Decoupling the structural and magnetic phase transformations in magneto-optic MnBi thin films by the partial substitution of Cr for Mn

Prabhakar R. Bandaru,[a] Timothy D. Sands, and Yukiko Kubota
Department of Materials Science and Mineral Engineering, University of California, Berkeley, California 94720

Ernesto E. Marinero
IBM Research Division, Almaden Research Center, 650 Harry Road, San Jose, California 95120

(Received 22 December 1997; accepted for publication 24 February 1998)

The first-order nature of the magnetic phase transformation at 360 °C and the presence of a Bi-rich eutectic at 265 °C have inhibited the application of MnBi thin films for high density magneto-optical data storage. It is suggested that partial substitution of Cr for Mn should both lower the Curie temperature, T_c, and decouple the lattice and magnetic transitions so as to allow reversible Curie point writing. It is found experimentally that 10% substitution of Cr for Mn reduces the apparent T_c to $\sim 250\,^{\circ}C$ while retaining a Kerr rotation angle greater than 1° at 633 nm, as measured through the silica glass substrate. Observations of increasing H_c with temperature in both MnBi and (Mn,Cr)Bi thin films suggest that the low-temperature phase is ferrimagnetic. © *1998 American Institute of Physics.* [S0003-6951(98)01717-3]

Since Curie-point writing with an electron beam was first demonstrated in 1958,[1] polycrystalline MnBi thin films have been considered to be promising candidates for magneto-optical (MO) data storage. In the quest for higher density storage exploiting the anticipated availability of low-cost, GaN-based blue lasers, MnBi assumes additional importance as it has the largest Kerr response in the blue wavelength regime of any known material at room temperature. This Kerr response contributes to a large intrinsic value of the figure of merit, $R^{1/2}\Theta_k$, where R is the reflectivity and Θ_k is the Kerr rotation angle. Furthermore, large perpendicular anisotropy[2] ($K_1 \sim 10^6$ J/m^3) is readily achieved in MnBi films as a consequence of uniaxial texture and a high intrinsic magnetocrystalline anisotropy.

Despite these outstanding attributes, efforts to develop MnBi for rewritable optical recording have been plagued by a first-order transformation from the high-temperature paramagnetic phase to the equilibrium low-temperature ferromagnetic phase.[3] This coupling of the magnetic transition with a first-order lattice transition at 360 °C leads to high media noise and poor reversibility, consequences of the presence of both equilibrium and metastable phases (e.g., the quenched high-temperature phase) following Curie-point writing. Another issue of contention is the steady increase of coercivity (H_c) with temperature[4] which could be a potential obstacle for Curie-point writing. This issue will be dealt with in detail in a later paper.[5] In this letter, an approach toward decoupling the lattice and magnetic transitions through the partial substitution of Cr for Mn is rationalized and preliminary results supporting this approach are presented.

The equilibrium low-temperature phase of MnBi (LTP) adopts the hexagonal NiAs structure with $a_0 = 0.429$ nm and $c_0 = 0.6126$ nm (Fig. 1) at room temperature.[3] In this structure, the Mn^{3+} ions are octahedrally coordinated by Bi, and ferromagnetic interactions predominate, possibly mediated via an ''exchange inversion''[6] superexchange mechanism through the Bi $6p$ orbitals.[7] During heating through 360 °C, a coupled magnetic and first-order lattice transition results in the formation of a paramagnetic high-temperature phase (HTP). This transformation is believed to involve the shuffle of approximately 15% of the Mn to the five-fold-coordinated bipyramidal interstices.[3,8] The resulting orthorhombic structure is a superstructure of the hexagonal unit cell, with pseudohexagonal lattice parameters of $a_0 = 0.434$ nm and $c_0 = 0.597$ nm (extrapolated to room temperature).[3] Upon quenching from above 360 °C, the HTP can be retained. This quenched HTP becomes ferrimagnetic below $\sim 180\,^{\circ}C$. It is speculated[3] that an antiferromagnetic exchange coupling between adjacent octahedral and bipyramidal Mn sites reduces the net magnetization per Mn ion from $\sim 4\,\mu_B$ for the LTP to $\sim 2\,\mu_B$ for the quenched HTP.

From the perspective of reducing media noise and improving reversibility, it is imperative that the magnetic tran-

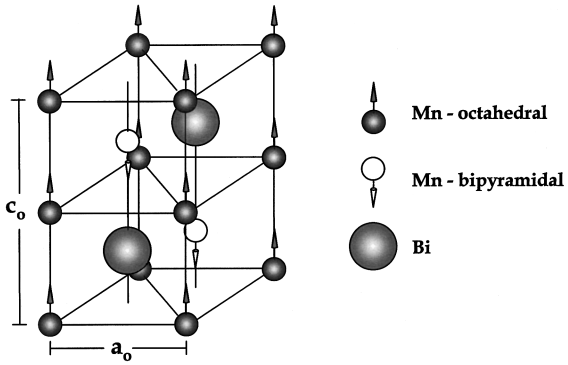

FIG. 1. Structure of low temperature MnBi. The octahedral sites are occupied by ferromagnetically coupled Mn. In the high temperature phase, the bipyramidal sites are partially occupied with Mn, which is antiferromagnetically coupled to the octahedrally coordinated Mn in the quenched high temperature phase.

[a]Electronic mail: bpr@uclimk2.berkeley.edu

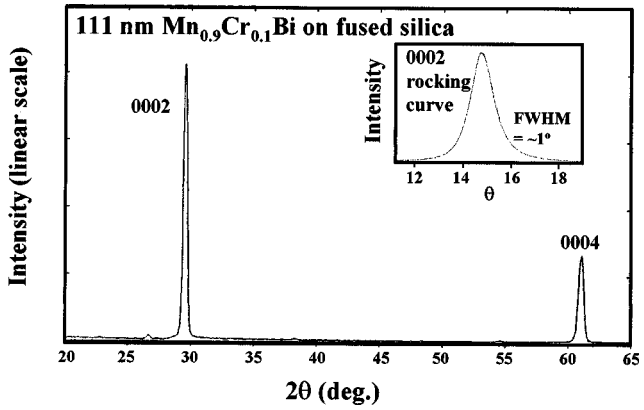

FIG. 2. Coupled θ–2θ x-ray (Cu $K\alpha$: 1.5406 Å) spectrum from a 111 nm thick ($Mn_{0.9}Cr_{0.1}$)Bi film on a silica glass substrate. The small peaks at ~27° and at ~54° correspond to the $K\beta$ (λ: 1.3922 Å) 0002 and 0004 reflections. X-ray rocking curve showing a FWHM of ~1° is inset.

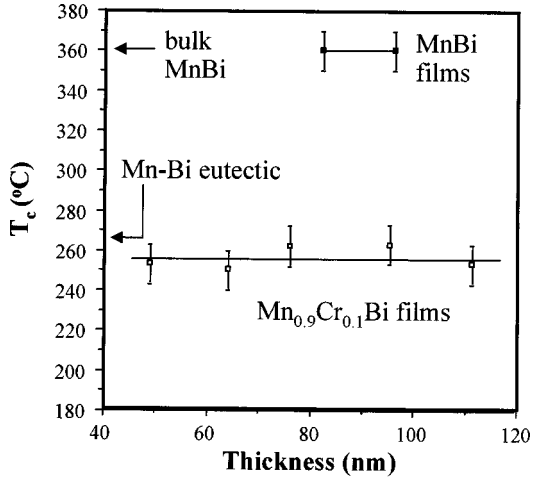

FIG. 3. Curie temperature (T_c) as a function of film thickness for MnBi and $Mn_{0.9}Cr_{0.1}Bi$.

sition to be used for MO recording be decoupled from any first-order lattice transition. Furthermore, the difficulty in completely eliminating Bi inclusions from MnBi films leads to the practical requirement that the magnetic transition (ideally second-order) involve a transition temperature below[9] the Mn–Bi eutectic temperature of 265 °C.[10] Previous attempts at addressing the phase transformation problem have endeavored to stabilize either the LTP or the quenched HTP through alloying with Ti;[11] Cu;[12] Zn, Sb, Te, Cr, Fe, Co, Ni, Ti, Sc;[13] Al, Si;[14] and Ru or Rh.[15] Superheating of the LTP and supercooling of the HTP using fast laser pulses comparable to the conditions of thermomagnetic recording has also been explored.[16] In several of these studies, the LTP→HTP transformation was suppressed,[11,15] but at the expense of a reduced MO figure of merit. For example, suppression of the LTP yields a low magnetic transition temperature characteristic of the quenched HTP, but with an associated reduction in Θ_k by as much as 50%.[11,12,13] Several alloying additions were reported to have resulted in new undesirable ternary phases (e.g., Cu, Zn, Ti)[11–13] or were found to inhibit the reaction to form MnBi (e.g., Cr and Fe).[13]

The approach adopted in the present study was to reduce the effective Curie temperature of the LTP by partial substitution of Mn with an ion that would reduce the net ferromagnetic coupling in the MnBi lattice. In the localized moment picture of magnetism, the Curie temperature (T_c) is proportional to the exchange integral J ($J>0$ for ferromagnetism and $J<0$ for antiferromagnetism). By choosing a trivalent ion that favors both antiferromagnetism and octahedral coordination in the MnBi lattice, it was speculated that the T_c of the LTP could be controllably reduced without the full penalty in the figure of merit associated with the quenched HTP. Although a previous alloying attempt[13] was unsuccessful, Cr was the obvious candidate. The affinity of an ion for a particular lattice position is measured by the relative crystal field stabilization energy (CFSE) of the site—higher values indicating greater stability. The excess octahedral CFSE of Cr^{3+} (octahedral CFSE—tetrahedral CFSE=157.6 kJ/mol) is the largest of the transition metal ions and is substantially greater than that of Mn^{3+} (95.3 kJ/mol).[17] Furthermore, partial substitution of Cr for Mn should reduce the magnitude of ferromagnetic coupling, J, due to the propensity for antiferromagnetic interactions between Cr ions.

Electron-beam evaporation (10^{-6} Torr) was used to sequentially deposit Bi, Mn, and Cr on silica glass disk substrates (Hoya Industries) and silicon nitride (60 nm)/silicon substrates. The deposition of Bi first is essential to developing the required c-axis texture. The Bi is highly textured as-deposited and this texture is imparted to MnBi as it nucleates at the Mn/Bi interface during heating as was observed in *in situ* transmission electron microscopy (TEM) studies.[5] Layer thicknesses were adjusted to yield an average composition of $Mn_{1-x}Cr_xBi$. It was found that very slow deposition rates (<2 nm/min) were necessary to obtain reproducible films. The thin films were then coated with a 60 nm SiO_2 layer for protection from the ambient, followed by vacuum annealing (10^{-7} Torr) at 360 °C for 30 min. X-ray diffraction (Siemens D5000) was employed for phase and texture determination. The magnetic and magneto-optic property measurements were obtained by the magneto-optic Kerr effect (MOKE). MOKE measurements utilized a He–Ne laser probe (633 nm) of 1.5 mm diameter on the sample placed within the pole pieces of a 20 kOe magnet. The remanent Kerr rotation was recorded from the substrate side (for the fused silica substrates) and from the film side (for the silicon nitride/silicon substrates). MOKE measurements as a function of temperature were used for the analysis of magnetization behavior and to determine the T_c. (T_c is defined here as the temperature at which the remanent Kerr rotation extrapolates to zero). The temperature was varied in 15 °C intervals with heating and cooling rates around 40 °C/h. The films were tested for magnetic reversibility by alternate heating and cooling cycles. At least three measurements were taken at each temperature to ensure accuracy and stability.

MnBi and (Mn,Cr)Bi films with a high degree of c-axis texture were obtained upon annealing the as-deposited multilayers (Fig. 2). Based on calibration with the (kinematically forbidden) 200 Si peak, the c_0 parameter was found to be 0.609 nm for MnBi and 0.6064 nm for $Mn_{0.9}Cr_{0.1}Bi$. No superstructure reflections were detected. A high degree of c-axis fiber texture was evidenced by rocking curve full width at half maximum (FWHM) values of of ~1° (see inset of Fig. 2).

In accordance with the qualitative predictions above, it was found that on substitution of 10% Cr for Mn, the T_c was

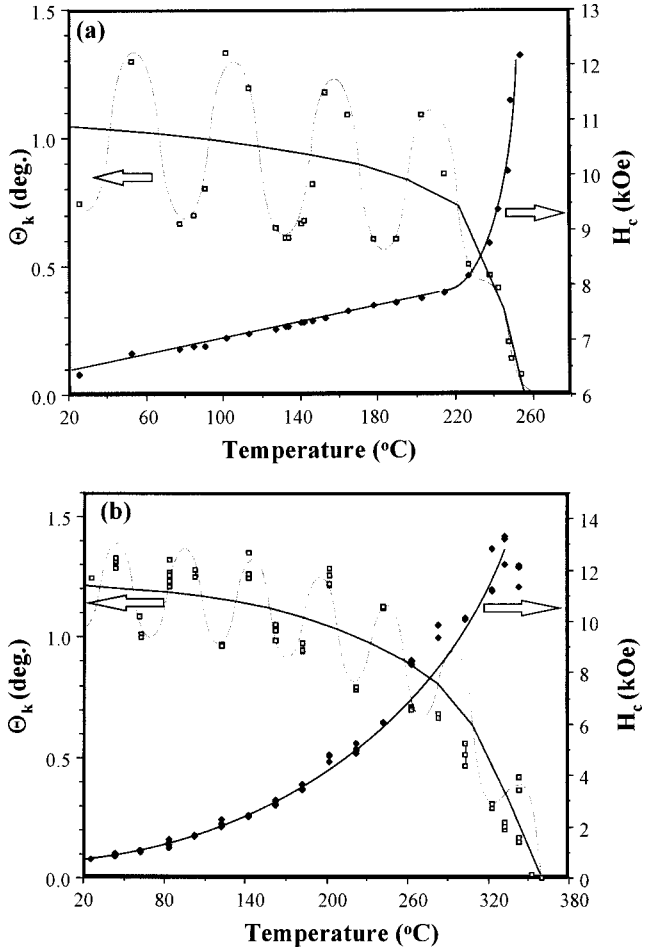

FIG. 4. Remanent Kerr rotation (Θ_k) and coercivity (H_c) as a function of temperature for (a) $Mn_{0.9}Cr_{0.1}Bi$ (111 nm thick) and (b) MnBi (96 nm thick) films on fused silica substrates. Data were acquired by measurement through the silica glass substrates at a wavelength of 633 nm. Oscillations in Θ_k with $\sim 50\,^{\circ}C$ periods are attributed to Fabry–Perot interference arising from the thermal expansion of the silica substrate. The curves representing the sinusoidal oscillations in the Kerr rotation are intended to be a guide to the eye.

decreased to $250 \pm 10\,^{\circ}C$. A similar result was obtained on substitution of 12.5% Cr and studies are in progress to ascertain the compositional dependence. The constancy of T_c over a range of film thicknesses suggests an intrinsic materials characteristic (Fig. 3).

Excellent figures of merit ($R^{1/2}\Theta_k \sim 0.63$) were obtained with remanent Kerr rotation (Θ_k) of 1.0°–1.2° and reflectivities (R) of 25%–40%. Figure 4(a) illustrates the remanent Θ_k (proportional to the magnetization) versus temperature behavior for a 111 nm ($Mn_{0.9}Cr_{0.1}$)Bi film on a silica glass substrate. The oscillations in the Θ_k are consequences of the thermal expansion of the flat silica glass substrates giving rise to Fabry–Perot etalons. The mean Kerr rotation is found by tracing a line through the inflection points of the oscillation (corresponding to zero interference). The (Mn,Cr)Bi films were found to be magnetically reversible after cycling beyond the T_c in contrast to the unalloyed MnBi films [Fig. 4(b)] which suffered degradation in Θ_k, presumed to be due in part to repeated segregation and melting of Bi.

Of particular interest is the steadily increasing coercive field (H_c) with temperature for both MnBi and (Mn,Cr)Bi films. Previous observations of increasing H_c have been attributed to the nucleation of another phase[11] or thermal activation of domain pinning sites.[4] The x-ray diffraction data from the films of the present study, however, do not reveal superstructure reflections, nor is there any evidence of thermal irreversibility in the (Mn,Cr)Bi as would be expected if the film were to transform from a quenched phase to the stable LTP. This magnetic behavior suggests competing ferromagnetic and antiferromagnetic interactions in the MnBi and (Mn,Cr)Bi thin films;[5] the increasing H_c with temperature being indicative of a ferrimagnetic compensation point at or near T_c, or a ferrimagnetically coupled interstitial fraction that increases steadily with temperature.[5,11] Preliminary data show ferrimagnetic behavior but this has yet to be fully confirmed.[18]

In conclusion, the partial substitution of Cr for Mn in MnBi has been shown to reduce the apparent Curie temperature to around 250 °C, below the Bi melting point and intermediate between the Curie temperatures of the LTP and the quenched HTP. This has been accomplished with very little degradation in the MO figure of merit. No indications of phase separation, lattice phase transitions, or irreversibility of the magnetic transition in (Mn,Cr)Bi have been observed in these preliminary studies, although future experiments using magneto-optic recording conditions are necessary before it can be concluded that the magnetic transition in (Mn,Cr)Bi is not coupled with a first-order lattice transition.

This work has been supported by NSF Grant No. ECS-9409730. The use of the facilities of the Berkeley Microlab, the Berkeley Integrated Materials Laboratory (NSF DMR-9214370) and facilities at the Lawrence Berkeley National Laboratory are acknowledged. The magnetic measurements were performed at the IBM Almaden Research Center, San Jose.

[1] L. Mayer, J. Appl. Phys. **29**, 1454 (1958).
[2] R. S. Tebble and D. J. Craik, Magnetic Materials (Wiley–Interscience, London, 1969).
[3] A. F. Andresen, W. Halg, P. Fischer, and E. Stoll, Acta Chem. Scand. **21**, 1543 (1967).
[4] X. Guo, X. Chen, Z. Altounian, and J. O. Strom-Olsen, J. Appl. Phys. **73**, 6275 (1993).
[5] P. Bandaru, T. Sands, Y. Kubota, and E. Marinero (unpublished).
[6] J. B. Goodenough, A. Wold, R. J. Arnott, and N. Menyuk, Phys. Rev. **124**, 373 (1961).
[7] P. W. Anderson, Phys. Rev. **115**, 2 (1959).
[8] B. W. Roberts, Phys. Rev. **104**, 607 (1956).
[9] The reduction of the Curie temperature to below the melting point of Bi is seen as an additional advantage as it was found in *in situ* TEM experiments that the incipient melting of Bi inclusions in MnBi films could result in a deterioration of film properties and could result in irreversibility (see Ref. 5).
[10] Binary Alloy Phase Diagrams, edited by H. Okamoto and P. R. Subramanian (ASM International, Materials Park, Ohio, 1990).
[11] W. K. Unger, E. Wolfgang, H. Harms, and H. Haudek, J. Appl. Phys. **43**, 2875 (1972).
[12] A. Katsui, J. Appl. Phys. **47**, 3609 (1976).
[13] H. Gobel, E. Wolfgang, and H. Harms, Phys. Status Solidi A **34**, 553 (1976).
[14] D. J. Sellmyer, R. D. Kirby, J. Chen, K. W. Wierman, J. X. Shen, Y. Liu, B. W. Robertson, and S. S. Jaswal, J. Phys. Chem. Solids **56**, 1549 (1995).
[15] K. Lee, J. C. Suits, and G. B. Street, Appl. Phys. Lett. **26**, 27 (1975).
[16] K. Kempter and E. Bayer, IEEE Trans. Magn. **MAG-12**, 62 (1976).
[17] A. R. West, *Solid State Chemistry and its Applications* (Wiley, New York, 1992).
[18] The Θ_k vs temperature data suggest the presence of a ferrimagnetic compensation point at a temperature near the Curie temperature. The implications of this behavior for Curie-point writing are not yet clear.