Ferromagnetism of MnAs Studied by Heteroepitaxial Films on GaAs(001)

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Thin epitaxial films of MnAs—promising canditates for the spin injection into semiconductors—are well known to undergo simultaneously a first-order structural and magnetic phase transition at 10–40 °C. The evolution of stress and magnetization of MnAs/GaAs(001), both measured quantitatively with our cantilever beam magnetometer at the coexistance region of α-MnAs and β-MnAs, reveal an orthorhombically distorted unit cell of the ferromagnetic phase, which provides important clues on the origin of ferromagnetism in MnAs.

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Manganese arsenide—a room temperature ferromagnet of the pnictides (MnX with $X = \mathrm{P}$, As, Sb, Bi)—is one of the rarely found ferromagnetic metals which can be easily combined with the two technologically leading semiconductor substrates, Si(001) and GaAs(001), yielding high quality epitaxial films by molecular beam epitaxy (MBE) [1–4]. Owing to the negligible interdiffusion, a main advantage of the MnAs films over, e.g., Fe/GaAs(001) [5], is the formation of sharp interfaces [6]. This makes it a promising material for the injection of spin information [7] in future semiconductor devices.

Furthermore, there is also great fundamental interest in MnAs. In the bulk, the magnetic phase transition is coupled to a structural one and proceeds abruptly at about 40 °C [8,9]. First order of the transition is confirmed by observations of a latent heat, a temperature hysteresis [10], and a discontinuity of the lattice parameter [11]. The ferromagnetic α-MnAs crystallizes in the hexagonal NiAs structure with alternating hexagonal planes of Mn and As atoms [Fig. 1(a)]. The lattice of the paramagnetic β-MnAs, on the other hand, is orthorhombic and contracted in volume by about 2% [11]; since the orthorhombic distortion is small, β-MnAs is often regarded as quasihexagonal [8]. In thin MnAs($\bar{1}100$) films on GaAs(001), on the contrary, the transition from α to β phase proceeds continuously. However, this is not due to a change to a second-order phase transition but to the coexistence of both phases in the temperature region of 10–40 °C [12]. What appears to be a violation of Gibbs's phase rule at first sight, is the result of the composition-dependent stress (equivalent to the thermodynamic pressure) of the thin film/substrate system, which stabilizes also the formation of a self-organized stripe pattern of the two phases [13–15].

The nontypical temperature-dependent disappearance of ferromagnetism via a first-order phase transition stimulated intense theoretical studies of the magnetic properties of MnAs. It is still under discussion whether the ferromagnetism should be described by a double exchange mechanism [16] due to the strongly directional, hybridized Mn-As bonds or has mainly itinerant character [17–21] because of the metallic behavior of MnAs. Furthermore it is not clear whether the change in volume [9,22] or the different symmetry [19] of α and β phases are responsible for the loss of magnetism during the phase transition.

Here we report on quantitative measurements by a cantilever beam magnetometer (CBM) of the stress and magnetism evolving in the phase coexistence region of MnAs/GaAs(001). From the deduced strain it can be concluded that—in contrast to the bulk phase—MnAs lattice of the thin film expands only uniaxially along the growth direction. Detailed analysis of the resulting orthorhombic structure of the ferromagnetic phase provides insight into the nature of ferromagnetism of MnAs, particularly demonstrating the important role of the Mn-As-Mn interaction.

As substrates, commercial 100-μm-thick epiready GaAs(001) wafers were routinely coated with a 100-nm-thick GaAs(001) buffer layer by standard solid-source MBE [15] after removal of the oxide. MnAs was deposited at a substrate temperature of 250 °C, at a $\mathrm{As_4/Mn}$ beam equivalent pressure ratio of 250, and at a rate of 20 nm/h. The epitaxial orientation with respect to the GaAs substrate is MnAs($\bar{1}100$) ∥ GaAs(001) [Fig. 1(b)]

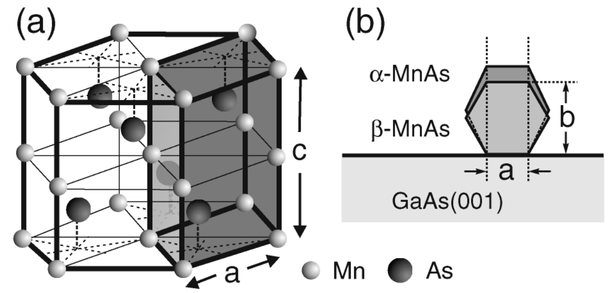

FIG. 1. (a) NiAs-type crystal structure of α-MnAs in the bulk. (b) Schematic illustration of the structural phase transition of MnAs($\bar{1}100$)/GaAs(001), where the in-plane lattice spacing a remains constant; note that due to the rigid geometrical constraints of the heteroepitaxial film/substrate system also α-MnAs is orthorhombic.

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and MnAs[0001] || GaAs[$1\bar{1}0$]. The key instrument for this study is our sensitive CBM [23], which enables quantitative measurements of both the stress and magnetic properties of thin films. As cantilever beam substrates we cut 25×5 mm^2 sized samples with either the MnAs[$11\bar{2}0$] or the MnAs[0001] direction along the length, and the film covering an area of 11×5 mm^2. The stress was evaluated by Stoney's formula [24] adapted to the geometry of the experimental setup. For the magnetic hysteresis measurements we ramped the magnetizing in-plane field [H in Fig. 3(a)]. Each value was calculated from the torque generated by shortly applying a small probing field perpendicular to the film plane (for details, see Ref. [23]). For calibration of the CBM the substrate deflection due to its weight after rotation by 180° was measured.

In Fig. 2(a) the magnetization of a 60-nm-thick film of MnAs($\bar{1}100$) on GaAs(001) is plotted in the temperature range of 0–50 °C, thus including the phase coexistence region. Each experimental data point corresponds to the remanent magnetization of complete hysteresis loops measured by CBM at the given temperature [Fig. 3(a)]. Above 40 °C no magnetization is detectable. Lowering the temperature, the magnetization increases gradually and saturates at about 10 °C, when the film is completely transformed to α-MnAs. This is confirmed by the experimental saturation value of 0.65 ± 0.05 MA/m, which is in good agreement with the magnetization of 0.67 MA/m reported for bulk α-MnAs at 10 °C [25]. Between cooling and heating a small hysteresis of 2.5 °C is observed. Figure 3(a) displays exemplarily two hysteresis loops measured in the temperature range of 0–50 °C by applying the magnetizing field along the MnAs[$11\bar{2}0$] direction. All hysteresis loops, except the ones close to 40 °C, are almost perfectly squarelike, indicating (i) that the easy axis of MnAs/GaAs(001) indeed lies along MnAs[$11\bar{2}0$] as found previously [2,4] and in agreement with bulk [10], and (ii) that also in the coexistence region the α phase is magnetically saturated, i.e., the stripes consist of single domains [see also magnetic force microscopy (MFM) image of Fig. 3(b)]. Particularly the latter point is an important finding. As predicted theoretically [13] and confirmed by atomic force microscopy (AFM) investigations [14,15], MnAs films form a periodic pattern of alternating α- and β-MnAs stripes at 10–40 °C in order to reduce elastic energy [see Fig. 3(b)]. Since the shape of the magnetization curve of Fig. 2(a) follows the temperature-dependent change in composition determined by x-ray diffraction [13] or scanning near-field optical microscopy (SNOM) [14], it can be concluded that the reduced magnetization in the phase coexistence region is the result of the changing composition and not due to thermal disorder as in common second-order phase transitions of ferromagnetic materials.

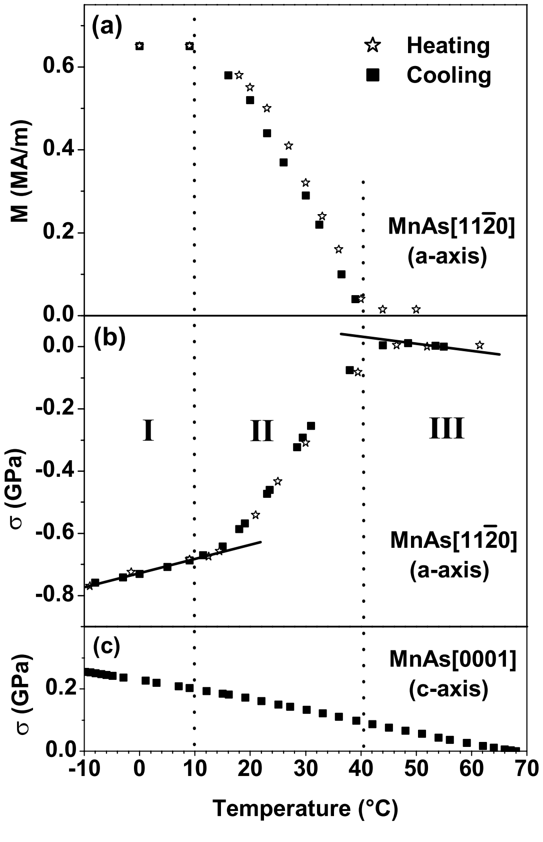

FIG. 2. Temperature dependence of magnetization M and stress σ of 60-nm-MnAs/GaAs(001) measured by CBM: (a) remanent ($\simeq$ saturation) M along the easy MnAs[$11\bar{2}0$] axis; (b) σ along MnAs[$11\bar{2}0$]; (c) σ along MnAs[0001]; temperature regions I, II, and III indicate pure α-MnAs, the coexistence region and pure β-MnAs, respectively.

Figure 2(b) displays the corresponding evolution of stress due to strain in the MnAs[$11\bar{2}0$] direction. Between 60 and -10 °C three different regions can clearly be identified: Upon cooling of the MnAs film small

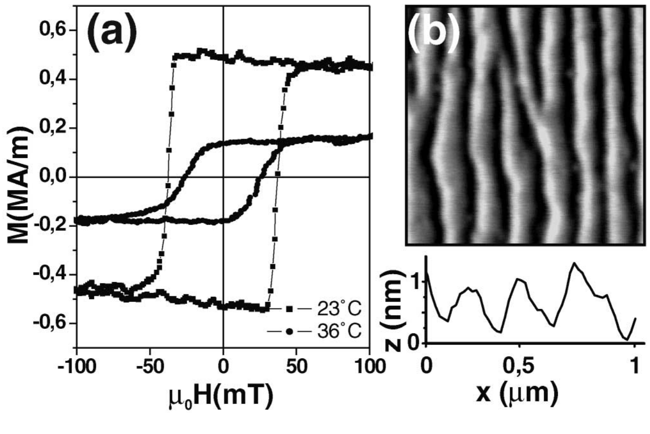

FIG. 3. Magnetic properties of 60-nm-MnAs/GaAs(001): (a) Hysteresis loops along the easy MnAs[$11\bar{2}0$] axis (not corrected for the diamagnetism of the substrate); (b) 2×2 μm^2 MFM image taken at 27 °C in zero magnetic field after magnetizing the film, which confirms the single domain configuration of individual α-MnAs stripes (bright) as well as a line scan measured by AFM in the contact mode.

tensile and compressive stress contributions develop in the pure phases of β and α MnAs, i.e., above 40 and below 10 °C, respectively (regions III and I). In the phase coexistence region II, on the other hand, a large compressive stress contribution dominates. We remark that the same temperature dependence of the stress is repeatedly obtained and reproduced even after more than 100 cooling/heating cycles, thus excluding plastic deformation. Therefore the stress is solely the result of a straining and destraining due to thermal expansion and/or the phase transition. Note that stress develops only when the film is prevented from assuming its equilibrium lattice dimensions. For instance, in region III the equilibrium lattice spacing of the β-MnAs film shrinks upon cooling. In the actual experiment, however, the in-plane lattice spacings are kept nearly constant by the substrate [26]. Therefore the β-MnAs film experiences an increasing tensile strain with decreasing temperature which is responsible for the tensile stress contribution in region III. An analogous argument, but with opposite sign, holds for α MnAs in region I, where the lattice spacing a is reported to increase upon cooling [11]. Consequently, a compressive stress contribution is observed in region I. To put the discussion on a quantitative base we calculated the thermal expansion of a from the temperature gradient of the stress along MnAs[$11\bar{2}0$], marked by straight lines in regions I and III of Fig. 2(b) [27]. We obtain values of $-1.1 \times 10^{-4}/°\mathrm{C}$ and $+6.3 \times 10^{-5}/°\mathrm{C}$ for the α and β phase, respectively, which are in good agreement with the thermal expansion of a determined by x-ray diffraction ($-1.0 \times 10^{-4}/°\mathrm{C}$ [11] and $-0.84 \times 10^{-4}/°\mathrm{C}$ [28] for α MnAs as well as $+5.8 \times 10^{-5}/°\mathrm{C}$ for β MnAs [11]). The stress evolution in regions I and III therefore can be fully ascribed to thermal expansion.

When passing from region III to the phase coexistence region II a large compressive stress contribution is observed, indicating an increase of the equilibrium lattice spacing a, see discussion above. As known from bulk studies a indeed increases during the transformation from β-MnAs to α-MnAs. Quantitatively, we obtain a value of 0.59 ± 0.05 GPa for the change of stress accompanied with the complete transformation of β MnAs into α MnAs or vice versa, which compares well with the stress of 0.61 GPa calculated from the respective change of a in the bulk [28]. Furthermore, from bulk studies it is known that the lattice spacing along the c axis is not affected by the phase transition [11,28]. As confirmed by Fig. 2(c), the same is true for the MnAs film. The stress evolution along the c axis, measured by a substrate with its length parallel to MnAs[0001], reflects solely the thermal expansion of c [29]. Obviously the MnAs film can change its volume only by uniaxial expansion in the growth direction [b in Fig. 1(b)]. AFM investigation of the MnAs film reveals an average height difference of 1 nm between the stripes of α and β MnAs [Fig. 3(b)]. The corresponding height change of about 1.7% compares well with the 1.9% calculated for a clamped bulk [28].

All in all, our experiments of MnAs/GaAs(001) reveal that—contrary to bulk samples—the two in-plane lattice spacings a and c of the MnAs film do not change in the course of the first-order phase transition [30]. Because of adhesion to the substrate the film can only expand vertically and therefore both phases, α *and* β MnAs, are orthorhombic [Fig. 1(b)] supported by transmission electron diffraction [31]. Surprisingly, despite the significant differences in the lattice dimensions and geometry compared to bulk, the MnAs film turns ferromagnetic at the structural phase transition with both the saturation magnetization and the transition temperature comparing well with the respective bulk values.

The appearance of ferromagnetic order under the rigid geometrical constraints of the heteroepitaxial film/substrate system provides new insight into the origin of ferromagnetism in pnictides. In older studies [9,22], ferromagnetism in MnAs was explained via a localized Heisenberg model in terms of magnetostrictive effects, because of the large volume change during the parallel structural phase transition. Modern first principle calculations based on density functional theory (DFT) [17–21], which treat the magnetism of (metallic) pnictides from the viewpoint of itinerant electrons, indeed reveal a narrow range for the Mn-Mn distance $d_{\text{Mn-Mn}}$, where a ferromagnetic alignment of the magnetic moments is energetically favorable. In fact, α-MnAs at 39 °C with $d_{\text{Mn-Mn}} = 0.286$ nm is ferromagnetic, whereas in bulk Mn $d_{\text{Mn-Mn}}$ for antiferromagnetic coupling is ~ 0.275 nm (see Ref. [32]). At smaller Mn-Mn distances, however (e.g., in room temperature MnP with $d_{\text{Mn-Mn}} = 0.269$ nm) a ferromagnetic phase is no longer stable, because the exchange interaction is too weak due to strong overlap of the d bands of Mn [20]. Notice that in pnictides the Mn atoms along the c axis are nearest neighbors with $d_{\text{Mn-Mn}} = c/2 = 0.286$ nm. Since c remains nearly constant during the phase transition—a fact well established in the bulk and shown here for a MnAs film—"exchange magnetostriction" in the sense of a varying $d_{\text{Mn-Mn}}$ can therefore be excluded as an explanation.

In the hexagonal MnAs(0001) plane direct exchange coupling of the Mn atoms is not possible, because $d_{\text{Mn-Mn}}$ is too large ($d_{\text{Mn-Mn}} = a \approx 0.37$ nm). Therefore coupling via different double exchange mechanisms [33,34] was considered in older work, where the parallel spin alignment is promoted by an electron transfer between the localized d states of the Mn cations through extended d or p type states of the anionic As [16]. The important role of the anion is also reflected in recent DFT calculations, where the p states of As are found to interact strongly with the d bands of Mn: the stronger the p-d hybridization, the lower the d-d exchange interaction and, consequently, the resulting magnetic moment [19,20]. The p-d hybridization is supported by the considerable negative polarization of the anion (e.g., $-0.23\mu_B$ for As) found by neutron scattering [35] and in accordance with theory

[20]. DFT studies of distorted lattices of MnAs with different c/a ratios brought Sanvito and Hill to the speculation that the reduction of magnetization of MnAs grown on GaAs may be due to large deformation of the hexagonal lattice [19]. However, this conclusion is not confirmed by our experiments since the orthorhombically distorted α-MnAs film still exhibits bulk-like magnetic properties, thus contradicting a major role of the lattice symmetry.

Using a two-band Hubbard model Schwieger and Nolting recently reported that small changes in the hybridization between a *d*- and a *p*-like band can lead to large changes in the magnetization of a ferromagnetic band [36]. Our results therefore provide strong evidence that slight differences in the Mn-As distance and/or the respective bond angle that affect the *p*-*d* hybridization of MnAs, are responsible for the dramatic changes in the spin alignment. In view of our experimental results and the extensive theoretical studies we conclude that it is indeed the change in Mn-As-Mn interaction which drives the transition from the paramagnetic to the ferromagnetic state. As stated in Ref. [36] a small change in *p*-*d* hybridization can give a "final kick" to a system that is close to a ferromagnetic transition.

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