Composition Dependent Magnetic Coupling in Fe-Cr Alloy Cluster Arrays

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Dense arrays of Fe-Cr alloy clusters with different Cr ratios were fabricated by gas-phase cluster beam deposition. The complex multiphase structure and various coupling effects in the cluster arrays were studied. A lattice mismatched tetragonal-like morphology of the Fe-Cr alloy cluster was observed at large Cr ratio. An exchange bias effect was observed and was shown to be dependent on the proportion of the Cr components in the alloy. With the increase of the Cr composition, the exchange bias field became smaller and stronger dipolar interactions between the clusters developed. Residual coercivity and magnetization, which were more remarkable in the tetragonal-like clusters, were observed above the ferromagnetic-superparamagnetic transition temperature. The experimental results of the coercive field and the bias field at different temperatures demonstrated that the tetragonal-like clusters had better thermal stability and greater anisotropy.

Key words: Fe-Cr alloy, Cluster arrays, Tetragonal-like phase, Exchange interaction

I. INTRODUCTION

Interfacial magnetic coupling in the antiferromagnetic/ferromagnetic heterostructures provides a way to control the ferromagnetic state. The exchange bias effect that arises from intimate exchange interaction between the antiferromagnet and ferromagnet at their interface [1-3], particularly for nanoscale thicknesses or geometries, can result in composite materials with unique and complex properties which are inaccessible through conventional intrinsic materials. The magnetic coupling can lead to various magnetic ordering phenomena, which are becoming critical for next-generation nanoscale magnetic and electronic devices. Fe-Cr composite has become a preferred research combination for magnetic coupling study, especially after the discovery of the giant magnetoresistance effect [4, 5] between two Fe layers separated by non-magnetic Cr spacers in the multilayered Fe-Cr film [6].

The magnetic coupling in alloys is strongly dependent on the composition as well as the chemical ordering state. Complex magnetic couplings exist in the Fe-Cr alloy system. According to the equilibrium phase diagram for the Fe-Cr system (see FIG. 1) [7, 8], above 830 °C, Fe-Cr alloy forms a single bcc α phase, whereas at T<450 °C, the α-FeCr phase disappears and the alloy decomposes to Fe-rich phases and Cr-rich phases (see FIG.1). Therefore, the composition of the Fe-Cr alloy is generally composed of a large amount of ferromagnetic α-FeCr phase, a small amount of ferrimagnetic σ-FeCr phase, and some antiferromagnetic phases. The proportion of the α-FeCr phase generally depends on the Fe-Cr ratio during the preparation process and reaches a maximum at a suitable Fe-Cr ratio [9]. The magnetic interactions in the Fe-Cr system include dipolar interactions between ferromagnetic α-FeCr phases, exchange coupling between antiferromagnetic layers and ferromagnetic layers, as well as other small effects on the magnetic properties of the whole system caused by a small amount of weakly magnetic α-FeCr phase [10].

It is widely known that nanoscale magnetic properties can depart remarkably from that of bulk. Com-
pared with Fe-Cr films [11] and bulk alloys, Fe-Cr alloy nanoparticles have more potential applications because of their complex structure, diverse phase composition and magnetic exchange interaction between the particles [12–14]. The magnetic properties of nanooalloys are very sensitive to their size, to their aggregation states, as well as to their chemical content and order. Fe-Cr nanoalloys have diverse structures and compositions. Isolated Fe-Cr core-shell nanoparticles with an Fe core and a Cr shell were prepared by vapor deposition [15], and it was found that at least two Cr atomic layers were required to stabilize the ferromagnetic/antiferromagnetic interface and generate the associated exchange bias and increase in coercivity. Kaur et al. [16] synthesized low concentration (<10 atom%) Cr-doped core-shell Fe/Fe-oxide nanoparticles, and observed a reversal from dipolar interaction to exchange interaction with Cr incorporation.

In this work, Fe-Cr alloy cluster arrays with different composition ratios were prepared by cluster beam deposition. The effects of the alloy compositions on the magnetic coupling were investigated by measuring the hysteresis loops under field cooling (FC) and zero field cooling (ZFC).

II. MATERIAL AND METHODS

Fe-Cr alloy cluster arrays were prepared with the gas phase deposition of Fe-Cr clusters generated from a magnetron plasma gas aggregation cluster source equipped with two magnetron discharge heads, installed with a Fe target and a Cr target, respectively. Further details on the experimental operation can be found elsewhere [17]. Briefly, a stream of argon gas with a flow rate of 56 sccm was continuously introduced through a ring structure close to the surface of the target into the aggregation tube to maintain the discharge. Another stream of argon gas was fed as a buffer gas through a gas inlet near the magnetron discharge heads. The magnetron discharges were operated at a constant total pressure of about 100 Pa. The magnetron discharges of the two targets were operated at controlled power separately. Atoms were simultaneously sputtered from the Fe target and the Cr target, and aggregated in the argon buffer gas to form clusters. The sputtering rates of each target were pre-calibrated with respect to their input power such that during the operation, the ratio of Fe to Cr atoms in the formed clusters could be easily controlled by selecting an appropriate input power. The clusters were ejected from the aggregation tube to high vacuum through a diaphragm and then deposited on the substrates that were attached on the sample holder. The substrate was a 5 mm×5 mm square silicon wafer. In the present studies, two samples with different ratios of Fe to Cr were fabricated. The sample with a Fe:Cr ratio of 2:1 was noted as the Fe-Cr alloy clusters with a 33 atom% Cr content, and the one with a Fe:Cr ratio of 1:1 was noted as the Fe-Cr alloy clusters with a 50 atom% Cr content. In these two samples, most of the clusters had a Cr content that was close to 33 atom% or 50 atom%, although only a few of them had exactly such Cr content. The mass of both samples was about 2 μg.

The morphologies of the Fe-Cr alloy cluster arrays were characterized with a transmission electron microscope (TEM). Amorphous carbon films on copper grids were used as substrates for TEM observation. Magnetization measurements were performed by using a superconducting quantum interference device (SQUID, MPMS-3) magnetometer. The cluster arrays were placed with the magnetic field in the sample planes for all measurements. Hysteresis loops were measured using a swept magnetic field up to an applied field of ±20 kOe after ZFC and after FC with a cooling field of 1 kOe. Temperature dependent measurements were carried out from 5 K to 300 K under FC conditions.

III. RESULTS AND DISCUSSION

FIG. 2 (a) and (b) show the TEM images the Fe-Cr alloy clusters with two different Fe:Cr ratios of 33 atom% and 50 atom%, respectively. As shown in the two figures, the Fe-Cr alloy clusters are randomly distributed on the surface of the substrate. Most of the clusters are isolated from each other without coalescence. On one hand, aggregations occur among most of the clusters. From FIG. 2(a), it can be clearly seen that most of the clusters are almost spherical. On the other hand, in the film of Fe-Cr alloy clusters with a 50 atom% Cr content, clusters with rectangular shapes become typical, as can be seen from FIG. 2(b). From the histograms shown in FIG. 2 (c) and (d), the average sizes of the clusters in the Fe-Cr alloy clusters with a 33 atom% Cr content and 50 atom% Cr content are about 8.3 nm and 8.8 nm respectively. Therefore, the size of Fe-Cr alloy clusters does not change significantly with the Fe:Cr ratio. From the HRTEM image (inset in FIG. 2(a, b)), it can be found that the shapes of the larger alloy clusters in the Fe-Cr alloy clusters with a 50 atom% Cr content are closer to tetragonal-like rather than cubic. This kind of tetragonal-like structure was not observed for Fe-Cr alloy clusters previously. The content of the tetragonal phase calculated from FIG. 2(b) is at least 43.6%. Actually, the content of the tetragonal phase should be larger than this value since the shapes of many smaller clusters could not be accurately identified so that they were not counted as tetragonal phases. From the histogram shown in FIG. 2(c), the average size of this tetragonal-like clusters is about 9.2 nm, slightly larger than the overall average size. Therefore, the tetragonal-like structure may originate from the distortion of the bcc-Fe lattices due to the internal strains caused by the appearance of residual Cr in the alloy clusters. When the Cr incorporation is
FIG. 2 TEM images of the Fe-Cr alloy clusters with (a) 33 atom% and (b) 50 atom% Cr content. The inset figures show HRTEM images. Histograms measured from the TEM images of the Fe-Cr alloy clusters with (c) 33 atom% (d) 50 atom% Cr content. (e) Size distribution histogram of the tetragonal-like clusters measured from (b).

sufficiently large, Cr atoms could not completely form binary phase structures with Fe atoms, instead, partial intragranular segregations of Cr atoms occur, resulting in the presence of residual Cr atoms in the alloy. Similar segregation phenomenon has been previously observed in Ni-Cr alloy clusters [18].

FIG. 3 (a) and (b) show the magnetic hysteresis loops measured at 5 K under FC and ZFC conditions. A significant left shift of the hysteresis loop can be observed, which indicates that there are exchange couplings between the ferromagnetic components and the antiferromagnetic components in the sample. Since both sample preparation and magnetic measurements were carried out under high vacuum, and the samples were immediately transferred with a very short time of air exposure, there should be no significant oxidation on the cluster surfaces. In fact, no significant oxide layers could be observed from TEM and HRTEM images. Therefore, it can be expected that oxides of Fe or Cr are not the main antiferromagnetic components. The bias of the observed hysteresis loop should be mainly derived from the exchange coupling between the antiferromagnetic components formed by Cr and the ferromagnetic components formed by bcc-Fe. The coercive force $H_C$ and the exchange coupling field $H_E$ are deduced from the hysteresis loops as

$$H_C = \frac{1}{2}(H_{\text{right}} + H_{\text{left}})$$  \hspace{1cm} (1)

where $H_{\text{right}}$ and $H_{\text{left}}$ are the reverse magnetizing fields which must be applied in forward direction and opposite direction to make the magnetization return to zero (The value of $H$ on the hysteresis curve at which the hysteresis loop intersected the horizontal magnetizing field axis). From FIG. 3 (a) and (b), we can see the coercive force $H_C$ drops from 1661 Oe in the Fe-Cr alloy clusters with 33 atom% Cr content to 1414 Oe in the Fe-Cr alloy clusters with 50 atom% Cr content under FC condition. The reduction of the coercive force with the increase of the Cr content is in coincidence with those observed in the most previous Fe-Cr alloy studies [9, 10]. The incorporation of Cr forms more antiferromagnetic components and a portion of ferrimagnetic components ($\sigma$-FeCr), all of which impair the ferromagnetism. However, the exchange bias field changes induced by Cr incorporations observed in our experiments are contrary to those reported for the Fe-Cr alloy nanoparticles with larger size (~25 nm) and lower concentrations of Cr (<10 atom%) [16], which showed an increase of exchange bias field with Cr incorporation. In our study, $H_E$ reduces from 1336 Oe in the Fe-Cr alloy clusters with 33 atom% Cr content to 839 Oe in the Fe-Cr alloy clusters with 50 atom% Cr content under FC conditions. This can also be attributed to the fact that the presence of residual Cr in the tetragonal-
FIG. 3 Magnetic field \((M-H)\) loops of the Fe-Cr alloy clusters with (a) 33 atom% and (b) 50 atom% Cr content measured at 5 K either under ZFC condition or under FC condition with a 1 T cooling field. Magnetization vs. temperature \((M-T)\) curve of the Fe-Cr alloy clusters with (c) 33 atom% and (d) 50 atom% Cr content sample after ZFC and FC under 1 T cooling field.

Like phase structure makes the phase contact interface more complicated, hindering the pinning effect [19] of the antiferromagnetic component on the ferromagnetic component, thereby reducing the exchange bias field.

FIG. 3 (c) and (d) show the magnetization vs. temperature curve \((M-T)\) under FC and ZFC conditions. For the Fe-Cr alloy clusters with 33 atom% Cr content, the FC curve and the ZFC curve bifurcate below about 32 K and coincide above 32 K. This behavior of the ZFC/FC curves is typical for an assembly of magnetic nanoparticles and can be explained by the spin freeze model [20, 21]. During the ZFC process, the ferromagnetic spin is frozen at low temperature and forms a spin-glass state, which cannot be flipped in time as the temperature rises, resulting in a bifurcation of the FC and ZFC curves. The crossover between the bifurcate and coincide regimes occurs in a temperature range near the blocking temperature \(T_B\) which corresponds to the onset of the superparamagnetic regime. The crossover range is relatively narrow and very close to the low temperature peak of the ZFC curve, indicating that the dispersion on the size and magnetic anisotropy energy in the cluster assembly are small.

For the Fe-Cr alloy clusters with 50 atom% Cr content, the FC curve is consistent with that of the Fe-Cr alloy clusters with 33 atom% Cr content, but its ZFC curve does not exhibit significant spin-glass state behavior at low temperatures. This indicates that as the Cr content increases, stronger dipolar interactions between the clusters develop at low temperature, so that the spins are not completely frozen. This long-range dipolar interparticle interactions are likely to be derived from the ferromagnetic \(\alpha\)-FeCr particles formed by the incorporation of Cr into the bcc-Fe. Furthermore, in the Fe-Cr alloy clusters with 50 atom% Cr content, most of the segregated residual Cr atoms in the tetragonal-like structure occupy the intragranular sites of bcc-Fe lattice, which causes some ferromagnetic spins to break away from the lattice. As a result, the degrees of freedom of these spins become higher, and they can be quickly flipped as the temperature rises even after being frozen, which leads to no obvious peak in the ZFC curve.

FIG. 4 (a) and (b) show hysteresis loops measured under FC condition at different temperature. The hysteresis loop gradually shrinks with the increase of the temperature and almost disappears at temperature higher than 50 K, indicating that the Fe-Cr clusters transform completely to superparamagnetic. The \(H_C\) and \(H_R\) calculated from the hysteresis loops are shown in FIG. 4 (c) and (d) as a function of temperature. The coercive field \(H_C\) monotonically decreases with increasing temperature, similar to those previously observed in the Fe-Cr alloy prepared by arc melting [22]. However, there is still a measurable coercive force and remanence even above 50 K, at which the \(M-T\) curves in FIG. 3 (c) and (d) show a ferromagnetic-superparamagnetic transition. The remanent coercive field is especially remarkable in the Fe-Cr alloy clusters with 50 atom% Cr content. In the magnetic nanoparticles, spins of the fer-
Magnetic core rotate easily under the thermal effect, while the surface/interface spins require additional energies to change their directions [16, 23]. For the Fe-Cr alloy clusters with 50 atom% Cr content, there are more surface/interface spins than those in the Fe-Cr alloy clusters with 33 atom% Cr content due to the presence of residual Cr atoms, which are distributed on the surface or interface of the tetragonal-like phase. Therefore, additional energy barriers were generated in the tetragonal-like structure. They can block the orientation changes of the surface/interface spins induced by temperature rising. Furthermore, surface/interface spin structures or magnetic domain structures can also generate additional net magnetic moments, resulting in greater coercivity and remanence in the Fe-Cr alloy clusters with 50 atom% Cr content at higher temperature. It therefore indicates that the thermal stability of the Fe-Cr alloy clusters with more tetragonal-like structure is enhanced.

It can also be seen from FIG. 4 (c) and (d), the Fe-Cr alloy clusters with 33 atom% Cr content have a lower blocking temperature \( T_B \), which corresponds to the temperature at which the exchange coupling field disappears. The anisotropy constant \( K_e \) can be estimated from \( T_B \) using the Arhenius-Neel relationship [24]

\[
T_B = \frac{K_e V}{25k_B} \tag{3}
\]

where \( k_B \) is the Boltzmann constant, and \( V = 4\pi R^3/3 \) is the particle volume. \( K_e \) is calculated to be \( 0.438\times10^5 \) erg/cm\(^3\) and \( 0.592\times10^5 \) erg/cm\(^3\) for the Fe-Cr alloy clusters with 33 atom% and 50 atom% Cr content respectively. Both of them are much smaller than that of bulk iron (\( 4.8\times10^5 \) erg/cm\(^3\) [25] due to the size effect. For the Fe-Cr alloy clusters with 50 atom% Cr content, although the lack of strong antiferromagnetic components may result in a smaller exchange bias field than the Fe-Cr alloy clusters with 33 atom% Cr content, the anisotropy of the morphology caused by the appearance of the tetragonal-like structure and the anisotropy of the composition caused by the distribution of the residual Cr increase the anisotropy constant. It should be noted that the Fe-Cr alloy clusters with tetragonal-like structure have more complex magnetic couplings and deserve further study.

**IV. CONCLUSION**

In summary, we have fabricated dense arrays of Fe-Cr alloy clusters with different Cr doping ratios by the gas phase cluster beam deposition method. The complex multiphase structure and various coupling effects of the alloy clusters arrays were analyzed. A lattice mismatched tetragonal-like Fe-Cr alloy phase was observed in the Fe-Cr alloy clusters with higher Cr contents, which may originate from the distortion of the bcc-Fe lattices due to the internal strains caused by the appearance of residual Cr in the alloy clusters. Due...
to the presence of the residual Cr atoms, the Fe-Cr alloy clusters with 50 atom% Cr content had a smaller exchange bias field than the Fe-Cr alloy clusters with 33 atom% Cr content. In addition, due to the strong dipolar interparticle interactions between the ferromagnetic clusters and the vanishing of the pinning effect, no obvious peak could be observed from the ZFC curve of the Fe-Cr alloy clusters with 50 atom% Cr content near the block temperature, at which a ferromagnetic-superparamagnetic transition was usually observed for the magnetic clusters. As temperature increases, the larger residual coercivity and magnetization revealed that the Fe-Cr alloy clusters with 50 atom% Cr content had better thermal stability. The change in the anisotropy constant calculated from the blocking temperature demonstrated that there were larger morphological anisotropy and compositional anisotropy in the tetragonal-like structure.

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