

Structure and magnetic properties of columnar Fe-N thin films deposited by direct current magnetron sputtering

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Abstract: Columnar Fe-N thin films with thickness ranging from 30 to 150 nm were deposited by direct current magnetron sputtering using an Ar/N₂ gas mixture ($V(\text{N}_2)/V(\text{N}_2+\text{Ar})=5\%$) on corning glass substrates. The structure, surface morphology and magnetic properties were investigated using X-ray diffractometry(XRD), scanning electron microscopy, atomic force microscopy, transmission electron microscopy(TEM) and superconducting quantum interference magnetometry. XRD investigation shows that Fe-N films exhibit amorphous-like structures; however, TEM measurements indicate the synthesis of mixture phases of $\alpha\text{-Fe}+\zeta\text{-Fe}_2\text{N}+\epsilon\text{-Fe}_3\text{N}$ in these films. The magnetic anisotropy and coercivity of Fe-N thin films exhibit strong dependence on the film growth behavior and surface morphology. With increasing the height of Fe-N films with column structures, the coercivity increases from 7.96 kA/m to 22.28 kA/m in the direction parallel to the film surface. In perpendicular direction the coercivity only increases slightly from 39.79 kA/m to 43.77 kA/m. However, the values of anisotropy field increase from 0.79×10^6 to 1.44×10^6 A/m, which is mainly attributed to the shape anisotropy of elongated columns due to the fact that the difference of magneto-crystalline anisotropy among these Fe-N films is small. The saturation magnetizations of Fe-N films vary with increasing film thickness from 23.5 to 85.1 A·m²/kg.

Key words: Fe-N thin film; coercivity; magnetic anisotropy; saturation magnetization

1 Introduction

Iron nitride thin films have attracted a great deal of attention for many years due to their variety of structural and magnetic properties for the potential applications as magnetic functional materials[1–8]. All nitrides with the composition of Fe_xN ($x \geq 3$) are ferromagnetics at room temperature. Among them, $\alpha''\text{-Fe}_{16}\text{N}_2$ (bct) has higher saturation magnetization (298 A·m²/kg) than that of bulk $\alpha\text{-Fe}$ (210 A·m²/kg) and $\gamma'\text{-Fe}_4\text{N}$ (fcc, 188 A·m²/kg) [9–10]. In addition, paramagnetic $\zeta\text{-Fe}_2\text{N}$ (orthorhombic) and nonmagnetic phases FeN ($\gamma'''\text{-NaCl}$ and $\gamma''\text{-ZnS}$) also have been paid much attention in these years[11–12]. Compared with the crystalline structures, amorphous magnetic Fe-N thin films are expected to have several advantages over crystalline Fe-N films such as lower

magnetic anisotropy because of the isotropic nature of the amorphous structure[13–14]. Some reports have been given on the synthesis of amorphous Fe-N films by sputtering technique. However, the synthesis conditions must be controlled carefully to avoid forming other Fe-N crystalline structures[15–17].

In this work, using DC magnetron sputtering technique, Fe-N thin films were deposited with various thicknesses on corning glasses substrate. The relationship of surface morphology and structure with magnetic properties including coercivity, saturation magnetization and magnetic anisotropy for synthesized Fe-N thin films was studied.

2 Experimental

Fe-N films with thickness ranging from 30 to 150

nm were deposited on corning glass substrates in mixed Ar/N₂ gas ($V(\text{N}_2)/V(\text{Ar}+\text{N}_2)=5\%$) using DC magnetron sputtering with high purity (99.99%) α -Fe target. The distance between the fixed 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 ethanol consecutively, then baked in a vacuum chamber at 250 °C for 2 h and cooled down to room temperature. During sputtering, the DC power and the magnet exciting power were kept constant at 100 W and 37.5 W ($I=2.50$ A, $U=15$ V) respectively, and the total pressure was fixed at 2.0 Pa. The deposition rate was about 0.1 nm/s.

The structure of the films was analyzed using X-ray diffractometer(XRD) with Cu K α radiation using a current of 150 mA and voltage of 40 kV (Rigaku, D/MAX-rA) and JEM-2000EX TEM operated at 180 kV and 160 kV. The surface morphology of the films was characterized using scanning electron microscope (SEM) (JOEL JSM-6700F) and non-contacted atomic force microscope(AFM) (Digital Instrument Nanoscope III scanning probe microscope). The radius of the Si₃N₄ tip was about 10 nm. The scan area was 1–5 μm , the scan speed was 1 Hz and the sampling rate was 256 points per line. Magnetic properties of the films were measured by superconducting quantum interference device (SQUIDS) magnetometer (MPMS-5S, Quantum Design, San Diego, CA, USA) in magnetic fields up to 5 T. The mass of the samples was measured using analytical balance (Sartorius BS210S).

3 Results and discussion

3.1 Film structures and surface morphology

Structures of the Fe-N thin films were analyzed using XRD. Fig.1 shows the XRD patterns of the Fe-N film samples (A1, A2, A3 and A4 corresponding to film with thickness of 30, 90, 120 and 150 nm, respectively) deposited on glass substrates. No obvious strong diffraction peak can be observed for these films, which indicates that the synthesized films are amorphous or crystal Fe-N films containing small crystalline grains without showing any preferred orientation growth. In order to well understand the crystal phases in samples A1, A2, A3 and A4, the structures of Fe-N films were investigated by means of TEM.

The TEM bright-field images shown in Fig.2 reveal that the nanocrystalline grain sizes increase from 5 nm to 50 nm with increasing film thickness. Compared with the analysis of XRD, it can be concluded that the broadened peaks should come from the reflections of Fe-N nanocrystalline, not from the amorphous structures. The

diffraction patterns of selected area for these Fe-N films are shown in Fig.3. The obtained diffraction rings in these figures attribute to reflections of ζ -Fe₂N+ ϵ -Fe₃N (Fig.3(a), for sample A1), ζ -Fe₂N+ α -Fe+ ϵ -Fe₃N (Fig.3(b), for sample A2), and ϵ -Fe₃N+ α -Fe+ ζ -Fe₂N (Figs.3(c), (d), for sample A3, A4, respectively). The broader diffraction rings in Fig.3(a) indicate that the size of grains for Fe-N film deposited for 5 min is much smaller than that of the others.

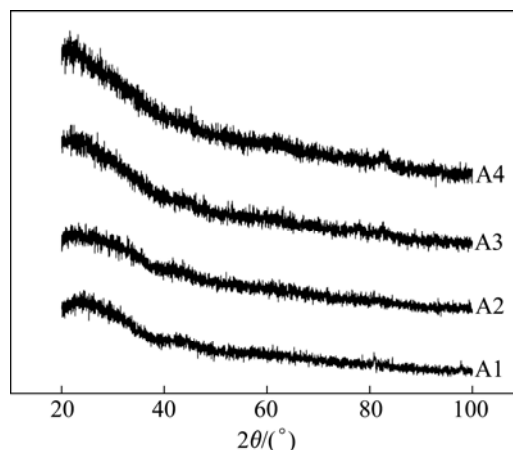


Fig.1 X-ray diffraction patterns for Fe-N film samples with various film thicknesses: (a) A1, 30 nm; (b) A2, 90 nm; (c) A3, 120 nm; (d) A4, 150 nm

Fig.4 exhibits the cross-sectional SEM images for the Fe-N films. After initial random nucleation of islands, the dominant columns are formed and grow vertically as a function of film thickness. In addition, it is shown that the column structures become denser and column edges become smoother with the increase of deposition time, which may be related to the growth mechanism of Fe-N thin film[11]. In order to further characterize the surface morphology and evaluate the surface roughness (σ), the AFM was used. The roughness for Fe-N films as a function of the film thickness is shown in Fig.5. It can be seen that with increasing Fe-N film thickness, the surface roughness increases from about 12.5 to 20.1 nm.

3.2 Magnetic properties

Fig.6 shows the magnetization curves of Fe-N films with various thicknesses. The $H_{//}$ lines indicate the hysteresis loops when a magnetic field is applied parallel to the substrate. When the magnetic field is applied normal to the substrate, the $H_{\perp}$ lines are obtained. In this case, the magnetic field is in the longitudinal direction of the column structures. All the magnetic hysteresis loops were measured without considering the diamagnetic component of the substrate background signal. The differences in H_c and the distinct loop shapes along two

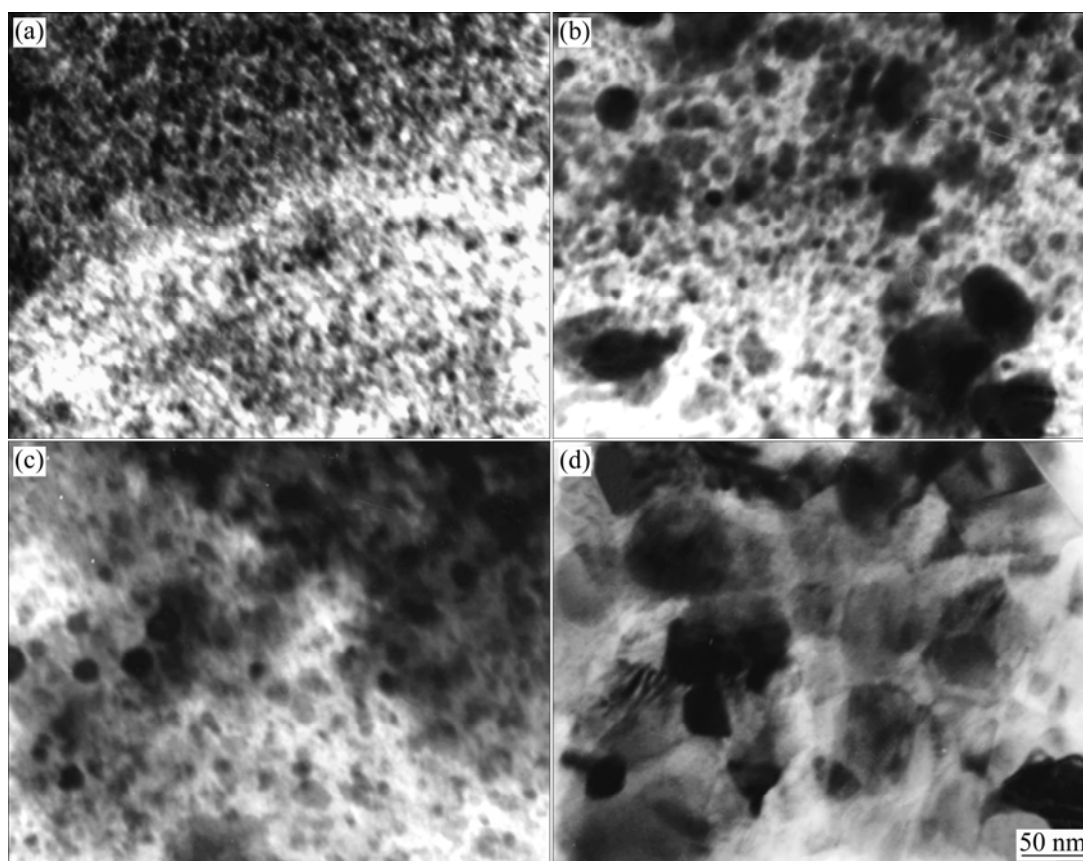


Fig.2 Bright-field SEM images for Fe-N film samples: (a) A1; (b) A2; (c) A3; (d) A4

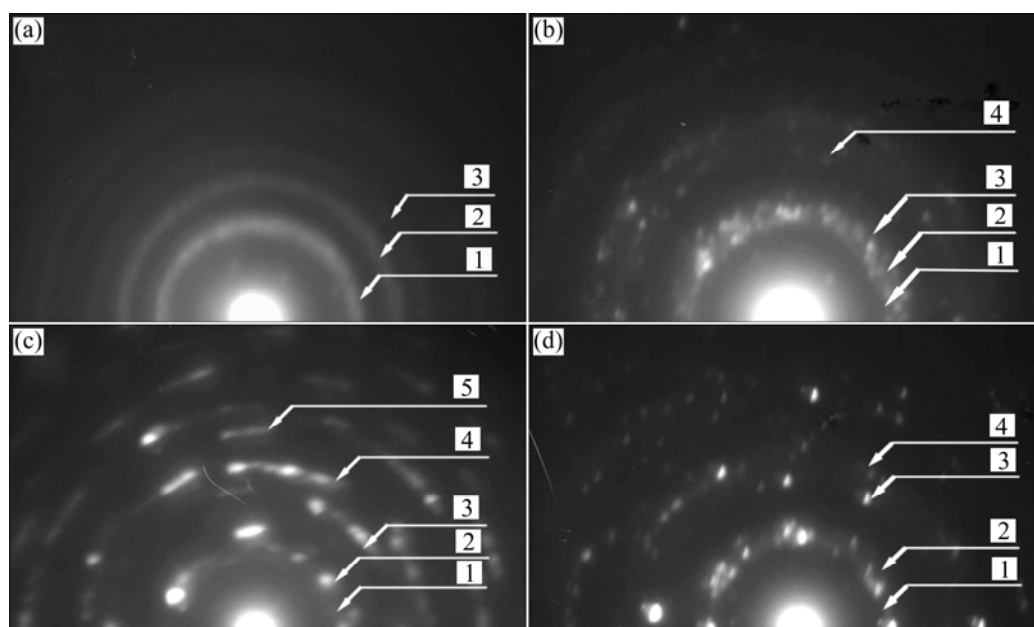


Fig.3 Electron diffraction patterns for corresponding samples: (a) A1, diffraction rings 1 to 3 belonging to ζ -Fe₂N (200), ε -Fe₃N (210) and ζ -Fe₂N (042), respectively; (b) A2, diffraction rings 1 to 4 belonging to ζ -Fe₂N (200), α -Fe (110), ε -Fe₃N (210) and ζ -Fe₂N (042), respectively; (c) A3, diffraction rings 1 to 5 belonging to ζ -Fe₂N (200), α -Fe (110), ε -Fe₃N (103) and ζ -Fe₂N (042), (240), respectively; (d) A4, diffraction rings 1 to 4 belonging to ε -Fe₃N (110), α -Fe (110), ε -Fe₃N (300) and ζ -Fe₂N (240), respectively

magnetic directions imply that magnetic anisotropy exists for columns grown at different deposition times. The value of magnetic anisotropy field increases from

0.79×10^6 to 1.44×10^6 A/m with increasing film thickness. As no obvious anisotropy growth of grains is observed by XRD, magneto-crystalline anisotropy can be

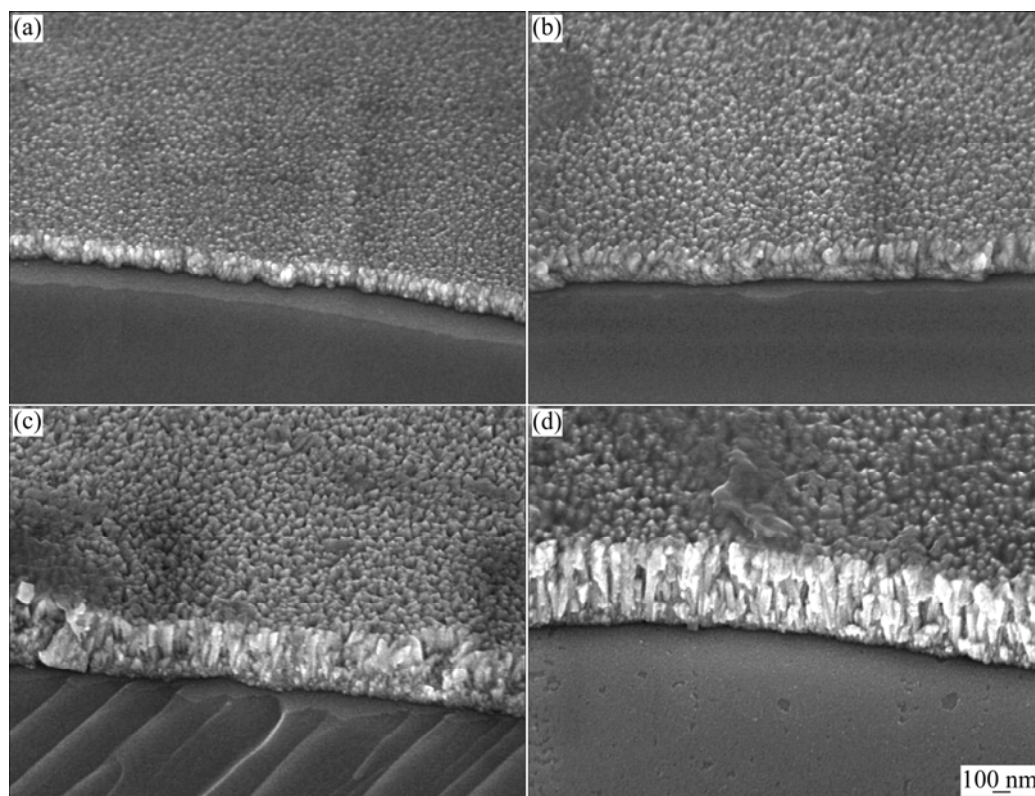


Fig.4 Cross-sectional SEM images for Fe-N films with various film thicknesses: (a) 30 nm; (b) 90 nm; (c) 120 nm; (d) 150 nm

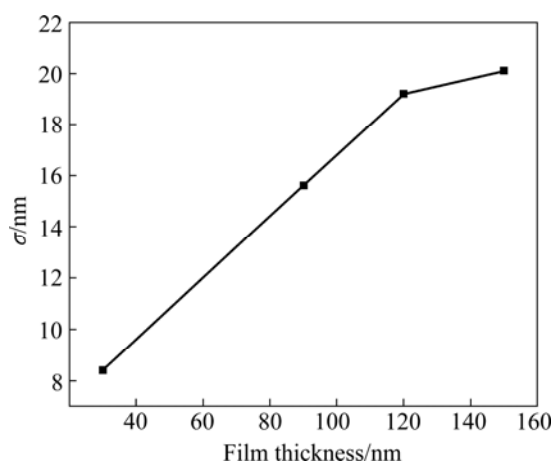


Fig.5 Surface roughness of Fe-N films vs thicknesses obtained from AFM data

expected to have few attribute to the magnetic anisotropy. Therefore, the shape anisotropy is supposed to play a key role in the magnetic anisotropy of these Fe-N films, which shows the increasing tendency with increasing film thickness. The easy axis of magnetization is found to be parallel to the substrate. The coercivities $H_{c//}$ and $H_{c\perp}$ vs film thickness are plotted in Fig.7. With increasing deposition time, the coercivity $H_{c//}$ increases obviously from 7.96 to 22.28 kA/m; however, $H_{c\perp}$ increases only slightly in the range of 39.79–43.77 kA/m. The influence of microstructures, such as grain size, surface roughness, on the magnetic properties of thin

films is extremely complicated. In this work, with increasing film thickness, nanocrystalline size of Fe-N thin film increased from 5 nm to 50 nm; consequently, $H_{c//}$ increased, which indicates that the critical size of single domain particle for Fe-N thin films might be above 50 nm[18–19]. The calculated saturation magnetizations for these Fe-N thin films are also shown in Fig.7, which are about 23.5, 41.8, 79.2 and 85.1 $\text{A}\cdot\text{m}^2/\text{kg}$, respectively.

3.3 Discussion

As mentioned above, the synthesized Fe-N films exhibit in-plane anisotropy. In addition to the possible influence of grain size on the coercivity of the synthesized Fe-N thin films, $H_{c//}$ also exhibits the same tendency with increasing surface roughness. According to Ref.[20], this tendency can be partly attributed to the increase of demagnetizing factor. Many magnetic properties including coercivity are each a function of the demagnetizing factor that depends on the surface roughness and type of magnetic domain walls. It is well known that there are mainly two kinds of magnetic domain walls: Bloch wall for bulk magnetic materials or thick films and Néel wall for thin films in which the magnetization rotates within the film plane when crossing the wall. In the case of Néel wall, the demagnetizing factor increases in the direction parallel to the film surface with increasing surface roughness as

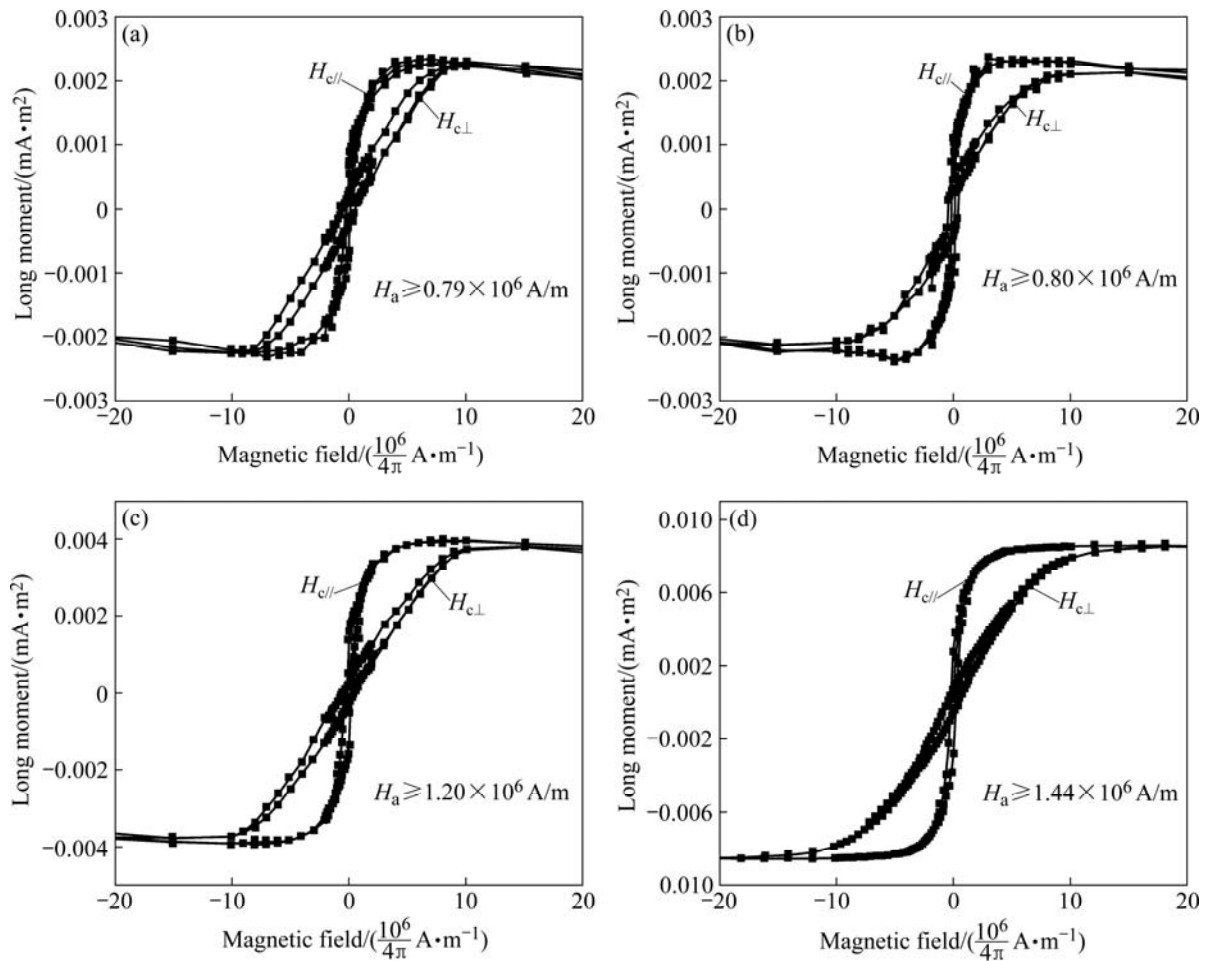


Fig.6 Magnetization curves for Fe-N films with various film thicknesses: (a) 30 nm; (b) 90 nm; (c) 120 nm; (d) 150 nm

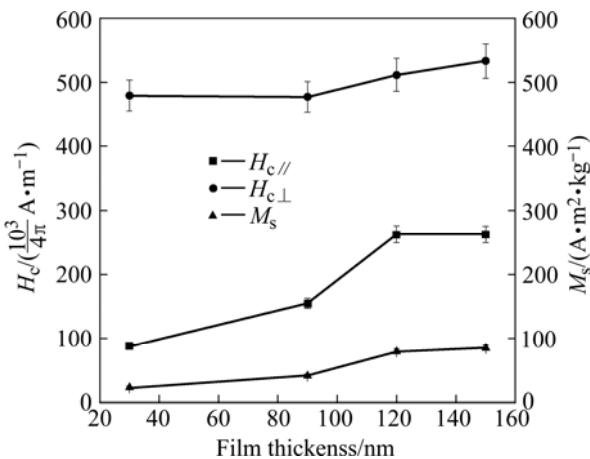


Fig.7 Coercivity(H_c) and saturation magnetization(M_s) for Fe-N films with various film thicknesses

$n_{xx} - \sigma^2$, where n_{xx} is the demagnetizing factor, and σ is the surface roughness. In this work, with increasing demagnetizing factor in the direction parallel to the film, $H_{c//}$ increased from 7.96 to 22.28 kA/m. However, the coercivity in the perpendicular direction $H_{c\perp}$ increased slightly from 39.79 to 43.77 kA/m. Saturation magnetization of Fe-N films exhibits a dependence on

the synthesized phases. With increasing deposition times for these Fe-N film samples, the amount of rich-Fe phase (ϵ -Fe₃N and α -Fe) in the films increases. Consequently, saturation magnetization increases.

4 Conclusions

1) Fe-N thin films, with various film thicknesses deposited at low N₂ fraction ($V(N_2)/V(N_2+Ar)=5\%$) exhibit columnar growth in the directions parallel and vertical to the film surface. With increasing film thickness from 30 to 150 nm, the surface roughness and grain size increase and those columns vertical to the substrates are elongated, which results in an increase of shape magnetic anisotropy for these films.

2) In the direction of magnetic field parallel to the substrate, $H_{c//}$ increases from 7.96 to 22.28 kA/m. In the direction of magnetic field perpendicular to the substrate, the value of $H_{c\perp}$ changes mildly from 39.79 to 43.77 kA/m with increasing film thickness.

3) The saturation magnetization(M_s) of Fe-N films exhibits a strong dependence on the synthesized Fe-N phases. The types of Fe-N phases in these films change

little with increasing deposition time; however, the amount of Fe-rich ferromagnetic phases increases after longer deposition time, which attributes to the increase of M_s .

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