Magnetic anisotropy and crystal structure of Co–P films synthesized by electrodeposition from alkaline electrolytes

X. Xu[a)]
Department of Chemical Engineering, University of Virginia, Charlottesville, Virginia 22904

G. Zangari
Department of Materials Science and Engineering, University of Virginia, Charlottesville, Virginia 22904

(Presented on 2 November 2005; published online 21 April 2006)

Co–P and Co films were electrodeposited on polycrystalline Au from a Co-sulphamate-based alkaline solution with ammonium citrate as complexing agent, with or without Na hypophosphite as the P source. Pure cobalt films exhibit a hexagonal-close-packed (hcp) structure. Scanning electron microscopy images show an acicular microstructure, with shorter features at larger current densities. In the presence of the P source, the films show diffraction peaks only at very small deposition current densities (up to 2 mA/cm^2), when more packed and slightly elongated grains are formed and x-ray-diffraction (XRD) patterns exhibit hcp (10.0) and (11.0) peaks. With increasing current density, P content in the films increases, the apparent grain size decreases, and the films lose crystallinity, as detected by XRD. Co films show in-plane magnetization and coercivity less than 100 Oe. The codeposition of P results in an increased coercivity of crystalline films, up to about 900 Oe at 100 nm thickness. Amorphous Co–P films obtained at high current density become very soft and for a thickness larger than 400 nm exhibit a stripe domain structure. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2167328]

I. INTRODUCTION

Electrodeposited Co–P films are versatile magnetic materials that can exhibit a wide range of magnetic properties in dependence of their microstructure and phosphorous content. In particular, they display properties of interest in applications ranging from magnetic recording to microelectromechanical systems.[1] These alloys are usually grown by electrodeposition from acid electrolytes,[2,3] where the growth process is influenced by hydrogen evolution and composition can be varied only to a limited extent by varying the current density, cd. Growth from alkaline electrolytes may provide for alternative and more convenient means to control composition, microstructure, and magnetic properties. We discuss here the electrodeposition of Co–P films from alkaline Co-sulphamate-based electrolytes using ammonium citrate as a complexing agent. Both relatively hard and soft Co–P films can be grown from this electrolyte, their properties being tailored simply by changes in the plating current density.

II. EXPERIMENTAL DETAILS

Co and Co–P films were prepared by electrodeposition onto polycrystalline, 100-nm-thick Au films, previously sputtered on glass. The electrolyte contained 0.1*M* cobalt sulphamate, 0.1*M* ammonium citrate, 0.1*M* glycine, and 0.1*M* sodium hypophosphite, the latter being the P source. *p*H was adjusted to 8 using diluted NaOH. Electrodeposition was performed at 65 °C, without stirring. Samples were grown at constant current, and sample thickness was controlled by varying the deposition time.

a)Electronic mail: xx4b@virginia.edu

Film morphology and composition were investigated by scanning electron microscopy (SEM) (JOEL JSM6700) along with energy dispersive x-ray spectroscopy (EDS), and the crystal structure was determined by x-ray diffraction (XRD) (Scintag Inc.). Magnetic properties were measured with a vibrating-sample magnetometer (ADE Technologies, VSM Model 886). Hysteresis loops were measured at room temperature with the magnetic field applied parallel to the film plane, up to a maximum field of 5000 Oe.

III. RESULTS AND DISCUSSION

Cobalt films were grown for comparison purposes from the same electrolyte, without the P source. The SEM surface morphology of these films (Fig. 1, left, cd=5 mA/cm^2) shows a platelet microstructure, with features decreasing in size at higher cd's (not shown). XRD patterns (Fig. 2) show that Co films exhibit a hexagonal-close-packed (hcp) structure in a wide range of current densities. hcp (10.0), (10.1)

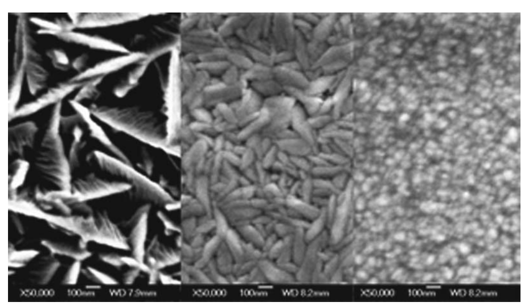

FIG. 1. SEM surface morphology of Co and Co–P films. Left: Co film deposited at 5 mA/cm^2. Center: Co–P (~10 at. % P) film deposited at 2 mA/cm^2. Right: Co–P (~13 at. % P) film grown at 5 mA/cm^2. The thickness for all films was 1 μm.

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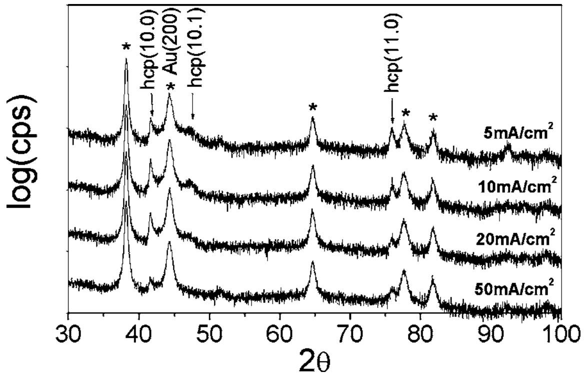

FIG. 2. XRD patterns of pure Co films (1 μm in thickness) deposited at various current densities, where cps is count per second. Peaks indexed with $*$ are reflections from the Au substrate.

(weak), and (11.0) orientations are all present (peaks marked by * belong to Au substrate). A possible (00.2) orientation is hidden by the Au (200) peak.

P codeposition with Co causes important changes in the microstructure (Fig. 1). At small current density ($2\ mA/cm^2$, ~ 10 at. % P, Fig. 1 center) crystal grains are elongated, smaller, and more compact than Co. The corresponding XRD pattern (Fig. 3) shows sharp hcp (10.0) and (11.0) peaks. As the current density increases and hence the P content increases beyond 10 at. %, grain size decreases (Fig. 1, right) and the films lose their crystallinity, as shown in the XRD patterns in Fig. 3. The only indication of a crystalline short-range order is the shoulder at the right of the Au (200) peak, decreasing in intensity with increasing current density, which should belong to the (00.2) reflection for hcp Co(P). The film amorphization that was achieved here by changing the deposition current density could be obtained in Ref. 2 only by varying the pH or H_3PO_3 concentration; both these methods are far less practical than varying cd. In both cases, however codeposition of P beyond 10 at. % results in the formation of an apparently amorphous structure, due both to the hindrance of surface diffusion of adsorbed Co ions during growth[2] and to the difference in atomic radius of Co and P. P content in the films increases with increasing current density (10%, 13%, and 15% for films deposited at 2, 5, and $20\ mA/cm^2$, respectively), opposite to what is observed in the deposition from acid solutions.[2,3]

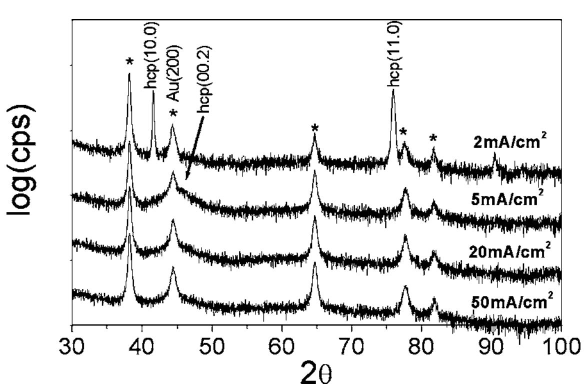

FIG. 3. XRD patterns of Co–P films (1 μm in thickness) deposited at different current densities. Peaks indexed with $*$ are reflections from the Au substrate.

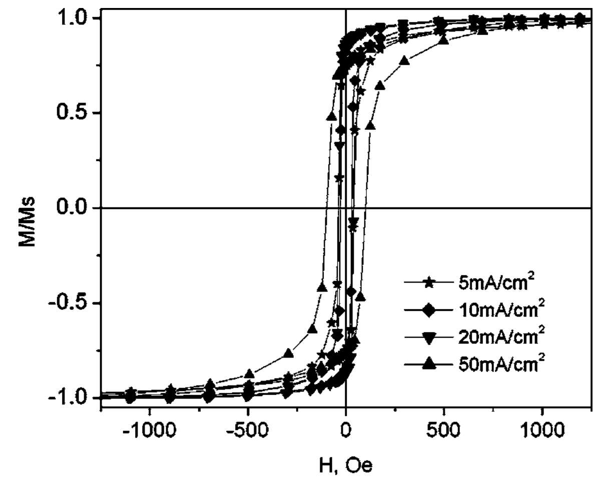

FIG. 4. Normalized hysteresis loops of 1-μm-thick Co films.

Figure 4 shows the normalized hysteresis loops of 1-μm-thick Co films deposited at different current densities. Magnetic anisotropy is clearly in plane and magnetization switches by domain-wall motion. The coercivity is small (30–90 Oe) and increases greatly as current density increases from 20 to $50\ mA/cm^2$, indicating an increase in defect density when growth is made to occur faster. This is also verified by the XRD patterns in Fig. 2, where the diffraction peaks of the film grown at $50\ mA/cm^2$ are much weaker than the other ones.

Co–P films with varying P contents on the other hand display very different magnetic properties. Figure 5 shows the in-plane hysteresis loops of Co–P films (1 μm in thickness) grown at different cd's. Crystalline Co–P (P ~ 10 at. %) films grown at $2\ mA/cm^2$ exhibit in-plane anisotropy—in agreement with their crystalline orientation—with a coercivity around 330 Oe. As the P content increases and the films become amorphous, the loops become typical of films exhibiting stripe domains.[4] In this configuration, local magnetization vectors lie in the plane normal to the film plane and oscillate between directions slightly upward and downward with respect to the film plane, which leads to a stripe pattern. The total energy in the material is minimized by this configuration and stabilized by a net perpendicular

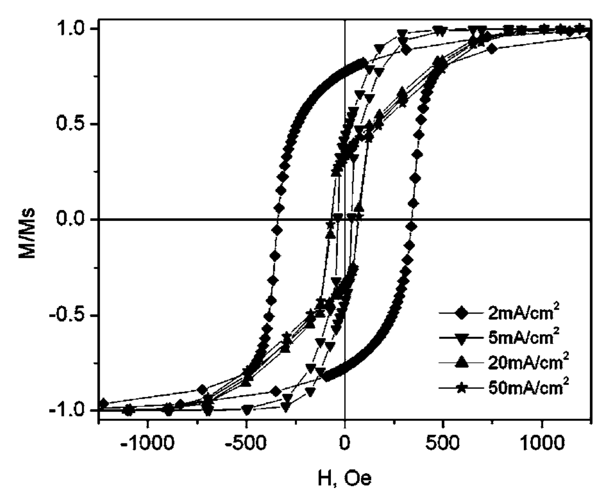

FIG. 5. Normalized hysteresis loops of 1-μm-thick Co–P films.

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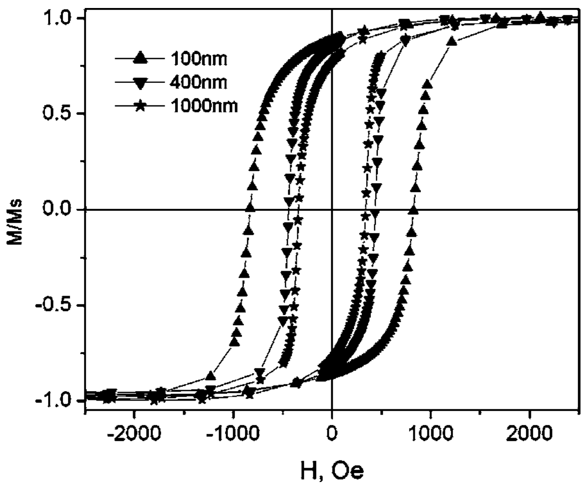

FIG. 6. Normalized hysteresis loops for Co–P deposited at 2 mA/cm^2 with different thicknesses.

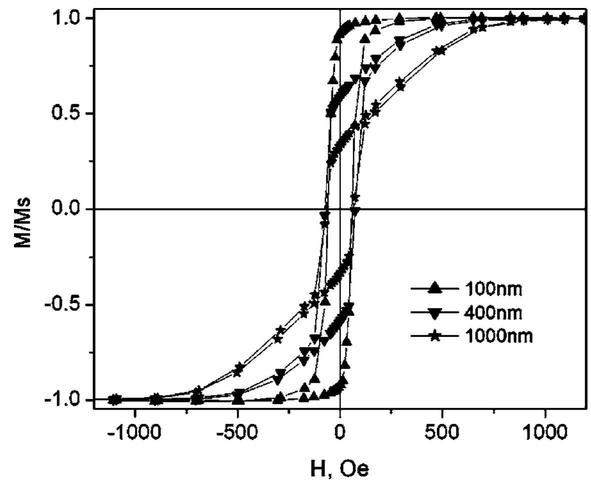

FIG. 7. Normalized hysteresis loops for Co–P deposited at 20 mA/cm^2 with different thicknesses.

anisotropy, which is most often of magnetoelastic origin. When a small external magnetic field is applied, the domains first rearrange and the stripes become aligned with the direction of the applied field. As the magnetic field increases, local magnetization vectors begin to rotate towards the direction of the external field and the films approach saturation. Higher fields are needed to saturate films with a larger P content, indicating that these films possess a higher effective anisotropy.

The magnetic properties of Co–P films were also found to differ with film thickness. Figures 6 and 7 show the hysteresis loops of Co–P films deposited at 2 and 20 mA/cm^2, respectively. Film thickness ranges from 100 to 1000 nm. The crystalline Co–P films in Fig. 6 exhibit similar magnetization behavior, with squareness and coercivity decreasing with increasing thickness. This is probably a consequence of the increase in grain size observed by SEM in thicker films (not shown). Assuming a rotational magnetization process of slightly interacting fine particles, in fact, film coercivity is inversely proportional to particle size.[5]

Figure 7 clearly shows that the stripe domain configuration in amorphous Co–P films is observed only above a critical thickness.[6,7] This is a consequence of the balance between shape and perpendicular anisotropy. Below a critical value of the film thickness, the local magnetization lies along the film plane due to the strong shape anisotropy. With increasing thickness, the in-plane anisotropy decreases and the net anisotropy switches in the perpendicular direction; hence, the stripe domain configuration appears.

In summary, we synthesized Co and Co–P films using a Co-sulphamate-based alkaline electrolyte with NaH_2PO_2 as the P source. The codeposition of P produces amorphous films except at very small deposition current density, i.e., 2 mA/cm^2. Pure Co films show in-plane magnetic anisotropy and small coercivity. Polycrystalline Co–P films deposited at small current densities still display in-plane anisotropy but larger coercivity, probably as a consequence of P codeposition that may induce grain decoupling. Co–P films with $P > 10$ at. % show amorphous structures and perpendicular anisotropy, increasing with P content.

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