Structure and high-frequency soft-magnetic properties of Co–TiN nano-composite films

Yiwen ZHANG,* Nobukiyo KOBAYASHI,** Shigehiro OHNUMA*,** and Hiroshi MASUMOTO*†

*Center for Interdisciplinary Research, Tohoku University, Sendai 982-8578, Japan
**Research Institute for Electromagnetic Materials, Sendai 982-0807, Japan

The interest in the soft magnetic nano-composite films has grown to realize down-sized microelectronic devices at GHz frequency. In this study, the good soft magnetic Co–TiN nano-composite films were successfully prepared at room temperature (RT) by a sputtering method. XPS results prove that the Co in the films is pure metallic state. The nano-composite films show good frequency response of permeability, which resonance frequency is as high as 1.3 GHz. The films have high magnetic loss absorption (Ploss) around 1.5 GHz range, which have a high potential for noise suppressors in high frequency devices.

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1. Introduction

Recently, the nano-composite film has attracted much attention owing to its valuable properties and simple process at room temperature (RT).1)–3) In particular, Co particles-oxide matrix nano-composite films (e.g. Co–AlO, Co–ZrO and Co–SiO2) show a good soft-magnetic property with high resonance frequency (f0), which can be used in inductor and electromagnetic compatibility (EMC) suppressor for down-sized microelectronic devices at GHz frequency. However, the permeability (μ) of (Co-metal)-(oxide-ceramic) system is relative lower than that of theoretical calculation, which can be due to easy oxidation of Co.4)–7)

In our study, TiN ceramic has been employed as structural (matrix) phase, considering the good chemical and thermal stability of TiN (a kind of diffusion blocking material). Recently, perpendicular magnetic Co–TiN films with large coercivity (Hc) have been studied for future high-density magnetic recording with the nano-fiber structure.30) However, there has been less study related to the soft magnetic Co–TiN nanogrannular films.3) In this article, the effect of film thickness on the Co–TiN nano-composite ceramic films, the structure and magnetic properties of Co–TiN nano-composite films have been investigated at RT.

2. Experimental procedure

Co–TiN films were prepared on Si, quartz and Pt/Si substrates by rf reactive magnetron sputtering method in a sputtering Ar gas pressure of 2 × 10⁻¹ Pa at RT. Composite targets were composed of a TiN disk and Co chips on the disk. The thickness of the films was controlled by sputtering time from 10 to 60 min. Film structures were investigated by X-ray diffraction analysis (XRD, Rigaku, RINT-2400) and field emission-scanning electron microscopy (FE-SEM, Hitachi 4300E). The chemical composition of the films was analyzed by Rutherford backscattering spectroscopy (RBS) and X-ray photoelectron spectroscopy (XPS). The magnetization vs. field was measured with a vibrating sample magnetometer (VSM, Riken densi, BHV-30SS). The μ from 10 MHz to 3 GHz was determined by a shielded loop coil method.10) A microstrip line (MSL, W = 3 mm × L = 75 mm) of Zc = 50 Ω connected at both ends to the network analyzer (Agilent 8753ES) was used to evaluate noise suppression effects of conduction current.1)

3. Results and discussion

The RBS test shows that the Co–TiN films are composed of Co55–(TiN)45 composite. XPS results prove that the Co chemical state is pure metallic state. In Fig. 1 the XRD results show that no crystalline peak of the films can be observed, when the thickness of Co–TiN films is lower than 100 nm. When the thickness of films is above 150 nm, the TiN (200) peak appears. From calculation by Scherrer Formula, the size of TiN particles decreases from 6 to 4 nm, when the thickness of films increases from 170 to 510 nm. And the TiN particle size keeps around 4 nm with the thickness from 510 to 920 nm. However, no obvious Co crystalline peak is observed in all the films, which means the Co should be of metallic amorphous phase in films. Cross-section
SEM figures (Fig. 2) show that Co-TiN films are smooth and dense. The column structure can be observed clearly in the films with thickness higher than 340 nm, which is consistent with the appearance of TiN (200) peak in XRD results.

Typical soft-magnetic hysteresis loops of Co-TiN composite films are shown in Fig. 3, with magnetic field applied parallel to film surface. The magnetization at 5 kOe is as high as about 8 kG, and it is independent of film thickness, which indicates the homogeneous distribution of Co content in the films. Owing to Co pure metallic state in the films, the magnetization is consistent with the theoretical calculation from Co content in all the films, which is a great advantage over the (Co-metal)-(oxide-ceramic) system reported.

Figure 4 shows the low-field (250 Oe) magnetic loops of in-plane magnetized Co-TiN films with thickness of 340, 520 and 920 nm. All the films have hard and easy axes of magnetization. It is noteworthy that the anisotropy of all the films is as high as about 25 Oe, which could lead to good high-frequency soft magnetic properties with high $f_r$ of $\mu$. With film thickness increasing, the $H_c$ decreases from 15 to 5 Oe, which could be owing to the stress and nano-particle size change with different film thickness. However, it is noticeable that the thin Co–TiN films (520, 340 nm) show high hard axis coercivity. As is well known, the ideal in-plane uniaxial magnetic films have near 0 Oe coercivity of hard axis. Therefore, the thin Co–TiN films could have easy axis dispersion, which are assumed to consist of many small regions having different local direction of easy axis to the average easy axis direction of the films. When the applied field is along the average hard axis, small regions with easy axis dispersion show the magnetization component on hard axis. After removal of the field, the average remanence ($M_r$) of these small regions appears along the hard axis, which is observed in the thin Co–TiN films (520, 340 nm). This analysis is also consistent with the results of frequency response on permeability ($\mu$-f response) of Co–TiN films in Fig. 5. In ideal in-plane uniaxial magnetic anisotropy films, no $\mu$-f response along easy axis can be observed at more than MHz range. However, the $\mu$-f response of 340 nm Co–TiN film [Fig. 5(c)] shows high $\mu$ value along both average easy and hard axes, which proves the existence of easy axis dispersion. This phenomenon is reasonable, because the uniaxial magnetic anisotropy in this film has been naturally induced, for example, by the Ar gas flowing effect during the sputtering deposition. If the uniaxial magnetic anisotropy is artificially controlled, e.g. by magnetic field, the sample may show no $\mu$-f response along the easy axis. In contract, the sample of 920 nm [Fig. 5(a)] shows higher $\mu$ value (around 300) only along the hard axis, which indicates good alignment of easy axis, i.e. the thick Co–TiN films (920 nm) is a nearly ideal uniaxial magnetic material. The resonance frequency of all the films is as high as 1.3 GHz. The resistivity of all the films is around 220 $\Omega$ cm. This experiment result is consistent with a theoretical calculation by the L. L. G. formula for soft magnetic thin films with in-plane uniaxial magnetic anisotropy. The $f_r$ can be calculated with following equation:

$$f_r = \frac{\mu \gamma}{2 \pi \sqrt{4\pi M_s \cdot H_k}}$$

Fig. 2. SEM cross section morphology of the Co–(TiN) samples with the thickness = 90, 340, 520, 920 nm.

Fig. 3. (Color online) Magnetic hysteresis loops of Co–TiN films with the thickness = 90, 340, 520, 720, 920 nm.
where $\gamma$ is the gyromagnetic ratio ($1.76 \times 10^7 \text{Oe}^{-1}\text{s}^{-1}$), $4\pi M_s$ is saturation magnetization ($B_s$). According to B-H loop test results in Figs. 3 and 4, the Co–TiN film of 920 nm has $4\pi M_s$ of 8.3 kGs and $H_k$ of 25 Oe. From calculation of Eq. (1), the $f_r = 1.28$ GHz.

The initial permeability is given by $\mu_i = 4\pi M_s/H_k = 330$. In Fig. 5, the $\mu-f$ response test result is accordant with theoretical calculation result here.

The magnetic damping effect, which has been considered for excellent noise suppressor in GHz frequency range, is in proportional to the imaginary permeability and thickness of the films in principle. Noise suppression capability is evaluated by the ratio of dissipated power at the magnetic film portion to the incident power, as

$$\frac{P_{\text{loss}}}{P_{\text{in}}} = 1 - (S_{t2}^2 + S_{r1}^2) \tag{2}$$

where $S_{t2}^2$ is transmission power ratio, $S_{r1}^2$ is reflection loss power ratio. By the MSL measurement, the Co–TiN composite films show frequency dependence of noise absorption effect ($P_{\text{loss}}/P_{\text{in}}$) with different film thickness in Fig. 6. This noise absorption ($P_{\text{loss}}/P_{\text{in}}$) is from pure magnetic loss, after removing the eddy current loss effect by test method (not discuss here). All the films show the absorption peak around 1.5 GHz, which is consistent with the $\mu-f$ response test result. With the thickness increasing, the absorption peak becomes higher and broader, owing to the change of thickness and imaginary permeability, respectively.

4. Summary

XPS results prove that the Co chemical state in Co–TiN nano-composite films is pure metallic state, which is a great advantage over the (Co-metal)-(oxide-ceramic) system reported. When thickness of the films is above the 150 nm, the TiN (200) peak appears in XRD. The particle size of TiN decreases from 6 to

Fig. 4. (Color online) Low-field magnetic hysteresis loops of the Co–TiN film with the thickness = 340, 520, 920 nm.

Fig. 5. (Color online) Frequency response on permeability ($\mu-f$ response) of the Co–TiN films along hard and easy axes: (a) 920 nm; (b) 520 nm; (c) 340 nm.
4 nm, when thickness of the films increases from 170 to 510 nm. No obvious Co crystalline peak is observed in all the films. The films show high $B_s$ at 5 kOe of about 8 kG, high $H_k$ of around 25 Oe, which are independent of film thickness. The $H_c$ decreases from 15 to 5 Oe with thickness increasing. The $\mu$-$f$ response of 340 nm Co–TiN film show high $\mu$ value along both average easy and hard axes. In contrast, the sample of 920 nm shows higher $\mu$ value (around 300) only along the hard axis, which should be a nearly ideal uniaxial magnetic material. The $\mu$-$f$ response test result is accordant with theoretical calculation result. Comparing to (Co-metal)-(oxide-ceramic) system, the Co–TiN films have higher $\mu$ value. Moreover, the films show the high magnetic loss absorption around 1.5 GHz, which is promising for using in various noise-suppress applications.

Fig. 6. (Color online) Measured ratio of the power loss to the incident power ($P_{\text{loss}}/P_{\text{in}}$) for Co–TiN films with the thickness = 340, 520, 920 nm.