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## Depth profiling of APTES self-assembled monolayers using surface-enhanced confocal Raman microspectroscopy

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### ABSTRACT

The internal structure of self-assembled monolayers (SAMs) such as 3-aminopropyltriethoxysilane (APTES) fabricated on a glass substrate is difficult to characterize and analyze at nanometer level. In this study, we employed surface-enhanced Raman spectroscopy (SERS) to study the internal molecular structure of APTES SAMs. The sample APTES SAMs were deposited with Ag nanoparticles to enhance the Raman signal and to obtain subtler structure information, which were supported by density functional theory calculations. In addition, in order to carry out high-resolution analysis, especially for vertical direction, a fine piezo electric positioner was used to control the depth scanning with a step of 0.1 nm. We measured and distinguished the vertical Raman intensity variations of specific groups in APTES, such as Ag/NH<sub>2</sub>, CH<sub>2</sub>, and Si—O, with high resolution. The interfacial bond at the two interfaces of Ag-APTES and APTES-SiO<sub>2</sub> was identified. Moreover, APTES molecule orientation was demonstrated to be inhomogeneous from frequency shift.

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### 1. Introduction

3-Aminopropyltriethoxysilane (APTES) is an aminosilane frequently used in silanization i.e. the functionalization of surfaces with alkoxy silane molecules. The functionalized surface could promote adhesion of polymer films to glass, attach metal NPs to silica substrate, and promote cell growth, etc. The APTES multilayers have been studied by many approaches, e.g., UV-visible absorption [1], ellipsometry [2], X-ray photoelectron spectroscopy [1,3], etc. Nevertheless, none of them could support the inner molecular structure of APTES SAMs in detail.

Many spectroscopic techniques have been successfully applied to study surface characterization, such as Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS) and time-of-flight secondary-ion mass spectroscopy (ToF-SIMS). New techniques are being developed to estimate and monitor the coating systems at higher resolution, including depth profile analysis of the entire coating thickness. Confocal Raman microspectroscopy (CRM) is a well-known in-situ measurement method to be used in elucidating molecular structure. It is particularly suitable for the depth profiling of polymer films, such as the dye in PET fibers [4], UV-cured coatings [5], the fungicide fluorfolpet in a PVC film [6], etc. However, CRM is not sensitive enough to scan all materials and thin films (such as monolayers). Although the accuracy of CRM depth profiling is limited, it could be improved by some approaches, e.g., the use of immersion oil objective could increase

the depth resolution [7,8]. In this study, we will use surface-enhanced Raman spectroscopy (SERS) and a high-performance depth-scanning stage controller to improve the depth profiling on APTES SAMs.

SERS coupled with SERS sensor could overcome the low sensitivity of the common Raman spectroscopic technique. The SERS sensor is essential for obtaining enhanced Raman signals of Au, Ag, Cu, etc. Ag nanoparticles (AgNPs) have often been used as a conventional sensor among all SERS sensors [9,10], and also in this study. So far, SERS has been widely employed in various fields, such as microbiology [11,12], organic materials [13], and electrochemistry [14,15]. It has a great potential for observing the subtle signals of molecular vibrations even at atomic level. Moreover, a piezo electric stage installed on Raman can support accurate displacement movement with a step of 0.1 nm and realize a depth profile at atomic level combing with SERS. Jiang et al. [16] have successfully characterized hydrazine adsorption on Cu surface at the nanometer scale using a plasmonic antenna enhancing Raman scattering. In this article, we attempt to carry out the depth profiling of APTES SAMs, in search of accurate and distinct inner molecular information, by using SERS. Some encouraging results were observed during this scanning, which are valuable of understanding APTES SAM internal structure.

### 2. Experimental Section

#### 2.1. Preparation of APTES SAMs

The reagents that we used include APTES (99%, SIGMA-ALDRICH), Toluene (99.5%, KANTO KAGAKU), ethanol (99.5%, KANTO KAGAKU),

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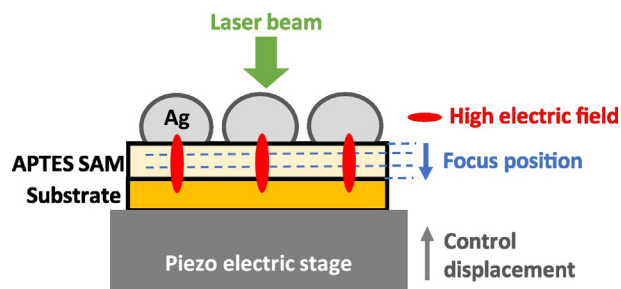


Fig. 1. Schematic diagram of the depth-profiling mode with SERS.

$\text{H}_2\text{SO}_4$  (KANTO KAGAKU) and  $\text{H}_2\text{O}_2$  (KANTO KAGAKU). The substrate used is TEMPAX® glass ( $20 \times 20 \times 1.0 \text{ t mm}^3$ , MUSASHINO FINE GLASS). The self-assembled APTES monolayers used in this study were prepared according to the following procedure (Fig. S1). First, a glass substrate was cleaned for 10 min by a solution consisting of sulfuric acid and hydrogen peroxide ( $\text{H}_2\text{SO}_4:\text{H}_2\text{O}_2 = 2:1$ ). Then, the cleaned substrate was immersed in 10 mL of toluene solution containing 0.043 mmol of APTES at  $60^\circ\text{C}$  for 10 min. APTES SAMs were formed and were washed by ethanol with ultrasonication for 2 min to remove any physisorbed APTES molecules. Finally, AgNPs with a diameter of 5 nm was prepared and evaporated on the amine-modified glass (molecular structure shown in Fig. S1), to enhance Raman scattering as a SERS sensor. The morphology was characterized by atomic force microscopy (AFM).

## 2.2. SERS and Depth Profile Measurement

The employed instrument was a confocal Raman microspectroscopy (Tokyo instrument Co.), with excitation wavelength of 785 nm (laser power of 3.8 MW), pinhole of  $10 \mu\text{m}$  diameter and resolution of  $3.3 \text{ cm}^{-1}$ . The numerical aperture (NA) of the objective lens is 0.95. The sample APTES SAMs was adsorbed with AgNPs to enhance the Raman signals (SERS). The estimated electric field is presented in Fig. 1 and Fig. S3, which illustrate the location of SERS hotspot. The penetrated electric field exponentially decayed, where the decayed depth in  $1/e$  is only 3 nm. This means we can observe the Raman spectrum nanometer-scale depth region. The depth resolution can be increased due to the enhanced electric field. Because Raman intensity is enhanced by  $10^4$  for SERS, the field gradient in depth direction is also extremely sharp, that is the equivalent to the sharp focusing depth.

For measuring the depth profiling of APTES SAMs, firstly, the laser beam was irradiated to APTES SAM surface, and then the focus position was moved from surface to substrate by using the piezo electric stage, which was installed to support accurate displacement movement with a step of 0.1 nm. The schematic of using piezo electric stage in combination with SERS is displayed in Fig. 1. Utilizing SERS and piezo electric stage, the resolution of depth profile can be achieved to the nanometer level, which has been demonstrated elsewhere [17].

## 2.3. Theoretical Calculation

For peak assignment, vibrational modes and their frequency values were theoretically analyzed using density functional theory, which is implemented in the Gaussian09 software package [18]. Adsorption

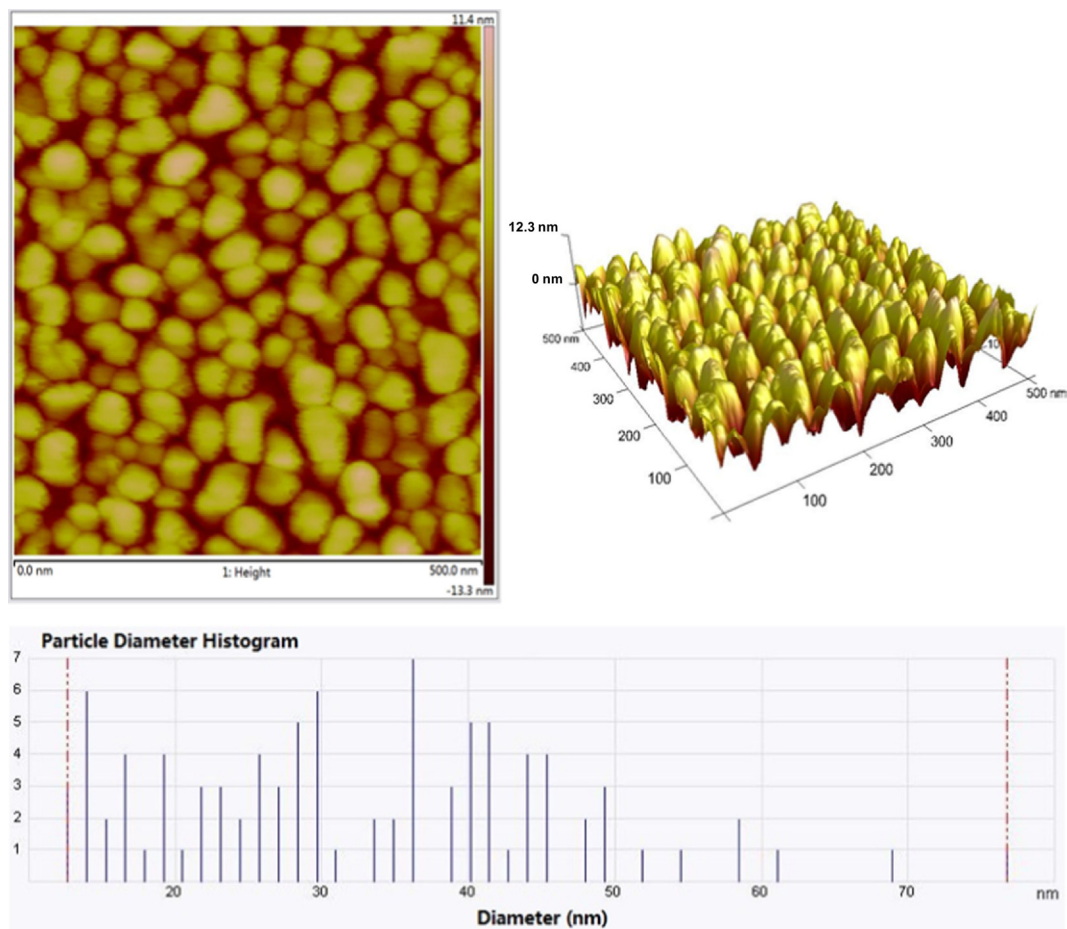


Fig. 2. AFM image of the morphology of APTES SAMs with Ag deposited and the particle diameter histogram of AgNPs. The island-like AgNPs with a diameter of several tens nm was observed.

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