

Oxygen-assisted room-temperature deposition of CoPt₃ films with perpendicular magnetic anisotropy

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Trace amounts of oxygen in the deposition environment are shown to induce perpendicular magnetic anisotropy and remanence in nominally cubic CoPt₃ grown by vapor deposition at or slightly above room temperature. Oxygen is known to act as a surfactant during epitaxial growth of Pt, and here is shown to affect the surface roughness of CoPt₃ films. The dependence on oxygen partial pressure and on growth temperature suggest that the oxygen may act to increase the surface mobility of the growing films, thereby enhancing the clustering which leads to anisotropy. A strong orientation dependence in the anisotropy is found, which was not seen in the absence of oxygen. CO by contrast uniformly reduces anisotropy. © 2002 American Institute of Physics. [DOI: 10.1063/1.1523161]

CoPt₃ grown by vapor deposition with the substrate held at a temperature between 200 and 450 °C has a strong perpendicular magnetic anisotropy (PMA).^{1–6} The bulk-equilibrium phase of this material has either an L10 cubic symmetry or a chemically disordered fcc structure.⁷ The cause of PMA in this seemingly cubic system is believed to be Co clustering on the growth surface which is preserved in the bulk,^{4–6} creating a structure which is locally similar to a Co/Pt multilayer. X-ray absorption fine structure measurements confirm the locally inhomogeneous nature of these alloys.⁸ The maximum anisotropy as a function of growth temperature occurs near 400 °C, which appears to be a result of competition between increasing surface mobility which facilitates clustering and more slowly increasing bulk mobility which eliminates it. When grown at temperatures below 200 °C, films do not show PMA. This significantly reduces their potential use for perpendicular media, where low temperature growth is greatly preferred due to stability of the substrates used. As a result, much effort has gone into studies of Co/Pt multilayers which can be grown with PMA at room temperature. The anisotropy in the CoPt₃ codeposited films is, however, a significant fraction of that found in the optimized multilayers, and the alloys may have some advantage of ease of preparation. In addition, the underlying reason for the Co clustering at the growth surface of these alloys is still not understood, nor how widespread the phenomena may be in codeposition of materials whose equilibrium phase diagrams indicate complete miscibility.

In this work, we have found that oxygen may be used as a surfactant to create PMA in CoPt₃ films grown at or slightly above room temperature. Films grown at 75 °C with as little as 4×10^{-10} Torr partial pressure of oxygen during growth exhibit perpendicular anisotropy including remanence, with no significant incorporation of oxygen into the films. We suggest that this is due to the oxygen reducing the surface roughness of the growing films, thereby increasing surface mobility and enhancing Co clustering. A rough growth surface, which would limit the formation of Co clus-

ters, is more likely at lower temperatures as arriving adatoms have less thermal energy to overcome step- and island-edge barriers. It is these barriers that a surfactant lowers, allowing adatoms to diffuse to lower-energy positions and producing flatter films; we suggest that this allows Co to cluster on the surface, creating PMA. Enhanced surface mobility resulting from a flatter growth surface has been previously observed in materials such as (100) FePd.⁹ We note, however, that in their work the increased mobility aided the formation of the L1₀ bulk-equilibrium phase at lower temperatures, while in our work the flatter films enhance a clustered surface state which is not the bulk-equilibrium state.

Oxygen is known to act as a surfactant during deposition of Pt on Pt, Cu on Cu and Co on Cu,^{10–12} causing flatter growth surfaces and improved epitaxy without significant incorporation into the films. The flatter films in Pt on Pt growth were shown to be due to increased interlayer transport,¹⁰ while in the Cu on Cu system the flattening was attributed to an increased density of islands forming on the growth surface.¹¹ Monolayers of Co grown on Pt in the presence of CO gas were also shown to be flatter due to enhanced interlayer transport.¹³

Samples were prepared by electron beam coevaporation from separate Co and Pt sources in an ultrahigh vacuum deposition system. The background pressure during deposition was approximately 8×10^{-9} Torr (not including any added oxygen); the background partial pressure of the various gases in the chamber was measured with a residual gas analyzer. The principal background gases were H₂O, N₂, and CO₂, with partial pressures of 2.1×10^{-9} , 0.5×10^{-9} , and 1.7×10^{-9} Torr, respectively, during a typical deposition. The measured background pressure of oxygen gas was within instrumental error of zero ($< 1 \times 10^{-11}$ Torr.) The partial pressure of oxygen in the chamber was controlled by manually adjusting a precision leak valve connected to a bottle of ultrahigh purity oxygen gas, and was controllable to within 10% of the desired value for all pressures used. Co and Pt were codeposited at a total rate of 0.5 Å per second to a final thickness of 450 Å. A seed layer of 100 Å Pt grown at high temperature (500 °C) was used to achieve epitaxy in the low-temperature growth. (0001)-oriented Al₂O₃ was the

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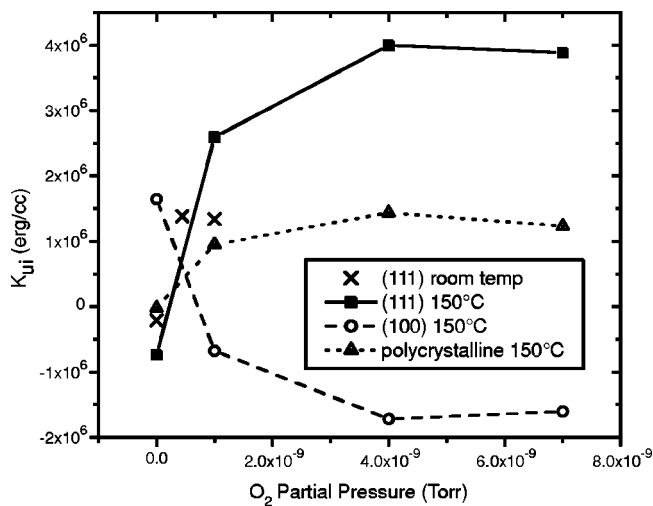


FIG. 1. Intrinsic anisotropy of films grown at 150 °C and room temperature vs oxygen background pressure. Error bars are smaller than symbol size.

substrate for the (111) films, while MgO (100) was used for the (100)-oriented films. Several nonepitaxial, but strongly (111)-textured samples have been included in the study as well, deposited directly on SiN_x-covered Si substrates with no seed layer.

We prepared two sets of samples, varying the oxygen pressure at a fixed deposition temperature in one and varying the temperature in a fixed partial pressure of oxygen in the other. We also studied the effect of CO gas on samples grown near room temperature. Compositions of the films in this study were primarily determined by Rutherford backscattering (RBS). Values were confirmed by analysis of the magnetic moments of films annealed to high temperatures (800 °C) after growth. Previous work has shown that after annealing and quenching to room temperature at even moderate quench rates, the samples are in the face-centered-cubic state where the magnetization is a well-determined function of composition.⁵ Low-angle x-ray reflectivity was used to determine film roughness and thickness; high angle x-ray diffraction was used to determine lattice constants.

The magnetic anisotropy at room temperature of the films was measured with a torque magnetometer. Torque τ on the samples is recorded as a function of the angle between the surface normal and the applied field α . Once the saturation moment of the samples is known, it is straightforward to convert α into the angle between the magnetic moment of the sample and the surface normal, θ . All of our films showed a $\tau = K_u \sin^2(\theta)$ dependence of the torque on this angle, as you expected for a simple uniaxial anisotropy, with K_u being the net perpendicular magnetic anisotropy. The intrinsic anisotropy K_{ii} is calculated by subtracting the shape anisotropy component equal to $-2\pi M_S^2$ from K_u .

K_{ii} of films grown at 75 °C as a function of oxygen partial pressure is shown as the crosses in Fig. 1. (111) epitaxial films grown at room temperature show a remarkable sensitivity to the presence of oxygen during growth. Without oxygen, these films exhibit in-plane anisotropy and very low coercivity. Films grown with as little as 4×10^{-10} Torr of oxygen gas however have significant PMA. By contrast, (111)-oriented samples grown near room temperature in the presence of CO gas show a rapid transition from no intrinsic

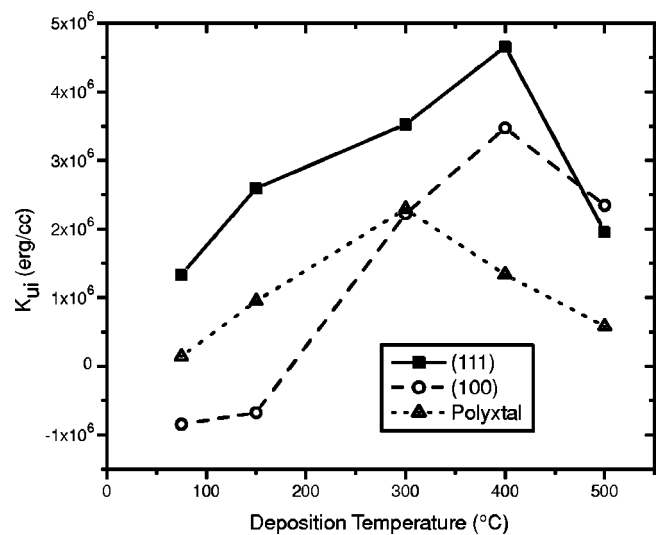


FIG. 2. Intrinsic anisotropy of films grown in 1×10^{-9} Torr O₂ vs deposition temperature. Error bars are smaller than symbol size.

anisotropy ($K_{ii} \approx 0$) to in-plane anisotropy ($K_{ii} < 0$) with increasing CO pressure. At 150 °C, both (100) and (111) films were prepared epitaxially. These show a strong dependence on the oxygen pressure as well, as shown in Fig. 1, but in opposite directions; the presence of oxygen creates PMA in (111) films, while a strong in-plane anisotropy is created in (100)-oriented samples. Polycrystalline samples lie between these.

Figure 2 shows K_{ii} as a function of growth temperature for films grown at a partial oxygen pressure of 1×10^{-9} Torr. A peak in K_{ii} at 400 °C is seen for both (111)- and (100)-oriented films, similar to the peak seen previously without oxygen. The peak in the anisotropy of the (111) films is much broader than found for no oxygen, with significant PMA present at 150 and 75 °C, below the threshold of 200 °C observed without oxygen, but the highest value of K_{ii} at 400 °C is unchanged.

The (100) films exhibit a crossover between 150 and 300 °C from strong in-plane anisotropy ($K_{ii} < 0$) to perpendicular anisotropy ($K_{ii} > 0$). Above 300 °C, K_{ii} for both (100) and (111) films is nearly identical to that seen in films grown without oxygen.^{4,5} K_{ii} for the polycrystalline films is lower than (111) films at all temperatures, with a peak at 300 °C, and again there is PMA in films grown below 200 °C.

Magnetization M versus field H was measured at room temperature with a vibrating sample magnetometer. As an example, the hysteresis loop for a (111) film grown in 1×10^{-9} Torr O₂ at 150 °C is shown as an inset in Fig. 3. In the absence of oxygen during growth, this sample would have no PMA and no remanence, but it shows relatively strong PMA including full remanence. The saturation magnetization M_S of films grown at 150 and 75 °C is shown in Fig. 3 as a function of the oxygen pressure. The composition of samples with no O₂ is 25.4 at. % Co, while the samples with 1×10^{-9} Torr O₂ are 23.1 at. % Co, and the higher-oxygen samples very close to the correct composition of 25 at. % Co. These small variations in composition are enough to explain most of the structure seen in the plot. Allowing for these small composition shifts, we see that the moment of the

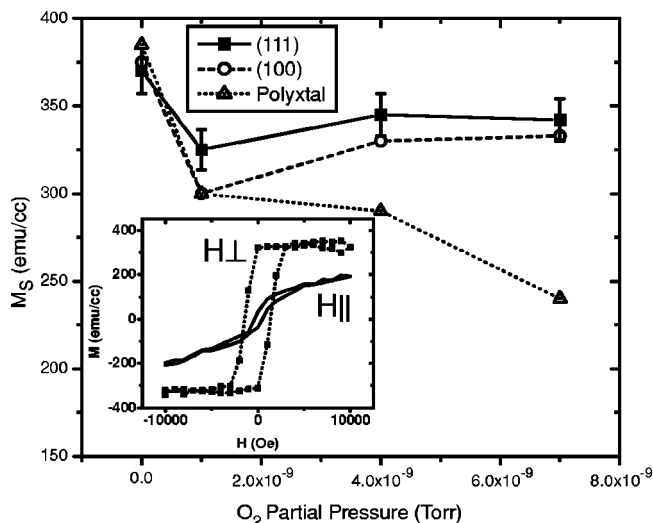


FIG. 3. Spontaneous magnetization of films grown at 150 °C vs oxygen background pressure; Zero-oxygen films are 26 at. % Co, 1×10^{-9} Torr oxygen films are 24 at. % Co, the rest are 25 at. % Co. Inset is hysteresis loop for film grown in 1×10^{-9} Torr O_2 . Error bars on (111) data are typical of all orientations; other error bars omitted for clarity.

epitaxial samples shows little dependence on oxygen dose, suggesting little or no incorporation of oxygen into the growing films. It is worth noting that the arrival ratio of Co and Pt atoms to O_2 molecules during the deposition is quite large; at 4×10^{-10} Torr, with a deposition rate of 0.2 monolayers of $CoPt_3$ per second, the ratio is 500:1. This small amount of oxygen, even if incorporated into the growing films, is unlikely to create a strong PMA through chemical modification of the alloy.

The moment of the (111) films in the as-grown state is enhanced by 10% over that found after annealing, indicating the presence of Co platelets in the as-grown films, similar to what has previously been observed in films grown at higher temperatures (e.g., 400 °C) with no oxygen.⁵ The dramatic increase in PMA is thus most likely due to an effect of the oxygen on the Co and Pt at the growth surface.

High angle x-ray characterization shows no significant dependence of lattice constant on oxygen pressure up to at least 7×10^{-9} Torr, again indicating no significant incorporation. RBS measurements on the polycrystalline samples with 1×10^{-9} Torr O_2 show no detectable oxygen peak, putting an upper limit of 3%–4% on the oxygen content in the films. At higher pressure, a reduction of M_S is seen, going to zero near 3×10^{-8} Torr O_2 , consistent with RBS data which shows some O_2 incorporation at this higher pressure.

The surface roughness of the films was characterized qualitatively from low-angle x-ray reflectivity measurements. A reflectivity which decays more slowly with increasing angle and with interference fringes extending to higher angles indicates a smoother film, while a short decay with less fringes indicates a rougher film. Based on our reflectivity data, the roughness of the (111) films decreases as more O_2 is added to the deposition environment, while the (100) films show increased roughness with increased oxygen dose. The roughening effect of the oxygen on the (100) films is perhaps due to increased (111) faceting of the films. These

opposing trends in the surface roughness parallel the anisotropy data, in which the (111) and (100) films have opposite trends with increasing oxygen dose. Adding CO to the system created an in-plane anisotropy in (111)-oriented films, and the low angle x-ray reflectivity data show a monotonic increase in roughness with increasing CO dose, similar to the results for the (100) samples in O_2 . These data support the contention that reducing surface roughness is a key component in the creation of PMA in these films.

In summary, we find that a small amount of oxygen in the deposition environment of $CoPt_3$ codeposited films causes large changes in the magnetic anisotropy. Films with a (111) orientation grown near room temperature with as little as 4×10^{-10} Torr oxygen have net PMA with close to full remanence, while films grown under identical conditions with no oxygen have no PMA. Conversely, (100) films that have a small net PMA when grown with no O_2 have an in-plane anisotropy when grown in the presence of oxygen. The changes in anisotropy are correlated with changes in the surface roughness, suggesting both that flatter growth surfaces lead to higher anisotropy, and that O_2 acts as a surfactant in the growth of (111) $CoPt_3$. The large effects are restricted to the lower-temperature samples, as samples grown above 200 °C are virtually unaffected by the presence of oxygen, possibly due to desorption of oxygen from the growth surface at higher temperatures. We have also shown that it is possible to grow polycrystalline $CoPt_3$ on an amorphous substrate with PMA by depositing near room temperature in the presence of oxygen, which may be of technological interest.

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