Strain-Mediated Phase Coexistence in Heteroepitaxial Films

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We present experimental evidence of the equilibrium coexistence between crystalline phases in heteroepitaxial films of MnAs on GaAs. The phases, which can coexist in the bulk system only at one temperature point, coexist in the epitaxial film over a wide temperature interval. An apparent contradiction with the Gibbs phase rule is resolved by the presence of strain in the film.

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The Gibbs phase rule limits the coexistence between phases with the same chemical composition to a single temperature. We present experimental evidence of an equilibrium phase coexistence in heteroepitaxial films over a wide temperature interval. In films of MnAs grown epitaxially on GaAs, we observe the coexistence of two structurally distinct phases, hexagonal αMnAs and orthorhombic βMnAs, in a range from the bulk phase transition temperature to at least 20 °C below it. The fraction of the low-temperature phase decreases almost linearly when approaching the phase transition temperature. Thermal cycling does not reveal any hysteresis. An apparent contradiction with the Gibbs phase rule is resolved by the presence of long-range elastic interactions in the strained heteroepitaxial film. The epitaxial coupling of the film to the substrate does not allow a change of the film sizes (and, hence, the mean strain) in the plane of the interface. As a result, the minimum of the free energy of the film, which includes the elastic strain energies of both phases, is realized by a coexistence of these phases.

MnAs on GaAs is a promising heteroepitaxial system which integrates magnetic and semiconductor properties. It has been intensively studied during the past years [1,2]. Figure 1 sketches the epitaxy of MnAs on a GaAs(001) surface. Below 40 °C, the bulk MnAs crystal is ferromagnetic and forms the hexagonal αMnAs phase (structure of bulk phases and the phase diagram of MnAs are reviewed in Ref. [3]). In epitaxy, the $(\bar{1}100)$ side facet of the hexagonal prism is attached to the GaAs(001) surface. At approximately 40 °C, the bulk αMnAs experiences a first-order phase transition to the paramagnetic orthorhombic phase βMnAs. Its unit cell is shown in Fig. 1 by the dashed line: the hexagon anisotropically shrinks in both directions, while the height of the prism (perpendicular to the plane of the figure) does not change. A further phase transition in bulk MnAs takes place at 125 °C. This transition is continuous and results in the γMnAs phase, which is hexagonal again.

The structure of bulk MnAs crystals [4], the epitaxial relationships of MnAs on GaAs [1,2], and the structure of the interface [2] are known. MnAs grows epitaxially on GaAs(001) despite a very large mismatch in the GaAs$[\bar{1}10]$ direction which amounts to 33%. The transmission electron microscopy studies [2] show that every sixth GaAs{220} plane fits into every fourth MnAs{0002} plane, which reduces the actual mismatch to 5%. This mismatch, as well as the mismatch along the perpendicular direction (7.7%), is released by regular arrays of misfit dislocations. The MnAs films reveal a unique epitaxial orientation on the polar GaAs(001) surface, namely, $(\bar{1}100)$ MnAs $\parallel$ (001) GaAs and [0001] MnAs $\parallel$ $[1\bar{1}0]$ GaAs, which was checked in the present study by *in situ* reflection high-energy electron diffraction. It is essential for the considerations below that the orientation of the film with respect to the substrate is unique. There are no rotationally equivalent domains (twins), albeit translational domains can be present.

At the αMnAs-βMnAs transition, the unit cell shrinks in the plane of the interface, as shown in Fig. 1, resulting in a strained film. Hypothetically, three scenarios are possible. If misfit dislocations can be generated to release the elastic strain energy, the phase transition would proceed exactly in the same way as in bulk MnAs. However, generation of misfit dislocations is hardly possible near room temperature. In the opposite case, if the dislocations could neither be generated nor moved by glide, the strain could not be released nor redistributed. It would be locally fixed, and the phase transition would proceed uniformly, albeit at a temperature different from the bulk transition temperature. The third possibility is realized when the dislocations cannot be generated because of the low temperature but the existing misfit dislocations can glide along the interface. Then, the strain can be redistributed, and only the mean strain over the whole sample is fixed. The free energy minimum of the film is reached through the coexistence of domains of two phases with different strain. The x-ray

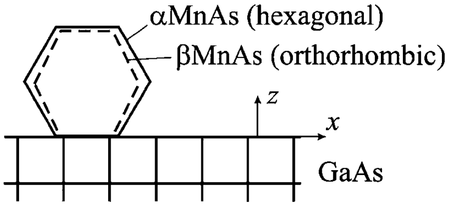

FIG. 1. Scheme of the epitaxy of MnAs on GaAs(001).

data presented below show that this latter scenario is realized near the αMnAs-βMnAs transition.

MnAs layers, 250 nm thick, were grown by solid source molecular beam epitaxy on 100 nm thick GaAs buffer layers at 250 °C with a growth rate of 19 nm h^{-1} [2]. The samples were transferred from the growth chamber through air to an UHV analysis chamber integrated in a six-circle diffractometer. The sample temperature was controlled by a radiative heating stage with an estimated systematic uncertainty in temperature determination of at most 5 °C. Large area Be windows allowed x-ray access to the sample. Temperature-dependent double crystal x-ray measurements were performed using an asymmetrically cut four-reflection Du Mond–Bartels-type Ge 220 monochromator placed at a distance of 20 cm from the sample. An 80 cm long x-ray capillary tube (angular acceptance 0.1°) was used to bridge the distance from the point focus of the sealed x-ray tube to the monochromator.

Figure 2(a) presents the ω-2θ x-ray diffraction scan of the MnAs/GaAs(001) film at 30 °C. (Here, ω denotes the glancing angle of incidence on the sample surface and 2θ the detector angle with respect to the incident beam.) The peak of the GaAs substrate and the peaks of αMnAs and βMnAs are clearly distinguished. When the temperature is changed, the intensities of the two MnAs film peaks also change. The structure factors of both reflections are almost equal, and, hence, the ratio of the integrated intensities of αMnAs and βMnAs peaks is equal to the ratio of the volume fractions of the phases in the film. The measurements were performed in two thermal cycles of stepwise cooling and heating between 45 and 27.5 °C with a measurement at each temperature. The ratio of the integrated intensities does not show any hysteresis and does not change from one cycle to another, which points to an equilibrium coexistence of the two phases.

The fraction of the αMnAs phase is plotted as a function of temperature in Fig. 2(b). In contrast to the bulk phase transition, only a small fraction of the film has the structure of the low-temperature phase αMnAs just below the transition. The fraction of this phase increases almost linearly with decreasing temperature in an interval of more than 20 °C. The presence of x-ray diffraction peaks from both phases in the MnAs heteroepitaxial films at room temperature was already noticed earlier [1,5]. However, no temperature-dependent measurements were performed.

Any equilibrium first-order phase transition proceeds as a discontinuous motion of the system from one minimum of its free energy to the other, which becomes deeper at the transition temperature. In the crystalline system under investigation, the shape and size of the unit cell changes at the transition. Since the linear dimensions of the film are fixed, the strain due to phase transformation cannot be released and gives rise to elastic strain. Near the transition temperature of the free crystal, the finite elastic energy density exceeds the free energy gain due to the transition into the deeper free energy minimum and makes a uniform phase transformation in the whole film unfavorable. A simple calculation presented below shows that the free energy minimum is reached by a phase transformation in parts of the crystal. The relative fractions of the two phases depend on temperature, and the phase coexistence takes place in a finite temperature interval.

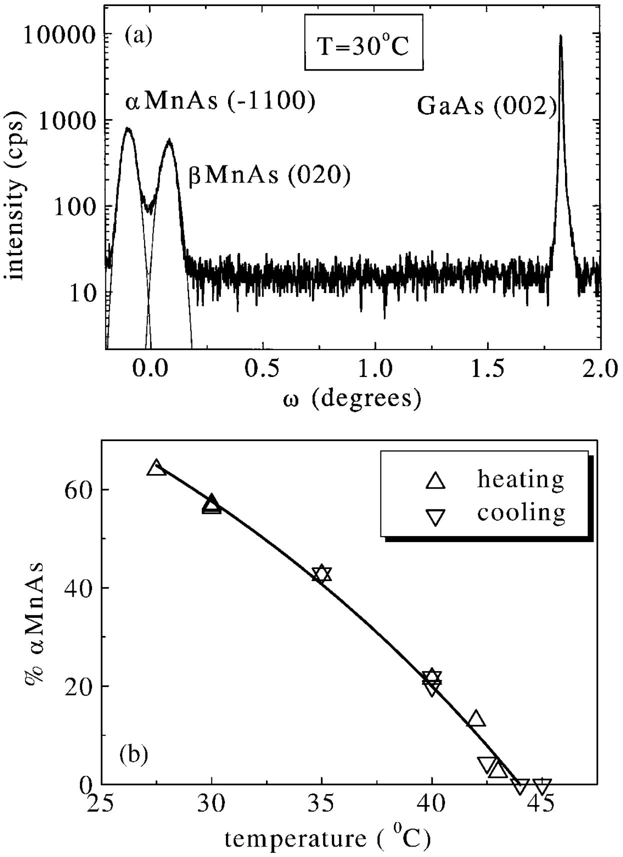

FIG. 2. (a) Diffraction curve (ω-2θ scan) near the GaAs (002) reflection measured at a temperature of 30 °C (CuK$_{\alpha 1}$ radiation). The αMnAs($\bar{1}100$) and the βMnAs (020) reflections are clearly distinguished. (b) Fraction of αMnAs calculated from the integrated intensities of the observed MnAs reflections.

The possibility of a similar two-phase coexistence in bulk crystals has been considered for a first-order phase transition accompanied by a volume change [6]. In that case, the inclusions of the product phase are strained, and the free energy minimum is achieved by phase coexistence, with the volume fraction of the product phase depending linearly on temperature. In epitaxial films, the requirement of a constant volume of the crystal is replaced by the constant linear dimensions of the film in the plane of the interface. A volume change at the phase transition is not necessary for such a phase coexistence. The coexistence can take place for shear transformation strain as well.

The phase coexistence driven by the constrained lateral size of the film has close similarity to the behavior of ferroelectric films. In the latter system, the symmetry of both initial and product phases are higher (e.g., cubic and tetragonal) and the elastic energy is minimized by polydomain structures consisting of domains of the product phase with different orientations (twins) [7]. The coexistence between the initial and the product phases was also considered theoretically [8]. It was shown that the transition is irreversible, because the equilibrium domain structures depend on the direction of the transition. In the system considered in the present paper, the crystallographic orientation of the film with respect to the substrate is unique, which results in a reversible transition.

Let us consider first, for the sake of clarity, a one-dimensional model system, and then extend the results to epitaxial films. The system can be thought of as beads on a string, and the phase transition consists in an abrupt change of the equilibrium mean distance between the beads. The difference between the free energy densities in the two phases $\Delta f = f_2 - f_1$ favors phase 1 on one side of the transition (where it is positive) and phase 2 on the other side. At the transition temperature, $\Delta f = 0$. If the system is free to expand, the change of the relative distances between particles at the transition (called the phase transformation strain) is η_0. We explore the situation when the system cannot change the total length and, hence, cannot reach the equilibrium distance between particles after the transition. Let us introduce the total strains ε_1 and ε_2 which are relative changes of the interatomic distances in the two phases in the actual state of the system.

The elastic free energy densities in the phases 1 and 2 are $\mathcal{E}\varepsilon_1^2$ and $\mathcal{E}(\varepsilon_2 - \eta_0)^2$, where $\mathcal{E}$ is the relevant elastic modulus. Then, if the phases are allowed to coexist and the fraction of the phase 1 is ξ, the mean free energy density is

$$f = \xi(f_1 + \mathcal{E}\varepsilon_1^2) + (1 - \xi)[f_2 + \mathcal{E}(\varepsilon_2 - \eta_0)^2]. \tag{1}$$

The requirement of the constant length of the system relates the total strains in the two phases:

$$\xi\varepsilon_1 + (1 - \xi)\varepsilon_2 = 0. \tag{2}$$

The minimum of the free energy (1) over the total strains ε_1 and ε_2, and the fraction ξ of phase 1, subject to the constraint (2) is reached at

$$1 - \xi = -\frac{\Delta f}{2\mathcal{E}\eta_0^2}. \tag{3}$$

When Δf takes small negative values near the transition temperature, the free system uniformly proceeds into phase 2. However, from Eq. (3) it follows that only some fraction of system of fixed length is in phase 2. This fraction linearly increases with the deviation from the transition temperature, since Δf is a linear function of $T - T_0$ near the transition (here T is the temperature and T_0 is the transition temperature). The free energy density at the minimum is equal to $f = -(\Delta f)^2/(4\mathcal{E}\eta_0^2)$, and it can be easily checked that this value is smaller than the values at the terminal points $\xi = 0$ and $\xi = 1$. Thus, we find that the restriction of the total length of the system gives rise to a strain-driven phase coexistence in a finite temperature interval given by Eq. (3) within $0 < \xi < 1$.

Proceeding to strained heteroepitaxial films, we take into account, as in the model above, only the elastic energies of the phases and the temperature-dependent difference between the free energy densities of a free crystal in the two phases Δf. We neglect the energy of the domain boundaries between the phases, the changes in the film-substrate interfacial energy, and the magnetic energy. We assume that at the transition (which is close to room temperature in the system under consideration) misfit dislocations are not generated but can glide along the interface, which imposes a restriction only on the total length of the film along the interface (or, equivalently, the mean strain in it). The energy of the domain boundaries and the magnetic energy are essential in determining the domain sizes and configurations, which are out of the scope of the present paper. We note that the domain boundary energy includes the energy of the misfit between the domains of different phases, since they have different spacings normal to the film-substrate interface.

The film can freely expand normal to its plane, and, hence, stress normal to the film is absent, $\sigma_{zz} = 0$. We introduce the elastic strain tensors $\hat{e}_\alpha$ and $\hat{e}_\beta$ for the two phases under consideration and use the condition $\sigma_{zz} = 0$ to relate the strain components: $e_{zz} = -[\nu/(1 - \nu)](e_{xx} + e_{yy})$. Here, $\hat{e}$ denotes the elastic strain tensor for a particular phase. The film is assumed to be elastically isotropic, ν is the Poisson ratio, and the z axis is normal to the film (see Fig. 1). Then, calculating the in-plane stress components, we express the strain energy density for a particular phase as

$$f^{\mathrm{el}} = \mathcal{E}_0(e_{xx}^2 + 2\nu e_{xx}e_{yy} + e_{yy}^2), \tag{4}$$

where $\mathcal{E}_0 = E/2(1 - \nu^2)$, and E is the Young modulus.

Let $\hat{\eta}_\alpha(T)$ and $\hat{\eta}_\beta(T)$ be the intrinsic strain tensors of the two phases. They describe the changes of the lattice spacings in free bulk crystals and include both the discontinuous jump at the first-order phase transition temperature and smooth variations of the spacings below and above the transition, in particular, thermal expansion. The latter contribution is important, since the linear thermal expansion coefficients of MnAs are anomalously large and can be estimated from the measurements on bulk crystals [4] as $(1 \pm 0.5) \times 10^{-4}$ K^{-1}, at least one order of magnitude larger than that of GaAs (6×10^{-6} K^{-1}). The uncertainty in the value above reflects discrepancies between different studies [4]. We also note that αMnAs has a negative thermal expansion in the hexagonal plane (i.e., $\eta_{\alpha xx} = \eta_{\alpha zz} < 0$).

The change of the lattice spacing in the film, measured in x-ray diffraction experiments, is described by the total strain $\hat{\varepsilon} = \hat{\eta} + \hat{e}$. The size of the film along the interface, and, hence, the mean total strain, does not depend on temperature (we neglect the thermal expansion of the GaAs substrate). Denoting by ξ the fraction of the αMnAs phase, we write this condition as

$$\xi \varepsilon_{\alpha xx} + (1 - \xi)\varepsilon_{\beta xx} = \varepsilon_x \,, \tag{5}$$

where ε_x is a constant. It is the xx component of the strain in the βMnAs phase in the film just above the phase coexistence region. The change of the unit cell parameters at the phase transition proceeds only in the xz plane, so that we have $\varepsilon_{\alpha yy} = \varepsilon_{\beta yy} \equiv \varepsilon_y$, where ε_y is a constant. The corresponding components of the intrinsic strain η_{yy} are equal in both phases and describe thermal expansion.

The fractions of the phases can be found from the minimum condition for the free energy density

$$f = \xi f_\alpha^{\mathrm{el}} + (1 - \xi)(\Delta f + f_\beta^{\mathrm{el}}), \tag{6}$$

subject to the additional constraint (5). The actual minimization is easily performed by substituting (4) into (6), expressing the elastic strain through total strain ($\hat{e} = \hat{\varepsilon} - \hat{\eta}$), excluding $\varepsilon_{\alpha xx}$ due to (5), and minimizing (6) with respect to $\varepsilon_{\beta xx}$ and ξ. The result is

$$\xi = \frac{\Delta f}{2\mathcal{E}_0 \eta_0^2} - \frac{\varepsilon_x + \nu\varepsilon_y - (\eta_{\beta xx} + \nu\eta_{yy})}{\eta_0}, \tag{7}$$

where $\eta_0 = \eta_{\beta xx} - \eta_{\alpha xx}$. Equation (7) reduces to Eq. (3) when one takes $\varepsilon_x = 0$, $\eta_{\alpha xx} = 0$, and $\nu = 0$.

The two-phase coexistence occurs when the right-hand side of (7) takes values within the interval $[0, 1]$. In particular, the temperature when the αMnAs phase appears is given by the condition $\xi = 0$. It depends on the strain in the film above the transition ε_x, ε_y and does not necessarily coincide with the temperature of the bulk phase transition (where $\Delta f = 0$). The temperature of the bulk phase transition αMnAs-βMnAs is known only to be in the interval between 33 and 44 °C [3]. This uncertainty, as well as a possible systematic error (within 5 °C) of temperature determination in our measurements, does not allow us to judge whether the temperature of the appearance of the αMnAs phase in the film [$T_0 = 44$ °C, cf. Fig. 2(b)] differs from the bulk transition temperature or not.

The numerators of both terms in Eq. (7) are linear functions of the temperature near the phase transition. If η_0 is taken, as a first approximation, equal to the phase transformation strain (i.e., thermal expansion is neglected), the fraction of the low-temperature phase ξ is a linear function of temperature. The thermal strain, as well as the nonlinearity of $\Delta f(T)$, explains some deviation of the observed $\xi(T)$ from a straight line. The bulk measurements [4] agree in the phase transformation strain at the αMnAs-βMnAs transition $\Delta\eta_0 = -0.012$ but, as noted above, differ in the temperature dependencies of η. We used the values $\eta_0 = -0.012 + 1.5 \times 10^{-4}(T - T_0)$ and $\varepsilon_x + \nu\varepsilon_y - (\eta_{\beta xx} + \nu\eta_{yy}) = -1.5 \times 10^{-4}(T - T_0)$, where the temperatures are in degrees centigrade. The fit of the data shown in Fig. 2(b) to Eq. (7) has been obtained with $\Delta f / 2\mathcal{E}_0 = -6 \times 10^{-6}(T - T_0)$. The contribution from the second term of Eq. (7) is roughly one-third of the total value.

In summary, we have observed an equilibrium phase coexistence between hexagonal αMnAs and orthorhombic βMnAs phases of MnAs/GaAs(001) heteroepitaxial films. The fraction of the low-temperature phase αMnAs linearly increases upon cooling below the bulk phase transition temperature in an interval of more than 20 °C. Thermal cycling does not show any hysteresis. An apparent contradiction with the Gibbs phase rule is resolved by the presence of elastic strain.

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