Magnetic and electrical properties of iron nitride films containing both amorphous matrices and nanocrystalline grains

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Abstract

We have investigated the magnetic and electrical properties of iron nitride films containing both amorphous matrices and nanocrystalline grains. It is found that both the number and the size of the grains in the amorphous matrix increase as the film thickness increases. The grain size varies in the range of 10–300 nm. The saturation magnetization and the coercivity increase as the number and the size of the grains increase. The electrical resistivity of the iron nitride films is higher than that of the iron film.

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1. Introduction

Iron nitride has been known for its variety of phases with different crystal structures due to different nitrogen contents. The phase and the structure of iron nitride change as the nitrogen concentration increases from α'-Fe2N (x ≈ 8, tetragonal) [1], α''-Fe16N2 (bct) [2], γ'-Fe3N (fcc) [3], ε-Fe3N (2 < x ≤ 3) (hcp) [4] to ζ-Fe2N (orthohombic) [5]. The magnetic properties are also changed by the nitrogen concentration in the iron nitride. For example, the saturation magnetizations of the α'-Fe2N (x ≈ 8, 4πMs = 22–24 kG) [6] and the α''-Fe16N2 (4πMs = 28–30 kG) [7] phases are higher than that of the α-Fe (4πMs = 21.6 kG) phase. The saturation magnetizations of the γ'-Fe3N (4πMs = 18–21 kG) [8] and the ε-Fe3N (4πMs = 16–17 kG) [9] phases are lower than that of the α-Fe phase.

The saturation magnetization of the ε-Fe3N (2 < x ≤ 3) phase decreases as x increases, and it disappears at room temperature above x of 2.3 [10]. The ζ-Fe2N phase does not show ferromagnetism at room temperature, and the Curie temperature is between 4 and 60 K [11 12]. On the other hand, it has been reported that the grain size is reduced by the addition of the nitrogen to metals [13, 14]. The grain size of the iron films is also reduced by the addition of the nitrogen. Therefore, if we control both the grain size and the crystal structure, the iron nitride films will have low coercivity and high saturation magnetization. The low coercivity and the high saturation magnetization are suitable for soft magnetic materials. Future hard disk drives require such soft magnetic materials for writing head materials. The iron nitride films are candidates for such materials because the coercivity of these films is lower than that of pure iron films. In the iron nitride films, the low coercivity is caused by the decrease of the crystal grain size due to the addition of nitrogen in the iron nitride films. There have been some reports about the iron nitride films with nanocrystalline or amorphous structures, which were prepared by mechanical alloying [15] and sputtering...
[16,17] under adequately controlled conditions. However, there have been few reports about the magnetic and electrical properties of the iron nitride films containing both the amorphous matrices and the nanocrystalline grains.

In this study, we investigate the magnetic and electrical properties of the iron nitride films containing both the amorphous matrices and the nanocrystalline grains. In our previous investigation, the grain was nanocrystallized when the flow rates of Ar and N\textsubscript{2} gases were chosen to be 12 and 3 sccm (standard cc/min), respectively. Therefore, we prepared the iron nitride films with various thicknesses using the above-mentioned flow rates.

2. Experimental procedures

The iron nitride (Fe\textsubscript{x}N) films were prepared by reactive dc magnetron sputtering onto surface-oxidized Si (001) substrates. The temperature of the substrates was not artificially changed. The substrate temperature was increased by plasma during sputtering, and then the temperature was between 320 and 370 K. The flow rates of Ar and N\textsubscript{2} gases during sputtering were 12 and 3 sccm (standard cc/min), respectively. The sputtering target used in the present study was an iron (3N5) disc (38.5 mm in diameter and 1.0 mm in thickness). The sputtering power was 20 W. The deposition rate of the iron nitride films was 0.06 nm/s. The thicknesses of the iron nitride films were 20, 40 and 120 nm.

Magnetization curves of the iron nitride films were measured using a vibrating sample magnetometer (VSM) with a maximum magnetic field of 18 kOe. The magnetic field was applied parallel and perpendicular to the film plane. Changes of the saturation magnetization due to the measurement temperature were determined using a superconducting quantum interference device (SQUID) magnetometer with an in-plane applied magnetic field of 10 kOe. Ferromagnetic resonance (FMR) spectra were measured using an electron spin resonance (ESR) spectrometer operating at 9.4 GHz and a maximum in-plane magnetic field of 5 kOe in the film plane, in order to investigate the saturation magnetization of each part of the iron nitride films. Changes in electrical resistivity due to the temperature were measured using the four-point terminal method with an applied in-plane current of 0.1 mA. The magnetization curves and the FMR spectra were measured at room temperature. The saturation magnetization and the electrical resistivity were measured in the temperature range of 10–300 K. The structure of the iron nitride films was investigated using an X-ray diffractometer (XRD) with Cu-K\textalpha radiation and a transmission electron microscope (TEM).

3. Experimental results

3.1. Magnetic properties

Fig. 1 shows the magnetization curves of the iron nitride films with various thicknesses. The figure also shows the magnetization curves of the iron film for comparison. As shown in Fig. 1(a), the saturation magnetization of the iron film (4\pi M\textsubscript{s} = 20.4 kG) is slightly lower than that of the bulk (4\pi M\textsubscript{s} = 21.6 kG). As shown in Fig. 1(b), the magnetization of the iron film is not saturated below the field perpendicular to the film plane of 18 kOe, because this Fe film has in-plane magnetic anisotropy. The saturation magnetization and the coercivity do not change in the thickness range of 30–50 nm at the iron films. On the other hand, as shown in Fig. 1(c), (e) and (g) the saturation magnetization of the iron nitride films slightly increase as the thickness increases. The coercivity of the 40-nm-thick iron nitride film is slightly higher than that of the 20-nm-thick iron nitride film. The coercivity of the 120-nm-thick iron nitride film is much higher than that of the 40-nm-thick iron nitride film. As shown in Fig. 1(d), (f) and (h) the saturation field increases as the thickness increases. It can be seen that the magnetic anisotropy of each iron nitride film is
parallel to the film plane. As mentioned above, it is understood that the magnetic properties of the iron nitride film depend on the film thickness.

Fig. 2 shows the saturation magnetization of the iron nitride films with various thicknesses as a function of temperature. The figure also shows the saturation magnetization of the iron film.

**Fig. 2.** Saturation magnetization of the iron nitride films with various thicknesses as a function of temperature. The figure also shows the saturation magnetization of the iron film.

On the other hand, the saturation magnetization of the iron nitride films decreases as the temperature increases. This behavior is similar to that of the iron film. The figure also shows that the saturation magnetization of the iron nitride films is lower than that of the iron film in the measurement temperature range. The saturation magnetizations of the 40-nm-thick and 120-nm-thick iron nitride films are almost the same at the temperature of 10 K, and are higher than that of the 20-nm-thick iron nitride film. Moreover, Fig. 2 shows that the quantity of the decrease in saturation magnetization due to the temperature depends on the film thickness. As the thickness of the film decreases, the quantity of the decrease in saturation magnetization increases. This is because the Curie temperature of the thin film is lower than that of the thick film. As mentioned above, it is understood that the magnetic properties of the iron nitride films are changed by the thickness. Even in the case of the thick films, the film structure near the substrate is similar to that for the thin films. For example, in the 120-nm-thick film, the film structure from the interface with the substrate plane to a location 20 nm away from the substrate plane is similar to the film structure of the 20 nm-thick film. Therefore, the magnetic properties of the initially deposited 20-nm-thick layer in the 120 nm-thick film must be similar to those in the case of the 20-nm-thick film. However, the magnetic properties are largely changed by the film thickness. This phenomenon indicates that the film structure varies as the distance from the substrate plane increases, and thus the magnetic properties vary as the distance from the substrate plane increases.

In order to understand the heterogeneity of the iron nitride films, we measured the FMR of the films. Fig. 3 shows the FMR spectra of the iron nitride films with various thicknesses. The figure also shows the spectrum of the iron film. Because the peak intensity is too weak, the scale of the absorption intensity of the iron film is magnified tenfold. From the spectrum, it can be seen that the iron film shows only a main resonance peak, which is located at a magnetic field of 0.53 kOe. The main resonance field of the iron nitride films increases as the thickness decreases. The saturation magnetizations estimated from the main resonance field are $M_s = 13.7, 14.9$ and $15.6$ kG for 20, 40 and 120-nm-thick iron nitride films, respectively. The magnetization estimated from the main resonance field is slightly higher than that obtained from the magnetization curves. However, the tendency of the changes in saturation magnetization as seen from the main resonance field and the magnetization curves is the same. In the cases of the 20 and 40-nm-thick iron nitride films, only the main resonance peak is observed. However, the 120-nm-thick iron nitride films shows not only the main resonance field, but also the small resonance peak at a field around 0.6 kOe. This indicates that the 120-nm-thick iron nitride film has different phases with different magnetic properties.

### 3.2. Electrical properties

**Fig. 4.** Electrical resistivity change of the iron nitride films with various thicknesses as a function of temperature. The figure also shows the electrical resistivity of the iron film. The electrical resistivity of the iron film
increases as the temperature increases. This behavior is a typical change in electrical resistivity in the metals. The electrical resistivity (15 μΩ cm) of the iron film is higher than that of the single crystalline iron film (around 10 μΩ cm) [19]. This increase in electrical resistivity is considered to be due to the electron scattering by the grain boundary because the iron film prepared in this study has a polycrystalline structure. The electrical resistivity of the iron nitride films is much higher than that of the iron film. The dependence of the electrical resistivity on the temperature is very small for the iron nitride films of each thickness. The electrical resistivity of the iron nitride films slightly decreases as the thickness increases. The relationship between electrical properties and film structures will be discussed in section 4.2.

3.3. Film structure

The above results show that the magnetic and electrical properties of the iron nitride films change as the thickness changes. To clarify the origin of the changes in these properties, we investigate the structure of the iron nitride films. Fig. 5 shows the X-ray diffraction profiles of the iron nitride films with various thicknesses and the profile of the iron film. The iron film shows a diffraction peak at 2θ = 44.7°. This peak comes from the diffraction of α-Fe (110). On the other hand, no diffraction peak was observed for the 20 and 40-nm-thick iron nitride films. A broad diffraction peak was observed between 40 and 50° for the 120-nm-thick iron nitride film as shown by the ellipse in the figure. In the 2θ angle range where the diffraction was observed, (121), (111) and (110) diffraction peaks of ζ-Fe2N, ε-Fe3N and α-Fe of the bulk crystal are located as shown by dotted lines, respectively. It is difficult to determine the phase in the 120-nm-thick iron nitride film by the X-ray diffraction experiment, because the diffraction peak is very broad.

As mentioned above, it is considered, based on the result of the X-ray diffraction experiment, that the crystalline iron nitride film grows as the thickness increases. However, the type of the formed iron nitride phase is not clear. Therefore, the structure of the iron nitride film was investigated by means of transmission electron microscopy. Fig. 6 shows the transmission electron micrographs and the selected area diffraction patterns. Fig. 6(a) shows the dark-field image of the 20-nm-thick iron nitride film. A gray matrix and three white small grains are observed. In order to
clarify the structure of the gray matrix, the diffraction patterns of the gray matrix are observed. As shown in Fig. 6(b), only a halo ring is observed for the gray matrix. Therefore, the gray matrix is considered to consist of the amorphous phase. Fig. 6(c) shows the dark-field image of the 40-nm-thick iron nitride film. As shown in Fig. 6(e), many grains are observed in the amorphous matrix. The number of grains, however, is higher in the 40-nm-thick film than in the 20-nm-thick film. Fig. 6(d) shows selected area diffraction patterns for the amorphous matrix containing the grains. One can observe the diffraction rings from the grain in addition to the halo ring. However, a sufficient number of diffraction rings are not observed to determine the phase. In the bright-field image of the 120-nm-thick film shown in Fig. 6(e), many black grains are observed in the gray matrix. The diameters of the grains in Fig. 6(e) are distributed from 10 to 300 nm. The shape of the grains changes from circular to a square-edge-like as the grain size increases. The gray matrix is considered to be amorphous in the 20-nm-thick and 40-nm-thick iron nitride films. Fig. 6(f) shows the bright-field image of the other areas of the same specimen as that in Fig. 6(e). The many crystallites approximately 300 nm in the size are observed. In order to clarify the phase of the crystallites, the diffraction pattern of the circular area indicated by the white circle in (f) is investigated as shown in Fig. 6(g). The obtained diffraction ring in Fig. 6(g) corresponds to the d-spacing value of the bulk $\varepsilon$-Fe$_3$N phase. From the results, it can be concluded that most parts of the grains observed in Fig. 6(f) have the $\varepsilon$-Fe$_3$N structure.

4. Discussions

4.1. Relationships between structures and magnetic properties of iron nitride films

As mentioned in Section 3.1, the saturation magnetization increased as the thickness of the iron nitride films increased. To clarify the origin of this tendency, the structure of the iron nitride films is investigated. It is found that the grains are dispersed in the amorphous matrix. As the thickness of the iron nitride films increases, both the number of grains and the size of the grains increase. The results of transmission electron microscopy reveal that the structure of the grain in the 120-nm-thick iron nitride film is found to be the $\varepsilon$-Fe$_3$N phase. The saturation magnetization of the $\varepsilon$-Fe$_3$N phase ($4\pi M_s = 16\sim 17$ kG) [8] is larger than that of the amorphous phase ($4\pi M_s = 14\sim 16$ kG). The coercivity of the $\varepsilon$-Fe$_3$N phase is considered to be larger than that of the amorphous phase which has no crystal magnetic anisotropy. Based on these results, the reason for the increase in saturation magnetization and coercivity in the iron nitride films is considered to be that the volume ratio of the $\varepsilon$-Fe$_3$N phase in the iron nitride films becomes large. The increase in volume ratio of the $\varepsilon$-Fe$_3$N phase is caused by the increase in thickness of the iron nitride film. As shown above, the changes in magnetic properties agree well with the changes in film structure and it was found that the growth of the $\varepsilon$-Fe$_3$N phase grain significantly affects the magnetic properties of the iron nitride films.

4.2. Electrical resistivity in iron nitride films

As mentioned in section 3.2, the change in electrical resistivity due to the measurement temperature is small in the iron nitride films. It has been reported that the change in the electrical resistivity due to the measurement temperature is small in amorphous materials [20]. Therefore, it is considered that the existence of the amorphous phase decreases the change in the electrical resistivity of the iron nitride films in this study. Moreover, it is known that the electrical resistivity of amorphous materials is higher than that of crystalline materials [21,22]. Therefore, in this study, the existence of the amorphous phase increases the electrical resistivity of the iron nitride films, and thus the electrical resistivity of the iron nitride films is higher than that of the iron film.

5. Conclusions

We investigated the magnetic and electrical properties of iron nitride film containing both amorphous and nanocrystalline grains. The following results were obtained.

1. The iron nitride films have both amorphous matrices and nanocrystalline grains.
2. The phase of the grains in the amorphous matrices is $\varepsilon$-Fe$_3$N.
3. Both the number and size of the $\varepsilon$-Fe$_3$N phase grains increase as the thickness of the iron nitride film increases.
4. The saturation magnetization and the coercivity at room temperature increase as the film thickness increases.
5. The electrical resistivity of iron nitride films is higher than that of iron film. The change in electrical resistivity due to the measurement temperature is small in the iron nitride films.

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