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MICROSTRUCTURAL EVOLUTION OF Fe GROWN ON A (001) Cu FILM AND ITS IMPLICATION TO THE ELASTIC ANOMALY IN METALLIC SUPERLATTICES

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ABSTRACT

A large softening of the shear modulus has been reported in metallic superlattices composed of insoluble bcc/fcc metals. In an attempt to understand this elastic anomaly, we have studied the microstructure of Fe/Cu bilayers as a function of the Fe thickness with transmission electron microscopy (TEM). Analysis of the moire fringes observed in plan-view TEM images revealed that the fcc Fe structure epitaxially grows on the (001) Cu up to a thickness of 2.0 nm. At 2.3 nm, the bcc Fe structure nucleates, accompanying lattice rotation around the growth direction with respect to the underlying fcc structure. As the Fe thickness further increases, the submicron polycrystalline grains formed. Based on these results, the microstructure of the metallic superlattices and its relation to the softening of the shear modulus will be discussed.

INTRODUCTION

Since Hilliard and coworkers [1-3] discovered anomalously large enhancement of the elastic moduli in various fcc/fcc superlattices, significant effort has been paid to understand this phenomenon both theoretically and experimentally. However, in recent years, this enhancement effect has been creating great controversies based on contradictory observations showing no enhancement [4-7]. In contrast, bcc/fcc superlattices have been found to exhibit substantial softening of the shear modulus [8-11]. Although the softening effect is a widely observed phenomenon in bcc/fcc superlattices [12], the mechanism is not well understood to date. Experimentally, variation of the lattice parameter in the superlattices has been reported to be relevant to the softening [9,13]. It has been shown theoretically that lattice rotation around the growth direction at the interface can cause variation of the lattice parameter and concomitant softening of the shear modulus [14]. In order to verify this theoretical prediction and to better understand the relation between the lattice parameter variation and the elastic anomaly, crystallographic information in a local scale is essential.

Our objective is to investigate the microstructure of superlattices and the crystallography of adjacent layers, which then will be sought for correlations to the elastic anomaly. This paper is the first in a series of

study on the superlattices. Here, we start with Fe/Cu bilayers, which are the basic unit of the superlattice structure. In the present work, a single crystalline Cu film was grown as a substrate for Fe deposition. A single crystalline film offers clear advantages in crystallographic analysis compared to previous studies in which textured polycrystalline multilayers had often been used. The bilayers enable us to investigate in detail the microstructure of deposited film, the local crystallography, and the defect morphology by using TEM moire fringe technique [15]. The Fe and Cu system was chosen because the crystallographic orientation relationships between bcc-Fe and fcc-Cu are well known [16], which is a prerequisite for the moire fringe analysis. Furthermore, Fe and Cu are hardly soluble with each other [17], thus, eliminating chemical contributions to the elastic properties.

Since the largest softening is generally observed at a layer thickness of a few nm [8-11, 13], the present work centers on the microstructural evolution of Fe films with thicknesses in the range of 2.0 to 15.0 nm. The bilayer results will be used to discuss the possible relation between the microstructure of the superlattices and the elastic anomaly.

EXPERIMENTAL PROCEDURE

A UHV electron-gun deposition system (the base pressure 2×10^{-8} Torr) was used to synthesize Fe/Cu bicrystals. A single crystalline Cu layer of 200 nm in thickness was formed by depositing pure Cu (99.999%) at an evaporation rate of 0.3 nm/s onto an air-cleaved rock salt heated to 430 °C. After cooling the film to room temperature, pure Fe (99.998%) was deposited at an evaporation rate of 0.3 nm/s to thicknesses varied from 2.0 to 15.0 nm. The bicrystal film was removed from the rock salt substrate by desolving it in water, and floated onto a Cu grid for following TEM examination. The microstructure and the local orientation relationship (OR) between bcc-Fe and fcc-Cu were investigated as a function of the Fe thickness with a Philips CM-30 operated at 300 kV.

The moire fringe technique was employed to analyze the local OR. When two crystalline layers with different structures overlap in the incident-beam direction, moire fringes are observed in the image. The spacing (D) and direction (θ) of the fringe depend on a set of planes which strongly diffract the incident beam, and can be calculated from the plane spacing (d_1 and d_2) of each layer and the angle (ϕ) between two planes by the following equations [15]:

$$D = \frac{d_1 d_2}{(d_1^2 + d_2^2 - 2d_1 d_2 \cos \phi)^{1/2}} ,$$

$$\theta = \sin^{-1} \left\{ \frac{d_1 \sin \phi}{(d_1^2 + d_2^2 - 2d_1 d_2 \cos \phi)^{1/2}} \right\} .$$

Here, the direction of the moire fringe is expressed as an angle of the fringe relative to the plane of spacing d_1 . These values were calculated by using the above equations for all possible OR's between bcc-Fe and fcc-Cu [16], and used to determine the local OR's. The calculated values and detail analysis are found in Ref. 18.

RESULTS

Figure 1 shows the plan-view bright field image and the corresponding diffraction pattern at an Fe thickness of 2.0 nm. Both the image and diffraction pattern show essentially the same features as a single crystal Cu. This is consistent with previous reports [19] in which Fe was found to adopt the fcc structure up to a thickness of approximately 2.0 nm. When the Fe thickness increases to 2.3 nm, moire fringes appear in the image, indicating the formation of different crystalline structure. The fringe directions are $[110]$ and $[\bar{1}10]$ and the spacing is approximately 1.4 nm. These values are explained by the formation of the bcc-Fe structure with four of the 12 variants of Pitsch OR. Although, it is not clear whether the bcc structure nucleates within the preexisting fcc-Fe or forms on top. The corresponding atomic arrangement at the structural interface is shown in Fig. 2. The parallel planes are $(001)_f // (110)_b$. The parallel directions are $[110]_f // [\bar{1}\bar{1}1]_b$, $[110]_f // [\bar{1}11]_b$, $[\bar{1}\bar{1}0]_f // [\bar{1}\bar{1}1]_b$, and $[\bar{1}\bar{1}0]_f // [\bar{1}11]_b$, where subscripts f and b represent fcc and bcc structures, respectively. This arrangement is the same as that predicted theoretically by the invariant line condition [20]. As treated in the theory, the fcc to bcc structural transformation is geometrically realized by uniform deformation of the fcc structure along the principal direction, $[100]_f$ and $[010]_f$, and subsequent lattice rotation by 9.7° around the $[001]_f$ direction.

As the Fe thickness further increases to 5.0 nm, more areas exhibit moire fringes with various directions and spacings, indicating the formation of bcc-polycrystalline layer. The diameter of polycrystalline grains, characterized by a set of the same type of fringes, are from 5 to 15 nm. These values are in the same range as those observed in the thicker Fe film, in which polycrystalline grains were more clearly observed [18]. Using the calculated directions and spacings [18], approximately 70% of the all grains in the image are explained by either the Kurdjumov-Sacks, Nishiyama, or Pitsch OR's [21]. The rest of the grains cannot be explained by the known OR's. This is probably due to the local bending of the film which causes the deviation of the fringe direction and spacing from the calculated values [22].

DISCUSSION

Based on the present results, the relationship between the microstructure of multilayer films and the elastic anomaly will be discussed. The microstructure of the Fe layer was found to develop in

three steps. (1) The Fe film initially adopts the fcc structure. (2) When the Fe thickness reaches to a nominal thickness of 2.3 nm, the bcc-Fe nucleates with the Pitsch OR, which is associated with a lattice rotation around the growth direction of 9.7° with respect to the underlying fcc structure. (3) As the Fe thickness increases to 5.0 nm, more bcc-Fe nucleates with various OR's, causing the formation of the polycrystalline layer. Now, suppose that Fe and Cu are alternately deposited on a Cu single crystal. We would expect the three variations of the microstructure similar to the bilayer case depending on the bilayer repeat length (λ), i. e., the thickness of an Fe layer plus a Cu layer. For a very small λ , fcc-Fe and Cu are likely to grow in perfect epitaxy without producing large elastic strains at the interface. At a slightly larger λ , the Fe layer would be partially bcc with associated lattice rotation around the growth direction. This will result in the lattice rotation at every interface and the creation of large misfit strains. For a larger λ , polycrystalline, most probably textured, layers will form. Each of the polycrystalline grains will be arranged in such a way to minimize the elastic strain.

The elastic anomaly observed in Mo/Ni [9] and Nb/Cu [11] multilayers also showed variation in three steps. (1) When λ was very small, the shear modulus was independent of λ . (2) As λ increased to a few nm, the shear modulus dropped to a minimum value, and (3) gradually increased, with increasing λ , to a level comparable to the value in the first regime. Similar observations have been reported in other bcc/fcc multilayers [8, 10, 13]. Note that the value of λ which divides the elastic properties into the first and second regimes are remarkably similar to the value at which we observed the bcc phase formation associated with lattice rotation.

The close correlation between the expected multilayer structure and the observed elastic anomaly can be explained as follows. Since previous observations [9,13] found concomitant variation of the shear modulus and the lattice parameter (i. e. elastic strain), it is expected that in the first regime, in which perfect epitaxial growth occurs, the shear modulus is independent of λ . With increasing λ to the second regime, where the bcc structure forms, the elastic strain is induced, resulting in the variation of the shear modulus. In this regime, the present results show that lattice rotation occurs at the interface. Theoretically, the lattice rotation has been demonstrated to cause the softening of the shear modulus. Therefore, sudden decrease in the shear modulus is expected when λ increases from the first regime to the second regime. With increasing λ into the third regime, the softening effect will decrease due to the decreasing interface volume.

SUMMARY

We have studied the microstructure of bilayer Fe/Cu films as a function of the Fe thickness. As the Fe thickness increases from 2.0 to 2.3, and to 5.0 nm, the microstructure of the Fe layer changes from an epitaxial

fcc structure to the bcc structure accompanying lattice rotation and misfit strain, and to the bcc polycrystalline layer. This microstructural evolution appears to be correlated with elastic anomaly observed in the metallic superlattice, suggesting that the anomaly is driven by lattice rotation and elastic strains. In order to clarify this point more directly, detail studies of the microstructure and elastic properties are now in progress.

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Fig. 1 Variation of the bright-field image as a function of the Fe thickness varied from 2.0 to 2.3, and to 5.0 nm.

Fig. 2 Lattice matching between fcc (open circles) and bcc (filled circles) lattices, representing one of the four equivalent variants of Pitsch orientation relationship.

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