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# GaAs:Mn Nanowires Grown by Molecular Beam Epitaxy of (Ga,Mn)As at MnAs Segregation Conditions

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## ABSTRACT

**GaAs:Mn nanowires were obtained on GaAs(001) and GaAs(111)B substrates by molecular beam epitaxial growth of (Ga,Mn)As at conditions leading to MnAs phase separation. Their density is proportional to the density of catalyzing MnAs nanoislands, which can be controlled by the Mn flux and/or the substrate temperature. After deposition corresponding to a 200 nm thick (Ga,Mn)As layer the nanowires are around 700 nm long. Their shapes are tapered, with typical diameters around 30 nm at the base and 7 nm at the tip. The wires grow along the ⟨111⟩ direction, i.e., along the surface normal on GaAs(111)B and inclined on GaAs(001). In the latter case they tend to form branches. Being rooted in the ferromagnetic semiconductor (Ga,Mn)As, the nanowires combine one-dimensional properties with the magnetic properties of (Ga,Mn)As and provide natural, self-assembled structures for nanospintronics.**

Self-assembled one-dimensional structures such as nanowires (NW) or nanowhiskers are currently the subject of intense research activity.[1,2] They are expected to possess great capabilities for a wide range of applications, including physical nanodevices such as diodes,[1] transistors in both classical and single electron operation mode,[3] nanosensors,[4,5] and biological nanoengineering tools.[6] In view of these perspectives it is highly desirable to master the ways of NW formation and to understand physical phenomena leading to self-assembled nanowire growth. Although the basic mechanism leading to the growth of nanowire structures was identified over four decades ago by Wagner and Ellis[7] as so-called vapor−liquid−solid (VLS) growth, nowadays several other mechanisms have been proposed, and their applicability is debated.[8,9] The "classical" VLS mechanism of NWs formation requires the presence of liquid nanodroplets of a catalyst material, which accommodates and dissolves the NW constituent elements, and delivers them, due to supersaturation, to the NW tip at the NW−catalyst interface. This mechanism has been used for successful description of NW growth in different materials systems, both single elements (Si, Ge) and multinary alloys (e.g., binary and ternary III−V and II−VI semiconductors).[1,10−12] However, there is quite a large variety of materials that do not need any catalyst for NW growth, e.g., GaN[13] or ZnO.[14] There are also reports that the catalyst nanoparticles at the NW tips do not necessarily need to be in the liquid phase to stimulate the NW growth.[8,15] Here we present an example of a material system, (Ga,Mn)As, in which the NW formation is rather unexpected, but as it occurs, it is particularly interesting in view of opening prospects to integrate two important research domains, spintronics and self-assembled nanostructures. In the (Ga,Mn)As ternary alloy a significant part of the Ga atoms (up to about 8 atom %) is replaced by Mn. The Mn atoms provide both the localized spins $S = {}^5/_2$ and charge carriers (valence band holes), because they act as shallow acceptors in the GaAs host. The coupling between spins of localized Mn ions and valence band holes leads to

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a ferromagnetic phase in (Ga,Mn)As for Mn content higher than about 0.5 atom % and sufficiently high concentration of valence band holes (in the range of $10^{20}$ $cm^{-3}$). (Ga,Mn)-As is nowadays considered as a prototype ferromagnetic semiconductor.[16] Because the equilibrium solubility of Mn in GaAs is below 0.1 atom % (Ga,Mn)As with the required Mn concentrations in the range of several atom % can only be obtained by a highly nonequilibrium growth method such as low-temperature molecular beam epitaxy (MBE). The typical MBE growth temperatures used for GaAs (590−640 °C) are not applicable for (Ga,Mn)As, because under high-temperature growth conditions the Mn delivered into the growing GaAs film segregates to MnAs nanoclusters.[17] As shown for the first time by Ohno et al.,[18] the use of very low growth temperatures, in the range 200−300 °C allows overcoming the Mn segregation problems and leads to formation of a (Ga,Mn)As ternary alloy. (Ga,Mn)As has been already demonstrated to be useful for fabrication of functioning spintronics components such as spin lasers,[19] or tunneling magnetoresistance structures.[20] There are reports on self-assembled NWs obtained in other magnetic semiconductor systems like (Ga,Mn)N, (Zn,Mn)O.[21,22] However, in these materials the realization of carrier-induced ferromagnetism is uncertain due to extreme difficulties in sufficiently high p-type doping levels, and evidence of segregation of additional magnetic phases identified in the corresponding layer structures.[23,24] In the case of (Ga,Mn)As the carrier induced ferromagnetism is very well established and quite well understood, at least in the layer geometries.[25] Recently, magnetoelectronic effects associated with single electron transport were reported in (Ga,Mn)As nanostructures obtained via chemical methods (e-beam lithography and wet chemical etching).[26] Thus, the possibility of obtaining self-assembled wire-like nanostructurers in this compound is particularly interesting. We note that two reports concerning Mn induced growth of GaAs nanowires have appeared recently. Martelli et al.[27] describe Mn-catalyzed formation of GaAs nanowires during GaAs MBE growth at moderate and high temperatures (450−620 °C). These authors deposited a thin metallic Mn layer prior to the NW growth and observed catalytic properties of pure Mn, revealing its presence at the NW tips. Jeon et al.[28] ascribe the development of defect-free (Ga,Mn)As nanowires (containing 20% Mn) to initial formation of (Ga,Mn)As islands due to lattice mismatch between the high concentration (Ga,Mn)As layer and the GaAs(001) substrate. However, as the lattice mismatch between (Ga,Mn)As and GaAs is quite small [about 0.4% for the highest Mn content possible (close to 10%); even for 1 $\mu$m thick (Ga,Mn)As layers deposited on GaAs(001) substrates the layer is coherently strained to the substrate without any lattice relaxation],[29] this mechanism is questionable. In this Letter we show that the mechanism leading to the development of nanowires in this system is the catalyzing action of MnAs nanodots appearing due to phase separation occurring during (Ga,Mn)As MBE growth at the temperature that is too high for the formation of a uniform (Ga,Mn)As ternary alloy.

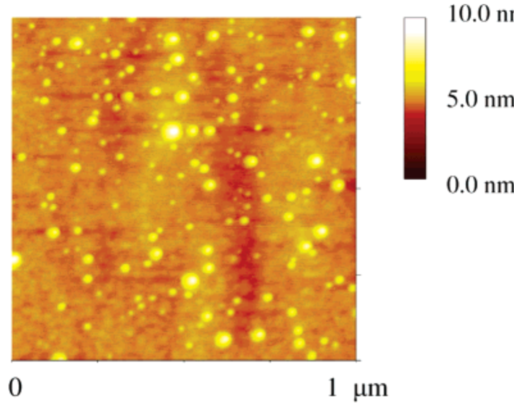


**Figure 1.** AFM image of a 50 nm thick $Ga_{0.94}Mn_{0.06}As$ layer with MnAs nanoislands segregated at the surface.

The samples were grown in a KRYOVAK MBE system dedicated to (Ga,Mn)As growth. As substrates we used epi-ready GaAs(001) and GaAs(111)B n-type wafers. To facilitate direct comparison, pieces of the two substrates were placed close to each other on the same substrate holder. The substrate temperature during growth was monitored by an infrared pyrometer operating in the 100−700 °C temperature range. After growing a thin GaAs buffer layer at high-temperature (590 °C), the substrate temperature ($T_S$) was decreased to 300−350 °C (depending on Mn flux: higher $T_S$ for lower Mn flux) and (Ga,Mn)As growth was started. The growth was performed using $As_2$ molecular flux generated by a valved cracker As source, with a As:Ga flux ratio of about 2. The Mn flux was evaluated via RHEED intensity oscillations recorded for (Ga,Mn)As thin film calibration samples. The substrate temperature used for NW growth was set to be above the maximum temperature growth of uniform (Ga,Mn)As layers.[17,30] MBE growth at these conditions leads to the appearance of 3D-features in RHEED, due to formation of MnAs clusters. In the case of (Ga,Mn)As with high Mn content (in the range of 5%) growth above a critical temperature results in an abrupt transition between 2D and 3D RHEED features. The morphology of a (Ga,Mn)As surface with MnAs clusters investigated by AFM is shown in Figure 1. The islands have diameters of 300−500 Å and heights in the range 20−50 Å.

For low Mn content (1% in the present case) the transition from the 2D to 3D surface is rather gradual, as shown in Figures 2 and 3. For both (001) and (111)B substrates the growth starts from smooth two-dimensional GaAs surfaces. The initial (001) surface (Figure 2a) has a 2-fold reconstruction in [110] and [−1,1,0] azimuths and 4-fold in [010] and [100], typical for the $c(4 \times 4)$ reconstructed GaAs(001) surface. After Mn and Ga shutters are opened, the 2-fold periodicity in the [110] azimuth disappears and surface roughening occurs, as manifested by 3D chevron-like features at the main diffraction streaks. After about 5 min of the growth the 2D diffraction streaks disappear and a purely 3D diffraction image is seen. The multiple diffraction spots are due to coherent twinning on the {111} plane. Figure 2g shows a scanning electron microscopy (SEM) image of the NWs grown on the (001) substrate after 1 h growth time. The SEM images were obtained with the incident electron

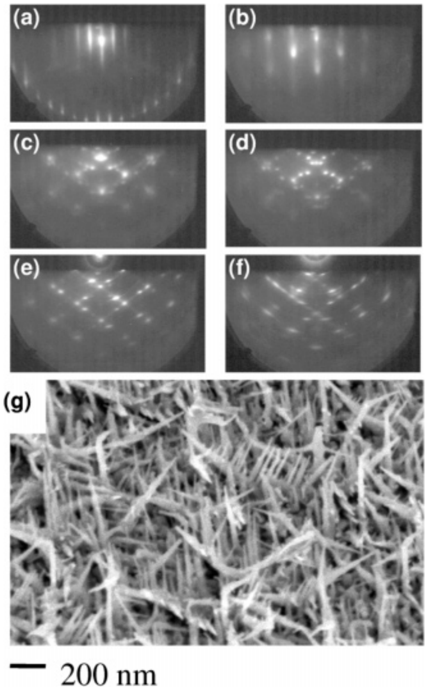


**Figure 2.** RHEED patterns along [110] azimuth at different stages of growth on GaAs(001): (a) initial GaAs(001) surface; (b)−(f) after 3, 6, 11, 25, and 60 min of growth; (g) SEM image after 60 min growth.

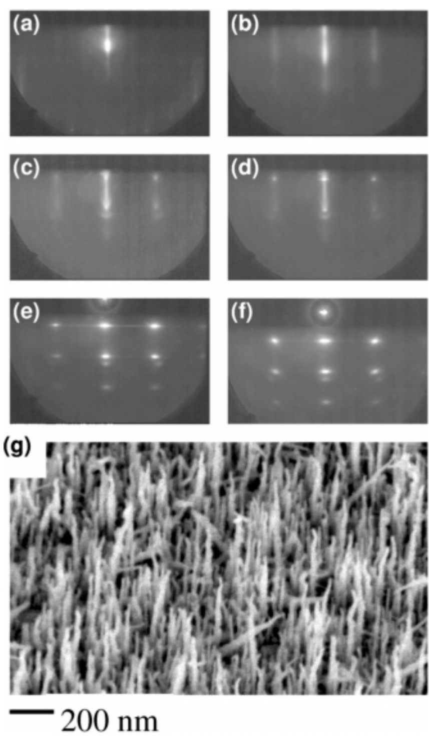


**Figure 3.** RHEED patterns along the [11−2] azimuth at different stages of growth on GaAs(111)B: (a) the initial GaAs(111)B surface; (b)−(f) after 2, 7, 10, 25, and 60 min of growth; (g) SEM image after 60 min growth.

beam inclined 45° with respect to the surface plane. The nanowires have different orientations and many of them have branches, pointing preferentially away from the substrate surface.

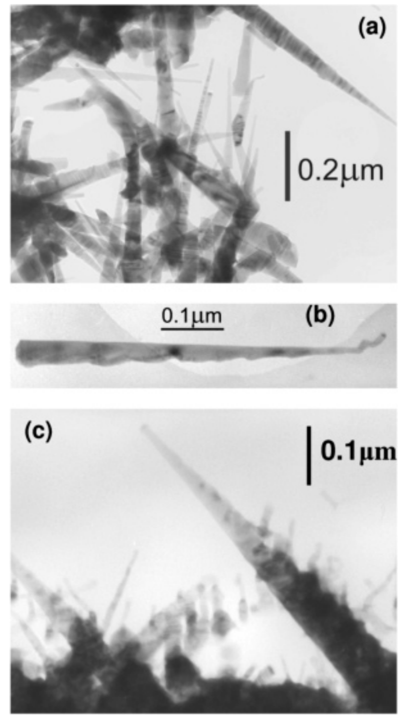


**Figure 4.** TEM images of (a) GaAs:Mn NWs scraped from the (001) substrate on a holey carbon film, (b) a single NW revealing its straight and rough sides, and (c) cross-sectional view along the ⟨110⟩ substrate direction. The downward NW sides are straight without secondary branches, contrary to the sides exposed to the effusion sources.

For nanowires grown on the GaAs(111)B surface the structure is much less disordered, as indicated by the RHEED patterns (Figure 3a−f). This is also seen in the SEM image (Figure 3g), which shows that the majority of nanowires are now perpendicular to the substrate surface (i.e., oriented along the ⟨111⟩ growth direction). In this case no additional spots are visible in RHEED between substrate diffraction streaks. All spotty patterns are located along the 2D RHEED streaks from the initially smooth GaAs(111)B surface, because the twinning planes are now parallel with the substrate surface.

Transmission electron microscopy (TEM) images from individual nanowires scratched off the (001) substrate and placed on a carbon film TEM grid are shown in Figure 4a. All the nanowires are tapered. The single nanowire shown in Figure 4b is quite smooth on one side and much rougher on the other. As noted above, the branches visible in SEM (Figure 2g) are found preferentially on one side of the NW. The NW morphology is more visible in a TEM picture made in cross-sectional geometry, where both the NW and substrate surface are shown. Figure 4c shows the cross-sectional TEM picture of a sample grown for 1 h with Mn content corresponding to 1 atom % in a uniform growth of (Ga,Mn)As layer. It is clear that the smooth NW side is facing the substrate, and the short branches occur on the "outer" side, i.e., the side facing the effusion sources. It seems likely that the roughness seen on one NW side in Figure 4b reflects an early stage of branch formation. Their geometrical distribution indicates that the branches are formed due to

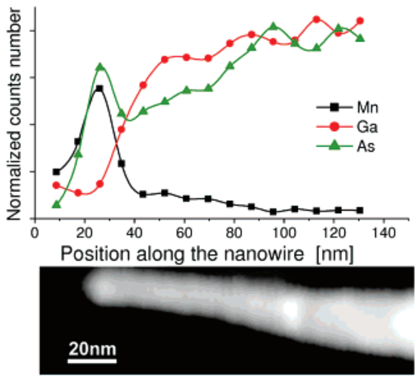


**Figure 5.** TEM image of a single NW and the corresponding EDX line scan.

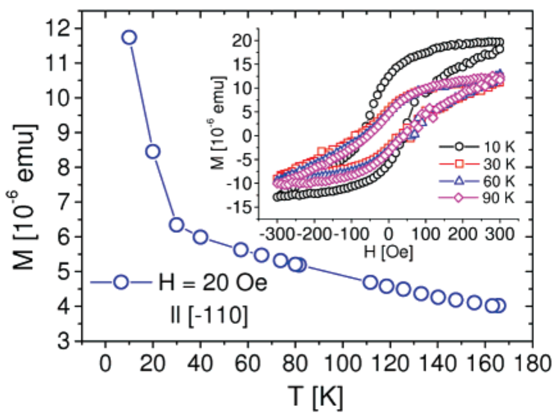


**Figure 6.** Temperature dependence of magnetization (main frame) and hysteresis curves (inset) for nanowires on GaAs(001). The M(T) dependence was measured with an external magnetic field of 20 Oe along the [-110] direction.

the action of impinging Mn atoms, which are known to have very low surface mobilities, especially at the low growth temperatures used. It is worth noticing that the density of branches increases with increasing Mn flux.

Figure 5 shows a result of an EDX measurement of an elemental composition along a top part of a selected nanowire. A clear enhancement of Mn and As signals at a tip is found. Because the Mn:As ratio at the tip is close to one, and no free Mn can occur in the III−V MBE system with high As overpressure, Mn at the tip region must be bound with As, forming a MnAs nanocluster.

The magnetic properties of one of the GaAs:Mn NW samples were analyzed by a SQUID magnetometer, see Figure 6. The sample was grown for 60 min on GaAs(100) at 320 °C, with a Mn flux corresponding to 6% Mn content in uniform (Ga,Mn)As and at a planar growth rate of 0.2 monolayer/s. Because the SQUID signal is collected from all parts of the sample (including GaMnAs layer, nanowires, and quantum dots), one can expect rather complex overall magnetic characteristics. Nevertheless, some significant features are observed. First, we note that the sample shows nonzero magnetization and hysteretic behavior up to 170 K (M(H) curves are displayed only up to 90 K). Second, we see that the magnetization curve (only field cooled data were recorded) has a clear break around 30 K. These observations can be correlated with results reported for Mn(Ga)As nanoclusters obtained by thermal annaling of (Ga,Mn)As layers.[31] Specifically, it was found that slow annealing in the growth chamber resulted in MnAs clusters in ZB structure, and clusters subjected to long term annealing at temperatures similar to those applied in the present work showed no room-temperature ferromagnetism. Instead, the samples exhibited superparamagnetic behavior with a blocking temperature around 30 K. Although further detailed magnetic charcterization of the present samples is needed, we tentatively associate the ferromagnetic signal up to 170 K with the (GaMn)As layer formed parallel with the nanowires, and the rapid increase in the magnetization below 30 K with the nanoclusters located on the nanowires.

In conclusion, we have observed formation of nanowires during MBE growth of (Ga,Mn)As at MnAs segregation conditions. Although the nanowires appear without any external catalyst, the NW growth is induced by surface segregated MnAs nanoclusters. The GaAs:Mn nanowires are tapered and grow along the ⟨111⟩ direction both on (001) and (111)B oriented GaAs substrate. NWs grown on the GaAs(001) substrate have a strong tendency to form branches at the sides exposed to the fluxes from effusion cells during the MBE growth.

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