Temperature dependence of coercivity behavior in iron films on silicone oil surfaces

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Received 17 April 2006; received in revised form 18 September 2006; accepted 22 September 2006
Available online 4 October 2006
Communicated by J. Flouquet

Abstract
A new iron film system, deposited on silicone oil surfaces by vapor phase deposition method, has been fabricated and its microstructure as well as magnetic properties has been studied. It is found that the temperature dependence of the coercive field \( H_c(T) \) of the films exhibits a peak around a critical temperature \( T_{\text{crit}} \): for the temperature \( T < T_{\text{crit}} \), \( H_c(T) \) increases with the temperature; if \( T > T_{\text{crit}} \), however, it decreases rapidly and then approaches a steady value as \( T \) further increases. Our study shows that, for \( T > T_{\text{crit}} \), the observed coercivity behavior is mainly dominated by the effect of the non-uniform single-domain particle size distribution, and for \( T < T_{\text{crit}} \), the anomalous coercivity behavior may be resulted from the surface anisotropy, the surface effect and the characteristic internal stress distribution in the films. The influence of the shape and size of the particles on the thermal dependence of the magnetization is also investigated.

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PACS: 75.60.-d; 75.70.Ak; 75.50.Tt
Keywords: Magnetic thin film; Coercivity; Liquid substrate

1. Introduction
The hysteresis loop (HL) was first studied more than a century ago [1], however, the understanding of the real magnetic process in thin magnetic films as well as in bulk magnets is still rather poor and many theoretical analyses and models are based on some simplified assumptions [2–5]. Current research on the ultrathin magnetic layers is largely focused on the magnetic domain structure and the mechanisms of the magnetization reversal. These studies are mainly driven by fundamental interests (including the origins and the shapes of magnetic domains, the understanding of the coercive field value governed by the nucleation process and domain-wall displacements, the dynamical magnetization, and the link with the nanostructure) and technical applications in the information storage media such as higher recording density, stability, and improvement of magnetic bits, etc.

It is well known that magnetic properties of thin films depend on the preparation methods, the post-deposition treatments and the nature of the substrates. Recently, vapor phase deposition of metals on liquid substrates is studied systematically [6–10]. The experiments show that the films deposited on the liquid substrates may exhibit characteristic microstructures and unique physical properties. All the anomalous properties of these free sustained films are closely related to both the free standing boundary conditions and the interactions among the atoms and atomic clusters in the films.

In this Letter, we investigate the microstructure and the temperature dependence of the coercive field \( H_c \) in an iron film system deposited on silicone oil surfaces. Our experiment shows the influence of the size and shape of the particles on the temperature dependence of coercivity and magnetization.
2. Experiment

The samples were prepared by thermal evaporation of 99.99% pure iron in a vacuum of $6 \times 10^{-4}$ Pa at room temperature (RT $= 18 \pm 2$ °C). Commercial silicone oil (Dow Corning 705 Diffusion Pump Fluid) with a vapor pressure below $10^{-8}$ Pa was painted onto a frosted glass surface, which was fixed 130 mm below the filament (tungsten). The resulting oil substrate with an area about $12 \times 20$ mm$^2$ had a uniform thickness of $\approx 0.5$ mm. The deposition rate $f$ for all samples was $0.8 \pm 0.1$ nm s$^{-1}$ and the nominal film thickness $d$ was in the range of 10–35 nm, which were determined by a quartz-crystal balance. After deposition, the sample was removed from the vacuum chamber.

After separated from the oil substrates and washed with acetone and ethanol, the iron films were measured immediately: the magnetic properties of the samples were measured by a Quantum Design PPMS (Physical Property Measurement System) magnetometer. The transmission electron microscopy (TEM, JEM-2010), atomic force microscopy (AFM, SPI3800N, Seiko) and X-ray diffraction (XRD, Rigaku D/Max 2500/PC with Cu $K\alpha$ radiation) were used to study the particle shape, size, composition and crystal structure of the films.

3. Results and discussion

The typical AFM image of the upper iron film surface is shown in Fig. 1(a). The dark part and white part in Fig. 1(a) mean low position and high position of the film surface, respectively. The 3-dimensional morphology of the AFM result in Fig. 1(a) is also shown in Fig. 1(b). It can be seen clearly from Fig. 1(a) and (b) that the vertical distance between the lowest and highest positions of the film is about 20 nm, indicating that the roughness of the film surface is significant with respect to its film thickness ($d = 30$ nm). The cluster size distribution obtained from Fig. 1(a) is found to resemble a Gaussian distribution as shown in Fig. 1(c), from which one finds that the median diameter of the clusters is $\phi_m = 41$ nm and the standard deviation is $\sigma_\phi = 7.0$ nm. In fact, for the iron films on oil surfaces, our experiment shows that the cluster size distribution is location dependence and furthermore the size distributions in upper and bottom surfaces of each film sample are also different, which we believe should be related to the large diffusion coefficient of the metallic atoms and atomic clusters on the liquid surfaces [6,8]. Therefore, the cluster size distribution in Fig. 1 is only a local character of the film.

On the other hand, the X-ray diffraction pattern shows that the iron film deposited on silicone oil surface exhibits a polycrystalline structure and the average size of the crystal grains in the film is in the range of 6–10 nm, which is also confirmed by the HRTEM measurement [10].

The general features of magnetic properties can be found from hysteresis loop. Here, we applied magnetic field parallel (i.e., in-plane) and perpendicular to the film planes in the temperature range of 2–300 K, and the typical in-plane and perpendicular hysteresis loops are shown in Fig. 2. It can be seen clearly that the perpendicular remanence $M_r(\perp)$ is very close to that of the in-plane $M_r(\parallel)$ and the ratio of $M_r(\perp)/M_r(\parallel)$ increases from 0.51 ($T = 300$ K) to 0.75 ($T = 2$ K). Fig. 2 also shows that the coercive fields in the two cases are nearly same. These results indicate that the magnetic moments of the particles are not all in the film plane but part of them are out of the film plane [11]. The existence of the out-plane magnetic moments may be explained in terms of the significant surface roughness (Fig. 1), which may induce the spin disorder in the film surface. As the temperature decreases, the disordered spins are trend to be frozen due to the magnetic interactions among them [10], therefore the out-plane magnetic moments are enhanced at low temperature.

Fig. 3 shows the temperature dependence of in-plane coercivity $H_c = H_c(T)$ of the Fe film samples with different film thicknesses $d = 10, 20, 35$ nm, defining samples S1, S2 and S3,
Fig. 2. In-plane (solid circle) and perpendicular (open circle) temperature dependent hysteresis loops of the sample with $d = 20$ nm. Solid lines are the guide to the eye. (a) $M_r(\perp)/M_r(\parallel) = 0.75$; (b) $M_r(\perp)/M_r(\parallel) = 0.72$; (c) $M_r(\perp)/M_r(\parallel) = 0.65$; (d) $M_r(\perp)/M_r(\parallel) = 0.51$.

Fig. 3. In-plane temperature dependence of the coercive field $H_c(T)$ of the iron films on oil surfaces, the film thickness $d = 10, 20, 35$ nm, representing samples S1, S2 and S3, respectively. S4 and the sign "a" represent the experimental result of the iron film on glass substrate with $d = 20$ nm. The solid lines are the guide to the eye.

respectively, where $H_c(T)$ are determined from the measured temperature-dependent in-plane hysteresis loops. For the purpose of comparison, iron films were also deposited under identical evaporation conditions on glass substrates and the typical in-plane coercivity $H_c(T)$ of the Fe films on glass substrates is also shown in Fig. 3 (i.e., sample S4). In Fig. 3, the coercivity peaks around a critical temperature $T_{\text{crit}} = 10–15$ K are obviously observed for the films on silicone oil surfaces and the thinner the film is, the higher value the peak reaches. It is found that, if $d > 35$ nm, the coercivity behaviors of the films on both oil and glass surfaces are similar and then $H_c(T)$ is independent of the nature of the substrates. For the sample S1, the peak of $H_c$ reaches 1400 Oe, which is much higher than those obtained in the Fe films on glass substrates (see the experimental data of the sample S4 in Fig. 3). In fact, no obvious coercivity peaks can be observed for the iron films deposited on glass substrates, which is in agreement with the results of the magnetic thin films deposited on other solid substrates [12–14]. On the other hand, it should be emphasized that this anomalous temperature-dependent coercivity behavior of the iron films deposited on liquid surfaces is identical to the temperature dependence of the maximum-energy product $(MH)_{\text{max}}$ of the hysteresis loops [10].

To explore the intrinsic properties of the iron films deposited on liquid substrates, the low field (100 Oe) zero-field cooled (ZFC) and field cooled (FC) magnetization curves were measured as the following. The sample was first cooled in zero-field from 300 to 2 K, then a field $H = 100$ Oe was applied and the ZFC magnetic moment $M_{\text{ZFC}}$ was recorded with temperature increasing from 2 to 300 K. After that, cooled the sample to 2 K again with the applied field unchanged. The FC magnetic moment $M_{\text{FC}}$ measured by heating the sample to 300 K again in the same field. The ZFC and FC magnetization curves obtained in the magnetic field $H = 100$ Oe are shown in Fig. 4(a).

It is noteworthy that the $M_{\text{ZFC}}$ in Fig. 4(a) does not show a defined maximum and that the ZFC and FC curves remain separated up to practically room temperature. This $M_{\text{ZFC}}$ behavior in the weak applied field implies that there exists wide size distribution of iron grains in the sample which, therefore, enter the superparamagnetic regime at different temperatures [15]. The effect of the superparamagnetism is to decrease the coercivity of the film, which can be seen in Fig. 3.

In addition, the temperature dependence of the saturation magnetization $M_s(T)$ was also measured in a saturation field ($H = 1000$ Oe), as shown in Fig. 4(b). It is found that the thermal saturation magnetization $M_s(T)$ approximately fits the well
known Bloch’s $T^{3/2}$ law [see the dash line in Fig. 4(b)] [16],

$$M_s(T) = M_s(0)(1 - BT^{3/2}) \quad (\text{for } T \ll T_{\text{Curie}} = 1043 \, \text{K}),$$  

where $M_s(0)$ is the saturation magnetization for $T = 0$ K, $B$ is the Bloch’s constant and $B = 3.3 \times 10^{-6} \, \text{K}^{-3/2}$ for bulk Fe. For the film sample in Fig. 4(b), the Bloch’s constant obtained from the fitting by the Bloch’s law is $B = 2.0 \times 10^{-5} \, \text{K}^{-3/2}$. The larger Bloch’s constant compared with the bulk value indicates that the grains in the iron films are smaller [16]. Therefore the fluctuation of the surface moments of the grains is larger than that of the interior of the grains [16], which will affect the magnetic properties of the iron film. It should be noted that the thermal dependence of saturation magnetization at low temperature (below 15 K), as shown in Fig. 4(b), does not consistent well with the Bloch’s law, which may be related to the anomalous low temperature coercivity behavior.

Since the non-uniformity of the particle size is recognized to be an important factor affecting $H_c$ [11–14], Kneller and Luborsky gave a treatment of the coercive force of the mixture of thermally stable, high coercive force particles with superparamagnetic and multidomain particles [17]. The coercive field $H_c$ for such a mixture of non-interacting particles can be expressed as follows [14,17]:

$$H_c = H_c' \left[1 + (H_c' \cdot a/T) \cdot x(T)/(1 - x(T))\right],$$  

where $H_c'$ is the coercive field of the blocked particles, which is assumed to be uniaxial and randomly oriented, i.e. $H_c' = H_c^0(1 - bT^{3/4})$ [18] with $H_c^0$ is the coercive field at $T = 0$ K,

$b$ is a constant depending on the effective anisotropy constant $K_{\text{eff}}$ and $x(T)$ is the volume fraction of superparamagnetic particles at temperature $T$. By employing the Gaussian particle size distribution of standard deviation $\sigma$ and mean volume $V_0$, furthermore, Vavassori et al. worked out the volume fraction of superparamagnetic particles $x(T)$ in Eq. (2) that can be written as [14]

$$x(T) = 0.5 \left[1 + \text{erf}\left((T - T_0)/\sqrt{2} \cdot \sigma'\right)\right],$$  

where $\sigma' = \sigma K/25k_B$ and $T_0 = V_0K/25k_B$ is the mean blocking temperature. We then fit the experimental data $H_c(T)$ in Fig. 5 with $H_c^0$, $\sigma'$ and $T_0$ as adjustable parameters. The agreement between the experimental data and the fits is excellent, as shown in Fig. 5. The best fit parameters are $H_c^0 = 2900 \, \text{Oe}$, $T_0 = 127 \, \text{K}$ and $\sigma' = 37 \, \text{K}$ for the sample S1 and $H_c^0 = 1080 \, \text{Oe}$, $T_0 = 115 \, \text{K}$ and $\sigma' = 34 \, \text{K}$ for the sample S2. Furthermore, the values of $T_0$ and $\sigma'$ correspond to the mean radii of the particles (assumed to be spherical) of 10.2 ± 1.7 nm and 9.8 ± 1.6 nm for the samples S1 and S2, respectively [14], which is in good agreement with the average size of the iron grains obtained from the XRD [10]. While for the film on glass substrate, i.e., sample S4, the mean radius of the particles is 8.1 ± 0.9 nm, which is smaller than that of the films on silicone oil surfaces. We find that, with the film thickness increases, the mean radius of the particles on oil surfaces decreases and approaches that of the films on glass substrates. In Fig. 5, the used anisotropy constant $K_{\text{eff}}$ is found to be of the order of $10^5 \, \text{erg/cm}^3$, which is approximately calculated by $H_cM_s/2$ for all the samples, where $H_c$ is the anisotropy field [12].

Based on the result above, for $T > T_{\text{crit}}$, the observed coercivity behavior is mainly due to the effect of the Gaussian distribution of particle sizes [14]. Although the anisotropy energy barrier is affected by magnetic interactions among the iron crystal grains [13], the good agreement between the experimental data and the fit shown in Fig. 5 indicates that the non-uniform particle size distribution may easily overwhelm the intergrain interaction effects on the temperature dependence of $H_c$ ($T > T_{\text{crit}}$).

For $T < T_{\text{crit}}$, the coercive field decreases rapidly with decreasing the temperature, as shown in Fig. 3. This unexpected behavior of $H_c$ seems rather confusing. However, several rea-
sonable factors still can be figured out: (1) As shown above, the surface anisotropy due to the disordered surface spins induced by the significant surface roughness is important in determining the coercivity behavior at low temperature since the disordered spins are trend to be frozen due to the magnetic interactions among them. The interactions between the surface frozen spins and in-plane spins may result in the anomalous coercivity behavior at \( T < T_{\text{crit}} \) \cite{10,19}; (2) For the thinner films, the effects of the underlying liquid layers on the microstructures of the films are stronger than those of the thicker films, which will enhance the disorder of the surface spins. Therefore, it is quite reasonable that the anomalous behavior of \( H_c \) below \( T_{\text{crit}} \) becomes more obvious in thinner films, as shown in Fig. 3; (3) The characteristic internal stress patterns in the nearly free standing films may also result in the anomalous coercivity behavior since the internal stress may also induce anisotropy in the films \cite{20–22}. To make the final conclusion, however, a flexible theoretical model, including the aspects of surface anisotropy, detailed magnetic interactions between the surfaces disordered spins and in-plane spins, and internal stress patterns and evolution with the temperature, is still needed.

4. Conclusion

In conclusion, we have described the temperature dependence of the coercivity behavior in the iron films deposited on silicone oil surfaces. A generalized model including the effects due to the non-uniform single-domain particle size distribution is presented to study the anomalous behavior of the coercive field of the films. The theoretical results are in good agreement with the experimental data, indicating that the non-uniform particle size distribution may play an essential role in determining the temperature dependence of coercivity for \( T > T_{\text{crit}} \). We also show that all the surface anisotropy, surface effect and internal stress patterns in the nearly free sustained iron film system would make contributions to the anomalous behavior of \( H_c \) below \( T_{\text{crit}} \). Unfortunately, the direct observation of the magnetic reversal process and the details of the relationship between the microstructures and the magnetic properties have not yet been carried out so far.

Our results above indicate that the effect due to the liquid substrates plays an important role in the temperature dependence of coercivity. Further research in this branch may allow a new class of thin film studies on different liquid substrates and study their properties, which may provide us a new way to investigate the magnetic reversal mechanism, the relaxation behavior of magnetic moments and so on.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (Grant No. 10174063) and by the Natural Science Foundation of Zhejiang Province in China (Grant No. Y604064).

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