GRAIN PREFERENTIAL ORIENTATION OF Ag/Ni MULTILAYERED FILM[①]

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ABSTRACT Grain preferential orientation of Ag/Ni multilayered films with different layer thicknesses (each Ag and Ni layer consists of 5, 8, 20 and 40 atomic planes for different films respectively) have been investigated by transmission electron microscopy. For Ag and Ni grains of fcc lattice structure, there is a dominant [111] preferential orientation along the growth direction, the film is mainly [111] textured. But the texture axis may deviate for about 20° and some extend of ⟨121⟩ texture may be formed as the result. Increasing of the layer thickness restrains this axial deviation and enhances [111] texture. The electron diffraction analysis indicates that multilayered film may consist of columnar structure, Ag and Ni grains in each column take the same orientation while grains in adjacent columns have correlated but somewhat different in-plane orientations. At the first stage of deposition of layers on the glass substrate, the grains show preferential orientation in growth direction only, the in-plane orientations are at random. The in-plane texture of the film is formed when the deposition is further proceeded.

Key words multilayered film electron diffraction preferential orientation texture

1 INTRODUCTION

The very thin metallic layers may exhibit different structural characteristics from those of bulk materials with the same composition, and the interaction between two elemental layers may probably induce new effects. Stimulated by these interesting features, metallic multilayered film have been a hot spot of study in the field of new materials in recent years. The influence of layer thickness on the elastic and magnetic properties of metallic multilayered films had been studied by some authors[1-3]. The grain structure and the structural correlations between grains in two elemental layers play important roles in the physical properties of multilayered materials. The present paper focus on the transmission electron microscopy (TEM) investigation of grain preferential orientation of Ag/Ni multilayered films, and the influence of layer thickness on it. Choosing of Ag/Ni system was based on the consideration that in the bulk state, the Ag-Ni system has a very limited mutual solubility[4], and both metals show fcc structure but with a large difference in lattice parameters (a_{Ag} = 0.4085 nm, a_{Ni} = 0.3523 nm, $f = \Delta a/a = 0.15$). Thus, Ag/Ni multilayered film has the features of having a periodic structure with sharp concentration modulations and a large lattice mismatch at the interfaces between two elemental layers.

2 EXPERIMENT

2.1 Samples

Ag/Ni multilayered films were provided by CENG (Central d' Etudes Nucleairs de Grenoble) of France. They were prepared by cathodic sputtering: alternately depositing Ag and Ni layers with several atomic planes on glass substrate, thus the artificial periodic structure of bi-metallic layers was formed. According to the nominal number (N_{Ag} and N_{Ni}) of atomic planes in Ag and Ni elemental layers, the samples are denoted as N_{Ag}/N_{Ni}, i.e. 5/5, 8/8, 20/20 and 40/40 respectively. The total thickness of these multilayered films is about 5 μm, the films could be

① Received Dec. 12, 1997; accepted Feb. 27, 1998

easily detached from the glass substrate.

2.2 TEM observations

TEM experiments were mainly carried out with JEOL-200CX transmission electron microscope. The observations were carried out mainly with plane-view specimens, thus the electron diffraction patterns contain in-plane structural information of the film. The plane-view TEM specimens were prepared by double-jet electropolishing and ion milling. For 40/40 multilayered film, besides the plane-view specimens, the cross-sectional specimen was also prepared with the method reported by Yang *et al*[5], and observed by TEM with incident electron beam parallel to the interfaces of the film. In order to measure the lattice spacings of the diffraction rings, very thin Cu polycrystalline film was deposited on some of the TEM specimens and its diffraction rings were taken as the calibration.

3 RESULTS AND DISCUSSION

At first, examine the electron diffraction pattern of 20/20 plane-view specimen as shown in Fig. 1(a). According to the values of lattice spacing d, the diffraction rings are indexed as (from low d spacing to higher d spacing) Ni(220), Ag(220), Ni(111), Ag(111) and Ag(422)/3 (see Fig. 1(a)) respectively. Near the inner side of Ni(111) ring, there is a very weak Ni(422)/3 ring could be observed. No (200) ring could be found. The intensities of the diffraction rings are not uniform but divided into arcs showing 6-fold symmetry, and with Ag and Ni diffraction arcs of the same indexes always in the same directions. According to the diffraction theory, for fcc Ag elemental layer, when the number of (111) close-packed atomic planes parallel to the interfaces is $N = 3n$ (n is an integer number, thus the layer consists of several complete fcc unit cells), (422)/3 is a forbidden diffraction and will not appear. When $N = 3n \pm 1$, i. e., besides the complete fcc unit cells, there are "surplus" atomic planes in each Ag layer, these "surplus" atomic planes cause the structural factor of the (422)/3 reflection being non-zero, and result in the appearance of Ag (422)/3 diffraction ring. The formation of this (422)/3 "forbidden" diffraction in fcc thin film had already been discussed by Cherns[6]. The existance of Ag(422)/3 and Ni(422)/3 forbidden rings in Fig. 1(a) indicates that the (111) planes of the lattice are parallel to the surface of the film, in other words, the grains in Ag/Ni multilayered film exhibit [111] preferential orientation along the film growth direction. The electron diffraction pattern of 5/5 specimen is shown in Fig. 1(b). The pattern of 8/8 film is similar to that of 5/5 film, while the pattern of 40/40 film is similar to that of 20/20 film. Judge from the similarity of these patterns, the structures of these samples are believed to be basically the same, although there may be some differences between them indicated by the small disparities in the diffraction patterns. For 40/40 film, the TEM bright field image of the cross-sectional specimen shows clearly the periodic layered structure. In the corresponding electron diffraction pattern, along the perpendicular direction of the layers the Ag(111) and Ni(111) spots appear much stronger than those in the other directions, confirming the existence of [111] texture along the growth direction in multilayered film. Comparing the diffraction patterns of 5/5, 8/8, 20/20 and 40/40 samples, it is found that the relative intensities of Ag(422)/3 and Ni(422)/3 forbidden diffractions increase with the layer thickness. It seems to indicate that the [111] texture of the multilayered film gets relative stronger with the increasing of layer thickness. It is well known that for electron diffraction, if the multilayered film is completely [111] textured, there would be no (111) diffraction for plane-view specimen; besides, in a single set of fcc lattice the (111) diffraction never exhibits six-fold symmetry. But in our experiment, the diffraction patterns show rather strong Ag(111) and Ni(111) rings. Moreover, these (111) diffractions exhibit six arcs with six-fold symmetry. This puzzling result may have the following two explanations.

The first explanation: Examine the stereographic projection of the fcc lattice as shown in Fig. 2, near [111] axis there are [121], [112] and [211] axes exhibiting three-fold symmetry

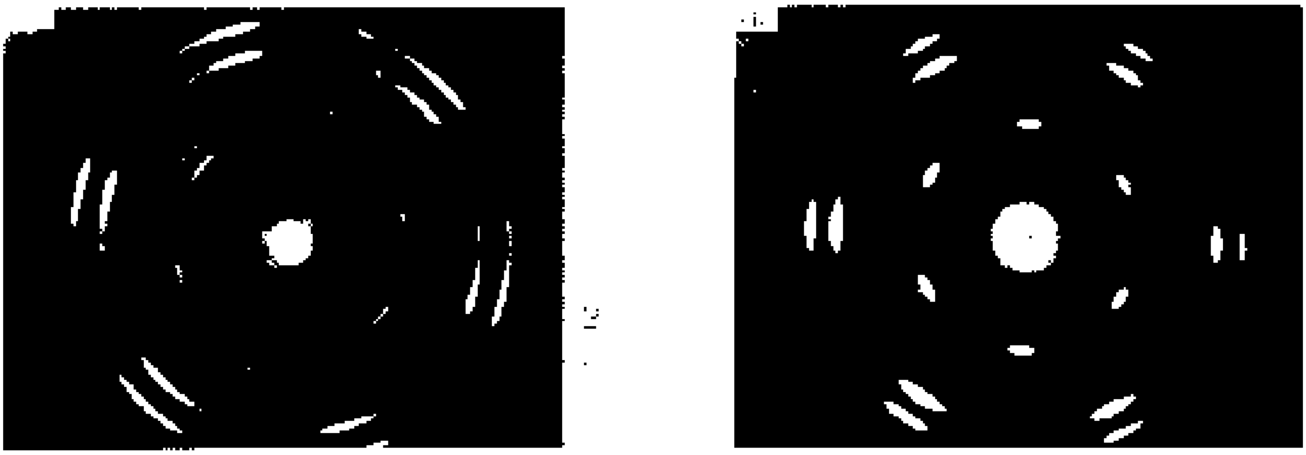

Fig. 1 Selected area electron diffraction patterns of 20/20 (a) and 5/5 (b) multilayered films

with each other around the [111] axis. The angles between [111] and these three ⟨121⟩ axes are the same, i.e. $\theta = 19.47°$, which is the smallest one among the angles between [111] and the other directions. The existance of (111) diffraction arcs is probably caused by the fact that in these samples, besides the [111] texture, there is some extend of ⟨121⟩ texture appearing as the result of the anisotropic deviation of the [111] texture axis. Such axis deviation has been observed by high resolution electron microscopy in an Ag/Ni cross-sectional specimen[7]. Its origin may be due to the steps necessary to achieve the relaxation of the Ag/Ni interfaces by misfit dislocations. Three sets of ⟨121⟩ preferential oriented grains with texture axes exhibiting three-fold symmetry around the [111] axis form the six-fold (111) and (220) arcs in the diffraction pattern (also no (200) diffraction). For fcc lattice, (111) is the most close-packed plane, thus [111] texture is the most energy favourable for the growth of Ag/Ni multilayers system. The deviation of the texture axis would enhance the total free energy of the system, so it is reasonable that with further progress of deposition of the layer (layer getting thicker), the deviation of the axis tends to be restrained and [111] texture tends to be enhanced.

The second explanation: Considering the very short periodicity of these multilayers, the

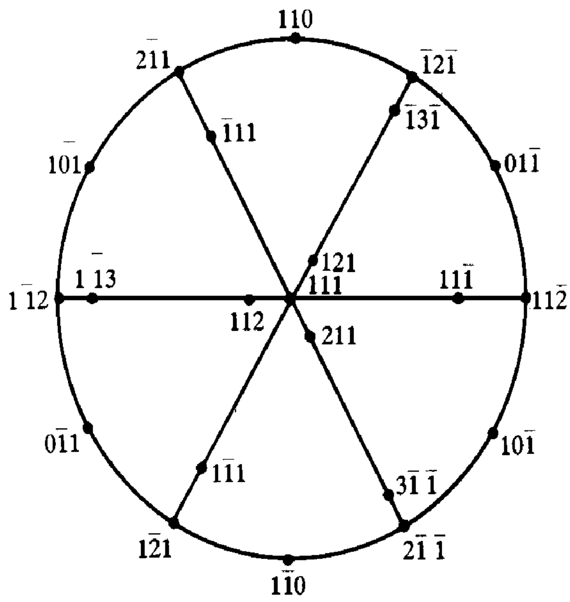

Fig. 2 Stereographic projection of fcc lattice

appearance of (111) diffraction rings may also be due to the higher-order Laue zone diffraction phenomenon of [111] preferential oriented grains. Since the elemental layers in the multilayered films are very thin, the reciprocal lattice spots appear as elongated rods with the elongation direction perpendicular to the layers. Thus it is possible that the Ewald sphere cuts the $11\bar{1}^*$ reciprocal rods at the first-order Laue zone which gives $(11\bar{1})$ diffraction. The angle between $[11\bar{1}]^*$ direction and $(111)^*$ plane is also

19.47°. The TEM specimen-tilting experiment shows that, when the specimen is gradually tilted around an axis, and the angle between the incident electron beam and the normal of the multilayered film is changed from 0° to about 20°, the (111) diffraction in the direction perpendicular to this axis gets continuously stronger. Then it tends to be weaker with further tilting. This result support the explanation stated above.

In the diffraction patterns of 20/20 and 40/40 samples, there is a strong diffracton ring near the incident spot with *d* spacing of about 1 nm. This *d* value is quite near the calculated spacing of the Moiré fringe formed by the parallel and same oriented Ag(220) and Ni(220) planes (d = 0.92 nm). In the bright field image of 40/40 sample heat treated at 200 ℃ as shown in Fig. 3, there are many parallel Moiré fringes with spacing agree with the above calculated value, which are believed to be formed by parallel Ag(220) and Ni(220) planes. Thus the small diffraction ring near the incident spot is the contribution of double diffraction from Ag(220) and Ni(220) planes. Such double diffraction has also been observed in Au/Ni superlattice films[8]. The appearance of strong double diffraction, and the fact that the diffractions from Ag and Ni planes of the same indexes are always in the same directions indicates that in a single column of the multilayers (which will be described later), most of the Ag and Ni grains keep the same orientation. It is found that the appearance of double diffraction is also dependent on the layer thickness: it is absent in 5/5 sample and begins to appear in 8/8 sample, although the intensity is very weak then. When the layer thickness increase, the double diffraction ring gets stronger. The ideal double diffraction is formed from two crystals whose lattices be undistorted and parallel to each other. The absence of double diffraction in 5/5 sample is probably due to the large coherency strains induced by the large lattice mismatch between two layers. Increasing of layer thickness enable the formation of misfit to dislocate at the interfaces and reduce the lattice strain[9], thus is favourable for the appearance of double diffraction.

For all of the samples, besides the preferential orientation of grains along the growth direction of the multilayers, the intensity anisotropy of the diffraction rings indicates that there are in-plane preferential orientations too. The orientational spread of the diffraction arcs reflects the distribution of this preferential orientations of the grains among the selected area. The orientaional spread of (220) diffraction arc for 5/5, 8/8 and 20/20 multilayered films is 11°, 15° and 21° respectively, the spread range increases with layer thickness. The selected area for electron diffraction is as large as 1 μm², which contains a large amount of grains. It seems that during the layer growth, there is some correlation between the orientations of adjacent new grains, but this correlation is weak that there may be small orientational deviation between the grains. With the increasing of layer thickness, and as its consequence, the number of grains, the cumulative in-plane orientational scatter gets larger and results in the increase of the spread range of the diffraction arcs. During TEM observations of all the samples, when the area selecting aperture is laterally displaced, the orientations of arcs in the diffraction patterns are simultaneously changed continuously. Referring to the report of columnar structure found in Au/Ni multilayered film[8], this phenomenon can be explained by the following morphological description: the Ag/Ni multilayered film consists of a lot of columns perpendicular to the layer with cross-sectional area much smaller than the TEM selected area.

Fig. 3 TEM bright field image of 40/40 sample showing the Moiré pattern

In each column the in-plane orientation of the grains is the same, while neighbouring columns show correlated but somewhat different in-plane orientations. In order to study the influence of glass substrate on the structure of multilayered film, for the 20/20 sample, the thin TEM specimens from the part contacting the substrate during deposition (the bottom side of the film) and from the part exposing to the air (the top side of the film) had been prepared by single-jet electro-polishing. The electron diffraction pattern of the bottom side specimen is shown in Fig. 4, compare it with Fig. 1(a) (taken from the central part of the 20/20 film), the diffraction rings do not split into arcs but are homogeneous in intensity, although the relative intensities of the rings are similar to that of Fig. 1(a). The diffraction pattern of the top side specimen is equivalent to that of Fig. 1(a). These results indicate that, at the first stage of deposition of multilayers on the glass substrate, there is preferential orientation along the growth direction only, the in-plane orientations of grains are at random. As deposition of layers being further proceeded, the in-plane preferential orientation (texture) is established progressively probably due to the correlation between neighbouring grains which tend to have the same orientation. It is probably the amorphous structure of the glass substrate which is unfavourable to the formation of the in-plane texture.

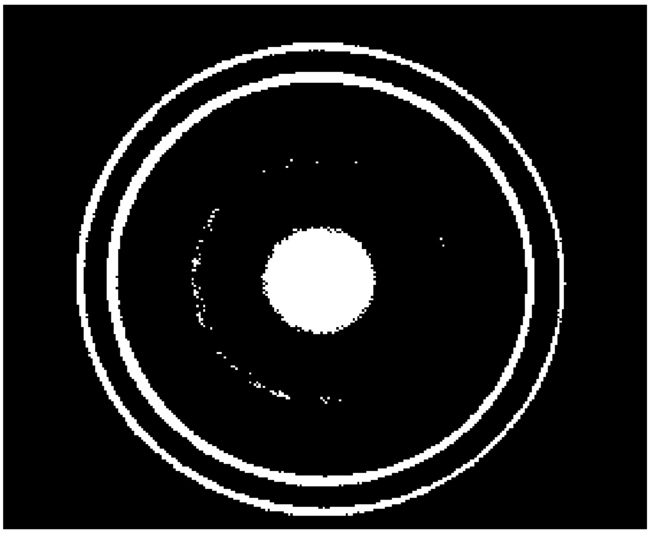

Fig. 4　Electron diffraction pattern of the foil contacted to the glass substrate during deposition of 20/20 sample

4 SUMMARY

For Ag/Ni multilayered film, there is a dominant [111] texture along the growth direction. The texture axis may exhibit orientational deviation for about 20° and result in the formation of ⟨121⟩ texture in some extend. With increasing of layer thickness, the deviation of texture axis tends to be restrained and [111] texture tends to be enhanced. It is proposed that the multilayered film consists of columnar structure, Ag and Ni grains in each column take the same orientation while grains in adjacent columns show correlated but somewhat different in-plane orientations. At the first stage of deposition of multilayers on glass substrate, the grains show preferential orientation in growth direction only, the in-plane orientations are at random. With further deposition, the in-plane preferential orientation is formed.

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(Edited by Zhu Zhongguo)