Effect of epitaxy and lattice mismatch on saturation magnetization of γ'-Fe_4N thin films

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We report the effect of epitaxial growth and lattice mismatch on the enhancement of saturation magnetization (M_s) of ferromagnetic γ'-Fe_4N thin films deposited on different single crystal substrates having lattice mismatches from 0% to 11%. It was found that M_s in the γ'-Fe_4N film increased with increasing degree of epitaxy and minimizing lattice mismatch between the film and the substrate. Maximum saturation magnetization of 1980 ± 20 emu/cm^3 (about 24% higher than previous result) was obtained with $LaAlO_3$(100) substrate having zero lattice mismatch after postannealing of 30 min, which is believed to originate from magnetovolume effect in well-ordered epitaxially grown films. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2940599]

Certain phases of iron nitride have been fascinating the researchers during the past several decades due to their apparently amazing magnetic properties.[1–6] Among these, γ' phase of iron nitride (Fe_4N) is the most stable phase with a metallic ferromagnetic unique structure and bearing high saturation magnetization.[7,8] The γ'-Fe_4N phase has face-centered cubic iron lattice with a nitrogen atom positioned at the body-center site.

In the past few years, single phase γ'-Fe_4N thin films were grown on Si(100) and NaCl(100) substrates;[9] epitaxial single phase γ'-Fe_4N films were deposited on single crystal Cu(100),[10] MgO(001),[11,12] and $SrTiO_3$(001) (Ref. 13) substrates. This material has potential applications in high-density magnetic write heads and magnetic recording media. Furthermore, it seems to replace those materials for which high magnetic flux density and low coercivity are required, e.g., 50% nickel permalloys. It could also be an attractive material in the case of current perpendicular-to-plane devices, where low resistance of the ferromagnetic materials could be an issue[13] and the possible development of all nitride epitaxial magnetic tunnel junctions (MTJs) with epitaxial γ'-Fe_4N as magnetic electrodes and epitaxial Cu_3N as an insulating layer.[14] Recently, MgO-based MTJs with γ'-Fe_4N electrode have been reported having relatively large inverse tunneling magnetoresistance effect.[15]

So far, a giant value of saturation magnetization has been reported in α''-$Fe_{16}N_2$ prepared by evaporating iron in low pressure nitrogen[2] and molecular beam epitaxy.[16] The exact origin of this giant value is not yet clear; anyhow, only the single phase epitaxially grown α''-$Fe_{16}N_2$ thin films have been found to reveal this value. Some other research groups[4,17] could not reproduce these results as α'' phase of iron nitride is a metastable phase and thermally less stable,[1] whereas γ' phase of iron nitride is considerably stable capable of showing strong ferromagnetic character which might be further strengthened by controlling the epitaxial growth. In this letter, we have investigated the epitaxy-dependent saturation magnetization achieved by optimizing annealing time in γ'-Fe_4N thin films and the subsequent effect of lattice mismatch on saturation magnetization using three different substrates MgO(100), $SrTiO_3$(100), and $LaAlO_3$(100) with lattice mismatches of 11%, 3%, and 0%, respectively.

To optimize the conditions for single phase epitaxial growth, several iron nitride thin films were deposited on MgO(100) substrates under various deposition conditions. Highly pure (99.95%) target of α-iron (50 mm in diameter) was placed at a distance of 10 cm from the substrate holder. The substrates were preheated at 450 °C in vacuum for 30 min before deposition. The base pressure of the chamber was better than 2×10^{-6} Torr. Optimized partial pressures of 5 and 0.5 mT of analytically pure Ar (99.95% purity) and N_2 (99.95% purity), respectively, with a total working pressure of 5.5 mT were injected into the chamber utilizing dc sputtering power of 30 W. 550 Å thick films were deposited with a deposition rate of 0.55 Å/s at the substrate temperature of 450 °C and *in situ* annealed for 10–40 min. The investigation of crystal structure, pole figure, and phi scan were carried out by Rigaku D/MAX-RC MPA x-ray diffractometer (XRD) utilizing Cu $K\alpha$ radiation. Surface morphology was characterized by a PSIA, XE-100 atomic force microscope (AFM). Film thickness calibrations being critical in this study for accurate volume estimation of the thin films were performed by AFM and cross-sectional images obtained by Hitachi S-4800 scanning electron microscope (SEM). Magnetic characterizations were carried out using a VT-800 (Riken Denshi Co Ltd.) vibrating sample magnetometer (VSM) with an applied field of up to ±15 kOe. The M–H loops were measured with the applied field parallel to the film plane.

Figure 1 shows the x-ray diffraction patterns of γ'-Fe_4N thin films deposited on MgO(100) at the substrate temperature of 450 °C and *in situ* annealed from 10 to 40 min. XRD patterns clearly illustrate the (100) and (200) peaks of γ'-Fe_4N at 2θ of 23.45° and 47.91°, respectively. All other peaks are from MgO substrate. For comparison, the x-ray diffraction pattern of pure single crystal MgO substrate used in this work is also shown in Fig. 1(e). The intensity of (100) and (200) peaks of γ'-Fe_4N films increases as the annealing time increases from 10 to 30 min The in-plane epitaxiallity

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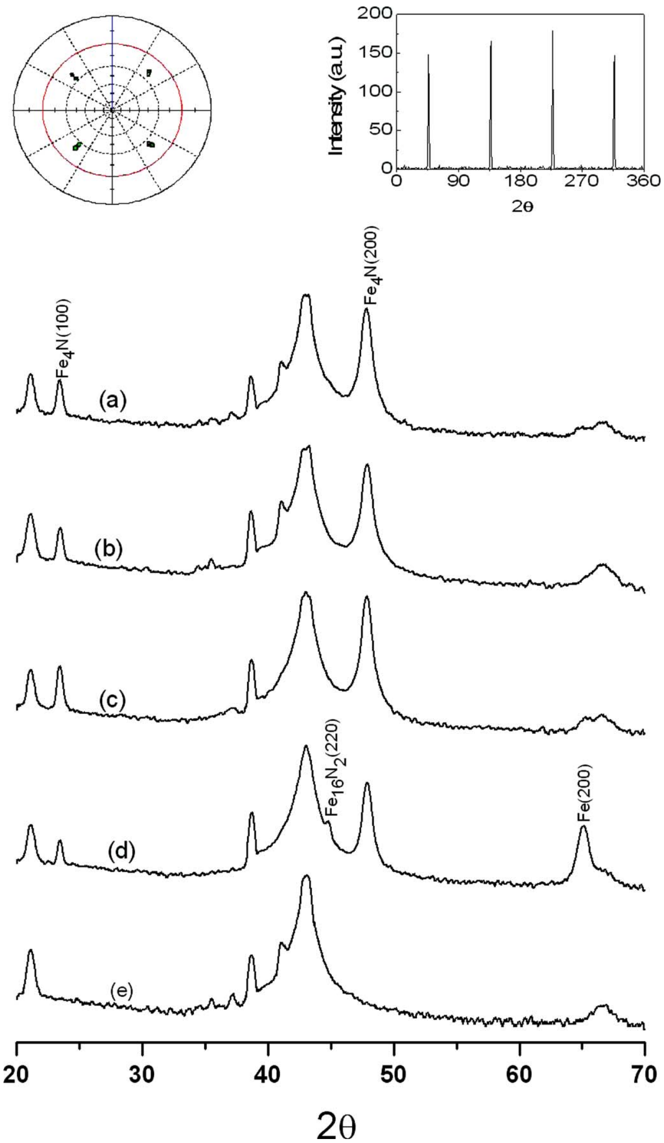

FIG. 1. (Color online) X-ray diffraction patterns of thin films with annealing time of (a) 10 min, (b) 20 min, (c) 30 min, and (d) 40 min together with (e) the x-ray diffraction pattern of MgO(100) substrate.

of the film annealed for 30 min was further verified by the pole figure and the phi scan obtained using XRD as shown in the top left and right corners of Fig. 1. The presence of four clear spots in the x-ray ψ-Φ pole scan and the appearance of only four sharp peaks in Φ-scan with 2θ fixed at (111) reflection for both scans evidently prove the high quality epitaxial nature of γ'-Fe_4N thin films. The rocking curves obtained for the (100) reflection of the samples annealed for 10–40 min showed the decrease in the full width at half maximum (FWHM) up to the annealing time of 30 min. The minimum value of FWHM was 0.37° observed for the sample annealed for 30 min which demonstrates that 30 min. annealing at 450 °C substrate temperature is the most favorable condition for single phase epitaxial growth of γ'-Fe_4N thin films on MgO substrate. Annealing the films for 40 min or more destroyed the epitaxial nature that might be due to the excessive escape of nitrogen atoms resulting in the appearance of some extra peaks of α-Fe (200) at 2θ=65.06° and α''-$Fe_{16}N_2$ (220) at 2θ=44.77°, as shown in XRD pattern in Fig. 1(d).

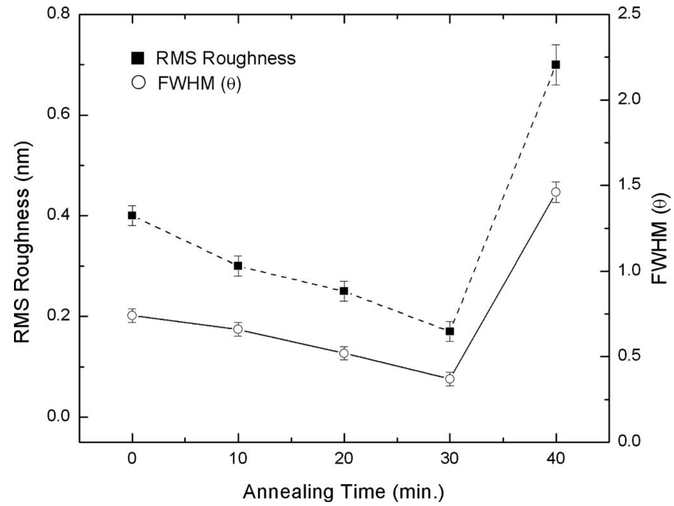

FIG. 2. Annealing time plotted against rms value of surface roughness (dashed line) and FWHM (solid line).

Figure 2 shows the effect of annealing time plotted against FWHM for (100) reflection and root-mean-square rms value of surface roughness of γ'-Fe_4N thin films deposited on MgO(100) at a substrate temperature of 450 °C and *in situ* annealed for 10–40 min. The rms value of surface roughness characterized by AFM decreased almost linearly with increasing annealing time up to 30 min for which the minimum value of surface roughness was observed to be 0.17 nm. Such a low value of rms roughness demonstrates epitaxial growth from smooth layer-by-layer growth process, in which first islands are formed that finally coalescence in full smooth layered texture.[7] The rms roughness and FWHM showed exactly the same behavior and decreased with the increase of annealing time up to 30 min. The lowest value of surface roughness (0.17 nm) and the minimum FWHM value of 0.37° were observed for this sample. The sample annealed for 40 min demonstrated a drastic change in structure: The values of rms roughness and the FWHM increased suddenly to 0.7 nm and 1.46°, respectively. This abrupt change in behavior of the film annealed for 40 min is obviously due to the nonepitaxial growth, which is consistent with the XRD result of the sample, as can be seen in Fig. 1(d).

Strong ferromagnetic behavior of γ'-Fe_4N thin films was revealed by the magnetic hysteresis loops with an in-plane applied magnetic field. The loops showed the easy axis in the ⟨100⟩ direction with distinct fourfold cubic anisotropy, characteristic of well-ordered single crystal epitaxial texture. Saturation magnetization (M_s) was calculated by careful volume estimation of thin films using cross-sectional SEM measurement. Figure 3(a) shows a plot of M_s vs FWHM for γ'-Fe_4N thin films deposited on MgO(100) substrates at a temperature of 450 °C and *in situ* annealed for 10–40 min. As seen in the figure, the value of saturation magnetization increases with the decrease in FWHM up to the sample annealed for 30 min showing a value of 1760 ± 20 emu/cm^3. This value is 16% higher than the previous reported value[7,8] and might be attributed to the high degree of epitaxy for this sample. The sample annealed for 40 min shows sudden decrease in M_s value (1140 emu/cm^3), which is obviously due to the nonepitaxial nature of the film.

To further explore the dependence of saturation magnetization on epitaxial growth, we have deposited γ'-Fe_4N thin films under the same deposition conditions on three different

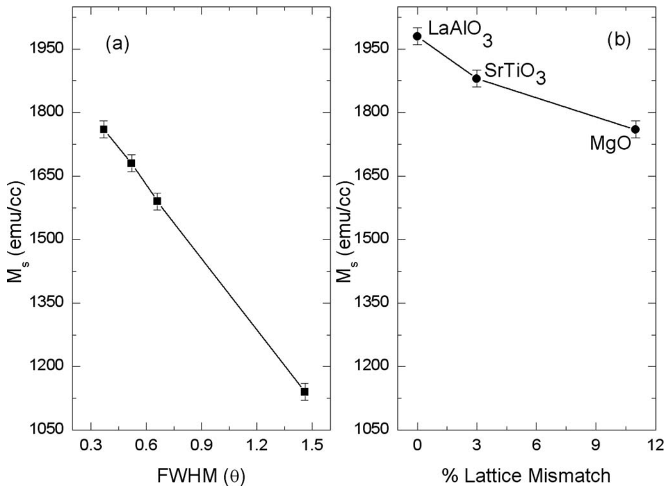

FIG. 3. (a) Plot of M_s vs FWHM of γ'-Fe_4N films deposited on MgO with 10, 20, 30, and 40 min annealing. (b) Plot of M_s vs lattice mismatch for γ'-Fe_4N.

substrates: MgO(100), $SrTiO_3$(100), and $LaAlO_3$(100) with lattice mismatches of 11%, 3%, and 0%, respectively. Although MgO has 11% lattice mismatch with γ'-Fe_4N, even then favorably can be employed for epitaxial growth as in our case, too, but such a large mismatch could affect the growth normals and the in-plane orientation relationship between the substrate and the deposit.[12] Having lattice mismatch of only 3%, $SrTiO_3$ offers relatively better template for epitaxial growth. X-ray diffraction pattern of the sample deposited on $SrTiO_3$(100) showed unique (200) peak of γ'-Fe_4N at 2θ value of 47.91°, indicating the epitaxial structural texture of the film. For perfectly matched lattice, $LaAlO_3$ should be the most appropriate substrate for the growth of epitaxial γ'-Fe_4N thin films. The constraint is, due to no lattice mismatch, the dominant peaks of both the deposit and the substrate comprehensively overlap each other, hence cannot be detected by XRD patterns in the case of thin films. The value of saturation magnetization observed for these three samples is plotted as function of lattice mismatch, as shown in Fig. 3(b). It can be shown that saturation magnetization increases with decrease of lattice mismatch and reached up to 1980 ± 20 emu/cm^3 at 0% lattice mismatch. Note that this value of saturation magnetization is about 24% higher than the experimentally observed value[7,8] reported so far for this material. Theoretical band calculation has been performed[18] for the structure of γ phase of iron by introducing empty spheres instead of nitrogen atoms in order to investigate the premises of high magnetic moment ascribed to the ferromagnetic phases of iron nitride. The value of magnetic moment evaluated for γ phase fcc iron with the same volume as that of γ'-Fe_4N was about $2.7\mu_B$ per Fe atom which is quite comparable to our experimentally observed value. The origin of this high magnetic moment in γ'-Fe_4N has been explained based on the volume expansion effect and charge transfer effect.[19,20] However, the N atom, on its interstitial insertion in fcc iron lattice, is considered to act as a hopping site for electrons that can help itineracy of conduction electrons. As a result, the bandwidth of 3*d* electrons is expected to spread which, consequently, may limit the increase of exchange splitting. Nevertheless, some local bonding between Fe and N atoms seems to play a key role in enhancing the saturation magnetization in uniquely structured ferromagnetic phases of iron nitride thin films.[20]

In conclusion, ferromagnetic γ'-Fe_4N grown on MgO(100) by dc magnetron sputtering showed epitaxial growth as the annealing time was increased from 10 to 30 min. The value of saturation magnetization showed strong dependence on the epitaxial growth and lattice mismatch of the substrates. The maximum value of saturation magnetization was achieved by using $LaAlO_3$(100) substrate with 0% lattice mismatch after 30 min post annealing at the temperature of 450 °C.

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