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Estimated phase transition and melting temperature of APTES self-assembled monolayer using surface-enhanced anti-stokes and stokes Raman scattering

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ABSTRACT

A structure's temperature can be determined from the Raman spectrum using the frequency and the ratio of the intensities of the anti-Stokes and Stokes signals (the I_{as}/I_s ratio). In this study, we apply this approach and an equation relating the temperature, Raman frequency, and I_{as}/I_s ratio to *in-situ* estimation of the phase change point of a (3-aminopropyl)triethoxysilane self-assembled monolayer (APTES SAM). Ag nanoparticles were deposited on APTES to enhance the Raman signals. A time-resolved measurement mode was used to monitor the variation in the Raman spectra *in situ*. Moreover, the structural change in APTES SAM (from ordered to disordered structure) under heating was discussed in detail, and the phase change point (around 118 °C) was calculated.

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1. Introduction

(3-Aminopropyl)triethoxysilane (APTES) is a typical organosilane agent for the preparation of amino-terminated films on silicon substrates. It is used to promote adhesion of polymer films on glass, promote protein adhesion and cell growth, and attach metal nanoparticles (NPs) to a silica substrate. APTES multilayers have been investigated by many methods, including ellipsometry,[1] UV–vis absorption,[2] X-ray photoelectron spectroscopy,[2,3] and atomic force microscopy (AFM).[4] However, all these studies focused on the characterization of APTES film formation, and there has been very little research on the phase transition (melting) process of an APTES self-assembled monolayer (SAM). The melting process of this ordered structure is significant for its application because a melted (disordered) APTES monolayer could weaken the device properties and performance. Regarding the phase change points, the melting and boiling points of standard bulk APTES are -70 and 217 °C, respectively. After APTES self-assembles on a silica surface, it can maintain the solid state even under an environmental temperature above its melting point. Therefore, there must be a higher melting point and a specific melting process for an APTES SAM than for a typical standard APTES sample. However, for a sample with such an extremely thin layer structure (several nanometers for mono-, bi-, or tri-layers), detailed analysis of the interior structural variation is fairly difficult to realize. To gain insight into the mechanism of the phase transition process inside an APTES monolayer and estimate the melting point, we attempted to employ anti-Stokes and Stokes surface-enhanced Raman scattering (SERS).

SERS, a type of Raman scattering, can be observed via the enhancement caused by rough metal NPs. It has great potential for providing information on small molecular vibrations, even at the atomic level. SERS is extensively applied in various areas including microbiology,[5,6] organic materials,[7] and electrochemistry.[8,9] To create local field intensity enhancement, effective SERS sensors are crucial. Ag NPs are often used as a conventional SERS sensor [10,11] and are used in this paper as well.

Anti-Stokes and Stokes Raman scattering represent two possible outcomes of Raman interaction. The material absorbs energy, and the emitted photon has a higher or lower energy than the absorbed photon; these two possibilities are called anti-Stokes and

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Stokes Raman scattering, respectively. Stokes scattering peaks are stronger than anti-Stokes scattering peaks. Their ratio depends on the temperature; this fact can be exploited practically for temperature measurement [12,13]. The intensity ratio of anti-Stokes to Stokes scattering can be theoretically expressed as

$$\frac{I_{as}}{I_s} = \exp(-\frac{h\nu}{kT}) \quad (1)$$

where ν is the Raman shift of one vibration, k is the Boltzmann constant, and h is the Planck constant. Anti-Stokes Raman scattering is generally rather weak, so it is hard to observe anti-Stokes Raman signals from materials with low Raman activity. Fortunately, Ag NPs deposited on an APTES SAM can enhance the Raman signals of not only Stokes scattering but also anti-Stokes scattering. Thus, it may become possible to observe the temperature during a heating process by a powerful Raman technique.

Therefore, we investigated the melting process of ultrathin APTES SAMs by surface-enhanced anti-Stokes and Stokes Raman scattering in this study. Ag NPs were adsorbed on top of the monolayers to create localized Raman enhancement (SERS). Consequently, the anti-Stokes scattering could be observed together with enhanced Stokes scattering, so the phase change point for APTES could be calculated using Eq. (1). A time-resolved measurement mode was used to monitor the variation in the Raman spectra *in situ*. The laser beam in this research was used not only to excite Raman spectra but also to heat the sample. The phase transition of APTES from ordered to disordered structure at the atomic level under laser heating is discussed and analyzed according to the variation in Raman peaks representing specific bonds.

2. Experimental methods

2.1. Sample preparation

APTES (99%, Sigma-Aldrich), toluene (99.5%, Kanto Kagaku), and ethanol (99.5%, Kanto Kagaku) were used. The substrate was TEMPAX® glass ($20 \times 20 \times 1.0\,t\,mm^3$, Musashino Fine Glass). The APTES SAM samples used in this study were prepared as follows. First, a glass substrate was cleaned using a solution of sulfuric acid and hydrogen peroxide (H_2SO_4:H_2O_2 = 2:1) for 10 min. Next, the cleaned substrate was immersed in 10 mL of toluene solution containing 0.043 mmol of APTES at 60 °C for 10 min, during which an APTES SAM layer formed. The SAM was rinsed with ethanol under ultrasonication for 2 min to remove physisorbed APTES molecules.

A film of nanometer-sized Ag NP was adsorbed on the amine-modified glass via evaporation (Fig. 1) to enhance the Raman scattering. Finally, island-like Ag film was formed as a SERS plasmonic sensor due to aggregation process, with the average thickness of over 10 nm (Fig. S1).

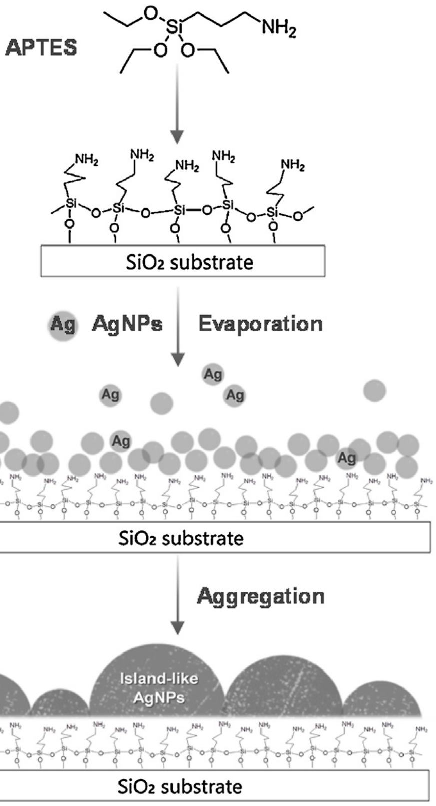

Fig. 1. Schematic diagram of estimated structure of APTES SAMs.

2.2. Atomic Force Microscopy (AFM)

AFM images were collected in tapping mode using a multimode scanning probe microscope produced by Veeco Instruments, Inc. The image for publication covered an area of 0.25 μm^2, which is the same size as the original image. The AFM image was processed using a third-order X–Y plane fit image.

2.3. Raman Spectroscopy and SERS

Confocal Raman spectroscopy was employed to obtain anti-Stokes and Stokes Raman signals. Microscopic confocal Raman spectroscopy (Tokyo Instrument Co.) was used with excitation wavelengths of 785 nm (the laser power was 13.8 mW) and a notch filter for recording anti-Stokes signals. The focused laser beam was used not only to excite Raman spectra but also to heat the sample. A time-resolved kinetic measurement mode was used, with an exposure time of 1 s and kinetic cycle time of 1.1 s. Ag NPs were adsorbed on the APTES SAM samples to enhance the Raman signal and obtain more subtle structural information.

2.4. Theoretical calculation

A density functional theory (DFT) calculation was performed using the Gaussian 09 package[14] to assign the experimental Raman peaks to appropriate vibrational modes. We optimized the geometry of the adsorption system containing the Ag particle and APTES molecule. The Ag particle was modeled as a tetrahedral cluster with 20 atoms because this cluster is applicable for full geometrical optimization. The APTES molecule was assumed to interact with the tip of the Ag cluster via–NH_2.

B3LYP was used as the exchange-correlation functional [15,16]. As basis sets, 6-31G** was applied to H, C, and Si atoms, and 6–31 + G** was applied to N and O atoms.[17] A different basis set was used for N and O because N and O are relatively electronegative and exhibit a strong tendency to accept electrons, so they require a larger basis set. For Ag, the effective core potential of Hay and Wadt [18] was selected as the substitute for the Ar core. Because the solvent environment was assumed to surround the adsorption system, a polarizable continuum model (IEFPCM)[19] having a dielectric constant of 78.35 was applied in the calculation.

3. Results and discussion

3.1. Surface-enhanced Raman spectra of APTES SAMs

APTES SAMs were prepared according to the fabrication process described in Section 2.1, and the morphology was characterized by AFM as described in Section 2.2. Fig. 2 shows an AFM image of a

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