Enhanced magnetic coercivity in magnetic granular solids

Gang Xiao and C. L. Chien
Department of Physics and Astronomy, The Johns Hopkins University, Baltimore, Maryland 21218

We have fabricated magnetic granular Fe-SiO_2 solids over a wide metal volume fraction range 15%–100%. The microstructure of the samples has been characterized by using transmission electron spectroscopy, electron diffraction, and Mössbauer spectroscopy. Giant magnetic coercivity, as high as 2500 Oe, has been observed in samples with nanometer particle size. The behaviors of coercivity across the metal volume fraction range are attributed to the change of particle size and percolation effect.

I. INTRODUCTION

Magnetic fine particles in the size range of a few to a few tens of nanometers have been of persistent scientific interest and of technological importance.[1–3] This is the size range near or below the critical size for the formation of single-domain particles in which superior magnetic properties, unattainable in bulk solids, are realized. Chemical methods (e.g., forced hydrolysis) are often used to produce relatively large (hundreds of nanometer) and free-standing particles. The fine particles must be prevented from coalescing into large aggregates, and in the case of metal particles, from oxidizing. This necessitates the use of an inert medium in which the fine particles are dispersed as evenly as possible through nontrivial processes.

A different, and in many respects, superior method for making ultrafine magnetic particles is the vapor deposition of metal-insulator composites. These granular metal films consist of ultrafine metal particles of only a few nanometers in size with rather uniform sizes and dispersion. It should be noted that in the vapor deposition method, the fabrication, the dispersion of the ultrafine particles, as well as coating onto a desirable surface are achieved simultaneously without additional processing.

Because of the unique microstructure of ultrafine particles, unusual properties have been realized in granular metal films.[1–3] In this paper, we will describe the fabrication and characterization of a magnetic granular system Fe-(SiO_2) where the ultrafine Fe particles are embedded in an amorphous SiO_2 matrix. A dramatically enhanced magnetic coercivity, as high as 2500 Oe, achieved in this granular system will be reported. Such coercivity is about 50 times higher than that of the bulk Fe.

II. EXPERIMENTS

The granular Fe-(SiO_2) samples were fabricated by using a high-rate rf magnetron sputtering system. Samples over a large Fe volume fraction range (p) of 15%–100% have been made. The sputtering targets were composite targets of pure Fe and SiO_2 with appropriate composition. The presputtering pressure in the vacuum chamber was in the 10^{-8} Torr range. Care was taken in maintaining constant sputtering conditions to assure a uniform size of the ultrafine granules. The samples, with thicknesses of 2–5 μm, were deposited onto various substrates kept at room temperature. The composition of the samples was crosschecked with atomic absorption, x-ray fluorescence analysis, and target composition, with general agreement within 5 at. %.

The microstructures of the samples were examined by transmission electron microscopy (TEM), electron and x-ray diffraction, and complimented by ^{57}Fe Mössbauer spectroscopy. Magnetic measurements were performed by using a SQUID magnetometer. The coercivity was determined from either a complete or a portion of a hysteresis loop with magnetic fields up to 50 kOe. Measurements were made at various temperatures from 2 to 400 K.

III. RESULTS AND DISCUSSIONS

Inherent to granular metal systems is the phenomenon of percolation. The percolation threshold (p_c), above which a connecting network of granules exist, is usually near a metal volume fraction (p) of about 50%–60%.[1] This is illustrated by the TEM micrographs shown in Fig. 1, where the structures of two samples, $Fe_{90}(SiO_2)_{10}$ and $Fe_{60}(SiO_2)_{40}$,

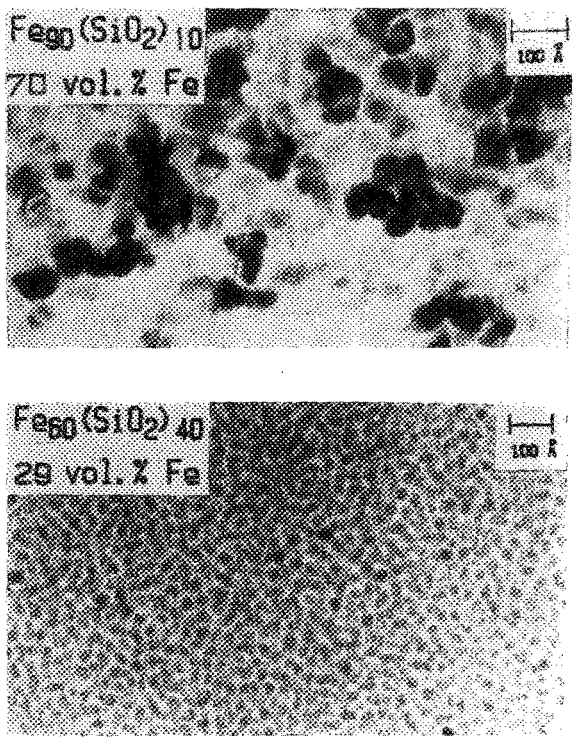

FIG. 1. TEM micrograph of granular $Fe_{90}(SiO_2)_{40}$ (70 vol. % Fe) and $Fe_{60}(SiO_2)_{40}$ (29 vol. % Fe) films.

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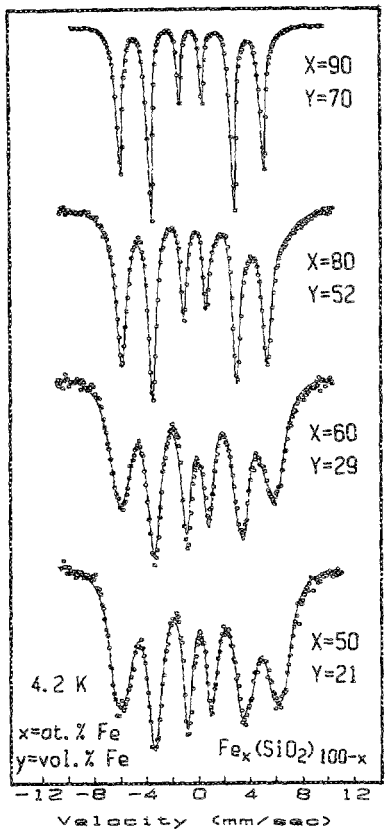

FIG. 2. Mössbauer spectra of various granular Fe-SiO_2 solids at $T = 4.2$ K.

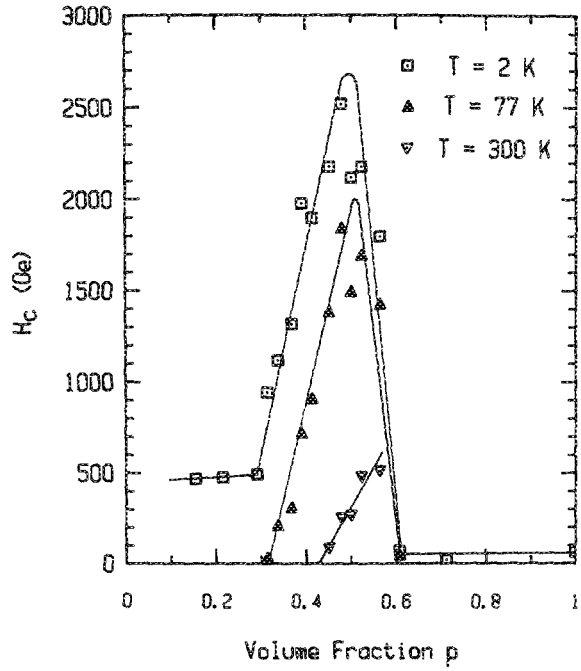

FIG. 3. Magnetic coercivities measured at $T = 2$, 77, and 300 K of Fe-SiO_2 granular films as a function of Fe volume fraction.

with respective Fe volume fractions of 70% and 29% (which are above and below the percolation threshold), are clearly displayed. The $Fe_{90}(SiO_2)_{10}$ sample consists of large connecting granules, while the small Fe granules are well separated in $Fe_{60}(SiO_2)_{40}$. With room-temperature substrates, we observed a monotonic increase of granule size with Fe volume fraction. Specifically, we obtained average granule sizes of 17, 38, 50, and 70 Å for samples with $p = 14\%, 29\%, 38\%$, and 70%, respectively. These approximately equiaxial granules exist in magnetic single-domain form because their sizes are smaller than the critical size for single-domain Fe particles (~ 200 Å).[4]

Electron diffraction established that, for samples with relatively large particles whose diffraction patterns are not excessively broad, the granules have a bcc structure, the same as α-Fe. Further confirmation came from ^{57}Fe Mössbauer spectroscopy. Figure 2 shows the Mössbauer spectra of a number of granular samples at 4.2 K. For sample with smaller granular sizes, as realized in samples with lower volume fraction, the spectra lines are broader as expected. The line positions are slightly different from that of bulk Fe. It is also apparent that there are no evidence of large contributions from Fe oxides. From these results one can conclude that the granules are essentially pure Fe granules.

In Fig. 3, the coercivity (H_c) data of the Fe-(SiO_2) system at 2, 77, and 300 K are presented as a function of the Fe volume fraction p. The results at 2 K are close to the ground-state properties, in which one observes a giant enhancement of H_c. Spectacular changes of H_c occur in the range of $29\% \leqslant p \leqslant 60\%$. Keeping in mind that H_c of bulk Fe is less than 50 Oe due to magnetic multidomain structure, we find that the granular Fe sample has an H_c as high as 2500 Oe at $p = 46\%$. Then H_c precipitously drops to a value of about $H_c \sim 50$ Oe, which is close to the value of the sputtered bulk pure Fe, and remains at that value from $p = 60\%$ to 100%. The precipitous decrease in H_c is attributed to the percolation effect. As p approaches the percolation threshold, formation of a connecting network of small granules starts to occur. As a result, magnetic coercivity reduces substantially.

As shown in Fig. 3, H_c decreases as temperature increases due to superparamagnetism.[4,5] According to Kneller

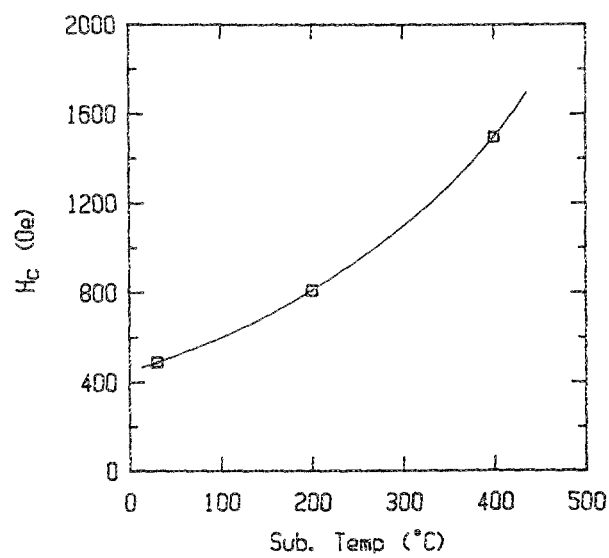

FIG. 4. Magnetic coercivity as a function of sample deposition temperature for a Fe-(SiO_2) sample with a volume fraction of 28%.

and Luborsky,[6] the temperature dependence of coercivity for noninteracting uniform particles is

$$H_c = H_{c0}(1 - \sqrt{T/T_g}), \quad (1)$$

where T_g is the onset temperature for superparamagnetism which is proportional to the magnetic anisotropy energy KV, with K being the anisotropy constant and V the granular volume.

For samples deposited at room temperature, larger particle sizes are realized in samples with higher values of p as mentioned earlier. This would normally result in a stronger dipole-dipole interaction, which tends to decrease H_c as established both theoretically[7] and experimentally.[8] Therefore, the observed increase of H_c must be associated with the effects due to the increase of particle size. This indeed is supported by the following experiment. We deposited three samples with the same volume fraction (29%) at three different temperatures 30, 200, and 400 °C. The high substrate temperature effectively enlarges the particle size. In Fig. 4, H_c is plotted against the substrate temperature. Clearly, high H_c is a result of enlarged particle size. It is noted that the strength of the dipole-dipole interaction in samples with the same volume fraction is about the same.

There are two essential features of the behavior of H_c in the granular Fe-SiO_2 system. First, H_c increases dramatically with particle size. Such a phenomenon, observed at 2 K, is not a thermal artifact due to magnetic relaxation,[5] but intrinsic to Fe-SiO_2. The second is the extremely high H_c values (at least 2500 Oe) achieved in the granular system.

According to conventional theories,[9] for Fe particles with sizes less than 120 Å, the rotation-in-unison mode of magnetization reversal is more favorable than bucking and curling modes. In this mode, the zero-temperature coercivity H_{c0} is $2K/M$, where M is the magnetization and K is the effective anisotropy constant from various contributions such as magnetocrystalline, shape, strain, etc.,[4] which are largely independent of size. Since the magnetization remains relatively constant in our Fe-SiO_2 system, the effective K would necessarily be size dependent in order to account for the experimental results. Further difficulties are encountered when very large H_c values are to be accommodated in various models. Both the magnetocrystalline anisotropy and the maximum strain induced coercivity of bulk Fe are only of the order of 600 Oe.[4] In the rotation-in-unison model, H_c was predicted to be as high as 5000 Oe but only for particles with an extremely large aspect ratio.[4] The chain-of-spheres fanning model[9] indicates a maximum H_c of 2700 Oe for an infinitely long chain in a random system. These extreme particle shapes and morphology were not revealed in our TEM micrographs, although there are evidences of neighboring granules in contact for samples near p_c. It should be pointed out that the enhancement of H_c is not due to the particles in contact near p_c where one may imagine the existence of some chain-of-spheres-like arrangement. Particle size is the dominant factor affecting H_c. One of the ample evidences is shown in Fig. 4, where H_c is enhanced with particle size. In these samples the volume fraction is much below p_c where particles are well isolated from each other. Other evidences can also be found in a related publication.[10] The fact that in ultrafine granules H_c is size dependent cannot be satisfactorily accounted for by existing models.

However, it must be recognized that the above-mentioned models, and indeed almost all the existing models, assume free-standing particles or particles dispersed in a nonbonding medium. In the granular Fe-SiO_2 system, the particles are strongly bonded to the insulating matrix and may be subjected to very larger stresses. For small particles, a large portion of the Fe atoms are at or near the surface. The number of surface atoms increases with particle size. The metal-insulator interfaces may dominate the coercivity in such systems. Under a reversing field, the moment reversal may well begin first at the surface and then propagate throughout the particle.

IV. SUMMARY

Granular Fe-SiO_2 solids over a large metal volume fraction range (15%–100%) have been made with a magnetron sputtering system. The granular nature of the samples has been characterized by transmission electron microscopy, electron diffraction, and ^{57}Fe Mössbauer spectroscopy. A giant magnetic coercivity of 2500 Oe is observed at 46% metal volume fraction. The H_c of the samples with higher volume fractions drops to the bulk Fe value. The observed behaviors of H_c are due to changes of particle size and percolation effect.

ACKNOWLEDGMENT

This work was supported by the Office of Naval Research Contract No. N0001485-K-0175.

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