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Strain-induced high ferromagnetic transition temperature of MnAs epilayer grown on GaAs (110)

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Abstract

MnAs films are grown on GaAs surfaces by molecular beam epitaxy. Specular and grazing incidence X-ray diffractions are used to study the influence of different strain states of MnAs/GaAs (110) and MnAs/GaAs (001) on the first-order magnetostructural phase transition. It comes out that the first-order magnetostructural phase transition temperature T_t, at which the remnant magnetization becomes zero, is strongly affected by the strain constraint from different oriented GaAs substrates. Our results show an elevated T_t of 350 K for MnAs films grown on GaAs (110) surface, which is attributed to the effect of strain constraint from different directions.
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Introduction

Today, there is growing interest for realization of new technologies utilizing spin degree of freedom of electrons in semiconductor devices [1]. The technology of manipulating spin in semiconductors promises devices with enhanced functionality and higher speed. A prerequisite for realization of such kind of devices is development of solid-state spin injectors at room temperature. Diluted magnetic semiconductors (DMSs) and ferromagnet/semiconductor hybrids are two important components for efficient spin injection. The exploitation of DMSs, however, is severely hindered by their low Curie temperature due to the low solubility of transition metals in semiconductors [2,3]. With room-temperature ferromagnetism and high crystal quality, MnAs has been epitaxied on (001)-, (110)-, (111)-, and (113)-oriented GaAs substrates [4-9]. Moreover, MnAs/GaAs having sharper interface than that of Fe/GaAs has been presented [10,11]; the sharp interface is considered to be crucial for obtaining higher transmission efficiencies. Recently, spin injection from MnAs into GaAs has been demonstrated [12], and the spin-dependent tunneling experiments show that the spin polarization at MnAs/

GaAs interfaces is high [13,14]. Therefore, MnAs/GaAs hybrid is attracting more and more attention for its potential applications in spin injection, magnetic tunneling junctions, and magnetically logic devices.

The first-order magnetostructural phase transition is a long-standing topic in magnetism [15-20]. Bulk MnAs shows a coupled first-order magnetostructural phase transition from the ferromagnetic hexagonal α-phase (P6(3)/mmc) to the paramagnetic orthorhombic β-phase (Pnma) which is contracted in volume by 2% at about 318 K. For epitaxial MnAs films on GaAs substrate, the transition proceeds continuously over a broad temperature range with coexistence of the two phases. The phase coexistence results in a considerable fraction of MnAs epitaxial films which are usually in paramagnetic phase at ~30°C, a strong limitation for room temperature spintronic devices. The first-order magnetostructural phase transition temperature T_t, at which the remnant magnetization becomes zero, can be enhanced either by applying an external magnetic field or by growing MnAs films on different oriented GaAs substrates [21]. For example, T_t for MnAs films grown on GaAs (111)B is higher than that grown on GaAs (001) [18,22,23].

Epitaxial MnAs films on GaAs (001) and GaAs (111)B have been thoroughly investigated [4-6], while little attention has been paid to MnAs films grown on GaAs (110) [7]. The spin relaxation time is considered crucial

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important for practical application of spin memory devices or spin quantum computers. In GaAs (110) quantum wells, the spin relaxation time is in nanosecond range, much longer than that in GaAs (001) where the spin relaxation time is in picoseconds range [7]. More work is expected for investigation of MnAs films grown on GaAs (110) surfaces. In this work, we will present that epitaxial MnAs films grown on GaAs (110) are with a different strain states from MnAs films grown on GaAs (001), and α-phase can coexist with β-phase to a higher temperature (remnant magnetization becomes zero when the temperature reaches 350 K).

Experimental procedure

The MnAs films were grown on GaAs (110) and GaAs (001) substrates by molecular beam epitaxy with a 12-keV reflection high-energy electron diffraction (RHEED) to monitor the growth process. Before growth of MnAs, a 100-nm GaAs buffer layer was grown to smoothen the surface. For MnAs films grown on GaAs (110), the buffer layer was grown at a lower substrate temperature T_s = 400°C and higher As_4/Ga beam equivalent pressure (BEP) ratio of 50, while for the buffer layer grown on GaAs (001), a standard procedure (T_S = 560°C, As_4/Ga = 12) was used. The growth parameters and thickness of MnAs films on GaAs (110) and GaAs (001) are shown in Table 1. During MnAs growth, the surface is (1 × 2) reconstructed. By analyzing RHEED patterns taken during growth of MnAs, we get the following epitaxial relationship: $(1\bar{1}00)$ MnAs//(110) GaAs, [0001] MnAs//[001] GaAs, and $(11\bar{2}0)$ MnAs//$[1\bar{1}0]$ GaAs. The streaky RHEED pattern becomes sharper after *in situ* cooling the sample from growth temperature to room temperature, indicating enhancement of crystal quality. The microstructure and interface of the MnAs films were characterized by high-resolution cross-sectional transmission electron microscopy (HRTEM), while the study of the magnetic domain structures was carried out by using magnetic force microscope (MFM). By using tapping/lift modes, the topographic and magnetic force images may be collected separately and simultaneously in the same area of the sample. The magnetic property of all the samples was measured by superconducting quantum interference device magnetometry with magnetic field parallel to the surface of samples. Anisotropic strain of the thin MnAs films was characterized by X-ray diffraction

(XRD). The XRD experiments were performed at the U7B beam line of National Synchrotron Radiation Laboratory of China using a 0.154-nm wavelength monochromatic beam, which is selected through a double-crystal Si (111) monochromator, and triple-axis mode was used in these measurements in order to achieve high resolution. Strain information was obtained through measurements of in-plane and out-of-plane diffractions in the $\omega/2\theta$ scan mode. Specially, grazing incidence geometry was performed for in-plane measurements (IP-GIXD).

Results and discussion

Atomic force microscopy (AFM) and MFM images taken from the growth surface are shown in Figure 1. One can see from Figure 1 that there is no evident stripe pattern in AFM images. Generally, all the samples in this study are very thin, and the stripe height is roughly 1% of the film thickness. As shown in Figure 1, the magnetic domains are randomly distributed in MFM images for MnAs films grown on both GaAs (110) and GaAs (001). We also observed the cross-sectional MFM images for MnAs/GaAs (001) and MnAs/GaAs (110). Although we can see sharp interfaces between MnAs and GaAs from Figure 2a,b, we cannot see evident borders between ferromagnetic α-phase and paramagnetic β-phase, indicating that the two phases are mixing together. Our results are different from observations in a 200-nm MnAs film epitaxied on GaAs (001) presented in [24], in which ferromagnetic α-phase and paramagnetic β-phase are obviously separated. We assumed this phenomenon resulted from the too thin thickness of MnAs layer. Figure 3 shows the HRTEM image of sample D, MnAs/GaAs (110), from which we can observe that MnAs films have a well-ordered crystal orientation and a sharp interface between MnAs and GaAs. Judged from the chromatic aberration of MnAs and GaAs substrate, the thickness of the epitaxial MnAs film is 11 nm.

The remnant magnetization M_r as a function of temperature T is plotted in Figure 4a. The linear decrease of M_r at low temperature is caused by thermal fluctuation, while the rapid decreasing at high temperature is caused by structural transition from hexagonal phase to orthorhombic phase. As the thickness can change magnetic property of MnAs epilayer [7,25], M_r becomes zero when the temperature reaches 340 and 350 K for samples B and sample D, respectively. In accordance

Table 1 Growth parameters and the thickness for samples A-D

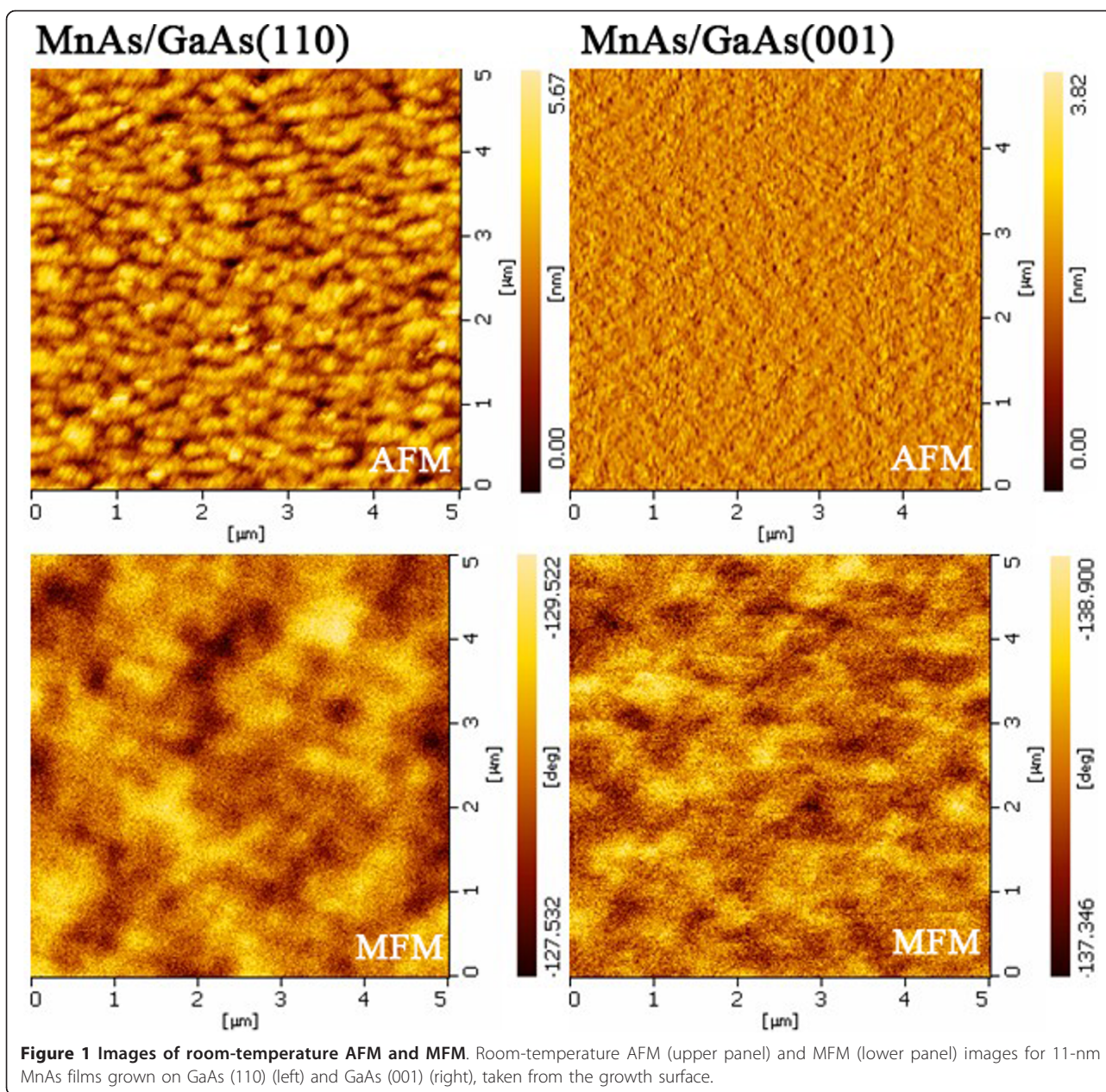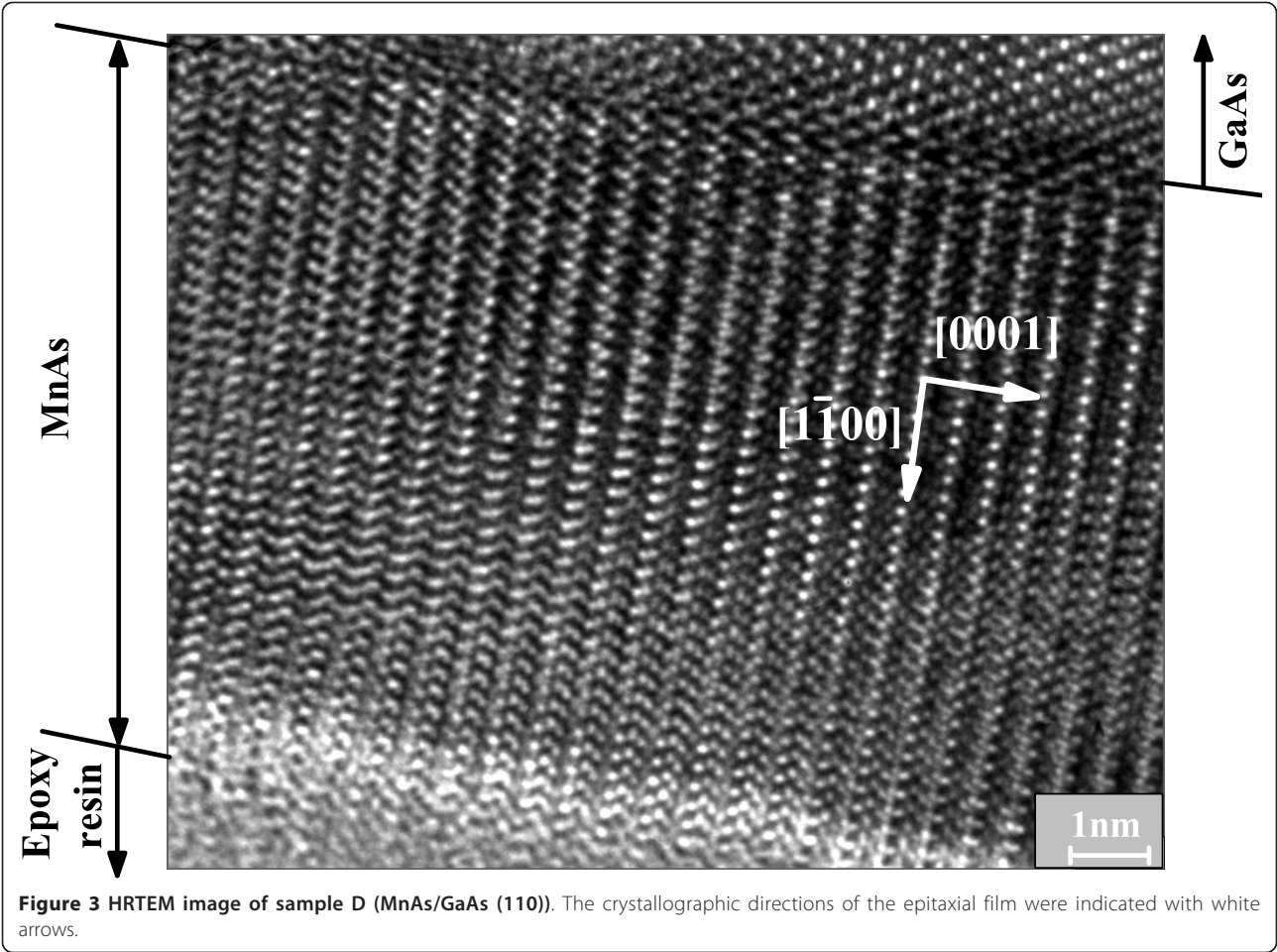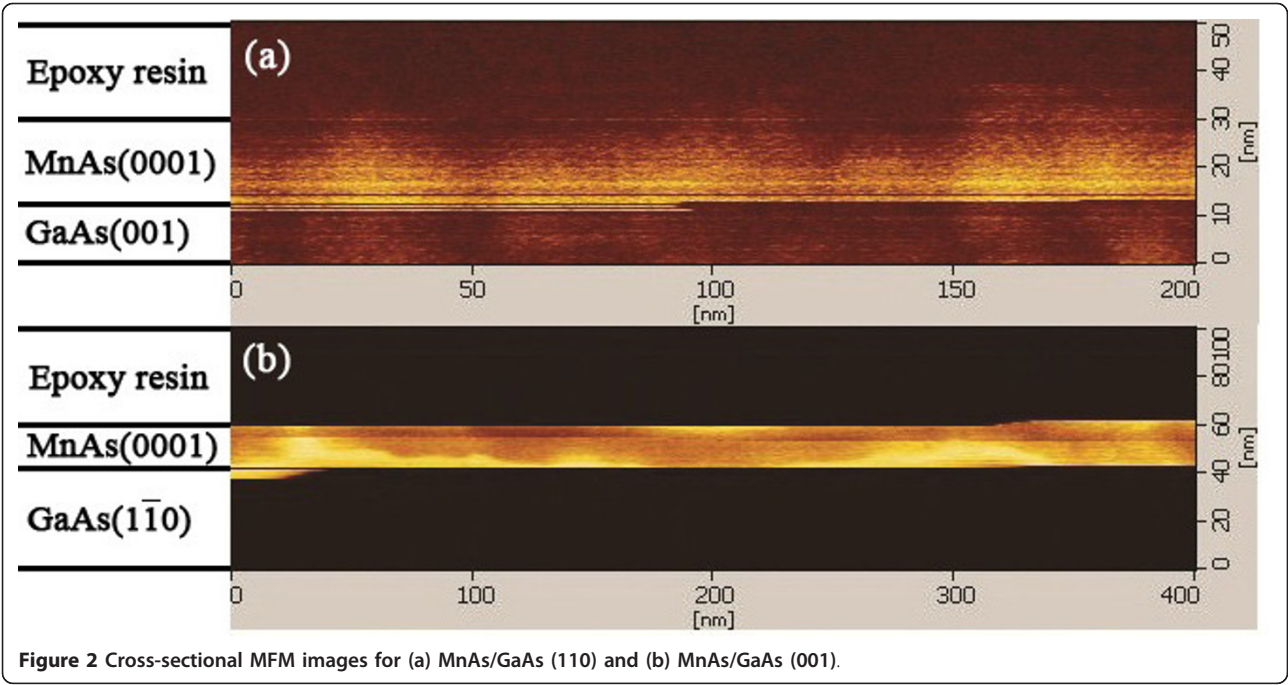| Sample	Growth temperature (°C)	As_4/Mn BEP ratio	Furnace cooling	Thickness (nm)	GaAs substrate
A	230	300	N	11	GaAs (001)
B	210	175	N	3	GaAs (110)
C	210	300	N	11	GaAs (110)
D	210	175	Y	11	GaAs (110)

Figure 1 Images of room-temperature AFM and MFM. Room-temperature AFM (upper panel) and MFM (lower panel) images for 11-nm MnAs films grown on GaAs (110) (left) and GaAs (001) (right), taken from the growth surface.

with RHEED pattern analysis given above, M_r exceeds 1,200 emu/cm^3 at 5 K for sample D, which is a bit larger than the saturation magnetization reported for MnAs/GaAs (001) at 10 K with little crystal defect and optimum intra- and inter-stripe magnetic coupling [26]. The remarkable magnetic property difference between sample C and sample D may originate from the different growth conditions, such as the low substrate temperature and over pressure of As$_4$ for sample C, or different stoichiometry. Figure 4b shows *M-H* hysteresis loops measured at room temperature with magnetic field applied along the direction of MnAs $(11\bar{2}0)$, the easy axis of magnetization. The magnetization hysteresis

loops show a perfect square form for all the samples studied here.

In order to probe the effect of anisotropic strain on the first-order magnetostructural phase transition, we performed synchrotron XRD measurements. The experimental results are shown in Figure 5. The orthorhombic notation is used for the α-phase lattice parameters, in which a_{ortho}, b_{ortho}, and c_{ortho} stand for the spacing between MnAs (0001), MnAs $(11\bar{2}0)$, and MnAs $(1\bar{1}00)$, respectively. The lattice parameters, primitive cell volume, and transition temperature are shown in Table 2. Early in the 1960s, Bean and Rodbell and Menyuk et al. concluded that T_t is proportional to the
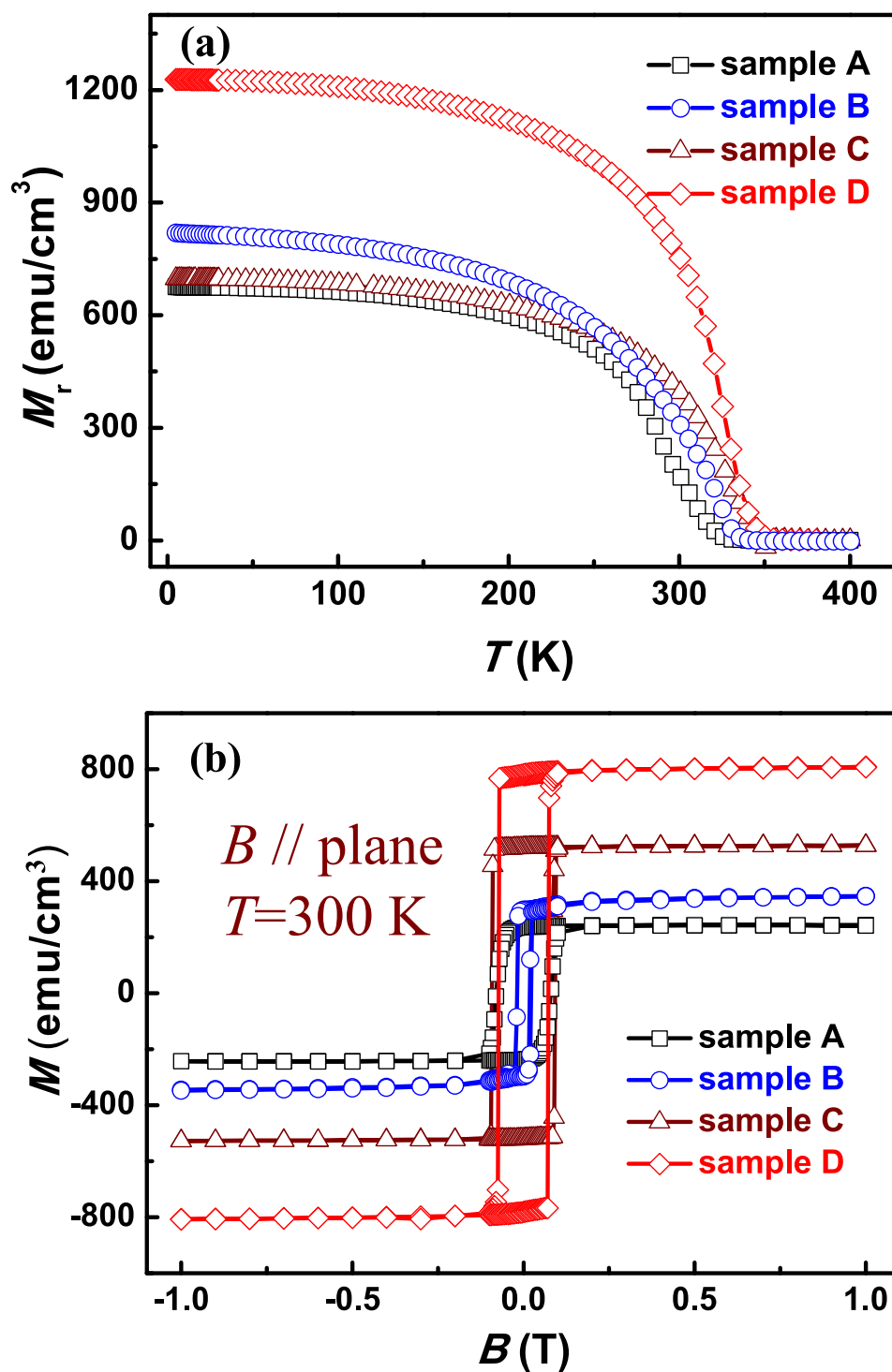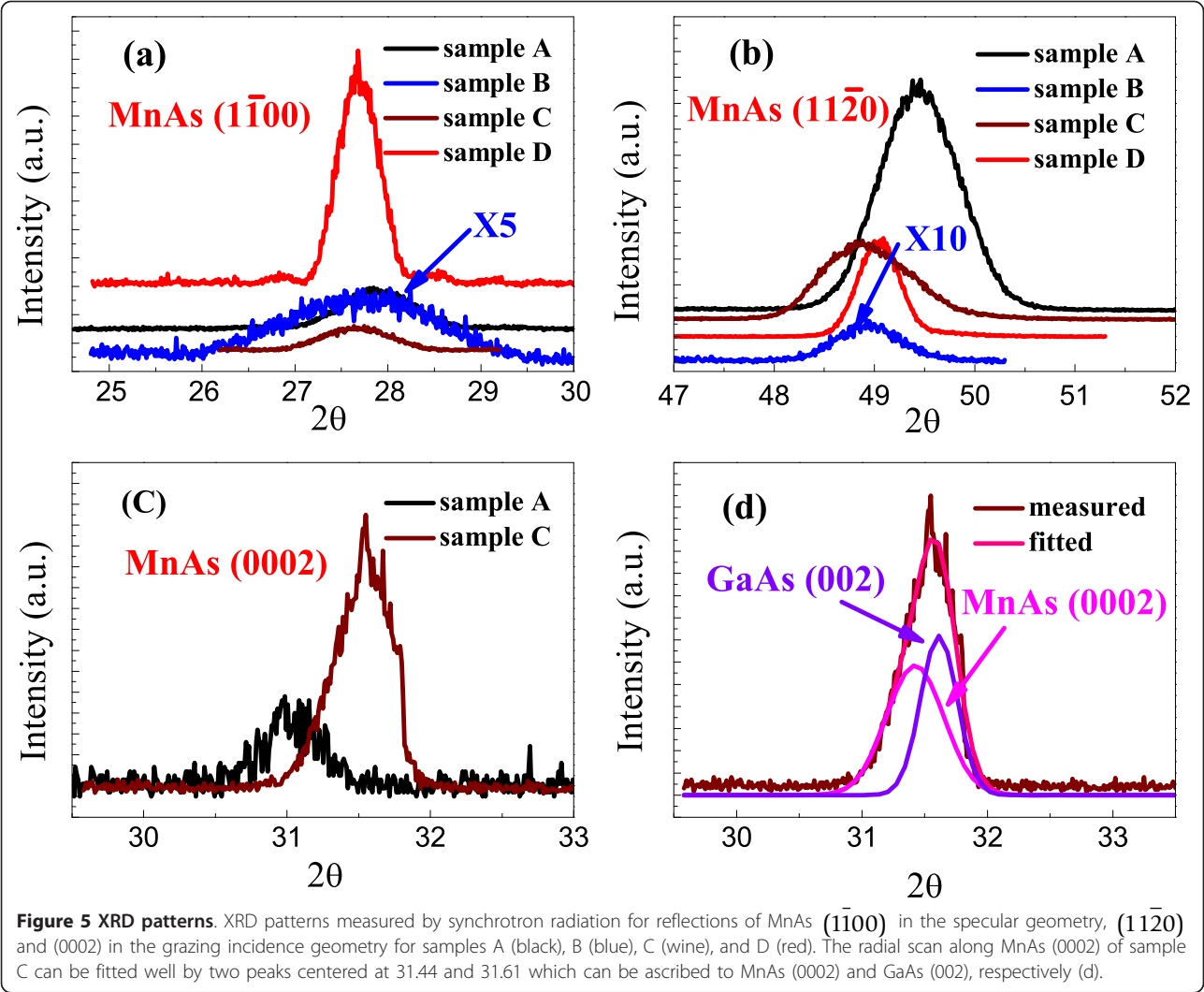
Figure 2 Cross-sectional MFM images for (a) MnAs/GaAs (110) and (b) MnAs/GaAs (001).

Figure 3 HRTEM image of sample D (MnAs/GaAs (110)). The crystallographic directions of the epitaxial film were indicated with white arrows.

Figure 4 Temperature dependence and magnetic field dependence of magnetization. a Temperature dependence of the remnant magnetization M_r for samples A-D. M_r remains over zero even when the temperature reaches 340 and 350 K for samples B and D, respectively. **b** The magnetic field dependence of magnetization for MnAs grown on GaAs (110) and GaAs (001) at 300 K, under a magnetic field applied along the easy axis of magnetization.

Figure 5 XRD patterns. XRD patterns measured by synchrotron radiation for reflections of MnAs $(1\bar{1}00)$ in the specular geometry, $(11\bar{2}0)$ and (0002) in the grazing incidence geometry for samples A (black), B (blue), C (wine), and D (red). The radial scan along MnAs (0002) of sample C can be fitted well by two peaks centered at 31.44 and 31.61 which can be ascribed to MnAs (0002) and GaAs (002), respectively (d).

primitive cell volume and a larger primitive cell volume (V) corresponds to a higher T_t based on the magnetostrictive model [15,16]. Clearly our experimental results cannot be explained by a simple effect of primitive cell volume variation, and T_t is not a linear function of V. For example, as to all the epitaxial films studied here,

the primitive cell volume is smaller than that of the bulk material, while ferromagnetic hexagonal α-phase can coexist with paramagnetic orthorhombic β-phase to a higher temperature. Furthermore, there is remarkable difference between lattice parameters for MnAs films grown on GaAs (001) and GaAs (110). For sample A, grown on GaAs (001), a_{ortho} is larger, while b_{ortho} and c_{ortho} are smaller than that for sample D, grown on GaAs (110). In good agreement with the experimental and theoretical results of Iikawa et al. [23], all these changes result in a lower transition temperature (stretching of the lattice parameters in the basal plane results in a higher T_t, while stretching of lattice parameters along the perpendicular direction lowers T_t).

Summary

In summary, we have shown that the ferromagnetic order in MnAs can be extended to higher temperature by growing MnAs on GaAs (110). Ferromagnetic

Table 2 Lattice parameters, primitive cell volume, and transition temperature of samples A-D and MnAs bulk [27]

	MnAs bulk	Sample A	Sample B	Sample C	Sample D
a (Å)	5.71	5.78	**5.71**	5.67	**5.69**
b (Å)	3.72	3.69	3.73	3.72	3.72
c (Å)	6.45	6.41	6.43	6.45	6.45
T_t (Å)	313	325	335	350	350
V (Å^3)	137.06	136.71	136.95	136.05	136.53

The lattice parameters shown in boldface were calculated from elastic constant tensor of MnAs.

α-phase can coexist with paramagnetic β-phase to 350 K. By XRD measurements, it is found that T_t is not a simple function of primitive cell volume, and stretching of lattice parameters in the basal plane or compressing of lattice parameter in the perpendicular direction results in a higher T_t. The result described here attests to a strong link between anisotropic strain and epilayer properties. Understanding and mastering these characterizations may open a possibility to control magnetic properties via selection of substrate orientation and provide new possibilities for using MnAs epilayer in spintronic devices.

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Authors' contributions
PX, JL, LC, SY, HM carried out the sample preparation. PX, JL and GP participated in the XRD Measurements. PX carried out the MFM and SQUID measurements, the statistical analysis and drafted the manuscript. JZ conceived of the study and participated in its design and coordination. All authors read and approved the final manuscript.

Competing interests
The authors declare that they have no competing interests.

References
1. Zhao YJ, Geng WT, Freeman AJ: **Structural, electronic, and magnetic properties of α- and β-MnAs: LDA and GGA investigations.** *Phys Rev B* 2002, **65**:113202.
2. Bonanni A: **Ferromagnetic nitride-based semiconductors doped with transition metals and rare earths.** *Semicond Sci Technol* 2007, **22**:R41.
3. Bonanni A, Simbrunner C, Wegscheider M, Przybylinska H, Wolos A, Sitter H, Jantsch W: **Doping of GaN with Fe and Mg for spintronics applications.** *Phys Stat Sol (b)* 2006, **243**:1701.
4. Schippan F, Trampert A, Däweritz L, Ploog KH, Dennis B, Neumann KU, Ziebeck KRA: **Microstructure formation during MnAs growth on GaAs(0 0 1).** *J Cryst Growth* 2000, **201/202**:674.
5. Tanaka M, Saito K, Nishinaga T: **Epitaxial MnAs/GaAs/MnAs trilayer magnetic heterostructures.** *Appl Phys Lett* 1999, **74**:64.
6. Däweritz L, Kästner M, Hesjedal T, Plake T, Jenichen B, Ploog KH: **Structural and magnetic order in MnAs films grown by molecular beam epitaxy on GaAs for spin injection.** *J Cryst Growth* 2003, **251**:297.
7. Kolovos-Vellianitis D, Herrmann C, Däweritz L, Ploog KH: **Structural and magnetic properties of epitaxially grown MnAs films on GaAs(110).** *Appl Phys Lett* 2005, **87**:092505.
8. Akinaga H, Miyanishi S, Tanaka K, Van Roy W, Onodera K: **Magneto-optical properties and the potential application of GaAs with magnetic MnAs nanoclusters.** *Appl Phys Lett* 2000, **76**:97.
9. Akinaga H, De Boeck J, Borghs G, Miyanishi S, Asamitsu A, Van Roy W, Tomioka Y, Kuo LH: **Negative magnetoresistance in GaAs with magnetic MnAs nanoclusters.** *Appl Phys Lett* 1998, **72**:3368.
10. Schippan F, Trampert A, Däweritz L, Ploog KH: **Kinetics of MnAs growth on GaAs(001) and interface structure.** *J Vac Sci Technol B* 1999, **17**:1716.
11. Lu J, Meng HJ, Deng JJ, Xu PF, Chen L, Zhao JH, Jia QJ: **Strain and magnetic anisotropy of as-grown and annealed Fe films on c(4 × 4) reconstructed GaAs (001) surface.** *J Appl Phys* 2009, **106**:013911.
12. Stephens J, Berezovsky J, McGuire JP, Sham LJ, Gossard AC, Awschalom DD: **Spin accumulation in forward-biased MnAs/GaAs schottky diodes.** *Phys Rev Lett* 2004, **93**:097602.
13. Garcia V, Jaffrès H, Eddrief M, Marangolo M, Etgens VH, George JM: **Resonant tunneling magnetoresistance in MnAs/III-V/MnAs junctions.** *Phys Rev B* 2005, **72**:081303(R).
14. Garcia V, Jaffrès H, George JM, Marangolo M, Eddrief M, Etgens VH: **Spectroscopic measurement of spin-dependent resonant tunneling through a 3D disorder: The case of MnAs/GaAs/MnAs junctions.** *Phys Rev Lett* 2006, **97**:246802.
15. Bean CP, Rodbell DS: **Magnetic disorder as a first-order phase transformation.** *Phys Rev* 1962, **126**:104.
16. Menyuk N, Kafalas JA, Dwight K, Goodenough JB: **Effects of pressure on the magnetic properties of MnAs.** *Phys Rev* 1969, **177**:942.
17. Zhao YJ, Zunger A: **Zinc-blende half-metallic ferromagnets are rarely stabilized by coherent epitaxy.** *Phys Rev B* 2005, **71**:132403.
18. Garcia V, Sidis Y, Marangolo M, Vidal F, Eddrief M, Bourges P, Maccherozzi F, Ott F, Panaccione G, Etgens VH: **Biaxial strain in the hexagonal plane of MnAs thin films: The key to stabilize ferromagnetism to higher temperature.** *Phys Rev Lett* 2007, **99**:117205.
19. Jenichen B, Kaganer VM, Kästner M, Herrmann C, Däweritz L, Ploog KH, Darowski N, Zizak I: **Structural and magnetic phase transition in MnAs (0001)/GaAs(111) epitaxial films.** *Phys Rev B* 2003, **68**:132301.
20. Kaganer VM, Jenichen B, Schippan F, Braun W, Däweritz L, Ploog KH: **Strain-mediated phase coexistence in MnAs heteroepitaxial films on GaAs: An x-ray diffraction study.** *Phys Rev B* 2002, **66**:045305.
21. Ney A, Hesjedal T, Däweritz L, Koch R, Ploog KH: **Extending the magnetic order of MnAs films on GaAs to higher temperatures.** *J Magn Magn Mater* 2004, **288**:173.
22. Das AK, Pampuch C, Ney A, Hesjedal T, Däweritz L, Koch R, Ploog KH: **Ferromagnetism of MnAs studied by heteroepitaxial films on GaAs(001).** *Phys Rev Lett* 2003, **91**:087203.
23. Iikawa F, Brasil MJSP, Adriano C, Couto ODD, Giles C, Santos PV, Däweritz L, Rungger I, Sanvito S: **Lattice distortion effects on the magnetostructural phase transition of MnAs.** *Phys Rev Lett* 2005, **95**:077203.
24. Rache Salles B, Marangolo M, David C, Girard JC: **Cross-sectional magnetic force microscopy of MnAs/GaAs(001).** *Appl Phys Lett* 2010, **96**:052510.
25. Däweritz L, Wan L, Jenichen B, Herrmann C, Mohanty J, Trampert A, Ploog KH: **Thickness dependence of the magnetic properties of MnAs films on GaAs(001) and GaAs(113)A: Role of a natural array of ferromagnetic stripes.** *J Appl Phys* 2004, **96**:5056.
26. Berry JJ, Potashnik SJ, Chun SH, Ku KC, Schiffer P, Samarth N: **Two-carrier transport in epitaxially grown MnAs.** *Phys Rev B* 2001, **64**:052408.
27. Willis BTM, Rooksby HP: **Magnetic transitions and structural changes in hexagonal manganese compounds.** *Proc Phys Soc Sect B* 1954, **67**:290.