Microstructure and magnetic properties of the FeTaCN nanocrystalline thin films

C. Y. Chou[a] and P. C. Kuo
Institute of Materials Science and Engineering, National Taiwan University, Taipei 106, Taiwan

Y. D. Yao
Institute of Physics, Academia Sinica, Taipei 115, Taiwan

S. C. Chen
Department of Mechanical Engineering, De Lin Institute of Technology, Taipei 236, Taiwan

A. C. Sun and C. T. Lie
Institute of Materials Science and Engineering, National Taiwan University, Taipei 106, Taiwan

(Presented on 13 November 2002)

FeTaCN films were deposited on quartz substrates by cosputtering of Fe and TaC targets at room temperature with different N_2 flow rate ratios in the sputtering gas. The as-deposited films were postannealed in vacuum for 30 min at various temperatures. The effects of annealing temperature on the N_2 flow rate ratio and film thickness on the magnetic properties and microstructure of the film were investigated. X-ray diffraction and transmission electron microscopy analyses show that the as-deposited FeTaCN film has a nanocrystalline structure or mixing phases of nanocrystalline and amorphous. Nanocrystalline as-deposited film with good soft magnetic properties (in-plane coercivity $Hc_{\parallel}=1\sim2$ Oe and $4\pi Ms=12-14$ kG) can be obtained by controlling the N_2 flow rate ratio and film thickness. The soft magnetic properties can be improved by postannealing the as-deposited film at 200–300 °C as the N_2 flow rate ratio is higher than 5 vol %. For the $Fe_{71.03}Ta_{6.1}C_{7.2}N_{15.67}$ film, the $Hc_{\parallel}$ value decreases as the film thickness is increased when the annealing temperature is lower than 400 °C. After annealing at 300 °C, its $Hc_{\parallel}$ is about 3.57 Oe as the film thickness is 50 nm and $Hc_{\parallel}$ will decrease to 0.18 Oe as the film thickness is increased to 1000 nm. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1555904]

Pure Fe film has a large magnetocrystalline anisotropy and large magnetostriction, which are undesirable from the point of view of soft magnetic properties. It has been known that the addition of some transition metals to Fe film will improve its soft magnetic properties.[1] Recently, the enhancement of the soft magnetic properties of these doped films with nitrogen or carbon incorporation has been extensively investigated.[2,3] Generally, the soft magnetic properties of Fe-based nanocrystalline films originate from the fine grain size and strong intergranular ferromagnetic exchange coupling, which will reduce the magnetocrystalline anisotropy.[4] However, good soft magnetic properties in these Fe-based alloy films are usually obtained by either substrate heating at elevated temperatures during deposition, or postannealing at temperatures around 400–600 °C (Ref. 5) to nanocrystallize the deposited films. This will restrict the application of them to the magnetic devices which require low temperature fabrication processes.

In this work, we investigated the magnetic properties and microstructure of the FeTaCN film and make an effort to obtain the as-deposited film with good soft magnetic properties and thermal stability by optimizing the sputtering parameters.

The FeTaCN film was fabricated on quartz substrate by dc-magnetron reactive cosputtering of Fe and TaC targets at room temperature. The TaC target was made by a Ta disk overlaid with C chips which covering about 18% of the disk surface area. The sputtering power density was fixed at 3.49 W/cm^2 for the Fe target and 1.97 W/cm^2 for the TaC target. The base pressure was below 4×10^{-7} Torr. The N_2 flow rate ratio, defined as $R(N_2)=F(N_2)/[F(Ar)+F(N_2)]\times100\%$, where $F(N_2)$ and $F(Ar)$ are the N_2 and Ar flow rates in the sputtering gas, respectively. $R(N_2)$ in the sputtering gas was varied from 1% to 15%. The film thickness was varied from 50 to 1000 nm. A SiN_x cap layer of about 20 nm was deposited on the FeTaCN film by rf magnetron sputtering of the Si_3N_4 target to prevent oxidation of the magnetic film. After deposition, the films were annealed in vacuum below 1×10^{-5} Torr for 30 min at a temperature between 200 and 500 °C, then quenched in ice water. The composition of the film was analyzed by x-ray photoelectron spectroscopy (XPS). The microstructure and crystal structure of the film were investigated by a Philips Tecnai F30 field emission gun (FEG) transmission electron microscopy (TEM) and a thin-film X-ray diffractometer (XRD) with Cu $K\alpha$ radiation. The magnetic properties of the films were measured by a vibrating sample magnetometer (VSM).

Figure 1 shows the x-ray diffraction patterns of the as-deposited and various annealed $Fe_{63.68}Ta_{6.06}C_{4.95}N_{25.31}$ films, which annealed at different annealing temperatures. The film thickness is 200 nm and the $R(N_2)$ during deposition is 15 vol %. No sharp x-ray diffraction peak is observed for the as-deposited film. We conjecture that the structure of the as-deposited film may be nanocrystalline or mixed phases of

[a]Electronic mail: a3150@ms3.hinet.net

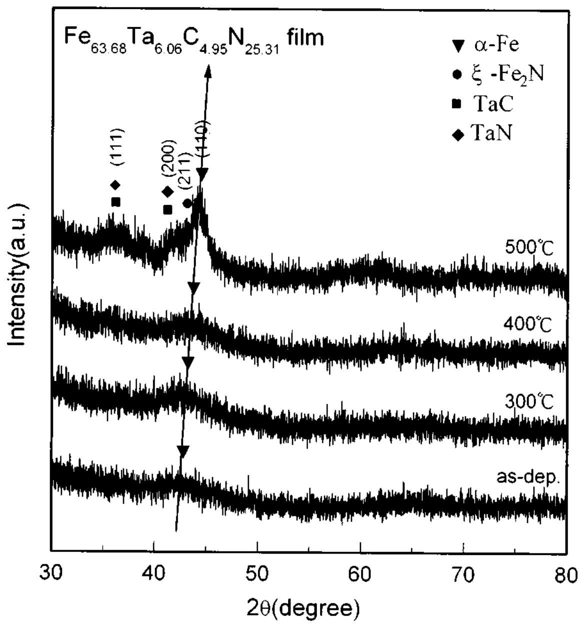

FIG. 1. X-ray diffraction patterns of the as-deposited and annealed $Fe_{63.68}Ta_{6.06}C_{4.95}N_{25.31}$ films.

nanocrystalline and amorphous. A broad peak is observed as the film is annealed at 300 °C. The broad peak is still observed when the annealing temperature is increased to 400 °C. This may be caused by the poor crystallinity of the film. Besides, no evidence is found for the existence of nitride or carbide phases. This may be due to the too small volume fractions of the nitride and carbide phases in the film that were difficult to detect by XRD. It can be also seen that the α-Fe(110) peak shifts to its typical peak position as the annealing temperature is increased. This means that the lattice spacing of the (110) planes is decreased as the annealing temperature is increased. It can be related to the stress relief, which is caused by diffusing out of C and N atoms from the α-Fe grain to reduce the Gibbs free energy. Some broad TaC(N) and ξ-Fe_2N diffraction peaks and a more clear α-Fe(110) peak were observed as the annealing temperature is increased to 500 °C. Precipitation of the ξ-Fe_2N phase, as shown in Fig. 1, will result in deterioration of the soft magnetic properties of the film.

Figure 2 shows the TEM bright field image and selected area diffraction (SAD) pattern of the as-deposited $Fe_{66.87}Ta_{7.09}C_{6.77}N_{19.27}$ film. The film thickness is 200 nm. The $R(N_2)$ during deposition is 10 vol % for this film. We

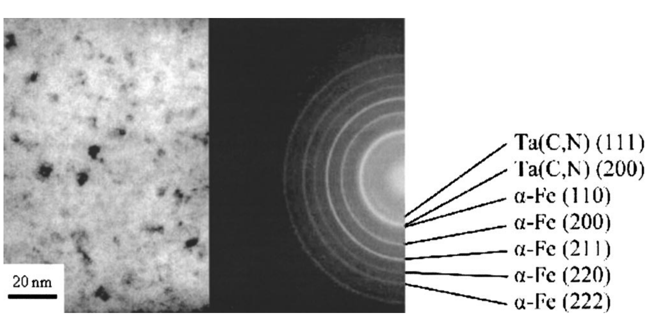

FIG. 2. TEM bright field image and electron diffraction pattern of the as-deposited $Fe_{66.87}Ta_{7.09}C_{6.77}N_{19.27}$ film.

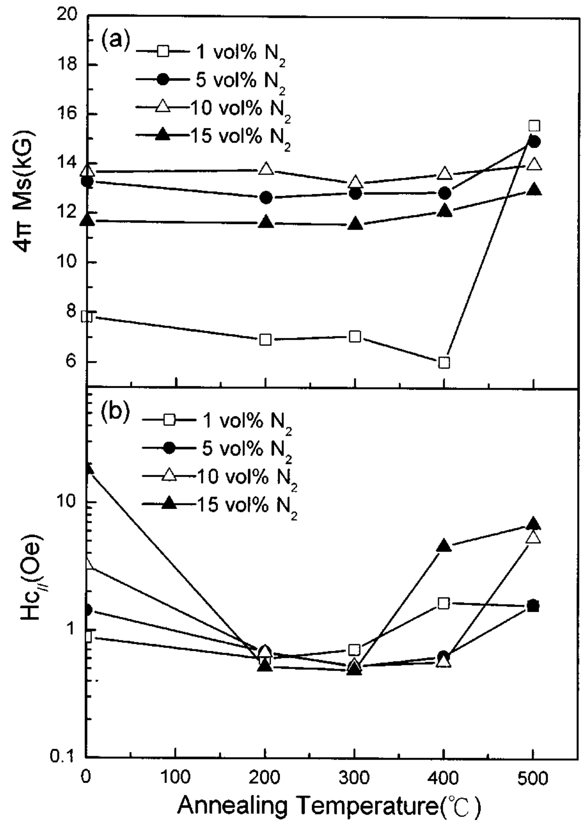

FIG. 3. Variations of (a) the saturation magnetization $4\pi Ms$ and (b) the in-plane coercivity $Hc_{\parallel}$ with annealing temperature for the FeTaCN films with different N_2 flow rate ratios.

can see that this film has a nanocrystalline structure. This film consists of small α-Fe grains and more smaller Ta(C, N) precipitates. The average grain size of α-Fe is about 6 nm, which is smaller than that of the $Fe_{71.03}Ta_{6.1}C_{7.2}N_{15.67}$ film [$R(N_2)$ is 5 vol %]. The average grain size of α-Fe observed by TEM is about 8 nm for the $Fe_{71.03}Ta_{6.1}C_{7.2}N_{15.67}$ film. Since the $R(N_2)$ of the $Fe_{66.87}Ta_{7.09}C_{6.77}N_{19.27}$ film is larger than that of the $Fe_{71.03}Ta_{6.1}C_{7.2}N_{15.67}$ film, it is believed that the number of TaN precipitates increases with $R(N_2)$ during film deposition owing to their large formation enthalpy. As a result, more α-Fe grains will nucleate from the TaN surface as $R(N_2)$ is increased. Therefore, the smaller grain size of the $Fe_{66.87}Ta_{7.09}C_{6.77}N_{19.27}$ film is formed.

Figures 3(a) and 3(b) show variations of saturation magnetization $4\pi Ms$ and in-plane coercivity $Hc_{\parallel}$ with annealing temperature, respectively, of various FeTaCN films deposited at different $R(N_2)$. The film thickness is 200 nm. From Fig. 3(a) we can see that the $4\pi Ms$ value is more sensitive to annealing temperature when the N_2 flow rate ratio is lower, especially 1 vol % N_2. The $4\pi Ms$ value increased drastically from 5.9 to 15.6 kG as the annealing temperature increased from 400 to 500 °C for the film with 1 vol % $R(N_2)$. The TEM observation shows that rapid increase of $4\pi Ms$ value when annealed at 500 °C is due to the change of microstructure of this film. This film is changed from low $4\pi Ms$ of mixing nanocrystalline and amorphous phases to the high $4\pi Ms$ crystalline α-Fe phase at this temperature.[6]

At an $R(N_2)$ below 10 vol %, the increase of $4\pi Ms$ with $R(N_2)$ is also due to the increase of crystallinity of the film. As $R(N_2)$ further increases to 15 vol %, the decrease of $4\pi Ms$ may be due to the reaction of supersaturated N atoms with Fe and Ta atoms, forming a nonmagnetic TaN phase and weaker ferromagnetic or nonmagnetic FeN_x phase. Therefore, the $4\pi Ms$ value of this film is lower than that of 10 and 5 vol % $R(N_2)$ films, as shown in Fig. 3(a). From Fig. 3(b), we can see that the as-deposited film has higher $Hc_\parallel$ value than that of the annealed film and $Hc_\parallel$ increases with the $R(N_2)$ for the as-deposited film. The higher $Hc_\parallel$ value for larger $R(N_2)$ film is ascribed to the distortion of crystal lattice that come from the occupation of N atoms in the interstitial sites. This resulting in large internal stress in the film, thus, impeding the domain wall motion and degrading the soft magnetic properties. The soft magnetic properties can be improved by postannealing the film at 200 to 300 °C as shown in Fig. 3(b). This is due to the stress relief result from the diffusing of C and N atoms out from α-Fe grains to reduce the Gibbs free energy, as discuss above. The $Hc_\parallel$ value increases as the annealing temperature is higher than 400 °C. It is related to the large residual stress resulting from quenching the film in ice water after high temperature annealing and the grain growth after annealed above 400 °C.

It should be noted that the $Hc_\parallel$ value of the 5 vol % $R(N_2)$ film ($Fe_{71.03}Ta_{6.1}C_{7.2}N_{15.67}$ film) is lower than that of 10 vol % $R(N_2)$ film ($Fe_{66.87}Ta_{7.09}C_{6.77}N_{19.27}$ film) after being annealed at 500 °C. Although the crystal phases of are identical, the average α-Fe grain size of the $Fe_{71.03}Ta_{6.1}C_{7.2}N_{15.67}$ film is larger than that of the $Fe_{66.87}Ta_{7.09}C_{6.77}N_{19.27}$ film after being annealed at 500 °C. From the TEM observation, the average α-Fe grain size of the $Fe_{71.03}Ta_{6.1}C_{7.2}N_{15.67}$ film is about 9 nm and the $Fe_{66.87}Ta_{7.09}C_{6.77}N_{19.27}$ film is about 6 nm after being annealed at 500 °C. The smaller $Hc_\parallel$ value of the $Fe_{71.03}Ta_{6.1}C_{7.2}N_{15.67}$ film is attributed to that it has appropriate size and amount of TaC or TaN particles. Owing to the excessive TaC or TaN precipitates in the $Fe_{66.87}Ta_{7.09}C_{6.77}N_{19.27}$ film that reduce the exchange coupling force between ferromagnetic grains, the $Hc_\parallel$ value of this film is larger than that of the $Fe_{71.03}Ta_{6.1}C_{7.2}N_{15.67}$ film as shown in Fig. 3(b).

Figures 4(a) and 4(b) are the variations of $4\pi Ms$ and $Hc_\parallel$ with annealing temperature, respectively, of the $Fe_{71.03}Ta_{6.1}C_{7.2}N_{15.67}$ films with various film thickness. It can be seen that the $4\pi Ms$ value is lower than 12.2 kG as the annealing temperature below 400 °C and the film thickness higher than 400 nm. This low $4\pi Ms$ value is related to more nonmagnetic atoms, such as Ta, C, and N atoms, dissolved into the Fe-based matrix. From Fig. 4(b), we can see that the $Hc_\parallel$ value decreases with increasing film thickness when the annealing temperature is lower than 400 °C. The decrease of the coercivity with increasing film thickness is consistence with the Hoffmann's magnetization ripple theory.[7,8] After being annealed at 300 °C, the $Hc_\parallel$ value is about 3.57 Oe as the film thickness is 50 nm, the $Hc_\parallel$ value will decrease rapidly to 0.18 Oe as the film thickness is increased to 1000 nm. But, the $Hc_\parallel$ value increases drastically as the film thickness is increased as the annealing temperature further increases to 500 °C, especially as the film thickness is larger than 400 nm. This is due to the large thermal stress forming in the film that is caused by the thermal expansion coefficient difference between the FeTaCN film and the quartz substrate after quenching from high temperature.

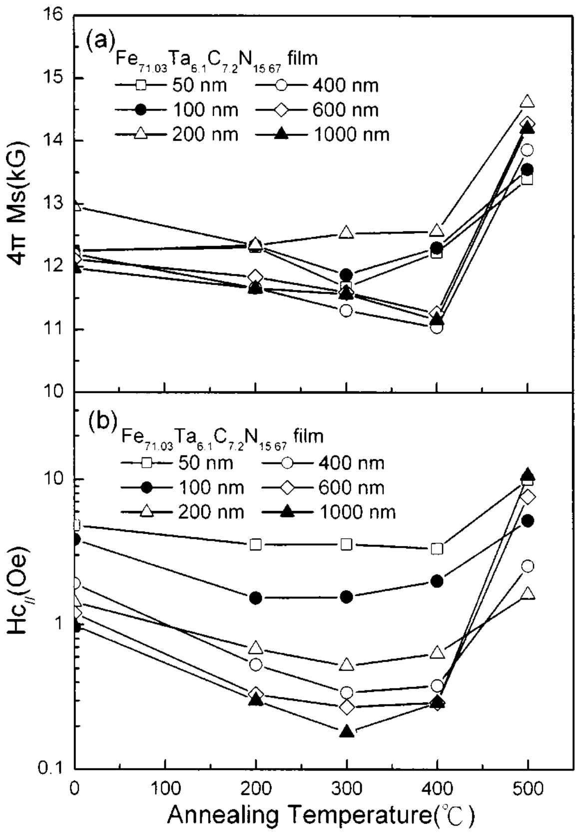

FIG. 4. Variations of (a) the saturation magnetization $4\pi Ms$ and (b) the in-plane coercivity $Hc_\parallel$ with annealing temperature for the $Fe_{71.03}Ta_{6.1}C_{7.2}N_{15.67}$ films with different thicknesses.

We have successfully achieved good soft magnetic properties for the as-deposited film by simultaneous addition of C and N to the FeTa alloy film. Comparing the conventional FeTaC and FeTaN alloy films, the high temperature annealing process is avoided by combination addition of C and N to FeTa alloy film. The magnetic properties of the FeTaCN films are very sensitive to the N_2 flow rate ratio. The fine crystalline α-Fe grain together with appropriate size and amount of TaC or TaN precipitates in the film are the essential factors to obtain the good soft magnetic properties.

This work was supported by the National Science Council of ROC through Grant No. NSC 90-2112-M-001-065. The authors would like to thank Hsueh-Ren Chen for TEM observations.

[1] N. Kataoka, M. Hosokawa, A. Inoue, and T. Masumoto, Jpn. J. Appl. Phys., Part 2 **28**, L462 (1989).
[2] B. Viala, M. K. Minor, and J. A. Barnard, J. Appl. Phys. **80**, 3941 (1996).
[3] M. Miura and A. Obata, IEEE Trans. Magn. **32**, 1952 (1996).
[4] G. Herzer, IEEE Trans. Magn. **26**, 1397 (1990).
[5] O. Kohmoto, IEEE Trans. Magn. **27**, 3640 (1991).
[6] M. Naoe, M. Kodaira, Y. Hoshi, and S. Yamanaka, IEEE Trans. Magn. **17**, 3062 (1981).
[7] H. Hoffmann, Thin Solid Films **58**, 223 (1979).
[8] J. Zhang, X. B. Yang, H. Ninomiya, and H. Hoffmann, J. Magn. Magn. Mater. **131**, 278 (1994).