Mn-assisted molecular-beam epitaxy growth (Ga,Mn)As nanowires

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Abstract. Arrays of (Ga,Mn)As crystal nanowires on a GaAs (100) substrate were obtained using molecular-beam epitaxy at the substrate temperature 485°C. From the high energy electron diffraction patterns, the crystallographic phase of the nanowires is detected to be cubic which is supporting by ex situ microscopy study.

1. Introduction

Recently, interest has continued in one-dimensional nanostructures—crystal nanowires (NWs) grown using different technological methods, including molecular-beam epitaxy. This interest is due to the unique properties of these structures associated with a small number of structural defects, as well as the possibility of the NWs growing on substrates with large mismatch in lattice parameters. As a rule, the NWs growth corresponds to the so-called vapor–liquid–crystal method with a catalyst based on different metals. To activate such growth, the most frequently used metal is Au [1–3]. Self-catalyzed growth of the crystal nanowires is also possible, i.e., growth using its own material. In the case of GaAs, for example, gallium may serve as the catalyst for NW growth [4, 5]. Also, successful synthesis of (Ga,Mn)As NWs on GaAs(111)B substrates when using Mn as the catalyst has recently been reported [6].

It is worth noting that semiconductor compounds based on (Ga,Mn)As are very promising materials as applied to spintronics, since they have properties that are inherent to semiconductors as well as magnetic materials. Such semiconductors are called diluted magnetic semiconductors. One
of the main problems in such materials use is that their Curie temperature is far from room temperature [7].

Transition to synthesis of nanostructures with reduced dimensionality, such as two-dimensional layers or quasi-structures like NWs, may be one of the ways to solve this problem. In contrast to the films, synthesis of the NWs opens more opportunities to create defect-free structures on a mismatched substrate.

In this paper, we showed the principal possibility to synthesize (Ga, Mn)As NWs on GaAs(100) substrates using Mn as a catalyst.

2. Experiments

The growth experiments were carried out using an EP1203 MBE system equipped with Ga, Mn atomic and As$_4$ molecular cells. First, epi-ready GaAs(100) substrates were thermally cleaned to eliminate native oxide layer at 620°C. The deoxidation process was monitored by the reflection high-energy electron diffraction (RHEED) method. The temperatures of the cells were equal to 1000°C, 373°C, and 720°C, for Ga, As, and Mn correspondingly. After completion of the oxide removing process, the temperature of the substrate was lowered by 40–50°C, and the growth of the GaAs buffer layer was carried out over 15 minutes to smooth out the surface. Then the temperature was decreased by another 10°C and Mn shutter was opened (As shutter was closed during Mn deposition stage) for 2 minutes to form Mn terminated nanoclusters used as a catalyst for the self-catalyzed growth of NWs later on. As the working temperature (485°C) was reached, the Mn, Ga, and As cells were simultaneously opened, and the (GaMn)As NWs started to grow. The time of NWs nucleation evaluated from RHEED pattern was 30 seconds. The total growth time was equal to 25 minutes at the GaAs growth rate equals to 1 ML/s. It should be noted, that the growth of NWs occurred under slightly metal stabilized growth conditions, i.e. the As$_4$/Ga flux ratio was 0.4.

3. Results

As it was noticed in [4], the predominant crystallographic phase of NWs was cubic, when GaAs NWs on a Si(111) surface were formed in Ga-stabilized conditions. The same type is characteristic for the obtained NWs array, as we detect from the RHEED patterns (Figure. 1), since the diffraction picture shows the presence of the cubic phase, only. The lack of characteristic reflections related to the hexagonal phase (in particular, 0001) indicates the absence of a wurtzite phase in the obtained structures. As was shown in [8, 9], in the process of GaAs NW growth on Si(100), Si(111), and GaAs(111)B substrates with Au as the catalyst, the predominant crystallographic phase is wurtzite. However, under definite growth conditions, a transition from a cubic structure to a hexagonal one and vice versa is possible. For our samples, such a transition is not characteristic, which is exclusively due to the influence of Mn. It should be noted that the NW formation on a substrate with orientation (100) can occur in four equivalent directions <111>. As follows from the RHEED pictures in our case, only two preferential directions of growth, which is likely caused by features of NW formation in this system one can observe.
The morphology of the NWs obtained was studied using a scanning electron microscope (SEM) Zeiss Supra 25. SEM images of (Ga,Mn)As NWs shown in Figure 2 (a, b) demonstrate that NWs have typical lengths between 0.8 µm and 4 µm and diameters 50–90 nm. The nanowire density is about $10^7$ cm$^{-2}$. Most of NWs have a preferential growth direction along $<111>$ and $<110>$. Some of them are oriented along $<310>$ crystallographic directions. Remarkably, (Ga,Mn)As NWs do not have any branches. Many of them are slightly tapered, which can be caused by the relatively low growth temperature resulting in limitations on Ga adatom diffusion lengths [10, 11].

The structural and chemical characterization of the grown samples was carried out by transmission electron microscopy (TEM). For this purpose, the samples were prepared in two different ways. First, the NWs were chopped from the substrate and suspended on a carbon grid. The growth direction of the NWs and their morphology were analyzed in a JEOL JEM 4010 microscope, which allowed a high-resolution TEM investigation (HRTEM) of the crystal structure, including lattice defects detection. Second, the chemical nature of precipitates found on the substrate surface as well as the chemical composition were investigated by high-angle angular dark-field scanning transmission electron microscopy (HAADFSTEM) combined with energy-dispersive X-ray analysis (EDX). For this analysis, we used a FEI TITAN 80/300 equipped with a probe corrector, which allowed a lateral resolution of 0.1 nm. Figure 3 shows a typical example of a $<110>$ oriented NW obtained as a result of TEM measurements. The NW has a length of 2 µm, diameter is lower 100 nm, which is changed due to slight tapering. Even in such long NWs, we could not find crystal defects, such as dislocations or
precipitates. However, some of them may have planar features as stacking faults lying parallel to the growth direction (see Figure 3). The NWs have pure zincblende crystal structure. The EDX analysis of (Ga,Mn)As also yields no local precipitation of the Mn within the detection limit of 0.5%. Thus, Mn is homogeneously distributed over the NWs with the concentration less the $10^{20}$ cm$^{-3}$.

Figure 3. TEM image of a $<110>$ oriented NW. The tip at the upper right contains the growth front and the catalytic droplet, which contains a high concentration of Mn. The dark features inside the NWs are caused by bending of the crystal lattice, known as "bending contours." In the center, a stacking fault (SF) is located lying parallel to the growth direction.

4. Conclusions
In summary, (Ga,Mn)As NWs have been grown by MBE on GaAs(100) substrates using Mn as a catalyst. The majority of the NWs have preferential growth direction along $<111>$ and $<110>$. The NWs do not have any extended defects, such as dislocations or precipitates. The EDX analysis of (Ga,Mn)As also yielded no local precipitation of Mn within the detection limit of 0.5%. Some of the NWs contain planar features such as stacking faults lying parallel to the growth direction.

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