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We have synthesized a series of granular Fe-SiO_2 solids consisting of Fe metal granules of nanometer sizes embedded in an insulating SiO_2 matrix. The ultrafine microstructures, revealed by TEM, are achieved by using a high-rate magnetron sputtering system. The magnetic properties of such solids are determined by the granular size and the metal volume fraction. Below the percolation threshold, isolated single-domain particles having large magnetic coercivity in the blocked state exhibit superparamagnetic relaxation, which has been studied by using SQUID magnetometry and Mössbauer spectroscopy. Above the percolation threshold, magnetic coercivity drops dramatically and the magnetic properties approach that of pure Fe. The anisotropy energy of the magnetic granules, much larger than that due to magnetocrystalline anisotropy, has been determined.

I. INTRODUCTION

Granular magnetic solids consist of small magnetic granules of nanometer sizes embedded in an insulating matrix. These ultrafine metal particles are much smaller than those achieved by powder metallurgy and chemical methods. Because of their unique microstructure, granular metal solids exhibit many unusual properties of fundamental interest as well as technological importance. The small physical sizes (15–150 Å) allow the exploration of finite size effects in solids as well as unusual electrical, magnetic, and optical properties.[1,2] Granular metals are also attractive media for potential applications since their superior properties can be tailored through process conditions.

In this work, we describe the behaviors of magnetic Fe-(SiO_2) solids. For samples with low metal volume fraction (p), the small Fe granules are separated in an amorphous SiO_2 matrix, where single-domain characteristics and magnetic relaxation phenomena are observed. For samples with high volume fraction, the connecting granules exhibit bulk magnetic properties. Percolation behavior occurs at about $p_c \sim 0.5$–0.6,[1] which marks the boundary between conducting and insulating samples.

II. EXPERIMENT

Granular metal can be fabricated by using vapor deposition methods, of which sputter deposition is the most versatile. In order to achieve granular metals, a number of sputtering modes and target geometries can be employed, in addition to selecting the proper combination of metal and insulator. All the samples of Fe-(SiO_2) used in this work have been made by magnetron sputtering with homogeneously mixed composite targets. The samples, of thickness about 2–5 μm, were deposited onto Kapton substates kept at room temperature with a 4-mTorr pressure of Ar as the sputtering gas. The samples are denoted by their atomic composition [e.g., $Fe_{60}(SiO_2)_{40}$] and metal volume fraction (e.g., $p = 0.29$), the latter can be easily obtained through a simple calculation. The magnetic properties are measured by using a SQUID magnetometer and Mössbauer spectroscopy, with characteristic measuring times of 10 and 10^{-8} s, respectively.[3] The high sensitivity and the small field capability of the SQUID magnetometer are imperative for the studies of the magnetic relaxation of granular magnetic solids.

III. RESULTS AND DISCUSSIONS

The microstructures of the samples were revealed through transmission electron microscopy (TEM). Examples of the TEM micrograph are shown in Fig. 1, where the structures of two samples $Fe_{90}(SiO_2)_{10}$ and $Fe_{60}(SiO_2)_{40}$

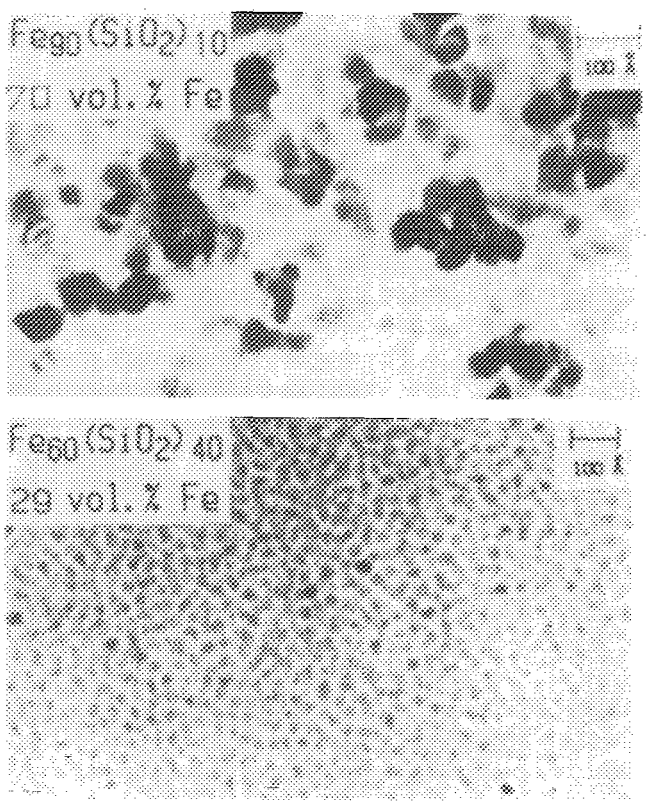

FIG. 1. TEM micrograph of $Fe_{90}(SiO_2)_{10}$ and $Fe_{60}(SiO_2)_{40}$ samples.

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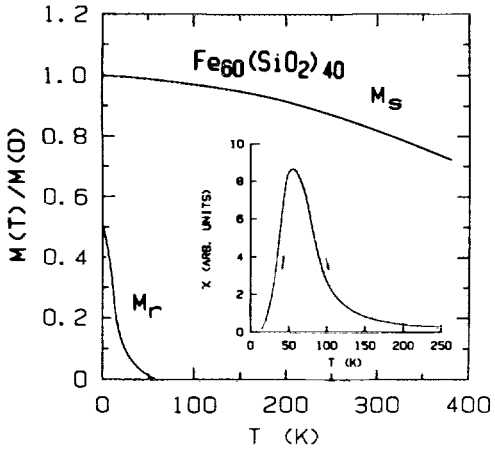

FIG. 2. Saturation magnetization (M_s) under a 50-kOe magnetic field and remanence (M_r) of granular $Fe_{60}(SiO_2)_{40}$. Insert: Initial susceptibility in the zero-field-cooled mode under an external field of 10 Oe.

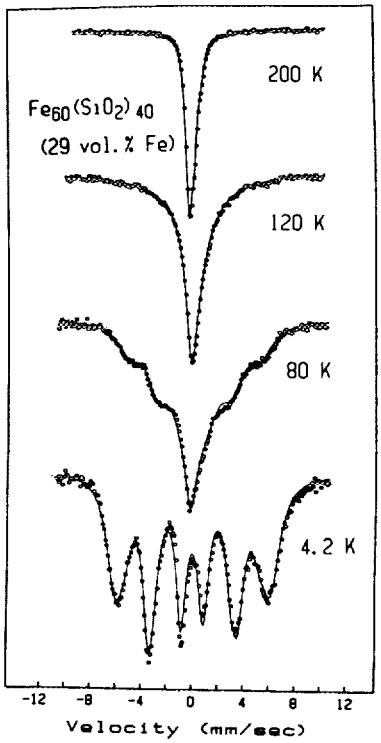

FIG. 3. Mössbauer spectra of $Fe_{60}(SiO_2)_{40}$ at various temperatures.

with the respective Fe volume fractions of 0.70 and 0.29, 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 $Fe_{60}(SiO_2)_{40}$.

Similar to the electrical conductivity, magnetic properties of granular solids also experience dramatic changes around the percolation threshold. We have measured the magnetic coercivity (H_c) of the Fe-(SiO_2) solids. Above the percolation threshold, H_c is very small, similar to that of bulk Fe, for example, the H_c value for $Fe_{90}(SiO_2)_{10}$ is only about 20 Oe. This is because the connecting granules form a multidomainlike structure. Below the percolation threshold, the granular solids exhibit single-domain behavior and the H_c can be enhanced a great deal depending on the size and shape of the single-domain particles. The H_c for $Fe_{60}(SiO_2)_{40}$ with a granular size about 38 Å was measured to be 450 Oe at $T = 2$ K, an order of magnitude larger than that of the high volume fraction samples.

For magnetic granular solids with small granules (smaller than the critical size for single magnetic domain) and low volume fraction, each granule is a single domain with a moment of μ. The magnetization of such granular solids is then $\Sigma_i \mu_i \cos\theta_i = n\mu\langle\cos\theta\rangle$. At low temperatures ($T \sim 0$ K) and without an external field, the ground-state configuration consists of an assembly of single-domain particles, whose moment axes are randomly oriented over a 4π solid angle. Hence the magnetization is zero. Saturation magnetization of $M_s = n\mu$ is obtained under a large external field. When the external field is turned off, a nonzero remanent magnetization (M_r) results. For isolated granules in the absence of magnetic interactions, it is necessary that $M_r = n\mu/2$. This is because the moment vectors are now randomly oriented only in a hemisphere, i.e., $\langle\cos\theta\rangle = 1/2$. Thus $M_r = M_s/2$ at low temperature is an experimental signature for isolated single-domains particles. This is indeed observed in the sample of $Fe_{60}(SiO_2)_{40}$ with $p = 0.29$ as shown in Fig. 2, where the saturation magnetization M_s was obtained under a large field of 50 kOe. The temperature dependence of M_s is indicative of ferromagnetically ordered particles. As T is increased, thermal energy through superparamagnetic relaxation tends to destabilize the moments. Consequently the value of M_r decreases with T. The temperature at which $M_r = 0$ marks the blocking temperature (T_B) of the superparamagnetic transition. A more informative way of examining superparamagnetism and blocking temperature is to perform initial susceptibility measurements. This is shown in the insert of Fig. 2, where the temperature dependence of susceptibility under an applied field of 10 Oe is displayed. The measurement was carried out in the zero-field-cooled (ZFC) mode, the sample was first cooled in zero field and then a 10-Oe field was applied. The ZFC data show a cusp which marks the blocking temperature. We found that the blocking temperature is sensitively dependent on the external field. For $Fe_{60}(SiO_2)_{40}$, the extrapolated zero field blocking temperature is $T_{B1} = 58$ K.

The superparamagnetic relaxation time, assuming an Arrehenius law,[4] has the form of

$$\tau = \tau_0 \exp\left(\frac{CV}{k_B T}\right), \tag{1}$$

where C is the magnetic anisotropy energy per unit volume and V is the volume. The blocking temperature T_{Bi} is defined by

$$T_{Bi} = \frac{CV}{k_B[\ln(\tau_i/\tau_0)]} \tag{2}$$

for an instrument with a measuring time of τ_i. With one characteristic measuring time τ_i, CV and τ_0 cannot be independently determined. We also employed ^{57}Fe Mössbauer spectroscopy which has a measuring time of 10^{-8} s. Mössbauer spectra of $Fe_{60}(SiO_2)_{40}$ at various temperatures are shown in Fig. 3. At low temperatures (e.g., 4.2 K), the relax-

ation of the magnetic moments is slow and the spectrum resembles that of pure Fe. As the temperature is increased, the effective hyperfine field gradually collapses even though the particles themselves remain ferromagnetically ordered. At high temperatures (e.g., 200 K) no hyperfine splitting can be seen. The blocking temperature (T_{B2}) is the temperature at which the magnetic hyperfine splitting first appears. Using a zero-velocity thermal scan method T_{B2} was determined to be 167 K. Because τ_2 for Mössbauer spectroscopy is nine orders of magnitude smaller than τ_1 for SQUID magnetometer, T_{B2} is totally different from T_{B1}. The ratio of T_{B1}/T_{B2}, however, is independent of CV, therefore, *independent* of the granule characteristics. This is confirmed in a number of granular Fe-(SiO_2) samples where a nearly constant value of $T_{B1}/T_{B2} \simeq 0.35$ has been found. In the present case of $Fe_{60}(SiO_2)_{40}$, the value of $T_{B1} = 58$ K, $T_{B2} = 167$ K allow $\tau_0 \simeq 10^{-13}$ s, and $CV = 2.3 \times 10^{-13}$ erg to be independently determined. From the TEM micrograph, the diameters of the granules are about 38 Å, leading to a value of $C = 8 \times 10^6$ erg/cm^3. This value is much larger than the bulk magnetocrystalline anisotropy energy of 10^5 erg/cm^3 for bulk Fe,[5] indicating that the magnetocrystalline anisotropy is not the major contribution.

In summary, magnetic granular Fe-(SiO_2) solids have been fabricated. Samples with volume fraction above and below the percolation threshold exhibit very different structural and magnetic behaviors. The well-isolated granules below the percolation threshold possess a large magnetic coercivity and its anisotropy energy is determined to be 8×10^6 erg/cm^3, while the connecting granules above the percolation threshold cause the coercivity to drop to a value similar to that of the bulk Fe.

ACKNOWLEDGMENT

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