

Distribution of α and β phases in the coexistence regime in MnAs(0001) layers grown on GaAs(111)B

Y. Takagaki,^{a)} E. Wiebicke, L. Däweritz, and K. H. Ploog

Paul-Drude-Institut für Festkörperelektronik, Hausvogteiplatz 5-7, 10117 Berlin, Germany

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The discontinuous change in the lattice constant that occurs at the first-order phase transition between α - and β -MnAs gives rise to a coexistence of the two phases in MnAs layers grown on GaAs substrates. When the GaAs substrates are oriented in the (111)B direction, the c axis of MnAs is aligned normal to the growth plane. We identify the domain structure of α - and β -MnAs for this crystal orientation by utilizing the different reactivities of the two phases against wet chemical etching. Submicrometer-size islands of α -MnAs are found to be interwoven in a honeycomblike network of β -MnAs. We also show that this domain structure combined with strain effects results in a formation of MnAs lumps by etching. © 2004 American Institute of Physics. [DOI: 10.1063/1.1786359]

For the controlled carrier transport across dissimilar materials, abrupt and structurally ordered interfaces are generally desirable. Epitaxial growth of ferromagnetic materials on semiconductor (paramagnetic) substrates, therefore, can provide an ideal system for a wide variety of spin injection. The epitaxially grown layers are suitable also for an integration of spintronic devices into conventional circuits. MnAs/GaAs heterostructures are one of such material systems with interesting prospects.¹ The Curie temperature of MnAs (≈ 40 °C) is above room temperature and GaAs possesses excellent optical and electrical properties to investigate and utilize the spin polarization of the carriers injected from MnAs.²

The physical properties of MnAs/GaAs heterostructures are unique because of a peculiarity of MnAs. That is, the first-order phase transition in the magnetic properties is accompanied by a structural transition. The low-temperature ferromagnetic phase, α -MnAs, has a hexagonal structure while the high-temperature paramagnetic phase, β -MnAs, is orthorhombic. More importantly, the structural transition involves a volume change. α -MnAs is about 2% larger in volume than β -MnAs.³ To be specific, the lattice constant remains nearly unchanged along the c axis at the phase transition. The size change takes place only in the directions perpendicular to the c axis. This fact leads to significant consequences in epitaxial MnAs layers grown on GaAs substrates. The abrupt phase transition is disrupted because of the constraint from the substrates. The two phases coexist over a wide temperature range around the bulk transition temperature in order to reduce the stress arising from the discontinuous volume change at the phase transition.⁴

At present, MnAs layers are grown epitaxially on (001)- or (111)-oriented substrates of GaAs. In case of the (001) substrates,⁵ the (110) plane of MnAs forms the growth surface, see Fig. 1(b). The [0001] and [1120] directions of MnAs are aligned along the [110] and [110] directions of GaAs, respectively. The phase transition of MnAs induces a stress in one in-plane direction but not in the other orthogonal in-plane direction. Therefore, the coexistence of α and β phases takes place by forming a stripe structure.

Submicrometer-wide narrow strips of α - and β -MnAs are repeated alternately in the MnAs[1120] direction.⁶ Besides the magnetic properties, the stripe structure manifests itself as a corrugationlike modulation in the layer thickness as the lattice constants of α - and β -MnAs differ in the direction normal to the surface.

The MnAs layers grown on (111)B substrates^{7,8} arrange their c axis along the growth direction, Fig. 1(a). The $[\bar{2}110]$ and $[01\bar{1}0]$ directions of MnAs are parallel to the $[\bar{1}10]$ and $[11\bar{2}]$ directions of GaAs, respectively. Therefore, the phase transition leads again to a stress in the epitaxial layers. X-ray diffraction from the layered system has provided evidence for the coexistence of the two MnAs phases.⁹ However, the surface topography observed by atomic force microscope (AFM) was not successful in being associated with the domain structure as the height modulation results merely as a secondary effect due to the nonidentical elastic properties of α - and β -MnAs and is below the resolution of AFM.

In this letter, we determine the distribution of the α and β phases in MnAs(0001) layers grown on GaAs(111)B. Our determination method is based on the marked difference in

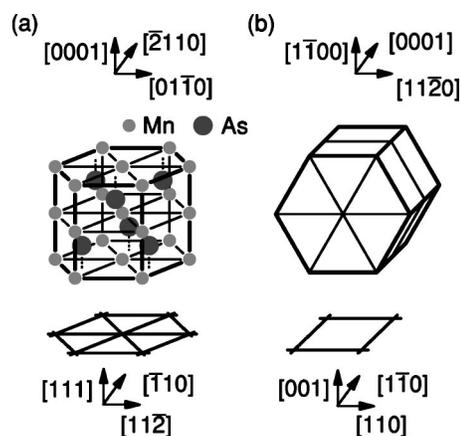


FIG. 1. Epitaxial relationships for (a) MnAs(0001) on GaAs(111) and (b) MnAs(1100) on GaAs(001). For the case of the GaAs(111)B substrate, the $[01\bar{1}0]$ and $[\bar{2}110]$ directions of MnAs are aligned along the $[11\bar{2}]$ and $[\bar{1}10]$ directions of GaAs, respectively. For the case of the GaAs(001) substrate, the $[1120]$ and $[0001]$ directions of MnAs are parallel to the $[110]$ and $[1\bar{1}0]$ directions of GaAs, respectively.

^{a)}Electronic mail: takagaki@pdi-berlin.de

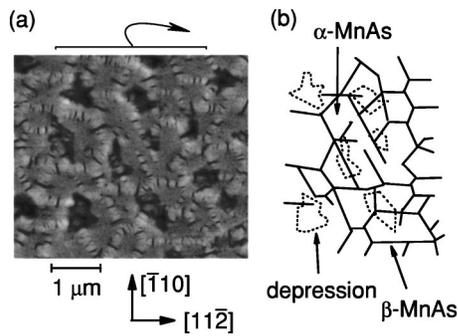


FIG. 2. (a) Scanning electron micrograph of the MnAs(0001) surface after a shallow wet chemical etching. Prominent features are illustrated in (b). The bright lines with black spots and the gray islands that fill the opening between the lines correspond to the domains of β -MnAs and α -MnAs, respectively. The dark islands, which are indicated by the dotted lines in (b), are the depressions formed by the terraces on the MnAs surface, originating from the surface morphology of the GaAs buffer layer. The as-grown thickness of the MnAs layer is 400 nm.

the reaction of α - and β -MnAs to wet chemical etch solutions. In addition, the domain structure is shown to produce submicrometer-size islands of MnAs in a self-organized manner by wet chemical etching.

For our experiments, a 400-nm-thick MnAs layer was grown on a GaAs(111)B substrate by molecular-beam epitaxy.¹⁰ The growth temperature was set to 225 °C for the initial ~ 2 nm of the MnAs layer. The subsequent growth was carried out at an elevated temperature of 300 °C. X-ray diffraction has revealed that α - and β -MnAs coexist in this heterostructure at temperatures between 40 and 50 °C.⁹ The fact that the temperature range for the coexistence is higher than the bulk transition temperature is a consequence of the MnAs layers experiencing tensile strain from the GaAs substrates. The layered system prefers α -MnAs to β -MnAs as the larger volume of α -MnAs is helpful to suppress the expansion of the layers enforced by the substrates. In contrast, the two phases coexist in MnAs layers grown on GaAs(001) substrates at temperatures lower than the bulk transition temperature, typically between 10 and 40 °C, as the layers are compressed by the substrates.⁴ That the temperature range for the coexistence is narrow for (111)B substrates in comparison to that for (001) substrates suggests the accumulated stress in the epitaxial layers being less for the former substrate orientation than the latter.

We investigate the domain structure of the two MnAs phases in the coexistence regime by means of an enhancement (or a creation) of the surface morphology through wet chemical etching. The idea is along the lines with the technique that makes crystal defects visible by a certain type of wet chemical etching. To the extent we have studied so far, any etch solution for GaAs etches MnAs as well. The etching of MnAs layers on GaAs(001) using HCl- and H₂SO₄-based solutions was examined in detail in Refs. 11 and 12. α -MnAs was found to be etched much faster than β -MnAs, leaving giant surface corrugations corresponding to the stripe structure for the (001) substrates when MnAs layers were etched for less than the whole layer thickness.¹²

Figure 2(a) shows a scanning electron micrograph of the surface of the MnAs/GaAs(111)B heterostructure after wet chemical etching. The etching was carried out at a temperature within the range of coexistence (≈ 42 °C) for 45 s using a HCl:H₂O₂:H₂O=4:1:12 solution. Due to the evaporation

of HCl and H₂O₂, which is inevitable at the relatively high temperature of the etching, precise control of the etch rate is difficult to achieve. We estimate that the MnAs layer was skimmed by 50–100 nm.

For a better understanding, critical features in the central area of Fig. 2(a) are sketched in Fig. 2(b). The most visible feature is a network of bright “broken” lines. The black elongated spots in the lines are cracks that are generated during the etching and seem to extend toward the MnAs/GaAs interface. Patches that appear as gray areas in Fig. 2(a) fill the opening within the network. The bright lines are about 30 nm higher than the gray islands. As the etching of α -MnAs is expected to be faster than that of β -MnAs also for the c -axis-oriented MnAs layer, we conclude that the network of the bright lines and the gray islands correspond to the domains of β - and α -MnAs, respectively. The bright lines stretch predominantly along three symmetrical in-plane directions, i.e., the GaAs[112] direction and its family related by the threefold symmetry of the epilayer and the substrate.¹³

The surface feature contains also polygon-shaped pits, which are seen as dark areas in Fig. 2(a). These pits are the depressions between the terraces that are characteristic for MnAs layers grown on singular GaAs(111)B surfaces. The depressions are formed during the growth of a GaAs buffer layer underneath the MnAs layer and hence exist prior to the etching. The step at the boundary of the terraces is about 30 nm in height, i.e., the depressions are about 30 nm deep. Notice that the network of the β -MnAs ridges is unaffected by the depressions as the step height is much smaller than the layer thickness.

As we stated above, the etching produces cracks within the ridges that presumably originate from the β -MnAs segments. The large strain in the MnAs layers imposed by the substrates is responsible for this crack generation. In MnAs layers grown on GaAs(001), cracks run in the direction perpendicular to the c axis of MnAs and extend far into adjacent regions of the MnAs layers that are protected from etching.¹² For the case of the GaAs(111)B substrates, however, the cracks are contained in the etching region. This provides additional evidence that the MnAs layers are less stressed on GaAs(111)B than on GaAs(001). Interestingly, it is the β -MnAs regions here that is important for the generation of cracks. This is in contrast to the situation in MnAs layers grown on GaAs(001), in which the presence of α -MnAs is essential for the crack generation.¹⁴

The textured domain structure is found to give rise to a formation of MnAs lumps when the etching further progresses.¹² In Fig. 3, we show a surface image when the etching was long enough for the etch front to reach the MnAs/GaAs interface. The image was taken from a boundary between the etched area and an area that had been covered by a resist to avoid the etching. In the border region, MnAs surfaces with various degrees of the wet chemical etching can be observed within a single frame of the micrograph, as is the case in Fig. 3. We can, therefore, acquire an overview of how this self-organized process proceeds. (We emphasize that the MnAs lumps emerge throughout the etched surface.)

At the center of Fig. 3, the domain structure of α - and β -MnAs is seen as the reversed triangle, indicated by the dotted lines, formed by the ridges. The large etch rate for α -MnAs in comparison to that for β -MnAs results in a pref-

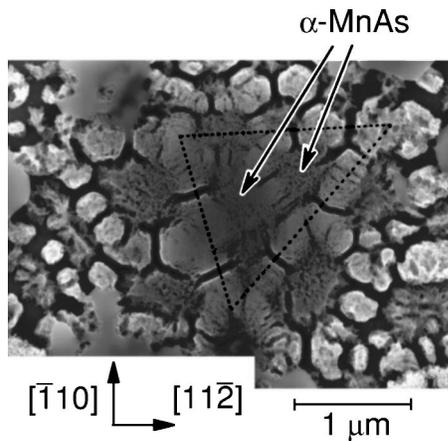


FIG. 3. Scanning electron micrograph of the MnAs(0001) surface after a deep wet chemical etching. The degree of etching increases from the center toward the periphery.

erential removal of the patches of α -MnAs encircled by the β -MnAs ridges, as we find in the adjacent areas on the left- and right-hand sides of the triangle. As the ridges are already divided into small segments by the cracks, these pieces are left as submicrometer-size lumps until they too are etched out. (See the peripheral areas in Fig. 3.)

We point out that the MnAs layers are anticipated to undergo complicated phase transitions during the etching process. The stress is partially released by the generation of the cracks and by the subsequent disappearance of MnAs that surrounds the lumps.¹² Given the circumstance that the etch temperature is fairly close to the bulk transition temperature, slight changes in the stress environment can induce phase fluctuations of MnAs. The formation process of the MnAs lumps is likely to be affected considerably by the etch temperature and the thickness of the MnAs layers. We show one such example in Fig. 4. The percentage of β -MnAs is larger in Fig. 4 than in Fig. 2 as the temperature was, presumably, just below the upper limit for the coexistence when the etching was performed. As a consequence of the dominance of β -MnAs, the MnAs lumps are large in size and cover almost the whole area, except for the small number of patches corresponding to the minority domain of α -MnAs.

In conclusion, the significantly different rates at which the α and β phases of MnAs are etched enable us to determine their distribution when the two phases coexist in the MnAs layers grown on GaAs(111)B substrates. Submicrometer-size segments of α -MnAs having polygonal shapes originating from the three-fold symmetry of the crystals are embedded in a honeycomblike network of β -MnAs. The large etch rate for α -MnAs and the etching-induced cracks that occur exclusively in the β -MnAs ridges forming

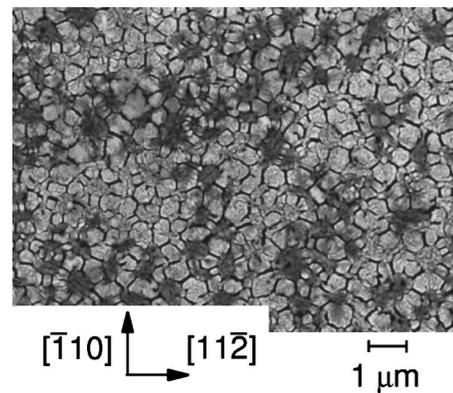


FIG. 4. Scanning electron micrograph when the etching was carried out presumably at a relatively high temperature. The dark areas correspond to the domain of α -MnAs.

the network give rise to a self-organized formation of MnAs lumps by wet chemical etching.

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