) In the case of oxygen-plasma treatment, all the characteristic Raman peaks of PS film stayed present in the spectra during the O$_2$ plasma treatments except the increasing peak intensity at 1574 cm$^{-1}$, which is related to the resultant carbon products during the plasma modification processes (see Fig. 6-8) [54-55]. The dominating peak at 1574 cm$^{-1}$ could also cover some new functional groups produced by O$_2$ plasma in the same wavenumber range. The products should be identified in detail by some other additional techniques, for example, XPS. The Raman spectrum showed only the characteristic peak of glass substrate
at (~1100 cm\(^{-1}\)) after the PS film was treated in O\(_2\) plasma for 15 seconds, indicating the complete removal of the PS film.

Fig. 6-8: In–situ Raman spectra of PS film modified by O\(_2\) plasma.

Fig. 6-9: In–situ Raman spectra of PS film modified by (Ar + H\(_2\)) plasma.

Fig. 6-10: In–situ Raman spectra of PS film modified by (N\(_2\) + H\(_2\)) plasma.
The reaction mechanisms of oxygen plasma were postulated as four stages: [62-63]:

Stage 1: Surface is bombarded by photons, electrons, ions, atoms and excited species, and the free-radical sites will be created in this stage;

Stage 2: The molecular oxygen will react with the free-radical sites on the polymer and lead to peroxides, alkoxy, and OH radicals;

Stage 3: The polymer chain will be cleaved, which leads to loss of the primary volatile species;

Stage 4: Gas-phase reactions of the primary volatile products will happen in the plasma.

All the above mentioned steps can be described by the following reactions:

(a) Abstraction:

\[ -C - C + O \rightarrow -\dot{C} - C + \dot{O} H \] \hspace{1cm} (6-1)

\[ -C = C + O \rightarrow -\dot{C} = C + \dot{O} H \] \hspace{1cm} (6-2)

\[ RH + \dot{O} H \rightarrow \dot{R} + H_2O \] \hspace{1cm} (6-3)

\[ RH + O : \rightarrow \dot{R} + \dot{R}^*O^* \] \hspace{1cm} (6-4)

(b) Addition to unsaturated moieties:

\[ -C = C + O : \rightarrow -\dot{C} = C - O^* \] \hspace{1cm} (6-5)

(c) Absorption of the O_2 dissociation energy:

\[ RH + 2O \rightarrow R^* + H^* + O_2 \] \hspace{1cm} (6-6)

In our case study, the abstraction reaction is supposed to be predominant in the process of oxygen plasma. The primary reaction should proceed readily at the tertiary C-H bond in polystyrene. The O_2 plasma first abstracted the hydrogen atoms from PS chains in the PS film and left the carbon backbone. With further oxygen-plasma modification, more hydrogen atoms were selectively removed and more carbon backbone remained, which could be corresponding to the increasing Raman intensity of peak at 1574 cm\(^{-1}\) (see the Raman spectra of PS with 10 seconds O_2 plasma in Fig. 6-8).

However, the increased Raman intensity at 1574 cm\(^{-1}\) could also be from the contribution of created phenol products in the PS film during process of O_2 plasma modification. It should be noted that the hydrogen atoms in the ring were not removed in this process, because the ring breathing mode (1004 cm\(^{-1}\)) and the aromatic CH stretch (3060 cm\(^{-1}\)) could still be
detected in the Raman spectra. Moss et al. [63-64] found that the aromatic polymers were more resistant to plasma oxidations and they thought the formation of phenol products contributed to this resistance. They postulated that the hydroxyl radicals and oxygen atoms in ground-state formed in the plasma will add to the aromatic ring rather than abstract a hydrogen atom during plasma oxidation of a polymer. In the presence of oxygen, the free-radical adduct will produce phenols and undergo some oxidative cleavage of the ring.

According to their postulations, when all the hydrogen atoms in the organic film were removed, the O₂ plasma reacted with the residual carbon atoms and components in the PS film to form the volatile products, which were evaluated finally. The final Raman spectrum only showed the characteristic Raman peak from the glass substrate. Although Raman is sensitive to the aromatic compounds and the information from the ring breathing and aromatic CH stretch can be detected in our spectra, the formation of phenol need to be confirmed by additional analysis tools further.

(2) The effect of (Ar + H₂) plasma was mainly physical etching effect and no new functional groups were observed during the whole plasma modification processes. The hydrogen abstraction could also have occurred in this process, which could be concluded from the increased Raman intensity at 1534 cm⁻¹ with increasing treatment time of (Ar + H₂) plasma. However, the ability to abstract hydrogen of (Ar + H₂) plasma is not as strong as that of O₂ plasma. The PS film was etched away after (Ar + H₂) plasma treatment for 225 seconds (see Fig. 6-9), whereas it is etched away in O₂ plasma for 15 seconds.

(3) The behavior of plasma mixture of nitrogen and hydrogen was supposed to be similar to an ammonia plasma, in which NH₂ radicals are considered as the reactive species and the important intermediary agent for the functionalization [65]. In our case, the most prominent Raman peak observed at about 1530 cm⁻¹ broadened and the peak intensity increased with the increasing plasma modification time of (N₂ + H₂) plasma (see Fig. 6-10). It could be assigned to the possible contributions from C=N functional groups in the substituted benzene ring or C≡C out-of phase stretching in benzene ring in the PS film. At the same time, the weak vibration of hydrogen-bonded N-H groups at 3450-3250 cm⁻¹ and the C≡N stretching vibration at 2260-2200 cm⁻¹ were not observed [21, 66]. The introduction of new functional groups should be interpreted by the additional information in the future. The hydrogenated amorphous carbon could be another possibility contributing to the broad peak...
at 1530 cm$^{-1}$ [67-68]. The Raman peak at 1530 cm$^{-1}$ of PS with 115 s (N$_2$ + H$_2$) plasma was fitted by the original software as shown in Fig. 6-11. Two Gaussian bands at 1356 and 1547 cm$^{-1}$ can be observed and attributed to the D and G band of hydrogenated amorphous carbon, respectively. In addition, the PS film was not etched away yet even after treated in (N$_2$ + H$_2$) plasma for 155 seconds.

Fig. 6-11: Fitted Raman peaks of PS film treated with 115 s (N$_2$ + H$_2$) plasma (from 1100 to 2000 cm$^{-1}$).

(4) From the above discussion it can be concluded that the etching effects of the three plasmas on PS films are significantly different. It is obvious that the etching rate of O$_2$ plasma is much faster than the other two plasmas. As can be simply calculated, the average etching rates are 1.3 nm/s for O$_2$ plasma, ~0.1 nm/s for (Ar + H$_2$) plasma and < 0.1 nm for (N$_2$ + H$_2$) plasma, respectively.

6.4 Conclusions

In the present work, SERS was successfully applied to in-situ characterize and monitor the processes of different plasma modifications preformed on the thin copper films, carbon nanotubes and thin polystyrene films supported by glass-based SERS-active substrates.

The thin copper film was exposed to a complete reaction cycle of plasma treatments from reduction to oxidation and again to reduction. The whole process was successfully investigated by surface-enhanced Raman spectroscopy. Surface contaminants were removed in the (Ar + H$_2$) plasma and metal hydroxides were formed in the following O$_2$
plasma. After the (Ar + H₂) plasma was introduced again, the copper film with metal hydroxide layer was reduced to its initial chemical composition. UV-Vis spectra showed the optical properties of the copper sample changed significantly after the plasma modifications, which can be attributed to the changed morphology induced by plasma modifications. FE-SEM images of the copper films before and after plasma modifications confirmed this point. The small metal particles grew into bigger ones and the copper surface became smoother than that before plasma treatments, which can be explained with Oswald ripening effect.

Following the described procedures and using the back-scattering geometry for the in-situ plasma chamber, the modifications of a number of surfaces by different plasmas could be in-situ investigated and characterized. In-situ investigation of carbon nanotubes exposed to nitrogen plasma was a successful example.

The modification effects of different plasmas on the thin polystyrene films were investigated and the Raman spectra were qualitatively interpreted by the reaction mechanisms postulated in the literature. The primary effect of O₂ plasma is hydrogen abstraction and the effect of (Ar + H₂) mixture plasma is mainly physical etching. Moreover, (N₂ + H₂) plasma can induce physical etching and introduce new nitrogen-containing functional groups, but detailed information by other characterization tools should be complemented in the future to confirm the proposed reactions further.

6.5 References


Chapter 7: In-situ Monitoring of the Organic Molecule Adsorption Combining SERS and QCM

7.1 Introduction

One of the main advantages of surface-enhanced Raman spectroscopy (SERS) is that it can be easily combined with many other techniques. For example, SERS has been applied to in-situ investigate the molecule adsorption/desorption dependent on electrode potential in electrochemistry research [1-3]. A hot topic named as tip-enhanced Raman spectroscopy (TERS) is a combination of SERS and atomic force microscope (AFM) or scanning tunneling microscope [4-5]. SERS can also be combined with scanning electron microscope (SEM) [6], transmission electron microscope [7] and quartz crystal microbalance (QCM), which will be introduced in this chapter.

QCM is very sensitive to mass changes as small as a few of ng/cm², thus it can provide accurate information at the initial stage of the adsorption process. Recently, QCM has been used to in-situ study the formation of self-assembly monolayers [8-9]. SERS and QCM have often been used to investigate the molecular adsorption processes, but these two sensitive techniques are usually applied as individual ones. In other words, these two sensitive techniques have not been combined to acquire Raman spectra and QCM data simultaneously in a single experimental process [8-11].

In this chapter, the adsorption process of 2-mercaptobenzothiazole (MBT) was in-situ investigated by combining SERS and QCM techniques. The experimental set-up and procedures are introduced in detail. The kinetics of the adsorption process and the structural information of the organic molecules were acquired simultaneously with our experimental set-up. Thin silver or gold layer was deposited on quartz crystals coated by rough SiO₂-like HMDS plasma polymer films and the whole system (Ag/SiO₂/quartz crystal or Au/SiO₂/quartz crystal) was used as the SERS-active substrate in this case study. Our principal aim was to achieve a fundamental understanding of the organic molecule adsorption on silver or gold. The results will give some hints for the future investigations of the interactions between organic molecules and other metals widely applied in industry.
7.2 Experimental Details

7.2.1 Materials and Preparation of Samples

The used quartz crystals for QCM measurements are planar AT-cut quartz crystals with a resonance frequency of 5 MHz (P/N 149273-1, 25 °C, Maxtek, Inc., USA). The quartz crystals were first polished and coated with Cr (3 nm) and Au (250 nm) layers. The collection of data was performed with the RQCM instrument from the same company.

2-mercaptobenzothiazole (MBT) has various and widespread industrial uses. It is well known to be an effective corrosion inhibitor and is recommended for the protection of lead, copper and its alloys [12]. MBT has a pKa of 6.93 at 20 °C and hence is present in acid media as the unionized protonated form (HMBT), which could adopt either thiol or thione structure. In basic media, MBT molecule is in the form of thiol ion (MBT\(^{-}\)). All the three configurations are shown in Fig 7-1 [13]. In this experiment, MBT powder (> 99%, Merck, Germany) was used as received without further purification. The MBT powder was dissolved in absolute pure ethanol (for analysis, 99%, Merck, Germany) and the concentrations from \(10^{-3}\) to \(10^{-5}\) M were used for different experiments.

![Fig. 7-1: Different configurations of 2-mercaptobenzothiazole in acid media in the form of: (a) thiol and (b) thione; in basic media (c) thiol ion (MBT\(^{-}\)), respectively [13].](image)

Quartz crystals were cleaned ultrasonically in ethanol for 10 minutes before they were introduced into the microwave plasma chamber. The parameters and the procedures for depositing the rough SiO\(_2\)-like plasma polymer films were described in section 3.2. For different purposes, 100 nm silver or 100 nm gold was deposited on the quartz crystals coated with rough SiO\(_2\)-like plasma polymer films by means of PVD.
For ex-situ experiments, the quartz–based SERS-active substrates were immersed into the freshly prepared MBT solution ($10^{-3}$ M) for 24 hours. The samples were rinsed with plenty of ethanol to remove the physically adsorbed MBT molecules and measured with Raman spectrometer immediately afterwards.

For infrared reflection adsorption spectroscopy (IRRAS) measurements, the smooth Si-wafers coated with 100 nm silver layer were immersed into the $10^{-5}$ M MBT solution for 1, 2, 4, 8, 16, 32, 64, 128 and 240 minutes, respectively. The samples were rinsed with a great amount of absolute ethanol and dried in a nitrogen stream before introduced into the IR spectrometer.

### 7.2.2 Surface Characterization and Analysis

The parameters and the information about the apparatus for the AFM, SEM and UV-Vis spectroscopy measurements are the same as shown in section 3.2.3. The FT-IRRAS measurements were performed on the MBT molecules adsorbed on 100 nm silver-covered Si-wafers using a Nicolet 870 spectrometer and the parameters for the XPS measurement are the same as described in section 5.2.2.

Surface-enhanced Raman spectroscopy measurements were performed using a modular system (Dilor LabRAM, ISA Instruments. SA, INC, France) and the excitation sources are Ar$^+$ green laser (514.5 nm) and He-Ne red laser (632.8 nm). For ex-situ Raman measurements, the laser power was set at 2 mW to avoid the possible decomposition of AgMBT complex [13], whereas for in-situ Raman measurements, the laser power was set at 10 mW and kept constant during the experiment process to achieve a good S/N ratio. The wavenumber range of Raman measurements was from 300 to 1700 cm$^{-1}$ and the spectra acquisition time was 10 seconds. For the gold substrates, He-Ne laser was used as excitation source because of the strong fluorescence induced by Ar$^+$ laser.

### 7.2.3 In–situ Experimental Set-up Combining SERS and QCM

The whole in-situ experimental set-up is presented in Fig. 7-2. In brief, the solution containing MBT molecules was pumped into the cell (the volume is 0.1 ml) and the molecules adsorbed on the Ag (or Au) layer deposited on the quartz crystals. SERS spectra and QCM data of the molecular adsorption process were collected simultaneously right from the beginning of the adsorption process.
Absolute pure ethanol was first pumped into the cell and the laser was focused on the surface of quartz-based SERS-active substrate through the glass window. The whole system was kept running about 30 minutes to wait for the system to be stable before the MBT solution was introduced into the cell. $10^{-3}$ M MBT solution was added into pure ethanol and the final concentration was adjusted to $10^{-4}$ M. To accelerate the diffusion of MBT solution and keep the solution homogeneous, a magnetic stir was used during the experiment. The flow rate of MBT solution was set as 1 ml/min and controlled by software. Raman spectra were collected immediately after the introduction of MBT solution.

![Fig. 7-2: Schematic representation of the in-situ experiment set-up combining SERS and QCM [I. Klueppel, G. G. Sun, G. Grundmeier, to be submitted].](image)

In the liquid-phase experiments, the QCM data should be carefully interpreted because it includes the effect of fluid on the piezoelectric movement of quartz crystals. When the quartz crystal is in contact with liquid phase, the oscillation is usually damped and results in a decreased resonance frequency [9]. Such a frequency change could be ignored in our case study, because both the initial and final states are under nearly identical conditions with respect to the density, viscosity, and temperature of the solution phase.

### 7.3 Results and Discussion

#### 7.3.1 Topography of the Quartz Crystal-based SERS-active Substrates

Surface-enhanced Raman spectroscopy is very sensitive to the surface conditions of the samples, such as the shape and size of particles, the interparticle distances. Thus, it is very important to know the information about the topography of the prepared surfaces. AFM and
FE-SEM were applied to characterize the surface structure of the quartz crystal-based SERS-active substrates. The corresponding results are shown in Fig. 7-3.

![AFM images of different surfaces: (a) quartz crystal coated with a nanoporous SiO$_2$-like plasma polymer film; (b) (a) coated with a 100 nm silver film.](image)

As shown in Fig. 7-3 (a), the surface of quartz crystal coated with a SiO$_2$-like plasma polymer film is similar to that of the Si-supported SiO$_2$-like plasma polymer film. A very rough (RMS > 20 nm), defect-rich surface was achieved in the deposition process of HMDS plasma polymer film, even when the supporting substrate was exchanged into quartz crystals. It confirmed that the process described in chapter 3 for preparing SERS-active substrates is versatile and flexible again. After a 100 nm silver layer was deposited on the quartz crystal coated with a rough SiO$_2$-like plasma polymer film, it inherited the fluctuant characters from the under layer, thus a very rough silver surface was produced to enable the SERS enhancement effect (see Fig. 7-3 (b)). The size distribution of silver particles is very broad, which is from 100 to 250 nm, even up to 500 nm for some aggregated silver particles.

The FE-SEM images show that the obtained surfaces of quartz crystal-based SERS-active substrates are similar to those of Si-based SERS-active substrates (not shown here, refer to Fig. 3-6 in chapter 3). It is expected that the obtained surface with rich defects is also easy to produce SERS effect according to the literature [14-17].

### 7.3.2 Ex-situ SERS Spectra of MBT Molecules Adsorbed on Ag

The enhancement effect of the SERS-active substrates prepared by the described processes in chapter 3 has been proved in the previous chapters. Fig. 7-4 presents the ex-situ Raman
spectra of $10^{-3}$ M MBT solution adsorbed on the quartz crystal-based SERS-active substrates (spectrum a) and normal Raman spectra of MBT powder (spectrum b). It has to be mentioned that no Raman peaks of MBT dissolved in ethanol adsorbed on normal substrates can be identified at such a low concentration except the Raman peaks from absolute ethanol (data is not shown here). Therefore, the Raman spectra of MBT adsorbed from a dilute solution on the quartz crystal-based SERS-active substrate in Fig. 7-4 must be enhanced.

The Raman peaks of the basic elemental groups in MBT molecule can be detected and assigned in Table 7-1 according to the data in the literature [13, 18-23]. All the peaks were broadened and shifted because of the chemisorption, which is due to the presence of additional states at Fermi energy resulting from bonding and the presence of additional relaxation channels [24]. A remarkable difference between two spectra in Fig. 7-4 (1) is that the moderate intense peak at 1425 cm$^{-1}$ assigned as NCS ring stretching in normal Raman spectrum (Fig.7-4-1 (b)) red shifted to 1395 cm$^{-1}$ and became the dominating peak in SERS spectrum (Fig.7-4-1 (a)). The dominating peak at 1254 cm$^{-1}$ assigned to CH bending or CN stretching in normal Raman spectrum became a moderate intensity peak and also red shifted to 1246 cm$^{-1}$ in SERS spectrum.

The molecular adsorption mechanisms of an adsorbate or the molecule structure information can be deduced from its SERS spectrum through a detailed analysis of the peak shift and peak broadening caused by the surface adsorption. On this basis it is worth to note that the peak positions as well as the bandwidths of the vibrational modes of MBT
adsorbate at 2645, 1498, 1395, 1273, 1254, 1076, 1031 cm\(^{-1}\) in spectrum (a) are barely the same as those in spectrum (b) in Fig. 7-4.

**Table 7-1**: Assignments of the Raman peaks of MBT powder and MBT adsorbed on quartz crystal-based SERS-active substrates [13, 18-23]

<table>
<thead>
<tr>
<th>Peak position (cm(^{-1}))</th>
<th>Raman</th>
<th>SERS</th>
<th>Assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td>3070</td>
<td>3070</td>
<td></td>
<td>CH stretching in Bz ring</td>
</tr>
<tr>
<td>2645</td>
<td></td>
<td></td>
<td>SH stretching</td>
</tr>
<tr>
<td>1600</td>
<td>1590</td>
<td></td>
<td>Bz ring stretching</td>
</tr>
<tr>
<td>1585</td>
<td>1564</td>
<td></td>
<td>Bz ring in plane stretching</td>
</tr>
<tr>
<td>1498</td>
<td></td>
<td></td>
<td>N-C=S stretching (thioamide I)</td>
</tr>
<tr>
<td>1460</td>
<td>1459</td>
<td></td>
<td>C-C stretching</td>
</tr>
<tr>
<td>1425</td>
<td>1395</td>
<td></td>
<td>NCS ring stretching</td>
</tr>
<tr>
<td>1320</td>
<td>1315</td>
<td></td>
<td>NH bending (thioamide II)</td>
</tr>
<tr>
<td>1273</td>
<td>1281</td>
<td></td>
<td>CH in-plane bending</td>
</tr>
<tr>
<td>1254</td>
<td>1246</td>
<td></td>
<td>CH bending or CN stretching</td>
</tr>
<tr>
<td>1133</td>
<td>1135</td>
<td></td>
<td>CH in-plane bending</td>
</tr>
<tr>
<td>1076</td>
<td></td>
<td></td>
<td>Bz ring or SCS antisymmetric stretching</td>
</tr>
<tr>
<td>1031</td>
<td></td>
<td></td>
<td>CH in-plane deformation</td>
</tr>
<tr>
<td>1011</td>
<td>1013</td>
<td></td>
<td>C-C-C bending</td>
</tr>
<tr>
<td>867</td>
<td></td>
<td></td>
<td>CH out-of-plane bending</td>
</tr>
<tr>
<td>705</td>
<td>717</td>
<td></td>
<td>C-S stretching</td>
</tr>
<tr>
<td>663</td>
<td></td>
<td></td>
<td>NH deformation</td>
</tr>
<tr>
<td>607</td>
<td>602</td>
<td></td>
<td>CS stretching in heterocyclic ring system</td>
</tr>
<tr>
<td>527</td>
<td></td>
<td></td>
<td>Bz ring deformation</td>
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<tr>
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<td>508</td>
<td></td>
<td>Bz ring deformation</td>
</tr>
<tr>
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<td>396</td>
<td></td>
<td>Bz ring deformation</td>
</tr>
<tr>
<td>315</td>
<td></td>
<td></td>
<td>Ag-S stretching</td>
</tr>
</tbody>
</table>

Comparing the data obtained in our study with those in the literature, the behavior of adsorbed MBT is similar to the MBT in basic media, in which the MBT exists as the thiol ion (MBT\(^{-}\)) [13]. It can be concluded that the MBT exists in the form of thiol ion when it was dissolved in the ethanol. Especially, the absence of peaks at 663 and 1498 cm\(^{-1}\)
assigned to NH deformation and N-C=S stretching, respectively in SERS spectrum confirmed this point further (see Fig. 7-4 (1) a). While the predominant species are thiones when the MBT is in solid state and the corresponding Raman bands at 397, 1254 and 1273 cm\(^{-1}\) are the most intense ones (see Fig. 7-4 (1) b).

The peak at 2645 cm\(^{-1}\) can be assigned to the SH stretching. It is weak but clear in the normal Raman spectrum of MBT powder, while it disappears in the SERS spectrum (see Fig. 7-7-(2)). It can be concluded that the adsorption of MBT molecule is achieved by the bond between the exocyclic sulfur atoms and the silver atoms on the surface.

According to the SERS selection rules [25, 26], vibrational modes, whose polarizability tensor elements are perpendicular to a metal surface, should be strongly enhanced in a SERS spectrum, i.e. those corresponding to \(\alpha'_{zz}\), where \(z\) is along the surface normal. Vibrations derived from \(\alpha'_{xz}\) and \(\alpha'_{yz}\) should be the next most intense modes and those corresponding to \(\alpha'_{xx}\), \(\alpha'_{yy}\), and \(\alpha'_{xy}\) should be least enhanced. It can be used to determine the orientation of the adsorbed molecules. In our case, the NCS ring stretching at 1395 cm\(^{-1}\) is the strongest band in SERS spectrum. That means the heterocyclic NCS ring plane is possibly perpendicular to the silver surface. The Raman intensities of C-N stretching in NCS bond and C-H bending at 1246 and 1281 cm\(^{-1}\) are relatively weak in the SERS spectrum, it can be concluded that molecular adsorption of MBT on silver was not through interactions between N atoms and the silver surface. In addition, the fact that the CH out-of-plane bending vibration at 867 cm\(^{-1}\) was much weaker than the CH in-plane bending vibration at 1135 cm\(^{-1}\) in SERS spectrum indicates that MBT is orientated either perpendicular or slightly tilted relative to the surface according to the SERS surface selection rules. However, concerning the orientation of MBT on Ag surface, a different opinion was put forward by Sandhyarani and Pradeep who thought the plane of MBT molecule is almost parallel to the surface [21, 27]. According to the results in our case study, we would like to propose that the plane of MBT molecule is either perpendicular or slightly tilted relative to the silver surface. The proposed orientation of MBT molecule adsorbed on the silver is shown in Fig. 7-5, which also agrees with the results in the literature [28].
7.3.3 Optical Properties of Glass-based SERS-active substrates before and after Adsorption

UV-Vis spectroscopy was applied to investigate the optical properties of the silver film on glass-based SERS-active substrates before and after adsorption. To avoid the baseline effect, the second derivative UV-Vis absorption spectra of quartz glass-based SERS-active substrates before and after MBT adsorption were used to present the changes of optical properties of silver films resulting from the adsorption as shown in Fig. 7-6. Second-derivative spectra display sharp minimum values where maximum values are located in the original spectra, hence the minimum values can be used to identify the surface plasmon resonance (SPR) positions.

Fig. 7-6: Second-derivative UV-Vis absorption spectra: (a) quartz glass-based SERS-active substrate; (b) (a) immersed in $10^{-4}$ M MBT solution for 1 hour.
Adsorption induced changes in the optical properties of SERS-active substrates can be illustrated by the red shift of the SPR band from 361 to 364 nm. The red shift, decreased intensity and the broadening of the SPR band may be attributed to the chemisorption of MBT molecules [28-29]. Several reactions could happen during the process of adsorption, such as reactions forming MBT molecular shells of various thicknesses around the silver particles and reactions involving charge transfer to and from the silver thereafter altering electronic states. It could also result from the complexes (or insoluble salts) formed between MBT and Ag and adsorbed on silver particles. This might be the main reason for the decrease of intensity and the broadening of the SPR peak.

7.3.4 In-situ Analysis of MBT Molecule Adsorption Process

7.3.4.1 In-situ SERS Measurements

The in-situ SERS spectra of MBT adsorbed on the quartz crystal-based SERS-active substrates were collected during the adsorption process. The Raman spectra with different interval of measurements are shown in Fig. 7-7 (a) and (b), respectively. Raman spectrum of absolute ethanol was first acquired and used as a background spectrum (see the lowest spectrum in Fig. 7-7-(a)). The Raman peaks from the ethanol are marked with asterisks in the Raman spectra in Fig. 7-7.

![In-situ SERS spectra of adsorbed MBT as a function of adsorption time: (a) from the beginning to 100 s with an interval of 10 s; (b) from 100 to 240 s with an interval of 30 s. (the spectra were shifted vertically for clarity.).](image)

It can be observed that the Raman intensity of MBT wasn’t detected until the injection occurred 40 seconds, because the solution need some time to flow into the cell. The Raman
intensity is very weak at the beginning because the molecular adsorption takes some time. At the initial stage of the adsorption only one new peak at 1395 cm$^{-1}$ was detected (see 40 s in Fig. 7-7 (a)), which can be assigned to the NCS ring stretching mode. The in-situ Raman spectra shows that the longer the adsorption time, the stronger the Raman intensity of peak at 1395 cm$^{-1}$. Other Raman peaks of MBT molecules also appeared in the SERS spectra, such as at 717, 1013, 1315, 1564 and 1593 cm$^{-1}$, whose Raman intensity also increased with the increasing adsorption time (see Fig. 7-7).

Raman intensity is proportional to the number of the molecule illuminated by the laser. In our case study, the evolution of the Raman intensity is related to two contributions: one is from the increased number of adsorbed MBT molecules and the other one is from the quartz crystal-based SERS-active substrates. To qualify the relative amount of MBT in the neighborhood of a silver surface, the peaks at 1395 cm$^{-1}$ was chosen as the probe peak, as it is a characteristic peak of MBT molecule. The evolution of Raman intensity with adsorption time for MBT molecule and ethanol during the adsorption process of MBT is shown in Fig. 7-8.

![Fig. 7-8](image.png)

*Fig. 7-8: Evolution of Raman intensity of ethanol and MBT molecule adsorbed on silver surface as a function of time after injection during the adsorption process.*

The Raman intensity of ethanol was almost constant, which proves that our system was stable during the adsorption process. As shown in Fig. 7-8, the Raman intensity of peak at 1395 cm$^{-1}$ increased sharply after the MBT solution was introduced to the cell (40 seconds after the injection). Four minutes later, the Raman intensity of peak at 1395 cm$^{-1}$ reached its peak value and kept almost constant for some time. The whole process is clearly shown in Fig. 7-8.
7.3.4.2 In-situ QCM Measurements

The frequency change of QCM as a function of time in the process of MBT adsorption is shown in Fig. 7-9 (a) and the Raman intensity of peak at 1395 cm\(^{-1}\) is also plotted for comparison with the QCM data. Fig. 7-9 (b) presents the complete curve of the QCM frequency change in the process of the MBT adsorption over 48 hours.

As can be seen in Fig. 7-9 (a), the frequency change of the quartz crystal in absolute ethanol was less than 1 Hz in the initial minutes. Minor frequency deviations can be neglected before \(10^{-3}\) M MBT solution was injected into the absolute ethanol (marked as ‘injection point’ in Fig. 7-9 (a)). It took about 40 seconds for the diluted MBT solution to enter the cell, and then the quartz frequency started to decrease, indicating the starting of the adsorption process. This is in agreement with the Raman results shown in Fig. 7-7 (a). The information of MBT molecule wasn’t acquired until 40 seconds later after the MBT solution was added into ethanol (marked as ‘starting point’ in Fig. 7-9 (a)).

The QCM curve shown in Fig. 7-9 (a) indicates that the adsorption process could be roughly divided into two stages. After the linear fitting (dash lines), the two adsorption stages and the turning point of the two adsorption stages are clearly shown in Fig. 7-9 (a). It can be seen that the slope of the QCM frequency change in the first adsorption stage is much steeper than that in the second adsorption stage. This suggests that the adsorption rate in the first stage was much faster than that in the second stage.

The adsorption process of MBT on quartz crystal-based SERS-active substrate can be interpreted by analyzing the QCM frequency change during the adsorption process as shown in Fig. 7-9 (a). The mass changes (\(\Delta m\)) corresponding to the delta frequency (\(\Delta f\)) can be calculated according to the Sauerbrey equation [9, 30]:

\[
\Delta f = - \frac{f_0^2}{N \rho_q L_q} \Delta m = -c_f \Delta m
\]

where \(\Delta f\) is the mean delta frequency resulting from a change in mass per unit area (\(\Delta m\)) by adsorption or desorption of molecules on a quartz crystal substrate, \(f_0\) is the resonance frequency of the quartz crystal (5 MHz), \(L_q\) is the thickness of the bare quartz disk 0.033 cm, \(N\) is the frequency constant (\(N = f_0 \cdot L_q = 1.65 \times 10^5\) Hz cm), \(\rho_q\) is the density for quartz 2.468 g/cm\(^3\), respectively, and \(A\) is the area of the silver-coated quartz (0.20 cm\(^2\)). From the
Sauerbrey equation it can be calculated that constant of $c_f$ is equal to $6.139 \times 10^7$ Hz g$^{-1}$cm$^2$.

![Image](image.png)

\(\Delta f\) (Hz)  

time (min)

**Fig. 7-9:** (a) Change of QCM frequency with fitted curves (dash lines) and Raman intensity of peak at 1395 cm$^{-1}$ as a function of adsorption time in the first 7 minutes of the adsorption process (in-situ); (b) change of QCM frequency over 48 hours during adsorption process with fitted curve (dash line).

The typical number of molecules to form a monolayer on the solid surface is $\sim 10^{15}$/cm$^2$ [31] and the calculated corresponding frequency change is 17.0 Hz based on equation 7-3. In our case, the QCM frequency change in the first stage of adsorption was around 7.5 Hz. Therefore, it is likely that a submonolayer of MBT was formed in the first adsorption stage. General speaking, the number of the molecules to form a monolayer can’t be decided, which really depends on the molecular volume, the orientation of the molecule on the surface. Therefore, it is reasonable to propose a submonolayer or a complete monolayer.
was formed in the first adsorption stage. In the second stage, the behavior of QCM curve could be attributed to the shift from quartz crystal and should be investigated further in the future. The curve of frequency change as a function of time was fitted by the software and the frequency change, $\Delta f$, of the complete adsorption process was determined to be about -196 Hz (see Fig. 7-9 (b)).

The interpretation of Raman data can also support the proposed adsorption process. Before the MBT monolayer completely formed, the Raman intensity of peak at 1395 cm$^{-1}$ increased very sharply with increasing amount of adsorbed MBT until passing the turning point of the two adsorption stages. According to the first layer enhancement mechanism, only the layer very close to the silver surface can get the maximum enhancement effect. The increased Raman intensity can be attributed to the increased MBT molecules and the enhancement from the quartz crystal-based SERS-active substrates. The latter is the main contribution corresponding to the fast increased Raman intensity in the first adsorption stage. For the behavior of Raman intensity in the second stage, it seems like multilayer formed, but it should be interpreted by combining the QCM data.

The effect of the surface coverage dependence could be another contribution to the behavior of the Raman intensity in the process of adsorption [32-34]. Stolberg et al. [32] found that for both low and moderate coverages, the SERS data tracked the surface concentration data very well. The integrated SERS intensity is directly proportional to the surface coverage for low coverages. While for higher coverages, the SERS intensity-coverage relation becomes inversed. This curving down at high coverages is commonly observed in SERS. It can be explained that the induced dipoles of adsorbed polarized molecules depolarize the external field and decrease the magnitude of the local microscopic field at the active site [35].

The evolution of Raman intensity could also related to the orientation change of the adsorbed MBT molecules during the adsorption process which will be investigated in the following part. Nevertheless, all the proposed adsorption process should be confirmed by the other further experiments using different analytical techniques.
7.3.5 Infrared Reflection Adsorption Spectroscopy (IRRAS)

Infrared reflection absorption spectroscopy (IRRAS) has emerged as one of the leading methods for structural analysis of monolayers at the metal-water interface over the past decades, since the early works by Dluhy et al. in 1985 [28]. The IRRAS technique not only allows the characterization of chain conformation and head group structure but also provides qualitative and quantitative information about molecular orientation [36]. To find out if the molecular orientation changed during the adsorption process, IRRAS measurements were preformed on the absorbed MBT on silver film. The obtained IRRAS spectra are shown in Fig. 7-10 (a).

![Fig. 7-10: (a) FT-IRRAS spectra of $10^{-5}$ M MBT adsorbed on Ag film for different time; (b) Plot of logarithm of absorbance of MBT at 1004 cm$^{-1}$ as a function of absorption time. The peak at 1003 cm$^{-1}$ can be assigned to the C-S stretching vibration in the AgMBT surface complex and the peaks at 1412 and 1451 cm$^{-1}$ are from C-C stretching and C-C in-plane stretching [37], respectively. The intensity of peak at 1003 cm$^{-1}$ in IRRAS spectra as]
a function of adsorption time was plotted in Fig. 7-10 (b). The absorbance intensity of the IR peak at 1003 cm$^{-1}$ increased with extending adsorption time. The increased intensity resulted from the increased number of chemically adsorbed MBT molecules, as the in-situ QCM results showed previously. Moreover, the relative intensity ratio between peaks at 1003 and 1412 cm$^{-1}$ changed when the adsorption occurred after 240 minutes. The intensity of peak at 1412 cm$^{-1}$ is stronger than that of the peak at 1003 cm$^{-1}$, while the relation between those two peaks was inversed when the adsorption time was less than 240 minutes. It could be attributed to the changes in the molecular orientation or reconstruction of the molecular monolayers. However, the detailed orientation alteration process should be investigated and confirmed by the complementary measurements in the future.

7.3.6 X-ray Photoelectron Spectroscopy (XPS)

In order to understand the chemical state of elements on the surface and to explore the changes of the substrate atoms upon adsorption, XPS investigation was performed on the MBT molecule adsorbed on the silver film. The resultant corresponding XPS spectra of Ag 3d, C 1s, S 2p and N 1s are shown in Fig. 7-11 (a)-(d).

The Ag 3d 5/2 and Ag 3d 3/2 appeared at 368.1 and 374.1 eV respectively, which indicates no changes in the silver surface (Fig. 7-11 (a)) [21]. The C 1s spectrum in Fig. 7-11 (b) shows two peaks at 284.6 and 286.0 eV, which can be attributed to the adsorbed hydrocarbons and the carbon linked to the nitrogen atom, respectively [21, 38-39]. MBT molecule contains two kind of sulfur atoms in different chemical state, the S 2p peak should be fitted into two different peaks in principle. However, in our case, three obvious peaks could be observed in S 2p region. The peak at 162.1 eV is assigned to the S 2p 3/2 from exocyclic thiolate S atom and the peak at 164.9 eV corresponds to S 2p 1/2 of the endocyclic S atom. As for the peak at 163.6 eV, it could be an overlap of the S 2p 1/2 in exocyclic thiolate and the S 2p 3/2 for endocyclic S atom within the ring. Hence S 2p spin–orbit doublet splitting is clearly visible here (see Fig. 7-11 (c)). The bonding to Ag exists mainly through the exocyclic S atom, since the one present in the heterocyclic ring has very weak coordinating ability due to its lone pairs participating in resonance structures of the molecule [40]. Furthermore The N 1s peak can be detected at 398.8 eV as shown in Fig. 7-11 (d) which confirms the adsorption of MBT on silver surface [41].
7.3.7 SERS Spectra of MBT Adsorbed on Gold Surface

The orientation of adsorbed MBT molecules on gold surfaces has been widely reported in the literature [27, 42-43]. However, concerning the bonding of MBT to gold surface there is still a controversy. For example, Bharathi et al. [41] have proposed that MBT adsorbs on gold surface in the thiol form. In contrast, Sandhyarani and Pradeep have proposed that MBT adsorbs on gold surface in the thione form [21, 27]. This controversy makes it difficult to understand the nature of the bond between Au and MBT molecules. The postulated orientation of MBT on gold in the literature is shown in Fig. 7-12, in which two sulfur atoms attach on the Au surface [41-43].

To better understand the bond structure and molecular orientation on Au surface, the SERS spectrum of MBT adsorbed on Au film was acquired as presented in Fig. 7-13. For comparison reasons, the SERS spectrum of MBT adsorbed on Ag film is shown in Fig. 7-13 as well. Two kinds of SERS-active substrates were immersed into the $10^{-4}$ M MBT
ethanol solution for 1 hour. The parameters of measurement are almost the same except the acquisition time of spectrum is 30 seconds for MBT on Au film by using He-Ne laser and 10 seconds for MBT on Ag film by using Ar+ laser, respectively.

![Fig. 7-12: Schematic representation of Au-MBT structure proposed by Bharathi [41-43].](image)

The SERS spectra in Fig. 7-13 are completely identical, which means the orientation and the bond conditions of adsorbed MBT on Au film and on Ag film could be same. In other words the MBT adsorbed on gold surface exists in thiol form as it adsorbed on silver surface discussed previously, which also agrees with Woods’ and Bharathi’s conclusions [13, 20, 42]. In addition, in the spectrum (b) in Fig. 7-13 (2) the peak at 1394 cm$^{-1}$ from MBT adsorbed on the gold surface is a smooth and symmetric single peak, thus, it could be concluded that only one kind of MBT species was adsorbed on the gold surface [13].

![Fig. 7-13: SERS spectra of MBT adsorbed on glass-based SERS-active substrates:](image)

(1) 350-900 cm$^{-1}$ range  (2) 900-1700 cm$^{-1}$ range

The orientation of MBT adsorbed on gold has been proposed that the plane of molecule is perpendicular to the gold surface by several groups [21, 41-42]. It can be deduced that orientation of MBT molecules on the silver surface is also perpendicular to the silver surface, which could support our conclusion in section 7.3.2 further. However, the
attachment of MBT molecules on Au or Ag should be investigated further to better clarify the bond between the sulfur atoms and the metal atoms.

### 7.4 Conclusions

In this chapter, in-situ investigation of the adsorption process of MBT on silver surface by combining SERS and QCM was first time successfully performed. The advantage of this in-situ experimental set-up is that the kinetics of the adsorption process (QCM data) and the information from the adsorbed molecules (Raman spectra) can be acquired simultaneously. The results showed that the in-situ set-up combining SERS and QCM can facilitate more profound insight into the nature of MBT adsorption on metal surfaces.

The behavior of MBT in ethanol is similar to that shown in basic medium comparing our results with those in the literature. The MBT adsorbed on the silver surface is in the form of thiol and the orientation of the adsorbed MBT molecules is likely either perpendicular or tilted relative to the silver surface. The adsorption of MBT on silver surface was achieved by the bond between the exocyclic sulfur atoms in MBT and the silver atoms on the surface. The change in molecular orientation or reconstruction of molecular layers could happen during the adsorption process according to the IRRAS results.

The adsorption process is qualitatively proposed by interpreting the combined QCM data and Raman results. QCM results showed that the adsorption process can be roughly divided into two stages. The first stage is the initial stage in which a submonolayer or a complete monolayer could form. In the first stage, the SERS intensity of MBT molecules kept increasing until a monolayer formed, which is due to the increased number of adsorbed MBT molecule and the enhancement effect from the SERS-active substrates. As for the second stage, it need investigate further in the future because of the possibility of the shift from the quartz crystal.

The Raman spectra of MBT adsorbed on the gold surface suggested that MBT molecules adsorbed on the gold in the form of thiol and only one kind of MBT species with single orientation was observed. However, more detailed investigation of MBT adsorption on gold and silver surfaces should be performed in the future to clarify the controversy in the literature.
7.5 References

Chapter 8: General Conclusions and Outlook

This work is aiming at the development of novel SERS-active substrates and the extension of the applications of the SERS-active substrates to different research fields, such as investigation of the growth of thin plasma polymer films; studying the phase transition of thin TiO₂ films with annealing treatments, in-situ characterization of plasma modification effects on thin metal or polymer films as well as in-situ monitoring the adsorption process of organic molecules by combining SERS and QCM techniques. The main conclusions drawn from the various investigations contained in this work are summarized as follows:

The fabrication of novel SERS-active substrates was accomplished by combining plasma enhanced chemical vapor deposition of organosilicon film and physical vapor deposition of silver. The obtained plasma polymer surface is rough, rich of defects and pores in the nanometer scale and shows a cauliflower-like morphology. The features inherited from the plasma polymer film still remained when a very thin silver layer was deposited on top of it, which was proved by AFM and SEM measurements. The enhancement effect of the achieved substrates was probed by the adsorption of BPE molecules on the obtained substrates and the enhancement factor was determined to be up to 10⁵-10⁷. The contribution of the increased surface area to the enhancement factor was also studied by means of electrochemical impedance spectroscopy. The result showed that the surface area of the rough silver surface is about 1 order of magnitude larger than that of the smooth silver surface. Therefore, the prepared substrates are really SERS-active, and the increase of the surface area is just a minor effect contributing to the enhancement effect. In addition, the prepared substrates show very good long-term stability under ambient conditions.

The relation between SERS intensity and the film thickness and the enhancement factor as a function of the film thickness were achieved by investigating the growth of thin organosilicon plasma polymer films. It was found that the Raman intensity always increases with increasing film thickness, but the enhancement factor decreases sharply in the first 20 nm thickness range. This can be explained by the proposed “first layer enhancement mechanism”. As the overlayer is over a few nanometers, the electromagnetic enhancement from the SERS-active substrates attenuates strongly.
The phase transition of the sputtered thin TiO$_2$ film with annealing treatments was investigated by the prepared SERS-active substrates. Raman intensity of TiO$_2$/SERS-active substrate system is enhanced at least two orders compared to that of the TiO$_2$/Si system and 20 times relative to that of the TiO$_2$/Ag/Si system. The enhanced signal of the TiO$_2$ thin films is due to the localized electromagnetic field from the surface plasmon excitation of metal Ag decoration. The investigation of the phase transition of the TiO$_2$ thin films by SERS shows the possible applications of SERS in analysis of other important metal/metal oxides in industry in the future.

In-situ plasma modifications of copper surfaces were performed on copper films deposited on the glass-based SERS-active substrates. A complete cycle of plasma oxidation and reduction of copper films was investigated by SERS. Surface contaminants were removed in the (Ar + H$_2$) plasma and metal hydroxides were formed in the following O$_2$ plasma. After the (Ar + H$_2$) plasma was introduced again, the metal hydroxide layer was reduced to the initial chemical composition. The significant change of the surface morphology could be attributed to Oswald Ripening effect, which leads to the growth of metal particles in the process of plasma modifications. The in-situ set-up was also applied to modify carbon nanotubes by N$_2$ plasma. The ratio between D-band and G-band from carbon nanotubes increased after the plasma modifications and this indicated that more defects were introduced during the plasma modification process. Different plasma modifications were carried out on the thin polystyrene films and the possible reaction mechanisms of plasma modifications were qualitatively discussed according to the Raman results.

In-situ monitoring of the adsorption process of MBT on silver surfaces by combining SERS and QCM techniques was performed on a home-built experimental set-up. The advantage of this set-up is that the kinetics of molecular adsorption process (QCM data) and the information of the adsorbed molecules (Raman spectra) can be acquired simultaneously in a single experiment. The results showed that the combination of SERS and QCM techniques is very useful for a profound insight into the nature of MBT adsorption on metal surfaces. The adsorption of MBT on silver surface is achieved by the bond between the exocyclic sulfur atoms in the MBT molecules and the silver atoms on the surface. MBT molecules adsorb on the silver surface in the form of thiol and the orientation of MBT molecules is likely either perpendicular or tilted relative to the silver surface, which is different from the
parallel orientation proposed by other researchers in the literature. The adsorption process is likely to be divided into two stages according to the QCM data. In the initial stage of the adsorption, MBT monolayer was proposed to form and multilayers formed in the second stage of the adsorption. The change of Raman intensity as a function of adsorption time agrees with the above-proposed adsorption mechanism.

In the future, the model TiO$_2$/SERS-active substrate system can be applied for the in-situ study of the photocatalytic effect of the anatase TiO$_2$ by detecting the photodegraded products of the adsorbed chemical compounds, which could be a very promising technique in waste water or gas treatment. As mentioned above, the back-scattering experimental set-up can be extended to in-situ characterize the plasma modification effects on many other metal/metal oxides or in-situ analyze the growth of different thin plasma polymer films in industry. Moreover, the adsorption of MBT on metals should be further investigated by using the experimental set-up combining SERS and QCM techniques. The adsorption/desorption of MBT molecules on metal surfaces will be investigated by applying the potential polarization or varying the pH value of the solution. This would provide more profound understanding of the adsorption of MBT molecules on metals.
## Abbreviations and Symbols

### Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>AF</td>
<td>Audio frequency</td>
</tr>
<tr>
<td>AFM</td>
<td>Atomic force microscope</td>
</tr>
<tr>
<td>ALD</td>
<td>Atomic layer deposition</td>
</tr>
<tr>
<td>BPE</td>
<td>Trans-1, 2-bis (4-pyridyl) ethylene</td>
</tr>
<tr>
<td>CE</td>
<td>Chemical enhancement</td>
</tr>
<tr>
<td>CNTs</td>
<td>Carbon nanotubes</td>
</tr>
<tr>
<td>CT</td>
<td>Charge transfer</td>
</tr>
<tr>
<td>DC</td>
<td>Direct current</td>
</tr>
<tr>
<td>DDA</td>
<td>Discrete dipole approximation</td>
</tr>
<tr>
<td>DTGS</td>
<td>Deuterated triglycine sulfate</td>
</tr>
<tr>
<td>EIS</td>
<td>Electrochemical impedance spectroscopy</td>
</tr>
<tr>
<td>EF</td>
<td>Enhancement factor</td>
</tr>
<tr>
<td>EM</td>
<td>Electromagnetic enhancement</td>
</tr>
<tr>
<td>EtOH</td>
<td>Ethanol</td>
</tr>
<tr>
<td>FT-IR</td>
<td>Fourier-transformation infrared</td>
</tr>
<tr>
<td>FE-SEM</td>
<td>Field emission scanning electron microscope</td>
</tr>
<tr>
<td>GIXRD</td>
<td>Grazing incidence X-ray diffraction</td>
</tr>
<tr>
<td>HMDS</td>
<td>Hexamethyldisilane</td>
</tr>
<tr>
<td>HMDSO</td>
<td>Hexamethyldisiloxane</td>
</tr>
<tr>
<td>HOMO</td>
<td>Highest occupied molecular orbital</td>
</tr>
<tr>
<td>IRRAS</td>
<td>Infrared reflection adsorption spectroscopy</td>
</tr>
<tr>
<td>LSPR</td>
<td>Localized surface plasmon resonance</td>
</tr>
<tr>
<td>LUMO</td>
<td>Lowest unoccupied molecular orbital</td>
</tr>
<tr>
<td>MBT</td>
<td>2-mercaptobenzothiazole</td>
</tr>
<tr>
<td>$M_n$</td>
<td>Number average molecular weight</td>
</tr>
<tr>
<td>ORC</td>
<td>Oxidation-reduction cycle</td>
</tr>
<tr>
<td>PDI</td>
<td>Polydispersity index</td>
</tr>
<tr>
<td>PECVD</td>
<td>Plasma enhanced chemical vapor deposition</td>
</tr>
<tr>
<td>PS</td>
<td>Polystyrene</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Full Form</td>
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<td>--------------</td>
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<tr>
<td>PVD</td>
<td>Physical vapor deposition</td>
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<tr>
<td>RF</td>
<td>Radio frequency</td>
</tr>
<tr>
<td>QCM</td>
<td>Quartz crystal microbalance</td>
</tr>
<tr>
<td>RMS</td>
<td>Root mean square</td>
</tr>
<tr>
<td>SAMs</td>
<td>Self-assembled monolayers</td>
</tr>
<tr>
<td>SEF</td>
<td>Surface-enhanced fluorescence</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscope</td>
</tr>
<tr>
<td>SEHRS</td>
<td>Surface-enhanced hyper-Raman spectroscopy</td>
</tr>
<tr>
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<td>Surface-enhanced infrared spectroscopy</td>
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<tr>
<td>SE-SFG</td>
<td>Surface-enhanced sum frequency generation</td>
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<tr>
<td>SE-SHG</td>
<td>Surface-enhanced second-harmonic generation</td>
</tr>
<tr>
<td>SH</td>
<td>Thiol</td>
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<tr>
<td>S/N</td>
<td>Signal/noise</td>
</tr>
<tr>
<td>SPP</td>
<td>Surface plasmon polariton</td>
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<tr>
<td>SPR</td>
<td>Surface plasmon resonance</td>
</tr>
<tr>
<td>STM</td>
<td>Scanning tunneling microscopy</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission electron microscope</td>
</tr>
<tr>
<td>TERS</td>
<td>Tip-enhanced Raman spectroscopy</td>
</tr>
<tr>
<td>THF</td>
<td>Tetrahydrofuran</td>
</tr>
<tr>
<td>UHV</td>
<td>Ultra-high vacuum</td>
</tr>
<tr>
<td>UV-SERS</td>
<td>Ultraviolet excited SERS</td>
</tr>
<tr>
<td>UV-Vis</td>
<td>Ultraviolet-visible absorption spectroscopy</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray photoelectron spectroscopy</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
</tr>
</tbody>
</table>
Symbols

$\alpha$  Polarizability of the molecule

$\alpha_0$  Polarizability at the equilibrium position

$A$  Surface area

$A(\nu)$  Field enhancement factor

$d$  Distance between the molecule and the metal sphere

$d$  Film thickness

$\varepsilon$  Complex dielectric constant

$E_0$  Amplitude of the external electric field

$E_M$  Field ($E_M = E_0 + E_{sp}$)

$E_{sp}$  Field of a dipole induced in the metal sphere

$f_0$  Resonance frequency of the quartz crystal

$\Delta f$  Frequency shift of the quartz crystal

$G(\nu_s)$  Stokes signal power

$h$  Planck constant

$I$  Raman intensity

$L_q$  Thickness of the bare quartz disk

$\Delta m$  Change in mass per unit area

$N$  Frequency constant ($N = f_0 \cdot L_q$)

$\rho_q$  Density of the quartz crystal

$r$  Radius of the metal sphere

$Q$  Vibrational amplitude

$Q$  Constant phase element (for EIS)
Abbreviations and Symbols

\( t \) Time
\( \mu \) Dipole moment
\( \nu_L \) Frequency of the incidence light
\( \nu_0 \) Vibration frequency of internal modes in molecule
\( \nu_L' \) Frequency of the scattered light
\( \Delta \nu \) Raman shift
\( V \) Vibration state (\( V=0, 1, 2, \ldots \))
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Publications Related to This Work


2. I. Klüppel, **G. G. Sun,** G. Grundmeier, “In-situ investigation of the kinetic adsorption process of 2-mercaptobenzothiazole by combining surface-enhanced Raman spectroscopy and quartz crystal microbalance”, in preparation.

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