Electron Microscopy of Au/Ni Artificial Superlattice Films

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Cross-sections of Au/Ni multilayered films with artificial superstructures have been observed by a transmission electron microscope. Images have revealed alternate coherent stacking of [111] oriented fcc Au and Ni layers. Electron diffraction patterns indicate that films have fiber texture structures. In-plane coherent grain sizes are less than 10 nm. The surface morphology is dependent on the artificial period; films with shorter periods have smoother surfaces. Interface roughness in the range of 3–4 lattice planes causes columnar structures for the multilayered films with longer periods.

(Received February 2, 1990)

Keywords: electron microscopy, multilayered films, artificial superstructure, gold/nickel, epitaxy, interface roughness

I. Introduction

Metallic multilayered films with artificial superstructures (ASF's: Artificial Superlattice Films) have been extensively investigated in this decade as a new class of material with novel properties. Perpendicular magnetic anisotropy of Co/Pt ASF's⁽¹⁾ and giant magnetoresistance of Fe/Cr ASF's⁽²⁾ are typical examples of new properties originated from their artificial superstructures. Structures of ASF's have been characterized mainly by X-ray diffraction because X-ray diffraction is a convenient non-destructive method of knowing average structures of ASF's⁽³⁾⁽⁴⁾. Also, transmission electron microscopy (TEM) studies of ASF's have been reported^{(5)–(11)}. Especially, cross-sectional TEM images of multilayered films for soft X-ray optical elements, such as W/C or Mo/Si multilayered films with non-epitaxial structures, have clearly revealed the degrees of surface and interface roughness, crystallinity and interfacial reaction^{(5)–(8)}. Several TEM studies in high resolution mode for epitaxially grown metallic ASF's have been also reported^{(9)–(11)}.

In this paper, cross-sectional TEM images of epitaxial Au/Ni ASF's are presented. Typical features of Au/Ni multilayered films are as follows. Both Au and Ni metals have fcc structures. Despite of a large difference in lattice constants ($a_{\text{Au}}=0.40786$ nm, $a_{\text{Ni}}=0.3524$ nm and $(a_{\text{Ni}}-a_{\text{Au}})/a_{\text{Au}}=-0.14$), epitaxial growth of Ni films on [111] oriented Au films have been reported⁽¹²⁾⁽¹³⁾. The orientational relationship of epitaxy is $(111)_{\text{Ni}}// (111)_{\text{Au}}$; $[2\bar{2}0]_{\text{Ni}}// [2\bar{2}0]_{\text{Au}}$. A phase diagram of a bulk Au-Ni alloy shows a simple miscibility gap with a critical temperature at 810°C and mutual solubilities of Au and Ni are very limited at lower temperatures⁽¹⁴⁾. Therefore, the combination of Au and Ni is suitable for the fabrication of ASF's especially with short periods. Multilayered films with short period and high X-ray reflectivity are avail-

able for normal incidence mirrors of soft X-ray microscopes⁽¹⁵⁾. Because of a large difference in atomic number, Au/Ni ASF's are expected to show high X-ray reflectivity. Yang *et al.* have reported an anomalous enhancement of Young modulus for Au/Ni ASF's with a short period⁽¹⁶⁾, which is one of the novel properties of ASF's called as "Super-modulus effect". Magnetic properties of Au/Ni ASF's are also interesting. Epitaxial Ni films sandwiched by Au have been reported to show a steep fall down of ferromagnetic Curie temperature with decrease of film thickness at around 1.2 nm⁽¹⁷⁾. It seems that these properties for Au/Ni ASF's with short periods closely relate to their structural properties. However, structures of Au/Ni ASF's have not been clarified in detail.

II. Experimental Procedure

Samples were prepared by electron beam evaporation in an ultra-high vacuum. Pressure during deposition was less than 5×10^{-7} Pa. Layer thicknesses were controlled by a high speed shutter system combined with quartz thickness monitors. Deposition rates were kept at about 0.03 nm/s. Substrates were polyimide films and glass plates. At first, a 25.0 nm thick Au layer was deposited on a bare substrate at room temperature and then the film was kept at 150°C for 1 h in ultra-high vacuum. After the film was cooled down to 50°C, multilayered films were deposited. It is known that annealing at 150°C results in the formation of [111] textured Au films with fairly large grain sized of about 200 nm and with atomically flat surfaces⁽¹³⁾⁽¹⁸⁾.

Samples were examined by X-ray diffraction to check the texture and artificial period. TEM observations were performed by a transmission electron microscope (JEOL JEM-2000EX) equipped with a top-entry goniometer stage, operating at 200 kV. Specimens for plane views were peeled off from a glass substrate using a copper mesh with mesh cement. Specimens for cross-sectional views were prepared by ultra-microtomy. Samples with polyimide substrate were embedded in epoxy resin and

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were sliced by a diamond knife edge. Thin fragments floated on water were collected on a microgrid supported by a copper grid mesh.

III. Results and Discussion

1. X-ray diffraction

Four samples have been investigated in the present work. Their nominal layer thicknesses are Au(5.0 nm)/Ni(5.0 nm)/Au(25.0 nm) (sample A), [Au(5.3 nm)/Ni(5.3 nm)]₁₀/Au(25.0 nm) (sample B), [Au(3.0 nm)/Ni(3.0 nm)]₁₇/Au(25.0 nm) (sample C) and [Au(1.0 nm)/Ni(1.0 nm)]₅₀/Au(25.0 nm) (sample D). Sample A is a sandwich film to check the epitaxy by plane views. Figure 1 shows X-ray diffraction patterns of these samples. Their scattering vectors are perpendicular to the film. They indicate [111] texture growth of both Au and Ni layers. No peaks indicating other orientations like [100] were detected. Samples B, C and D show superlattice reflections (satellite reflections) of which spacings agree with nominal bilayer thicknesses. The observed periods were 10.7, 6.0 and 1.9 nm for samples B, C and D, respectively. The numbers of (111) lattice planes in the individual Au and Ni layers, n_{Au} and n_{Ni} , estimated by preliminary analyses of peak intensities are as follows: $n_{\text{Au}}=21$ and $n_{\text{Ni}}=27$ for sample B, $n_{\text{Au}}=12$ and $n_{\text{Ni}}=15$ for sample C and $n_{\text{Au}}=4$ and $n_{\text{Ni}}=5$ for sample D. Detailed analyses of X-ray diffraction intensities are in progress and will be published elsewhere.

2. Plane views of a buffer layer and a sandwich film

Figure 2 shows plane views of a 25 nm thick Au film and sample A. An electron diffraction pattern (EDP) of the Au film shown in (a) indicates that the orientation of crystallites in the film plane is at random but that the film has an [111] texture. The grain sizes range from 50 to 500 nm as shown in (b). A selected area EDP and a Moiré fringe pattern of sample A are shown in (c) and (d). A small selected-area aperture, of which radius is about 0.3 μm on the image, was located on a fairly large grain of Au so as to give a single crystalline EDP. For the Moiré fringe observation, an objective aperture with its radius of 7 nm^{-1} was located on the 000 spot. The EDP shows a net pattern corresponding to (111)* reciprocal planes of both fcc Au and Ni. Many satellite spots are visible around each spot because of the double diffraction effect. The spacing and direction of satellite spots indicate an in-plane epitaxial orientation of $[\bar{2}\bar{2}0]_{\text{Ni}} // [\bar{2}\bar{2}0]_{\text{Au}}$. The sharpness of spots indicates that there exists not so much rotation of in-plane orientation throughout from the bottom Au layer to the top Au layer. There appear forbidden spots at $(n/3)(422)_{\text{Au}}^*$ (n : integer) and their equivalent positions. These forbidden spots have been already reported by Renard and Nihole for Au/Ni/Au and Au/Co/Au sandwich films⁽¹³⁾. Their intensities arise when the number of Au(111) lattice plane is not a multiple number of 3: namely the unit period of fcc stacking. The appearance of these forbidden spots implies the

Fig. 1 X-ray diffraction patterns of sample A: Au(5.0 nm)/Ni(5.0 nm)/Au(25.0 nm) sandwich film, sample B: [Au(5.3 nm)/Ni(5.3 nm)]₁₀/Au(25.0 nm) ASF, sample C: [Au(3.0 nm)/Ni(3.0 nm)]₁₇/Au(25.0 nm) ASF and sample D: [Au(1.0 nm)/Ni(1.0 nm)]₅₀/Au(25.0 nm) ASF.

flatness of Au layers.

Moiré fringe patterns of fcc/fcc hetero-epitaxial films have been discussed by Bassett *et al.*⁽¹²⁾. The parallel Moiré fringe spacing under the $[\bar{2}\bar{2}0]_{\text{Ni}} // [\bar{2}\bar{2}0]_{\text{Au}}$ configuration is 0.92 nm when the Au and Ni layers have the same lattice spacings as the bulk metals. The observed fringe spacings are about 1.0 nm and agree with the calculated value. Under the present observation condition, the Moiré patterns should be dot patterns because of the 6-fold symmetry of the (111) lattice plane. The observed image in Fig. 2(d) shows a dot pattern locally with heavy modulation. The modulation indicates a small in-plane coherence length of the Ni layer and also tilting of the Ni(111) lattice plane with respect to the Au(111) plane.

3. Cross-sectional views of multilayered films

Figure 3 shows low magnification cross-sectional images of samples B, C and D with periodic multilayered structures. The black and white stripe contrast is indicative of the alternate stacking of Au and Ni layers. The black and white contrasts correspond to Au and Ni layers, respectively. Stripe contrast is visible even for Sample D with the shortest period of 1.9 nm. Surface morphology depends on the period. Sample D with the shortest period has much more flat surface than samples B and C with

Fig. 2 Plane views of a Au buffer layer and a Au/Ni/Au sandwich film. (a) an electron diffraction pattern and (b) a bright field image of 25 nm thick Au film. (c) a selected area electron diffraction pattern and (d) a Moiré fringe pattern of sample A.

Fig. 3 Low magnification images of cross-sections of multilayered films (samples B, C and D).

longer periods. The surface roughness of samples B and C is ascribable to the columnar structures in the multilayered regions. In-plane dimensions of the columns increase with decreasing artificial period. Typical values of grain sizes are about 30 nm for sample B and 50 nm for sample C. The image of sample D with the shortest period of 1.9 nm does not show any distinct columnar structure. It is to be noted that multilayered structures near the Au buffer layers are fairly flat even in the case of samples B and C. The boundaries of columns are not necessarily located at grain boundaries of buffer Au layers.

Figure 4 shows selected area EDP's of the cross-sections for samples B, C and D of which images are shown in Fig. 3. The radius of the selected-area aperture was about $0.3\ \mu\text{m}$ on the images. Therefore, the diffraction patterns give information on multilayered films with a few grains of the Au buffer layer. However, the observed EDP's are all fiber diffraction patterns. A schematic EDP for the Au[111]/Ni[111] fiber texture structure is sup-

plemented on the lower right hand portion of Fig. 4. The observed EDP's well agree with this pattern and indicate the preferred orientation of the Au and Ni (111) lattice planes. The EDP for sample D, which was observed by locating the selected-area aperture on a fairly large grain of the buffer Au layer, shows sharp diffraction spots from the Au buffer layer as indexed in the figure. They form a net pattern corresponding to the $[11\bar{2}]$ -zone EDP of fcc-Au. The multilayered film is not a single crystalline but has a fiber texture structure even on a grain of the Au buffer layer. The broadening in an arch form of the diffraction spots on the fiber axis indicates the orientational distributions for both Au(111) and Ni(111) lattice planes in the range within $\pm 5^\circ$. Off-axial diffraction spots, like (200), (11 $\bar{1}$) or ($2\bar{2}0$), are very broad and diffuse especially in the case of samples C and D with shorter periods. Coherent grain sizes in the film plane are much smaller than that of the Au buffer layer. Thus, the multilayered film on a grain of the Au buffer is composed of small crystallites of which overall orientations are at

Fig. 4 Selected area electron diffraction patterns of cross-sections for samples B, C and D of which images are shown in Fig. 3. A schematic diffraction pattern for Au[111]/Ni[111] fiber texture structure is also shown.

Fig. 5 Lattice images of sample C (a) and D (b) for regions near the buffer layers.

random. Therefore, no difference in diffraction contrast is observed among the columns. However, neighboring Au and Ni crystallites keep the in-plane epitaxial orientation $[2\bar{2}0]_{\text{Ni}} // [2\bar{2}0]_{\text{Au}}$ locally near the buffer layer as revealed by the plane views shown in Fig. 2(c) and (d). It seems that there occur gradual rotations of the in-plane orientation with increasing layer number for both Au and Ni layers.

Figure 5(a) and (b) show lattice images of samples C and D, respectively. In the image of sample C, some Au(111) and Ni(111) lattice fringes extend continuously into the black and white stripe regions arising from compositional modulation. This observation indicates that Au(111) and Ni(111) lattice planes are coherently stacked. However, the observed lattice fringe patterns are somewhat wavy and strong diffraction contrast is visible

at some parts. Also, the boundaries of Au and Ni layers are not strictly parallel to the lattice fringes. These observations indicate a small in-plane coherence length of less than 10 nm and an interface roughness in the range of 3–4 monolayers of (111) lattice planes. The interface roughness increases as the interface moves apart from the buffer layer. A significant bending of stripe contrast is seen at the upper part of the photograph marked by a white arrow, which corresponds to an onset of boundary for columnar structure in the image shown in Fig. 3. The interface roughness is enhanced with increasing layer number. A possible mechanism is as follows. A large misfit between Au(111) and Ni(111) lattice planes causes a loss of in-plane coherency and a rougher growth front with increasing layer number. The columnar structure is formed with the so-called shadowing mechanism after

the growth front becomes fairly rough.

The lattice image of sample D also shows the (111) lattice fringes of fcc structure indicative of coherent stacking of Au and Ni layers. Lattice fringe patterns are wavy and diffraction contrast is also visible. The black and white stripe contrast is not so clear as that in sample C. Because the interface roughness is in the range of 3–4 monolayers as observed in sample C, the interfaces of sample D with an average period of 9 lattice planes ($4\text{Au}(111)+5\text{Ni}(111)$) are heavily disordered. Further details of interface structures are not clear because the observed image is a projection along the thickness of probably more than 30 nm. In spite of large interface roughness, the (111) lattice fringes are nearly continuous and there exists no distinct disorder in the growth orientation like the [100] orientation. The uniformity suggests large lattice strains both in Au and Ni layers and a smaller lattice misfit in this sample. X-ray diffraction measurements of in-plane lattice dimensions and in-plane coherence lengths are in progress. Their pre-

liminary results have revealed a 2% contraction of $\text{Au}(2\bar{2}0)$ lattice spacing and an 4% expansion of $\text{Ni}(2\bar{2}0)$ lattice spacings compared with bulk lattice spacings for sample D.

IV. Summary

The results are summarized as follows.

- (1) A 5.0 nm thick Ni layer sandwiched by Au layers grows epitaxially with an orientational relationship of $\text{Ni}(111)\parallel\text{Au}(111)$; $\text{Ni}[2\bar{2}0]\parallel\text{Au}(2\bar{2}0)$. Moiré fringe pattern indicates a layered overgrowth of Ni layers. However, many defects were detected.
- (2) Alternate stacking of Au and Ni in the multilayered films was revealed by cross-sectional images even for a sample with the shortest period of 1.9 nm. The surface morphology of multilayered films is dependent on the period and it was found that films with shorter periods have smoother surfaces.
- (3) Multilayered films have fiber texture structures

with the [111] orientation of fcc structure. The lattice images have clearly shown the coherent stacking of Au(111) and Ni(111) lattice planes. Lattice fringe patterns indicate many defects both in Au and Ni layers and small in-plane coherence lengths.

(4) Interface roughness is within 3–4 atomic planes. The cumulative interface roughness causes columnar structures for multilayered films with a longer period.

Acknowledgment

This work has been supported in part by Grant in-aid for Scientific Research on Priority Areas, "X-ray Imaging Optics", Contact Number 01651003 from the Ministry of Education, Science and Culture, Japan.

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