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MBE fabrication of Mn_xP nanowhiskers

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Abstract. MnP and Mn_2P nanowhiskers have been grown by molecular-beam epitaxy (MBE) technique on InP(100) and GaAs(111)B substrates. The catalyst-free growth of nanowhiskers is found to be depended on the formation of Mn-based nanoclusters. The magnetic properties of the samples have been investigated by the measurements in a vibrating sample magnetometer.

1. Introduction

The fabrication of one-dimensional nanostructures such as nanowhiskers or nanowires attracts more and more attention due to their versatile device application [1,2]. Contrary to the routine vapour-liquid-solid (VLS) method of the nanowhiskers growth which relies on the use of metal catalyst nanoparticles [2-4], so called catalyst-free (or self-catalytic) method [5-8] allows to avoid any contaminations of nanowhiskers from a metal catalyst as well as to obtain completely self-assembled formation of nanowhiskers and therefore is of importance for the creation of the new devices.

The present work is devoted to the investigation of self-catalytic growth of Mn_xP nanowhiskers and their properties. It should be pointed out that bulk orthorhombic MnP is very promising material because it exhibits very interesting properties such as ferromagnetism with relatively high Curie temperature (T_c = 291.5 K [9]), catalytic and magnetocaloric properties. Therefore the creation of one-dimensional nanostructures on the basis of MnP might have even more potential for the spintronics applications, yet has not been thoroughly investigated. Recently MnP nanorods have been successfully synthesized by the solution-phase thermal decomposition of continuously delivered Mn-tri-n-octylphosphine (TOP) complex using a syringe pump [10]. Here we report on different line of attack which is based on the growth of Mn_xP nanowhiskers by molecular beam epitaxy (MBE).

2. Experimental techniques

Originally Mn_xP nanowhiskers have been found simultaneously with Ge nanowhiskers during MBE growth of $MnGeP_2$ thin films [11]. MnP and Mn_2P nanowhiskers have been grown by MBE technique without any preliminary deposited metal catalyst on InP(100) and GaAs(111)B substrates. Mn was supplied using conventional Knudsen cell, whereas P_2 was obtained by decomposition of tertiarybutylphosphine (TBP) inside the cracking cell. The time of the growth was varied from 30 min

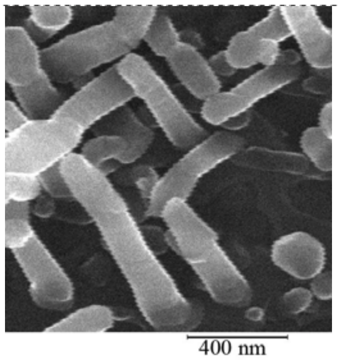

Figure 1. SEM image of nanowhiskers grown on InP(100) substrate. (T_{growth}=510°C)

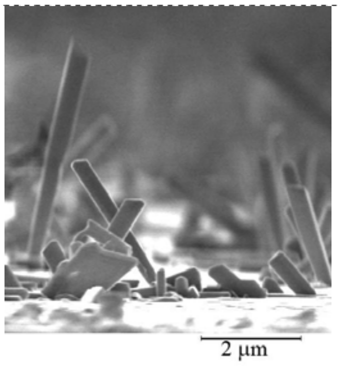

Figure 2. SEM image of nanowhiskers grown on GaAs(111)B substrate. (T_{growth}=535°C)

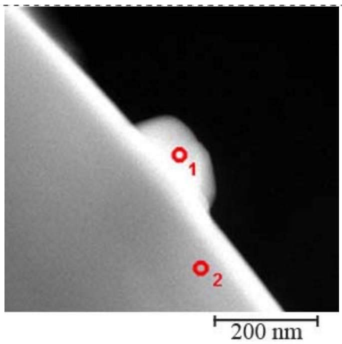

Figure 3. STEM image of Mn-based nanocluster on InP(100) substrate. (point 1 – composition of Mn:P ~ 20:14 %,point 2 – InP.

up to 2 hours. The temperature of the substrates was held between 480-545°C. The flow rate of TBP was set in the range of 2.0-2.3 sccm using mass flow controller. The temperature of Mn K-cell was varied in the range of 630-660°C.

A scanning electron microscope (SEM, HITACHI S-4500) and a transmission electron microscope (TEM, FEI TECNAI-F20) equipped with scanning TEM (STEM) and energy-dispersive X-ray spectrometer (EDX) were used for microstructure analysis of nanowhiskers. TEM specimen was prepared by transferring nanowhiskers from the substrate surface onto Cu grid. Magnetic properties of the samples have been examined by the measurements in a vibrating sample magnetometer (VSM, TOEI VSM-5-19).

3. Results and discussion

The typical microstructure of self-assembled nanowhiskers obtained on InP(100) and GaAs(111)B surfaces are shown on Figures 1 and 2 correspondently. SEM images demonstrate that the nanowhiskers grown on InP and GaAs substrates differ not only in sizes but also in crystallographic shapes. For example, nanowhiskers obtained on InP(100) surface have diameters close to 150 nm, lengths up to 2 μm, whereas nanowhiskers grown on GaAs(111)B surface have lengths up to 30 μm, widths up to 600 nm and, it should be especially emphasized, clear atomic facets (see Figure 2).

As mentioned above, in our growth procedure we do not deposit any preliminary metal catalyst layer. Nonetheless, it was found that some of nanowhiskers grown at higher temperatures on InP substrates have more complicated structure consisting of two parts similar to the nanowhiskers obtained according to VLS growth mechanism using metal catalyst nanoclusters as a seeds for the growth. The number of such nanowhiskers was increasing with the time of growth. Moreover, STEM investigations have revealed that the growth of nanowhiskers on both GaAs(111)B and InP(100) surfaces is apt to be caused by the formation of Mn-based nanoclucters on the substrate surface (see Figure 3). It seems likely that crystallographic structure of Mn-based nanoclusters and evidently shapes of nanowhiskers depend on surface reconstruction of the substrates. However, the process of the nucleation of Mn-based nanoclusters has not been thoroughly investigated and it is one of the goals for the current studies.

The study of chemical composition of elements of nanowhiskers has been performed using EDX spectrometer. The results obtained have shown that chemical composition of nanowhiskers grown on GaAs(111)B substrate is close Mn_2P phase (see Figure 4). On the top of nanowhiskers we have not found any precipitated droplets of other phase.

Such self-catalytic growth of nanowhiskers appears to be partially explained taking into account diffusion-induced mechanism [8,12,13]. According to this mechanism, top surface of nanowhiskers

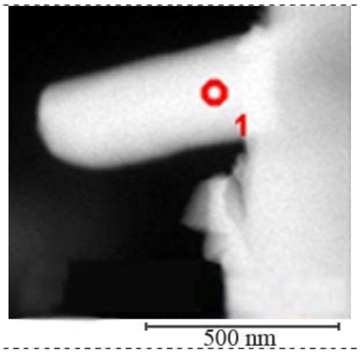

Figure 4. STEM image of the nanowhisker grown on GaAs(111)B substrate. (point 1 – composition of Mn:P ~ 48.8:25.4 %).

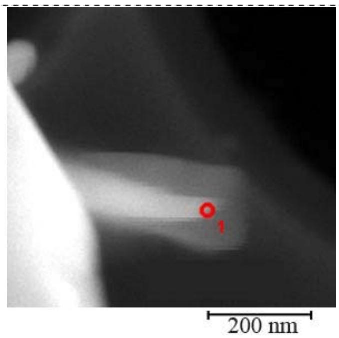

Figure 5. STEM image of the nanowhisker grown on InP(100) substrate. (point 1 – composition of Mn:P ~ 38.50:38.48 %).

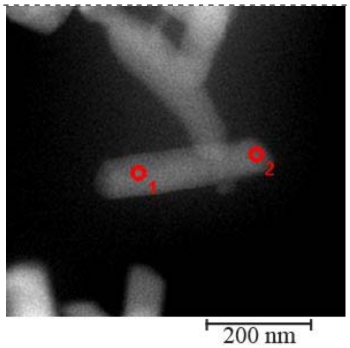

Figure 6. STEM image of the nanowhisker grown on InP(100) substrate. (point 1 – composition of In:Mn:P ~ 34.47:13.2:36.5 %, point 2 – In:Mn:P ~ 6.04:40.87:42.24).

due to low chemical potential attracts adatoms diffusing towards the tip on side facets [8]. Depending on the relation between the diffusion and nanowhiskers lengths, shapes of nanowhiskers can be different. If the length of nanowhisker is longer, the tapering of nanowhisker occurs. In case of GaAs substrate for our growth condition, it seems that we deal with relatively big values of the diffusion lengths because we have not found nanowhiskers of that type, whereas for the growth on InP(100) surface such kind of nanowhiskers can be observe.

The chemical composition of elements measured for nanowhiskers grown on InP substrate seems to be correspond to MnP phase (see Figure 5), though some of nanowhiskers obtained (see Figure 6) surprisingly contain a parts which can be related to InP phase despite of the fact that our MBE apparatus does not equip with any In supply source. As it was mentioned above, the number of such nanowhiskers is found to be depended on the growth temperature and the time of growth. In this case, MnP nanowhiskers which were nucleated at initial stage of the growth supposedly act as a catalyst for the growth of InP nanowhiskers. It seems likely, that at elevated temperatures with the increasing time of the growth the rate of evaporation of In atoms from InP substrate increases. That may result in the growth of InP nanowhiskers in frameworks of diffusion-induced mechanism described above. By this expedient a new potentialities for the growth of nanowhiskers using as a building material evaporated atoms of the host substrate are opened to consider.

Furthermore, the magnetic properties of the samples have been studied using VSM magnetometer from room to 77K temperature range. It was found, that samples obtained on GaAs(111)B substrates

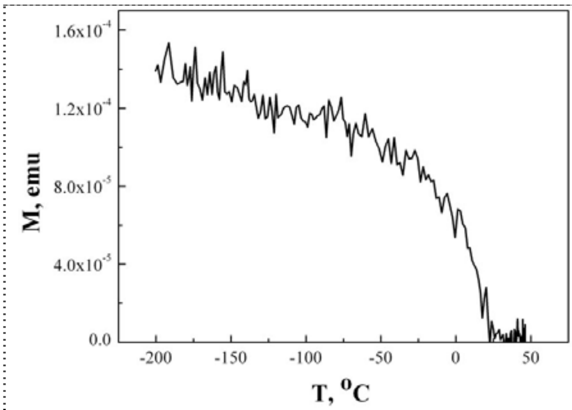

Figure 7. Temperature dependence of magnetization measured with an applied field of 100 Oe for the sample with MnP nanowhiskers grown on InP(100) substrate

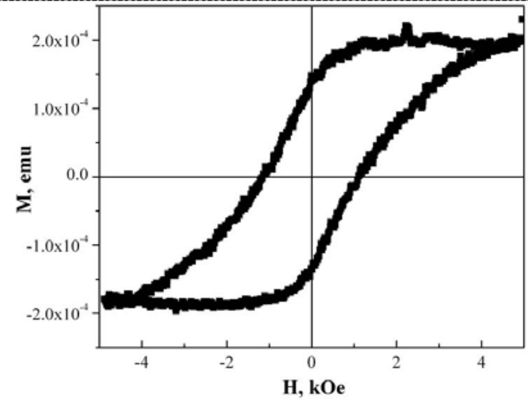

Figure 8. Magnetic field dependences of magnetization measured at 77 K for the sample with MnP nanowhiskers grown on InP(100) substrate

do not exhibit any ferromagnetic ordering in this temperature range which is coincident with the data on the chemical composition of nanowhiskers obtained by EDX, since it is known that bulk Mn_2P is antiferromagnetic [14].

More interesting results have been obtained for the samples with nanowhiskers grown on InP(100) substrates (see Figure 7 and 8). The magnetization of the samples as you can see on Figure 7 exhibits ferromagnetic properties up to room temperature range.

4. Acknowledgments

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