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Surface morphological modification of Pt thin films induced by growth temperature

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Grazing-incidence x-ray reflectivity (GIXR), x-ray diffraction, and atomic-force microscopy (AFM) are used to characterize surface structures of Pt thin films grown on ultrasmooth SiO_2 substrates. The GIXR spectra of the Pt thin films are found to be strongly dependent on the growth temperature. The surface roughness of the Pt thin films shows a minimum (1.21 nm) at the optimum temperature of 773 K, which is in good agreement with that obtained by the AFM measurements. The surface morphology of the Pt thin film grown at 300 K is three dimensional and has mountainlike islands with smaller grain sizes of 10–20 nm. In contrast, the surface of the Pt thin film grown at 773 K is composed of ridges, troughs, and flat facets. [S0163-1829(98)06531-X]

I. INTRODUCTION

Polycrystalline metal thin films have attracted much interest due to their widely industrial applications in electronic, magnetic, and optical devices.[1–4] In particular, the highly reliable electrodes of Pt thin films are required for semiconductor devices with ultra-large-scale integration.[5] However, the performances of metallic thin films are strongly affected by their grain size distribution, crystalline orientation, interface and surface structures, etc.[6,7] In order to clearly evaluate their natures and to control a better fabricating condition, an accurate determination of the physical parameters of metallic thin films is very essential for both fundamental and technological reasons.

Although atomic-force microscopy (AFM) is a powerful tool to measure the surface topography and can present a more ''visible'' result,[8] local information of the order of a few micrometers in size can be obtained. The grazing-incidence x-ray reflectivity (GIXR) has been recognized as a promising technique for studying thin films in the past few years,[9–11] because of its nondestructive and quantitative measurement. In a recent paper,[12] we have reported that a highly accurate thickness, density, and surface roughness could be obtained by GIXR technique for 5-nm Pt thin film on ultrasmooth SiO_2 substrate within the error of about 1.8%. In this work, the GIXR and AFM were employed to systematically measure the surface roughness of the Pt thin films produced at different growth temperatures. X-ray diffraction (XRD) was used to study the growth orientations of the Pt thin films. Our aim was focused on two aspects. First, to observe the surface roughness of the Pt thin films influenced by growth temperatures. Second, to study the difference of growth mechanism of the Pt thin films at low and high temperatures. We found that a Pt thin film with low roughness and large grain size could be grown on ultrasmooth SiO_2 substrate at 773 K.

II. EXPERIMENT

A 76.2-mm-diameter and 0.5-mm-thick ultrasmooth SiO_2 substrate with a surface roughness of 0.45 nm measured by AFM was cut into four pieces of approximately the same area. These small SiO_2 pieces were cleaned in acetone solution with an ultrasonic cleaner for 30 min. The Pt thin film was grown in a molecular-beam epitaxy (MBE) chamber, which was described elsewhere.[12] Before growing the Pt thin film, the SiO_2 substrate was cleaned by heating it to 1073 K for 1 h. Finally, the samples with the respective growth temperatures of 300, 623, 773, 923, and 1073 K were fabricated with a growth rate of 0.10 nm/s.

The GIXR measurements were performed using a high-resolution 18-kW rotating anode x-ray diffractometer (Rigaku SLX-2000). The Cu $K\alpha$ beam from the rotating anode was monochromatized with flat Ge(220) double crystals. The x-ray reflection intensities were collected by a scintillation counter with an incident collimating slit of 50 μm and a reception slit of 50 μm. The scanning rates were 0.010°/min with a 0.002° step. The x-ray diffraction measurements of the Pt thin films were performed with a Philips PW-1800 x-ray diffractometer.

The AFM observations were measured by contacted mode using a Digital Instruments Nanoscope III system: the stylus was made of microfabricated silicon.

III. RESULTS

The x-ray reflectivities of the Pt thin films at different growth temperatures are illustrated in Fig. 1. It can be observed that there are large differences in the respective oscillation peak region. Only a few oscillation peaks appear in the relatively smaller 2θ angle region for the Pt thin film grown at 300 K, while the oscillations are preserved to higher reflection angles for the Pt thin films grown at higher temperature. However, no monotonous change is exhibited with increasing growth temperature. In particular, the oscillation peaks extend to 4.5° for the Pt thin film grown at 773 K. This suggests that a lower surface roughness could be obtained for the Pt thin film grown at 773 K rather than at 300, 623, 923, and 1073 K. The fitting results of the surface roughness obtained from the GIXR measurements are summarized in Table I.

The surface morphologies of the Pt thin films grown at 300, 773, and 1073 K are shown in Fig. 2. It is readily observed that the surface topography of the Pt thin film grown at 300 K is composed of three-dimensional, well-separated, mountainlike islands with about 1.81 nm roughness and grain size of about 10–20 nm. When increasing the growth temperature to 773 K, the surface structure of the Pt

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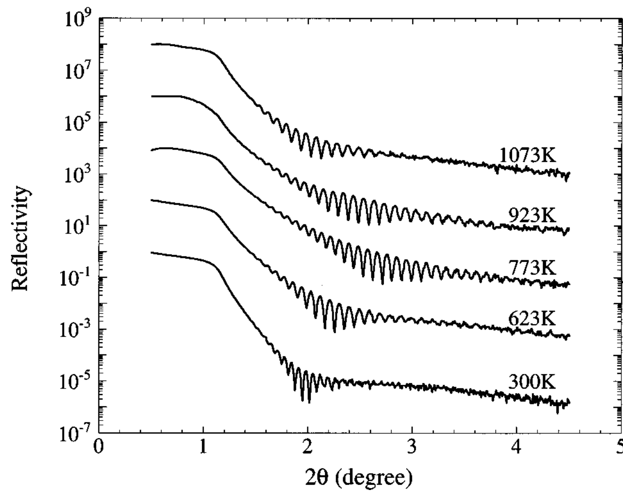


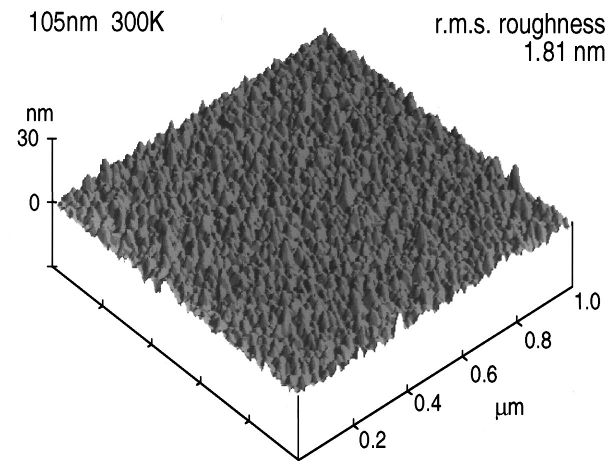
FIG. 1. Reflectivity spectra for the Pt thin films grown at the temperatures of 300, 623, 773, 923, and 1073 K.

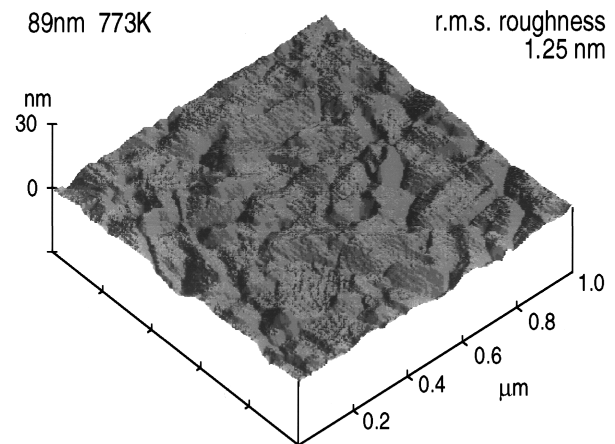
thin film attains a topography composed of ridges, troughs, and flat facets. The size of the ridges and troughs is about 200–500 nm and surface roughness is 1.25 nm for the Pt thin film grown at 773 K. The troughs become deeper and ridge sizes increase when the growth temperature of the Pt thin film is 1073 K.

The x-ray diffraction patterns of the epitaxial Pt thin films are shown in Fig. 3. The two peaks at 39.75° and 85.70° corresponding to the Pt (111) and (222) planes appear for all the Pt thin films. Furthermore, the (111) and (222) diffraction peaks become sharper and stronger with increasing growth temperature. For the Pt films grown at the higher temperatures, no evidence for the diffraction peak due to the (220) plane could be found. The XRD results suggest that at higher growth temperatures the Pt thin films are preferentially grown with (111)- and (222)-plane orientations. In contrast, it can be seen that there are weak diffraction peaks due to the (200), (220), and (113) planes in the Pt thin film grown at 300 K. This XRD result indicates that the Pt thin film grows randomly at 300 K.

IV. DISCUSSIONS

With the GIXR technique, You *et al.*[13,14] and Lee and Tseng[15] have studied the growth of Pt/Si(111) and Al/Si(100) at room temperature during the sputtering and electron beam evaporation process. Their results have indicated





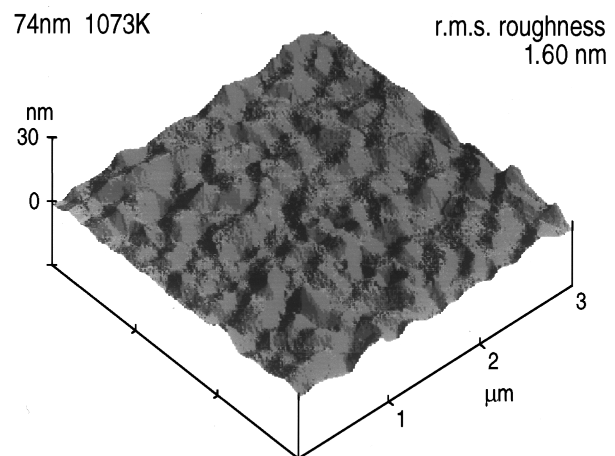


FIG. 2. AFM images of the Pt thin films grown at temperatures of 300, 773, and 1073 K.

that the Pt thin film shows an island growth on the Si substrate in the initial stage. They explained that the deposition of Pt atoms on preexistent Pt clusters proceeds faster than the continued nucleation on Si substrate. As the film becomes thicker, the islands gradually fill the surface and start to coalesce and continuously grow to form a homogeneously rough surface. Our AFM result demonstrates that the Pt thin film is favorable to three-dimensional island growth on a SiO_2 sub-

TABLE I. Surface roughness of Pt thin films as measured by GIXR and AFM. The errors are double standard deviation; T^* represents the growth temperature of the Pt thin films.

			Surface roughness (nm)	
Pt film	T^*(K)	Thickness (nm)	GIXR	AFM
Sample 1	300	105.27±0.29	2.11±0.05	1.81±0.10
Sample 2	623	89.68±0.21	1.59±0.03	1.50±0.10
Sample 3	773	89.45±0.20	1.21±0.03	1.25±0.10
Sample 4	923	90.02±0.20	1.50±0.03	
Sample 5	1073	73.98±0.22	1.68±0.03	1.60±0.10

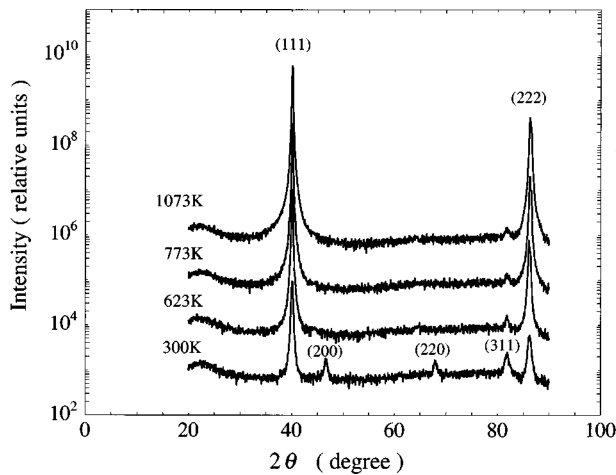


FIG. 3. XRD patterns of the Pt thin films grown at temperatures of 300, 623, 773, and 1073 K. The diffraction intensities are expressed on a logarithm scale.

strate at 300 K. It seems that there is a similar growth mechanism for the Pt thin film grown on the Si and SiO_2 substrates at room temperature.

Table I shows that the surface roughness with an identical change in the growth trend could be obtained from the GIXR and AFM measurements for the Pt thin films grown at various growth temperatures. From the GIXR results, the surface roughness (2.11 nm) of the Pt thin film grown at 300 K is larger than that (1.68 nm) grown at 1073 K. A minimum surface roughness (1.21 nm) appears at growth temperature of 773 K. Why does the higher growth temperature result in a lower surface roughness? There are three possible ways to interpret the growth temperature dependence of the surface roughness of the Pt thin films. First, the higher temperature is useful to increase the surface nucleation rate and to form small size islands. Second, the higher temperature tends to increase the Pt atomic migration capability on the surface of thin film. Third, the interface interaction between Pt atoms and SiO_2 substrate is useful to decrease the surface roughness. It is possible that the chemical reaction can take place in the interfacial Pt atoms and Si or O atoms at the higher growth temperature. However, even if the reaction between Pt atoms and surface Si and O can decrease the interfacial roughness, it is difficult to explain the lower surface roughness for 89.45-nm Pt thin film grown at 773 K. Kellerman *et al.*[9] have reported that the surface roughness of the Fe film decreases with an increase of the substrate temperature in the region between 448 and 473 K, using the x-ray reflectivity measurement. STM results of Adams *et al.*[16] further revealed that the Fe nucleation rate increases with elevating substrate temperature, giving a higher density of stable nuclei, resulting in smaller island sizes and a smoother steady-state surface morphology. However, the growth temperature dependence of our Pt thin films cannot be explained by the viewpoint of Kellerman *et al.* and Adams *et al.* since the AFM images in Fig. 2 and XRD patterns in Fig. 3 show that the grains in the Pt thin films become larger with increasing the growth temperature.

It is an interesting result that the large Pt polycrystalline grains forming at higher growth temperature can produce a smoother Pt thin film surface, compared with the film grown at 300 K, where small Pt grains are obtained. The XRD results in Fig. 3 suggest that the Pt thin films are preferentially grown with (111)- and (222)-plane orientations at higher growth temperatures, and that the Pt thin film grows randomly at 300 K. The results show that there are significantly different growth mechanisms for the Pt thin films at lower or higher growth temperature. The Pt thin films favor a three-dimensional island growth at lower temperature, but have a tendency to grow layer by layer at high temperature, which is consistent with the AFM results. Meanwhile, we find that the lower surface roughness of films grown on SiO_2 at 773 K corresponds to the initial crystallization temperature of Pt thin film in the 5-nm period Pt/C multilayers as grown by Lodha *et al.*[17] This result strongly indicates that a flatter Pt thin film could be grown at its initial crystallization temperature. For the Pt film grown at 773 K, we suggest that the deposited Pt atoms utilize the additional thermal energy after dropping onto the SiO_2 substrate surface to overcome the migration barrier and hence can diffuse rapidly into the neighboring spaces between the Pt grains. This means that the Pt atoms deposited at 773 K tend to promote the coalescence of neighboring Pt grains and thus flatten the rough surface. For the Pt thin film grown at 300 K, the surface roughness of the Pt thin film increases with thickness.[18] It can be interpreted that the diffusion capability of Pt atoms is small and that the migration of Pt atoms is localized. Therefore, many small mountain-shaped Pt grains are formed on the surface of the Pt thin film, as shown in Fig. 2. At much higher growth temperature, such as 1073 K, the Pt grains crystallize to form very large grains, so that the ridges are higher and the troughs become deeper. Hence, this condition is not useful for the Pt thin film growing smooth surfaces.

V. CONCLUSIONS

The surface structures of the Pt thin films with various growth temperatures have been studied by GIXR, XRD, and AFM techniques. The GIXR and AFM results have shown that a minimum surface roughness (1.21 nm) of the Pt thin films grown by MBE occurs at an optimum growth temperature of 773 K, which corresponds to the initial crystallization temperature of the Pt thin films. The XRD results indicate that at higher growth temperatures the textures of the Pt thin films favor (111)- and (222)-plane growth orientations. We have demonstrated that the Pt thin films favor a three-dimensional island growth with small grain size at 300 K, and that high temperatures suit the layer-by-layer growth with large grains.

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