Enhanced Curie temperatures in Fe and Co magnetic nanoparticle assembly on single-crystalline Al_2O_3/NiAl(100) with normal metal capping layer

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The ferromagnetism of Fe nanoparticle assembly on Al_2O_3/NiAl(100) is observed above 150 K with the coverage larger than 5 ML (monolayer). Cu capping layer induces an enhancement of the Curie temperature (T_C) in both Fe and Co magnetic nanoparticle assembly. The T_C of Fe nanoparticle assembly with 2 and 6 ML Cu capping layer is enhanced by ~20 K and even higher, indicating the critical effects of metallic capping layer in such magnetic nanostructures as nanoparticle assembly. The capping layer effect would be crucial for the *ex situ* measurements and the nanostorage-related applications. © *2006 American Institute of Physics*.
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In low dimensional systems, such as the ultrathin films and nanoparticles, the magnetic properties are strongly affected by variation of the surface condition, for example, the capping of normal metal (NM) such as Cu, due to the large ratio of surface to bulk atom number. In the reported studies, usually both the magnetic moment and Curie temperature (T_C) of magnetic ultrathin films are reduced by the NM capping layer.[1–6] The proposed reasons include the modification of surface anisotropy,[7] the surface interdiffusion,[8] etc. Although in some cases, there exists a nonzero magnetic moment in the NM layer right beside the FM film, the reduction in the magnetization of the FM film is always even larger.[3,5,6] As the nanoparticle systems are concerned, the NM capping effect is considered to be more complicated. The larger ratio of surface to bulk atom number in nanoparticles than the ultrathin films might result in more significant reduce of magnetization and T_C. In another aspect, for the Fe nanoparticle assembly prepared by buffer layer assistant growth (BLAG),[9] the metallic substrate, such as Cu(111), is shown to provide an additional coupling between the magnetic nanoparticles and significantly enhances the T_C, as compared with the substrate of Ge(111).[9] The questions thus raise that what kind of effect might be indeed caused by capping of NM layer on magnetic nanoparticle assembly and which one will dominate the final results? The magnetization and T_C might be either reduced just as the cases of ultrathin films[1,2] or enhanced since the NM metallic layer may provide additional coupling through the metallic connecting as the case of Fe dots/Cu(111) prepared by BLAG.[9] It is a very crucial and practical issue for the magnetic nanoparticle assembly in both the scientific and technical aspects, since the protective capping layer is unavoidable for the *ex situ* measurements and applications.

Recently many methods are developed for the fabrication of nanoparticle assembly.[9–19] However, most of the magnetic samples are *ex situ* measured with a protective capping layer,[15,18] which, as indicated in this letter, actually induces complicated effects on the magnetic behavior of nanoparticle assembly. In this experiment, the Fe and Co nanoparticle assembly are prepared on Al_2O_3/NiAl(100). The morphology and ferromagnetic behavior are *in situ* characterized. The insulating Al_2O_3 layer not only provides a superior template for the growth of nanoparticles but also terminates the possible magnetic interaction through the metallic substrate between the nanoparticles. Thus as compared with the nanoparticle assembly grown on bare metallic substrate,[9,11] the more direct comparison between the magnetic behaviors before and after NM capping (without and with NM connection between nanoparticles) can be made in this experiment.

The experimental apparatus and the preparation of Al_2O_3/NiAl(100) template are described in our previous report.[19] The Fe, Co nanoparticles, and Cu capping layers were deposited at room temperature (RT). Since the deposition rates were calibrated from the epitaxial growth on Cu(100),[2,20] 1 ML (monolayer) was defined as the atom density on Cu(100) surface: 1.54×10^{15} at./cm^2. The morphology of the sample was investigated by scanning tunneling microscopy (STM) with $V=1.6-2.0$ V and $I=0.8-1.0$ nA. The magnetic properties were characterized by magneto-optical Kerr effect (MOKE). Figure 1 shows the STM images of Fe nanoparticle assembly on Al_2O_3/NiAl(100) (Ref. 19) with the deposition coverage ranges between 3 and 13 ML. With the higher coverage, the particle size increases obviously. However, the morphology still retains the shape

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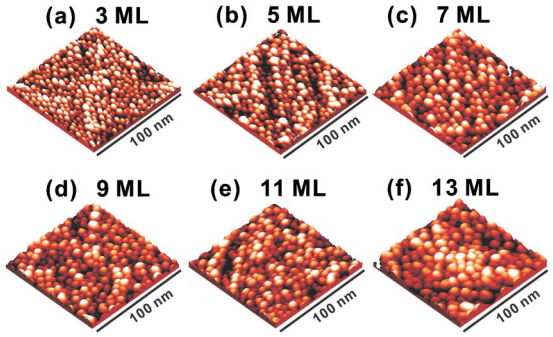

FIG. 1. (Color online) STM images of 3–13 ML Fe nanoparticle assembly on Al_2O_3/NiAl(100). The particle size increases with coverage, and the shape of particles sustains up to 13 ML.

of nanoparticle even with the deposition coverage up to 13 ML. Although the average size increases, the full width half maximum (FWHM) of size distribution dose not increase significantly with coverage. As shown in Fig. 1, no particle of very large size can be observed with 3–13 ML Fe coverage, implying that the growth mechanism might be different from the classical behavior. In the sample of 3 ML coverage, the alignment of nanoparticles is still observable. But for the higher coverage the alignment becomes more and more invisible. Although there exists the enlargement effect due to the finite size of STM tip, the gaps between nanoparticles are still observable, and the shape of nanoparticles also sustains. The significant reduction in the magnetic long-range exchange coupling of nanoparicale assembly as compared with the thin film system (Figs. 2 and 3) will also evidence the fact that the nanoparticles are still separated, at least in the sense of long-range exchange coupling.

Figure 2 exhibits the in-plane MOKE hysteresis loops of Fe nanoparticle assembly recorded at 150 K with different deposition coverage of 3–13 ML. Since the absence of hysteresis loop in polar MOKE is also confirmed, the 3 ML Fe nanoparticle assembly is nonferromagnetic above 150 K, and its T_C should be much lower. Not until 5–7 ML the onset of hysteresis loops is observed at 150 K, which is much lower than that in the Fe and Co/Cu(100) thin film systems.[1,2] There is no preferred easy axis in the plane for the longitudinal magnetization. It is reasonable since the shape of nanoparticles is isotropic in the plane and the alignment is also not significant. Since the nanoparticles are deposited at RT, the assembly is supposed to be stable at and lower than RT.

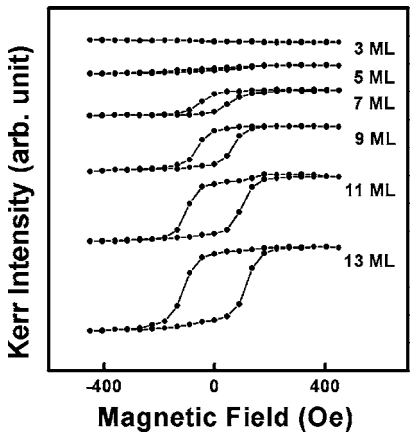

FIG. 2. The in-plane MOKE hysteresis loops of 3–13 ML Fe nanoparticles on Al_2O_3/NiAl(100) measured at 150 K. After 5 ML, the onset of remanent magnetization is observed.

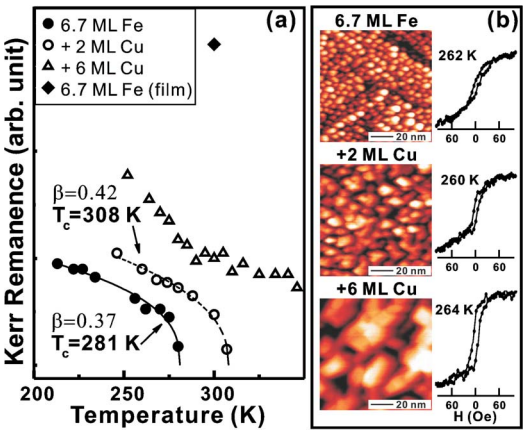

FIG. 3. (Color online) (a) The Kerr remanence (M_R) shown as a function of temperature for 6.7 ML Fe with 0, 2, and 6 ML Cu capping layers. Significant T_C enhancement is observed. For comparison, M_R of 6.7 ML Fe/NiAl(100) thin film grown and measured at RT is exhibited. (b) The corresponding STM images and MOKE hysteresis loops.

In order to avoid the possible diffusion or percolation caused by annealing to temperature much higher than RT, the experiment is focused on the investigation of Fe nanoparticle assembly with 5–7 ML coverage, in which the T_C is near RT. Figure 3(a) shows the Kerr remanence (M_R) of 6.7 ML Fe nanoparticle assembly as a function of temperature. As indicated, T_C is determined to be ~281 K. For comparison, the M_R of the 6.7 ML Fe/NiAl(100) thin film grown and measured at RT is also indicated. Obviously both the M_R and T_C of 6.7 ML Fe thin film are much larger than that of 6.7 ML Fe nanoparticle assembly, indicating a weak long-range coupling in the nanoparticle assembly, which is probably due to the separation of individual particles particularly in the sense of electron overlapping. In Fig. 3(a), after capping 2 ML Cu on the 6.7 ML Fe nanoparticle assembly, the significant increase in T_C from 281 to 308 K is observed. The sequential capping of another 4 ML Cu layer (6 ML in total) also helps increasing the magnetization signal. (Due to possible annealing effect, further measurement for T_C is not performed.) Figure 3(b) exhibits the corresponding STM images and MOKE hysteresis loops (at ~260 K) for the 6.7 ML Fe nanoparticle assembly with 0, 2, and 6 ML Cu capping layer. After capping 2 ML Cu, the M_R increases but keeps nearly the same M_S with the uncapped sample. With the 6 ML Cu capping layer, both the M_R and M_S increase. The STM images also reveal that the capping of Cu significantly changes the morphology and provide connections between the Fe nanoparticles.

As shown in the studies on 1–2 ML Co/Cu(100),[21] the annealing-induced percolation of two-dimensional islands drastically produces a T_C jump of 100 K and enhance the M_R to the level of thin films. In fact, after annealing the 6.7 ML Fe nanoparticle assembly capped with 6 ML Cu to more than 450 K, the remanent (M_R) and saturation (M_S) Kerr signal drastically increase to the same level as that of 6.7 ML Fe thin film due to the percolation between nanoparticles. It also evidences that the reduction of magnetization in nanoparticle assembly, as compared with the thin film system, indeed originates from the finite size effect in the isolated nanoparticles, not from such extrinsic reasons such as oxidation, etc.

Similar phenomenon of the T_C enhancement by capping Cu layer is also observed in the 8 ML Co nanoparticle assembly. Figure 4(a) shows that the T_C of uncapped sample is

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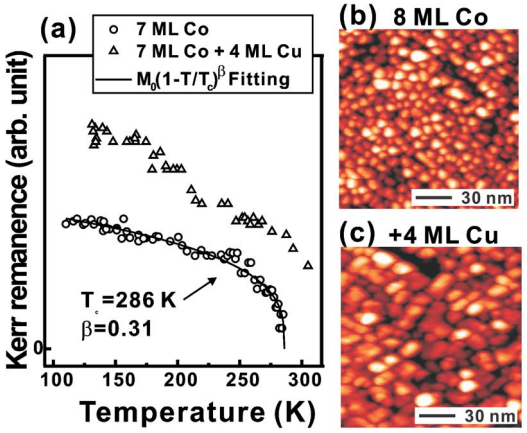

FIG. 4. (Color online) (a) The Kerr remanence shown as a function of temperature for the coverage of 8 ML Co before and after capping of 4 ML Cu. Significant T_C enhancement is observed. (b) and (c) are the STM images before and after capping of 4 ML Cu.

investigated to be ~286 K. After capping 4 ML Cu, both the magnetic Kerr signal and the T_C are enhanced. The STM images in Figs. 4(b) and 4(c) also indicate that the Cu capping layer covers the assembly and provides connections between the Co nanoparticles. The repeat in both Co and Fe nanoparticle assembly demonstrates that the effect is universal in various magnetic nanoparticles.

The critical exponent β is also estimated by fitting the curves for M_R as a function of temperature: $[M_R=M_0(1-T/T_C)^{\beta}]$ (Refs. 20 and 22) (Figs. 3 and 4). It ranges from 0.31 to 0.42, which is very similar to the results of the *in situ* measurements for Fe dots/Cu(111) prepared by BLAG.[9] The fitted β values are quite close to the prediction in three-dimensional (3D) Heisenberg (β=0.365) and Ising (β=0.325) models,[20,22] and far away from that of two-dimensional systems[20,22] (β=0.125–0.24 in experimental and theoretical reports). The tendency of β values toward 3D models also informs the intrinsic magnetism in nanoparticles.

Besides, the Cu capping effect on 9–11 ML Fe nanoparticle assembly is also investigated. The reduction of remanent and saturated Kerr signal for samples with 6 ML Cu capping layer can be observed, just the same as the reports on thin film systems. However, from the data in the previous sections, when the magnetic nanoparticles are still small and close to each other, the connection provided by the Cu capping layer dominates over the usual reducing effect caused by the reduction of surface anisotropy, strengthens the magnetic coupling between the nanoparticles, and eventually results in the enhancement of T_C.

In summary, Fe nanoparticle assembly is shown to sustain the particle shape up to 13 ML coverage and the ferromagnetism is observed above 150 K after 5 ML. Capping of Cu overlayer on Fe and Co nanoparticle assembly induces significant T_C enhancement. The Cu capping layer connects the nanoparticles, providing additional channels for the magnetic coupling between the individual nanoparticles and resulting in the increase of T_C. Such a pronounced capping effect may be avoided by using insulating layers.[23] Since the protective capping layer is always needed for the application of magnetic nanodevices, this effect might become a crucial issue in the near future for modulating their magnetic properties.

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