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Using Ion Beams to Modify Nanocrystalline Composites: Co Nanoparticles in Sapphire

A. Meldrum,[1] K.S. Beaty,[1] M. Lam,[1] C.W. White,[2] R.A. Zuhr,[2] L.A. Boatner[2]
[1] Dept. of Physics, University of Alberta, Edmonton, AB, CANADA
[2] Solid State Division, Oak Ridge National Laboratory, Oak Ridge, TN, USA

ABSTRACT

Ion implantation and thermal processing were used to create a layer of Co nanoclusters embedded in the near-surface region of single-crystal sapphire. The Co nanoparticles ranged in size from 2-20 nm and were crystallographically aligned with the host sapphire. Specimens were irradiated with Xe and Pt ions, and the microstructural evolution of the nanoclusters was investigated by transmission electron microscopy. With increasing Pt or Xe ion dose, the Co nanoparticles lost their initially excellent faceting, although they remained crystalline. The host Al_2O_3 became amorphous and the resulting microstructure consisted of a buried amorphous layer containing the still-crystalline Co nanoparticles. EDS mapping and electron diffraction were used to determine the distribution of the implanted species, and the magnetic properties of the composite were measured with a SQUID magnetometer. The results show that ion beams can be applied to modify and control the properties of ferromagnetic nanocomposites, and, combined with lithographic techniques, will find applications in exercising fine-scale spatial control over the properties of magnetic materials.

INTRODUCTION

Ion irradiation is an established and widely used technique for modifying and controlling the microstructural and electronic properties of thin films. Frequently, the injected ions pass through the film, creating displacement defects and ion mixing effects, but no intrinsic chemical changes. In recent years, several investigations have used ion irradiation as a means of controlling or patterning film properties. For example, the magnetic exchange bias of ferromagnetic-antiferromagnetic thin film multilayers can be modified and controlled by ion irradiation [1]. Ion irradiation has also been used to alter magnetic hysteresis behavior, and it has been possible to use lithographic masking combined with He-ion irradiation to pattern the magnetic properties of thin film materials [2].

In contrast, the effects of ion irradiation on nanocrystalline composites have not been extensively investigated despite over 50 years of radiation damage studies on bulk materials. As is the case for thin films, ion irradiation is expected to radically alter the microstructural and electronic properties, physical strength, and hardness of nanocomposites. These effects may be particularly important where nanocrystalline materials are to be used in high-flux environments (e.g., space flight). Furthermore, ion irradiation offers an excellent opportunity to create or pattern materials with novel properties.

The profusion of unique and/or novel properties displayed by nanocomposites produced by ion implantation suggests many applications [3]. However, one difficulty has been the fine-scale control of opto-electronic and magnetic effects. For example, Co particles produced by ion implantation into sapphire or other substrates show relatively low coercivities – regardless of the implant dose and post specimen processing (e.g., see Refs. 3,4). Using ion irradiation, it is possible, however, to increase the coercivity of Co-nanocomposite-based magnetic materials –

due to at least partly to radiation-induced amorphization of the host material. The optical properties of semiconductor nanoparticles may also be controlled or otherwise modified. New studies have recently shown that the characteristic red luminescence of Si nanoclusters embedded in SiO_2 can be strongly reduced, or even shifted in wavelength [e.g., Refs. 5,6,7]. These investigations have suggested the utility of ion irradiation for modifying opto-electronic properties of interest. In the present work, we focus on the results of experiments in which ion beams are used to modify the microstructural and magnetic properties of embedded Co nanocluster composites.

EXPERIMENTAL

High-purity sapphire wafers were implanted with 140 keV Co^+ to a dose of 8 x 10^{16} ions/cm^2 at room temperature. Thermal treatment was carried out for two hours at 1100°C under flowing Ar + 4%H_2. After 120 minutes, the specimen was retracted from the hot zone and allowed to cool. X-ray diffraction and transmission electron microscopy were used to determine the structure and orientation of the resulting Co nanoparticles. The Co-sapphire nanocomposite was then irradiated at room temperature with either 244 keV Xe or 320 keV Pt ions to varying ion fluences. The corresponding dose was calculated by using the Monte Carlo computer code SRIM-2000 [8] in the full cascade mode to obtain the number of displacements per ion per nm, using displacement energies for Al and O of 20 and 50 eV, respectively. Since the ion dose varies as a function of depth, for simplicity we will refer to the dose at a depth of 60 nm (corresponding to the observed center of the Co-nanoparticle profile). Samples were prepared for TEM by conventional thinning and polishing methods. *Ex-situ* cross-sectional and plan-view electron microscopy was used to investigate the resulting particle microstructure. Cross-sectional TEM was also done in the scanning mode to determine the chemical distribution of implanted elements. *In-situ* ion irradiation experiments using 1.0 MeV Xe^{2+} were conducted directly in an electron microscope at the IVEM Facility (Argonne National Laboratory). The room-temperature magnetic properties of the bulk specimens were measured using a SQUID magnetometer or by magnetic circular dichroism (MCD).
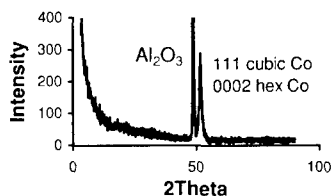

Fig. 1. X-ray diffraction results.

RESULTS AND DISCUSSION

Figure 1 shows the X-ray diffraction results from Co-implanted and annealed sapphire. A single peak due either to the [0002] axis of hexagonal Co or to the [111] axis of cubic Co was observed. We have previously used four-circle diffraction techniques to show that a mixture of the hexagonal and cubic phases is present [4]. Plan view and cross sectional TEM images are given in Fig. 2. In plan view, most of the nanocrystals appear well faceted, having triangular or hexagonal shapes with edges parallel to the in-plane crystallographic axes of the sapphire. In cross section, there is a distinct boundary at a depth of ~55 nm in the sapphire, below which the nanocrystals are more-or-less rounded, and above which they show good crystal facets. The well-faceted particles are somewhat elongated parallel to the specimen surface. The 55-nm
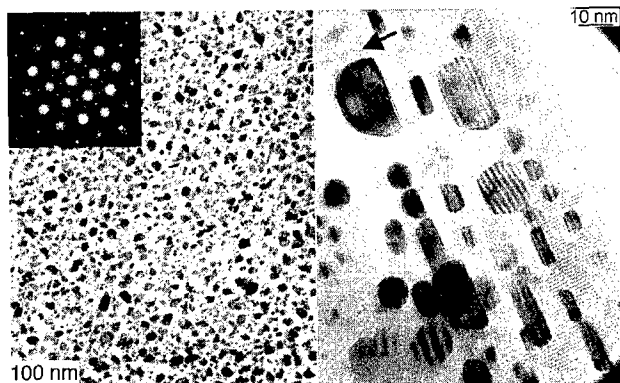
Figure 2. Plan view (left) and cross-sectional (right) images of the Co-implanted and annealed Al_2O_3 wafer. The arrow marks the depth above which the Co precipitates are well faceted.

boundary corresponds to the approximate depth at which the sapphire becomes amorphous during the room-temperature Co ion implantation. When the sapphire recrystallizes during thermal processing, the nanoclusters forming in the initially amorphous regions become well faceted, although the exact diffusion-related mechanism for this process remains to be investigated. The precipitates range in size from 2 to 20 nm (long axis). An [0001] zone axis electron diffraction pattern is shown as an inset to Fig. 2. There is a complex arrangement of double diffraction spots that are due to both the cubic and hexagonal Co, as well as top-bottom effects (the rings of double diffracted spots immediately surrounding the main sapphire maxima are due to the effects of the electron beam passing first through a Co precipitate and then through sapphire, and vice-versa).

Figure 3 shows the microstructural effects of 244 keV Xe irradiation. With increasing ion dose, the faceting gradually disappeared and all the particles were rounded, with some mottled internal contrast. Dark-field imaging suggested the presence of dislocation defects and possibly void or bubble-like structures within the particles. The sapphire was highly damaged, but the Co nanoparticles remained crystalline and relatively well aligned, although with poor or absent faceting. In the *in-situ* experiments, the host sapphire gradually became amorphous, and the loss of precipitate faceting was also observed. Amorphization of sapphire has not previously been reported in *in-situ* ambient-temperature irradiation experiments. Here, we irradiated to doses exceeding 10 dpa and used a low ion energy (200 keV) in order to mimic both the displacement damage and chemical effects occurring in bulk implanted specimens.

Co-sapphire nanocomposite specimens were also implanted with Pt, and both cross-sectional and plan-view electron microscopy was used to investigate the microstructure (Fig. 4). The Pt ion fluence was selected to give approximately the same displacement dose as for the 244 keV Xe irradiation. Compared to Fig. 2, the Co nanoparticles are again poorly faceted although they are still crystalline, and they are embedded within a buried amorphous layer formed in the sapphire. Overall, the effects of Xe
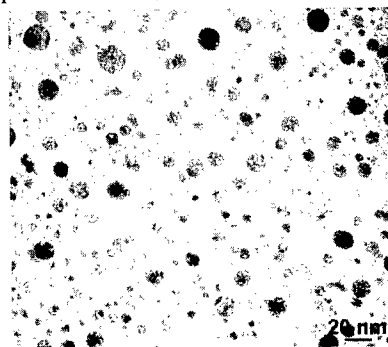

Fig. 3. Co-sapphire specimen in Fig. 2 irradiated with 244 keV Xe to a dose of ~17 dpa.

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and Pt irradiation on the particle microstructure were similar: in both cases the precipitate faceting disappeared; and although the particles remained crystalline, and the sapphire host material was damaged or amorphized.

EDS mapping was used to investigate the location and distribution of the implanted material. Particularly in the case of the Pt-implanted Co nanocomposite, it is important to know whether the Pt is preferentially attracted to the pre-existing Co nanoparticles (e.g., to produce a Co-Pt alloy). Figure 5 shows a set of EDS maps for Co and Pt. The Co particles appear clearly in the Co map, but the Pt retains its implant distribution and is not preferentially located within the pre-existing Co particles. There was also no evidence of a Co-Pt alloy in the electron diffraction patterns. Therefore, the observed *microstructural* changes are probably due largely to the effects of radiation damage and less to any chemical reaction between the Co and the Pt.

The magnetic measurements were done using magnetic circular diochroism (e.g., see Ref. 4). The magnetic coercivity of the annealed Co-sapphire composite is ~50 G and the saturation magnetization is 0.014 MCD units. After Xe irradiation to a fluence of 9 x 10^{15} ions/cm^2, the coercivity increased to 464 G and the saturation MCD signal was 0.0071 units. The Pt-irradiated sample had the highest coercivity (1,500 G) and the saturation magnetization was 0.0081 units. For both Xe and Pt irradiated samples, the coercivity increases rapidly at first, but then reaches a saturation value at approximately 20 dpa (Fig. 6).
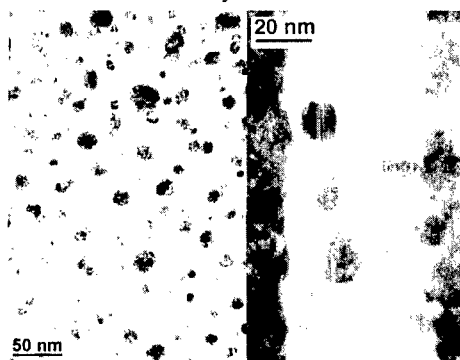

Fig. 4. Plan view (left) and cross-sectional images for Pt-irradiated Co nanocrystals in sapphire (dose = 14.4 dpa). The light band in the cross-sectional image is amorphous sapphire and the darker bands are still-crystalline sapphire. The surface was to the right of the cross sectional image.
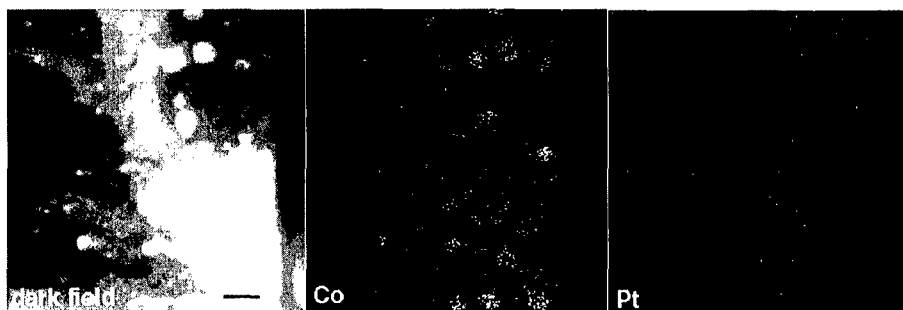

Fig. 5. Dark field image and corresponding energy-dispersive X-ray maps for Co and Pt. Scale bar is 20 nm.

Pt implantation increases the coercivity of the Co-sapphire composite by a factor of 2-3 more than the Xe implantation, for similar displacement doses. However, the EDS mapping and

electron diffraction do not suggest alloy formation in the Pt-implanted substrate on a scale larger than ~2 nm. Since the Pt implant has a greater effect on the coercive field than the Xe implant for the same ion dose, a chemical effect of some type must be involved. In initial work, we have found that nanocrystals of tetragonal CoPt alloy formed by co-implantation and annealing of sapphire have coercivities ranging up to several kG. If atomic-scale domains of this phase form within the pre-existing Co precipitates, the magnetic hardness could increase more than it would due to radiation damage alone. Further high-resolution electron microscopy will provide more information on the atomic-level structure of these particles.

These results suggest that ion irradiation has a considerable effect on the microstructural and magnetic properties of magnetic nanocluster composites. Careful selection of the irradiation conditions can be used to control or tailor the coercivity and saturation magnetization. Control over the lateral distribution of irradiated material would, for the first time, provide spatial control over the magnetic properties of magnetic nanocomposites formed by ion implantation. To this end, we have recently begun experiments employing lithographic masking techniques to control the distribution of the implanted material and to radiation-pattern the resulting composite. Figure 7 shows a preliminary result, where the letters "U of A" are written as conglomerates of embedded nanoscale precipitates formed by implantation of iron into an SiO_2 wafer. Experiments are ongoing [9].
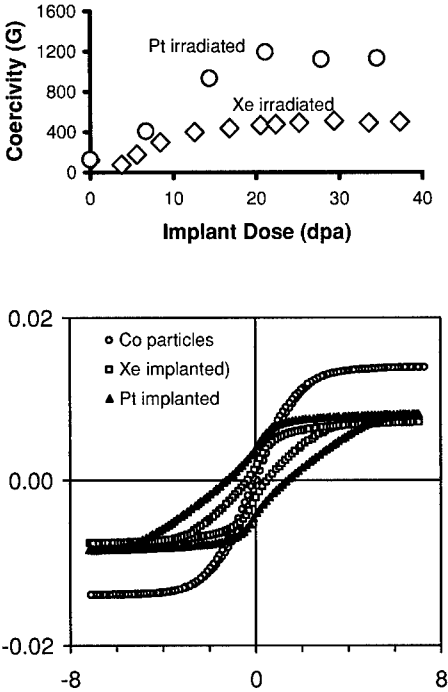
Fig. 6. Top: Coercive field as a function of implant dose for Xe- and Pt-irradiated Co nanocrystals in sapphire. Bottom: hysteresis loops for the 3 samples shown in Figs. 2-4. The abscissa is the applied field in kG and the ordinate is the magnetic circular dichroism (arbitrary units)

CONCLUSION

This work describes ion irradiation effects on the microstructural and magnetic properties of Co-sapphire nanocomposites confirming that the magnetic properties of Co particles can be modified and controlled by ion bombardment. However, considerable work remains to be done

in order to obtain a complete understanding of both irradiated and unirradiated Co-sapphire nanocomposites. While ion irradiation can clearly be used in controlling the microstructure and magnetic properties of Co-nanocluster composites, the technique can also be used to modify other materials of interest (examples include the absorption and emission characteristics of semiconductor nanocrystals). Our ongoing ion-beam patterning experiments will permit fine-scale spatial control over the properties of interest, and we have also recently demonstrated that unusual microstructural effects can occur during irradiation of embedded nanocrystals [10]. Despite recent funding cuts at several American ion-beam laboratories, we believe that some of the most interesting times for implanted nanoparticle research are just beginning.

Fig. 7. Optical image showing "letters" written with Fe nanoclusters implanted into fused silica. The letters are 68 microns high and 5 microns wide.

ACKNOWLEDGMENTS

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