

Evidence of a Surface-Mediated Magnetically Induced Miscibility Gap in Co-Pt Alloy Thin Films

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(100) and (111) oriented single-crystal CoPt_3 films were deposited over a range of growth temperatures from -50 to 800°C . The Curie temperature is increased by 200°C over the value expected for the homogeneous alloy in the as-deposited films (of both orientations) grown near 400°C . We interpret this as evidence for a previously unobserved, surface-mediated, magnetically driven miscibility gap in vapor-deposited CoPt_3 films. Large perpendicular magnetic anisotropy is also observed in the as-deposited films (of both orientations) grown near 400°C .

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Co-Pt alloys have been extensively studied for a wide variety of purposes, including the order-disorder transformation at high temperatures [1], the influence of magnetism on phase diagrams [2,3], studies of catalytic activity [4,5], and thin film magnetic effects such as perpendicular magnetic anisotropy and the possibility of magneto-optic recording [6–9]. The Co-Pt phase diagram is believed to be well understood; it exhibits continuous solid solubility in the fcc structure at high temperatures and forms long range ordered (LRO) phases at lower temperatures. Co-Pt has strong ferromagnetic interactions and a Curie temperature of nearly 1400 K for pure Co, dropping monotonically to below 1 K not until well below 1 at. % Co. Magnetic interactions introduce a positive energy of mixing which drives the system toward clustering of the magnetic species [2,3,10–12]. However, careful calculations of the Co-Pt phase diagram including these magnetic interactions still show solubility near the long range order compositions in bulk materials [2,3,11]. We have observed, however, that CoPt_3 films grown near 400°C exhibit a Curie temperature (T_c) that is enhanced by over 200°C relative to the value expected for the homogeneous alloy. This result can only arise from significant Co clustering, presumably driven by magnetic energy and either caused or at least permitted by the surface-driven nature of the thin film growth process.

The effects of vapor-deposition growth on materials is a topic of considerable importance. In addition to kinetic effects associated with growth from the vapor, there are effects due uniquely to thin film or surface equilibrium states during growth which may be distinct from bulk equilibrium. For example, strain caused by epitaxial or atomic size mismatch can induce miscibility in vapor-deposited mixtures that are immiscible in bulk, including the formation of LRO phases that are not present in the bulk phase diagram [13,14]. Growth-induced *immiscibility*, on the other hand, in systems which are *miscible* in the bulk (as we are suggesting for Co-Pt) has not been previously observed. Other surface equilibrium phenomena, such as segregation, reconstruction, or relaxation, result in a surface structure that may differ significantly from a

simple termination of the bulk structure. Vapor deposition is characterized by mobility at the growing surface, which is many orders of magnitude greater than bulk mobility. As a result, the growing surface may find a local surface equilibrium state which is then trapped in the bulk by the further deposition of additional layers of material. We suggest that the Co clustering we have observed in CoPt_3 films grown near 400°C represents a surface equilibrium phase in this temperature regime, which becomes trapped in the bulk during subsequent film growth.

We have used molecular beam epitaxy techniques [7,8] to grow (100) and (111) $\text{Co}_{1-x}\text{Pt}_x$ films epitaxially on (100) MgO and on (0001) Al_2O_3 , respectively, over a range of substrate temperatures from -50 to 800°C with $x = 0.75 \pm 0.02$ as determined by electron microprobe and Rutherford backscattering. The films were codeposited at a total rate of 0.5 \AA/s from individual Co and Pt sources using electron beam evaporation. All of the films are 3000 \AA thick as determined by low angle x-ray scattering. The measured mosaic spread about the (200) and (222) reflections in the as-grown films varies between 0.09° and 0.32° for films grown at temperatures $350 \leq T \leq 800^\circ\text{C}$; it increases in films grown below 350°C , reaching a value of 1.7° in films grown at 200°C . Films were also grown below room temperature with a mosaic spread of under 1.5° , presumably a result of the reentrant layer-by-layer growth phenomenon observed in pure Pt films. Reflection high-energy electron diffraction (RHEED) patterns observed during growth for all these films indicated good crystal quality.

Below an order-disorder transition temperature of 685°C [1], CoPt_3 has a Cu_3Au -type ($L1_2$) LRO phase, in which the corner sites of the fcc unit cell are populated by Co atoms and the face sites are populated by Pt atoms. We have determined the LRO parameter S at room temperature in the as-deposited films from the ratio of integrated intensities of the fundamental (200) and superlattice (100) x-ray diffraction peaks corrected for Lorentz-polarization factors, temperature dependent factors, static displacement factors [1], and angle dependent absorption factors. The results are shown in Fig. 1.

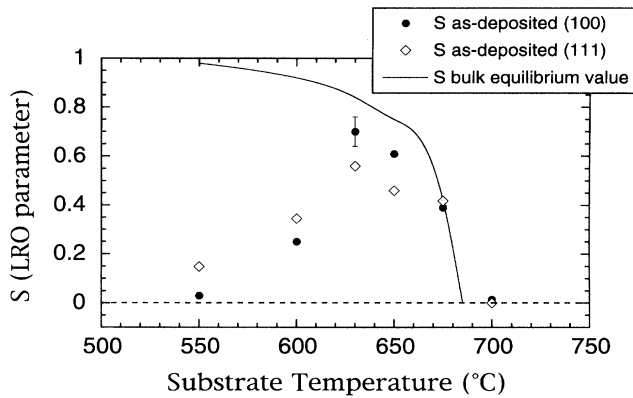


FIG. 1. Long range order in as-grown CoPt₃ films as a function of substrate temperature during growth. Bulk equilibrium curve from Ref. [1]. Error bar reflects uncertainty in all data points.

The LRO in the as-grown CoPt₃ films matches the bulk equilibrium value at 675 °C and follows the general trend toward increasing order with decreasing temperature seen in the equilibrium curve [1] down to 630 °C. Below 630 °C the grown-in LRO falls significantly below the equilibrium value. 630 °C is approximately equal to half the melting temperature, and bulk diffusivity is expected to be low below this temperature. We suggest that LRO may be formed *not* at the growth surface, but may nucleate and grow in the *bulk* of the film during deposition (100 min to grow a 3000 Å film). Estimates of the domain size of the LRO phase based on the width of the superlattice peaks are consistent with measurements of the domain size formed by the annealing of initially disordered bulk material between 600 and 685 °C for 50 to 100 min [1].

Chemically disordered fcc CoPt₃ has a magnetic ordering temperature T_c of 210 °C [3]. In the LRO phase, Co atoms have no Co nearest neighbors. Thus, as LRO develops in the alloy, direct exchange between Co atoms is greatly attenuated and T_c is depressed [3]. T_c of the CoPt₃ films was determined by measuring $M(T)$ upon heating in a 200 Oe external field (the resulting anneal is brief and to 400 °C only and resulted in no change in any property). For reasons that will be discussed later, we define T_c as the temperature at which the magnetization is 5% of its value at 25 °C. T_c as a function of substrate temperature during growth is shown in Fig. 2. $T_c = 218$ °C for the films grown at 800 °C, well within error bars (due to compositional uncertainty) of the expected value (210 °C) for the chemically disordered, homogeneous alloy. The depression in T_c in films grown at substrate temperatures in the range $500 < T < 700$ °C corresponds exactly with the presence and temperature dependence of the LRO phase as seen in Fig. 1. Below 500 °C, we expect $T_c \cong 210$ °C, since the LRO parameter S is below the limit of detectability in these films. We find, however, that T_c increases by 200 °C above what

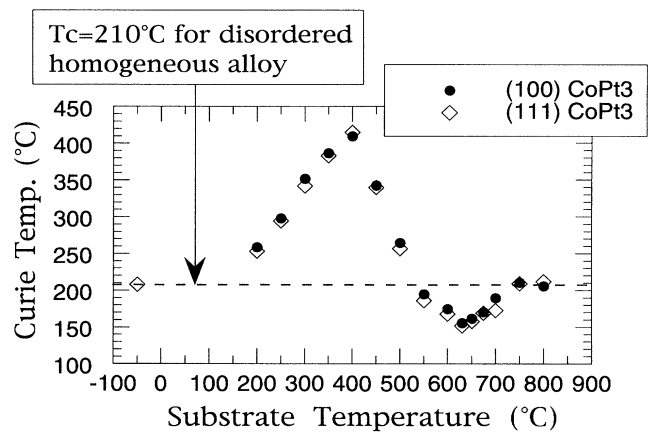


FIG. 2. Curie temperature (T_c) of as-deposited CoPt₃ films as a function of substrate temperature during growth. Error bars are smaller than symbol size and are not displayed.

would be expected for a homogeneous CoPt₃ alloy (ordered or disordered). T_c reaches a peak value of 415 °C at a growth temperature of 400 °C. This high value of T_c corresponds to a local Co concentration of 40 at. % Co [3], indicating a significant degree of Co clustering in these films. As the growth temperature is reduced below 400 °C, T_c drops back toward the value expected for the homogeneous alloy.

The normalized magnetization as a function of temperature for representative (111) CoPt₃ films grown at 800, 630, 400, and -50 °C is shown in Fig. 3. The films grown at 800 and -50 °C exhibit sharp transitions indicative of a homogeneous magnetic environment. The film grown at 630 °C exhibits a slightly broadened transition and a substantially reduced T_c due to the presence of the LRO phase. The film grown at 400 °C, however, exhibits a broad transition from room temperature to above 400 °C, consistent with a material containing a spectrum of magnetic environments. The presence of more than one magnetic phase necessitated a somewhat arbitrary definition of T_c ; other choices would not materially affect the results shown in Fig. 2.

Magnetic hysteresis measurements at room temperature [$M(H)$ curves] for films grown below 300 or above 700 °C are square with saturation magnetization of 340 emu/cm³ (the expected value for the chemically disordered homogeneous alloy), low coercivity, and no anisotropy above the shape anisotropy of a thin film. Films grown between 685 and 550 °C show reduced saturation magnetization, as expected for films with measurable LRO [3]; $M(H)$ curves are still square with low coercivity and anisotropy. Films grown near 400 °C exhibit substantially enhanced magnetization (450 emu/cm³), a perpendicular easy axis with a significant perpendicular magnetic anisotropy (discussed further below), large coercivity ($H_c = 1600$ Oe), and changes in slope upon reversal that indicate the presence of several magnetic phases.

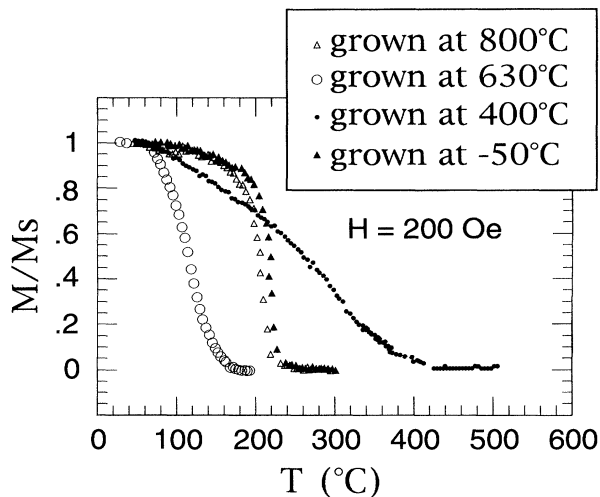


FIG. 3. Normalized magnetization as a function of temperature in a 200 Oe external field for (111) CoPt_3 films grown at 800, 630, 400, and -50°C . Data for (100) films qualitatively the same.

High angle x-ray diffraction measurements of the lattice constant in all samples yielded a value of $3.853 \pm 0.001 \text{ \AA}$ in agreement with that of bulk CoPt_3 [15]. The uncertainty reflects variation from sample to sample rather than the precision of the measurement which is $\pm 0.0002 \text{ \AA}$. The lattice constant of Co-Pt alloys is a sensitive function of composition, and the lattice constant of bulk $\text{Co}_{0.4}\text{Pt}_{0.6}$ (which has a T_c of 415°C) varies from that of CoPt_3 by nearly 1% [15]. The lattice constants of the films grown near 400°C were identical within 0.01% to films grown at 800°C . The high angle Θ - 2Θ reflections from the 400°C films show no unusual broadening or evidence of a second peak, and Θ - 2Θ scans reveal no other lattice constants or orientation. In other words, the phase-separated Co-rich and Pt-rich regions appear to have the same structure and lattice constant as the homogeneous alloy, and probably do not represent discrete compositions. Because lattice mismatch and attendant strain between different Co-Pt compositions with the same lattice constant are relatively large, the critical length of dislocation formation is small, thus limiting the maximum possible size of the Co-rich and Pt-rich regions in the inhomogeneous films. It is also possible that the proposed surface equilibrium phase separation occurs within a spinodal region where there is no energy barrier separating the homogeneous and inhomogeneous phases so that initial compositional fluctuations are continuous.

CoPt_3 has cubic symmetry in both its LRO (L_{12}) and disordered (fcc) phases, and uniaxial magnetic anisotropy would not be expected in this alloy. Nonetheless, uniaxial perpendicular magnetic anisotropy has been reported in thin-film, vapor-deposited Co-Pt alloys (and multilayers) including CoPt_3 [6–8]. Room temperature torque mea-

surements on our CoPt_3 films reveal a large uniaxial perpendicular magnetic anisotropy that is dependent on the growth temperature, independent of crystallographic orientation, and found exclusively in those films that are phase separated into Co-rich and Pt-rich regions, as indicated by their high values of T_c relative to that expected for homogeneous CoPt_3 . The net anisotropy K_\perp was determined using Miyajima's 45° method, and the intrinsic anisotropy K_u is given by $K_u = K_\perp + 2\pi(M_s)^2$. K_u as a function of substrate temperature during growth is shown in Fig. 4. Any residual cubic anisotropy was below the limit of detectability. Strain, as determined from high resolution, high angle x-ray diffraction measurements of in-plane and out-of-plane lattice parameters, is less than 0.03% in all films (consistent with previous results [8]) and thus cannot account for the observed anisotropy. The symmetry breaking of the cubic phase, as evidenced by the presence of uniaxial magnetic anisotropy, is apparently linked both to the vapor-deposition process and to the presence of Co-rich regions within the coherent cubic structure. Chemical heterogeneity has been previously suggested as a source of the magnetic anisotropy in Co-Pt alloys [7]. While we cannot suggest a specific model, it seems likely that the vapor-deposition process introduces an anisotropy in the Co-Co coordination within the segregated material (e.g., a network of oriented Co-rich regions, such as is seen in simulations of phase separation during growth [16]).

Films grown above 700°C and below 300°C exhibit all the properties of the chemically disordered, homogeneous alloy, indicating that the Co clustering in the films grown near 400°C is not the result of kinetic or geometrical effects (e.g., shadowing) during growth. The dramatic enhancement of magnetization, Curie temperature, and magnetic anisotropy observed in these films is not accompanied by any significant structural changes. Furthermore, films grown at 400°C , but at different deposition rates (0.15 and 1.5 \AA/s) exhibit the same anomalous magnetic properties as films grown at 0.5 \AA/s .

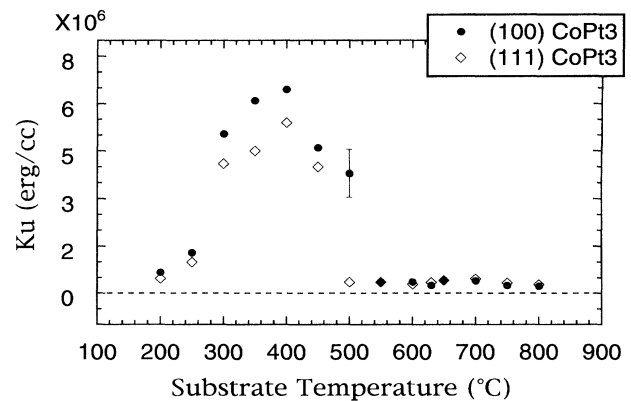


FIG. 4. Intrinsic uniaxial perpendicular magnetic anisotropy in CoPt_3 films as a function of substrate temperature during growth. Error bar reflects uncertainty in all data points.

Previous studies of clean (100) and (111) fcc (chemically disordered) $\text{Co}_{0.2}\text{Pt}_{0.8}$ [4] and $L1_2$ (LRO) CoPt_3 [5] surfaces indicate that, at the surface, energy considerations may be appreciably different than in bulk, changing, for example, the sign of the energy difference between the fcc and the $L1_2$ phase. These surfaces are not bulk terminated: Both (111) and (100) surfaces are terminated with a pure Pt layer with substantial Co enrichment in the second layer and a quasihexagonal reconstruction on the (100) surface similar to that observed in pure (100) Pt [4,5] [implying that both the (100) and (111) surfaces during growth can be represented by a triangular net]. Studies of ultrathin films also indicate suppression of LRO; a Co monolayer deposited on a (111) Pt surface forms a seemingly stable 2 monolayer thick fcc (chemically disordered) alloy after annealing at 375 °C (annealing at 630 °C results in complete diffusion of Co into the Pt) [9]. (We note the possibility that their ultrathin fcc alloy could be phase separated.) These results are unusual as most materials show the opposite behavior: even immiscible elements often form long range ordered surface alloys [13].

There are two distinct possible interpretations of the phenomena we observe. One is that the commonly accepted bulk phase diagram is incomplete; there is a miscibility gap in CoPt_3 opening below 550 °C not previously observed because of the difficulty of reaching equilibrium through bulk annealing at these temperatures. Theoretical Co-Pt phase diagrams [3,11], however, show LRO at low temperatures and do not support the existence of such a gap. It may be, however, that if LRO is suppressed, the energy of the clustered state is lower than the chemically disordered homogeneous alloy near 400 °C, due to the positive magnetic mixing energy, i.e., that the clustered state is metastable. Suppression of the LRO could be simply kinetic (due to a nucleation barrier) or due to surface energetic effects which apparently do not favor LRO [5].

The other possibility, perhaps more likely, is that the observed phase separation is purely a surface equilibrium effect. In this interpretation, LRO in CoPt_3 is suppressed at the surface at all temperatures and only forms in the bulk of the film when bulk mobility is sufficiently high. Near 400 °C, the clustered phase represents an equilibrium phase of the growth surface and this local equilibrium becomes trapped in the bulk by the deposition of subsequent adlayers. Appreciable bulk mobility during growth at temperatures above 600 °C would cause the bulk of the film to homogenize and form the LRO phase. The local stoichiometry in those films that exhibit significant Co clustering would not favor the formation of the LRO phase, thus it may not be coincidence that as-grown LRO vanishes and phase separation begins at a growth temperature which is the limit of appreciable bulk diffusivity.

To summarize, vapor-deposited single-crystal CoPt_3 films grown near 400 °C exhibit various anomalous mag-

netic properties, including a 200 °C increase in Curie temperature, indicating significant Co clustering. This clustering is likely a surface equilibrium effect driven by magnetic energy as T_c is a steep function of composition for the Co-Pt alloy and T_c for pure Co is high (1130 °C) relative to the growth temperature. X-ray measurements of the phase-separated films indicate a single lattice constant, implying that the Co-rich and Pt-rich regions must be small. Large perpendicular magnetic anisotropy is found exclusively in the films grown near 400 °C that have high Curie temperature and enhanced magnetization, suggesting that an explanation for the anisotropy must involve the phase separation.

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