Structure and magnetism of dilute Co(Zr) nanoclusters

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Co(Zr) nanoclusters having a small fraction of Zr (<7.8 at. %) were produced using a cluster-deposition method and aligned using a magnetic field of about 5 kOe prior to deposition. This study shows that Zr addition to Co nanoclusters improves the fraction of hexagonal close-packed structure, magnetic anisotropy, and easy-axis alignment process. Co(Zr) nanoclusters having 7.8 at. % of Zr exhibit a considerably enhanced magnetic anisotropy constant $K_a \approx 6.7$ Mergs/cm$^3$ and coercivity $H_c \approx 700$ Oe at 300 K as compared to those of Co nanoclusters ($K_a \approx 2.9$ Mergs/cm$^3$ and $H_c \approx 180$ Oe). © 2013 American Institute of Physics.

Research on specially designed magnetic nanoparticles provides new insights into nanoscale phenomena and also may lead to new materials for additional technological requirements.1–3 Recently, simple ferromagnetic nanoparticles such as Fe or Co doped with substitutional or interstitial additives have gained significant attention in order to create nanoparticle building-blocks with improved magnetic anisotropies for alternative permanent-magnet materials. They are also of interest from the viewpoint of fundamental understanding of nanoscale effect on electronic structure and magnetism.4–6 It is worth noting that experimental and theoretical investigations on bulk and thin films of Fe and Co already have shown appreciable changes in magnetic properties on doping with various transition metals.7–9

The fabrication of nanoparticles, however, requires sophisticated methods that ideally have precise control over the size, size-distribution, crystal structure, and composition. In this regard, the gas-aggregation-type cluster-deposition method has been shown to produce assemblies of magnetic nanoclusters smaller than 15 nm with a narrow size distribution and having standard or new crystal structures and stoichiometries.10–16 Most importantly, the easy axes also can be aligned by applying a magnetic field to the nanoclusters before deposition and this is an important processing step for implementing nanoclusters in practical applications.10 In the present study, we have used a cluster-deposition system to produce dilute $(\text{Co}_{1-x}\text{Zr}_x)$ nanoclusters having different at. % of Zr ($0 \leq x \leq 7.8$) and investigated their structural and magnetic properties.

The experimental set up has a water-cooled gas-aggregation chamber,10 where a composite target of Co-Zr is sputtered by a direct current (DC) magnetron sputtering using a mixture of argon and helium gases to form Co(Zr) nanoclusters. These nanoclusters were extracted as a collimated beam travelling towards the deposition chamber and deposited on a single crystalline Si (001) substrate kept at room temperature. X-ray diffraction (XRD, Rigaku D/Max-B diffractometer), superconducting quantum interference device (SQUID) magnetometer, and energy dispersive x-ray analysis (EDX, JEOL JSM 840A scanning electron microscope) were used to characterize the nanoclusters. For high-resolution transmission-electron microscopy (HRTEM, FEI Tecnai Osiris (Scanning Transmission Electron Microscope) studies, carbon-coated copper grids were used as substrates for deposition.

XRD patterns of nanoclusters of Co and Co(Zr) having 6.3 at. % of Zr are shown in Fig. 1(a). The standard positions and relative intensities of XRD peaks corresponding to the hexagonal close-packed (hcp) and face-centered cubic (fcc) structures of Co are given as vertical-solid and -dotted lines, respectively.17,18 XRD pattern of Co nanoclusters shows the most intense diffraction peak close to (002) reflection of the hcp Co, but the presence of a low-intensity (200) reflection also reveals a minor fraction of fcc phase. In the case of Co(Zr) clusters, the (200) reflection of the fcc phase completely disappears and the position of the most intense XRD peak has a good agreement with that of the (002) reflection of the hcp phase as shown in the XRD pattern of Co(Zr) nanoclusters having 6.3 at. % of Zr. These results indicate that Co(Zr) do not have a detectable amount of fcc phase by XRD, revealing predominant hcp structure According to the equilibrium Co-Zr binary phase diagram, Co$_{100-x}$Zr$_x$ solid solution forms up to 0.2 at. % of Zr.19 In the present study, non-equilibrium cluster-deposition method produces Co$_{100-x}$Zr$_x$ nanoclusters for 0 < x < 7.8 and this presumably leads to the stabilization of hcp structure in Co(Zr) nanoclusters. TEM studies show that Co(Zr) nanoclusters have an average size ($d$) of about 8.0 nm with an rms standard deviation of $\sigma/d = 0.16$ (not shown here). In comparison, Co nanoclusters have a slightly larger average size of about 10 nm. In addition, the HRTEM image of the Co(Zr) nanoclusters indicates a high degree of atomic ordering (Fig. 1(b)), and the corresponding

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and 

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((c) revealing a poor alignment, where 

\( H_c \)

Zr exhibit 

saturations and remanent magnetizations, respectively. We also have estimated the magnetic anisotropy constant \( K_1 \) as compared to standard bulk values, presumably due to disorder and surface effects in nanoclusters. 

In addition, the magnetic anisotropy constant \( K_1 \) was estimated by fitting the high field region of \( M-H \) curves of unaligned Co and Co(Zr) nanoclusters using the law-of-approach-to-saturation method, widely used for randomly oriented magnets. 

This analysis shows significantly enhanced magnetic anisotropies of Co nanoclusters on Zr addition. For example, the estimated values of \( K_1 \) for the nanoclusters of Co and Co(Zr) having 7.8 at. % of Zr are 2.8 and 6.7 Mergs/cm\(^3\), respectively. 

As compared to aligned nanoclusters, \( M-H \) curves of the unaligned Co and Co(Zr) clusters deposited in the absence of a magnetic field show identical hysteresis loops with \( M_s/M_s \), in the range of about 0.40–0.49, suggesting a random distribution of easy axes (not shown here). Note that \( M_s/M_s \) is 0.5 for non-interacting randomly oriented nanoclusters. In the present study, Co and Co(Zr) nanoclusters are not embedded in a matrix, and thus some dipolar and exchange interactions are expected between the nanoclusters. The unaligned Co and Co(Zr) nanoclusters, however, exhibit only slightly less \( M_s/M_s \) (about 0.40–0.49) indicating relatively weak or competing exchange and dipolar interactions. In addition, the magnetic anisotropy constant \( K_1 \) as compared to standard bulk values, presumably due to disorder and surface effects in nanoclusters. 

In addition to the increase in anisotropy, Co(Zr) nanoclusters also show appreciable magnetic polarization \( J_s \) (\( J_s = 4\pi M_s \)) in the range of 14.3–10.7 kG on varying Zr content from 2.6 to 7.8 at. %.

The measured values of \( H_c \) and \( M_s/M_s \) of aligned Co(Zr) nanoclusters as a function of Zr at. % along the easy and hard directions are shown in Figs. 3(a) and 3(b), respectively.
\(H_a\) and \(M_s/M_s\) are relatively high along the easy axis as compared to those values along the hard axis for Co(Zr) nanoclusters having 6.3 and 7.8 at. % of Zr, revealing a high degree of easy-axis alignment in Co(Zr) nanoclusters by applying a magnetic field prior to deposition. We also estimated the probability distribution of easy axes \(P(\gamma)\) of the aligned nanoclusters, 24–28 where \(\gamma\) is the angle between the easy axis and the applied magnetic field \(H_{\text{eff}}\) during the deposition as schematically shown in Fig. 3(c). The Co(Zr) nanoclusters show a narrow \(P(\gamma)\) as compared to that of Co nanoclusters.

Co nanoclusters show the following changes of structural and magnetic properties upon Zr addition. First, Co(Zr) nanoclusters show predominanthcp structure, as compared to a mixture of hcp and fcc structures observed in the case of Co nanoclusters. Note that fcc Co has an order of magnitude lower magnetic anisotropy as compared to that of hcp Co and this is supported by significantly enhanced \(K_1\) in Co(Zr) as compared to Co nanoclusters. In conjunction with this result, Co(Zr) nanoclusters show a high degree of alignment by applying a magnetic field prior to deposition.

Note that the actual alignment in the gas phase is a complicated process. The magnetization is rigidly coupled to the crystal in hard-magnetic nanoclusters so that the whole external field \(H_{\text{eff}}\) acts on these nanoclusters and aligns them within a few nanoseconds \(H_{\text{eff}} = H_{\text{eff}} < H_a\), whereas \(H_{\text{eff}}\) and \(H_a\) are effective magnetic field used for the alignment and anisotropy field, respectively. In the case of soft-magnetic nanoclusters such as fcc Co, only the anisotropy field can be exploited \(H_{\text{eff}} = H_a < H_{\text{eff}}\), and thus the crystal follows with a certain relaxation delay. At the same time, \(H_a < H_{\text{eff}}\) means that thermal excitations are more effective in randomizing the direction between spin and lattice. Qualitative estimates are \(MH_{\text{eff}}V/k_BT = 0.5\) for fcc Co and \(MH_{\text{eff}}V/k_BT = 5\) for hcp Co, where \(k_B\), \(V\), and \(T\) are the Boltzmann constant, volume of the nanoclusters, and temperature, respectively. Furthermore, alignment of the cubic nanoclusters is intrinsically difficult to realize, because interchanging a, b, and c axes does not alter the hysteresis loops.

In summary, a gas-aggregation cluster-deposition system was used to produce dilute Co\(_{1-x}\)Zr\(_x\) nanoclusters having 0 \(\leq x \leq 7.8\) and their structural and magnetic properties were investigated. XRD and HRTEM studies show that dilute Co(Zr) nanoclusters have predominantly the hcp structure as compared to a mixture of fcc and hcp phases observed in Co nanoclusters. Co(Zr) nanoclusters also were aligned using a magnetic field of 5 kOe before deposition and the magnetic anisotropy constant was evaluated as a function of Zr content. These results reveal that the addition of Zr to Co nanoclusters improve the magnetic anisotropy and easy-axis alignment process. Co(Zr) nanoclusters having 7.8 at. % of Zr exhibit an appreciable \(K_1 \approx 6.8\) Mergs/cm\(^3\) at 300 K as compared to \(K_1 \approx 2.1\) Mergs/cm\(^3\) for Co nanoclusters.

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