Analysis of microstructure of magnetic Fe$_3$C nanograins embedded in amorphous carbon films

Y. H. Lee, a) T. C. Han, and J. C. A. Huang
Department of Physics, National Cheng-Kung University, Tainan 70101, Taiwan, Republic of China

C. R. Lin
Department of Mechanical Engineering, Southern Taiwan University of Technology, Tainan 710, Taiwan, Republic of China

(Received 20 June 2002; accepted 16 May 2003)

The dc magnetron co-sputtering technique was used in fabricating amorphous carbon films containing magnetic Fe$_3$C nanograins. A composite target of a 2-in.-diam graphite disk plus several pieces of iron rods, 2 mm in diameter and 4 mm in length, were used. The films containing pure Fe$_3$C grains could be obtained only in proper sputtering conditions. Films containing only grains of Fe$_3$C phase were subjected to postdeposition annealing at temperatures of 250 to 600 °C for 60 and 90 min, respectively. Auger electron spectroscopy was used to determine the atomic concentration and its fluctuations. The microstructure and phases of grains were determined by high-resolution transmission electron microscopy (HRTEM) and selected area diffraction patterns. Very good crystallinity appeared at $T_a$~250 °C. From the HRTEM image, lattice spacings of 6.7 Å—corresponding to Fe$_3$C (001) planes—and 4.3 Å—corresponding to Fe$_3$C (100) planes—were observed. Higher annealing temperature and larger annealing time caused an increase of grain size. The largest grain (18 nm) was obtained at $T_a$=550 °C. © 2003 American Institute of Physics.

[DOI: 10.1063/1.1589590]

I. INTRODUCTION

High density, on the order of 100 Gb/in.$^2$, and low noise recording medium are a target of many scientists striving for ever-increasing storage capacities and speed in retrieving and storing information. Many different materials and methods$^{1-5}$ have been proposed to achieve this objective. Recently, both nonmagnetic films containing magnetic nanograins and nanocomposites of magnetic particles with nonmagnetic overcoatings have received much attention. The coercivity at room temperature are promising in having stable recorded information. Materials having high coercivity and thermal stability becomes an important factor in having stable recorded information. Materials having high coercivity are promising in having enough thermal stability.

We begin with a summary of some past results due to others, focusing on Fe–C composites. Hirano and Tajima$^{7,8}$ have reported iron carbide (Fe$_2$C$_2$,Fe$_3$C$_3$) particles synthesized by chemical methods. Bi et al.$^9$ used CO$_2$ laser pyrolysis to make Fe$_3$C and Fe$_2$C$_3$ nanoparticles. Later, Tajima and Hirano$^{10}$ proposed to take advantage of the exemption from binders and made polycrystalline films of Fe$_3$C by using rf magnetron sputtering. Watanabe$^{11}$ and Sorowardame,$^{12}$ respectively, proposed making polycrystalline ion carbide films (Fe$_2$C, Fe$_3$C, and Fe$_7$C$_3$) by a getter sputtering technique and plasma enhanced chemical vapor deposition. The films synthesized by Babonneau et al.$^{13}$ using ion-beam sputtering co-deposition were iron crystallites encapsulated in graphite-like nanocages. The room-temperature coercivity of the polycrystalline carbide films of Tajima and Hirano was 250 Oe and that of Babonneau et al. was 430 Oe.

In our study, we found that pure Fe$_3$C nanograins embedded in amorphous carbon films can be obtained under proper sputtering conditions on quartz (SiO$_2$) substrate without intentional heating. The highest room-temperature coercivity of 965 Oe was obtained for a film with 72 at. % C after annealing at 550 °C for 60 min. Magnetic properties of the films are closely related to the structures, sizes, phases and even shapes of the embedded grains, which are in turn related to the sputtering conditions. In this article, we pay attention to the effects of the sputtering pressure and the annealing temperature on the structures and phases of magnetic grains. The magnetic property is discussed in a separate article.$^{14}$

II. EXPERIMENT

Our samples were prepared by using a dc magnetron sputtering system with a basic evacuated pressure of 1×10$^{-6}$ Torr. The argon gas pressure was varied from 15 to 4 mTorr. Films were deposited on the substrates of SiO$_2$ without intentional heating. The substrate of a carbon coated copper grid was used for transmission electron microscopy (TEM) measurements. A composite target of a 2-in.-diam graphite plate (99.99%) plus 0.5, 1, 3, and 7, respectively, pieces of iron rods (99.99%) were used. Each piece of iron rod was cut in 4 mm length from a 2-mm-diam iron wire. The thickness of the films was measured by using a surface...
FIG. 2. Relation of the carbon concentration to the argon gas pressure and the number of pieces of iron rods. Dashed line indicates a region of lower pressures and higher carbon concentrations in which pure Fe3C grains were obtained.

profiler (DECTEC II) and maintained at about 100 nm. The samples were sealed in the evacuated quartz tubes for post-deposition annealing. Two different annealing times of 60 and 90 min were used and the annealing temperature, $T_a$, was varied from 250 to 600 °C. Auger electron spectroscopy (AES, Fison Microlab 310D) was used to determine the atomic concentration and its distribution through the thickness of the film. High-resolution transmission electron microscopy (HRTEM, JEOL 3010) was used for the study of the microstructure.

III. RESULTS AND DISCUSSIONS

Figure 1 shows both the atomic concentration and its distribution in the depth of the film. The depth of the film was expressed in terms of the sputtering time. The zero sputtering time in the abscissa of Fig. 1 corresponds to the film surface. The sputtering rate was $\sim 3.6$ nm/min. We observed only atoms of carbon and iron and no other elements in the films. The carbon and iron concentrations, 72% and 28%, respectively, were maintained throughout the film except close to (<5 nm) the substrate surface. For the as-deposited films, lower carbon and higher iron concentrations (dotted lines) were observed. But after annealing, the iron/carbon concentration is increased. Both distributions became almost flat at $T_a = 450$ °C. The sample of 85 at. % C were annealed at an $T_a = 450$ °C, see Fig. 3. The sample of 85 at. % C were annealed at an $T_a = 450$ °C. The carbon and iron concentrations, 72% and 28%, respectively, were maintained throughout the film except close to (<5 nm) the substrate surface. For the as-deposited films, lower carbon and higher iron concentrations (dotted lines) were observed. But after annealing, the iron/carbon concentration is increased. Both distributions became almost flat at $T_a = 450$ °C. See the solid curves in Fig. 1. For simplicity, only the results of $T_a = 350$ and 450 °C are shown in Fig. 1. A completely flat distribution was observed at $T_a = 500$ °C. We also found that the good adhesion to the substrate in the as-deposited films was gradually lost after annealing at $T_a = 450$ °C. It was obvious that more iron atoms appeared near the substrate surface of the as-deposited films and provided a good bonding between the film and the substrate surface. But the bonding between the iron atoms and the substrate surface was destroyed at $T_a = 450$ °C. Similar behaviors were observed in films of other carbon concentrations.

We could vary the carbon concentration by changing either the argon gas pressure or the number of pieces of iron rods. Figure 2 shows that the carbon concentration decreases with increasing the number of iron rods at constant sputtering pressure. At a given number of iron rods, carbon concentration decreases with decreasing pressure. Therefore, two equal carbon concentrations could be obtained by using either more pieces of iron rods at a high pressure or little pieces of iron rods at a low pressure. It seemed that the higher sputtering rates of iron atoms was obtained at lower pressures. But the iron atoms sputtered at low pressures are not inclined to form the iron grains. From analysis of the TEM results below, we found that low pressure suppressed the growth of iron grains and favored the growth of carbide grains.

We had taken the TEM images and the corresponding selected area diffraction (SAD) patterns for each carbon concentration at different constant pressures. In Fig. 3, we showed only the standard results of 42 and 85 at. % C, respectively, obtained at a constant pressure of 8.5 mTorr. The black spots in the TEM images, Fig. 3(a) and 3(b), are iron or/and iron carbide (Fe3C) grains, and the white background is carbon matrix because iron has a much larger atomic weight than carbon. In the SAD pattern of Fig. 3(c), many rings are indexed as belonging to the crystal planes of Fe3C phase. But there are still two rings indexed as belonging to iron crystal planes of (211) and (310). It indicates that both iron and iron carbide grains exist in the film of 42 at. % C. As the carbon concentration is increased, not only the number of diffraction rings of iron phase decreased, but the rings also became broad and vague. When the concentration reached 85 at. % C, no rings indexed as iron phase can be found in the SAD pattern [see Fig. 3(d)]. It can be that the iron grains were too small to show clear diffraction rings or there were really no iron grains. Films of 42, 65, and 80 at. % C, all made at a constant pressure of 8.5 mTorr, were subjected to postdeposition annealing at $T_a = 250$ °C for 60 min. Large iron spots (10–20 nm) were observed in the TEM images in all three films. Only the TEM image of 42 at. % C is shown in Fig. 4(a). The sample of 85 at. % C were annealed at an
even higher temperature $T_a = 350 ^\circ \text{C}$ for 60 min, but still no iron spots appeared in the TEM image [see Fig. 4 (b)]. The results showed that the sample of 85 at. % C contained only pure Fe$_3$C nanograins, because any tiny iron grains in the film will become the seed of growing grains which will soon aggregated and grow into large iron grains under heat treatment.

We shall now compare two films with roughly the same carbon concentration but with one fabricated at a high and the other at a low argon pressure. For example, the films of 56 at. % C made at 15 mTorr and of 60 at. % C at 4 mTorr, or the films of 79 at. % C made at 15 mTorr and of 78 at. % C at 6 mTorr (as shown in the Fig. 2). From both the TEM images and the SAD patterns (not shown), the films made at the lower pressures always contain larger carbide grains and less or even no iron grains. It seems that iron atoms sputtered at lower pressures favored forming a Fe$_3$C phase. We found that there was a region of lower pressures and higher carbon concentrations in which pure Fe$_3$C nanograins could be obtained. In this region the smaller carbon concentration provided larger Fe$_3$C grains. We pointed out this region by using a dashed line in Fig. 2.

The sample of 72 at. % C made at the pressure of 4 mTorr had pure and relatively large carbide grains. This film was thus chosen for post deposition heat treatments. We show the HRTEM image of the film annealed at $T_a = 250 ^\circ \text{C}$ for 60 min in Fig. 5. The crystalline planes can be seen clearly. The lattice spacing of 6.7 Å was assigned to Fe$_3$C (001) planes and 4.3 Å, which is close to the bulk value of 4.5 Å, to Fe$_3$C (100) planes. The slightly enlarged spacing of 6.9 Å was also observed. There was not only an improvement in crystallinity but also an increase in grain size from 4.5 to 9.0 nm (double) by the effect of annealing at a temperature as low as 250 °C. The film was further annealed at higher temperatures and for different annealing times. Grain sizes estimated from the TEM images are summarized in the Table I. From Table I, we observe that grain size increased with increasing either the annealing temperature or the annealing time. But the more prominent effect was obtained from increasing the annealing temperature. The constant annealing time of 60 min was thus used for $T_a = 350 ^\circ \text{C}$. The grain size of 18 nm obtained at $T_a = 550 ^\circ \text{C}$ was the largest among the films of pure Fe$_3$C grains. In Fig. 6, we show the SAD pattern of $T_a = 600 ^\circ \text{C}$, in which the indices are given directly next to the diffraction spots. We observed both the diffraction spots of Fe and Fe$_3$C. It indicates that the decom-

![FIG. 3. TEM images and the corresponding SAD patterns of the films with 42 and 85 at. % C, respectively, deposited at the pressure of 8.5 mTorr.](image)

![FIG. 4. TEM images of the films annealed at $T_a = 250 ^\circ \text{C}$ for (a) 42 at. % C, and at $T_a = 350 ^\circ \text{C}$ for (b) 85 at. % C.](image)

![FIG. 5. HRTEM image of the film with 72 at. % C, made at the pressure of 4 mTorr and annealed at $T_a = 250 ^\circ \text{C}$ for 60 min.](image)

<table>
<thead>
<tr>
<th>Sample Diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-deposited</td>
</tr>
<tr>
<td>250 °C 60 min</td>
</tr>
<tr>
<td>250 °C 90 min</td>
</tr>
<tr>
<td>350 °C 60 min</td>
</tr>
<tr>
<td>450 °C 60 min</td>
</tr>
<tr>
<td>550 °C 60 min</td>
</tr>
</tbody>
</table>

TABLE I. Grain sizes estimated from TEM images for the sample with 72 at. % C made at 4 mTorr for different annealing temperatures and annealing times.
position of Fe$_3$C had occurred, consistent with the observations of Senateur$^{15}$ and Kehrer.$^{16}$ They had pointed out that Fe$_3$C transformed into α-Fe and carbon at $T > 600^\circ$C. Even when decomposition occurs, large Fe$_3$C single crystalline grains still exist which are responsible for the diffraction spots. It seems that both the decomposition and recombination happened in the carbon films in which the Fe$_3$C grains were embedded. Among the diffraction rings of Fig. 6, none is indexed to iron crystalline plane, but except for the indicated graphite plane the rest are of Fe$_3$C planes. It indicates that only large Fe single crystalline grains existed at $T_a = 600^\circ$C but fine and large Fe$_3$C grains of single and polycrystalline coexisted.

One ring in Fig. 6 is indexed as graphite (002) plane. This shows that the carbon matrix was crystallized at $T_a = 600^\circ$C. At $T_a < 600^\circ$C, the carbon matrix was amorphous. This can be deduced from both the HRTEM images where no features between neighboring grains were observed, and the SAD patterns where no diffraction rings of crystalline carbon were observed.

**IV. CONCLUSION**

Amorphous carbon films containing magnetic nanograins of pure Fe$_3$C phase were made by a dc magnetron co-sputtering system. The crystallinity and the size of Fe$_3$C grains were largely improved from the as-deposited films by annealing. The largest grain size of 18 nm was obtained at the annealing temperature of 550$^\circ$C. It provided the room temperature coercivity of 965 Oe.

**ACKNOWLEDGMENTS**

The authors acknowledge L.C. Wang for technical assistance in TEM measurements. The authors would like to thank the financial support by the Republic of China’s National Science Council under Grant No. NSC90-2112-M006-031.