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Sy_Hwang Liou
University of Nebraska-Lincoln, sliou@unl.edu

S. Malhotra
University of Nebraska - Lincoln

Z.S. Shan
University of Nebraska - Lincoln

David J. Sellmyer
University of Nebraska-Lincoln, dsellmyer@unl.edu

S. Nafis
University of Nebraska - Lincoln

See next page for additional authors

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Authors

Sy_Hwang Liou, S. Malhotra, Z.S. Shan, David J. Sellmyer, S. Nafis, John A. Woollam, C.P. Reed, R.J. DeAngelis, and G.M. Chow

The process-controlled magnetic properties of nanostructured Co/Ag composite films

S. H. Liou,[a] S. Malhotra,[a] Z. S. Shan, [a] D. J. Sellmyer,[a] S. Nafis,[b]
John A. Woollam,[b] C. P. Reed,[c] and R. J. DeAngelis[c]
*Center for Materials Research and Analysis, University of Nebraska-Lincoln, Lincoln,
Nebraska 68588-0111*

G. M. Chow[d]
*Center for Bio/Molecular Science and Engineering, Naval Research Laboratory, Washington,
DC 20375-5000*

Nanostructured Co/Ag composite films were prepared by magnetron sputtering using a single target. The average crystallite sizes of Co and Ag in the films depend on the deposition conditions. As the substrate temperature increases from 100 °C to 600 °C, the average Ag crystallite size increases from 39 to 452 Å, and the average Co crystallite size increases from <30 to 297 Å in the film with 39 vol. % of Co. The films with 39 vol. % of Co and prepared at 400 °C substrate temperature showed a maximum magnetic coercivity of 565 Oe at 6 K. We have studied the correlation between the structure and magnetic properties of these films.

INTRODUCTION

Several methods have been developed during the last decades to prepare small particles.[1,2] Fine dispersed magnetic particle systems are of interest because of the opportunities they present for atomic engineering of materials with specific properties. Specifically, the magnetic coercivity of nanometer size particles is greatly enhanced because a particle contains a single magnetic domain. For example, coercivities up to 3 kOe, which is two orders of magnitude higher than that of pure Fe, have been achieved in granular Fe materials. These 2–20 nm Fe clusters were embedded in insulators such as SiO_2 or Al_2O_3.[3] Such materials may have the potential to be used in high density magnetic recording, optical devices, and sensors.

Previous studies have been carried out on small magnetic clusters dispersed in a metal matrix, such as Fe in a Ag matrix[4] and Fe in a Cu matrix.[5] In this article we show that a nanostructured composite material can also be formed by mixing Co and Ag. The average crystallite size of these films can easily be controlled during the sputtering process by varying the substrate temperature. The correlations between the microstructural characteristics, in particular the crystallite size in the films, and the magnetic properties, are discussed.

EXPERIMENTS

The Co/Ag composite metal films were prepared by dc magnetron sputtering using a single target. The sputtering targets were made by sintering a mixture of Co and Ag

powders. The films were prepared with the substrate temperature varied from 100 °C to 600 °C. The sputtering gas was 4 mTorr of Ar. The process conditions for making Co/Ag composite films are similar to those of Fe/Ag.[4] Film compositions were determined by using energy dispersive x-ray analysis in a scanning electron microscope. The structure of films was investigated using a Rigaku x-ray diffractometer with a Cu source. The magnetization and coercive force were measured using a commercial SQUID magnetometer.

RESULTS AND DISCUSSION

The films used in this study have compositions near $Co_{19}Ag_{81}$ (13 vol. % of Co) and $Co_{50}Ag_{50}$ (39 vol. % of Co). The variation in composition of the films prepared at different substrate temperatures was less than 5 at. %.

The x-ray diffraction patterns of Co/Ag composite films with 39 vol. % of Co prepared at substrate temperatures (T_s) from 100 °C to 600 °C are shown in Fig. 1. It clearly shows that the films prepared at higher substrate temperature are mixed with the crystallites of the face center cubic (fcc) Ag and fcc Co. We would like to discuss some of features in this figure: the fcc Co(200) peaks in the films with $T_s \geqslant 400$ °C, the peak position shift of the Ag(111) and Co(200) with variation in T_s, and systematical decreasing line widths of the diffraction peaks with increasing T_s. The strong fcc Co(200) diffraction peaks observed in these films indicate that most Co clusters have the fcc structure. The d spacings of Ag(111), which were calculated from the 2θ value of Ag(111), increases from 2.33 to 2.35 Å as the T_s increased from 100 °C to 300 °C. The d spacing of Ag(111) prepared at a low substrate temperature (<300 °C) is smaller than that of the bulk silver element. This is expected if we allow a small amount of cobalt to mix with the silver during deposition. Al-
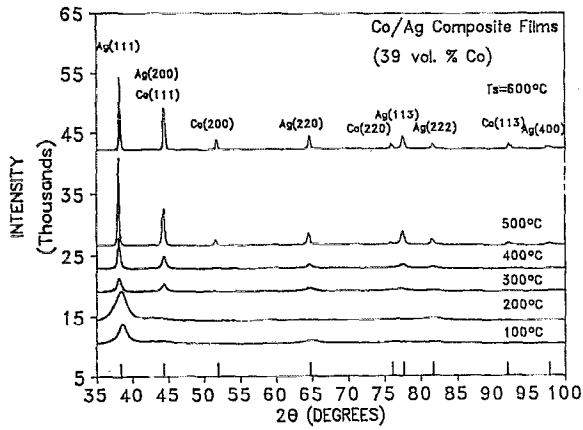

FIG. 1. Co/Ag composite films prepared at substrate temperatures of (a) 100, (b) 200, (c) 300, (d) 400, (e) 500, and (f) 600 °C.

though the mutual solubility of Ag and Co under equilibrium conditions is very low in both the solid and liquid form, an alloy of Co-Ag may form under fast quenching conditions. The amount of Co mixed in the Ag crystal matrix in the film prepared at a 100 °C substrate temperature is estimated to be about 5% if we assume that the alloying of Co and Ag follows Vegard's law.[6] The films prepared at a $T_s \geqslant 300$ °C have much less alloying between the Co and Ag as evidenced by the closeness of the d spacing of the film's fcc Ag(111) and Co(200) planes with that of the bulk Ag and Co, respectively. These results are similar to the results obtained on Fe/Ag films prepared under the same conditions.

The line width of the Ag(111) and Co(200) Bragg peaks decrease with increasing T_s, as can be seen in Fig. 1. This clearly indicates that the crystallite size of Ag and Co is changing with T_s. The average crystallite sizes were calculated from the shape of the Ag(111) and Co(200) peaks using the theory of Warren and the computational technique described previously.[7,8] The average crystallite size of Co and Ag in the Co/Ag films with 39 volume fraction of Co vs T_s is shown in Fig. 2. As T_s increases from 100 °C
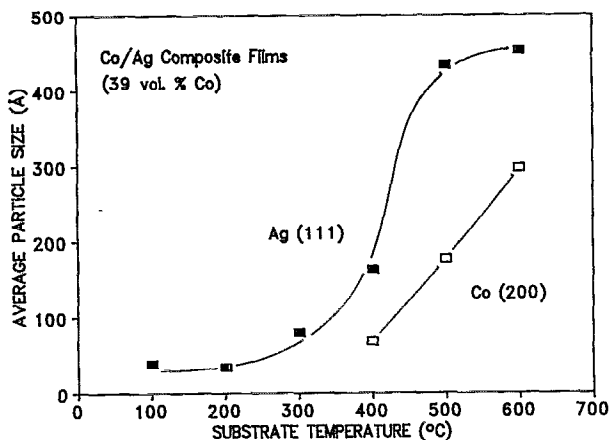

FIG. 2. Average particle size in Co/Ag composite films (39 vol. % of Co) vs substrate temperature.
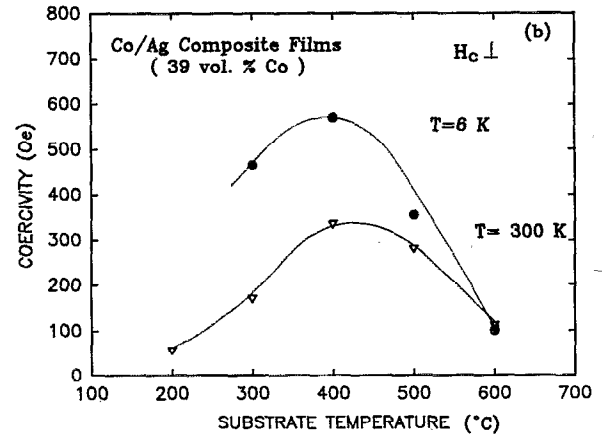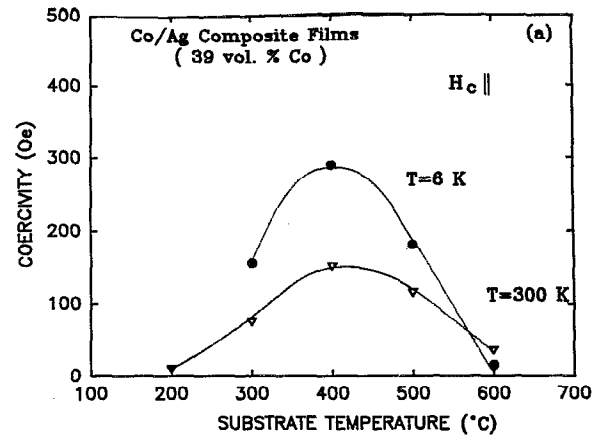

FIG. 3. Magnetic coercivities at 300 and 6 K of Co/Ag composite films containing 39 vol. % of Co deposited at various substrate temperatures. (a) measured when the applied field was parallel to the film surface; (b) measured when the applied field was perpendicular to the film surface.

to 600 °C, the average Ag crystallite size in the film increases from 39 to 452 Å, and the average Co crystallite size increases from 68 Å at $T_s = 400$ °C to 297 Å at $T_s = 600$ °C, respectively. The Co(200) peaks of the films prepared at $T_s < 300$ °C were not able to be resolved even at counting times of 20 s per 0.002° step in 2θ. This is considered to be due to an extremely small crystallite size < 30 Å.

The magnetic coercivity measured at 300 K and 6 K of films with 39 vol. % of Co versus the substrate temperatures is shown in Fig. 3. The H_c measured with the magnetic field parallel to the film surface is shown in Fig. 3(a) and the H_c measured with the magnetic field perpendicular to the film surface is shown in Fig. 3(b). The H_c's increase with increasing T_s and reach a maximum for the films prepared at 400 °C substrate temperature. An H_c as high as 565 Oe at 6 K has been achieved [see Fig. 3(b)]. It is known that the coercivity of the particles has a striking dependence on their size. As the particle size is reduced, it is typically found that the coercivity increases, goes through a maximum, and then tends toward zero. This magnetic behavior is due to the mechanism of the magnetization reversal which depends on the particle size. At large sizes, magnetization is changed by domain wall motion which takes much less energy. The result is small
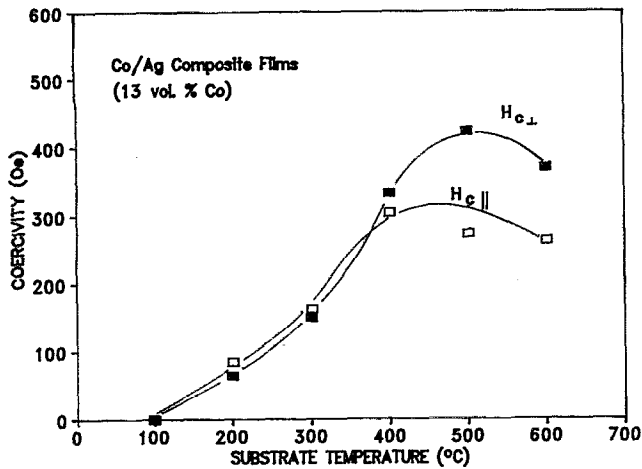
FIG. 4. Magnetic coercivities measured at 300 K with the applied field parallel and perpendicular of Co/Ag composite films containing 13 vol. % of Co deposited at various substrate temperatures.

FIG. 5. The coercivity vs temperature of films with 39 vol. % of Co prepared at $T_s = 400$ °C.

coercivity. Below a critical diameter D_s, which depends on the alloys, the particles become single domains. In this size range the coercivity reaches a maximum and their magnetization is changed by spin rotation which usually requires a larger energy than domain wall motion. Below a critical diameter D_s, the coercivity decreases again because of thermal effects which will cause the spontaneous rotation of spin. Such particles are called superparamagnetic. The behavior of H_c found in Co/Ag composite films, as shown in Fig. 3, can be correlated with their particle sizes. When H_c is a maximum, the magnetic particles are single-domain sized. The critical diameter for a cobalt crystallite is about 100 Å which is in good agreement with the single domain size reported by Luborsky.[9]

The magnetic coercivity measured with the applied field parallel ($H_{\parallel}$) and perpendicular ($H_{\perp}$) to the film surface versus substrate temperature of films with a lower volume fraction of Co (13 vol. % of Co) is shown in Fig. 4. The magnetic properties of these films are similar to those observed in the films of high volume fraction cobalt, with two notable exceptions. The maximum coercivity occurs 100 °C higher at a $T_s = 500$ °C. The other difference is the decrease in the anisotropy observed in the 13 vol. % Co compared with the 39 vol. % Co films.

The magnetic coercivity versus the temperature of films prepared at $T_s = 400$ °C is shown in Fig. 5. H_c is observed to decrease as the temperature increases. This is due to the thermal effects for the single domain particles. The temperature dependence of coercivity for noninteracting spherical or equiaxial single-domain particles is given by

$$H_c = H_{ci}[1 - (T/T_B)^{1/2}], \qquad (1)$$

where H_{ci} is the coercivity at 0 K and T_B is the blocking temperature, above which the material is superparamagnetic. The magnetic coercivity of film at a temperature above T_B is zero.[10] The T_B of films prepared at $T_s = 400$ °C is much higher than 400 °C; therefore, the direct
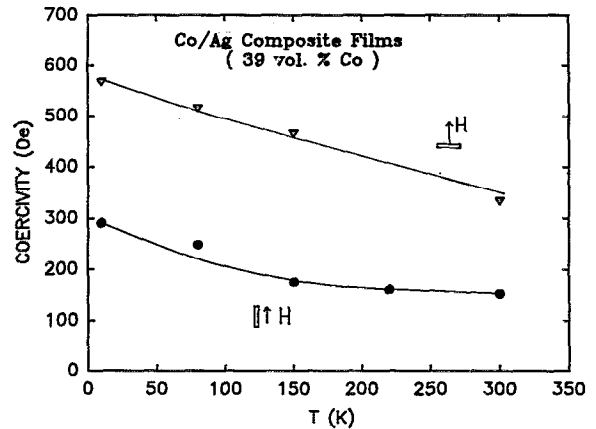
measurement of T_B is not possible. As shown in Fig. 5, the observed H_c versus temperature measured with magnetic field both perpendicular and parallel to the film surface is clearly not a function of $T^{1/2}$. The non-$T^{1/2}$ dependence is a strong indication that this film contains interacting crystallites. One would expect that the growth morphology in metal-metal films is under partial wetting conditions which may produce complex shaped networks rather than those made up of spherical clusters.

SUMMARY

We have synthesized Co/Ag composite metal films with nanometer sizes of Co and Ag crystallites. Both Co and Ag crystallites have a fcc structure. The sizes of crystallite increase with increasing substrate temperature. A much enhanced magnetic coercivity was observed when the average Co crystallite size was the size of a single domain.

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