Observation of exchange bias in nanoscale AuFe alloy film

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Abstract

We report on observation of the exchange bias effect in AuFe co-sputtered alloy films in the as-deposited state and following swift heavy ion irradiation. The Mössbauer spectrum for the as-deposited film shows a broad paramagnetic doublet together with a small contribution from hyperfine magnetic sextets. The magnetization behavior exhibits a spontaneous exchange bias effect at room temperature without application of an external triggering field. The magnitude of exchange bias in the as-deposited sample increases with decreasing temperature, at first gradually down to about 50 K and then more rapidly down to 5 K. Irradiation of AuFe film with 100 MeV Au4+ ions transforms the Mössbauer spectrum into a broad magnetic sextet, with asymmetric broadening characteristic of the formation of α-Fe magnetic nanoclusters surrounded by shells of reduced Fe concentration. At room temperature the exchange bias field is in the same sense as that for the as-deposited sample, but decreases with temperature until it reverse its sign at below about 50 K. In both the as-deposited and irradiated samples a well-defined uniaxial magnetic anisotropy, consequent on a stress induced texturing of the Fe precipitate distribution, is observed.

Introduction

Since the first observation in 1956 of the exchange bias (EB) effect by Meikjohon and Bean in ferromagnetic/antiferromagnetic Co/CoO nanoparticles [1], an increasing study of the phenomenon has been driven by fundamental interest and by its existing and potential applications (see for example Chandra et al [2] and references contained therein). The characteristic signature of the EB effect is a shift in magnetic hysteresis loop from the origin along the applied magnetic field axis together with an increase in coercive field. A variety of systems, including nanoparticles, epitaxial bilayers and polycrystalline thin films [3–8] have been observed to manifest the EB effect. The EB effect is generally achieved either when a ferromagnetic/antiferromagnetic (FM/AFM) binary system is cooled from a temperature in the range TN < T < TC (i.e. between the Neel and Curie temperature) to TN < 1. The sense of the EB field is opposite to the direction of an applied magnetic field during cooling.

Generally it is found necessary to apply a magnetic field during the cooling process in order to trigger the EB effect. However, some recent reports of the observation of spontaneous EB in several spin-glass-FM/AF nanocomposite systems, under zero-field cooling procedure, have been published [8–10].

In general, the EB field is found to be of either sign, but tunable sign reversal is rare. Zhang et al [11] report the tuning and EB sign reversal in Mn0.7Fe0.3NiGe alloy resulting from the increase of the maximum measuring field, while Kulkarni et al [12] and Manna et al [13] report on EB sign reversal by varying the temperature in Sm0.975Gd0.025Cu4Pd and La0.5Ce0.8CrO3, respectively.

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The present study on the EB effect in AuFe alloy film was prompted by the intriguing range of magnetic behavior displayed by AuFe films, from spin glass behavior in films of very low Fe content, through soft ferromagnetic to ferromagnetic behavior as the Fe concentration is increased. This progression in AuFe films has been the subject of many studies over the past forty years (see for example [14–24]). These studies show that the system behaves as a spin glass for Fe concentrations below 13 at%. At 15.5 at% a percolation limit is reached above which clusters of Fe with sufficient Fe-Fe near neighbour interactions to allow for ferro- or antiferromagnetic behavior in the clusters/precipitates to occur. The overall magnetic behavior of the system is governed by the average behavior of these clusters and by their mutual interaction. A recent comparative study, using several techniques, including, inter alia, Mössbauer Spectroscopy, magnetization, SEM and MOKE, by Stanciu et al [25] of AuFe films with 15 and 30 at% Fe, finds that, in the 15 at.% sample, the magnetic properties of AuFe granular films is due to an isotropic superparamagnetic behavior of a random distribution of very fine Fe precipitates/clusters and in the 30 at % sample, to the ordering of Fe precipitates into a regular lamella structure normal to the film thickness. This gives rise to a uniaxial anisotropy of the magnetization in the plane of the film with the Fe precipitates acting with Stoner-Wohlfarth behavior and long range interaction.

The object of the present study is to investigate the EB effect in the AuFe system and its modification/tuning by modifying the Fe cluster configurations by means of swift heavy ion irradiation. This approach has been reported previously, but mostly in the low implantation energy regime. Schmalhorst et al [26] have observed that by ion bombardment in the presence of magnetic field, exchange bias can be initiated without field cooling. Ehremann et al [27] have verified, both theoretically and experimentally, that the modification of multidomains by ion bombardment has an influence on the EB effect, presumably because of the generation of crystalline defects.

**Experimental**

RF magnetron co-sputtering technique was used to deposit AuFe alloy films onto Si substrates. The sputtering target consisted of a 5 cm diameter Fe target with Au foils and Fe foils, the latter enriched in the stable $^{57}\text{Fe}$ isotope, glued onto it. The enrichment allowed for study using Mössbauer spectroscopy. The thickness, composition and uniformity of the films were determined by Rutherford backscattering spectrometry (RBS), while their structural and phase characteristics were determined from x ray diffraction (XRD) and conversion electron Mössbauer spectroscopy (CEMS) measurements. The XRD measurements were conducted at the MCX beam line at the Elettra Synchrotron Facility, Italy, using a 1.0419 Å wavelength x rays. Irradiation of the films with 100 MeV Au ions up to a fluence of $5 \times 10^{13}$ ions cm$^{-2}$ was conducted using the 16 MV Pelletron accelerator at the Inter University Accelerator Centre, New Delhi.

Magnetic measurements of the as-deposited and Au irradiated films were performed using a superconducting quantum interference device (SQUID) and a magneto optical Kerr effect (MOKE) spectrometer.

**Results and discussion**

The RBS spectrum of the as-deposited AuFe film is shown in figure 1, where the solid line presents the fit to the data using the RBS analysis code RUMP [28]. The analysis yields a film thickness of approximately 63 nm and Au and Fe fractions of 44 at% and 56 at%, respectively. The Au and Fe contents in the film were found to be constant throughout the film. Figure 2 presents XRD patterns of the as-deposited and irradiated AuFe films for which the out of plane diffraction geometry [29] was used in the measurements. Each diffraction pattern has two clear peaks corresponding to reflections of the FCC, Au (111) plane and the BCC Fe (110) plane, together with a broad, central peak due to FCC AuFe (111) reflection. Lee et al [14] report that the FCC structure of the AuFe films is preserved up to 80 at% of Fe. The intensity of the AuFe (111) peak increases, at the expense of Au (111) and Fe (110) peaks, with irradiation, indicating an increase in the relative content of the AuFe alloy. Fits to the AuFe (111) peak yield crystallites of diameters of approximately 8.6 nm and 15.1 nm in the as-deposited film and in the irradiated film, respectively. The crystallite size corresponding to Au (111) and Fe (110) peaks are quite large compared to AuFe (111) peak. The AuFe (111) peak also shows a shift towards a higher diffraction angle, suggesting the presence of irradiation generated stress fields in the film. Lee et al [14] report that with increasing Fe concentration the strain field in AuFe films increases, and that beyond 80 at.% Fe content it leads to a structural lattice transformation of the AuFe alloy from FCC to BCC.

The CEM spectra of the as-deposited and irradiated films, obtained at room temperature, are presented in figures 3(a) and (b), respectively. The as-deposited film shows a central paramagnetic doublet, consistent with that reported by Mishra et al [30] for alloys of the same Au/Fe concentrations. The spectrum was analyzed in...
terms of contributions from distributions of quadrupole splittings (QS) and (small) hyperfine magnetic sextets (Bhf). The distribution probabilities, P(QS) and P(Bhf), are shown on the right-hand side (rhs) of figure 3. The quadrupole splitting distribution, ranging from approx. 0.2 to 1.2 mm s\(^{-1}\) with peaks at approx. 0.45 mm s\(^{-1}\) and 1.0 mm s\(^{-1}\), reflects the broad distribution of the configurations of Fe clusters. A small contribution (approximately 10\%) from a distribution of magnetic hyperfine fields, with the main contribution in the range B_{hf} = 22–28 T, gives an improved fit to the data. The isomer shift of 0.40 mm s\(^{-1}\) is commensurate with that observed by Stanciu et al\([25]\) for a 15 at\% Fe concentration in Au and is attributed to a random distribution of very fine superparamagnetic (above the blocking temperature) Fe clusters embedded in the Au matrix. In the present system at a 56 at\% Fe concentration the ZFC and FC curves (figure 4) for the as-deposited sample show that the reduced magnetic moment, m(T), behavior does not scale as H/T, thus ruling out superparamagnetic behavior in the clusters. The relatively small contribution in the CEM spectrum (figure 3(a)) of the small hyperfine magnetic sextet relative to the broad paramagnetic doublet, due to the Fe clusters, is considered to be a consequence of a relatively low inter cluster interaction.

On irradiation of the AuFe film with 100 MeV Au\(^{9+}\) ions, the CEM spectrum transforms into a broad magnetic sextet (figure 3(b)) with asymmetric broadening, characteristic of the formation of Fe nanoclusters with different Au/Fe concentrations at the interface with the Au substrate\([31]\). The probability distribution of the magnetic hyperfine field, P(B_{hf}), is shown on the rhs of figure 3(b) and in the interval 20 < B_{hf} < 40 T, it shows peaks at 33.0 T, 28.2 T and 22.5 T, in reasonable agreement with the results of Blachowski et al\([32]\) who,
for Au/Fe concentrations similar to the present, also observe a broadened magnetic sextet structure with probability distribution showing peaks at mean hyperfine fields of 33.1 T, 30.1 T and 26.6 T.

The relative intensities of the lines in a Mössbauer sextet of a sample with magnetic order are in the ratio 3:1:1:x:3, where $x = 4 \sin^2 \theta / (1 + \cos^2 \theta)$ and $\theta$ is the angle between the angle of incidence of the $^{57}$Fe gamma rays and the direction of alignment of the magnetic moment vector (see, for example, [33]). The present data yields relative line intensities of the magnetic components in the ratio 3:3.8(1):1, showing an in-plane alignment of the magnetic moment vector.

Field cooled and zero field cooled (FC-ZFC) magnetization data on the sample in the as-deposited and irradiated states, obtained with a SQUID magnetometer, are presented in figure 4. A field of 50 Oe was applied during the collection of the FC data. The blocking temperature of the as-deposited sample corresponds to the temperature at which the EB changes sign. For the irradiated sample, above a temperature of about 60 K the FC and ZFC curves show a slow linear decrease, without intersecting. This is attributable to magnetic order resulting from strongly interacting clusters and is confirmed by the observed ferromagnetic sextets in the CEM spectrum (figure 3(b)).
Temperature and field dependent magnetic moment measurements were made with a SQUID magnetometer. The hysteresis loops of the as-deposited and irradiated AuFe films, determined at temperatures 300 K, 100 K, 50 K and 5 K, are presented in figures 5 and 6, respectively.

The as-deposited film displays a positive shift of the hysteresis loop from the origin at room temperature, showing the existence of EB in the AuFe film. The shift in the hysteresis loop increases from +3.5 Oe to +38.3 Oe as the temperature is gradually reduced to 5 K. Note that in the present study no magnetic field was applied during deposition of the film, nor was any field cooling procedure carried out to induce ordering of spins or an EB effect.

The exchange bias observed in the as-deposited film may be attributed to interfacial stress induced by lattice mismatch between Au and Fe ion lattices. This interfacial stress will be temperature dependent leading to a change in the EB effect with temperature [8]. The compaction of magnetic nanoparticles under external pressure has been reported to lead to the development of surface spin disorder [34] which can be highly anisotropic and can contribute to an increase in magnetic anisotropy [2]. The coupling of these disordered or spin-glass like surface spins with core spins of nanoparticles results in exchange bias. This phenomenon is frequently seen in many exchange coupled nanoparticle systems where the pinning layer is a metastable disordered state [35, 36]. Such a stress induced magnetic unidirectional anisotropy can be along an easy axis, either in positive or negative direction depending on the compressive or tensile stress in the film leading to a temperature dependent exchange bias field.

The hysteresis curve at 5 K shows evidence of the training effect, i.e. a reduction of the exchange bias with consecutive hysteresis loops (annotated in figure 5). Below the blocking temperature (38 K for the as-deposited
the magnetic configuration in the AuFe crystallites is trapped in a metastable state which gradually evolves to a stable configuration (with lower exchange bias field) with consecutive cycling of the hysteresis loops [37].

The hysteresis loops for the Au-irradiated AuFe film at the temperatures indicated are presented in figure 6. After the irradiation with $5 \times 10^{13}$ cm$^{-2}$ 100 MeV Au ions, the hysteresis loop shifts completely from the origin towards positive field with an exchange bias field of +13.5 Oe at 300 K.

As the temperature is decreased, the hysteresis loop is observed to gradually shift in the opposite direction and shifts completely to negative field values at 5 K. This phenomenon, known as sign reversal, has been observed previously [38]. There is almost no shift in hysteresis loop around the maximum blocking temperature, which is 57 K. This last result has been reported by several groups, studying many different alloys with different values of $T_B$ which varies widely with the relative elemental concentration in the alloys [39–41].

The sign reversal of the exchange bias field observed at 5 K in figure 5 could be interpreted as follows. The stress induced magnetic anisotropy field $B_A$ can be expressed as [8]:

$$B_A = -\frac{3\lambda_s\sigma}{M_s}$$  \hspace{1cm} (1)

where $\lambda_s$ is the magnetostriction coefficient, $\sigma$ the stress and $M_s$ the saturation magnetization of the film. For tensile or compressive stress, $\sigma$ has positive or negative sign, respectively. According to equation (1), the magnetic anisotropy field changes its direction depending on the nature of the stress present in the film. For tensile stress $B_A$ is negative, and for compressive stress, it is positive. In the irradiated film, the stress most probably changes from tensile to compressive as the temperature is gradually lowered to 5 K, resulting in a change in the magnetic anisotropy field from negative to positive, and hence of the exchange bias field reversing its sign. This, therefore, suggests that it is possible to tune the exchange bias field in either direction with a variation in temperature.

Figure 7(a) presents the azimuthal angle dependent Kerr hysteresis loops for the as-deposited and irradiated samples. The maximum magnetic field applied for the MOKE measurements was 200 Oe. In corroboration with the SQUID results, the MOKE measurements also show shifted hysteresis loops, a signature of the exchange bias effect and typical Stoner–Wohlfarth behavior for the aligned ferromagnetic Fe clusters. After irradiation, the Stoner-Wohlfarth behavior is somewhat degraded by the induced defects with some loss of well-defined
anisotropy (figure 7(b)). The increased moment on the Au–Fe clusters now gives a long-range inter-cluster interactions that yields the hyperfine sextet structure in the CEM spectrum.

In order to better understand the magnetic anisotropy of the film, the magnetization reversal with external magnetic field applied in different in-plane orientations was investigated. The azimuthal angle dependence of the remanence magnetization (polar plot) of the as-deposited and irradiated film is presented in figure 7(b).

In addition to tuning, sign reversal of the exchange bias and uniaxial magnetic anisotropy, the magnetization saturation field in these AuFe films is very small (<100 Oe), making them suitable candidates for low field sensors.

Conclusions

AuFe co-sputtered thin films deposited by RF magnetron co-sputtering technique were irradiated with 100 MeV Au ions to fluences up to $5 \times 10^{13}$ ions/cm$^{-2}$. The as-deposited film displays stress induced spontaneous exchange bias at room temperature which further increases with decrease in the temperature of the films. These films have a well-defined uniaxial magnetic anisotropy. Further, our results show that temperature dependent tuning and sign reversal of the exchange bias is possible in swift heavy ion irradiated AuFe co-sputtered films, a desirable property for fabrication of MRAM devices. Magnetization saturation values in these films are less than 100 Oe which makes them suitable candidates for low field sensor applications.

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Data availability statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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