# Growth of *M*-plane MnAs on GaAs(111)B by molecular beam epitaxy

Y. Takagaki,[a)] C. Herrmann, B. Jenichen, J. Herfort, and O. Brandt
*Paul-Drude-Institut für Festkörperelektronik, Hausvogteiplatz 5-7, 10117 Berlin, Germany*

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We describe a growth procedure utilizing molecular beam epitaxy that produces a $(1\bar{1}00)$-oriented MnAs layer on GaAs(111)B despite the incompatible unit mesh symmetry. An amorphous MnAs layer is deposited at a low temperature beyond the critical thickness for coherent growth. When solid-phase epitaxy is initiated by reducing the background $As_4$ pressure, the layer crystalizes in the *M*-plane orientation with its *c* axis being along the $\{11\bar{2}\}$ directions of the substrate. The magnetization components associated with the coexisting *c*-axis orientations are independent of each other, suggesting that the structural domains are much larger in size than the atomic scales.  [DOI: 10.1063/1.2896616]

The phenomenon of epitaxial stabilization is, in general, based on specific interface structures defined by a minimum in total energy. These interfaces correspond to the preferred orientation-relationships between the lattices of the deposit and the substrate which are usually characterized by a low lattice mismatch. If the substrate and the epitaxial layer have lattice planes of the same symmetry and a mismatch $<8\%$, the initial growth will be pseudomorphic, i.e., coherently strained and with the orientation of the substrate. Thicker layers will relax by misfit dislocations when the strain energy exceeds the energy for dislocation formation.

In this paper, we present a growth procedure utilizing molecular beam epitaxy (MBE) that provides a surface orientation which is different from that obtained in conventional growth. In spite of the incompatible symmetries of the respective lattice planes, a layer of hexagonal MnAs is aligned on a GaAs(111)B substrate exhibiting the *M* plane as the growth surface, instead of the symmetry-matched *C* plane which is ordinarily obtained in MBE. X-ray diffraction (XRD) and magnetization measurements were carried out to inspect this surprising epitaxial orientation.

MnAs is an attractive material for spintronic applications as it is ferromagnetic at room temperature (the Curie temperature is about 40 °C) and can be grown epitaxially on GaAs, which is a widely used material for spin manipulation.[1,2] Bulk MnAs possesses a strong uniaxial magnetocrystalline anisotropy, in which the magnetic hard axis is oriented along the *c* axis. A control over the *c*-axis alignment to be perpendicular or parallel to the surface is thus advantageous for applications.

In our experiment, a 100-nm-thick GaAs buffer layer was grown on a (111)B-oriented substrate at a growth temperature of 600 °C. The $As_4/Ga$ beam-equivalent pressure (BEP) ratio was 24. During growth, a $(\sqrt{19}\times\sqrt{19})$ reconstruction was observed by reflection high energy electron diffraction (RHEED). The RHEED pattern changed to a $(2\times 2)$ structure while cooling the substrate to 200 °C. We emphasize that the substrate temperature $T_s$ was set here to a value which is significantly lower than that commonly used for growing MnAs. At this temperature, MnAs was deposited with an $As_4/Mn$ BEP ratio of 420. The RHEED pattern originating from the GaAs surface totally vanished, indicating that the MnAs layer was amorphous as a consequence of the low temperature. The nominal layer thickness was 2 nm with a nominal deposition rate of 0.3 nm/min (extrapolated based on the values for ordinary epitaxial growth at high $T_s$). We then increased $T_s$ to 270 °C, which is the optimum temperature for MnAs growth on GaAs(111)B.[3] During the increase of $T_s$, a RHEED pattern associated with the MnAs layer emerged, as shown in Fig. 1, indicating that solid-phase epitaxy took place. Using this crystalized layer as a template, an epitaxial MnAs layer with a thickness of 50 nm was grown by means of conventional MBE with an $As_4/Mn$ BEP ratio of 28 (the $As_4$ pressure was kept the same, whereas the Mn flux was increased). The growth rate was about 2.5 nm/min.

We have found that the MnAs layers prepared by the above-mentioned method are $(1\bar{1}00)$ oriented, in contrast to the (0001) orientation normally realized in the epitaxy on GaAs(111)B.[2] In Fig. 2, we show an XRD $\omega$-$2\theta$ scan across the GaAs(111) reflection. Apart from the substrate reflection, the MnAs$(1\bar{1}00)$ reflection is detected. The interference fringes indicated by the dotted bars in Fig. 2 manifest the smoothness of the MnAs surface and the abruptness of the MnAs–GaAs interface. In Fig. 2, we also indicate the expected angular position of the MnAs(0002) reflection. The amount of *C*-plane MnAs is seen to be small. We note that the XRD profile rules out the possibility that the *M*-plane growth is a consequence of the formation of facets during the preparation of the GaAs buffer layer.[4] While *M*-plane MnAs may favorably grow on certain surface orientations of GaAs

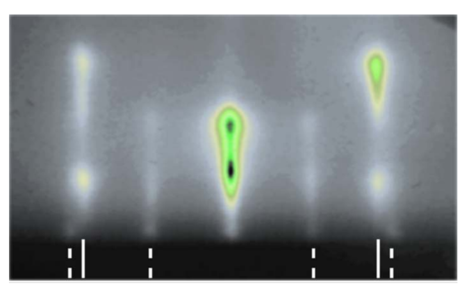

FIG. 1. (Color online) RHEED pattern of the low-temperature-deposited MnAs layer at 270 °C along the $[1\bar{1}0]$ azimuth of GaAs(111)B. The dashed and solid bars indicate the superposition of two distinct diffraction patterns resulting from the spacing of the (0002) and $(11\bar{2}3)$ planes, respectively.

[a)]Electronic mail: takagaki@pdi-berlin.de.

 

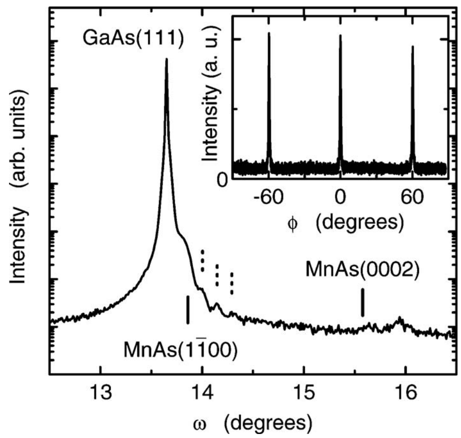


FIG. 2. XRD $\omega$-$2\theta$ scan of the 50-nm-thick MnAs layer on GaAs(111)B. The dotted bars indicate the interference fringes in the vicinity of the MnAs($1\bar{1}00$) reflection. The inset shows a skew-geometry $\phi$ scan of the ($\bar{2}201$) reflection of MnAs.

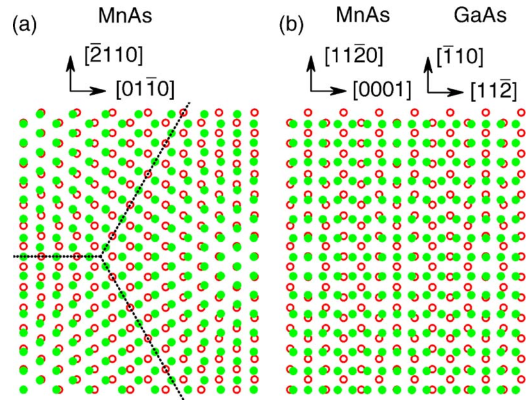


FIG. 3. (Color online) Comparison of the matching between the GaAs(111)B plane and the (a) *C* and (b) *M* plane of MnAs at growth temperature. The filled and open circles illustrate the configuration of the As atoms in MnAs and GaAs, respectively.

realized by faceting, we find no indication of the resultant inclination of the *c* axis of MnAs with respect to the nominal surface plane in the XRD profile.

In order to determine the actual orientation-relationship, we performed skew-geometry $\phi$ scans of the $(\bar{2}201)$ reflection of MnAs. The azimuthal in-plane angle $\phi$ is defined relative to the $[11\bar{2}]$ direction of the substrate. As shown in the inset of Fig. 2, the $(\bar{2}201)$ reflection is observed at integer multiples of 60°. The *c* axis is thus concluded to be aligned along the $\{11\bar{2}\}$ directions of the substrate. As the reflection amplitudes are the same within experimental accuracy, the hexagonal crystal is found to be arranged evenly in the six equivalent directions, resulting from the threefold symmetry of the substrate and the parallel and antiparallel alignment of the *c* axis. This epitaxial orientation is in agreement with the RHEED pattern, which can be interpreted as a superposition of twofold and fourfold degenerate patterns, as indicated by the bars in Fig. 1.

The *M*-plane orientation was established by the solid-phase epitaxy that occurred during the increase of $T_s$. In fact, faint reflections already appeared in the RHEED pattern when the As shutter was closed at 200 °C, prior to the increase of $T_s$ to 270 °C. This finding evidences that solid-phase epitaxy was initiated by the enhanced surface migration of Mn adatoms in the absence of an excess $As_4$ coverage of the surface. No diffraction ring was observed throughout the evolution of the RHEED pattern. The absence of a polycrystalline state suggests that the crystallization was under an overwhelming influence of the MnAs–GaAs interface.

In a separate experiment, we did not observe any reflections in the RHEED pattern if the As shutter was left open at $T_s$=200 °C. The RHEED pattern also remained absent when the As shutter was subsequently closed and even after $T_s$ was set to 270 °C, indicating that an initial excess $As_4$ coverage of the surface is detrimental for solid-phase epitaxy. A further increase of $T_s$ to 320 °C eventually resulted in the appearance of a RHEED pattern identical to that observed above, i.e., the MnAs layer is again *M*-plane oriented. The preference of the *M* to the *C* plane is, therefore, demonstrated to be robust and is unlikely to be a mere consequence of a subtle surface kinetics. The RHEED pattern in the latter case was, however, weak in intensity, implying that a quick enhancement of migration in an $As_4$-free environment immediately after the deposition of the amorphous layer is crucial for improving the quality of the layer.

The mechanism that leads to this specific orientation-relationship by solid-phase epitaxy is unclear at present. However, we would like to point out a scenario that could account for the unconventional epitaxial orientation-relationship. We presume that the thickness of the amorphous layer plays an important role. From the variation of the lattice constant during epitaxy monitored by RHEED, the critical thickness for MnAs on GaAs(111)B was estimated to be less than 1 nm.[5] The coherent layer formed by conventional high-temperature growth obviously corresponds to a minimum free energy and thus dictates the growth surface to be the *C* plane. Once chosen, the (0001) orientation is maintained throughout the growth even when the layer relaxes with introduction of misfit dislocations, regardless of the free energy of the relaxed layer. In contrast, the amorphous layer formed in our growth procedure is thicker than the thickness permitted for coherent growth. Therefore, when solid-phase epitaxy sets in, a relaxed layer is formed directly without going through the coherent growth stage. The experimental fact that we obtain purely *M*-plane-oriented layers suggests that the free energy of a relaxed *M*-plane layer is lower than that of a relaxed *C*-plane layer.

This inevitable conclusion from the results of our growth experiments is, however, counterintuitive when comparing the matching between the GaAs(111) plane and the MnAs(0001) [Fig. 3(a)] and MnAs($1\bar{1}00$) planes [Fig. 3(b)].[6] For the symmetry-matched case [Fig. 3(a)], the number of broken bonds can be reduced significantly by introducing misfit dislocations along the $[01\bar{1}0]$ directions, as indicated by the dotted lines.[2] In contrast, a dramatic reduction of the number of broken bonds appears to be hard to accomplish for *M*-plane MnAs on GaAs(111)B [Fig. 3(b)]. Microscopic investigations of the interfacial atomic configuration are needed to check the feasibility of our scenario.

It is worth noting that once the *M*-plane template has formed by solid-phase epitaxy, epitaxial growth can be resumed at $T_s$ of 200 °C. When the growth was carried out entirely at a fixed $T_s$ of 220 °C, the MnAs layer consisted of a mixture of the ($1\bar{1}00$) orientation (84%) and the (0001) orientation (16%). The epitaxial orientation is thus found to be significantly influenced by $T_s$ in this temperature regime.

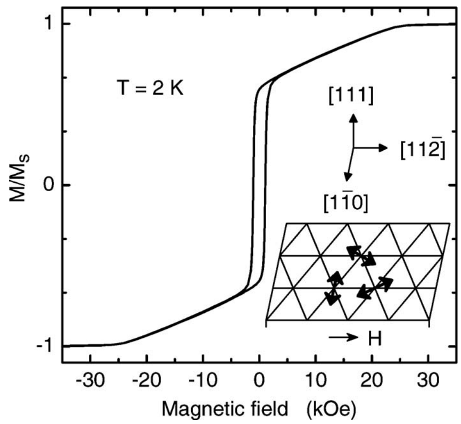


FIG. 4. Magnetization $M$ of a 50-nm-thick $M$-plane MnAs layer on GaAs(111)B normalized to the saturation magnetization $M_s$ at a temperature of $T=2$ K. The external magnetic field $H$ was applied along the $[11\bar{2}]$ direction of the GaAs substrate. The diamagnetic contribution of the substrate has been subtracted. The inset shows a schematic view of the orientation of the structural domains within the MnAs layer. The double arrows indicate the direction of the magnetic easy axes associated with the coexisting structural domains of MnAs.

It may be noteworthy that, while the principle epitaxial orientation of MnAs on GaAs(111)A is the $C$ plane, Morishita *et al.*[7] reported that the $(\bar{1}101)$ orientation became dominant for low growth temperatures using conventional MBE.

We have examined the magnetic properties of the $M$-plane MnAs layers using a superconducting-quantum-interference-device magnetometer. In Fig. 4, we show the dependence of the magnetization on an external magnetic field $H$ at a temperature of 2 K. The in-plane field was applied along the $[11\bar{2}]$ direction of the substrate. The magnetization curve reveals two components: an easy-axis-like component that gives rise to a hysteresis with the coercive field of about 1 kOe and a hard-axis-like component with the saturation field of about 25 kOe. The magnetization ratio of the two components is 2:1. As illustrated in the inset of Fig. 4, the external field is parallel to the magnetic hard axis for one third of the structural domains, resulting in the hard-axis behavior. For two thirds of the structural domains, the external field is tilted by 60° from the hard axis toward the easy axis. These domains provide the hysteresis with the coercive field enlarged by a factor of 1.15 in comparison to that when the field is along the magnetic easy axis.

The sizes of the structural domains are presently unknown. As the magnetization curve can be interpreted as a simple superposition of the contributions resulting from the different angles between the magnetic axes and the external field, the magnetic interaction between the structural domains is indicated to be insignificant. An individual structural domain is thus suggested to be large enough to sustain a well-defined magnetic domain. If the size of the structural domains is on the order of $1,\ldots,10$ nm, the magnetic coupling between atomic magnetic moments would be altered fundamentally.

We have also applied the same growth procedure to MnAs on a GaAs(001) substrate.[8] In conventional MBE growth, in which MnAs is normally $(1\bar{1}00)$ oriented, the $c$-axis orientation can be switched between being along the $[1\bar{1}0]$ and $[110]$ directions of the substrate (the so-called type A and type B orientations) by adjusting the growth conditions.[1] The epitaxial orientation realized by our growth method was a mixture of $(1\bar{1}00)$ (30%) and $(1\bar{1}01)$ (70%). Interestingly, the $c$ axis of MnAs$(1\bar{1}00)$ was aligned exclusively along the GaAs$[1\bar{1}0]$ direction.[9]

In conclusion, we have presented a growth procedure which provides $(1\bar{1}00)$-oriented MnAs layers on GaAs(111)B despite the symmetry mismatch of the participating lattice planes. This procedure consists of the deposition of an amorphous layer with a thickness exceeding the critical thickness for strain relief, and subsequent solid-phase epitaxy at elevated temperature. It is of great interest to see whether this method can also be applied to other heteroepitaxial systems, thus possibly enabling us to realize crystal orientations which cannot be easily synthesized with a direct epitaxial approach.

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[9]Broader peaks (by a factor of about 5) were additionally detected by XRD at angles of $\phi=\pm 60°$ tilted from the GaAs $[1\bar{1}0]$ direction.