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Magnetism of dilute Co(Hf) and Co(Pt) nanoclusters

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An investigation of the magnetic properties of Co-rich nanoparticles alloyed with a small fraction of Pt and Hf is presented. Co(Hf) and Co(Pt) nanoparticles with less than 15 at% of dopants were produced using a cluster-deposition method. The nanoparticles have sizes of less than 10 nm and show improved magnetic properties upon doping. Maximum coercivities of 900 Oe (at 300 K) and 2000 Oe (at 10 K) were observed for Co nanoparticles alloyed with 14.1 at% of Hf. Doped nanoparticles also exhibit high anisotropies, such as $K_I = 9.98$ Mergs/cm$^3$ (14.1 at% of Hf) and $K_I = 8.24$ Mergs/cm$^3$ (9.5 at% of Pt), as compared to Co nanoparticles ($K_I = 6.21$ Mergs/cm$^3$).


Synthesis of magnetic nanoparticles of size below 10 nm provides unique opportunity to study their nanoscale magnetic properties—in order to create building blocks for applications in areas such as permanent magnetism, magnetic recording, catalytic chemistry, and biomedicine.1–4 As material length scale approaches the nanoregime, magnetic properties of a simple ferromagnetic material such as Fe or Co will be a complex function of dimensionality, defects, and surface effects in addition to any effects of doping or alloying.5–7 Nanoparticles of Fe and Co and their intermetallic compounds with heavy transition (Pd and Pt) and rare-earth metals (RE = Y, Sm, etc.) have been previously investigated in detail.8–10 An increasing demand of RE metals and high costs of Pt and Pd, however, point toward minimizing the fractions of these metals in Co or Fe-based magnetic alloys.11,12

Recently, ab-initio calculations have shown that doping of Fe or Co with low concentrations of heavy transition metals (Pd or Pt) added a large anisotropy contribution13 and provide the impetus for investigating the magnetic properties of Co-rich nanoparticles with a small fraction of Pt or Pd or other heavy metals. In the case of Co-Pt, stoichiometric L10-ordered CoPt nanoparticles and thin films have been investigated extensively in the past14–16 and interestingly, an increase in magnetic anisotropy of CoPt thin films having 8 to 40 at.% Pt on applying bias to the substrate during the growth has also been observed.17 In comparison, the research on Co-Hf systems is limited with a few reports that focus on amorphous Co-Hf thin films having less than 20 at% of Hf.18–20 These films, however, exhibit soft magnetic properties with room-temperature coercivities in the range of 0.5 to 1.5 Oe.18–20 In the present study, we have fabricated nanoparticles of Co alloyed with small fractions of Hf and Pt (< 15 at%) using a plasma-condensation-type cluster-deposition method7–10,21 and investigated their structural and magnetic properties.

Co, Co(Hf), and Co(Pt) nanoparticles were deposited on Si substrate and carbon coated copper grids using our cluster-deposition system based on a direct current (DC) magnetron plasma-sputtering discharge described elsewhere.3,10 A mixture of argon (300 SCCM (standard cubic centimeter per minute)) and helium (100 SCCM) was used as sputtering gas, whereas Co and Co(Pt) nanoparticles were deposited at $P_{dc} = 150$ W and $P_{dc}$ used for producing Co(Hf) nanoparticles is 200 W. The cluster-deposited nanoparticles were characterized using superconducting quantum interference device (SQUID) magnetometer, energy dispersive x-ray analysis (EDX, JEOL JSM 840A scanning electron microscope), x-ray diffraction (XRD, Rigaku D/Max-B diffractometer), and transmission electron microscopy (TEM, JEOL 2010 with an acceleration voltage of 200 kV) measurements. The deposition rate of the nanoparticles was measured in situ using a quartz crystal thickness monitor—in order to quantify the nanoparticles for estimating the magnetization.

XRD measurements were used to investigate the structural properties of Co(Hf) nanoparticles (Co$_{100-x}$Hfx) as a function of atomic concentration of Hf (x). As shown in Fig. 1(a), XRD peaks of Co(Hf) nanoparticles with $x \leq 10.1$ at% are in good agreement with the standard positions of diffraction peaks corresponding to the hexagonal closed-packed structure of pure Co (vertical-dotted lines22) as revealed in the case of XRD pattern of Co(Hf) nanoparticles with $x = 7.7$ at%. As compared to Co(Hf) nanoparticles with $x \leq 10.1$ at% (curve i), Co-Hf nanoparticles with $x = 14.1$ at% (curve ii) have entirely different XRD peaks (Fig. 1(a)). An intermetallic compound with a stoichiometry of HfCo$_7$ is reported to form one of the following structures: tetragonal, hexagonal or orthorhombic for $x = 12.5$ at%.20,23–25 Interestingly, XRD peaks of Co(Hf) nanoparticles with $x = 14.1$ at% (curve ii in Fig. 2(a)) are in agreement with the diffraction peaks corresponding to the orthorhombic structure of melt-spun HfCo$_7$ bulk alloys (vertical-solid lines in Fig. 1(a)).26

\footnotesize
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Magnetic properties of Co(Hf) nanoparticles deposited on Si substrates show a coercivity ($H_c$) of 130 Oe for isolated nanoparticles having $x = 7.7$ at% and $x = 14.1$ at% of Hf. The standard positions of diffraction peaks corresponding to bulk Co (vertical-dotted lines) and bulk HfCo$_2$ (vertical-solid lines) are also shown. The transmission electron microscope image of Co-Hf nanoparticles with 14.1 at% of Hf, where the corresponding particle-size histogram fitted with a Lorentzian distribution is given as an inset. $\sigma$ and $\bar{d}$ are the standard deviation and average particle size, respectively.

Generally, the average particle size ($d$) of Co and doped Co nanoparticles was observed to be less than 10 nm as shown in the TEM micrograph (Fig. 1(b)) and corresponding histogram showing $d = 8.8$ nm (inset of Fig. 1(b)) for Co(Hf) nanoparticles with $x = 14.1$ at% produced at $P_{de} = 200$ W. For comparison, $d$ values of Co and Co(Pt) nanoparticles with 9.5 at% Pt produced at low $P_{de} = 150$ W are about 7.0 nm and 5.5 nm, respectively. The particle size estimated from Scherrer’s equation (for example 7.6 nm in the case of Co(Hf) with $x = 14.1$ at% Hf) is comparable, but slightly less than that of TEM analysis (8.8 nm). This is mainly due to the contribution from the presence of stress/strain in these nanoparticles to the width of the x-ray peaks.

Magnetic properties of Co(Hf) nanoparticles deposited on Si substrate as a function of $x$ were investigated by measuring the magnetization $M$ as a function of applied magnetic field $H$ from $-70$ kOe to 70 kOe at 300 K and 10 K. The expanded room-temperature hysteresis loops for Co-Hf nanoparticles deposited on Si substrates show a coercivity ($H_c$) of 130 Oe and a remanence ratio of $M_r/M_s = 0.34$ for $x = 7.7$ at%. and $H_c = 900$ Oe and $0.48$ for $x = 14.1$ at% as shown in Fig. 2(a). $M_r$ and $M_s$ are the remanent ($M$ at $H = 0$) and saturation magnetizations, respectively. As shown in Fig. 2(a), the $M_r$ of Co(Hf) nanoparticles with $x = 7.7$ at% is substantially reduced as compared to that of Co(Hf) nanoparticles having $x = 7.7$, presumably due to the formation of entirely different crystal structure at $x = 14.1$ at%. $H_c$ of Co(Hf) nanoparticles measured at 300 and 10 K as a function $x$ shows a systematic increase of $H_c$ on increasing $x$ from 7.7 to 14.1 at% as shown in Fig. 2(b), which can be attributed to an increase in magnetic anisotropy upon Hf alloying. A further increase of $x$ to 24.1 at%, however, leads to a substantial decrease of $H_c$, presumably due to the formation of cubic phases such as Co$_{23}$Hf$_6$ and Co$_7$Hf$_2$ at such high concentration.

As compared to Co(Hf) nanoparticles, hysteresis loops measured at 300 K for pure Co and Co(Pt) nanoparticles with 9.5 at% of Pt exhibit a very low $H_c < 50$, but reveal $H_c = 800$ Oe (Co) and $H_c = 2000$ Oe (Co(Pt)) at 10 K (not shown here). The magnetic anisotropy constant $K_1$ at 10 K was estimated by fitting the high field region of $M$ vs. $H$ curves (H > 20 kOe) at 10 K using the law of approach to saturation method (not shown here). $K_1$ values for Co, Co(Pt) and Co(Hf) nanoparticles are 6.21, 8.24, and 9.98 Mergs/cm$^3$, respectively. An increase in $K_1$ observed in the present study is agreed with our previous density functional calculations on Co doped with heavy transition metals, such as Pt and Pd.

In order to study the properties of isolated nanoparticles, nanoparticles of Co, Co(Hf) with $x = 7.7$ and 14.1 at% of Hf, and Co(Pt) with 9.5 at% of Pt were dispersed in SiO$_2$ to reduce the exchange coupling. For this, sequential depositions of nanoparticle layers with nominal thicknesses of about 0.5 nm and SiO$_2$ layers with thicknesses of 5.0 nm were carried out as schematically shown in Fig. 3(a). The numbers of nanoparticle and SiO$_2$ layers are 20 and 21, respectively. The coverage density is approximately 10–15% in these samples on the assumption of random distribution. However, nanoparticles can land close to each other on the substrate and may lead to the possibility of low-intense exchange coupling.

Fig. 3(b) shows the room-temperature $M(H)$ for isolated nanoparticles in SiO$_2$. The Co(Hf) nanoparticles with 7.7 at% and 14.1 at% of Hf, respectively, exhibit coercivities of 190 Oe (curve iii) and 850 Oe (curve iv) at 300 K. By contrast, Co:SiO$_2$ (curve i) and Co(Pt):SiO$_2$ nanoparticles (curve ii) show superparamagnetic-like behavior with $H_c < 10$ Oe. The zero-field-cooled (ZFC) and field-cooled (FC)
and Pt also increases the magnetic anisotropy to depending on dopant concentrations. Alloying of Co with Hf particles show appreciable room-temperature saturation maximum coercivities of 900 Oe and 2000 Oe at 300 and 10 the first time and also show hard magnetic properties with peak, probably due to intergranular exchange. In the case of increases with temperature but does not show a well-defined about 150 K (curve i). The ZFC curve of Co(Pt) (curve ii) magnetization curves are shown in Fig. 3(c). The Co nano-

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FIG. 3. (Color online) Cluster-deposited nanoparticles dispersed in SiO2 matrix layers: (a) Schematic view, and (b) room-temperature hysteresis curves and (c) field-cooled (solid circle) and zero-field-cooled (open circle) magnetization curves at an applied field of H = 50 Oe for (i) Co, (ii) Co(Pt) with 9.5 at% Pt, (iii) Co(Hf) with 7.7 at% Hf, and (iv) Co(Hf) with 14.1 at% Hf. These curves are presented in arbitrary units—in order to distinguish them clearly.