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Superparamagnetic behavior of ultrathin Fe films grown on $Al_2O_3(0001)$ substrates

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We have studied superparamagnetic behavior of ultrathin Fe films grown on an $Al_2O_3(0001)$ substrate at various growth temperatures. It is demonstrated that 1-nm-thick Fe films are in the superparamagnetic state, and the blocking temperature is strongly dependent on the growth temperature. The blocking temperature has a minimum value of 30 K for a growth temperature of 473 K, while it is ~70 K at other growth temperatures. In order to clarify the behavior, we consider the Fe growth mechanism and the magnetic interactions between Fe particles. Fe grows as three-dimensional islands at all temperatures studied and forms particles. The volume of the particles is observed via atomic force microscopy to increase with increasing growth temperature. In the case of growth at 323 and 373 K, Fe forms small particles that are close together and that interact with each other. For growth at 673 and 773 K, Fe forms relatively large particles and the magnetic properties are dominated by the individual particles. [DOI: 10.1063/1.1628408]

I. INTRODUCTION

Recently, the density of magnetic storage media has been increasing at the rate of 100% per year. Each element storing magnetic information must consist of ultrafine particles in order to yield high-density magnetic storage media. The ultrafine particles might magnetically interact weakly which would create a low signal-to-noise ratio. Further, as the magnetic elements continue to decrease in size, they approach the superparamagnetic limit. Below a critical size, in the range of 10 nm in diameter, each magnetic particle can be in a single domain state. At low temperatures, the ordered magnetic moments of these particles are frozen in place along an easy direction. However, above a certain temperature, known as the blocking temperature, thermal fluctuations can overcome the anisotropy barrier, causing the net magnetization of the system to vanish. Then, the system is said to be superparamagnetic.

A number of ideas have been proposed to suppress the superparamagnetic limit. One is to use material that possesses a high magnetic anisotropy in the bulk, such as $L1_0$-type FePt.[1,2] The surface magnetic anisotropy provides another way to enhance the magnetic anisotropy. The interface between a magnetic material and its oxide can also possess a high interfacial magnetic anisotropy.[3–5]

Ultrathin magnetic films grown on a metallic substrate have been investigated extensively.[6–10] But those grown on oxide substrates, such as Al_2O_3 and MgO, had been investigated only in limited cases, such as for Fe on MgO,[11–14] but not in the ultrathin region. In this article, we report the superparamagnetic behavior of ultrathin Fe films grown on $Al_2O_3(0001)$ substrates. We will discuss the influence of interparticle interactions on the superparamagnetic behavior. Our motivation is to perform fundamental research related to magnetic storage media.

II. EXPERIMENTAL PROCEDURES

The ultrathin Fe films were grown by molecular-beam epitaxy (MBE) using a VG-80M MBE system. The base pressure before and during growth was typically below 4×10^{-9} and 5×10^{-8} Pa, respectively. The growth rate of Fe was 0.005 nm/s. The thickness of Fe was fixed at 1.0 nm. In this study, the growth temperature was varied as a parameter in the range of 323–773 K, since temperature is an important parameter in MBE growth.[9,10] To investigate the magnetic properties, the Fe films must be exposed to air. To avoid oxidation, a 10-nm-Au capping layer was deposited at room temperature on the Fe films. We confirmed the lack of oxidation indirectly from the fact that the magnetization curves at 10 K show no shift after cooling in field (10 kOe). α-$Al_2O_3(0001)$ was used because it has atomically flat terraces.[15,16] In a previous paper, we reported that the surface structure of α-$Al_2O_3(0001)$ is very sensitive to thermal annealing.[15] In this study, the α-$Al_2O_3(0001)$ was annealed for 3 h at 1273 K based on guidelines from our previous work. Steps that are 0.216 nm in height and terraces that are 65.5 nm in width form in a regular manner on the substrate using such a heat treatment. The detailed substrate preparation procedure is described in Ref. 15.

The magnetic properties of the Fe films were investigated by means of the magneto-optic Kerr effect (MOKE) and superconducting quantum interference device (SQUID)

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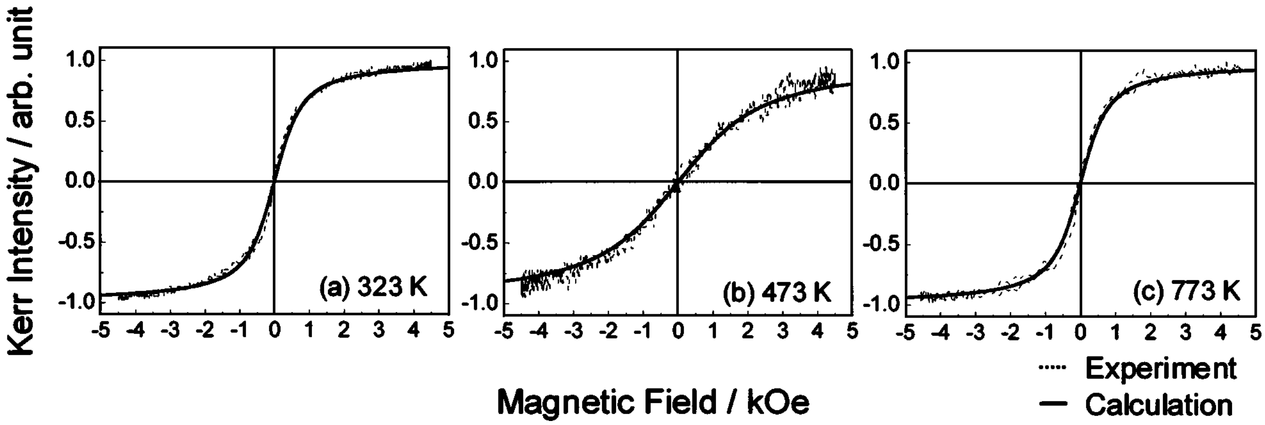

FIG. 1. Magnetization curves of ultrathin Fe films grown at (a) 323, (b) 473, and (c) 773 K, measured using MOKE. The measurement was performed in longitudinal configuration. Dotted and solid lines represent experimental and calculated results, respectively.

magnetometry. The magnetization curves were measured using MOKE at room temperature in fields up to 4.5 kOe. The measurements were performed in longitudinal and polar configurations. The temperature dependence of the magnetization $M(T)$ was measured using the SQUID magnetometer in the range of 10–300 K in a constant magnetic field. Changes were measured while heating after both field cooling (FC) and zero-field cooling (ZFC). If the system is in a superparamagnetic state, it should exhibit blocking phenomena in the magnetization. The blocking temperature was determined as the peak temperature of the $M-T$ curve after ZFC. We also measured the magnetic field dependence of the blocking temperature in order to investigate the interaction between magnetic particles. The structure of the Fe film was investigated using noncontact atomic force microscopy (NC-AFM). The investigation of surface structure was performed *in situ* before Au coating to eliminate the influence of the Au capping layer.

III. RESULTS AND DISCUSSION

We found that the 1.0-nm-thick Fe films were superparamagnetic, based on two types of experimental evidence. First, the magnetization curve at room temperature does not saturate. The magnetization curves measured using MOKE in the longitudinal configuration are shown in Fig. 1 as dotted lines. The growth temperature is 323, 473, and 773 K for Figs. 1(a)–1(c), respectively. The magnetization does not saturate even for applied fields of 4.5 kOe and the curves do not exhibit remanence or coercivity. This behavior is in agreement with the fact that the magnetization curve for a superparamagnetic system is represented by the Langevin function $L(a)=\coth(a)-1/a$, where $a=MH/k_BT$, M is the saturation magnetization for one Fe particle, H is the magnetic field, k_B is the Boltzmann constant, and T is temperature. Assuming that the saturation magnetization is $M=M_{\mathrm{Bulk}}[T]\cdot V[m^3]$, where M_{Bulk} is 2.16 T, the volume of an Fe particle can be roughly estimated by fitting the magnetization curve using the Langevin function with one fitting parameter V. Examples of fitting of magnetization curves are also shown in Fig. 1 as solid lines. The magnetization curves are well reproduced by the Langevin function. The magnetization for Fe grown at 473 K is more difficult to saturate than that for Fe grown at the other temperatures. This behavior is due to the change of magnetic interactions. The other type of evidence in support of superparamagnetism concerns the blocking phenomenon of the magnetization. $M-T$ curves after FC and ZFC in a magnetic field of 0.1 kOe are shown in Fig. 2. The growth temperature is 323, 473, and 773 K for

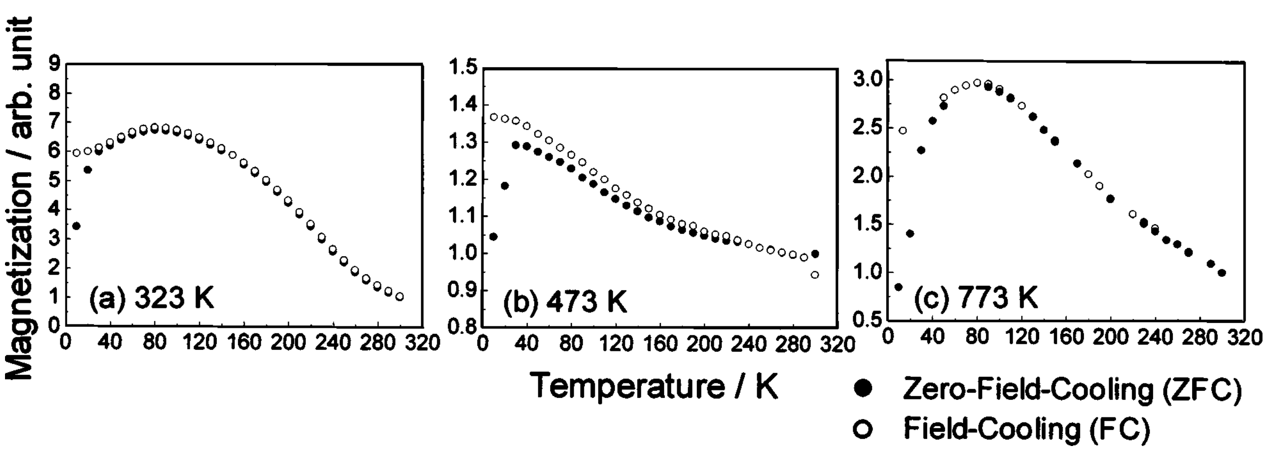

FIG. 2. Magnetization vs temperature ($M-T$) curves after FC (opened circles) and ZFC (closed circles) under the magnetic field of 0.1 kOe for ultrathin Fe films grown at (a) 323, (b) 473, and (c) 773 K. Magnetization is normalized by the value measured at 300 K.

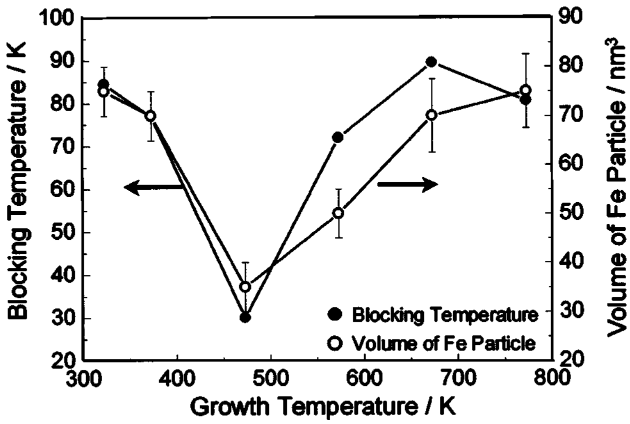

FIG. 3. Changes of the blocking temperature and the estimated volume of Fe particle as a function of growth temperature.

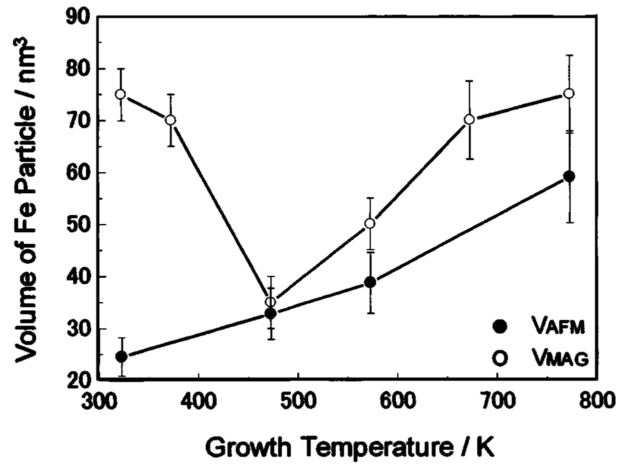

FIG. 5. Changes of the estimated Fe volume as a function of the growth temperature. Open and closed circles represent the value estimated from magnetization curve (V_{MAG}) and NC-AFM image (V_{AFM}), respectively.

Figs. 2(a)–2(c), respectively. In the low-temperature region, the $M-T$ curves after FC and ZFC differ from each other in that the ZFC curve has a peak. This feature indicates that the systems show blocking phenomenon and are thus in the superparamagnetic state. We determined the blocking temperature (T_B) of each Fe film from the peak temperature of the $M-T$ curve after ZFC. The peak of $M-T$ curves after FC should be due to the difference in cooling and heating rates.[17] The difference in the two curves in the temperature region $T>T_B$ is attributed to the volume dispersion of the Fe particles.[18] The volume dispersion leads to a distribution of T_B values. Changes in the blocking temperature and the estimated volume of the Fe particles with growth temperature, shown in Fig. 3, are observed to have similar dependences on growth temperature. The blocking temperature and the volume of the Fe particles have a minimum value of 30 K and 35 nm^3, respectively, at the growth temperature of 473 K. The above two features; the magnetization curves and the $M-T$ curves after FC and ZFC, are typical of superparamagnetic systems.

We now discuss the growth temperature dependence of the blocking temperature and Fe particle volume with respect to the Fe growth mechanism and the magnetic interactions between Fe particles. First, we describe the Fe growth mechanism. Fe grows in Volmer–Weber mode at all growth temperatures studied. NC-AFM images of the Fe films and cross-sectional views are shown in Fig. 4. The Fe forms particles randomly on the substrate at all temperatures studied, and the influence of steps on the substrate to Fe growth can be negligible. Nevertheless, regarding the Fe particle size and discreteness, these two parameters are dependent on the growth temperature. As shown in Figs. 4(a) and 4(b), the heights of the Fe particles are low for a growth temperature of 323 K. This indicates that small Fe particles coalesce and form quasi-two-dimensional (2D) continuous films. On the other hand, the Fe growth mechanism is obviously of a three-dimensional (3D) mode above 473 K as shown in Figs. 4(c)–4(f). Specifically, the Fe grown at 473 K forms almost completely discrete particles [Figs. 4(c) and 4(d)]. The changes with growth temperature of the average Fe particle volume estimated from the NC-AFM images, V_{AFM}, are shown in Fig. 5. The Fe volumes estimated from the magnetization

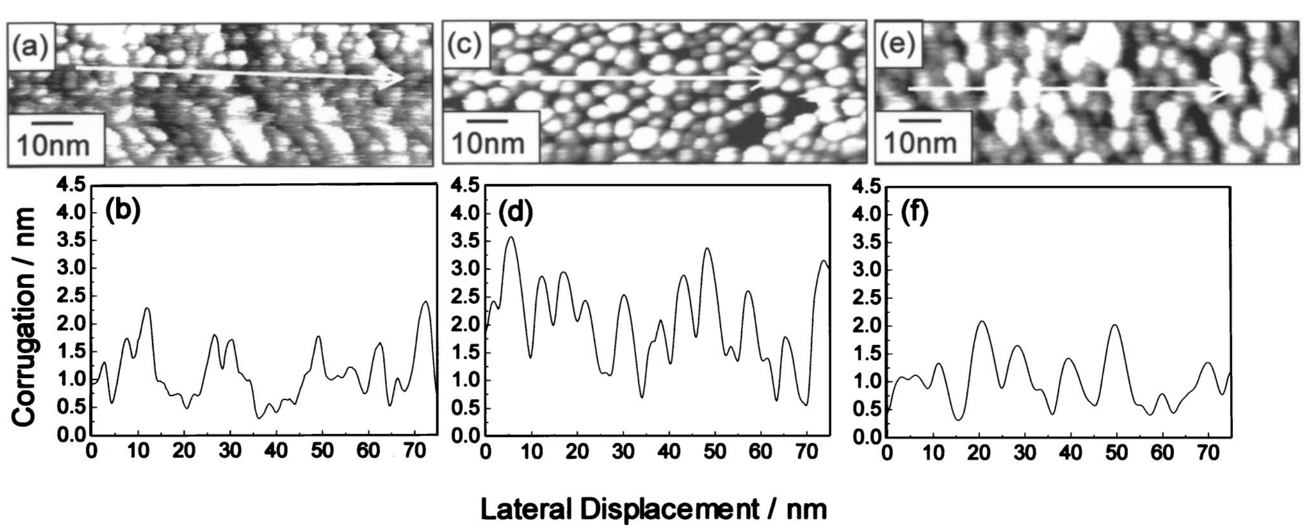

FIG. 4. NC-AFM images and these cross-sectional views of ultrathin Fe films grown at (a), (b) 323, (c) and (d) 473, and (e) and (f) 773 K.

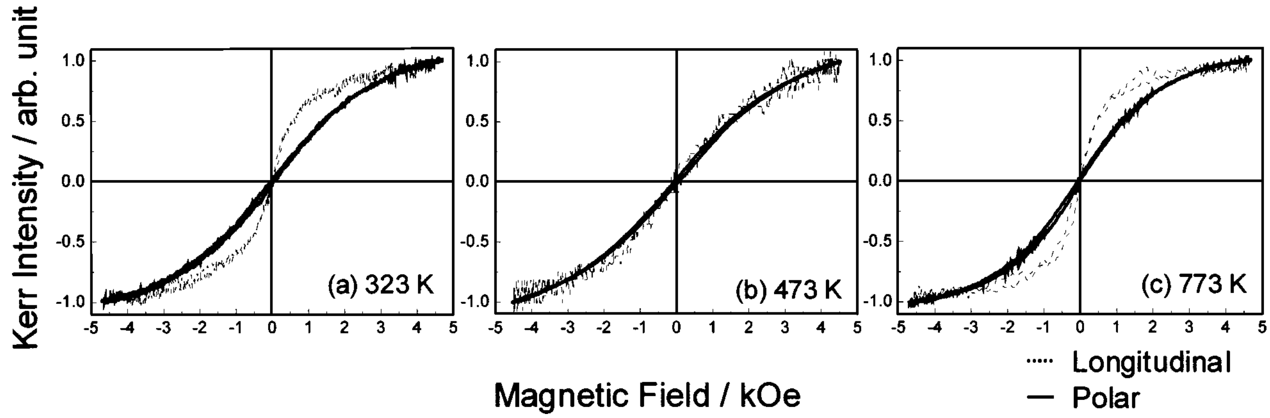

FIG. 6. Magnetization curves of ultrathin Fe films grown at (a) 323, (b) 473, and (c) 773 K, measured using MOKE. Solid and dotted lines represent the magnetization curves with the magnetic field perpendicular and parallel to the film plane, respectively.

curve using the Langevin function, V_{MAG}, are also plotted in Fig. 5. V_{AFM} increases monotonically with increasing growth temperature, while V_{MAG} has a minimum value, as described in Fig. 3. The difference between V_{AFM} and V_{MAG} in the low growth temperature region, such as 323 and 373 K, indicates that the interaction between Fe particles is not negligible; V_{MAG} is strongly influenced by magnetic interactions. At a low growth temperature, the Fe particles are close together [Figs. 4(a) and 4(b)] and the interactions between Fe particles can be large. The difference of V_{MAG} and V_{AFM} for Fe particles grown at a high temperature is due to the volume distribution of Fe particles. Langevin function considering log-normal distribution in Fe volume, in which the median and standard deviation of Fe volume are estimated from the NC-AFM images, well reproduce the experimentally obtained magnetization curves (not shown).

Next, we further discuss the interactions between Fe particles. In superparamagnetic systems that consist of interacting particles, the blocking temperature is expected to be higher than that for noninteracting systems.[19–21] In our case, the blocking temperature has a minimum value at a growth temperature of 473 K. Considering the monotonic increase with the growth temperature of the Fe particle volume, as estimated from the NC-AFM image, this increase in blocking temperature should be caused by the magnetic interactions between Fe particles. In order to confirm the existence of magnetic interactions between the Fe particles in the films grown at low temperature, we show two experimental results. The first result was the magnetization curves, shown in Fig. 6, which were measured using polar MOKE. At a low growth temperature, the magnetization should be in the film plane [Fig. 6(a)]. This feature supports the picture of quasi-2D growth due to coalescence of small Fe particles, or the existence of in-plane magnetic interactions between Fe particles. In the case of midrange growth temperatures, the two magnetization curves are almost identical, as shown in Fig. 6(b). This indicates that the Fe particles are discrete magnetically, and the magnetization behaves in the manner of a random 3D system. The ultrathin Fe film deposited at 473 K consists of structurally discrete particles, as shown in Figs. 4(c) and 4(d). These experimental findings are consistent. Figure 6(c) also shows the difference of the two magnetization curves for films grown at a high temperature. We believe that such a difference is due to the shape of the Fe particles. As shown in cross-sectional view [Fig. 4(f)], the heights of Fe particles, h, are smaller than their own diameters, d. This means that Fe particles grown at a high temperature have a low aspect ratio, h/d. Thus, the difference of two magnetization curves, in which the magnetic field is parallel and perpendicular to the plane, might be due to the shape anisotropy and not interparticle interaction. The existence of interparticle interactions is further confirmed by the

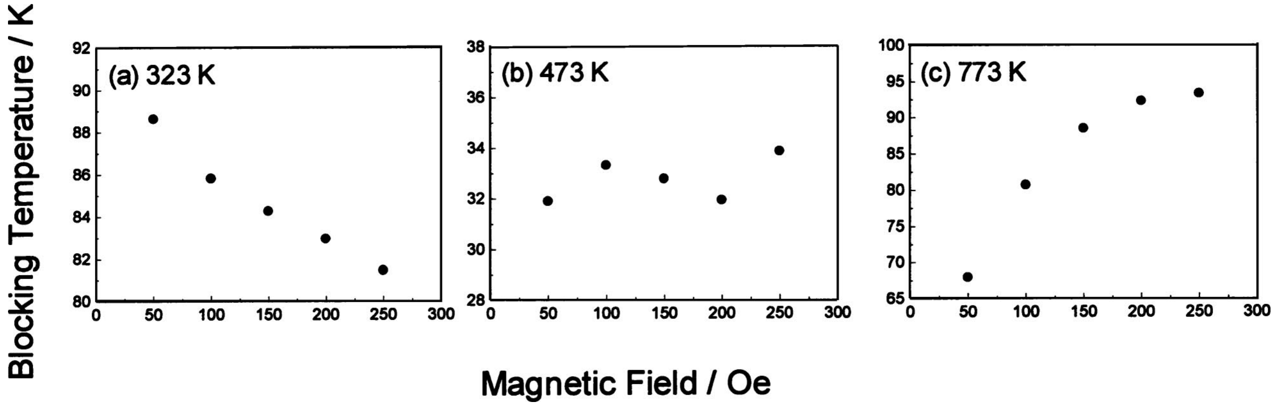

FIG. 7. Changes in blocking temperature as a function of measured magnetic field for ultrathin Fe films grown at (a) 323, (b) 473, and (c) 773 K.

measured magnetic field dependence of the blocking temperature, which is shown in Fig. 7. It is known that the blocking temperature increases with increasing field for systems of noninteracting superparamagnetic particles,[22,23] while the blocking temperature decreases for interacting systems.[23] We find that the blocking temperature decreases with increasing field for Fe grown at a low temperature, while the blocking temperature increases for a high growth temperature. Normally, the blocking temperature decreases with increasing field and is proportional to $H^{2/3}$ considering the change in the relaxation time.[24,25] On the other hand, the increase of blocking temperature with the magnetic field, which is observed in a few cases,[22,23] is a unique phenomenon for noninteracting systems and can be interpreted as a consequence of the nonlinear field dependence of the magnetization of unblocked particles.[23] These observations support the idea that magnetic interactions exist between Fe particles that are prepared at a low growth temperature, while magnetic interactions do not exist in the case of a high growth temperature. The effects of anisotropy on the superparamagnetic behavior are also important and are taken into consideration. The effects of anisotropy, such as surface anisotropy and strain anisotropy, are the topics of future investigations.

IV. CONCLUSION

We have investigated the superparamagnetic behavior of ultrathin Fe films grown on $Al_2O_3(0001)$ substrates. Although 1.0-nm-thick Fe is in the superparamagnetic state independent of the growth temperature, in the range studied of 323–773 K, the blocking temperature and the average volume of the Fe particles are strongly dependent on the growth temperature. The blocking temperature and the Fe particle volume estimated from the magnetization curve have minimum values of 30 K and 35 nm^3, respectively, for Fe growth at 473 K. This correlation between the blocking temperature, the Fe particle volume, and the growth temperature is attributed to the change of the Fe growth mechanism with growth temperature, and to the resultant changes in the magnetic interactions between the Fe particles.

ACKNOWLEDGMENTS

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