Spectroscopic analysis of a nanostructure roughness of plasma-deposited Au films using organic monolayer

M Shindo, T Sawada, K Doi, K Mukai and K Shudo
Faculty of Engineering, Yokohama National University, 79-5 Tokiwadai, Hodogaya-ku, Yokohama 240-8501, Japan

Abstract. The morphology and roughness of nanostructure of Au film are discussed using an atomic-force microscope (AFM) and a laser Raman spectroscopy. The Au films are deposited on mica and Si substrate by means of a dc plasma sputtering technique, and a self-assembled monolayer (SAM) of benzene-thiol is formed on the Au films. The cluster size and roughness on the surface increase with substrate annealing during the deposition on mica substrate, while they decrease on Si substrate. Raman spectra show a surface-enhanced Raman scattering (SERS) occurs at the optimum roughness \( R_A \sim 0.3 \) of the substrate.

1. Introduction

Organic thin films have been studied widely in relation with fabricating self-integrated devices, where a self-assembled monolayer (SAM) is widely used [1]. A SAM is created by the chemisorption of organic molecules onto specific metal/semiconductor surfaces. For example, a benzenethiol (BT) molecule, which is known to easily form a SAM, contains the most fundamental aromatic functional that offers a variety of applications and binds at the sulfur site to gold (Au)[2-4]. As molecular vibrations of the SAMs on the surfaces are fingerprints of adsorbed structures, the observations of those molecules clarify the molecule-substrate interaction at the nanometer scale.

The molecules in such monolayer films are detectable with surface-enhanced Raman scattering (SERS) [5,6], since SERS offers very high sensitivity spectroscopically; the enhancement can be at the order of 10^6, compared with ordinary Raman process. Although a SERS is usually used for nano-sized particles [7-11], the surface roughness will also induce SERS effect. Actually, this was confirmed by an ultrafast measurement of coherent molecular motion of adsorbed Au layers [12], on which the SAM of BT was adsorbed [13]. Detected signals of the ultrafast motion of molecules depended on the molecular array and surface morphology. Thus, a SERS measurement will give us the information on the surface roughness of Au thin films.

In this study, films of Au, which are deposited on mica and Si substrates using a dc plasma sputtering technique, are observed with an atomic-force microscope (AFM) to see their surface morphology including roughness. Then a SAM of BT is formed on the Au surface and observed by laser Raman spectroscopy to discuss the relationship between the roughness and onset of SERS. The effect of the substrate annealing during the deposition process is also discussed.

2. Experimental

Au atoms were attached to (001) surfaces of mica [14-17] after cleavage with a scotch tape and silicon substrates[18-20] at room temperature (RT) and 400°C by plasma dc sputtering using JFC1500 (JEOL).
The silicon surfaces usually have native oxide with non-uniform structures. The deposition rate was kept constant at approximately 0.5 nm/sec and the film thickness (θ) was controlled in the range of 0.3–20 nm. Several authors demonstrated that the surface morphology is not as sensitive to the deposition rate as to the annealing temperature [21,22]. After the surface morphology was observed with an atomic-force microscope (AFM), substrates were soaked into BT-ethanol solution (1 mM) for 24 hours at RT to make SAM. After rinse with ethanol, monolayer films were left on the surface. A laser Raman spectra of the surface rinsed with ethanol were measured using a 532 nm laser with a spot size of 1 μm in diameter.

3. Results and discussion

3.1 Au film deposited on mica substrates

Typical AFM images of Au thin film surfaces deposited on mica substrate are three-dimensionally shown in figure 1. The surface roughness with varied θ is summarized in table 1. Here, the diameter of the clusters designates for \( k_{\text{max}} \) where \( k_{\text{max}} \) is the wavenumber of a peak in two-dimensional fast Fourier transformation (FFT) spectra (for example, see figure 1(c)) from AFM surface profiles. This represents the average of the clusters very well: for instance, \( k_{\text{max}} \approx 0.053 \text{nm}^{-1} \) at the peak in FFT for \( \theta = 20 \text{nm} \) provides the cluster size \( k^{-1} \approx 19 \text{nm} \). The height of the clusters is evaluated in terms of two indexes, \( R_A \) and \( R_{\text{RMS}} \). One notes that \( R_{\text{RMS}} \) is 20–30% larger than \( R_A \). The amplitude in FFT component at \( k_{\text{max}} \) is very close to these two indexes. Two times of the index (\( R_A \), \( R_{\text{RMS}} \) or the FFT amplitude at the peak) approximates the height of clusters of the average diameter. The average diameter is increased as \( \theta \) is increased. However, the roughness is increased as \( \theta \) is increased except for \( \theta = 2 \text{nm} \).

![Figure 1](image.png)

**Figure 1.** Topographic AFM images of Au films deposited on mica substrate at RT at (a) \( \theta = 5 \text{nm} \) (b) \( \theta = 20 \text{nm} \). The cluster size is consistent with the inverse of the wave number at a peak in FFT spectrum (c) obtained with the surface profile (b). Note that the amplitude at \( k_{\text{max}} \) is \( \approx 0.4 \text{ nm} \). See table 1 and text for detail.
Table 1. The surface roughness of Au films estimated from AFM images. Film thickness specified with superscripts * showed the enhanced Ramana scattering (SERS) signal.

| Substrate | Thickness (nm) | Diameter | $R_A$ | $R_{RMS}$ |
|-----------|----------------|----------|--------|-----------|
| Mica      | 2nm            | 56.53    | 1.24   | 1.66      |
|           | 5nm*           | 32.28    | 0.076  | 0.102     |
|           | 10nm*          | 21.41    | 0.269  | 0.341     |
|           | 20nm           | 19.04    | 0.395  | 0.500     |
|           | 5nm*           | 50.04    | 1.04   | 1.33      |
|           | 0.3nm          | 29.09    | 0.69   | 1.48      |
|           | 0.3nm*         | 20.17    | 0.34   | 0.54      |
|           | 1nm            | 35.16    | 1.09   | 1.37      |
|           | 1nm            | 19.25    | 0.595  | 0.78      |
|           | 3nm            | 33.99    | 0.78   | 1.01      |
| Si        | 3nm            | 18.47    | 0.85   | 0.66      |

$\theta$: thickness specified with superscripts * showed the enhanced Ramana scattering (SERS) signal.

$R_A$: Arithmetic mean value $R_A = \sqrt{\frac{\int_{-\infty}^{\infty} (x, y) - z_0 \, dx \, dy}{\int_{-\infty}^{\infty} z(x, y) \, dx \, dy}}$.

$R_{RMS}$: Root mean square (RMS) value $R_{RMS} = \sqrt{\frac{\int_{-\infty}^{\infty} (z(x, y) - z_0)^2 \, dx \, dy}{\int_{-\infty}^{\infty} z(x, y) \, dx \, dy}}$.

$z_0$: average in the height $z(x, y)$ over position $(x, y)$ in the observed area.

This indicates that the diffusive process of Au on mica in the initial phase of the deposition is different from that on Au after the surface is enough covered with Au.

Figure 2 shows Raman spectra of the films for various $\theta$. A clear peak of C=C bond at 1570 cm$^{-1}$ appeared only for $\theta = 5$ and 10 nm in RT deposition. This suggests that the surface roughness is optimum for SERS at $\theta = 5$–10 nm. The C=C bond peak shifted to the lower energy with $\theta$ increased (at the order of a few cm$^{-1}$), indicating that the surface roughness tilted BT orientation with respect to the surface [23,24].

3.2. Annealing effect to Au deposition on mica substrates

Au film deposition was also carried out with the substrate annealed at 400 °C for $\theta = 5$ nm. An AFM image and Raman spectrum of Au film deposited on mica substrate annealed at 400 °C are shown in figure 3. The annealing process during the deposition did not form a single crystal but increased the size of Au clusters and surface roughness. This is because Au on mica substrate has a large diffusion coefficient [25] and form (111) surface only at high-temperature (> 473°C) regardless to deposition rate[26]. However, this fact is in contrast to a post-process annealing of Au thin films on mica substrate forming a large single crystal typically at 400–500°C [14-16]. Therefore, Au cluster seems to have a high crystallinity on the substrate after deposition at high temperature. The annealed surface yields the strong SERS as shown in figure 3(b). The diameter of RT-deposited surface with $\theta = 2$ nm, whose roughness and diameter are similar to the annealed case, does not give SERS. This indicates that the larger cluster yields the stronger SERS, and that SERS needs a density of clusters.

Figure 2. Raman spectra of BT on Au film deposited on mica substrate.
Typical signals of BT-derived vibrations are marked.

![Figure 3](image)

**Figure 3.** An AFM image (a) and Raman spectra (b) of Au film deposited on mica substrate annealed at 400°C to \( \theta = 5 \) nm. Raman peaks from BT are strengthened at the annealed deposition while a substrate component does not change.

### 3.3. Au film deposited on Si substrate

AFM images of Au film deposited on Si substrate with \( \theta = 0.3 \) nm at RT and 400°C are shown in figure 4. Actually, the surface of Si was covered with native SiO\(_x\) (\( x \approx 2 \)) layer, and it has non-uniform amorphous-like structure. Thus, one cannot identify the deposition plane in the case of Si. Annealing during plasma sputtering decreased both the size and roughness of Au clusters. On the other hand, it is reported that a post-process annealing of Au thin films on Si substrate induces grain growth [14], indicating this process is different from our high temperature deposition. In our case, the deposition at high temperature did not grow grains but enhanced the cluster size. The height of the clusters corresponds to few monolayers of Au atom. This is because the lateral diffusion of Au on SiO\(_2\) surfaces dominates the vertical growth [27]. From Raman spectra in figure 5, the intensity of the peak was enhanced most at \( \theta = 0.3 \) nm with annealing, at which the roughness is optimum for SERS. It is concluded that BT was adsorbed on the ultimately thin Au surface and that SERS is effective on atomic-scale islands. We note that the roughness optimum for SERS is \( R_A \approx 0.3 \) nm, which agrees with \( R_A \) for mica substrate.

![Figure 4](image)

**Figure 4.** AFM images of Au films deposited on Si substrates with \( \theta = 0.3 \) nm at (a) RT and (b) 400°C.
4. Summary

BT-SAM on Au films deposited on mica and Si substrate were observed by means of Raman spectroscopy. Au deposited by dc plasma sputtering with and without annealing was compared. The cluster size and roughness of the surface increase on annealed mica substrate, while they decrease on Si substrate. It is found that a SERS yields strong signals at the specific diameter of Au clusters deposited with the thickness of more than a few monolayers of Au atoms and that a SERS offers a sensitive response to the surface roughness.

References

[1] Pensà E, Cortes E, Corthey G, Carro P, Vericat C, Fonticelli M H, Benitez G, Rubert A A and Salvarezza R C 2012 Accounts of Chem. Res. 45 1183
[2] Price R C and Whetten R L 2005 J. Am. Chem. Soc. 127 13750
[3] Kang H, Lee H, Kang Y, Hara M and Noh J 2008 Chem. Commun. 12 5197
[4] Kang H, Park T, Choi I, Lee Y, Ito E, Hara M and Noh J 2009 Ultramicroscopy 109 1011
[5] Zaera F 2012 Chem. Rev. 112 2920
[6] Rycenga M, Cobley C M, Zeng J, Li W, Moran C H, Zhang Q, Qin D and Xia Y 2011 Chem. Rev. 111 3669
[7] Hossain M K, Shibamoto K, Ishioka K, Kitajima M, Mitani T and Nakashima S 2007 J. Luminescence 122-123 792
[8] Elias J, Gizawska J M, Brodard P, Widmer P, deHazen Y, Graule T, Michler J and Philippe L 2012 Nanotechnology 23 255705
[9] Wang J, Zhu T, Song J and Liu Z 1998 Thin Solid Films 327-329 591
[10] Laor U and Schatz G C 1981 Chem. Phys. Lett. 82 566
[11] Bell S E J and McCourt M R 2009 Phys. Chem. Chem. Phys. 11 7455
[12] Katayama I, Koga S, Shudo K, Takeda J, Shimada T, Kubo A, Hishita S, Fujita D and Kitajima M 2011 Nano Lett. 11 2648
[13] Shudo K, Doi K, Katayama I, Kitajima M and Takeda J 2012 European Phys. J. Web Conf. in press
[14] Ferrero S, Piednoir A and Henry C R 2001 Nano Lett. 1 227
[15] Kowalczyk P, Kozlowski W, Kluse Z, Olejniczak W and Datta P J 2007 App. Surf. Sci. 253 4715
[16] Li F, Tang L, Zhou W and Guo Q 2011 Surf. Sci. 605 1016
[17] Ostendorf F, Schmitz C, Hirth S, Kuehnle A, Kolodziej J J and Reichling M 2008 Nanotech. 19
[18] Chan K, Aspanut Z, Goh B, Muhamad M R and Rahman S A 2011 Thin Solid Films 519 4952
[19] Ruffino F, Canino A, Grimaldi M G, Giannazzo F, Roccaforte F and Raineri V 2008 J. Appl. Phys. 104 024310
[20] Wang J, Zhu T, Song J and Liu Z 1998 Thin Solid Films 327-329 591
[21] Liu Z H, Brown N M.D 1997 Thin Solid Films 300 84
[22] Malinsky P, Slepicka P, Hnatowicz V and Svorcik V 2012 Nanoscale Res. Lett. 7 241.
[23] Benkataramanan M, Skanth G, Bandyopadhyay K, Vijayamohanan K and Pradeep T 1999 J. Colloid and Interface Sci. 212 553
[24] Joo S W, Han S W and Kim K 2001 J. Colloid and Interface Sci. 240 391–399
[25] Ruffino F, Torrisi V, Marletta G and Grimaldi M G 2011 Nanoscale Res. Lett. 6 112
[26] Higo M, Fujita K, Tanaka Y, Mitsushio M. Yoshidome T 2006 Appl. Surf. Sci. 252 5083
[27] Ruffino F, Grimaldi M G, Bongiorno C, Giannazzo F, Roccaforte F, Raineri V 2008 Superlattices and Microstructures 44 588