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Surface enhanced infrared absorption spectra on pulsed laser deposited silver island films

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ABSTRACT

Infrared absorption spectra for self-assembled monolayer of p-nitrothiophenol on Pulsed Laser Deposited (PLD) silver films have been measured at normal incidence of radiation. For a PLD film grown in non-equilibrium conditions, it was confirmed that the particle diameter and the interparticle distance were small compared with those of a vacuum-evaporated film. A film with such morphology is advantageous for infrared absorption enhancement. Results show that the best film for the infrared absorption enhancement is probably that generated with PLD.

1. Introduction

Silver films vacuum-evaporated onto dielectric substrates enhance the infrared absorption of adsorbed molecules [1–12]. Most investigations have demonstrated that physical effects that enhance absorption can result from surface electric field enhancements associated with collective electron resonance in metal islands. Nevertheless, the interpretation of those enhancements remains indeterminate. Understanding the morphology of island films involved in enhancement is expected to be useful to elucidate absorption enhancement mechanisms [13,14]. For that purpose, vacuum evaporation method is useful. To date, we have controlled film morphology by changing the film thickness [1,3,5], evaporation rate [4], substrate temperature during evaporation [2], and post-annealing temperature [15]. However, control of the film morphology using each of these methods is limited, probably because film growth in evaporation is done under thermal equilibrium processing. Pulsed Laser Deposition (PLD) is a simple and effective method for fabrication of thin films. A non-equilibrium condition in PLD process is especially of great benefit for the deposition of films with metastable phases. In addition, PLD has the excellent feature of supporting the synthesis of high-purity films better than a vacuum evaporation method using high-temperature evaporators. Despite these advantages, few studies have clarified the shape and surface morphology of Ag films prepared using PLD [16–18]. It is expected that PLD films have different morphology from that of evaporated films. The purposes of this study are deposition of the Ag film using PLD with features like those described above and evaluation of the possibility of applying the PLD film to IR enhancement.

2. Experimental details

Deposition of Ag thin films was performed in a high vacuum chamber with base pressure of 3.0×10^{-5} Pa. The pressure during deposition was less than 5.0×10^{-5} Pa. The 20 × 20 mm Ag target (99.99 %) was rotated at 7 rpm during laser ablation. The substrate used was a Si wafer that had been cut to ca. 20 × 20 mm^2. The substrate temperature was room temperature (RT). We degassed the substrates before deposition at 200–500 °C for 30 min to avoid incorporation of water desorbed from the sample holder and the deposition chamber walls during deposition. A KrF excimer laser (248 nm wavelength, COMPEX 102; Lambda Physik) with 30 ns pulse duration was used for Ag targeted ablation. The laser was focused onto the target in the vacuum chamber by a lens with normal incidence. The laser repetition rate was set to 5 Hz. The laser fluence was varied from 66 to 147 mJ/pulse. The PLD conditions for this experiment are presented in Table 1. Infrared absorption spectra were obtained at normal incidence of radiation using a Fourier transform infrared spectrophotometer (MB-100; ABB Bomem) equipped with a standard deuterated triglycine sulfate (DTGS) detector averaging 128 scans at 4 cm^{-1} resolution. As absorbing material, we used a reagent grade of p-nitrothiophenol (PNTP; Wako Pure Chemical Industries Ltd.)

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Table 1
List of PLD conditions.

Sample	Laser Power [mJ]	Exposure Time [min]
A1	66	20
A2	66	25
B1	93	10
B2	96	10
B3	96	10
C1	147	5
C2	147	10
C3	147	15

without further purification because of its self-assembling properties. A self-assembled monolayer of PNTP on the silver film on a Si substrate was prepared upon immersion of a silver film on Si into 2 mM ethanolic solutions of a PNTP for 2 h at room temperature. Then the monolayer was rinsed thoroughly with twice-distilled water. Morphologies of the Ag films deposited on a Si wafer were observed using a field-emission scanning electron microscope (FE-SEM, JSM-7000F; JEOL) at 10 keV. A schematic drawing used to evaluate the sizes of the particles and gaps is presented in Fig. 1. Lines were drawn at regular intervals in the photograph, the points of intersection of the edges of the islands and the lines were measured, and the sizes of the islands and gaps were evaluated.

3. Results and discussion

Fig. 2(a) presents typical infrared absorption spectra of PNTP chemisorbed onto PLD silver films. This isolated absorption band assigned to $\delta(NO_2)$ is suitable for the evaluation of absorbance. Fig. 2(b) presents infrared absorption spectrum of 50 nm thickness PNTP cast onto the Si substrate. Absorption intensities of the PNTP monolayer on silver thin film and a 50-nm-thick PNTP layer are almost identical. Therefore, it is clear that absorption enhancement is attributable to the silver thin film. Fig. 2(c) presents typical infrared absorption spectra of PNTP chemisorbed onto vacuum evaporated silver films that have similar island size and gap size with PLD film (147 mJ, 5 min) presented in Fig. 2(a). The more intense absorbance is observed in PLD film.

Fig. 3 presents a series of FE-SEM micrographs of a silver island-shaped film deposited on Si taken at 10 keV. The Ag film morphology did not depend upon the laser power or deposition time. Samples A1, A2, and C2 showed fine Ag particle morphology, with random dispersion on the substrate. In samples B1, B2, and B3, these islands started coming into contact with neighbors, eventually coalescing into a semi-continuous film (percolation threshold). In sample C1, these particles were clumped into three-dimensional islands with various heights and sizes. Sample C3 was an almost continuous film, but intricately shaped openings (gaps) remained in the film.

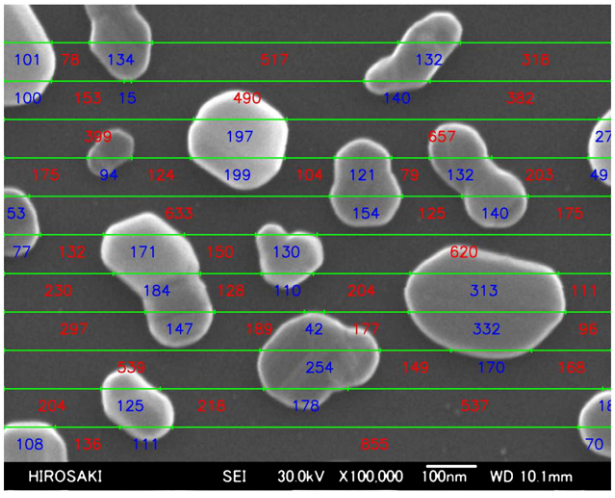

Fig. 1. Schematic drawing of parameter evaluation from FE-SEM micrograph. The lines were drawn at regular intervals in the micrograph (shown as green), and at the points of intersection at the particle edge. The lines were measured, and the particle sizes (shown as blue) and gap sizes (shown as red) were evaluated.

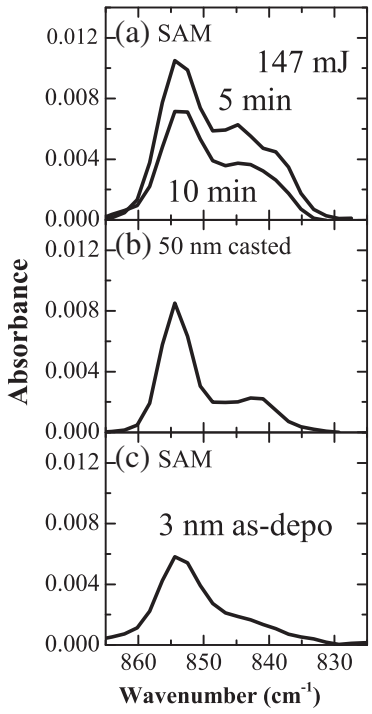

Fig. 2. (a) Typical infrared absorption spectra of the self-assembled monolayer of PNTP chemisorbed onto the pulsed laser deposited silver films. The PLD conditions are shown in the figure. (b) Infrared absorption spectra of 50 nm thickness PNTP casted onto the Si wafer. (c) Typical infrared absorption spectra of the self-assembled monolayer of PNTP chemisorbed onto the vacuum evaporated silver films. The evaporation conditions are shown in the figure.

Figs. 4 and 5 present size distribution histograms of islands and gaps as evaluated from Fig. 3. To evaluate the typical island size and gap size for each film thickness, a Gaussian curve was fitted to the histogram and the center of the Gaussian curve was calculated. The results are presented in Table 2 with IR absorbance. No IR absorption band was observed in sample C3 because no radiation was transmitted. Therefore, it is not evaluated here. An increase in the laser power and the exposure time will engender an increase in the film thickness. However, different from the case of vacuum evaporation, the particle did not grow along with the increase of these values. Moreover, the film morphologies mutually differ even though the preparation conditions were identical (B2 and B3). In other words, the reproducibility of morphologies of the island-like thin films prepared by PLD is not so good.

Next, the relations between parameters and the absorbance are discussed. Research results of the evaporated film [8] and the gold nanoparticles dispersed in polymer film show a positive dependency on the volume fraction of metal [19]. They also show that IR absorbance is inversely dependent on the particle size and gap size. The relations between parameters and the absorbance of PLD samples are presented in Table 2. For B, both the dependence on the particle size (Fig. 6(a)) and gap size (Fig. 6(b)) of IR absorbance showed negative dependence. For A and C, the dependence on the gap size of IR absorbance also showed negative dependence. These results support those obtained in studies that have used evaporated Ag thin film [2,3] and small Au particles dispersed in polymer [9]. However,