

MBE growth and characterization of MnP and Ge nanowhiskers

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Abstract. Ge and MnP nanowhiskers have been grown by molecular beam epitaxy (MBE) concurrently on InP and GaAs substrates. The growth of MnP nanowhiskers appears to be caused by catalytic free growth mechanism, whereas the growth of Ge nanowhiskers is found to be amenable to vapour-liquid-solid (VLS) mechanism of growth. The measurements of temperature and magnetic field dependences of magnetization have shown that the samples containing mostly Ge nanowhiskers exhibit ferromagnetic behaviour up to room temperature.

Keywords: nanowhiskers, molecular beam epitaxy, magnetic properties

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INTRODUCTION

Nanowhiskers, nanowires, nanorods and other one-dimensional nanostructures have been subject to intense scrutiny recently. Among them magnetic nanowhiskers deserve special attention because their fabrication will make possible the utilization such materials not only for data storage and nanoscale spintronics applications, but also for the investigation of the fundamental magnetic properties of low-dimensional system. Mn-doped nanowhiskers have been successfully synthesized using different methods [1-7] therewith it should specifically be mentioned about MnP nanorods which were obtained via thermal decomposition of continuously delivered metal-phosphine complexes [7].

In this paper, we report on MBE growth and the characterization of MnP and Ge self-assembled nanowhiskers on InP and GaAs substrates.

METHODS

Self-assembled (SA) nanowhiskers were grown on InP(100), GaAs(100) and GaAs(111)B substrates by molecular beam epitaxy using conventional Mn and Ge K-cells as well as cracking cell for the decomposing of tertiarybutylphosphine (TBP) into P₂ flux. It should be noted that firstly SA nanowhiskers were found during MBE growth of MnGeP₂ thin films [8] and we used similar technology for their growth later on. The growth temperature was held between 430 – 660 °C. The time of the growth process was varied from 30 minutes till 2 hours. The beam flux of Mn was adjusted in the range between 0,5 – 0,9 · 10⁻⁸ Torr and Ge in the range between 0,9 – 1,5 · 10⁻⁸ Torr. The flow rate of TBP gas

was set at 2.0 sccm.

The study of the samples was carried out with scanning electron microscope (SEM), scanning transmission electron microscope (STEM), energy-dispersive X-ray spectrometer (EDX) attached to the SEM and STEM apparatus as well as X-ray diffraction (XRD) system and superconducting quantum interference device (SQUID).

RESULTS

SA nanowhiskers with typical diameters close to 20 nm and length up to 2 μm have been obtained by MBE without use of any preliminary deposited catalysts on InP(100) surface (Fig. 1). With increasing the growth temperature instead of widely distributed individual nanowhiskers (Fig. 1a), the arrays of SA nanowhiskers those have random (Fig. 1b, c) distribution on the substrate can be grown. Besides, at elevated temperatures similar nanowhiskers have been grown on GaAs(100) substrates (Fig 1d) that can be of importance for the future device applications. TEM and EDX investigations of the samples have shown that we had obtained Ge nanowhiskers and MnP nanowhiskers simultaneously therewith the amount of MnP nanowhiskers was decreased with increasing of the growth temperature. Notwithstanding the fact that we did not use any tailor-made catalyst compound, the growth of Ge nanowhiskers is found to be amenable to vapour-liquid-solid (VLS) mechanism of growth. The role of the catalyst for the growth of nanowhiskers in this case plays Mn-based nanoclusters which seem to be self-assembled at an initial stage of the growth with atomic composition of elements close to Mn:P:Ge 78:5:6 %. According to the results of TEM and SEM measurements Ge nanowhiskers obtained

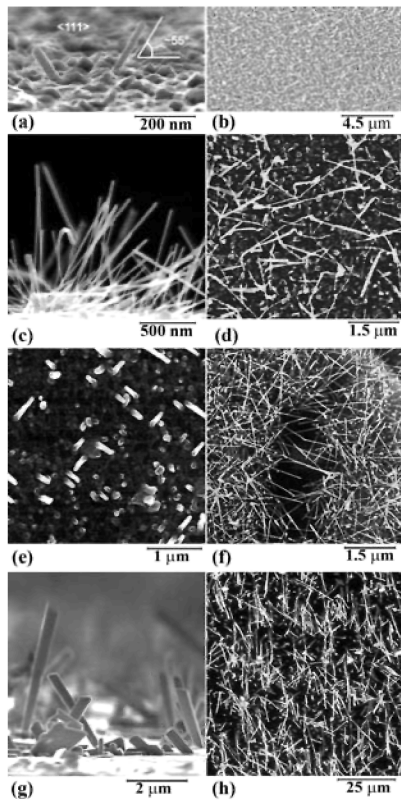


FIGURE 1. SEM images of individual (a), (d) and arrays of SA nanowiskers (b), (c) grown on InP(100)(a-c) and GaAs(100) (d) surfaces as well as MnP nanowiskers (e-h) grown on InP(100)(e), (f) and GaAs(111)B (g), (h) surfaces. The temperature of the growth: (a) 435°C; (b) 500°C; (c) 500°C; (d) 660°C; (e),(f) 510°C, (g),(h) 535°C.

are straight and uniform in diameters along their length with lattice fringe spacing 0.327 nm which corresponds to (111) plane.

By varying the composition of elements through the change of K-cells being in use MnP nanowiskers have been grown on InP(100)(Fig. 1e, f) and GaAs(111)B substrates(Fig. 1g, h); in doing so we have obtained neither GeP nor MnGe nanowiskers up to now. MnP nanowiskers obtained have lengths up to 30 μm, widths up to 600 nm and clear atomic facets without any terminated nanoclusters. Therefore, the growth of MnP nanowiskers is apt to be caused by catalytic free growth mechanism.

The investigation of the magnetic properties of the samples containing mostly Ge nanowiskers has demonstrated that magnetization of both a sample with nanowiskers and peeled nanowiskers themselves exhibit ferromagnetic behaviour up to room temperature (Fig. 2). Ferromagnetic properties of the samples can be attributable to the existence of MnGeP₂, MnP or Mn₅Ge₃ phases, but SA nanowiskers exhibit behaviour of mag-

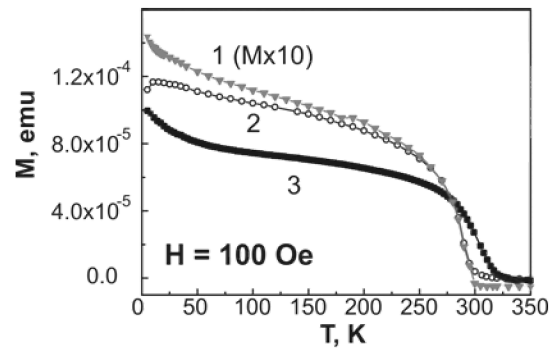


FIGURE 2. The temperature dependence of magnetization measured with an applied field of 100 Oe for (1) Ge nanowiskers grown on InP substrate at 520°C; (2) MnGeP₂ thin film grown on GaAs(100) substrate with Ge buffer layer [8] and (3) Ge nanowiskers grown at 520°C peeled off from the InP(100) substrate.

netisation that is distinct from that of MnGeP₂ thin film (see Fig. 2) [8]. In turn, the measurements of magnetic field dependences of magnetization performed at different temperatures for MnP nanowiskers grown on InP and GaAs substrates have shown that they do not exhibit ferromagnetic behaviour. Therefore ferromagnetic properties of the samples with prevailing concentration of Ge nanowiskers may be caused most likely by the presence of Mn₅Ge₃ phase.

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REFERENCES

1. Y. Q. Chang et al., *Appl. Phys. Letters* **83**, 2503–2504 (2003).
2. U. Philipose et al., *Appl. Phys. Letters* **88**, 263101 (2006).
3. D. S. Han et al., *Appl. Phys. Letters* **86**, 032506 (2005).
4. U. Philipose et al., *Appl. Phys. Letters* **88**, 263101 (2006).
5. K. Ip et al., *J. Vac. Sci. Technol. B* **21**, 1476-1481 (2003).
6. P. V. Radovanovic et al., *Nano Lett.* **5**, 1407-1411 (2005).
7. J. Park et al., *J. Am. Chem. Soc.* **127**, 8433-8440 (2005).
8. K. Sato et al., *J. Phys. Chem. Solids* **66**, 2030-2035 (2005).