Influence of an Au capping layer on the magnetic properties of CoPt nanowires

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Equiatomic CoPt nanowires with a gold cap layer have been fabricated by electrochemical template synthesis. Au improves the structural and magnetic properties of the $L1_0$ ordered CoPt, leading to coercivities of up to 1.43 T. The anisotropy constant K_1 was estimated as 3.9(9) MJ m^{-3} from the approach to saturation, and four effective anisotropy constants were determined from analysis of torque curves in a 14 T field. Multisegmented magnetic nanowires are produced using gold interlayers. © *2011 American Institute of Physics*. [doi:10.1063/1.3601748]

Binary Co–Pt alloys with an $L1_0$ structure have been widely investigated for high density magnetic recording media, microelectromechanical systems, giant magnetoresistance sensors, and bio-sensors. When their composition is close to equiatomic, CoPt alloys undergo a phase transformation from a disordered face-centered cubic (fcc) structure to the ordered face-centered tetragonal (fct), $L1_0$ structure on annealing below 825 °C.[1] Magnetocrystalline anisotropy is then ≈5 MJ m^{-3}. Permanent magnets with a large coercivity and a high magnetization (810 kA m^{-1}) can be produced.[2,3]

Electrodeposition of Co–Pt films is a simple alternative to sputter deposition. Electrochemical template synthesis in anodisc aluminum oxide membranes also enables the fabrication of CoPt nanowires with controllable dimensions.[4] A postdeposition annealing process is required to obtain the $L1_0$ ordered phase. Rhen *et al.*[5] achieved a coercivity of 1.30 T for CoPt nanowires while Liu *et al.*[6] obtained coercive fields of 1.35 T and 0.45 T parallel and perpendicular to the wire axis, respectively. Their method involved fabricating Co/Pt multilayered nanowires and subsequent annealing which produced a mixture of fcc and fct phases due to incomplete mixing of the Co and Pt segments.

Previous work has shown that the addition of a third, nonmagnetic element, such as Sn, Pb, Sb, Bi, Cu, Ag, and Au can reduce the annealing temperature required to obtain well-ordered $L1_0$ CoPt films.[7–9] Gold combines unique optical, electrical, and chemical properties with biocompatibility.[10,11] The effect of an Au spacer layer on the magnetic properties of CoPt films prepared by sputtering has been examined.[12–14] The diffusion of Au into CoPt improves the phase transformation from disordered fcc to ordered fct. Yuan *et al.*[14] achieved a coercive field of 1.20 T in CoPt/Au thin films. Min *et al.*[15] showed an enhancement in coercivity and improved squareness in the hysteresis curves of Au doped CoPt nanowires, and they found that CoPt nanowires with larger diameter wires (200 nm) formed a tetragonal phase but 50 nm diameter formed a cubic phase with reduced coercivity contrary to the results of Shamaila *et al.*[16]

Here, equiatomic CoPt nanowires have been fabricated by electrochemical template synthesis. An Au cap layer was then deposited above CoPt wires using a dual bath technique. Postdeposition annealing produces $L1_0$ CoPt/Au nanowires. Structural and magnetic properties of these wires are presented and a proof of principle is given for the fabrication of multisegmented CoPt/Au nanowires.

The nanowires were deposited into commercial membranes with an average pore diameter of 200 nm. They were 20 mm in diameter and 60 μm thick, with a pore density of $\approx 1 \times 10^9$ pores cm^{-2} and a fill factor of 0.68. A 600 nm Ag layer was sputtered onto the back of the membrane to provide a conducting substrate. The electrolyte contained 0.10 M cobalt sulfamate, 0.04 M diamminedinitritoplatinum, and 0.10 M diammonium hydrogen citrate.[5] The pH was adjusted to 6.5–6.7 using sodium hydroxide. A three-electrode cell with an Ag/AgCl (sat KCl) reference electrode and a Pt wire counter electrode, with an area of 0.95 cm^2 was used. Equiatomic nanowires were deposited at −0.85 V in open atmosphere at room temperature. Then the membrane was rinsed with ethanol and a gold layer was deposited on top of the CoPt wires. The electrolyte contained 0.05 M potassium dicyanoaurate and 0.50 M potassium perchlorate in anhydrous dimethyl sulfoxide (DMSO).[17] The gold electrodeposition was done in a glovebox with an O_2 level <1 ppm and $H_2O \approx 3$ ppm to avoid the formation of hydrogen cyanide. The length of the Au spacer layer could be precisely defined since there was no hydrogen evolution in the DMSO. The length was determined by monitoring the charge passed during deposition,[18,19] at a potential of −1.65 V relative to a nonaqueous Ag/Ag^+ (sat $KClO_4$ in DMSO) reference electrode. Once deposition was complete the Ag underlayer was removed using diamond lapping paper before annealing the membrane with the nanowires in forming gas (5 vol. % H_2 and 95 vol. % Ar) at temperatures ranging from 500 to 850 °C and annealing times of 10 to 120 min at 700 °C. Morphological and structural characterization was carried out using scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDAX), and X-ray diffraction with Cu-K_α radiation. The magnetic properties were examined using a 5 T Quantum Design MPMS superconducting quantum interference device (SQUID) magnetometer, and a 14 T PPMS system, at room temperature. An SEM image of CoPt/Au nanowires released from the alumina membrane by dissolving it in 1 M NaOH is shown in Fig. 1(a). CoPt wires had a length of 5.5 μm while the Au segments were 2 μm long with good adhesion at the interface. The EDAX elemental line profile indicates a clear transition from CoPt to Au within a single nanowire and the ratio of Co:Pt was determined as 49:51. Figure 1(b) shows the room temperature

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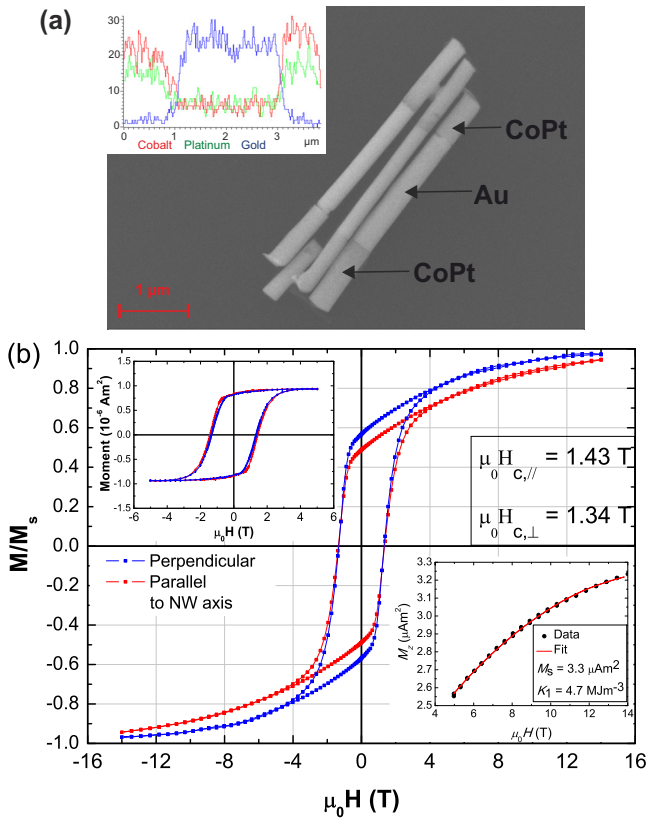

FIG. 1. (Color online) (a) SEM image and EDAX elemental line profile of CoPt/Au/CoPt nanowires. (b) High field PPMS magnetization curve for CoPt/Au nanowires. Insets shows hysteresis curve corrected for the high field slope, and the numerical fit of the approach to saturation.

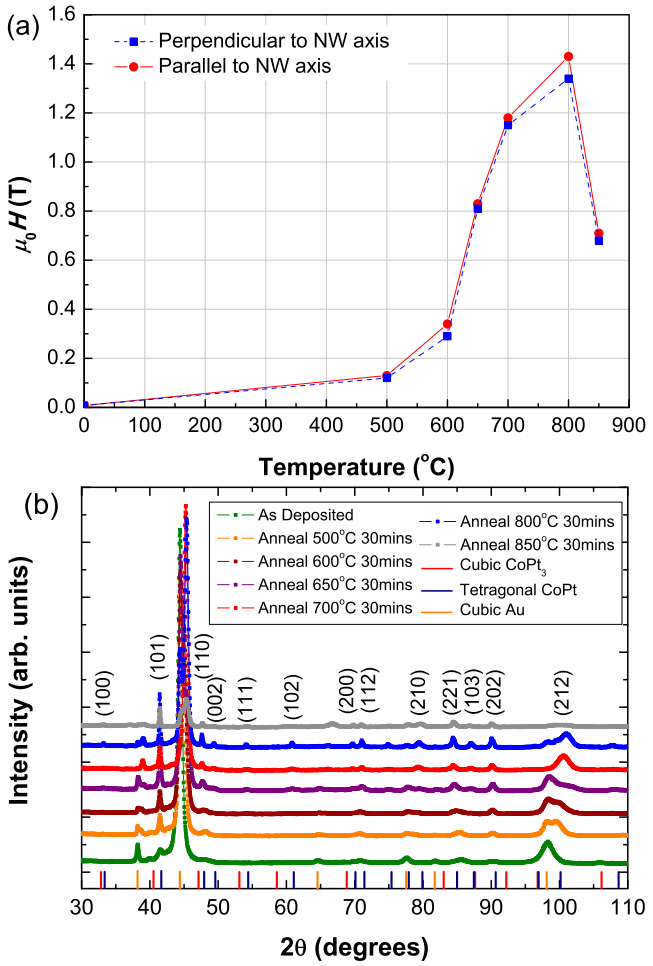

FIG. 2. (Color online) (a) Coercivity dependence and (b) X-ray diffraction pattern of CoPt/Au nanowires annealed at different temperatures for 30 min.

hysteresis curves for the membrane with the CoPt/Au nanowires annealed at 800 °C for 30 min. An effective demagnetization factor of $N=0.34$ was estimated, based on close-to-homogeneous magnetization of the individual wires. The coercive field is 1.43 or 1.34 T when the field is applied parallel or perpendicular to the wire axis. The sample was almost isotropic indicating an almost random distribution of the c-axis within the wires. The average remanence ratio, M_r/M_s is 0.53, showing a little remanence enhancement due to exchange coupling of the CoPt crystallites. Numerical fits to the high-field magnetization curve give a value of the leading anisotropy constant $K_1=3.9(9)$ MJ m^{-3}, which is close to the literature bulk value of 4.9 MJ m^{-3}.[20]

As-deposited CoPt/Au wires are magnetically soft (see Ref. 21 for high field PPMS and SQUID magnetization curve for as-deposited CoPt/Au nanowires, Fig. S1). Coercivity appears on annealing at 500 °C and it increases with annealing temperature as the disordered fcc structure transforms to the ordered fct structure reaching a maximum at 800 °C [Fig. 1(b)]. The Au capping layer increased the coercivity by 50% compared to the uncapped wires. This may be due to the diffusion of Au in CoPt wires as previously observed by Yokota *et al.*[12] The XRD patterns in [Fig. 2(b)] show the progressive onset of atomic order with annealing, leading to an increase in the (101) and (110) reflections, and the splitting of the peaks at approximately 78° and 99°, due to the development of the $L1_0$ order. Splitting of the (200) peak at 47° was apparent at 600 °C for CoPt/Au nanowires whereas for CoPt nanowires it appeared at 650 °C (see Ref. 21 for the XRD pattern of CoPt nanowires annealed at various temperatures for 30 min, Fig. S3). This indicates that Au facilitates the crystallization of ordered CoPt. The diffraction patterns at 700 and 800 °C, show complete transformation to the ordered phase. The shift in diffraction peaks around 98° toward higher angles was associated with the chemical ordering of the $L1_0$ tetragonal structure.[12] Above 800 °C the $L1_0$ phase transformed back to the cubic structure again, with broadening of the diffraction peaks accompanied by magnetic softening and reduced coercivity. The variation in the coercivity after 30 min shows a maximum associated with complete ordering.

The torque pattern was measured using a cantilever-based torque magnetometer, in the 14 T PPMS, for CoPt/Au nanowires as deposited and annealed at 800 °C for 30 min (Fig. 3). The sample area was 1.7 mm^2 or 0.9 mm^2, respectively. The magnetoresistance of the strain bridge causes an offset in each case. The large harmonic with period π reflects the uniaxial magnetocrystalline anisotropy and the crystallographic texture of the sample. There is already some atomic order in the unannealed sample evident from both torque and the (101) reflection shown in [Fig. 2(b)]. In the annealed state higher order harmonics $\cos(2n\theta)$ with $n=2$, 3, and 4 are also observed. Fitting the torque data to $\tau=\Sigma_{n=0}^{4}\tau_n \cos(2n\theta+\phi_n)$ with four anisotropy coefficients τ_i and phase function ϕ_n gives an offset $\phi_n \approx 5°$ for all harmonics and ratios τ_2/τ_1, τ_3/τ_1, and τ_4/τ_1 of 0.33, 0.08, and 0.02, respectively. τ_1 itself is related to the leading anisotropy constant K_1 multiplied by

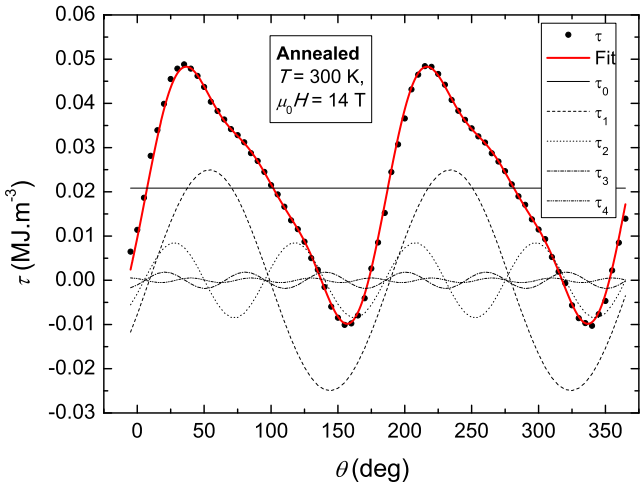

FIG. 3. (Color online) Torque curves measured with a 14 T applied field at room temperature for CoPt/Au nanowires annealed at 800 °C for 30 min.

a texture factor f^2. Using $K_1 = 3.9(9)$ MJ m^{-3} determined by fitting the approach to saturation, as shown in Fig. 1, we deduce a texture factor $f \approx 0.05$.

We are able to fabricate multisegmented CoPt/Au/CoPt nanowires using our method (Fig. 1). The composition and magnetic properties of each CoPt segment can be controlled by altering the deposition conditions. For example, one CoPt segment may be equiatomic and magnetically hard while the other segment may be Pt rich and thus magnetically soft ($Co_{46}Pt_{54}$). Two-segment CoPt/Au/CoPt and three-segment CoPt/Au/CoPt/Au/CoPt nanowires have been produced.

In conclusion, the incorporation of a gold cap layer in CoPt nanowires fabricated by electrochemical template synthesis significantly improves the coercivity and ordering of the $L1_0$ CoPt phase. The formation of the $L1_0$ CoPt ordered phase began at temperatures as low as 500 °C, and after annealing times of just 10 min at 700 °C. The coercive field values of 1.43 or 1.34 T, with the field applied parallel or perpendicular to the nanowire axis obtained by annealing at 800 °C are the highest yet reported. The magnetic anisotropy constant, K_1, was determined as 3.9(9) MJ m^{-3} from the approach to saturation of the samples. The slight crystallographic texture allows four anisotropy coefficients to be determined from torque curves. The fabrication method has been extended to multisegmented CoPt/Au nanowires which have potential for use as magnetic barcode labels.

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