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Influences of ultra-thin Ti seed layers on the dewetting phenomenon of Au films deposited on Si oxide substrates

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ABSTRACT

The influences of a Ti seed layer (1 nm) on the dewetting phenomenon of Au films (5 nm) grown onto amorphous SiO_2 substrates have been studied and compared. Atomic force microscopy results indicated that the introduction of Ti between the substrate and Au promoted the dewetting phenomenon. X-ray diffraction measurements suggested that the initial deposition of Ti promoted crystallinity of Au. A series of Auger electron spectroscopy and X-ray photoelectron spectroscopy results revealed that Ti transformed to a Ti oxide layer by reduction of the amorphous SiO_2 substrate surface, and that the Ti seed layer remained on the substrate, without going through the dewetting process during annealing. We concluded that the enhancement of Au dewetting and the improvement in crystallinity of Au by the insertion of Ti could be attributed to the fact that Au location was changed from the surface of the amorphous SiO_2 substrate to that of the Ti oxide layer.

1. Introduction

With the development of various fabrication tools, the ability to generate polymorphous nanostructures has been increasing in recent years. One of the simplest approaches for the low-cost fabrication of nanostructures by self-organization is based on spontaneous thermal agglomeration (or dewetting) of thin films. Post-deposition annealing at a temperature below the melting point sometimes induces such a thermal agglomeration process. This occurs while the thin film remains in the solid state, which is therefore called solid-state dewetting [1]. Solid-state dewetting is driven by a lowering of the total energy of the system with respect to the initial energies of the surfaces of the film and substrate, as well as the energy of the interface between the film and the substrate. Dewetting is also greatly influenced by atomic surface diffusion [2–4] and the thermal stresses that result from the heat treatment of thin films [5–7]; and thus the rate of dewetting increases with increasing temperature. Controlling dewetting would open the possibility of starting from a homogeneous thin film to obtain objects with a pre-defined statistical size and spatial distribution. It offers the advantage of avoiding complicated and expensive 'top-down' processes, such as lithographic subtractive ones.

As mentioned above, control of the thermodynamic and kinetic state, and stress conditions during film growth are therefore essential to obtain high-quality nanodot structures. However, during the growth of thin films, it is often the case that the desired nanostructure of the film is not thermodynamically and/or kinetically favorable under a given experimental condition. One of the useful options to control the dewetting behavior of noble metal film onto the substrate is to insert a thin seed layer between the film and substrate [8,9]. The addition of the seed layer is often effective in promoting agglomeration; for example, formation of Ag nanodots at a lower annealing temperature through additions of Ti and Fe seed layers have been reported [10–12]. In this seed layer assisted agglomeration (SLAA) process, the insertion of an ultrathin transition metal seed layer changes the thermodynamics and stress state between the noble metal layer and the substrate. Therefore, the use of a seed layer approach is of high technological interest, as it allows for the stabilization of multiple crystal structures and/or orientations of a given element, without the need for a complicated fabrication step. A summary of previous studies reveals that the insertion of a thin seed layer for the fabrication of noble metal nanodots provides the following advantages: (1) a manufactured thin film has strong adhesion to the substrate, (2) the annealing temperature to obtain the nanodots structure is decreased, (3) the epitaxial growth of the nanodots is enhanced, and (4) fabricated nanodots have a characteristic nanostructure that reflects the surface symmetry of the substrate [8–14].

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Among metals showing the localized surface plasmon resonance (LSPR) effect, the Au nanodots have proven to be very reliable, due to their good chemical stability and biocompability. Au nanodots can also act as a catalyst in the synthesis of semiconductor nanowires [15]. The LSPR of Au nanodots on a SiO_2 surface is considered to be useful for biosensors [16], waveguides [17], and photocatalysts [18]. As a general trend, these fascinating optical properties of nanostructures are strongly dependent on the surface morphology. Therefore, precise control over the size, density, and configuration of Au nanodots offers an efficient way to enhance and optimize the performance of various LSPR-based applications.

The aim of the present study is to investigate the influence of a thin Ti seed layer on the dewetting behavior of Au on an amorphous SiO_2 surface. The dewetting process can vary with different substrate surface. Thus, it would be interesting to study how the insertion of a thin seed layer influences the dewetting behavior of the thin film. Therefore, this research focuses on the dependence of the dewetting behavior of Au and Au/Ti films on the annealing temperature.

2. Experimental procedure

DC magnetron sputtering experiments were performed in this study. Before deposition, the chamber was evacuated to a base pressure of 6.7×10^{-5} Pa. Si(001) single crystals were used as substrates, which had approximately 3.0 μm of thermally grown amorphous SiO_2 (a-SiO_2). The a-SiO_2/Si(001) substrates were ultrasonically cleaned with acetone and ethanol. The thickness of the Au layer was set to 5 nm, in order to obtain relatively small nanodots, as has been reported in previous studies [19,20]. Two series of samples were deposited, namely the Au layer directly onto the substrate, and the Au layer deposited onto the substrate covered with an ultra-thin Ti seed layer. In this study, the thickness of the Ti seed layer was selected as 1 nm on the basis of our previous result [11]. During the deposition of the films, the working pressure was maintained at 6.7×10^{-1} Pa. The deposition rates of Au and Ti were 0.080 ± 0.003 and 0.091 ± 0.009 nm/s, respectively. All the layers were deposited at room temperature. After the deposition, the samples were heated at 150–450 °C at 5 h under the vacuum condition.

The morphologies of the surfaces after annealing of the samples were determined by atomic force microscopy (AFM) in tapping mode. The crystallographic structures of the samples were analyzed by X-ray diffraction (XRD) using Cu-*Kα* radiation. The microstructure of the sample was measured by electron back-scattered diffraction (EBSD; TSL OIM) in a scanning electron microscope (SEM; Hitachi High-Technologies S-4300SE) with an electron beam energy of 20 keV, and a step size of 50 nm. Auger electron spectroscopy (AES) was used to determine the elemental surface mapping. The samples were analyzed using a scanning Auger electron microprobe PHI700Xi (ULVAC-PHI) with an electron beam energy of 10 keV, probe current of 10 nA, and diameter of approximately 20 nm. X-ray photoelectron spectroscopy (XPS) on a PHI-Quantera (ULVAC-PHI) was also used to determine the detailed chemical composition of the samples, using Al-*Kα* X-rays as the exciting source, at a beam diameter of about 100 μm.

3. Results

Fig. 1 shows typical AFM images of the surface of (a) Au(5 nm), and (b) Au(5 nm)/Ti(1 nm) thin films deposited on the a-SiO_2/Si(001) substrates before and after annealing (150–450 °C for 5 h). We also quantitatively investigated the surface morphology of the Au and Au/Ti films on the annealing temperature, by analyzing the AFM images of Fig. 1. Fig. 2 shows the surface coverage and root-mean-square (RMS) roughness of the samples as a function of the annealing temperature. Fig. 1(a-1) and (b-1) show the AFM surface topographies without annealing of Au and Au/Ti films, respectively. From the result of Fig. 2, the RMS roughness values of these images are (a-1) 0.32 ± 0.05, and (b-1) 0.39 ± 0.02 nm, indicating that the surfaces before annealing are almost flat. This means that the Au and Au/Ti films grow as a 2D layer growth onto the substrates at room temperature. However after annealing, noticeable differences in the dewetting process between the Au single layer and Au/Ti bilayer can be seen. In the case of Au single layer as shown in Fig. 1(a), dewetting progresses through the following stages with an increase in the annealing temperature between 150 and 350 °C: (a-2) small grain formation, (a-3) grain growth, and (a-4) breakup of grains into strand structure. Fig. 1(a-5) shows that after annealing at 450 °C for 5 h, the surface morphology changes into the formation of nanodot array of diameter ~60 nm. The dewetting of the Au single layer observed in this study seems to follow the typical grain boundary grooving process [21]. As compared to the Au single layer case, the dewetting process of the Au film drastically changes with the insertion of a 1-nm-thick Ti seed layer through the following stages with an increase in the annealing temperature shown in Fig. 1(b): (b-2) hole nucleation formation, (b-3) hole growth, (b-4) strand structure, and (b-5) breakup of strand into nanodot formation. In the case of the Au/Ti bilayer, the dewetting process is similar to the conventional void growth type dewetting phenomenon reported elsewhere [1,22,23]. The diameter of the fabricated nanodot with the 1-nm-thick Ti seed layer (Fig. 1(b-5)) is relatively large (~200 nm), as compared to that of the Au single layer (Fig. 1(a-5)). We think that this result may be attributed to the difference in the grain size formed in the films. Furthermore, as shown in Fig. 2, the surface coverage of the Au/Ti bilayers is smaller than that of the Au single layers in the entire measuring range of the annealing temperature in this study. This result indicates that the thin Ti layer inserted the Au film and the a-SiO_2/Si(001) substrate works as an effective seed layer to enhance the dewetting phenomenon of the Au film.

Fig. 3 shows the results of XRD measurements (θ-2θ scan) of the (c, e) Au, and (d, f) Au/Ti films deposited on the a-SiO_2/Si(001) substrate after annealing at (c, d) 250 °C, and (e, f) 450 °C for 5 h, respectively. For references, XRD patterns of (a) a-SiO_2/Si(001) substrate without annealing and (b) Ti single layer film (5 nm) after annealing at 350 °C for 5 h are also displayed in Fig. 3. As compared to Fig. 3 (a), in the case of the Ti single layer deposited onto the a-SiO_2/Si(001)(Fig. 3 (b)), the XRD pattern does not reveal any clear Ti peaks, except the diffraction peaks originating from the substrate. Therefore, the thin Ti single layer grown onto the a-SiO_2/Si(001) substrate showed an amorphous structure in this experimental condition. When an Au film was deposited directly on the substrate, fcc-Au(111) and (222) peaks were observed in both of the annealing temperatures, as shown in Fig. 3(c)and (e). These results reveal that after annealing in this experimental condition, the Au film on the a-SiO_2/Si(001) substrate has the fcc-(111) crystallographic orientation. Similar to the results of Au single layer samples, the XRD patterns of Au/Ti samples shown in Fig. 3(d) and (f) also consist of the fcc-Au(111) and (222) peaks. However, the intensities of these two peaks are greater than those of the no seed layer samples. The crystalline quality of the samples was also characterized by XRD rocking curve (ω-scan). Fig. 4 shows ω-scans taken around the fcc-Au(111) reflection of (a, c) Au, and (b, d) Au/Ti films, after annealing at (a, b) 250 °C, and (c, d) 450 °C for 5 h, respectively. Fig. 4(a) and (c) show that in the cases of the Au films without Ti seed layer, the fcc-Au(111) peaks are very broad. Therefore, the full-width at half-maximum (FWHM) values of these peaks cannot be accurately measured. On the other hand, the fcc-Au(111) peaks of the Au/Ti films (Fig. 4(b) and (d)) are relatively strong. The FWHM values of the Au/Ti films after annealing at (b) 250 °C, and (d) 450 °C are 1.9°, and 0.84°, respectively, which indicates that the fluctuation of the crystalline orientation of Au films prepared on the a-SiO_2/Si(001) substrate covered with an ultra-thin Ti seed layer is smaller than that of the films directly deposited on the substrate. Therefore, the crystallographic orientation of the dewetting Au film on the a-SiO_2/Si(001) substrate is enhanced by the introduction of the Ti seed layer between the Au film and substrate.

EBSD study was carried out at a dewetting stage of the Au/Ti film after annealing at 250 °C for 5 h. Fig. 5 shows the EBSD maps of a hole growth stage shown in Fig. 1(b-3). Fig. 5(a) is an image quality (IQ) picture of the Au/Ti surface measured over an area of 5.0×5.0 μm^2.