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Film Growth and Magnetic Anisotropy of Thin Ni Electrodeposits on (001) Cu Films

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Thin electrodeposits of Ni prepared on (001) single-crystal Cu films are studied with an electron microscope. The perpendicular and crystalline anisotropies are also measured using a torque magnetometer. Misfit dislocations are observed from the thinnest deposit thickness (11 Å) examined. The elastic strain determined from spacings of misfit dislocations and moire fringes shows a lower decrease with Ni thickness than for vapor-deposited films. The measured anisotropy constants $2\pi M_s^2 + K_\perp$ and K_1 show strong thickness dependence. When the Cu substrate is removed from the Ni deposit, $K_\perp$ approaches zero and K_1 takes the bulk value. Effects of strain through the interaction with magnetostriction are discussed, and the calculated strain from $K_\perp$ agrees reasonably with the strain determined from electron microscopy.

Dünne Nickelschichten, elektrolytisch auf die (001)-Fläche einkristalliner Kupferschichten niedergeschlagen, werden mit dem Elektronenmikroskop untersucht. Außerdem werden die senkrechte und die Kristall-Anisotropie mit einem Torsionsmagnetometer gemessen. Von der dünnsten Niederschlagsdicke (11 Å) an werden Fehlanpassungsverschiebungen beobachtet. Die Spannung, bestimmt aus den Abständen der Fehlanpassungsverschiebungen und der Moiré-Streifen, zeigt eine geringere Abnahme mit der Nickeldicke als dies bei aufgedampften Schichten der Fall ist. Die gemessenen Anisotropiekonstanten $2\pi M_s^2 + K_\perp$ und K_1 zeigen eine starke Abhängigkeit von der Nickeldicke. Wird die Kupferunterlage von der Nickelschicht entfernt, nähert $K_\perp$ sich dem Werte null und K_1 nimmt den Wert des kompakten Materials an. Der Einfluß der Spannung durch die Wechselwirkung mit der Magnetostriktion wird diskutiert. Die aus $K_\perp$ errechnete Spannung stimmt leidlich mit der aus der Elektronenmikroskopie bestimmten Spannung überein.

1. Introduction

The epitaxial growth of Ni on Cu is of special interest because of the small misfit of 2.5%. Experiments have been reported for Ni/Cu bicrystal films [1 to 3], and in agreement with predictions of theory [4] one has observed the following facts: (i) the misfit is eliminated by elastic strain, i.e. the lattice spacing of Ni in the film plane assumes that of Cu, in the very early stage of film formation, and (ii) exceeding a critical film thickness interfacial or misfit dislocations are generated to accomodate a part of the misfit, so that the Ni lattice spacing approaches the bulk value as the film thickness increases.

On the other hand, the magnetic anisotropy is modified in very thin ferromagnetic films. The perpendicular anisotropy which tends to direct the magnetization normal to the film plane has been observed in amorphous [5], polycrystalline [6], and epitaxial films [6, 7]. It is interpreted in terms of the surface anisotropy which arises from the absence of neighboring atoms at the surface. In epitaxial films the presence of misfit strain may give rise to the perpendicular anisotropy [8] and modify the anisotropy in the film plane as well.

The aim of the present work is to study the electrolytic growth and the magnetic anisotropy of Ni on (001) Cu films. We measured the misfit strain by electron microscopy and perpendicular and crystalline anisotropies by torque magnetometry as a

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function of Ni thickness. It may be interesting to see whether the surface anisotropy is present or the anisotropies are attributed to effects of the misfit strain.

2. Experimental

We used electrodeposition to prepare thin Ni deposits. In case of evaporation the diffusion between Ni and Cu may cause difficulties in interpreting results; an appreciable amount of reduction of the magnetization is observed in Ni evaporated even at 200 °C on Cu films [9].

Single-crystal Cu substrates were prepared by evaporation on the air-cleaved (001) surface of rock salt at 310 °C in a vacuum of 10^{-6} Torr. The Cu films were floated on the electrolyte by immersion so that the subsequent deposition took place on the surface which had been adjacent to the rock salt [10]. Electrical contact was made to the floating film with a strip of Cu foil.

Ni was electrodeposited at room temperature and at a current density of 1 mA cm^{-2}. The electrolyte was made of 300 $NiSO_4 \cdot 6\,H_2O$, 6.2 H_3BO_3, and 3.1 g l^{-1} NaCl with pH 4.3. The thickness of Ni was measured with an X-ray microanalyzer which had been calibrated by a direct weighing method assuming a density 8.9 g cm^{-3} of bulk material. The real thickness of the magnetic Ni may be smaller than this due to possible oxidation at the surface. If we assume one or two atomic layers of the oxide, though no trace of oxidation was observed in transmission electron diffraction patterns, a reduction in thickness of 20% or less is estimated for the thinnest films of 40 Å for which magnetic quantities were measured. Thus the general dependence of K_1 and $K_\perp$ on Ni thickness is unchanged. The Ni specimens deposited on 1600 Å thick Cu were used for transmission electron microscopy. For magnetic measurements the specimens deposited on 3000 to 4000 Å Cu were prepared.

The magnetic anisotropy was measured with a torque magnetometer in a field of 10 kOe. By analyzing torque curves measured in the (001) film plane in a way similar to [11], the magnetocrystalline anisotropy constant K_1 was determined. On the other hand, from peak values of the perpendicular torque measured in the (100) plane at right angles to the film surface, the quantity $2\pi M_s^2 + K_\perp$ was determined. Here the anisotropy energy is defined as $E = (2\pi M_s^2 + K_\perp) \cos^2 \theta$, θ being the angle between the magnetization and the normal of the film surface. In this method the contribution from the crystalline anisotropy can be neglected, since the maximum torque occurs at $\theta = 45°$ where the torque from the K_1-term is just zero.

3. Results and Discussion

3.1 Observation of Ni/Cu bicrystal films

No features characterizing three-dimensional nuclei and their growth were observed in electron micrographs of thin Ni deposits on Cu. It was found that misfit dislocations were present even in the thinnest deposit of 11 Å examined. The dislocation lines were short and widely spaced, but became longer and closely spaced to form a network (Fig. 1) as the deposit thickness increased. They were parallel to both ⟨110⟩ directions in the (001) film plane. It turned out from micrographs taken under various diffraction conditions that the Burgers vectors of the dislocations were of type $\frac{1}{2}\,a\,\langle 110\rangle$ and were inclined at 45° to the film plane. Cross-slipped dislocations were also observed, which may give a support to this result [12].

Besides the dislocation images electron micrographs revealed a pronounced dark-light type contrast when the Ni deposit was less than 20 Å. Examination with the Ni surface facing down in the electron microscope showed similar contrast effects as Gaigher and Van Wyk [13] observed, which indicates that the dark-light type contrast

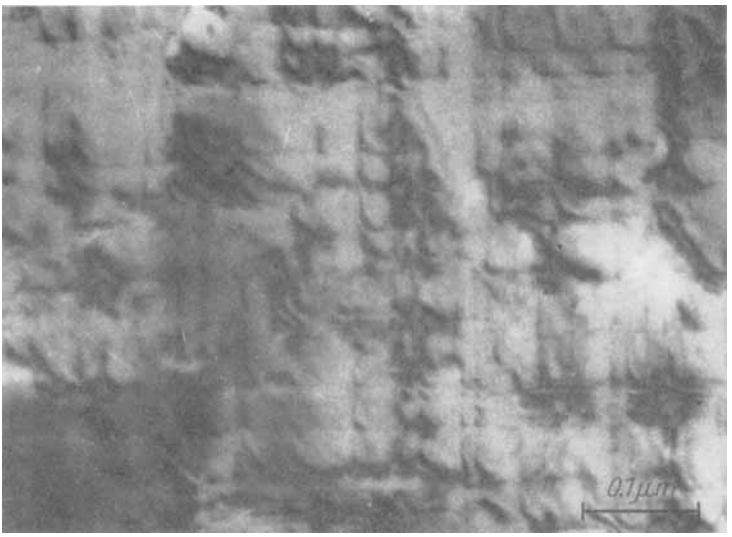

Fig. 1. Transmission electron micrograph of 67 Å thick Ni deposit showing a network of misfit dislocations. The borders of the figure are parallel to [110] and [1$\bar{1}$0] directions

is caused by strain fields probably at grooves of the Cu substrate. The presence of the substrate grooves was confirmed from micrographs taken for the Cu films. The grooves may be a consequence of three-dimensional growth of Cu on the rock salt; when islands of Cu coalesce into a continuous film, channels between the islands result in the grooves.

As the thickness of Ni increased to more than 40 Å moiré fringes became visible. The separation of the moiré fringes decreased with Ni thickness, showing that the misfit taken up by elastic strain decreased.

3.2 Elastic strain in Ni deposits

The misfit accomodated by dislocations can be calculated from their average spacing. Then the difference of the misfit from that between bulk lattice parameters of Ni and Cu gives the elastic strain left in the Ni deposit. Similarly, the strain is also calculated from the spacing of moiré fringes. Fig. 2 shows the obtained result of the strain as a function of Ni thickness.

It can be seen that the strain from moiré fringes is somewhat lower than that from dislocations. Yagi et al. [14] observed a lack of definite correspondence between moiré fringes and misfit dislocations for their evaporated bicrystal films, and interpreted this in terms of the loss of coherency in some places. Such a local incoherency between the

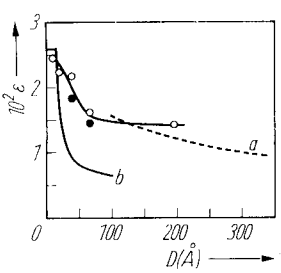

Fig. 2. Elastic strain ε obtained from the average spacing of misfit dislocations (open circle) and moiré fringes (solid circle) as a function of Ni thickness D. Curves a and b are the results of other authors for electrodeposited [13] and evaporated [3] films, respectively

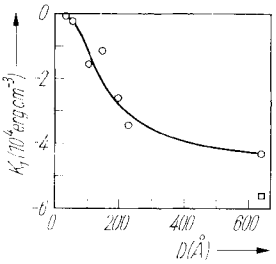

Fig. 3. Variation of magnetocrystalline anisotropy K_1 with thickness D. The square symbol is for the deposit from which the substrate has been removed

Ni deposit and the Cu substrate was observed in our films, which may account for the disagreement of the strains obtained from moiré fringes and misfit dislocations.

There are several previously reported measurements of the strain versus thickness relation for evaporated [2, 3] and electrodeposited [13] Ni/Cu bicrystal films. Some of them are compared with the present result in Fig. 2. A feature commonly seen for the strain in electrodeposited Ni (curve a and the present data) when compared with the strain in evaporated Ni (curve b) is a moderate decrease with increase in thickness. As Gaigher and Van Wyk [13] pointed out, such behaviour probably arises from the incorporation of foreign substances which cause an expansion of the Ni lattice and/or act as obstacles to the passage of dislocations.

There is, however, a distinct disagreement between the present and Gaigher and Van Wyk's observations. They did not observe misfit dislocations for deposits thinner than 100 Å, while the deposit of 11 Å (with a probable error of 3 Å) revealed dislocations in our case. Our observation is close to that of Matthews and Crawford [3] for evaporated Ni (curve b in Fig. 2), where they obtained a value of 15 Å for the critical thickness above which misfit dislocations were generated.

3.3 Magnetic anisotropy

Fig. 3 shows the measured magnetocrystalline anisotropy constant K_1 of the Ni/Cu bicrystal films as a function of Ni thickness. We also measured K_1 of a film with 640 Å thick Ni from which the substrate Cu was chemically dissolved. The obtained value (shown in Fig. 3) was -5.6×10^4 erg cm^{-3} and was in reasonable agreement with the bulk value of -5.0×10^4 erg cm^{-3} [15]. The same film before dissolving the substrate gave a lower K_1 of -4.3×10^4 erg cm^{-3}. Thus the difference of K_1 before and after removing the substrate is a contribution from substrate constraint; the strain which can be relieved when the substrate is removed is probably affecting K_1. Such strain effects may cause the variation of K_1 with Ni thickness.

The present result of K_1 is quite different from the corresponding measurement by Andrä et al. [16]. They did not observe any distinct thickness dependence of K_1 for electrodeposited (001) Ni films. One possible reason of this discrepancy is that they used electropolished surfaces of single-crystal Cu as substrate. In our former experiments using (110) faces of single-crystal Cu, we observed the formation of an oxide layer of Cu_2O, which had the same orientation as the original Cu face, after electropolishing. We also observed the epitaxial growth of Ni after subsequent electrodeposition. Thus the resulting strain in the Ni films may have a behavior different from the present case; the mismatch in lattice parameter between Cu_2O (a_{Cu_2O} measured is 4.27 Å) and Ni is 18%.

As seen from a plot of $2\pi M_s^2 + K_\perp$ versus Ni thickness in Fig. 4, the perpendicular anisotropy was observed for all the bicrystal films in a way that $K_\perp$ increased in magnitude as the Ni thickness decreased. The negative value of $2\pi M_s^2 + K_\perp$ observed for the films thinner than about 250 Å means that the magnetization remains perpendicu-

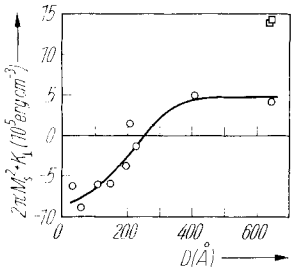

Fig. 4. Variation of perpendicular anisotropy $2\pi M_s^2 + K_\perp$ with thickness. The square symbol is for the deposit from which the substrate has been removed

lar to the film plane even without a magnetic field. Such a sign reversal of the perpendicular torque was reported by Gradmann [8] for (111) oriented Ni/Cu films. He interpreted this in terms of the elastic strain which resulted from the pseudomorphic growth of Ni up to 10 Å thickness.

If the perpendicular anisotropy is described by the surface anisotropy, $K_\perp$ may be proportional to K_s/D (K_s being the anisotropy constant and D the thickness). Such a variation of $K_\perp(D)$ was found for thin amorphous Fe [5], Ni and Co [6], and 48 Ni/Fe [7] films and values of K_s of order of 10^{-1} erg cm^{-2} were estimated. A plot of the present data of Fig. 4 as a function of (Ni thickness)$^{-1}$, however, did not show a straight line; in our films the surface anisotropy is not the dominant source of $K_\perp$.

We measured $2\pi M_s^2 + K_\perp$ for two Ni deposits of 640 and 645 Å after the substrate Cu was removed, and obtained values of 1.37 and 1.41 $\times$ 10^6 erg cm^{-3} (see Fig. 4), respectively. These values agree well with the shape anisotropy $2\pi M_s^2$ assuming the bulk M_s-value of 485 G, that is, $K_\perp$ disappeared in the unstrained films. We could not determine the contribution to $K_\perp$ from the surface anisotropy in these films. An estimation gives that K_s of 10^{-1} erg cm^{-2} yields a deviation of $K_\perp$ of only 1% of $2\pi M_s^2$. Thus the strain present in the Ni deposits attaching to the substrate is thought to give rise to $K_\perp$. One possible reason of the lack of observation of the surface anisotropy is such a strain effect, since the surface anisotropy is normally evident for very thin deposits where the strain increased rapidly in our epitaxial films.

3.4 Estimation of strain from anisotropy constants

We assume here that the interaction between magnetostriction and strain in the Ni deposit, i.e. the magnetoelastic effect, contributes to the measured K_1. Possible contributions from directional ordering of oxygen atoms (suggested for evaporated films [17]), imperfections, or impurities can be neglected, since no uniaxial component of the anisotropy was observed in the film plane. We also neglect the anisotropy coming from the constraint of the Ni/Cu bicrystal film to the glass substrate (on which the film was mounted and dried after deposition of Ni); the situation that the film does not deform freely by magnetostriction alters K_1 by the amount of 10^3 erg cm^{-3} [15], which is much smaller than the variation of K_1 with thickness.

For a (001) cubic crystal film on which a uniform strain ε is exerted the effective crystalline anisotropy constant K is given by [18]

$$K = K_1 + \frac{\varepsilon}{S_{11} + S_{12}}\left(\frac{2}{3}h_4 - 2h_3\right), \tag{1}$$

where K_1 is the anisotropy constant in the absence of strain, and h_i and S_{ij} are the magnetostriction constants and elastic compliances, respectively. We assume a value of -5.6×10^4 erg cm^{-3}, obtained for the unstrained film of 640 Å thick Ni, as K_1 in (1). Then we obtain ε of the Ni deposit at each thickness equating the observed K_1 (Fig. 3) to K.

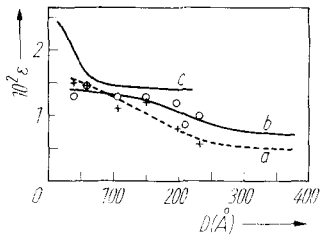

Fig. 5. Elastic strain calculated from magnetic anisotropies (a) K_1 and (b) $K_\perp$. (c) The result from transmission electron microscopy (TEM) in Fig. 2 is also shown

Several sets of h_3- and h_4-values measured for Ni crystals are available [19 to 22], but they are far from being free of errors due to the difficulty in measuring the high-order magnetostriction constants beyond h_2. The use of the h_i-values of different authors results in a difference in ε of a factor six between the extremes. Therefore, we used h_3 and h_4 averaged over the values from [19 to 22], while the S_{11}- and S_{12}-values of Alers et al. [23] were employed. (The values of S_{ij} or C_{ij} (elastic constants) measured by different authors are in good agreement [23].) The result of ε as a function of Ni thickness is shown in Fig. 5. The general tendency of the decrease of ε with thickness is well represented.

In order to consider effects of strain on $K_\perp$ we must know the value of $2\pi M_s^2$, since the measured quantity is $2\pi M_s^2 + K_\perp$. Measurements of M_s for very thin epitaxial films were reported in [7]. It was shown that a noticeable reduction of M_s occurred below about 50 Å film thickness, above which M_s remained constant. Our measurements of M_s from the L/H versus H plot as in [24] were not successful to obtain accurate values. The thinnest Ni for which the anisotropy constants were measured was 40 Å being limited by the sensitivity of the torquemeter used. We, therefore, assume here a $2\pi M_s^2$ value of 1.4×10^6 erg cm^{-3} (M_s of 472 G) independently of thickness. This value was obtained for unstrained deposits of about 640 Å as mentioned before.

We next assume as in the consideration of K_1 that the magnetoelastic effect is solely responsible for $K_\perp$. Then from the calculation in a way similar to [18] the following expression[2]) for $K_\perp$ is obtained:

$$K_\perp = \frac{\varepsilon}{S_{11} + S_{12}} (h_1 + h_4) . \tag{2}$$

The resulting ε using the experimental data of $K_\perp$ (Fig. 4) is shown in Fig. 5, where we used the h_i-values of Bozorth and Hamming [19]. Since the value of h_1 is one order larger than h_4 the uncertainty of h_4 does not affect the ε-value.

As compared in Fig. 5 there is a reasonable agreement between ε from $K_\perp$, though slightly less, and that obtained from electron microscopy. It should be remembered here that ε from electron microscopy was mostly determined from the spacing of misfit dislocations (see Fig. 2); the misfit strain after being relieved partly by dislocations was measured, so that other contributions to the strain, if any, were not included. Considering possible strain sources, contributions from grain growth and from the thermal effect, i.e. the difference in thermal expansion or contraction between the Ni deposit and the Cu substrate, are not present in our films. It is commonly seen for electrodeposits that the inclusion of foreign materials such as hydrogen and coordinated water expands the lattice contributing a compressive strain. Such additional effects which relieve the misfit strain may account for the difference between ε determined from $K_\perp$ and from electron microscopy.

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[2]) The corresponding expression in [18] may be $K_\perp = \varepsilon/(S_{11} + S_{12})(h_1 - h_3 - 8h_4/3)$. That (2) differs from this is due to a different way of torque magnetometry in determining $K_\perp$.

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