Epitaxial structure and magnetic anisotropies of metastable single crystal $Co_{0.70}Mn_{0.30}$ film

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Alloy films of $Co_{0.70}Mn_{0.30}$ were grown on GaAs (001) substrates by molecular beam epitaxy at room temperature. The metastable tetragonally distorted single crystal structure was confirmed by reflection high energy electron diffraction and x-ray diffraction measurement, which exhibited a 2.87 Å in-plane lattice parameter. Ferromagnetic resonance measurements and theoretical fitting were performed and showed that, with a Mn capping layer, a uni-directional anisotropy existed. In addition, a fourfold tetragonal magnetocrystalline anisotropy as well as a uniaxial term in the film plane was also confirmed. The hysteresis loops recorded by longitudinal magneto-optical Kerr-effect also demonstrated the existence of different kinds of in-plane magnetic anisotropy. The origins of the anisotropy are explained tentatively. *© 1997 American Institute of Physics.* [S0021-8979(97)03204-0]

Molecular beam epitaxy (MBE) has been shown to be suitable for growing single crystal films of transition metal on semiconductor substrates.[1,2] Various metastable phases have been grown and stabilized at room temperature on lattice-matched substrates. For example, metastable body-centered-cubic (bcc) Co and body-centered-tetragonal (bct) Mn films were grown on the GaAs(001) surface[3] and on the Pd(001) surface,[4] respectively. However, the epitaxy of alloy films has seldom been reported. As a continuation of the previous work of epitaxial growth of face-centered-cubic (fcc) Mn films on GaAs(001) surfaces,[2] we prepared single crystal $Co_{0.70}Mn_{0.30}$ alloy films on GaAs(001) substrates at room temperature and studied their structure and magnetic characteristics. To our knowledge, this study is the first one to involve epitaxial growth on this particular alloy.

The sample fabrication was carried out in a MBE system connected with a VG-ESCALAB electron spectrometer.[2] Reflection high energy electron diffraction (RHEED) is equipped to monitor the growth *in situ*. After sputtering with Ar^+ ions at 800 eV for 55 min, the GaAs(001) substrate was then annealed at 500 °C in ultrahigh vacuum for 25 minutes until a streaklike RHEED pattern was observed, implying a ''good'' flat surface. The pressure during evaporation was below 1×10^{-7} Pa. The absence of contamination of oxygen and carbon was indicated by Auger electron spectroscopy (AES) and x-ray photoelectron spectroscopy (XPS) analyses. Finally, the $Co_{0.70}Mn_{0.30}$ alloy film was deposited by direct co-evaporation of Co and Mn on the GaAs(001) surface at the appropriate deposition rates measured by a quartz-crystal thickness monitor. The composition of the Co–Mn alloy film was analyzed once by XPS and confirmed the approximate coincidence with the nominal composition (but the data of the resonance fields of two samples in Fig. 2 implies that composition deviations may exist). The substrate temperature was maintained at T=300 K during deposition.

Upon deposition, the RHEED pattern of GaAs(001) faded. Continuing the film growth up to about 5 Å yielded a new pattern shown in Fig. 1(a) with the incidence electron beam along [110] direction (the crystal azimuth in this article refers to the GaAs crystalline axis unless special description is made). This RHEED pattern did not change during growth up to 150 Å. A Cu layer was utilized to prevent oxidation. The rectangular distribution of the streaks corresponds to the projection of the three-dimensional reciprocal lattice along the [110] direction. When the sample was rotated 90° around the normal direction, so that the electron beam was along the $[1\bar{1}0]$ direction, the resulting RHEED pattern was exactly the same as that obtained from the [110] direction, which indicates that the in-plane lattice net is square. Fig. 1(b) displays the RHEED pattern for the sample rotating 45° with the e-beam along [010] direction. By comparing with the RHEED data of the clean GaAs(001), the lattice constant *a* of the surface net was estimated to be 2.87 Å. It is difficult to determine the out-of-plane lattice spacing from the observed RHEED pattern alone because RHEED is generally not sensitive to the vertical lattice spacing; therefore, we performed x-ray diffraction on the same sample *ex situ*. It is found that in the obtained XRD spectrum (not shown here) the huge peak around 66° and a peak at 58.9° are diffractions of the GaAs(004), respectively. At about 74.2°, corresponding to the lattice spacing of 2.56 Å, a peak appears which is the only diffraction peak from the $Co_{0.70}Mn_{0.30}$ thin film,

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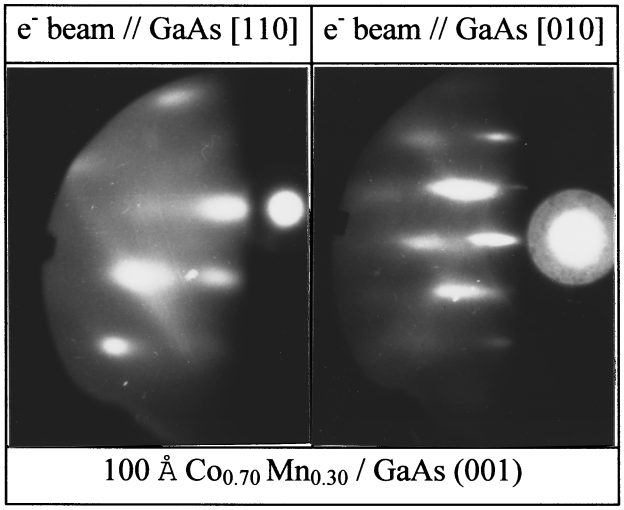

FIG. 1. RHEED patterns for a 100 Å Co–Mn film epitaxially grown on the GaAs(001) surface with (a) e-beam∥ [110] and (b) [010], respectively.

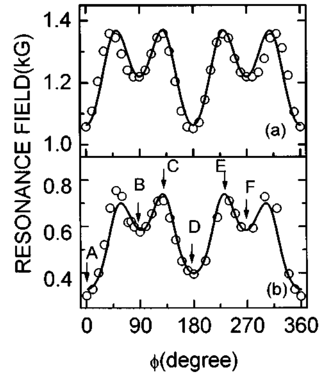

FIG. 2. In-plane angular dependence of the FMR field H_{res} for Co–Mn alloy films with different overlayers. The open circles are the experimental data and the solid line represents a theoretical fit using the parameters listed in Table I for (a) Cu(20 Å)/Co–Mn(65 Å) and (b) Mn(30 Å)/Co–Mn(50 Å).

however, the corresponding value does not accord with a fcc or a bcc structure. Then it is realized that the Co-Mn films were neither rotated fcc nor unrotated bcc structures,[2] but rather a bct or an equivalent face-centered-tetragonal (fct) structure. Considering its fcc structure for bulk phase,[5] in this article we assume the Co–Mn film to be a rotated fct structure which shows (001) plane that rotating 45° with respect to the plane of the substrate, so $[110]_{GaAs} \| [100]_{Co-Mn}$, $[\bar{1}10]_{GaAs} \| [010]_{Co-Mn}$.

The magnetic properties of Co–Mn alloy films were studied at room temperature by means of ferromagnetic resonance (FMR) and longitudinal magnetic optical Kerr effect (LMOKE) *ex situ*. The FMR experiments were performed at the X band of 9.78 GHz with the external magnetic field rotated in the film plane, starting from the $[100]_{Co-Mn}$ direction. The angular dependences of the ferromagnetic resonance field H_{res}, for Co–Mn films with different overlayers of Mn and Cu are displayed in Fig. 2. In the case of a 20 Å Cu capping layer, it can be speculated from Fig. 2(a) that a fourfold anisotropy exists which corresponds to the tetragonal magnetocrystalline anisotropy in the (001) plane, besides a contribution of a uniaxial term with the easy axis along $[100]_{Co-Mn}$ direction. For the film with 30 Å Mn overlayer, it is seen from Fig. 2(b) that $H_{res}(0°)$ is not equal to $H_{res}(180°)$. This means that an additional uni-directional anisotropy field H_D is present, causing $[100]_{Co-Mn}$ to be the easiest direction. Following the above idea, a theoretical fitting of FMR field was made by using the following expression of total free energy density:

$$E = -HM \sin\theta \cos(\phi_H - \phi) + K_1 \sin^2\theta + K_2 \sin^4\theta + K_2' \sin^4\theta \cos 4\phi - K_u \sin^2\theta \cos^2\phi + 2\pi M^2 \cos^2\theta + K_D \sin\theta \cos\phi \quad (1)$$

which includes the contributions from the Zeeman energy, the tetragonal magnetocrystalline anisotropy terms (K_1, K_2, K_2'), the in-plane uniaxial anisotropy (K_u term), the demagnetizing energy, and a uni-directional anisotropy term K_D. θ, ϕ, and θ_H stand, respectively, for the angles of the magnetization vector in spherical coordinates and the azimuthal angle of the magnetic field in the film plane. The three edges of tetragonal crystal structure are taken as the reference axes of the coordinates. Note that the easy axes of the fourfold, uniaxial, and uni-directional anisotropy are all along the $[100]_{Co-Mn}$ direction which is also the [110] axis of GaAs. The general condition for ferromagnetic resonance[6] yields the following resonance equation:

$$(\omega/\gamma)^2 = [H \cos(\phi_H - \phi) + (4\pi M - 2H_1) + 4(H_2 + H_2' \cos 4\phi) + 2H_u \cos^2\phi - H_D \cos\phi] \times [H \cos(\phi_H - \phi) + 2H_u \cos 2\phi - 16H_2' \cos 4\phi - H_D \cos\phi)], \quad (2)$$

in which we define $H_i = K_i/M$. By assuming the gyromagnetic ratio γ to be the value of bulk Co, the best fitting shown in Figs. 2(a) and 2(b) was achieved by taking the parameters listed in Table I. It is found that K_u is comparable to K_1 and K_D (if not zero), which could also be deduced from the relative values of H_{res} in Fig. 2. It is noted that $K_D(-5\times10^4\ \mathrm{erg/cm^3})$ for Co–Mn film with Mn overlayer is smaller than the corresponding value of $Jt = H_{ex}M = 16\times10^4 \mathrm{erg/cm^3}$ in Ref. 7 where stronger exchange coupling existed.

The easy axis of the uniaxial anisotropy K_u term was found along $[110]_{GaAs}$ in all the samples we made, which gives us an insight into its origin. Considering the fact that there is a slight miscut of about 2° from (001) to (110) plane, which leads to steps along $[110]_{GaAs}$ direction, the uniaxial term may result from step-induced anisotropy as proposed in Ref. 8. In a Co/Mn/Co sandwich system it was found that a stronger induced uniaxial anisotropy also resulted from the substrate steps.[9] As for the uni-directional anisotropy K_D, it could be considered to originate from an exchange interaction between the ferromagnetic Co–Mn alloy and the Mn overlayer. In the early 1960's, Kouvel discovered the existence of exchange anisotropy in Co–Mn disordered alloys of about 25, 30, and 35 at. % Mn, and explained it with a sta-

TABLE I. Anisotropy constants deduced from the FMR data of Co–Mn film with different coverages ($\times 10^4$erg/cm^3).

Sample	K_1	K_2	K_2'	K_u	K_D
Mn(30 Å)/Co–Mn(50 Å)	8.0	4.0	−1.1	7.5	−5.0
Cu(20 Å)/Co–Mn(65 Å)	3.4	2.3	−0.4	2.45	0

tistical composition fluctuation model.[10] However, in this experiment the absence of K_D when the Mn overlayer was replaced by Cu indicates that it could not be due to the inhomogeneity of the Co–Mn film. Recently, it was discovered by Henry and Ounadjela[11] that in Co/Mn multilayers the exchange interaction existed at the Co/Mn interfaces, which supports our experimental results.

The experimental LMOKE setup we used to record the magnetic hysteresis loops of the Mn/Co–Mn system is similar to that described by Qui *et al.*[12] By rotating the sample around the normal direction of the film plane, the hysteresis loops with the magnetic field along different directions in the film plane were recorded.

Figures 3(a)–3(d) display typical hysteresis loops of the sample Mn(30 Å)/Co–Mn(100 Å) with varying angle ϕ between the $[100]_{\mathrm{Co-Mn}}$ direction and the incidence plane of light. Fig. 3(a), 3(b), 3(c), and 3(d) are the Kerr loops with ϕ=0°, 90°, 135°, and 180°, which correspond to the four directions marked by A, B, C, and D in Fig. 2(b). It is found that the rectangular loop in Figs. 3(a) and 3(d) is characteristic of the two easy magnetization directions of $[100]_{\mathrm{Co-Mn}}$ and $[\bar{1}10]_{\mathrm{Co-Mn}}$, in which the former is the easiest due to the positive uni-directional anisotropy field, causing the shift of the loop to negative side while 3(d) is shifted to positive side. A complicated hysteresis loop composed of two steps in Fig. 3(b) appears in the $[010]_{\mathrm{Co-Mn}}$ direction along which the total anisotropy energy is at a minimum with higher energy at position B in Fig. 2(b). To change the direction of magnetization by 180°, corresponding to the one branch in the hysteresis loop, requires the magnetization to go through two potential maxima, e.g., from B to D across C and from D to F across E, which may be the origin of the stepped loop. The tilted loop of Fig. 3(c) shows the feature of the hard $[\bar{1}10]_{\mathrm{Co-Mn}}$ direction. It is obvious that under the maximum field of about 150 G the sample cannot be saturated, which causes the unique unsaturated loop. This is in contrast to the other three loops, which show a nearly saturated state under the same maximum field. However, the inconsistency of the experimental value of coercive force of about 40 G and the calculated value is explained by assuming a coherent rotation process,[13] which means that the magnetization process in the loop is not likely through uniform rotation. It should be a domain nucleation and domain wall displacement process. Therefore a quantitative explanation for the different loop shapes needs more study.

In conclusion, the metastable single crystal $Co_{0.70}Mn_{0.30}$ alloy film with tetragonal symmetry has been prepared on GaAs(001) surface via MBE. FMR studies show that with the Mn capping layer, a uni-directional anisotropy appears besides the fourfold magnetocrystalline anisotropy and a uniaxial term in the film plane. It is proposed that this results from the exchange interaction between the Co–Mn alloy and the Mn overlayer. The anisotropy of the hysteresis loops recorded by the LMOKE measurement can be understood qualitatively as a result of the interplay of three anisotropies.

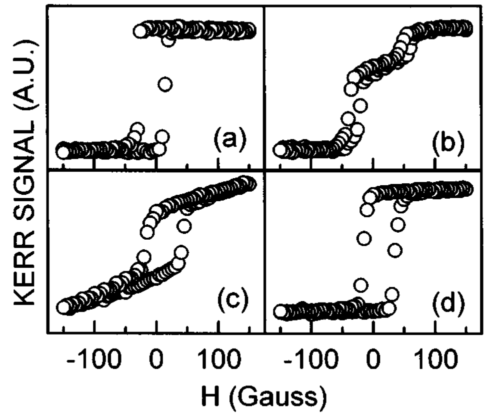

FIG. 3. Hysteresis loops for samples of Mn(30 Å)/Co–Mn(100 Å) measured by LMOKE with the applied field in-plane along different ϕ from [110] direction: (a) 0° (b) 90°, (c) 135°, (d) 180°, respectively.

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Note added in proof. Recently, we found that the Co–Mn film is conclusively bct, which changes the values of anisotropy constants and the easy directions with no influence on the whole physics.

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