Temperature and thickness driven spin-reorientation transition in amorphous Co-Fe-Ta-B thin films

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Magnetic properties of amorphous Co-Fe-Ta-B thin films are investigated. A tailorable spin reorientation transition (SRT) from in-plane single-domain-like state to out-of-plane multidomain state with increasing film thickness and temperature is obtained up to ~2.5 μm thick films, in contrast to previously reported ultrathin ferromagnetic films of transition metals consisting of about half a dozen of monolayers. Atomic relaxation is shown to have significant influence on the SRT. Our results showed that the atomic randomness and the strains are responsible for the SRT in magnetic materials.

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Controlled growth and tailorable properties of nanostructured magnetic materials have become a very active field for realization of various types of magnetic devices. The intrinsic magnetic anisotropy energy is one of the key quantities, which governs the magnetization direction. In recent years, the spin-reorientation transition (SRT) that is changes in the magnetization direction as a function of temperature, film thickness or the composition in ultrathin ferromagnetic multilayers consisting of few monolayers (ML) has attracted much interest.[1–4] For example, when Fe is deposited on Cu(100), a ferromagnetic ordering exist with perpendicular magnetization between 2 to 5 ML, and on increasing the Fe layer thickness magnetization rotates into the film plane.[5,6] Experimentally, similar SRT has been observed in ultrathin films of Fe/Ag(001), Fe/Cr(110), CeH_2/Fe(111), Fe/Tb(111), Co/Au(111), Co/Ru(111), and Co/Pd(111) with increasing film thickness and temperature.[7] An exceptional case is so called "reverse SRT," i.e., SRT from in-plane to perpendicular is also observed, and the most well known example for this kind of behavior is Ni on Cu(001).[8] Much effort has gone into understanding the occurrence of SRT in such systems. The SRT in such systems is suggested to accompanied by the structural transformation,[9] or the change in the magnetic anisotropy energy due to lattice relaxation[1,2,4] or variation in orbital magnetic moment due to broken symmetry at the film-substrate interface.

In case of epitaxially grown ultrathin films (or single crystal) where atoms are arranged in a particular type of lattice (such as bcc, fcc), the lattice distortion caused by the mismatch in the lattice parameters of the film, and the substrate can result in the metastable phases or the slight variation in atomic positions. Out come of this can be an unusual magnetic behavior (such as SRT) because of variation in exchange interactions, which are very sensitive to location of individual atoms. The lattice distortions or more precisely the randomness in atomic arrangement can be obtained in bulk materials if they are not bound to a particular type of crystal structure, and such a situation we can expect in case of amorphous magnets. Magnetic and nonmagnetic atoms in an amorphous magnet completely lose the periodicity of the lattice in its crystalline counterpart.[10] As the orientation of atomic moments are determined by the location of individual atoms, the random arrangement of atoms in an amorphous magnet can result in a situation where unexpected magnetic properties can be obtained in bulk form as compared to crystalline materials, only exhibiting the same property in few MLs.

In this paper we report on the surprising observation of "reverse SRT" in amorphous Co-Fe-Ta-B film of thickness nearly up to 2.5 μm, in contrast to previously reported ultrathin (~ six MLs) ferromagnetic films of transition metal elements.[1–9] We have shown that the atomic relaxation plays a significant role in controlling the SRT.

Amorphous (or glassy) thin films of Co-Fe-Ta-B were deposited by sputtering technique. The sputtering chamber was evacuated to a base pressure of $\sim 5\times10^{-6}$ Pa. The $Co_{43}Fe_{20}Ta_{5.5}B_{31.5}$ alloy (purity ~99.99%) target made by arc melting technique was sputtered in a high purity argon gas with a sputtering pressure, and dc powder of 0.2 Pa and 100 W, respectively. Films (thickness 0.04 to 5.5 μm) were deposited on fused quartz substrates. Substrate temperature (T_s) during deposition ranges from room temperature (~25 °C) to 300 °C. The average composition of the films measured by electron probe microanalysis (EPMA) at different locations (C_{Co} 44.2 at. %; C_{Fe} 20 at. %; C_{Ta} 3.8 at. %; C_B 32 at. %) was found close to the target composition. There is a deviation in Ta content and is due to the low sputtering rate of Ta compared to other elements present in the target. The presence of a broad peak around ~45° in the x-ray diffraction (XRD) curve for the film deposited at 25 °C (similar XRD curves were obtained for the films deposited at T_s as high as 300 °C) suggests the amorphous

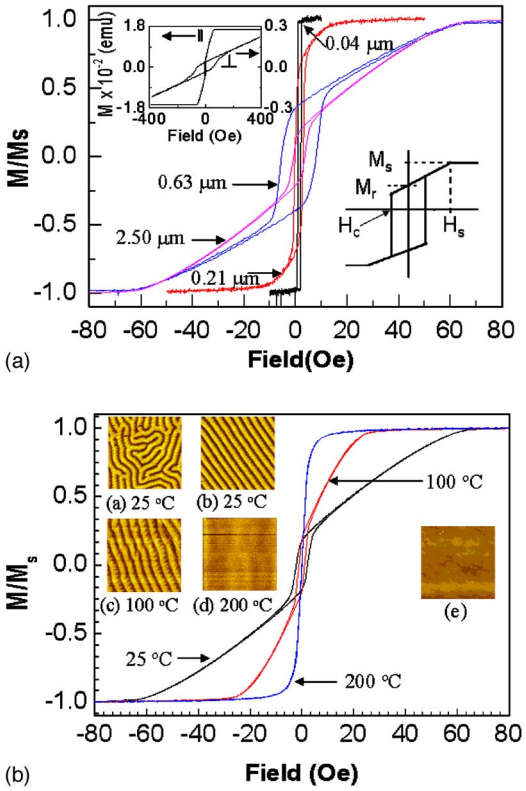

FIG. 1. (Color online) Hysteretic loops for Co-Fe-Ta-B thin films (A) deposited at room temperature (~25 °C), having different values of film thickness: Inset shows the inplane (∥) and out of plane (⊥) hysteretic loops for 2.5 μm thin film; (B) deposited at different T_s (film thickness ~2.5 μm). Insets: the MFM images (area 20 μm×20 μm) for (a) film deposited at 25 °C, Virgin state, (b) at 25 °C, in remanence state, (c) at 100 °C, in remanence state, (d) at 200 °C, in remanence state, and (e) typical topography of Co-Fe-Ta-B thin films.

nature. Moreover, completely amorphous nature of the films (which is similar to the bulk material, see Ref. 11) was also confirmed by high-resolution transmission electron microscope image, and the presence of hallow ring pattern in the selected area diffraction pattern. The differential scanning calorimetry (DSC) curve for the same film showed a glass transition temperature (T_g) at 909 K, and crystallization temperature (T_x) at 950 K with a large supercooled liquid region ($\Delta T_x = T_x - T_g$) of 41 K. Films were also found to be mechanically hardest among all the known metals, and glassy metals.[11] Details of the physical characterization will be reported elsewhere.

Magnetic properties of the films were studied by using a Quantum Design SQUID magnetometer, and vibrating sample magnetometer (VSM), with a magnetic field applied parallel to the film surface. Figure 1 shows the hysteretic loops measured at 300 K for the films deposited at a T_s ~ 25–200 °C, having different values of film thickness. A strange shape of the hysteresis loops can be noticed from Fig. 1 [Fig. 1(a), thickness >0.21 μm, and Fig. 1(b), 25 and 100 °C]. These types of hysteresis loops have been previously observed in the literature, and named as "transcritical hysteresis loop."[12,13] The shape of the hysteresis loops was found to change from square (characteristic of single domain type) to characteristic transcritical type [Fig. 1(a)], and transcritical to square type [Fig. 1(b)] with increasing film thickness and T_s, respectively. The square shaped loops ($M_r/M_s \approx 0.8$) exhibit a very low value of coercivity ($H_c < 1$ Oe). An increase in H_c with a reduction a in M_r/M_s ratio was observed for the transcritical type loops. The transcritical hysteresis loops are known to be associated with the presence of perpendicular magnetization.[12,13] We imaged the surface magnetic structure of the films using a magnetic force microscope (MFM) [Fig. 1(b) inset (a)–(e)]. Randomly oriented stripe domains were observed for the films having a transcritical type loop [Fig. 1(b) inset (a)], while the films possessing a square loop showed the absence of magnetic structure at the film surface [Fig. 1(b) inset (d)]. The randomly oriented domains were found to align or arranged in parallel stripes [Fig. 1(b) inset (b) and (c)] once the samples were exposed to magnetic field. From the Fig. 1, it can be conclude that the transcritical loops are associated with perpendicular magnetization, and the square loops with in-plane magnetization. Therefore we can say, a spin reorientation from in-plane single domain sate to perpendicular multidomain sate, and perpendicular to in-plane occurred with increasing film thickness[14] and T_s, respectively.

It is known that there can be two types of stress viz. macrostress and the microstress present in the films, which can influence the magnetic properties. Separating the film from the substrate relieves the macrostress, while the microstress can be relieved by depositing the films at elevated temperatures or by heat treating the films after deposition. In the present study, the hysteresis loops were found to be unchanged after separation of the films from the substrate. It can be noticed from Fig. 1(b) that the transcritical type loops are more pronounced for the films deposited at room temperature as compared to films deposited at elevated T_s, and indicate the role of microstress or atomic relaxation in the SRT. To understand the effect of atomic relaxation, we heat treated the film deposited at 25 to 200 °C in vacuum, and measured the hysteresis loop at 300 K, and again heated the same sample to 300 °C and measured the hysteresis loop at 300 K. The results showed a transition from transcritical to square type loop similar to the films deposited at increasing T_s. This suggests that the irreversible SRT from perpendicular to in plane magnetization at room temperature with increasing substrate temperature is due to atomic relaxation or the change in local short-range ordering of magnetic elements in the amorphous state. The effect of atomic relaxation on magnetic properties of Co adatoms and clusters studied by *ab initio* calculations also suggested that the strong tendency of perpendicular magnetization is totally suppressed by the atomic relaxation, and fully relaxed geometry results in the in-plane magnetization.[15]

Figure 2 shows the temperature dependent magnetization at 10 Oe in zero field cooled (ZFC) and field cooled (FC) state for the films of thickness ~2.5 μm. A decrease in magnetization at ~150 and ~250 K can be noticed from Fig. 2 for the films deposited at 25 and 100 °C, respectively, while the film deposited at 200 °C did not exhibit such a transition. The hysteresis loops measured at different temperatures (5 to 325 K) for the films deposited at 25 °C (thickness ~2.5 μm) showed a surprising change in the shape with

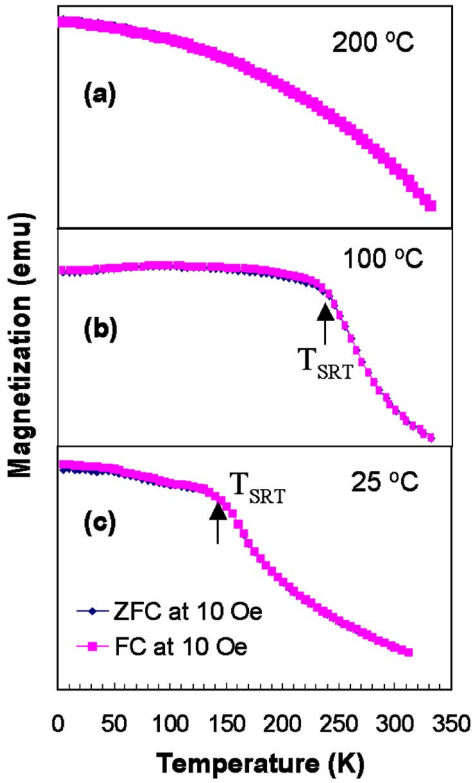

FIG. 2. (Color online) Temperature dependent magnetization in zero field cooled (ZFC) and field cooled (FC) state at 10 Oe for the film of thickness ~2.5 μm deposited at (a) 200 °C, (b) 100 °C, and (c) 25 °C.

increasing temperature (Fig. 3). The square shaped hysteresis loop observed below 150 K changed to transcritical type above 150 K (see Fig. 2, this temperature corresponds to decrease in magnetization). The remnant magnetization (M_r)

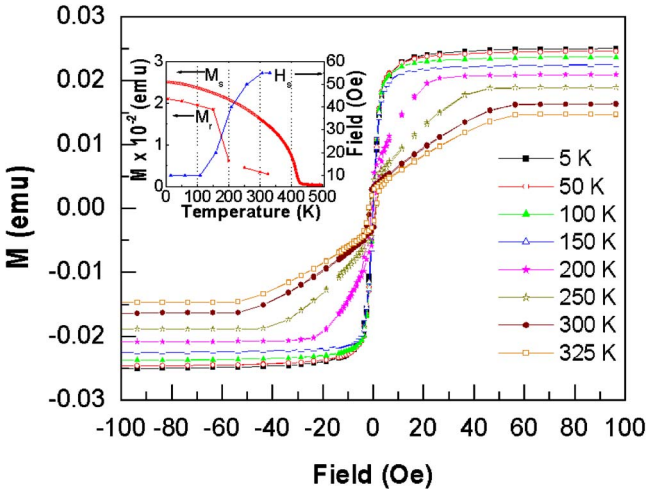

FIG. 3. (Color online) Hysteresis loops $M(H)$ measured at different temperature for Co-Fe-Ta-B thin film (thickness ~2.5 μm) deposited at room temperature (25 °C), and shows the spin-reorientation transition (~150 K) from in-plane to out of plane. Inset shows the variation in saturation magnetization (M_s), remnant magnetization (M_r), and the saturation field (H_s) with temperature. The value of T_c is ~450 K.

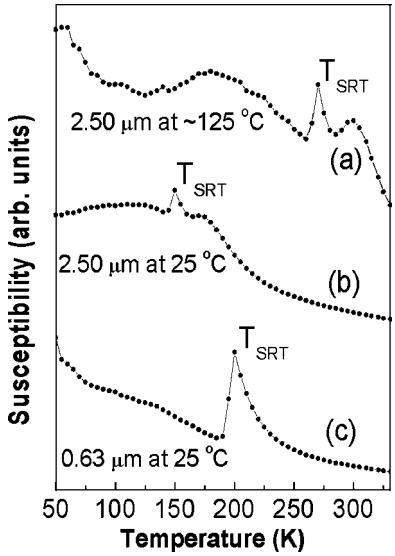

FIG. 4. Variation in susceptibility with temperature measured by applying an oscillating magnetic field of frequency 350 Hz for (a) 2.5-μm-thick film deposited at ~125 °C (ac field=0.1 Oe), (b) 2.5-μm-thick film deposited at ~25 °C (ac field=0.05 Oe), and (c) 0.63-μm-thick film deposited at ~25 °C (ac field=0.1 Oe).

also starts decreasing above 150 K, and it appears that the Curie-temperature (T_c) is close to 150 K, but the measured T_c is ~450 K (Fig. 3, inset). Similar changes in the shape of the hysteresis loops were also observed above ~250 K for the film deposited at 100 °C (see Fig. 2), while we did not observed any such changes in case of film deposited at 200 °C (Fig. 2). Figures 2 and 3 clearly establish the SRT from in-plane to perpendicular with increasing temperature, which is found to be reversible and can be tailored by varying the T_s during the film growth. It is worth to mention that we did not observed SRT in bulk samples (ribbons) made by melt-spinning technique. The magnetic properties of the ribbons were found similar to the film deposited at elevated temperatures. The T_c of the thin film samples (independent of the existence of SRT) and the bulk samples were found close to ~450 K.

The magnetic properties of Gd (0001) films epitaxially grown on W(110) also attracted lot of interest due to the possibility of a SRT at low temperature and film thickness (10–130 nm) from in plane to perpendicular.[16] It is suggested that the SRT in Gd films of thickness greater than 95 nm is governed by the changes in temperature-dependent magnetocrystalline anisotropy, and is not considered as a real SRT. The real SRT in Gd films was only observed for thickness less than 95 nm.[16] In order to verify the presence of real SRT in Co-Fe-Ta-B thick films, ac susceptibility measurements were performed (similar to Ref. 16). Figure 4 shows the real part of temperature dependent ac susceptibility for the 2.5-μm- and 0.63-μm-thick films. The existence of a peak in the ac susceptibility near SRT clearly point towards the existence of real SRT. A striking difference that is the saturation of susceptibility below SRT can be noticed in case of thick films as compared to thin films [Figs. 4(b) and 4(c)], and seems due to the variation in perpendicular anisotropy.[16] Although films in the present study are amorphous, but the

development of perpendicular anisotropy (or short-range ordering) with increasing film thickness cannot be ruled out because of perpendicular landing of atomic species during the sputter deposition process. Heat treatment of the film seems to deteriorate this anisotropy, which can be clearly noticed from the variation in susceptibility below the SRT, and enhancement in peak intensity near the SRT [Fig. 4(a)]. Moreover, the heat treatment also causes a shift in the SRT that can be linked to atomic relaxation.

At a first glance it seems that most of the magnetic properties are governed by the spin magnetism (M_s), but concerning the magnetic anisotropy, orbital magnetic moment (M_o) may play vital a role. In order to probe the effect of orbital magnetism and to understand the reason for the occurrence of real SRT in thick amorphous films, we also studied them by x-ray absorption spectroscopy (XAS), and x-ray magnetic circular dichrosim (XMCD). X-ray experiments were performed on the $\sim$2.5-μm-thick film below and above the SRT (298 and 20 K) at beamline 4.0.2 at the Advanced Light Source, Berkeley National Laboratory, USA.[17] We measured two sets of spectra with opposite field and opposite polarization. The x-ray angle of incidence was 30°, and the magnetic field of ±0.2 T was applied parallel to the x-ray beam. The calculated values for the ratio of orbital and spin moment M_o/M_s, obtained from the XMCD spectra measured at 298 K, and 20 K are $[(M_o/M_s)\mathrm{Fe}=0.033\pm0.005; (M_o/M_s)\mathrm{Co}=0.084\pm0.005]$ and $[(M_o/M_s)\mathrm{Fe}=0.047\pm0.005; (M_o/M_s)\mathrm{Co}=0.077\pm0.005]$, respectively, and are close to the values reported for the bulk Fe and Co $[(M_o/M_s)\mathrm{Fe}=0.043; (M_o/M_s)\mathrm{Co}=0.095)]$.[18] A small variation in the M_o/M_s ratio can be noticed for the Co-Fe-Ta-B thin films below and above the SRT and can be due to the instability in M_o.

Based on the previous studies, it can be noticed that SRT is generally observed in case of ultrathin films (Gd, Fe, Co, and Ni), where the interface between the film and the substrate played a crucial role.[1–8,16] It is known that the orbital magnetic moment is almost quenched due to the high symmetry of the arrangement of the surrounding atoms in the crystal. However, in ultrathin layers this quenching may partly lifted due to the broken symmetry at the surface, strains, and the exchange of electrons at the interface between two coupled layers.[19] The instability of orbital magnetism can produce a magnetic anisotropy energy via spin-orbit coupling, and can result in a SRT.[20] Now from the present study and the reported literature, we can conclude that the SRT observed in present study is related to the atomic randomness, and it is not necessary to have SRT only in ultrathin films. Atomic relaxation plays an important role in the observation of SRT and the relaxed state leads to disappearance of SRT. To our knowledge, this is the first study where SRT is observed in thick amorphous films.

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