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著者	岡本 聡
journal or publication title	Journal of Applied Physics
volume	79
number	9
page range	6880-6883
year	1996
URL	<a href="http://hdl.handle.net/10097/47594">http://hdl.handle.net/10097/47594</a>

doi: 10.1063/1.361510

# Effect of surface free energy of underlayer materials on crystal growth of Co polycrystalline films

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(Received 3 April 1995; accepted for publication 23 January 1996)

Crystallographic texture of polycrystalline Co films prepared by sputtering on a variety of underlayers has been investigated. The texture of polycrystalline Co films greatly depends on underlayer material, and this dependence is well explained by taking into account the surface free energy difference between the underlayer material ( $\gamma_u$ ) and Co ( $\gamma_{Co}$ ). When  $\gamma_u$  is larger than  $\gamma_{Co}$ , Co films can be grown with a well-defined crystallographic texture of hcp-Co(001), which is the lowest surface energy crystal plane in order to minimize the total surface energy. In contrast, if  $\gamma_u$  is much smaller than  $\gamma_{Co}$ , no remarkable underlayer effects can be observed in the crystallographic structure of Co films. © 1996 American Institute of Physics. [S0021-8979(96)01209-3]

## I. INTRODUCTION

It is well known that the existence of underlayers causes remarkable changes in the structural and physical properties of thin films. Some underlayers play very influential roles in improving the magnetic and magnetotransport properties of thin films and superlattices.<sup>1-5</sup> For instance, usage of some kinds of materials, such as Ta, Hf, and so on, as underlayers greatly improves the crystallographic texture of spin-valve structures, such as substrate/underlayer/Ni-Fe/Cu/Ni-Fe/FeMn, resulting in an intensive increase of giant magnetoresistance.<sup>5-7</sup> Similar results were obtained in Co/Cu superlattices.<sup>8</sup> Unfortunately, it is still uncertain why these underlayers enhance the crystallographic texture of metallic layers, due to a lack of understanding of the thin film growth process. Nevertheless, we can easily imagine that the following two factors greatly influence the thin film growth process on underlayers: (1) the lattice mismatch at underlayer/film interfaces; (2) the difference of surface free energies between under- and overlayer materials. We report the crystallographic texture of polycrystalline Co films prepared by sputtering on a variety of underlayers having different surface free energies.

## II. EXPERIMENT

The Co films with various underlayers were deposited on surface oxidized Si(100) at room temperature in a dc magnetron sputtering system, with a base pressure of  $3 \times 10^{-7}$  Torr and an argon deposition pressure of 3 mTorr. Deposition rates of Co and various underlayers were held nearly constant ( $\sim 100$  Å/min) because film structures generally depend on the deposition rate.<sup>3</sup> The Co films are 700 Å thick except when specified otherwise. For a part of our samples annealing was carried out at 200 °C in a high vacuum furnace with a pressure of less than  $3 \times 10^{-6}$  Torr in order to remove the internal stress in the films. The crystallographic texture was studied by x-ray diffraction (XRD) using Cu  $K\alpha$  radiation.

## III. RESULTS AND DISCUSSION

A lot of classical experiments have revealed a relationship between film morphology and the melting point of film material ( $T_m$ ), that is, the density of deposited islands usually decreases with an increase of  $T_m$ .<sup>9-13</sup> This fact can be explained by considering the dependence of the adatom diffusion constant  $D = D_0 \exp(-E_a/kT)$  on  $T_m$ , where  $D_0$  is the constant and  $E_a$  is the activation energy for surface diffusion which is related to  $T_m$ .<sup>14</sup> Therefore, different ways of substrate coverage can be expected for different underlayer materials in an extremely thin thickness region. According to the recent calculation by Amar, Family, and Lam,<sup>15</sup> the diffusion constant plays an influential role in the dynamical growth process of a submonolayer film. In order to realize nearly complete coverage of the substrate surface by an underlayer, we set the underlayer thickness relatively large, to at least 100 Å.

Thin film growth modes are mainly governed by the surface free energies, the interface energy, and the strain energy.<sup>16,17</sup> The deposited film will nucleate as three-dimensional islands (Volmer-Weber growth) if  $\gamma_s - \gamma_f - \gamma_i - \gamma_e < 0$ , where  $\gamma_s$  is the substrate surface free energy,  $\gamma_f$  is the film surface free energy,  $\gamma_i$  is the interface surface free energy, and  $\gamma_e$  is the strain energy. To date there is still an enormous lack of experimental data on interface and strain energies for the various combinations of metal and substrate surfaces, so that the prediction for the growth of thin films is very difficult. However, it can be qualitatively anticipated that the films tend to wet the substrate easily and to form flat two-dimensional-like islands with an increase of  $\gamma_s$ . If  $\gamma_s$  is very large so as to satisfy  $\gamma_s - \gamma_f - \gamma_i - \gamma_e \geq 0$ , the deposited film will grow in two dimensions or layer by layer (Frank-van der Merwe growth). For the present bilayer system which comprised of an underlayer and a Co layer, if the surface free energy of the underlayer material ( $\gamma_u$ ) is much larger than that of Co ( $\gamma_{Co}$ ), it is expected that Co spreads out over the underlayer surface and takes a relatively flat, two-dimensional equilibrium shape to minimize the total surface energy. In this case, according to the discussions given by Feng, Laughlin, and Lambeth,<sup>3</sup> crystal planes with

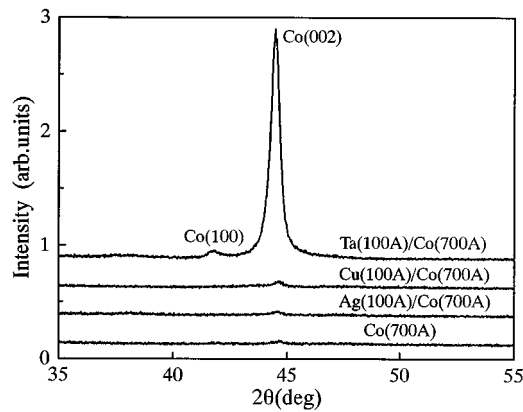


FIG. 1. The x-ray diffraction profiles of the Co films deposited on 100-Å-thick Ta, Cu, Ag with no underlayers.

the lowest surface energy of Co should cover the largest area of the underlayer surface. In order to check the validity of this model experimentally, we prepared a few kinds of bilayers of the form Si(100)/M(M:Ag,Cu,Ta)(100 Å)/Co(700 Å). Their (XRD) profiles are shown in Fig. 1. We note that Ag and Cu underlayers have little influence on the crystal structures of Co films. In contrast, Ta greatly enhances growth of the (001) texture of the Co film. Diffraction peaks from the underlayers were not found in these three samples. Comparing the surface free energies of these underlayer materials, the values of Ag (1.302 J/m<sup>2</sup>) and Cu (1.934 J/m<sup>2</sup>) are much smaller than that of Co (2.709 J/m<sup>2</sup>), while Ta (3.018 J/m<sup>2</sup>) is larger than Co.<sup>18</sup> This result suggests that the surface free energy of an underlayer material plays an influential role in the thin film growth process. Figure 2 shows the integrated diffraction intensity of Co(002) as functions of Co film thickness for Si/Co(*t*Å) and Si/Ta(100 Å)/Co(*t*Å) samples. We note that the Ta underlayer greatly enhances the crystallographic texture of the Co layer, and the integrated intensity of Co(002) is nearly proportional to the Co film thickness. This result indicates that the Ta underlayer promotes preferential crystal growth of Co films from its initial growth stage.

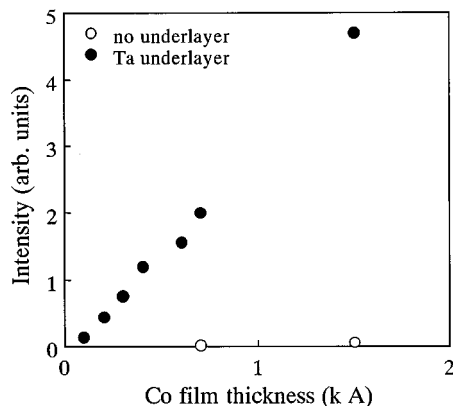


FIG. 2. The integrated diffraction intensity of hcp-Co(002) from Ta (100 Å)/Co (*t*Å) and Co (*t*Å) samples as a function of Co film thickness. The solid and open circles indicate the values obtained with and without Ta underlayers, respectively.

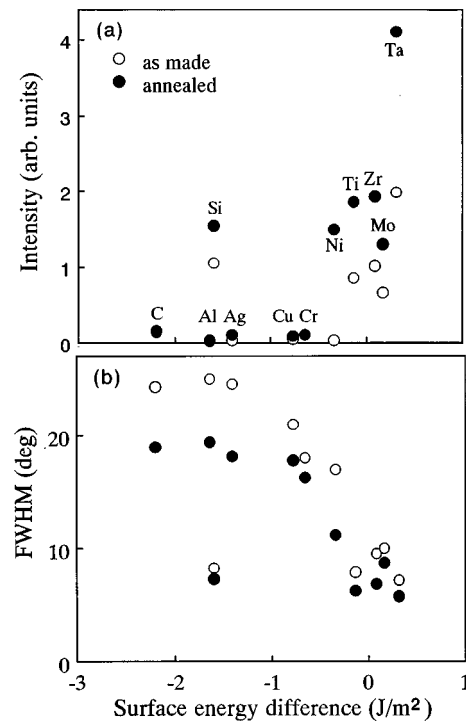


FIG. 3. (a) Diffraction intensity and (b) the FWHM of Co(002) from M (100 Å)/Co (700 Å) bilayers as a function of the surface free energy difference ( $\gamma_u - \gamma_{Co}$ ) between the underlayer material M and Co. As indicated C, Al, Si, Ag, Cu, Cr, Ni, Ti, Zr, Mo, and Ta were used as underlayer materials to vary the value ( $\gamma_u - \gamma_{Co}$ ). The open and solid circles indicate the data of as-prepared and annealed samples, respectively.

Figures 3(a) and 3(b), respectively, show the diffraction intensity from Co(002) and the full width at half-maximum (FWHM) of Co(002) rocking curves for underlayer (100 Å)/Co(700 Å) bilayer structures as a function of surface free energy difference ( $\gamma_u - \gamma_{Co}$ ). Any distinct diffraction peaks due to the underlayers cannot be detected in all samples. It can be noticed that the surface free energy difference ( $\gamma_u - \gamma_{Co}$ ) between underlayer material and Co is one of the most influential factors which determines the crystal structures of Co films. As the sign of ( $\gamma_u - \gamma_{Co}$ ) changes from minus to plus, diffraction intensity tends to increase along with a reduction of FWHM. That is, preferential growth of Co(001), which is the lowest energy crystal plane of hcp-Co, is enhanced when the Co film is grown on a higher energy underlayer surface. In order to investigate the relationship between diffraction intensity and FWHM, simple calculations were performed assuming that the rocking curves take the Gaussian form of  $I(\theta) = I_0 \exp[-(\theta - \theta_0)^2 / \sigma^2]$ , where  $I_0$  is the constant,  $\theta_0$  is the Bragg angle, and  $\sigma$  is the measure of Co (001) axis dispersion with respect to the film normal and has a relationship with FWHM as  $FWHM = 2(\log 2)^{1/2} \sigma$ . It can be noticed in Fig. 4 that the calculated result (solid line) can be well fitted to all the experimental data appearing in Fig. 3. This agreement between the calculation and the experiments indicates that the observed intensity is exclusively governed by dispersion of the crystallographic orientation of Co.

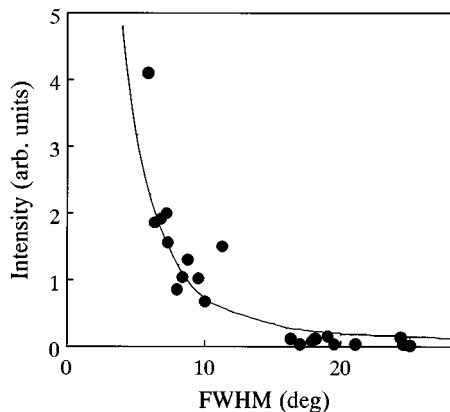


FIG. 4. The diffraction intensity vs the FWHM value obtained from Fig. 3. The solid curve indicates the calculated relationship between intensity and the FWHM.

As mentioned above, the surface free energy difference ( $\gamma_u - \gamma_{Co}$ ) between the underlayer material and Co is found to be deeply related to the crystallographic texture of a Co film in the underlayer/Co structures. In contrast, a Si underlayer exhibits a peculiar behavior different from other metallic materials, as noticed in Fig. 3. Although, at present, the reason for this behavior of Si is unclear, it is possible to consider that many dangling bonds at a Si surface might affect the underlayer/Co bond and thereby change the growth kinetics of the Co film.

It should also be pointed out that the underlayer thickness influences the texture of a Co film. Figure 5 shows the variation of the diffraction intensity from Co films as functions of the underlayer thickness for various materials. In the case where an underlayer material has a larger surface free energy than Co, such as Mo, Ta, and Zr, increasing the underlayer thickness deteriorates the crystallographic texture of Co polycrystalline films. According to XRD measurements (see, e.g., Fig. 6), we found that these underlayers effectively promote the preferential growth of Co(001) when they are amorphous, whereas a phase transition of the above underlayers from amorphous to crystalline states with an increase

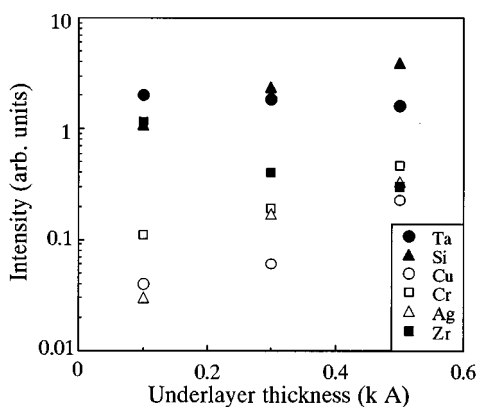


FIG. 5. The diffraction intensity of Co from M ( $\text{\AA}$ )/Co ( $700 \text{\AA}$ ) bilayers as a function of underlayer film thickness.

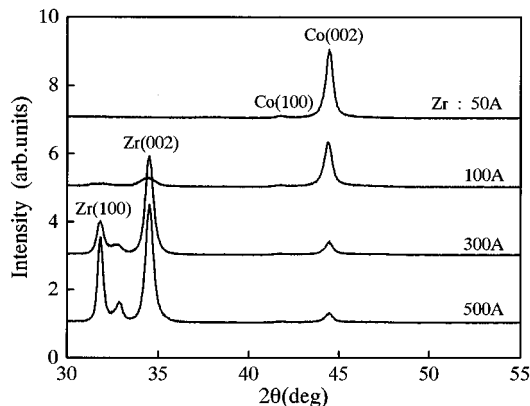


FIG. 6. Variation of the x-ray diffraction profiles of Zr ( $t \text{\AA}$ )/Co ( $700 \text{\AA}$ ) bilayers with the thickness of a Zr underlayer.

of thickness causes a deterioration of the texture of Co films. In contrast, Si underlayers were amorphous in the whole thickness range examined here and were always very effective in improving the crystallographic texture of Co films. The above results lead us to think that, once a crystallization process becomes distinct in the underlayer, one should deal with the thin film growth process in terms of other kinetics. Since bcc-Mo (lattice constant  $a = 3.146 \text{\AA}$ ), bcc-Ta ( $a = 3.302 \text{\AA}$ ), and hcp-Zr ( $a = 3.230 \text{\AA}$ ,  $c = 5.133 \text{\AA}$ ) crystals have large lattice mismatches with respect to hcp-Co ( $a = 2.507 \text{\AA}$ ,  $c = 4.069 \text{\AA}$ ), it is energetically unfavorable for crystal growth of Co because of the intensive increase of strain energy.

#### IV. CONCLUSION

In summary, the crystallographic texture of polycrystalline Co films greatly depends on underlayer material. This dependence is well explained by taking into account the surface free energy difference between the underlayer material and Co. When a high surface energy material, such as Mo, Ta, and Zr is used as an underlayer material, a Co film has a well-defined crystallographic texture. The reason considered here is that Co spreads out over the underlayer surface and takes the equilibrium shape of flat two-dimensional islands with preferential growth of Co(001), which is the lowest energy crystal plane that will minimize the total surface energy. In contrast with Mo, Ta, and Zr metallic underlayers, amorphous Si enhances the crystallographic texture of Co although its surface free energy is lower than that of Co. In this case, many dangling bonds at a Si surface might affect underlayer/Co bond strength and thereby change the growth kinetics of the Co film. More intensive structural studies are required to clarify the effects of underlayers on the growth dynamics of thin films.

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