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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/cm³ (14.1 at% of Hf) and $K_I = 8.24$ Mergs/cm³ (9.5 at% of Pt), as compared to Co nanoparticles ($K_I = 6.21$ Mergs/cm³).

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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 past^{14–16} 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 method^{7–10,21} 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}Hf_x) 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 HfCo₇ 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 HfCo₇ bulk alloys (vertical-solid lines in Fig. 1(a)).²⁶

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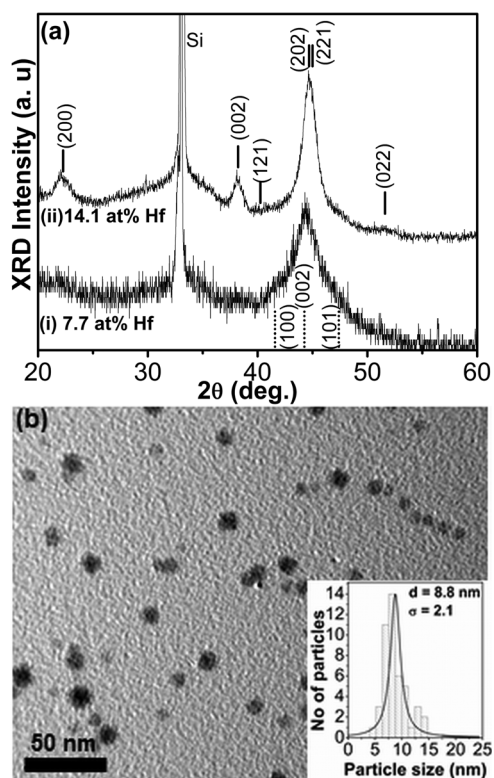


FIG. 1. (a) X-ray diffraction patterns of Co-Hf nanoparticles having (i) 7.7 at% and (ii) 14.1 at% of Hf. The standard positions of diffraction peaks corresponding to bulk Co (vertical-dotted lines) and bulk HfCo₇ (vertical-solid lines) are also shown. (b) Transmission electron microscope image of Co-Hf nanoparticles with 14.1 at% of Hf, where the corresponding particle-size histogram fitted with Lorentzian distribution is given as an inset. σ and 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 $P_{dc} = 200$ W. For comparison, d values of Co and Co(Pt) nanoparticles with 9.5 at% Pt produced at low $P_{dc} = 150$ 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 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_s of Co(Hf) nanoparticles with $x = 14.1$ 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

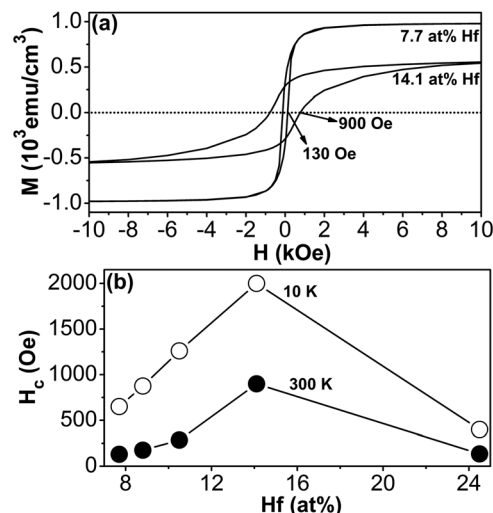


FIG. 2. (a) Hysteresis loops measured at 300 K for Co-Hf nanoparticles having 7.7 at% and 14.1 at% of Hf. (b) Coercivities at 300 K and 10 K for Co-Hf nanoparticles as a function Hf concentration.

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 Co₂₃Hf₆ and Co₇Hf₂ at such high concentration.²³

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_I 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).^{27,28} K_I values for Co, Co(Pt) and Co(Hf) nanoparticles are 6.21, 8.24, and 9.98 Mergs/cm³, respectively. An increase in K_I 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.¹³

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 SiO₂ to reduce the exchange coupling. For this, sequential depositions of nanoparticle layers with nominal thicknesses of about 0.5 nm and SiO₂ layers with thicknesses of 5.0 nm were carried out as schematically shown in Fig. 3(a). The numbers of nanoparticle and SiO₂ 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 SiO₂. 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:SiO₂ (curve i) and Co(Pt):SiO₂ nanoparticles (curve ii) show superparamagnetic-like behavior with $H_c < 10$ Oe. The zero-field-cooled (ZFC) and field-cooled (FC)

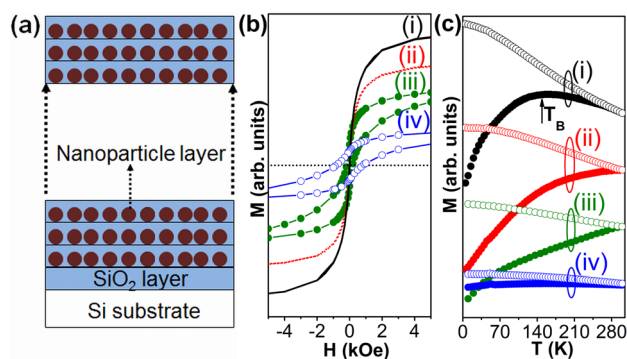


FIG. 3. (Color online) Cluster-deposited nanoparticles dispersed in SiO_2 matrix deposited by sequential depositions of nanoparticle and matrix (SiO_2) layers: (a) Schematic view, and (b) room-temperature hysteresis curves and (c) field-cooled (solid circle) and zero-field-cooled (open circle) magnetization 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.

magnetization curves are shown in Fig. 3(c). The Co nanoparticles have an approximate blocking temperature (T_B) of about 150 K (curve i). The ZFC curve of Co(Pt) (curve ii) increases with temperature but does not show a well-defined peak, probably due to intergranular exchange.⁸ In the case of Hf-Co nanoparticles, they are ferromagnetic at 300 K and thus do not show T_B in ZFC curves (curves iii and iv).

In conclusion, Co(Hf) nanoparticles were produced for the first time and also show hard magnetic properties with maximum coercivities of 900 Oe and 2000 Oe at 300 and 10 K, respectively for 14.1 at% of Hf. Co(Hf) and Co(Pt) nanoparticles show appreciable room-temperature saturation magnetization in the range of about 600 to 1000 emu/cm^3 , depending on dopant concentrations. Alloying of Co with Hf and Pt also increases the magnetic anisotropy to $K_I = 9.98$ and 8.24 Mergs/ cm^3 , respectively, as compared to pure Co nanoparticles ($K_I = 6.21$ Mergs/ cm^3).

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