

Crystal structures and magnetic properties of Fe–N thin films deposited by dc magnetron sputtering

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(Received 11 June 2004; accepted 21 September 2004)

Fe–N thin films were deposited on glass substrates by dc magnetron sputtering under various Ar/N₂ discharge conditions. Crystal structures and elemental compositions of the films were characterized by X-ray diffraction and X-ray photoelectron spectroscopy. Magnetic properties of the films were measured using a superconducting quantum interference device magnetometer. Films deposited at different N₂/(Ar+N₂) flow ratios were found to have different crystal structures and different nitrogen contents. When the flow ratios were 60%, 50%, and 30%, a nonmagnetic single-phase FeN was formed in the films. At the flow ratio of 10%, two crystal phases of γ' -Fe₄N and ε -Fe₃N were detected. When the flow ratio reduced to 5%, a mixture of α -Fe, ε -Fe₃N, FeN_{0.056}, and α'' -Fe₁₆N₂ phases was obtained. The value of saturation magnetization for the mixture was found to be larger than that of pure Fe. © 2004 International Centre for Diffraction Data. [DOI: 10.1154/1.1814980]

Key words: XRD, XPS, magnetic properties

I. INTRODUCTION

Iron nitride films have attracted a great deal of attention for many years (Cocke *et al.*, 1989). Initially, they were studied because of their abilities to improve surface hardness and wear resistance. Recently, nitrogen-poor phases such as γ' -Fe₄N, ε -Fe_{2.3}N, and α'' -Fe₁₆N₂ have been widely investigated because of their attractive magnetic properties (Mohm and Matar, 1999; Ortiz *et al.*, 1994; and Coey, 1994). It was reported by Kim and Takahashi (1972) that α'' -Fe₁₆N₂ phase was an important compound and may have an application in high-density magnetic recording owing to its giant saturation magnetization (310 emu/g). However, recent measurements showed that α'' -Fe₁₆N₂ had relatively lower values of saturation magnetization. For example, Takahashi and Shoji (2000) reported that the saturation magnetization of α'' -Fe₁₆N₂ was 218 emu/g. Besides saturation magnetization, coercivity is another important property for these nitrogen-poor iron thin films. Coercivity is an extrinsic property of material and is closely related to the magnetic reversal mechanism. Different values have been obtained for the same ferromagnetic phase by different investigators (Sugita *et al.*, 1994; Gupta *et al.*, 2001). The reasons for the different reported values of coercivity for the same phase remain un-

clear. The nonmagnetic cubic nitrogen-rich FeN phase has also attracted much attention in recent years. FeN can be incorporated in a multilayer superstructure of nuclear Bragg monochromator of type ⁵⁶FeN/⁵⁷FeN (Rohlsberger *et al.*, 1993; Chumakov *et al.*, 1993). Although FeN films have many potential applications and can be produced by a number of techniques, the preparation of a pure FeN film turns out to be rather difficult.

Using dc magnetron sputtering from a pure iron target, we deposited iron nitride films on glass substrates at room temperature by changing N₂ flow rate in a mixture of N₂/Ar discharge. The compositions, structures, and magnetic properties of the films were analyzed. Films of single FeN phase and multiple phases containing α'' -Fe₁₆N₂ with high saturation magnetization have been successfully obtained.

II. EXPERIMENTAL

Iron nitride films were deposited on Corning glass substrates in mixed Ar/N₂ discharges by dc magnetron sputtering from a high purity (99.99%) α -iron target (60 mm in diameter). The distance between the substrate holder and the target was 6.5 cm. The base pressure was 5×10^{-5} Pa. Prior to deposition, the substrates were cleaned ultrasonically in acetone and alcohol consecutively, and then baked in a vacuum chamber at 250 °C for 2 h and cooled down to room temperature. During sputtering, the dc power was kept con-

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TABLE I. Binding energies and atomic ratios for samples N60, N50, N30, N10, N5, and N0.

Samples	N 1s(eV)	Fe 2p _{3/2} (eV)	N/Fe
N60	396.7	710.7	1.06
N50	396.5	710.7	1.19
N30	396.9	710.7	1.10
N10	396.4	707.5	0.34
	397.2	711.0	
N5	396.3	707.3	0.11
	397.2	711.0	
N0		707.2	

stant at 110 W, and the total pressure was fixed at 2.0 Pa. Pure argon (99.999%) and nitrogen (99.999%) gases were introduced into the chamber, controlled by two independent mass-flow controllers. The argon gas flow was fixed at 43.7 sccm, while the nitrogen gas flow was controlled so that the nitrogen fractions in six sputtered films were 60% (N60), 50% (N50), 30% (N30), 10% (N10), 5% (N5), and 0% (N0). The deposition rate was about 0.11 nm/s, and the nominal thickness of the films was 200 nm.

The chemical binding states and compositions of the films were determined by X-ray photoelectron spectroscopy (XPS) (VG ESCALAB MK II). XPS was performed using Mg K α radiation (operating power: 15 mA and 15 kV). The crystal structures of the films were analyzed by X-ray diffraction (XRD) with Cu K α radiation ($\lambda=0.15406$ nm) generated by a rotating anode X-ray generator operated at 150 mA and 40 kV (Rigaku, D/MAX-rA). Magnetic properties of the films were measured by a superconducting quantum interference device magnetometer (MPMS-5S, Quantum Design, San Diego, CA, USA) in magnetic fields up to 5 T. The weights of the samples were measured using an analytical balance (Sartorius BS210S).

III. RESULTS AND DISCUSSION

Wide XPS scans of the Fe–N samples were used to determine the film compositions, and narrow XPS scans to analyze the chemical bonding between atoms. The measured binding energies of N 1s and Fe 2p_{3/2} spectra and the atomic ratios of nitrogen and iron atoms for the films deposited at the N₂ fractions of 60%, 50%, 30%, 10%, 5%, and 0% are listed in Table I. The atomic ratios of N/Fe for samples N60, N50 and N30 were close to the ideal value for the FeN phase. For samples N60, N50, and N30, the peaks at 710.7 eV energy in the XPS Fe 2p_{3/2} spectrum are related to Fe³⁺ and the peaks at 396.7±2 eV energy in the N 1s spectrum correspond to the FeN phase. For sample N10, the atomic ratio of N/Fe was almost the same as the value for ϵ -Fe₃N, suggesting that ϵ -Fe₃N was a dominant phase in the N10 film. For sample N5, the atomic ratio N/Fe was 0.11, which is between the values for α'' -Fe₁₆N₂ and FeN_{0.056}. Since the N 1s signal was very weak in the XPS spectrum for the N5 film, it is difficult to obtain a precise value of the atomic ratio of N/Fe. Thus the N/Fe ratio of 0.11 only qualitatively indicates that the nitrogen content in Fe–N film was very low. The N 1s peaks for all samples were in the range of 396.3–397.9 eV, and this indicates that the nitrogen atoms were bounded to the Fe atoms.

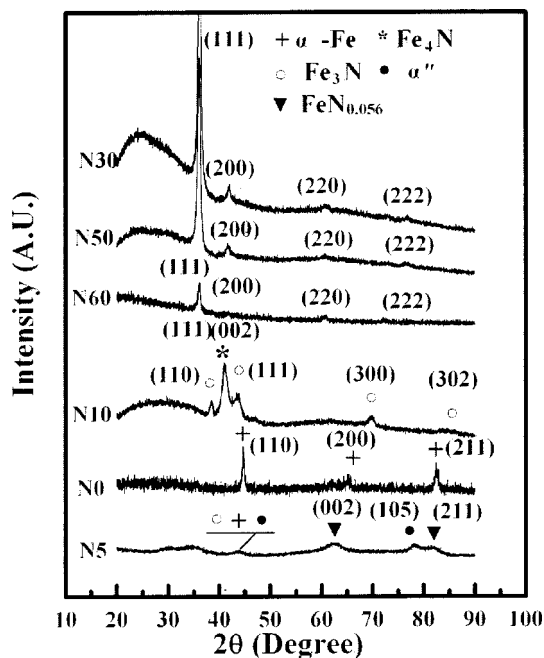


Figure 1. XRD patterns for iron nitride films grown at six different N₂/Ar flow rates: N30, N50, N60, N10, N0, and N5.

Figure 1 shows the XRD patterns of the six Fe–N films deposited on glass substrates. The diffraction patterns of samples N60, N50, and N30 were identified to be cubic nitride FeN with lattice parameter $a=0.4310\pm0.0001$ nm. This value is slightly smaller than the value of 0.4355 nm reported by Rissanen *et al.* (1998, 1999). All three patterns show FeN (111) preferred orientation, and the intensities of their FeN (200), FeN (220), and FeN (222) peaks increase with decreasing N₂ fraction. When the N₂ fraction decreases to 10% for the N10 film, magnetic phases of hcp ϵ -Fe₃N and fcc γ' -Fe₄N appear. The lattice parameters for ϵ -Fe₃N were calculated to be $a=0.4698\pm0.0001$ nm and $c=0.4379\pm0.0001$ nm (space group: $P6_322$), while that for γ' -Fe₄N to be $a=0.3795\pm0.0001$ nm. These lattice constants of ϵ -Fe₃N and γ' -Fe₄N are in agreement with those reported by Jacobs *et al.* (1995). A mixture of α -Fe, ϵ -Fe₃N, FeN_{0.056} (tetragonal with lattice parameters $a=0.2859$ nm and $c=0.3016$ nm) and α'' -Fe₁₆N₂ (bct with lattice parameters $a=0.5720$ nm and $c=0.6290$ nm) were formed for the N5 film. The two small X-ray diffraction peaks at $2\theta=44.5^\circ$ and 77.9° were identified to be α'' -Fe₁₆N₂ (220) and α'' -Fe₁₆N₂(105). At N₂ fraction=0 (only Ar gas discharge), the N0 film was found to be pure α -Fe with lattice constant $a=0.2866$ nm. The XRD results are in agreement with those obtained by XPS.

The magnetic measurements of samples N30, N50, and N60 showed that these films were nonmagnetic. Figures 2(a)–2(c) show in-plane hysteresis loops of samples N0, N10, and N5, respectively. Within experimental errors, the saturation magnetization of about 216 emu/g obtained from the sample N0 is essentially equal to the value of 218 emu/g for a pure α -Fe thin film. A hysteresis effect for the pure iron film of sample N0 was detected with coercivity of 95 Oe [see Figure 2(a)]. The saturation magnetization of sample N10 was found to be 130 emu/g, which is lower than those of ϵ -Fe₃N (153 emu/g, $\rho=7.204$ g/cm³) and

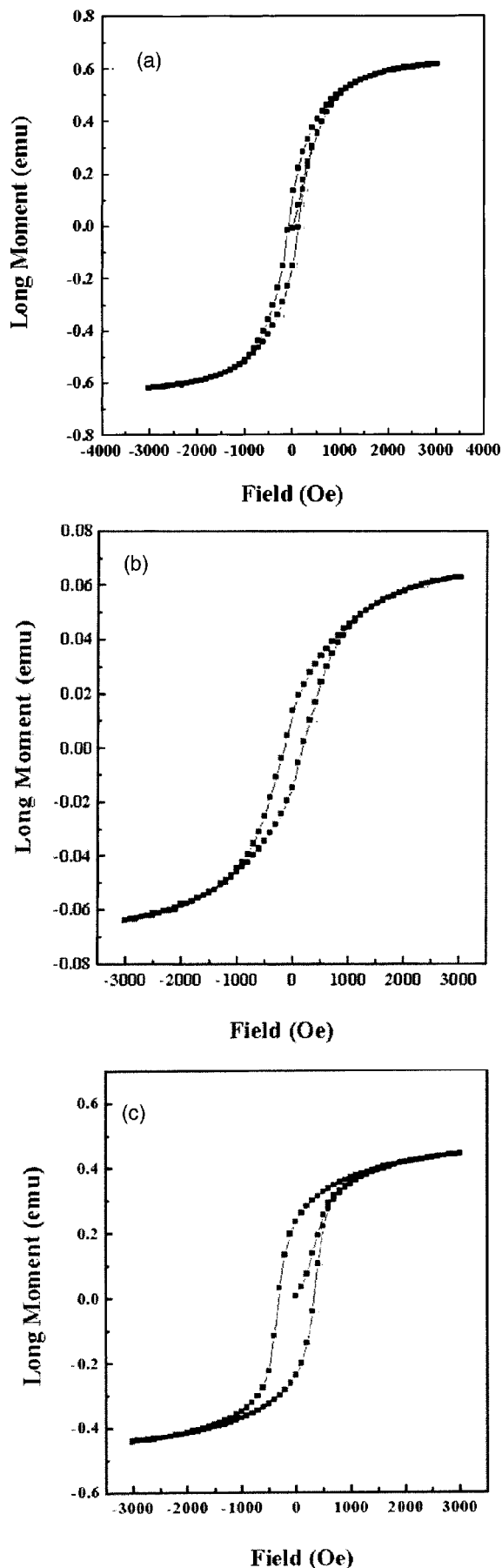


Figure 2. (a) Magnetic hysteresis loop for sample N0. (b) Magnetic hysteresis loop for sample N10. (c) Magnetic hysteresis loop for sample N5.

γ' -Fe₄N (186 emu/g, $\rho=7.242$ g/cm³). Since the saturation magnetization of sample N10 is near to that of ϵ -Fe₃N, this suggests that ϵ -Fe₃N is dominant in sample N10. As shown in Figure 2(b), the coercivity of sample N10 was 160 Oe. For sample N5, its saturation magnetization was 246 emu/g, which is higher than that of a pure iron film. Sample N5 had the highest coercivity of 320 Oe, see Figure 2(c). The coercivity of molecular beam epitaxial Fe₁₆N₂ films was 10–50 Oe (Sugita *et al.*, 1994), whereas the coercivity for a multi-phase film containing α'' -Fe₁₆N₂ was about 200 Oe (Borsa *et al.*, 2002). Since the coercivity is an extrinsic property of a material, the reason for this discrepancy needs a further study.

IV. CONCLUSIONS

The iron nitride films on glass substrates were successfully deposited by dc magnetron sputtering from a pure iron target under various N₂/Ar discharge conditions. Several crystal phases in the Fe–N films were formed by changing the N₂ fraction in the mixture of N₂/Ar gas flow. When the N₂/Ar flow rates were 60%, 50% and 30%, a single nonmagnetic phase FeN was found. At the N₂/Ar flow rate of 10%, two magnetic phases of ϵ -Fe₃N (hcp structure) and γ' -Fe₄N (fcc structure) were detected. When the N₂/Ar flow rate reduced further to 5%, a mixture of α -Fe, ϵ -Fe₃N, FeN_{0.056}, and α'' -Fe₁₆N₂ phases was found in the N5 film. The value of saturation magnetization for the N5 film was found to be 246 emu/g, which has a higher saturation magnetization than that of pure α -Fe. The observed high saturation magnetization in the N5 film can be attributed to the α'' -Fe₁₆N₂ phase.

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