Formation of nanomagnetic thin films by dispersed fullerenes

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A method of forming magnetic materials using dispersed fullerenes in ferromagnetic materials has been studied. Fullerenes (C_{60}) have been integrated into the matrix of Co, Fe, CoFe thin films by thermal vapor codeposition. The size effects and interaction of the C_{60} molecules to the metallic atoms promote a self-assembly grain growth mode to produce thin films with unique evoluted microstructures characterized by nanosize columnar grains with uniformly dispersed C_{60} on the grain boundaries. These nanocrystalline films have displayed a series of promising magnetic properties, such as high out of plane remanence, high coercivity, fast magnetic switching, and unusual hysteresis behavior. © 2000 American Institute of Physics. [S0003-6951(00)03646-9]

Most of the current approaches to make materials based on fullerenes attempt to synthesize fullerene-based materials by either exohedrally doping or endoherally doping fullerenes.¹ Though exciting properties have been found, the instability and the low production efficiency of these materials have limited their applications. Herein, we propose a near term use of fullerenes in developing nanomagnetic materials by adding fullerenes as a minor component to other magnetic material systems. Because of their advanced properties, nanomagnetic materials have had great impacts in the high density magnetic storage media,² advanced soft magnetic materials,³ and improved magnetocaloric materials.⁴ Since such advanced properties stem from the nanosize grain structures, we attempt to develop materials by manipulating these structures on the nanoscale by using fullerenes due to their unique closed-cage molecular morphology, chemical inertness, and other properties. Besides its relative abundance, C_{60} was introduced for the following reasons: (1) C_{60} is stable at pressure up to 20 GPa,5 possessing high impact strength and temperature stability.⁶ (2) C_{60} is spherical like an atom but with an outer shell diameter of 1 nm, bigger than any atomic species in the periodic table. (3) Single C_{60} molecules can be obtained by subliming at temperature as low as 400 °C.⁷ (4) Despite their relative inertness, C_{60} molecules interact strongly with many other atomic species.⁸⁻¹¹ We visualize the C₆₀ molecule as a large "pseudoatom."

We manufactured the C_{60} /metal thin films by thermally subliming high purity C_{60} powder while evaporating ferromagnetic metals in an ultrahigh vacuum. The starting vacuum was better than 1×10^{-9} Torr and deposition occurred at $10^{-7} - 10^{-8}$ Torr. The metal sources were pure Co and Fe metal rods. The fullerene had a purity of 99.95% C_{60} . The source materials were placed into alumina-coated tungsten crucibles and resistance heated. A small thermocouple was buried in the fullerene powder in the crucible to monitor the temperature. Deposition temperature ranged from 500 to 650 °C. Deposition rates were controlled by changing the current and followed by a thickness monitor. All films were grown to a nominal thickness of 100 nm on amorphous silicon nitride coated Si substrates. The concentration of the as-deposited thin films were measured by wavelength dispersive spectrometry and expressed in a formula of M_xC_{60} . A mass spectrometer was used to identify C_{60} and investigate the desorption of C_{60} as a function of temperature by heating a small amount of the metal- C_{60} film at a ramp rate of 100 °C/min up to 750 °C. A Raman spectrometer was used to investigate the metal- C_{60} interactions in the intact films. The grain microstructures of these films were observed by transmission electron microscopy. Magnetic measurements were carried out in a vibrating sample magnetometer (VSM).

The mass spectrometry confirmed the stability of C_{60} in the magnetic films. Figure 1(a) shows the spectrum for a $Co_{162}C_{60}$ film of 27 at. % carbon. The peaks at 720 and 360 correspond to C_{60}^+ and C_{60}^{2+} . Peaks at other mass/Z numbers could come from organic impurities or fragment of C_{60} .



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FIG. 1. (a) Mass spectrum of a $\text{Co}_{162}\text{C}_{60}$ film. (b) Intensity of C^+_{60} (M/Z=720) vs the heating temperature in mass spectrometry.

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FIG. 2. Raman spectra of the metal- C_{60} films, the pure C_{60} film and the graphite rod.

However, these peaks are far weaker than the C₆₀ peak, implying that the cage structure of the majority of the C_{60} is not altered. Figure 1(b) shows the 720 peak intensity versus temperature for three films. The starting desorption temperature at which the intensity of C_{60}^+ starts to stand out in the pure C_{60} film, $Co-C_{60}$ film and $Fe-C_{60}$ film are 450, 570, and 680 °C. These results are similar to those observed in the noble metal/ C_{60} systems¹² and indicate that the Co-C₆₀ and Fe- C_{60} bonds are stronger than the C_{60} - C_{60} bond.

With the surface enhanced Raman spectroscopy, peak shifts and additional features have been observed in monolayer C_{60} /noble metal (Au, Ag, Cu) systems.^{10,11,13} These changes are contributed to the perturbation of the perfect symmetry of the C₆₀ by the strong interaction at the metal-C₆₀ interface and the charge transfer from the metal to the C₆₀. Figure 2 shows the Raman spectra of the metal-C₆₀ films, a pure C_{60} film and a graphite rod. $A_g(2)$, the pentagonal pinch mode (1468 cm⁻¹ in pristine C₆₀) has been split in the Co-C₆₀ film and shifted to 1442 cm⁻¹ (26 cm⁻¹ to the left) in Fe-C₆₀ and CoFe-C₆₀ films. For the $A_g(2)$ mode, the downshift of 26 cm^{-1} in the Co, Fe, CoFe metal films is in line with the shift in Ag of 26-28 cm⁻¹ and higher than Cu of 23 cm⁻¹ and Au of 15–18 cm^{-1,10} The increase in the downshift is indicative of the increasing interaction between metal and C₆₀ and is consistent with the order of the work function of the metals (Ag of 4.3 eV, Cu of 4.7 eV, and Au of 5.1 eV).¹⁰ The work functions of Fe and Co are 4.4 and 4.3 eV^{14} and they seem to give shifts similar to Ag. Though the peak in 1298 cm^{-1} is close to one of the graphite peak, the mass spectrometry confirms that most of the fullerenes do not graphitize and therefore this peak may be just a coincidence with that in graphite.

Figures 3(a) and 3(b) are the bright field TEM plane view and cross-section view images of the $Co_{162}C_{60}(27 \text{ at. }\% \text{ C})$ film. The diffraction rings from the cobalt matrix is consistent with the hcp structure with no indication of a fcc phase. No graphite or C₆₀ crystal diffraction patterns were detected. The grains were highly columnar and uniform through the film, and had a diameter of 11 nm. They are much finer than the grains in the pure Co film (22 nm). The grain boundaries were well-defined and outlined by a bright phase with a diameter of 1-2 nm. This bright phase was not observed in the pure Co sample under the same microscopic operation conditions and, therefore, is concluded to be carbon containing interface since carbon has a lower atomic number and will appear white in a bright field image. As the mass spectrometry and Raman spectroscopy



FIG. 3. TEM plane view with diffraction pattern and cross-section images revealing grain structures that have been evolved by integrating C60 molecules into the Fe and Co magnetic films; (a) and (b) are from the $Co_{162}C_{60}$ film; (c) and (d) are from the $Fe_{73}C_{60}$ film; (e) and (f) are from the pure Fe film

show that most of the fullerenes are stable in the films and the TEM diffraction shows no graphite phase, the carbon interfacial phase is mainly composed of fullerenes.

Figures 3(c) and 3(d) are the plane view and crosssection TEM images of the $Fe_{73}C_{60}$ (42 at. % C) film. Figures 3(e) and 3(f) are images from a pure Fe film made under the same deposition conditions. The diffraction patterns from both films are identified to be bcc Fe with no indication of graphite or iron carbide. In the Fe73C60 film, grains are also well-defined and extremely uniform with a diameter of 5 nm. These nanosize grains aligned consistently and perpendicularly to the substrate. Most of these grains have lengths more than 50 nm. In the pure Fe film, the grains are much coarser $(\sim 15 \text{ nm in diameter})$ and randomly oriented.

From a series of samples, we observed that the grain size of the metallic matrix decreases with increasing C₆₀ concentration and the grains are commonly columnar with C₆₀ dispersed on the grain boundaries. Based on these findings and the observations of C₆₀ interactions with metal surfaces via scanning tunnel microscopy,^{13,15,16} the following selfassembly grain growth model is constructed: In the initial stage of the deposition, C₆₀ migrates to the edges of the metallic nuclei, reducing interface energy and defining the primitive grain boundaries. Because of the large size of the Downloaded 07 Jun 2010 to 129.6.180.4. Redistribution subject to AIP license or copyright; see http://apl.aip.org/apl/copyright.jsp



FIG. 4. (a) Out of plane hysteresis loops of the Co, $Co-C_{60}$ films. (b) The magnetization curve of the $Fe_{73}C_{60}$ is highly unusual in that the virgin curve goes out of the major loop.

 C_{60} molecule compared to the metallic atoms, the boundary C_{60} molecules form an interconnected structure on the substrate and confine the metallic atoms inside the network. The diameter of the individual cell of the network defines the grain size. Metallic layers build until they outreach the first layer of C_{60} and expose another layer of metallic edge to facilitate C_{60} to assemble exactly on top of the previous layer, raising the boundary. This self-assembly process results in the formation of the very slim columnar grains with C_{60} on the boundaries. The final grain size of the metallic matrix is determined by the deposition ratio of C_{60} to metal.

Figure 4(a) shows the out of plane hysteresis loops for the Co–C₆₀ films. Both the remanence and the coercivity increase significantly in the Co₁₆₂C₆₀ film. These values are comparable to the promising perpendicular recording media, Co–Cr and Co–CrTa.¹⁷ These C₆₀ comprising media have the potential to achieve ultrahigh storage density because the C₆₀ molecules limit grain growth, reside at grain boundaries, and reduce the magnetic coupling between grains which can lower media noise.¹⁸ Hayashi *et al.*¹⁹ have reported the use of graphite-like carbon to encapsulate Co grains using a tedious post-annealing process in order to decouple the grains. The advantage of using C₆₀ over graphite carbon is that C₆₀ molecules spontaneously go to the grain boundaries even in the as-deposited films.

Figure 4(b) shows the in-plane major hysteresis loops and the virgin magnetization curve of the $Fe_{73}C_{60}$ film. The virgin curve was obtained by magnetizing a demagnetized sample starting from zero field. Note that the virgin curve lies largely "outside" the major hysteresis loop. This is a very unusual feature and we have not found it in the pure Fe, the $Fe_{147}C_{60}$, or other Co, Co–C₆₀ films. From the ac and dc curves, it was found that a threshold field of about 68 Oe (stage 1) was needed to produce a noticeable change in the remanence. Above the threshold (stage 2), both the magnetic moment and remanence increased steadily with the external field. The third stage was characterized by a nearly constant remanence. Using the magneto-optical indicator film technique,²⁰ we observed dynamically the domain formation and growth process above the threshold field during the magnetization process from the demagnetized state. However, after the sample was saturated, we did not observe any domains. This implies that either a stable single domain was formed or the growth speed of a reversed domain was too fast to be caught in our observation. The fast switching property suggests this material had the potential to use in magnetic memory, magnetic switches, spin valves, magnetic springs, and other magnetic devices. The uniformity of the grains and distribution of C_{60} shown by the TEM in Fig. 3(c) may contribute to this fast switching ability.

We have manufactured a type of nanomagnetic thin films with interesting and promising properties achieved by introducing C_{60} molecules into the thin films of Fe, Co, and CoFe. The microstructure evolution caused by C_{60} is unique and dramatic. The higher order fullerenes and their derivatives and nanotubes may also be useful to develop advanced materials. Further study will enable us to understand better the process and utilize these molecules as an efficient tool for the production of nanomaterials.

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