

Nucleation at the phase transition near 40 °C in MnAs nanodisks

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The phase transition near 40 °C of both as-grown thin epitaxial MnAs films prepared by molecular beam epitaxy on GaAs(001) and nanometer-scale disks fabricated from the same films is studied. The disks are found to exhibit a pronounced hysteresis in the temperature curve of the phase composition. In contrast, supercooling and overheating take place far less in the samples of continuous layers. These phenomena are explained in terms of the necessary formation of nuclei of the other phase in each of the disks independent from each other. The influence of the elastic strains in the disks is reduced considerably. © 2006 American Institute of Physics.

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Manganese arsenide on GaAs is a promising material combination for spintronic applications based on spin injection.¹ MnAs is ferromagnetic at room temperature and has a large carrier spin polarization. It can serve as a source of spin polarized electrons. Furthermore MnAs may be applied for sensors and actuators thanks to its magnetoelastic response.² The room temperature ferromagnetic α phase is metallic and crystallizes in the hexagonal NiAs($B8_1$) structure. Near 40 °C MnAs transforms into the orthorhombic β phase exhibiting the MnP ($B31$) structure. The temperature dependence of the magnetization near the transition was investigated in (Refs. 2 and 3), and a 20 K wide hysteresis loop was observed. At this first order structural phase transition a significant change in the lattice parameter a is found, which amounts to $\approx 1.2\%$.^{4,5}

During epitaxy^{6,7} the MnAs($1\bar{1}00$) film on GaAs(001) is attached by the side facet of the hexagonal unit cell (Fig. 1), so that the c lattice direction MnAs[0001] is parallel to GaAs[$1\bar{1}0$]. The deformations in the layer lead to the phenomenon of phase coexistence, i.e., the phase content ξ does not change abruptly between zero and unity at a certain temperature as expected from the Gibbs phase rule. Two coexisting phases are found, on the contrary, in a wide temperature range.⁸ Elastic domains of both phases form a periodic stripe pattern⁹ in a self organized way. The domain period amounts to approximately five times the film thickness.^{10,11} Application of hydrostatic pressure^{12,13} or biaxial stress¹⁴ has a considerable influence on the transition temperatures.

The phase transition can be affected further by imposing artificial constraints on the stripe pattern. Significant effects are expected from a lateral confinement when a film is patterned to small disks. Such disks with smaller sizes than the widths of the elastic domains enable elastic relaxation of the laterally periodic stresses accumulated inside the epitaxial layer. The tight restriction of the MnAs lattice along the interface is then released. As a consequence the formation of elastic domains in MnAs nanodisks seems to be no longer energetically favorable. The distribution of magnetic domains in such MnAs disks was investigated in Ref. 15. The

aim of the present work is to study in more detail the influence of such a lateral structuring on the phase coexistence of α - and β -MnAs. We investigate the temperature dependence of the phase composition in epitaxial MnAs films prior to and following the artificial modification using microfabrication technologies.

The MnAs layers were grown by solid source molecular beam epitaxy (MBE) as described elsewhere.^{7,16,17} The nanostructuring was carried out using electron beam lithography and Ar ion milling. The resulting disks were assembled in the form of a square array as shown in the scanning electron micrograph in Fig. 2. In this sample, the diameter of the disks is smaller than 100 nm, i.e., well below the equilibrium size of the elastic domains in the original continuous MnAs layer.¹⁸ Temperature dependent synchrotron x-ray diffraction experiments were performed at the MAGS beamline at the BESSY storage ring using a Si(111) double crystal monochromator and 8 keV radiation.¹⁹ A six circle diffractometer equipped with a special cryostat was employed for the measurements. Preliminary experiments were performed at a similar diffractometer of the KMC 2 beamline at BESSY. In addition we performed laboratory experiments using a Panalytical X'Pert System with Ge(220) hybrid monochromator and Ge(220) analyzer crystal.

The phase contents of the MnAs samples were obtained from the ratio of the integrated intensities of the corresponding α -MnAs and β -MnAs reflections measured in symmetrical $\omega/2\theta$ scans (Fig. 3). The ($\bar{3}300$) and (060) or the ($\bar{1}100$) and (020) were analyzed,^{11,20} and the layer reflections were fitted by Gaussian curves. The intensity ratio changes with temperature in the phase coexistence range.⁸ The samples

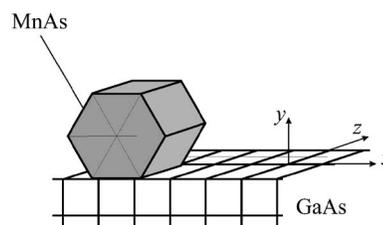


FIG. 1. Schematic view of the epitaxial relationship of MnAs on GaAs(001).

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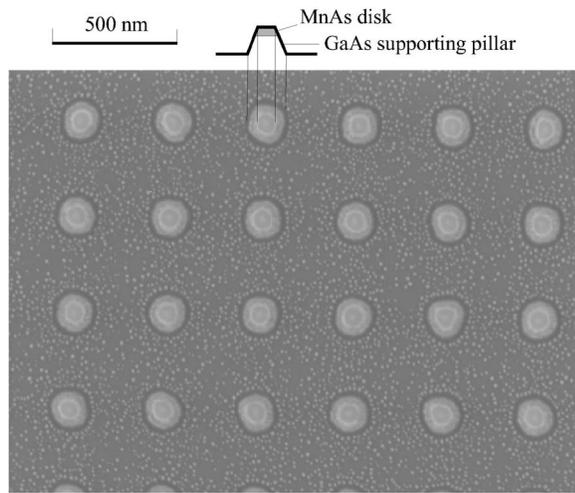


FIG. 2. Scanning electron micrograph of MnAs disks on GaAs supporting pillars. The diameter of the disks is below 100 nm, i.e., below the size of the elastic domains in the original MnAs epitaxial layer.

reached their equilibrium composition almost immediately after a certain temperature had been set, i.e., the relaxation times are significantly small. Samples consisting of MnAs disks having various diameters on the GaAs substrate were compared to their parent unstructured samples. Here we demonstrate the results from the smallest disks shown in Fig. 2. The lateral period of the domain structure of the original MnAs epitaxial layer can be obtained from the distance between satellite maxima $\Delta\omega_S$ in the x-ray triple crystal ω scan (Fig. 4). The period Λ_d is calculated from the formula $\Lambda_d = 2\pi/(\Delta Q_x) = \lambda/(2\Delta\omega_S \sin \Theta_B)$, where ΔQ_x is the distance of the satellite maxima in reciprocal space, λ is the x-ray wavelength, and Θ_B is the Bragg angle.²³ The x axis is defined to be perpendicular to the c direction of MnAs and parallel to the interface (see Fig. 1). The angular distance of the satellite maxima in Fig. 4 measured at room temperature yields an average lateral period of the domain structure of 247 nm. The thickness of the original MnAs film was determined to be 38 nm using x-ray reflectivity measurements.¹¹ The equilibrium domain period is thus estimated to be 190 nm.⁹ As

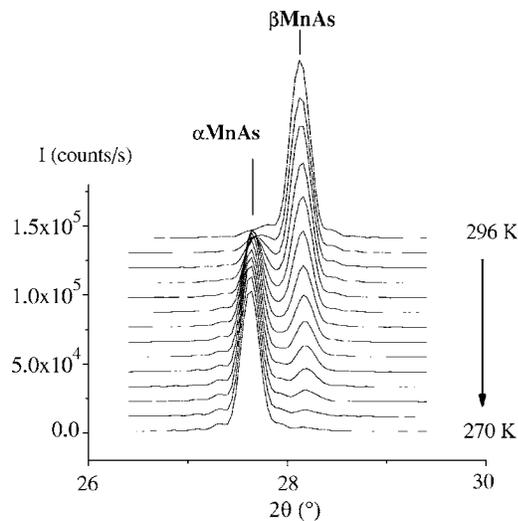


FIG. 3. X-ray reflections associated with α -MnAs($\bar{1}100$) and β -MnAs(020) of the MnAs disks obtained upon cooling the sample from 296 to 270 K in steps of 2 K. The curves are shifted vertically for clarity.

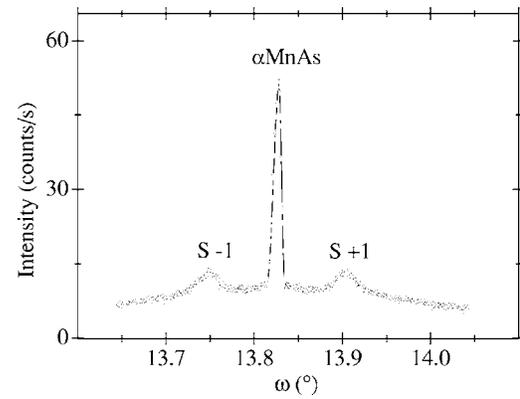


FIG. 4. X-ray triple crystal ω scan of the continuous layer measured at room temperature 27 °C near the reflection α -MnAs($\bar{1}100$) revealing additional satellite reflections (marked by S-1 and S+1) due to a lateral periodicity of the elastic domains of 247 nm.

the diameters of the smallest disks are sufficiently small (≈ 80 nm) only one elastic phase domain exists in an individual disk, which was confirmed at room temperature using magnetic force microscopy.¹⁵

The full triangles in Fig. 5 show the temperature dependence of the phase content ξ of α -MnAs in the unpatterned continuous epitaxial layer. As reported in Ref. 8 the heating and cooling curves roughly coincide and hence the temperature hysteresis in the range of phase coexistence is negligible. In the present sample this range extends quite broad between 270 and 315 K. The overall phase coexistence range amounts to 45 K. In the vicinity of the transition temperature of 315 K the α -MnAs content rises from zero almost linearly. When lowering the temperature further the rise of the phase content weakens and the content gradually reaches the saturation level at unity. The temperature dependence of the phase content ξ in the small MnAs disks is also shown in Fig. 5 (hollow symbols). When cooling down the MnAs disks, α -MnAs first emerges in the disks only at a temperature as low as 298 K. We observe a significant supercooling of the disks, i.e., all of them remain to be in the β phase.

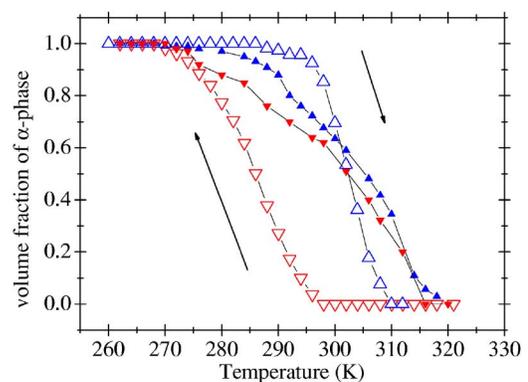


FIG. 5. (Color online) Temperature dependence of the volume fraction ξ of the MnAs α phase illustrating the coexistence of the two phases in the MnAs layer (full symbols) and the MnAs disk (hollow symbols) system. Upward (downward) directed triangles correspond to the heating (cooling) curve. The changes of the composition with temperature are more steep in the disk system than in the continuous layer system. The range of phase coexistence in the layer system is as large as 45° and only a very small hysteresis is observed. The disk system changes from one phase to the other within 15°–20° and a strong hysteresis (width 20 ± 5 K) of the temperature curve is found.

Subsequently, the α -MnAs content rises with further cooling until all the disks are transformed to the α phase at 270 K. Once the α phase had been realized entirely in all the disks, the sample was heated. Similar to the cooling case the temperature was as high as 285 K when the disks began transforming into the β phase. Therefore, a significant extent of overheating takes place in the disks in contrast to the continuous MnAs layer. The behavior of the MnAs nanodisks at the first order phase transition is similar to that of bulk MnAs.^{2,3} The same widths of the hysteresis in the temperature dependencies of the magnetization in bulk MnAs (Ref. 2) and of the phase content $\xi(T)$ in the MnAs disk ensemble are found. Moreover no phase coexistence takes place in the individual disks,¹⁵ indicating that the contribution of the elastic deformations during the phase transition is reduced considerably in the disk system. Nevertheless, the phase transition in the disk ensemble does not occur abruptly at a certain temperature. The slope of the temperature curve $d\xi/dT$ has increased only by a factor of 2–3 compared to that of the layer curve. The fact that the experimental disks are not perfectly identical due to small fluctuations in their sizes and shapes as well as the random presence of defects may be responsible for the finite temperature window at the phase transition. The strong temperature hysteresis observed in the experiment (Fig. 5) manifests the supersaturation in individual disks. The development of the other phase is retarded by a barrier, the energy Δf^* of formation of critical nuclei of the other phase.²⁴ This energy barrier seems to be connected mainly to the energy of the created phase boundary as in the case of bulk MnAs. The influence of the elastic energy, which was most important in the case of MnAs epitaxial films, is reduced.

In conclusion, we compared the first order phase transition in MBE-grown MnAs films on GaAs and in nanodisks prepared from the same MnAs films. The disks show supercooling (overheating) effects and as a consequence a pronounced hysteresis in the temperature dependence like in bulk MnAs. A stable nucleus of the other phase is required in each of the disks, since the individual disks are independent from each other. On the contrary, fewer nuclei are needed in the continuous layer as they can grow larger to fill the whole layer without restriction.

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