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# Fabrication of MnAs microstructures on GaAs(001) substrates and their electrical properties

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Dedicated to the occasion of the 75th birthday of Prof. Hans Georg von Schnering

#### **Abstract**

We explore wet and dry etching processes of thin MnAs layers grown on GaAs(001) substrates for microstructuring. Most of the common wet chemical etch solutions for GaAs react with MnAs strongly and in a peculiar manner. Unidirectional cracks are generated when the MnAs layers are thicker than 100 nm. We demonstrate that the crack generation can be avoided by choosing a suitable etch solution or etch temperature. We fabricate submicrometer-wide MnAs wires using Ar ion milling. The resistivity of the narrow channels is measured over a temperature range covering the phase transitions in MnAs between the  $\alpha$ ,  $\beta$ , and  $\gamma$  phases. The resistivity along the MnAs[0001] direction is found to be smaller than that along the MnAs[11\overline{2}0] direction regardless of the phase. A nearly linear temperature variation of the phase fraction is deduced in the  $\alpha$ - $\beta$  phase coexistence regime. The temperature coefficients of the resistivities are negative for the nonmagnetic phases.

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#### 1. Introduction

In devices whose operation is based on the manipulation of the spin instead of, or in addition to, the electron charge, injecting and detecting spin currents play an essential role. A straightforward way to accomplish these tasks is attaching ferromagnets to nonmagnetic conducting channels. MnAs is one of the prospective materials for constructing such device elements as it is ferromagnetic at room temperature and can be grown epitaxially on GaAs [1]. The latter is advantageous since ferromagnetic components can be integrated into the electrical and/or optical devices prepared in GaAs with nearly perfect interfacial properties.

MnAs is attractive also for magnetic storage devices. Since the 1950s, the data storage density has increased steadily at a rate of one order of magnitude in six years [2,3].

\*Corresponding author. Fax: +49 30 2037 7515. *E-mail address:* takagaki@pdi-berlin.de (Y. Takagaki). In near future, the size of the storage cells is expected to enter the regime of superparamagnetism. Ferromagnetic particles cannot hold their magnetization when the anisotropy in the magnetic energy, which is in proportion to the volume of the particles, is small compared to the thermal energy  $k_BT$ . The thermal instability thus imposes a limit on the storage density. The relaxation of the magnetization in small MnAs dots was demonstrated to be slow owing to the large uniaxial magnetocrystalline anisotropy [4]. In spite of the benefits of stabilizing the magnetization, the uniaxial anisotropy cannot be made too large in practice as the external magnetic field for recording magnetic data scales in proportion to the strength of the anisotropy. While the magnetization can be kept rigid at room temperature down to considerably small sizes, the coercivity of MnAs diminishes at the Curie temperature  $T_c \approx 40\,^{\circ}\text{C}$ . The material is, therefore, ideal for thermally assisted magnetic recording [5], which is a scheme performing the recording at an elevated temperature to reduce the coercivity. Moreover, MnAs has a unique magnetic property which is ideal for this application, i.e., the ferromagnetism in MnAs is lost discontinuously [6]. The magnetization is, therefore, unusually large even for temperatures just below  $T_c$ , and the magnetic anisotropy can be substantial to prevent the thermal randomization.

In fabricating these so-called spintronic devices or recording elements, processing MnAs layers turns out rather cumbersome due to the remarkable chemical reactivity of Mn [7.8]. In this paper, we investigate various features which MnAs layers develop when they are subject to etching. The generation of unidirectional cracks during wet chemical etching using ordinary etch solutions, if the layer thickness is larger than a critical value, is probably the most problematic phenomenon. We demonstrate methods to avoid the crack generation. With respect to dry etching, MnAs is highly resistive to reactive ions. Ar ion milling appears to be the only possibility so far, except under special circumstances [8], to fabricate submicrometer channels. We examine the electrical properties of the thus defined narrow channels in the temperature regime where MnAs transforms itself between the  $\alpha$ ,  $\beta$ , and  $\gamma$  phases.

### 2. Epitaxial MnAs layers on GaAs

We employ in our investigations MnAs layers grown on GaAs substrates by molecular beam epitaxy (MBE). A number of crystal orientations of the MnAs layers can be realized by choosing appropriate surface orientations of the substrates and optimizing the growth conditions [9-12]. Throughout this paper, the surface planes of the MnAs layers and the GaAs substrates are set to be (1100)- and (001)-oriented, respectively. The growth temperature was 230-250 °C under an As<sub>4</sub>/Mn beam equivalent pressure ratio of 70 [13]. The epitaxial orientation relationship is such that the  $[0\ 0\ 0\ 1]$  and  $[1\ 1\ \overline{2}\ 0]$  directions of MnAs are parallel to the [1 \(\bar{1}\) 0] and [1 \(\bar{1}\) 0] directions of GaAs, respectively. Bulk MnAs possesses a strong uniaxial magnetocrystalline anisotropy with the magnetic hard axis along the [0 0 0 1] direction. While the (0001) plane is the magnetic easy plane, the magnetic moments in the epitaxial thin films are oriented along the  $[1 \ 1 \ 2 \ 0]$  direction due to the shape anisotropy.

Two phase transitions occur in bulk MnAs between the above-mentioned growth temperature and room temperature. The low-temperature phase,  $\alpha$ -MnAs, is ferromagnetic and has a hexagonal crystal structure. A first-order phase transition takes place at about 40°C. At 126°C, MnAs undergoes a second-order phase transition. The medium-temperature phase,  $\beta$ -MnAs, loses the ferromagnetism and the crystal structure transforms to be orthorhombic. The phase during the epitaxial growth is the  $\gamma$  phase, which is paramagnetic and the crystal structure is hexagonal. A bulk MnAs crystal exhibits inherent characteristics of a first-order phase transition at  $T_c \approx 40$  °C, i.e., an abrupt transition and a thermal hysteresis (about 10 °C). However, this is no longer the case for epitaxial thin layers. The  $\alpha$  and  $\beta$  phases coexist over a wide temperature

range around  $T_c$  [14]. As we show below, the wet chemical etching of MnAs is profoundly influenced by the simultaneous presence of the two phases.

The phase coexistence originates from the stress evolution in MnAs/GaAs heterostructures [14]. During the MBE growth, MnAs layers are nearly free of the stress as misfit dislocations are incorporated at the MnAs/GaAs interface. The difference in the lattice constants between MnAs and GaAs can thus be disregarded. In cooling the sample from the growth temperature, the thermal expansion mismatch results in tensile strain in the MnAs layers. A crucial fact is that the thermal expansion coefficient of MnAs is significantly large,  $5.8 \times 10^{-5}$ /°C for the  $\beta$  phase [15] and  $2 \times 10^{-5}$  or the  $\gamma$  phase [16]. In comparison, the thermal expansion coefficient of GaAs  $5.9 \times 10^{-6}$ /°C. The accumulation of the thermal stress continues steadily with decreasing the temperature down to  $T_c$ . When the first-order phase transition sets in, however, the stress suddenly reverses its sign. The phase transition between the  $\alpha$  and  $\beta$  phases involves a discontinuous volume change due to magnetostriction, i.e., α-MnAs is 1.9% larger than  $\beta$ -MnAs. Correspondingly, the stress in the MnAs layers imposed by the substrate changes to be compressive when the temperature is lowered beyond  $T_c$ . (The abrupt lattice expansion/contraction is so huge that bulk MnAs crystals were observed to generate microcracks after thermal cycles [17,18].) The simultaneous existence of both of the phases is energetically favored as the thermal and phase-transition stresses are compensated with each other [19]. The temperature range for the coexistence shifts according to the relative strength of the two stresses. The range extends to the high- or low-temperature side of  $T_c$  if the thermal or phase-transition stress is dominant, respectively.

The distribution of the two phase-domains depends on the orientation of the c-axis of MnAs with respect to the surface plane. The sudden volume change at the phase transition takes place in the directions normal to the c-axis. The lattice constant along the c-axis is almost identical between the  $\alpha$  and  $\beta$  phases. The anisotropic change of the lattice constants gives rise to a periodic repetition of  $\alpha$ - and  $\beta$ -MnAs in the MnAs[11 $\bar{2}$ 0] direction with submicron-scale periods in MnAs(1100)/GaAs(001) heterostructures. The period d increases almost linearly with the film thickness t as  $d \approx 4.8t$  [20]. As we see below, the wet chemical etching of MnAs layers suffers from the fact that the stress retains the full strength in the MnAs[0001] direction, as there exists no stress reduction mechanism in that direction. We note that the shape of the phase domains possesses a quasi-sixfold symmetry when the substrates are GaAs(111)B, for which MnAs is  $(0\,0\,0\,1)$ -oriented. Submicrometer-size islands of  $\alpha$ -MnAs are interwoven in a honeycomb-like network of  $\beta$ -The etching characteristics of the MnAs(0001)/GaAs(111)B heterostructures are qualitatively similar to those of MnAs(\bar{1} 100)/GaAs(001) heterostructures.

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