Nucleation at the first order phase transition in MnAs nanodisks

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The first-order phase transition near 40°C in 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, i.e. supercooling and overheating take place in the disks whereas they are far less in the samples with continuous layers. These phenomena are explained in terms of the necessary formation of nuclei of the new phase in each of the disks independent from each other. The influence of the elastic strains in the disks is reduced considerably compared to the continuous layer.

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. The room temperature ferromagnetic α-phase is metallic and shows a hexagonal NiAs($B8_1$) structure. Near 40°C MnAs transforms into the orthorhombic β-phase exhibiting the MnP(B31) structure. During this first-order structural phase transition a significant change in the lattice parameter a is found, which amounts to $\approx$1.2% [2, 3] and is caused by magnetostriction [4]. The temperature dependence of the magnetization in bulk MnAs near the first order phase transition was investigated in [5, 6] and a temperature hysteresis of a width of about 20 K was observed near the transition temperature. During epitaxy [7, 8] the MnAs($1\bar{1}00$) film on GaAs(001) is attached by the side facet of the hexagonal unit cell , so that the c lattice parameter MnAs[0001] is parallel to GaAs[$1\bar{1}0$]. For MnAs epitaxial layers on GaAs(001) 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 [9]. Elastic domains of both phases form a periodic stripe pattern [10] in a self organized way. The domain period of the alternating stripes of α and β MnAs inside the epitaxial layer can be detected by x-ray diffraction. It amounts to approximately five times the film thickness [11]. Application of hydrostatic pressure [4, 12] or biaxial stress [13] has a considerable influence on the transition temperatures. The phase transition may be influenced further by imposing artificial constraints on the stripe pattern. Significant effects may be expected from a lateral confinement when a film is patterned to small disks. Such a disk pattern with diameters smaller than the size of the elastic domains enables elastic relaxation of the laterally periodic stresses accumulated inside the epitaxial layer. The tight restriction of the MnAs lattice along the interface
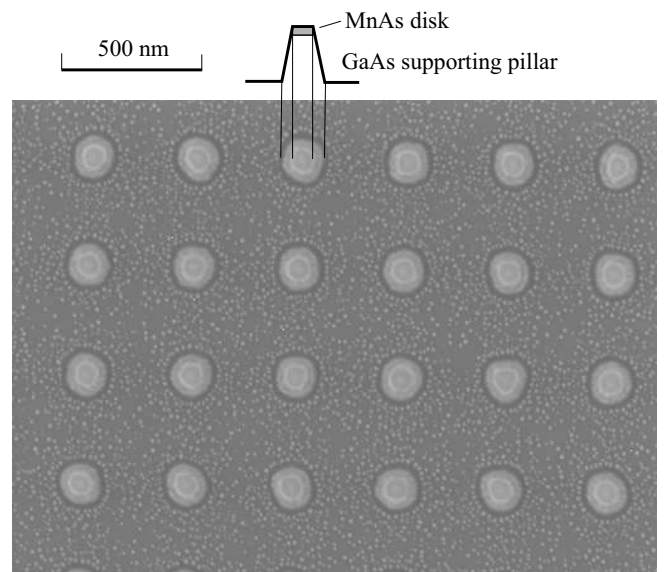

FIG. 1: SEM micrograph of the disk pattern demonstrating that the diameter of the disks is below 100 nm, i.e. below the size of the elastic domains in the MnAs epitaxial layer of 38 nm thickness.

is then released. The distribution of magnetic domains in such MnAs disks was investigated in [14]. 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 βMnAs. 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). Commercially available GaAs(001) epi-ready substrates without intentional miscut were used. A 100nm thick GaAs buffer layer was grown first at 550°C under RHEED control [7, 8]. Then, the nominally 40 nm thick MnAs layer was grown on the
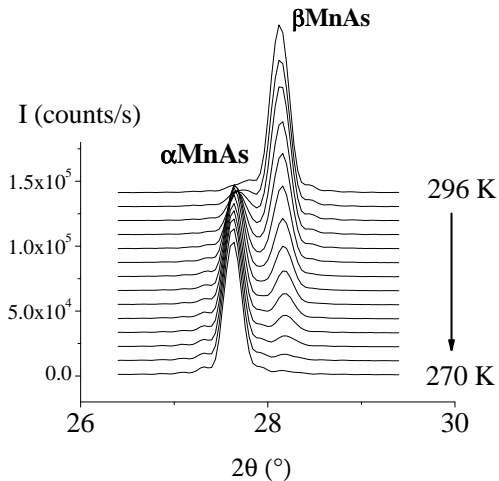
FIG. 2: X-ray reflections αMnAs($\bar{1}$100) and βMnAs(020) of the MnAs disks with a diameter of $\approx$80 nm and a thickness of 38 nm on a GaAs substrate obtained on cooling the sample from 296 K till 270 K in steps of 2 K. The curves are shifted vertically for clarity.

c(4×4)-reconstructed GaAs template at 250°C with a growth rate of 1.5 nm h^{-1} under As rich conditions. The microstructuring 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 (SEM) in Fig.1. The diameter of the disks is smaller than 100 nm, i.e. well below the equilibrium size of the elastic domains in the MnAs epitaxial layer [19].

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. A (3+3) 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 αMnAs and βMnAs reflections measured in symmetrical $\omega/2\theta$-scans (Fig. 2). The ($\bar{3}$300) and (060) or the ($\bar{1}$100) and (020) were analyzed [11, 15]. The layer reflections were fitted by Gaussian curves. The intensity ratio changes with temperature in the phase coexistence range [9]. We confirmed, that the samples 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 a GaAs substrate were compared to their parent unstructured samples. Here we show only the results from the smallest disks. The lateral period of the domain structure of
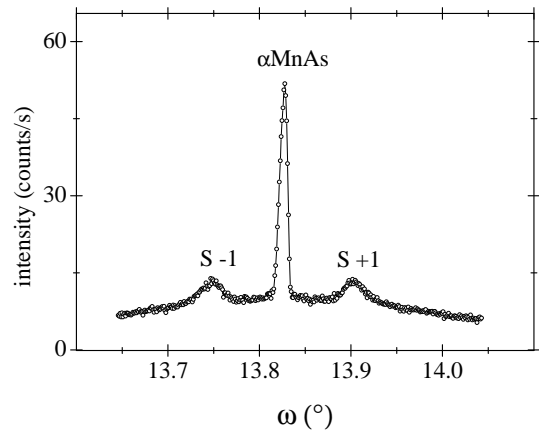

FIG. 3: Triple crystal ω-scan of the continuous layer near the reflection αMnAs($\bar{1}$100) revealing additional satellite reflections (marked by S -1 and S +1) due to a lateral periodicity of the elastic domains of 247 nm.

the original MnAs epitaxial layer can be obtained from the distance between satellite maxima $\Delta\omega_S$ in the ω-scan (Fig. 3). 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 [16]. The x-axis is defined to be perpendicular to the c-axis of MnAs
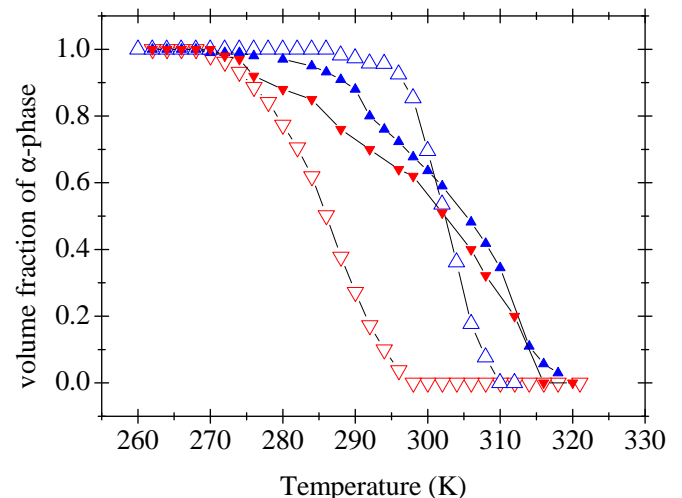

FIG. 4: (Color online) Temperature dependence of the volume fraction ξ of the MnAs α-phase illustrating the coexistence of the two phases in the MnAs layer (full symbols) and the MnAs disk (hollow symbols) system. Upwards (downwards) directed triangles correspond to the heating (cooling) curve. The changes 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 degrees and only a very small hysteresis is observed. The disk system changes from one phase to the other within 15 to 20 degrees and a strong hysteresis (width $20\pm5\ K$) of the temperature curve is found.

and parallel to the interface. The angular distance of the satellite maxima in Fig. 3 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] and SEM. The minimum equilibrium domain period is thus estimated to be 190 nm [9]. As the diameters of the smallest disks are are sufficiently small ($\approx$80 nm) only one elastic phase domain exists in an individual disk, which was confirmed, at least, at room temperature using magnetic force microscopy [14]. The full triangles in Fig. 4 show the temperature dependence of the phase content ξ of αMnAs in the unpatterned continuous epitaxial layer. As previously reported in [9] 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. So the overall phase coexistence range amounts to 45 K. In the vicinity of the transition temperature of 315 K the αMnAs content rises from zero almost linearly. In 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. 4 (hollow symbols). In cooling down the MnAs disks αMnAs 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. Subsequently the αMnAs content rises with further cooling until all the disks are transformed to be in the α-phase at 270 K. Once the α-phase had been realized entirely in all the disks, the sample was heated. Similarly 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 [5, 6]. The same widths of the hysteresis in the temperature dependencies of the magnetization in bulk MnAs [5] and of the phase content $\xi(T)$ in the MnAs disk ensemble are found. Moreover no phase coexistence takes place in the individual disks [14]. However, the phase transition in the disk ensemble still does not occur at a certain temperature, although the slope of the temperature curve $d\xi/dT$ has increased by a factor of 2-3 compared to that of the layer curve. The strong temperature hysteresis observed in the experiment (shown in Fig. 4) manifests the supersaturation in individual disks. The development of the new phase is retarded by a barrier, the energy Δf^* of formation of critical nuclei of the new phase [20]. A stable nucleus of the new phase is inevitable in each of the disks, since the individual disks are independent from each other, whereas in the continuous layer fewer nuclei are needed.

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[19] We take into account that the disks have a conical shape and take as the disk diameter the size of the smaller ring shaped contrast. The base of every disk is etched deeply into the GaAs material and has a larger diameter.

[20] In the isotropic approximation we find from the width of the hysteresis loop in the temperature curve of the MnAs disks $\Delta f^* = (4/3)\pi r_c^2 \sigma_b$, where $\sigma_b \approx 0.19 \ \mu cal/cm^2$ is the interface tension of the phase boundary and $r_c \approx 9 \ nm$ is the critical radius of the nuclei of the new phase [17, 18].