Available online at www.sciencedirect.com
ScienceDirect
Journal of Magnetism and Magnetic Materials 316 (2007) 221–224
Journal of magnetism and magnetic materials
www.elsevier.com/locate/jmmm

Growth and characterization of ferromagnetic MnAs films on different semiconductor substrates

M. Bolzan[a], I. Bergenti[b], G. Rossetto[a], P. Zanella[a], V. Dediu[b], M. Natali[a,*]

[a]ICIS-CNR, Corso Stati Uniti 4, Padova 35127, Italy
[b]ISMN-CNR, Via P Gobetti 101, Bologna 40129, Italy

Available online 28 February 2007

Abstract

MnAs thin films were grown by metalorganic vapour-phase epitaxy (MOVPE) on GaAs(0 0 1), Si(0 0 1) and oxidised silicon substrates. All films are crystalline and contain only the ferromagnetic α-MnAs phase. X-ray diffraction (XRD) and atomic force microscopy (AFM) measurements show that films on GaAs(0 0 1) have strong preferential orientation, developing elongated grains parallel to [1 –1 0] GaAs while films on bare and oxidised Si are polycrystalline with irregular-shaped, randomly oriented grains. Magneto-optic Kerr effect (MOKE) measurements show good magnetic properties for films on GaAs, such as strong in-plane anisotropy and squareness of the hysteresis loop in the easy direction. A Curie temperature of 340 K, remarkably higher than the bulk material (315 K), was found for a 65 nm thick film on GaAs. Films grown on bare and oxidised silicon wafers had lower Curie temperature and were magnetically isotropic.

PACS: 81.15.Gh; 75.50.Dd; 75.70.−i

Keywords: MOVPE; Ferromagnetism; Spintronics; Thin film; Epitaxy

1. Introduction

The semimetallic compounds MnAs and MnSb recently have attracted a lot of attention in the field of spintronics due to their room-temperature ferromagnetism and the possibility to grow high-quality epitaxial films on different semiconductor substrates [1–4]. These materials have so far mainly been grown by molecular beam epitaxy (MBE) while only recently there have been reports [5] on their deposition by metalorganic vapour-phase epitaxy (MOVPE), which is the deposition technique preferred by the semiconductor industry. In the present work, we investigate the structural, morphological and magnetic properties of MnAs thin films grown by means of MOVPE on GaAs(0 0 1), Si(0 0 1) and oxidised silicon substrates.

*Corresponding author. Tel.: +039 049 8295930; fax: +039 049 8702911.
E-mail address: natali@icis.cnr.it (M. Natali).

0304-8853/$ - see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.jmmm.2007.02.086

2. Experimental

Films were grown using a low-pressure Aixtron AIX200 MOVPE cold wall reactor. Precursors used were AsH_3 for As and methylcyclopentadienyl-manganese-tricarbonyl for Mn, respectively. Pd-purified H_2 gas was used as carrier gas. Films were simultaneously grown on bare GaAs(0 0 1) and Si(0 0 1) wafers and oxidised Si wafers (covered by a 200 nm thick SiO_2 film). Film thickness was measured by profilometer scans by scratching the film with a metal tip. Phase identification was performed by X-ray diffraction (XRD) measurements using a Philips PW1830 powder diffractometer, using Ni-filtered CuK_α radiation. Here, the reported measurements were performed using a parallel-plate collimator before the Xe gas proportional detector. Composition analysis was performed by SEM-EDS measurements using a Philips XL30 SEM [6]. The surface morphology of the films was investigated by atomic force microscopy (AFM) with a DME dualscope instrument using Si cantilever tips from NT-NDT.

Magneto-optic Kerr effect (MOKE) measurements were performed in longitudinal geometry using an He–Ne laser with a wavelength of 632.8 nm and an output power of 5 mW as light source. The MOKE measurements were performed in the temperature range 10–350 K.

3. Results

In Fig. 1 are shown grazing-incidence XRD spectra of MnAs films grown on GaAs, Si and SiO_2/Si substrates together with ICCD pattern # 71-0923 of hexagonal α-MnAs. The α-MnAs peaks are clearly observed in all three samples. We attribute the additional peaks to substrate and sample holder peaks. From the literature, α-MnAs is known to be ferromagnetic with a bulk Curie temperature $T_c = 315$ K. No peaks of the paramagnetic β-MnAs phase could be detected in any of the samples.

To investigate the texture of the samples we performed ω scans and ϕ scans on selected peaks as illustrated in Fig. 2. From the ω scan of the (10–12) peak, four preferential orientations are found that are pairwise symmetric with respect to the [0 0 1]GaAs surface normal. From the two strong/broad peaks, named C in Fig. 2b, we deduce inclinations of the α-MnAs [0 0 0 1] direction (*c*-axis) of $\pm 55°$ with respect to the [0 0 1]GaAs surface normal. These angles are the same as that of inclined (1 1 1)GaAs planes. We speculate that although the GaAs surface nominally is a (0 0 1) surface, its roughening before the MnAs growth eventually leads to the development of nanoscale (1 1 1) facets that could induce MnAs(0001)//GaAs(1 1 1) epitaxy, thus explaining peaks C. The two weaker/sharper peaks in Fig. 2b, named B, correspond to inclinations of the *c*-axis of $\pm 61°$ with respect to the [0 0 1]GaAs surface normal or equivalently $\pm 29°$ with respect to the surface plane. These orientations are typical of the so-called "B-type" growth [7]. A ϕ scan performed on one of C-type peaks is shown in Fig. 2c. A strong in-plane anisotropy is observed, compatible with a situation in which the in-plane projection of the *c*-axis aligns parallel to the [1 1 0] GaAs direction. Two symmetrically inclined α-MnAs unit cells are sketched in Fig. 2d. The presence of similar symmetric orientations has been previously observed in Ref. [8] for MnAs grown on GaAs(0 0 1) pre-coated with few monolayers of InAs self-assembling as nano-islands. Formation of microtwins was explained by the role of inclined (1 1 1) InAs island facets.

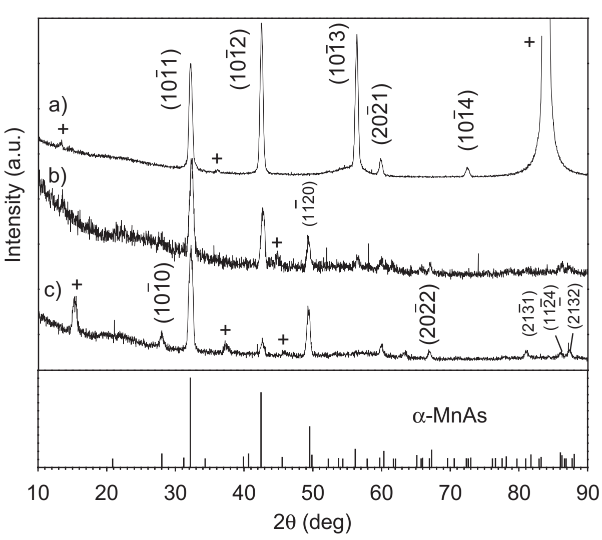

Fig. 1. XRD grazing-incidence ($\omega = 7°$) spectra of MnAs films deposited at $T = 475\,°C$ $P = 50$ mbar on different substrates. Film thickness and stoichiometry are (a) GaAs substrate: $t = 70 \pm 15$ nm Mn = 57.8 at% (b) Si(1 0 0) substrate: $t = 100 \pm 17$ nm Mn = 47.5 at%, (c) oxidised Si substrate: $t = 141 \pm 6$ nm Mn = 42.0 at%. Crosses indicate substrate and sample holder peaks.

No structural anisotropy was found in the XRD spectra of our films grown on bare and oxidised Si wafers that on the contrary, indicate an almost random polycrystalline texture.

In Fig. 3 are shown AFM images of samples grown on bare and oxidised silicon as well as on GaAs substrates. The morphology of the films is granular with apparently randomly distributed grains in the case of bare and oxised Si substrates and elongated, oriented grains parallel to [1 –1 0] in the case of GaAs substrates. By comparing the XRD and AFM data, we deduce that for growth on GaAs the inclined *c*-axis of MnAs is perpendicular to the long axis of the grains.

To investigate the magnetic properties we performed MOKE measurements. MOKE loops of a 65 nm thick MnAs film grown on GaAs (Mn = 58.8 at%), measured with the external field sweeping along the [1 –1 0] and [1 1 0] GaAs directions, are shown in Fig. 4. The film exhibits strong magnetic anisotropy: hysteresis is not observed when the field H is applied along the [1 1 0]GaAs direction while a squared loop is observed when the field H is applied along [1 –1 0]. The observation of a nearly square hysteresis loop is consistent with the fact that [1 –1 0]GaAs in our samples is parallel to a <11–20> α-MnAs direction that is known as MnAs easy axis. The hard axis of α-MnAs is known to be the *c*-axis. When the field is applied parallel to [1 1 0]GaAs, it is neither parallel to the easy axis nor to the hard axis. The absence of hysteresis is in agreement with MOKE measurements on similar "B-type" MnAs/GaAs films reported in Ref. [7].

For our 65 nm thick MnAs film a Curie temperature of about 340 K was found, obtained by following the temperature dependence of the coercive field along the easy magnetisation direction. This value is similar to that obtained on epitaxial MnAs film grown on GaAs (0 0 1) by MBE [9]. MnAs films grown on bare and oxidised silicon substrates do not show any magnetic anisotropy, confirming the randomness of the grain distributions. The coercive field for a 100 nm thick MnAs grown on bare Si measured at room temperature is $H_C = 433 \pm 5$ Oe, while for a 140 nm thick film grown on oxidised Si $H_C = 250 \pm 5$ Oe. The hysteresis loops (Fig. 5) are rounded compared to that of MnAs grown on GaAs indicating a magnetic disorder.

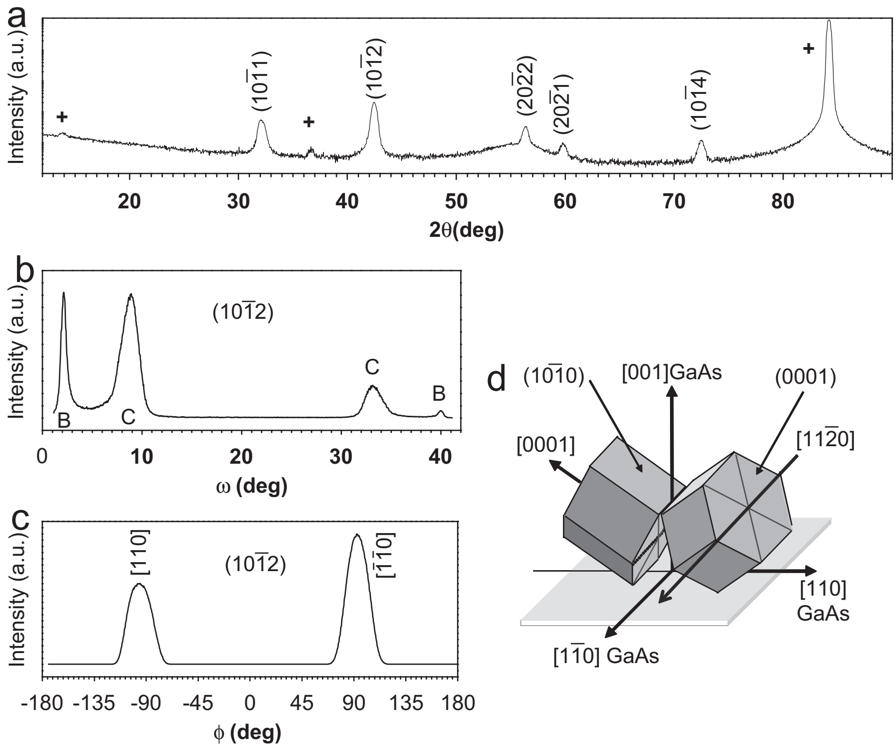

Fig. 2. XRD spectra of α-MnAs film on GaAs(0 0 1) substrate ($t = 90 \pm 10$ nm Mn = 49.9 at%): (a) 2θ scan recorded at grazing incidence angle $\omega = 7°$. Substrate and sample holder peaks are indicated by crosses, (b) ω scan for the (10–12) α-MnAs reflection and (c) ϕ scan for $\omega = 9°$, $2\theta = 42.4°$ corresponding to the C-type (10–12) α-MnAs peaks.

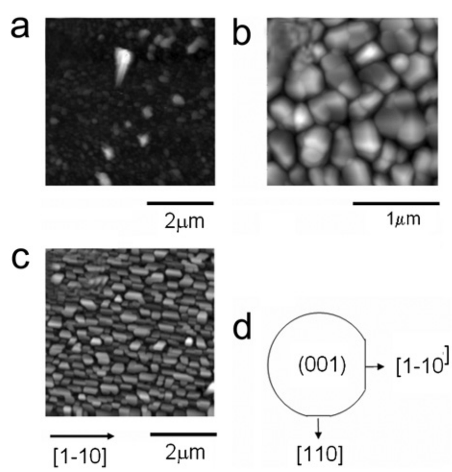

Fig. 3. AFM images of MnAs films grown at $T = 475\,°C$ $P = 20$ mbar on a) bare Si(0 0 1), (b) oxidised Si and (c) (0 0 1) GaAs substrates. In (d) is illustrated the SEMI-2 flat specification of the GaAs wafer used.

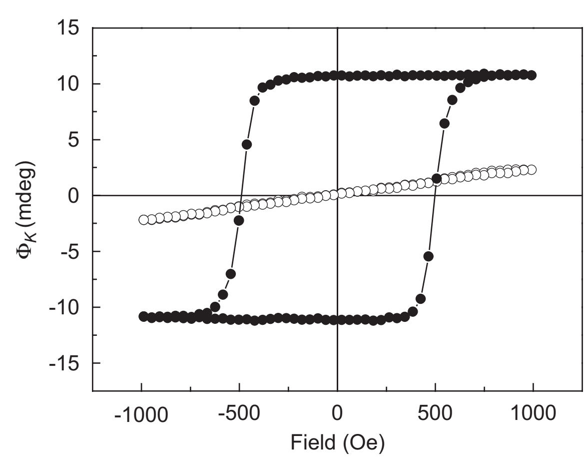

Fig. 4. Room-temperature hysteresis loop of MnAs films grown on (0 0 1)GaAs substrate. The magnetic field is applied perpendicularly (open circles) or parallel to (full circle) the [1 –1 0] of GaAs substrate.

The Curie temperature of MnAs films on Si was $T_C = 330$ K.

Concerning the absence of β-MnAs in our samples, we note that in Ref.[10], the existence of the β-phase below the Curie temperature was attributed to compressive strain, arising during the β–α phase transition during cooling down from the growth temperature, due to the constraint with the substrate. We speculate that the high surface roughness of our films is effective in relaxing such strains, thereby suppressing the β-phase at room temperature. Concerning the increased Curie temperature compared to the bulk value, tensile strain is known to play an important role [4,9]. Structural measurements to determine the strain of our samples as well as temperature-dependent XRD measurements are work in progress.

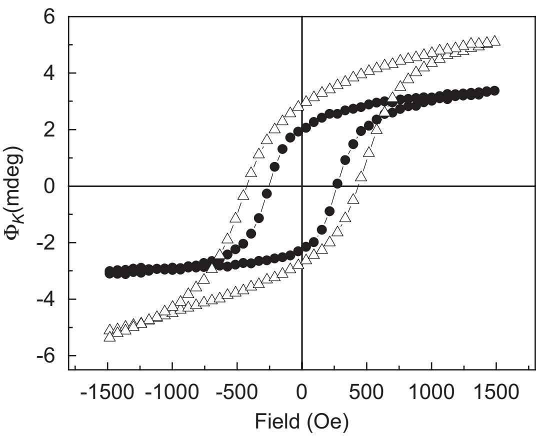

Fig. 5. Room-temperature hysteresis loops of MnAs films grown on bare Si (open triangle) and oxidised silicon (full circle).

4. Conclusions

Ferromagnetic α-MnAs films were grown by MOVPE on different semiconductor substrates. Films grown on (0 0 1) GaAs show ansiotropic structural, morphological and magnetic behaviour and a significantly increased Curie temperature compared to bulk MnAs ($T_C = 340\,K$), whereas films on bare and oxidised (0 0 1) Si are isotropic and have a lower Curie temperature.

References

[1] K. Ono, T. Uragami, M. Miziguchi, H. Fujioka, M. Oshima, M. Tanaka, H. Akinaga, J. Cryst. Growth 209 (2000) 556.
[2] M. Tanaka, Physica E 2 (1998) 372.
[3] A.K. Das, et al., Phys. Rev. Lett. 91 (2003) 87203.
[4] A. Ney, T. Hesjedal, L. Däweritz, R. Koch, K.H. Ploog, J. Magn. Magn. Mater. 288 (2005) 173.
[5] P.A. Lane, B. Cockayne, P.J. Wright, P.E. Oliver, M.E.G. Tisley, N.A. Smith, I.R. Harris, J. Cryst. Growth 143 (1994) 237.
[6] In the case of films on GaAs substrates the Mn:As ratio was determined by considering that the As signal is the sum of film and substrate contributions: %As(tot) = %As(sub) + %As(film). Since %As(sub) = %Ga(sub) we find %As(film) = %As(tot)—%Ga(sub).
[7] M. Tanaka, J.P. Harbison, M.C. Park, Y.S. Park, T. Shin, G.M. Rothberg., Appl. Phys. Lett. 65 (1994) 1964.
[8] H.S. Lee, T.W. Kim, D.U. Lee, H.C. Jeon, T.W. Kang, K.H. Lee, J.Y. Lee, Appl. Phys. Lett. 87 (2005) 71907.
[9] Y. Park, Y.-J. Shin, J. Kor. Phys. Soc. 37 (2000) 569.
[10] V.M. Kaganer, B. Jennichen, F. Schippan, W. Braun, L. Däweritz, K.H. Ploog., Phys. Rev. Lett. 85 (2000) 341.