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<td><strong>Author(s)</strong></td>
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An investigation of structure, magnetic properties and magnetoresistance of Ni films prepared by sputtering

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Abstract

Ni films were deposited by magnetron sputtering with a relatively high deposition rate (0.5 nm/s). We have investigated the structure and magnetic properties of Ni films with different thicknesses. Strongly reduced magnetization has been found in the as-deposited Ni film. Our structural investigation (high-resolution TEM, EXAFS) reveals the presence of amorphous structure. The crystallinity increases with increasing film thickness, accompanied by an increase of magnetization. In 15 nm film or below, circular crystallites were found after annealing at 500 °C. Anisotropic magnetoresistance (AMR) has been observed and it is strongly dependent on the microstructure.

Keywords

Ni film; Sputtering; Magnetization; Amorphous structure; Anisotropic magnetoresistance (AMR)

1. Introduction

Ni is one of fundamental elements in magnetic materials. Ni films have been widely studied due to their potential application in the recording media and semiconductor technology [1–3]. Many interesting phenomena have been observed in Ni thin films [4–6].
Today, nickel films can be fabricated by a variety of methods (sputtering, MOCVD, MBE, PLD, electro-deposition, etc). Sputtering is one of the most commonly used methods for the film growth.

Thin film growth by sputtering has been widely used for its quick film growth, and composition control [7]. The microstructure and properties of thin films prepared by sputtering are strongly influenced by the preparation condition, such as substrate material, substrate temperature, thickness, and deposition rate [8,9]. It has been reported that thin films prepared by sputtering have shown excellent magneto-transport properties [10].

Anisotropic magnetoresistance (AMR) is one of important types of magnetoresistance in spintronics [11]. It was first discovered in Ni-based materials in 1930s [12] and has also been observed in other magnetic materials, such as Co, Co–Ni and Fe–Ni [12]. The mechanism of AMR has not been well understood yet. McCurie et al. [13] suggested that AMR is resulted from the spin–orbit scattering and d-orbit splitting. Recently, many works have shown that AMR in Ni thin films is strongly dependent on microstructures and morphologies [14,15]. Many research groups are still investigating the structure, magnetic and magneto-electronic properties of Ni films in order to understand the AMR mechanism [11,16,17].

In this work, Ni thin films have been fabricated by sputtering technique. Structure and magnetic properties were studied in dependence on preparation condition (thickness and annealing temperature). AMR of these Ni films has been investigated in correlation with microstructure and magnetic properties.

2. Experimental detail

A nickel target (with a purity of 99.97%) was used for the fabrication of Ni films using a DC magnetron sputtering system (Discovery 18, Denton). The base pressure was 2.5 x 10⁻³ mTorr and the work pressure was approximately 7.5 mTorr. Ni films were deposited on glass substrates at room temperature. The film thickness varied from 15 to 400 nm controlled by sputtering time under a constant sputtering power (200 W). The deposition rate was estimated to be 0.5 nm/s. Annealing process was carried out in a vacuum furnace at 500°C for 1 h.

Film thickness was measured using a surface profilometer (P-12, Tencor Instruments) with a vertical resolution of 5 Å. A micro-balance with a resolution of 10⁻⁶ g was used for the estimation of deposited mass by calculating from the difference between the weight before and after the deposition. Magnetic properties were measured using a vibration
sample magnetometer (VSM, Maglab, Oxford) with a maximum magnetic field of 90 kOe. Magneto-resistance (MR) of the films was taken with the four-point probe method. XRD (Philips, CuKα PW1729 X-ray generator and PW1820 diffractometer), SEM (Philips FEG-XL-30), HRTEM (JEOL, JEM 3010), AFM and MFM (DI, Nanoscope IIIa) were used to study the microstructure and surface morphology of Ni films. The thin films were also studied using extended X-ray absorption fine structure (EXAFS) spectroscopy at the beam-line 3C1 of the Pohang Light Source in South Korea. X-ray magnetic circular dichroism (XMCD) and X-ray absorption spectra (XAS) experiments were performed at the SINS beamline of the Singapore synchrotron light source (SSLS) at National University of Singapore.

3. Results and discussion

Fig. 1 shows X-ray diffraction patterns of Ni films with different thicknesses. When the thickness is 15 nm, there is only a very weak peak detectable, which is corresponding to the (111) peak of FCC-Ni. After the film is annealed at 500 °C, the (111) peak in the spectrum becomes much pronounced, while the condition of XRD remains unchanged. This result implies the possible presence of disordering (very small grain size and/or amorphous structure). When the thickness increases to 50 and 100 nm, there are three peaks, which are expected for the poly crystalline FCC-Ni. There was no significant change in the XRD spectrum when the two films (50 and 100 nm) were annealed at 500 °C. However, the intensities of the FCC-Ni peaks were higher, showing the growth of grain size or better crystallinity.

Fig. 2 shows the high-resolution TEM micrographs of Ni films with different thicknesses in the as-deposited state. In Fig. 2a, small Ni crystallites surrounded by areas without lattice pattern are observed. During the HRTEM examination, no lattice pattern can be obtained in these areas. The result indicates the presence of amorphous structure. When the thickness increases to 50 nm (Fig. 2b), the amount of amorphous phase is strongly reduced. In the 100 nm Ni film, only a little amount of amorphous phase is found in grain boundaries. Fig. 2a shows that the average crystal size is about 4 nm in the 15 nm film. The average crystal size of 50 and 100 nm Ni films is approximately 5 nm, which is slightly larger than that in the 15 nm Ni film.

Fig. 3 shows the HRTEM micrographs of the 15 nm film after annealing. The microstructure is not uniform from the image. Large Ni grains (>20 nm) have been observed as shown in Fig. 3a. There are also a large number of circular structures in the 15 nm film after annealing, as shown in Fig. 3b. The presence of circular structure indicates the existence of a certain type of disordering. For thicker films (50 and 100 nm), only large grains are observed (similar as shown in Fig. 3a). The mechanism of the
formation of the circular structure in the 15 nm film after annealing needs to be investigated further. It may be related to the interaction between the substrate and the film, induced stresses during annealing and/or the formation of islands as discussed later (Fig. 6a).

XRD spectra and HRTEM images have shown the presence of disordered structure in the as-deposited Ni films. EXAFS is another effective way to obtain some information of the microstructure [18]. The EXAFS data of Ni films were analyzed using a standard WinXAS 97 procedure [19,20]. A cubic spline fit was used to remove the non-oscillatory background. The data were then converted into photoelectron wave vector $k$. The data were then Fourier transformed to real space to obtain radial distribution function by choosing a Gaussian window function. Fig. 4 gives the spectra of the Fourier transform (FT) amplitudes of the as-deposited and subsequently annealed 100nm Ni films. The coordination number of as-deposited film is estimated to be 7.1, which is much lower than that of Ni foil as a reference (coordination number=12 for FCC-Ni). It is to note that the magnitude of the first peak depends on both the coordination number $N$ and the disorder about the average distance. The disorder introduces typically a Debye–Waller $\sigma^2$. Thus, the Debye–Waller factor lowers the signal at large $k$ values. However, the fitting results of the samples showed little difference between the $\sigma^2$ values. Hence, the trend of amplitudes can be a good reflection of the coordination numbers. The local environment and the low coordination number of Ni films support the presence of disordering in the structure [21]. After annealing the film at 300 and 500 °C, the coordination number increases to 9.23 and 10.26, respectively, confirming the increasing crystallinity. The coordination numbers are still lower than that of standard Ni foil. It may be due to the presence of voids and defects in the Ni films. It should be noted that no sign of oxidation was evident in the EXAFS spectra.

Fig. 5 shows the surface morphology of the as-deposited Ni film with a thickness of 100nm. The surface is not very smooth according to the roughness analysis of the image. The roughness is probably due to the deposition with a relatively high sputtering rate (0.5nm/s). The image shows that the particle size is about 40–50 nm, which is much larger than the grain size as obtained from HRTEM (4–5 nm), implying that these particles were agglomerates of small grains. We also investigated the surface morphology of 15 and 50nm Ni films by AFM. The morphology was similar to that of the 100 nm film but with a lower roughness.

Fig. 6 shows that the SEM images of the Ni films with different thicknesses after annealing at 500 °C. It can be seen that islands are formed in the 15 nm film. The island size is about 1 $\mu$m. From the AFM study (not shown here), one island is composed of many smaller particles with a diameter of about 100 nm. The 50 nm Ni film shows some
voids, indicating in the beginning state of island formation. The formation of islands with heat treatment may be employed to fabricate patterned films [22]. No formation of islands is observed in the 100 nm film after annealing at 500°C. But the surface becomes rougher. Some small porosity can be seen from the SEM image. The particle size is much larger than that in the as-deposited counterpart. Again, one particle consists of many small grains (approximately 20 nm from our HRTEM study, as shown in Fig. 3).

Fig. 7 shows magnetic properties (saturation magnetization $M_s$ and coercivity $H_c$) of Ni films in the state of as-deposited and after annealing. For the 15 nm Ni film in the as-deposited state, magnetization is very low (215 emu/cm$^3$), which is only about 50% of that as expected of bulk-Ni (480 emu/cm$^3$). The low value of magnetization is probably due to the disordered structure in the thin film [23,24]. $M_s$ increases with the increase of thickness, as crystallinity increases with the increase of thickness, which has been observed in our XRD and TEM studies (Fig. 1 and Fig. 2). For thicker films, magnetization is still below that of bulk Ni (300–400 emu/cm$^3$ for film thicknesses in the range of 100–600 nm). This is probably due to a certain degree of disordering presented, as observed in Fig. 2c. After annealing at 500 °C, magnetization is close to that of bulk Ni. The magnetization of the 15 nm Ni film is slightly lower than that of thicker Ni films. This is probably associated with the circular structure as observed in the TEM study (Fig. 3b). Coercivity $H_c$ reaches a maximum of 700 Oe at 50 nm for the as-deposited films (Fig. 7). It has been reported [25] that voids and oxidation in the grain boundary may serve as pinning centers for high coercivity. In this study, the disordered structure (amorphous structure) may play an important role for the relatively high value of coercivity. For the annealed Ni films, there is a relatively smooth curve of coercivity (250–400 Oe). As shown above, Ni films in the state of as-deposited and after annealing have different magnetic properties and different microstructures. In this work, magnetic force microscopy (MFM) was performed to study the domain structure in the two states (as-deposited and annealed) to confirm the difference. Fig. 8 shows the MFM images of as-deposited and annealed Ni films with a thickness of 100 nm. A fine domain structure has been observed in the as-deposited film (Fig. 8a). After annealing at 500 °C, stripe-like domain structure appears. Similar domain structures (stripe-like) have been often observed in different magnetic thin films [26–29].

Fig. 9 shows the thickness dependence of resistivity of as-deposited and annealed Ni films. For the as-deposited films, resistivity had a relatively high value (35 $\mu$Ω cm) in the 15 nm film, probably due to the presence of a large amount of disordered structure. Resistivity decreases with increasing thickness. At thickness 400 nm, the resistivity (10 $\mu$Ω cm) is still higher than that of bulk Ni (7 $\mu$Ω cm), indicating a certain degree of disordering in the film. After annealing, the resistivity of the 15 nm film is very high (280 $\mu$Ω cm). This high resistivity is due to the formation of islands. For annealed Ni films in
the range of 50–400 nm, resistivity decreases with the increase of film thickness. The curve of resistivity versus thickness can be relatively well described with the Fuchs-Sondheimer Model [30,31]. The resistivity of 400 nm thick film is 7.4 μΩ cm which is very close to that of bulk Ni, showing a good crystallinity of the film.

The above discussion showed that a relatively high sputtering rate (with a relatively high sputtering power of 200W) led to the formation of some amorphous Ni on glass substrate when the film was thin (15 nm). With increasing film thickness, a certain amount of amorphous structure still remained. The presence of amorphous structure resulted in low magnetization. In this work, a separated experiment was performed, in order to confirm that the formation of amorphous Ni was associated with a relatively high sputtering power during deposition.

In Table 1, magnetization is listed in dependence on sputtering power and on substrates in 100nm Ni films. It can be seen that sputtering power can affect the crystallinity and magnetization greatly. Magnetization increases with the decrease of sputtering power, from 319 emu/cm³ at 200W to 462 emu/cm³ at 10W. It is to note that 462 emu/cm³ is very close to the magnetization of bulk Ni (480 emu/cm³). Our XRD study also confirmed that a low sputtering power benefited film crystallinity. On the other hand, we can see from the table that substrates also play an important role in the crystallinity of Ni films. Under the same condition (sputtering power=200W and thickness=100 nm), magnetization of Ni films on quartz and silicon wafer is higher than that of Ni film deposited on glass substrate. When Cu foil is used as the substrate, the magnetization of Ni film increases to 436 emu/cm³, which is not far below the expected value of bulk Ni. These results indicate that the crystallinity of Ni film can be strongly affected by the substrate. High magnetization of Ni film on Cu substrate is probably due to the same structure of FCC-Cu and FCC-Ni. In addition, their lattice parameter is close to each other.

X-ray magnetic circular dichroism (XMCD) has been extensively used for the measurement of magnetic moment of ferromagnetic materials [32]. In this study, XMCD and X-ray absorption spectra (XAS) experiments were carried out. The magnetic moment of as-deposited Ni film (15 nm) were measured by XMCD at room temperature. Before XMCD experiments, the sample was etched with Ar ion sputtering. A standard poly-Ni foil (Goodfellow, UK) was measured as a reference. Fig. 10 shows the XMCD spectra of as-deposited Ni film and reference Ni foil. Before XMCD experiments, the sample was fully magnetized by a magnetic coil in the horizontal plane. The dichroism spectroscopy was then obtained by reversing either the helicity of the circularly polarized light or the magnetization direction. The results show that the total magnetic moment of Ni foil is about 0.6 μB as expected in the reference of Ni foil [32]. The total magnetic moment of
as-deposited Ni film is about 20% lower than that of Ni foil, confirming the low magnetization in the as-deposited thin films.

As reported previously, anisotropic magneto-resistance (AMR) and positive magneto-resistance have been observed in Ni films [14]. In this work, we have investigated AMR in dependence on microstructure (amorphous structure and thickness). Fig. 11 shows magnetoresistance curves of different Ni films. The magneto-resistance is defined as MR = (R_H − R_0)/R_0, where R_0 is the film resistance at zero field and R_H is the resistance under magnetic field H. It can be seen that no significant AMR effect is present in the as-deposited Ni film since a large amount of amorphous structure is evident. After annealing at 500 °C, small AMR effect appears. However, no positive magneto-resistance is detected when magnetic field is parallel to the current. For the Ni films with a thickness of 50 nm, magneto-resistance remains small in the as-deposited state. After annealing, a relatively large negative MR is obtained in the perpendicular direction. The as-deposited Ni film with a thickness of 100nm has a significant positive MR. After annealing, larger positive MR is observed in the parallel direction, while a relatively large negative MR is present in the perpendicular direction which is nearly the same value as that of 50nm film (as shown in Fig. 11). Our results have shown that AMR is very small, when there is a large amount of amorphous structure. For as-deposited films, AMR increases with the increase of thickness as the crystallinity increases. The AMR of annealed 15nm films is low, probably due to the formation of the island structure. The AMR of thick films (200 and 400nm) is very similar to that observed in the annealed 100 nm film.

In this work, we have investigated the temperature dependence on resistance and AMR. Fig. 12 shows the resistance and AMR as a function of temperature for the 100 nm Ni film in the as-deposited and annealed state. The resistance of both samples (as-deposited and annealed) nearly has a linear relationship with temperature, as expected by the Matthiessen’s rule [33]. AMR first increases with the decrease of temperature and reaches a maximum at 150–160K. Similar results have been reported previously [34].

4. Conclusion

Ni films with different thicknesses were prepared by magnetron sputtering. Our XRD, HRTEM and EXAFS studies revealed there is a large amount of amorphous structure presented in relatively thin films (15nm) in the as-deposited state. Crystallinity increased with increasing film thickness. The as-deposited Ni films consisted of very small Ni grains (4–5 nm). After annealing (500 °C), large grains (20 nm) were observed. For the 15 nm Ni film, island formation was observed, and some circular structure was evident under HRTEM.
Sample with a large amount of amorphous structure was characterized by a very low saturation magnetization (compared with bulk Ni). Magnetization increased with the increase of thickness as the crystallinity increased. For the as-deposited films, large resistance was observed. After annealing at 500°C, increase in magnetization and decrease in resistance were observed. For thick Ni films (100–400 nm), magnetization and resistance were very close to those of bulk-Ni.

Magneto-resistance (MR) and AMR were strongly dependent on microstructure. The presence of amorphous structure led to a significant reduction in MR and AMR. For thick Ni films (100–400 nm), AMR values were comparable with those reported for Ni. [9] For the both 100 nm films (as-deposited and annealed), a maximum of AMR was found in the temperature range of 150–160 K.
References

List of Figures

Figure 1  X-ray diffraction spectra of Ni films: 15 nm in the as-deposited state; 15 nm after annealing at 500°C for 1 h; as-deposited 50 nm; and as-deposited 100 nm.

Figure 2  HRTEM micrographs of as-deposited Ni films with different thicknesses: (a) 15 nm, (b) 50 nm, and (c) 100 nm (the arrows indicate amorphous regimes).

Figure 3  HRTEM micrographs of the 15 nm Ni film after annealing.

Figure 4  EXAFS spectrum of Ni film with and without annealing: plot of $k\chi(k)$ of (a) 100-nm Ni film annealed 773 K, (b) 100 nm film annealed at 573 K, (c) as-deposited 100-nm Ni film and (d) Ni foil as the reference (right). The amplitudes of Fourier transform as a function of radial distance are shown on the left side.

Figure 5  AFM image of the as-deposited Ni film with a thickness of 100 nm (the image area is 2 x 2 μm). The data bar for roughness is from dark for 0 nm to light for 20 nm.

Figure 6  SEM images of annealed Ni films with different thicknesses of 15 (a), 50 (b) and 100 nm (c).

Figure 7  Magnetization and coercivity in dependence on the thickness of as-deposited and subsequently annealed Ni films.

Figure 8  MFM images of 100nm Ni films: (a) in the as-deposited state; (b) after annealing at 500 °C. The imaged area is 5 x 5 μm.

Figure 9  Resistivity as a function of the film thickness for as-deposited Ni films (upper) and after annealing at 500 °C.

Figure 10  (a) Ni L edge X-ray absorption spectra for as-deposited Ni film and standard poly-crystalline Ni foil, respectively. Spectra for both magnetizations are represented by different triangles: parallel (solid triangles) and antiparallel (open triangles) alignment of photon spin and sample magnetization directions. (b) Dichroism spectra calculated from
(a) as intensity difference shown by solid lines for Ni foil and dashed lines for as-deposited Ni, respectively.

Figure 11 Magnetoresistance (MR) curves of Ni films with different thicknesses (15, 50 and 100 nm) in the as-deposited state (down) and after annealing at 500 °C (upper). The magneto resistance was measured with two configurations: (a) the magnetic field was applied parallel to the electric current (solid). (b) the magnetic field was applied perpendicular to the current (dash).

Figure 12 Temperature dependence of AMR of the 100 nm Ni films in the as-deposited state and after annealing at 500°C (left). AMR is defined as $(\rho || - \rho \perp) / \rho_{av}$, where $\rho ||$ is the resistivity when magnetic field is parallel to electric current, $\rho \perp$ is the resistivity when field is perpendicular to current, and $\rho_{av}$ is the average resistivity. In the right site, resistance under zero field is plotted as a function of temperature.
List of Table

Table 1        The dependence of saturation magnetization $M_s$ of 100 nm Ni films on sputtering power and substrate
Figure 1

[Graph showing X-ray diffraction patterns for different film thicknesses, labeled 15nm, 50nm, 100nm, and 15nm after annealing. Peaks are labeled (111), (200), and (220).]
Figure 3
Figure 4
Figure 5
Figure 6
Figure 7
Figure 9

Graph showing the change in resistivity (μΩ cm) as a function of thickness (nm) for samples annealed and as-deposited.
Figure 10
Figure 11
Figure 12
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Table 1