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MBE growth and TEM analyses in Mn–Ge–P compounds

K. Minami[*, 1], **A. D. Bouravleuv**[1,2], **Y. Sato**[1], **T. Ishibashi**[1], **N. Kuwano**[3], and **K. Sato**[1]

[1] Department of Applied Physics, Tokyo Univ. of Agriculture and Technology, Koganei, 184-8588 Tokyo, Japan
[2] A. F. Ioffe Physico-Technical Institute, 194021 St. Petersburg, Russia
[3] Art, Science and Technology Center for Cooperative Research, Kyusyu Univ., Kasuga, 816-8580 Fukuoka, Japan

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Ternary $MnGeP_2$ thin films have been grown on GaAs substrate using MBE technique. The films prepared at 435 °C showed ferromagnetism at room temperature. TEM observation revealed a segregation of MnP tile-shaped grains. Films grown at 585 °C showed no trace of ferromagnetic secondary phases in XRD profiles and were found to show no ferromagnetic behaviors down to 77 K. This is consistent with theoretical prediction that stoichiometric $MnGeP_2$ is antiferromagnetic, and our previous experimental results that the $MnGeP_2$ layer existing at the top of $ZnGeP_2$:Mn has no contribution to ferromagnetic properties of the latter.

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1 Introduction

We have been working with chalcopyrite-based magnetic semiconductors (MS) prepared by thermal diffusion of Mn into the bulk II–IV–V_2 single crystals, and discovered that these materials exhibit ferromagnetic properties at room temperature (RT) [1–6]. In addition, reflection high energy electron diffraction (RHEED) observation during the deposition of Mn at 400 °C and *in-situ* photoemission studies indicate that novel chalcopyrite-type material $MnGeP_2$ was formed on the top surface layer of Mn-doped II–IV–V_2 semiconductors [7]. Additionally, photoemission and magnetic studies suggested that the $MnGeP_2$ top layer was non-magnetic and the origin of ferromagnetism of $ZnGeP_2$:Mn was due to the Mn-substituted MS layer. On the basis of these previous results, we started to prepare the novel ternary compound $MnGeP_2$ by a molecular beam epitaxy (MBE) technique. We have succeeded in preparation of well-defined $MnGeP_2$ on InP(001) substrates at the substrate temperature of 435 °C [8]. In order to improve the surface morphology of the epitaxial films we used Ge buffer layer and succeeded in obtaining a very flat surface [9]. The films were found to show ferromagnetism with the Curie temperature (T_c) as high as 320 K [10]. However, the origin of ferromagnetic properties was not clarified.

In this article, we analyzed crystalline properties of the ternary film grown on the Ge buffer layer using a transmission electron microscopy (TEM), from which an existence of a secondary ferromagnetic phase was confirmed. In order to avoid the secondary phase formation we prepared the ternary compounds at an elevated substrate temperature, in which magnetic properties were investigated.

* Corresponding author: e-mail: minami_5@cc.tuat.ac.jp, Phone: +81 42 388 7432, Fax: +81 42 387 8151

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2 Experiments

The crystal growth of ternary compound thin films was performed using an MBE technique [9]. Mn and Ge were evaporated using conventional Knudsen cells (K-cell) at temperatures of 620–680 °C and 1000 –1050 °C, respectively. The both beam flux intensity of Mn and Ge were adjusted at 0.6–0.64 × 10^{-8} Torr. Phosphorus was supplied as P_2 by cracking the tertiary butyl phosphine (TBP) gas source using a cracking cell at 835 °C. The flow rate of TBP was fixed at 2.0 sccm using mass flow controller. GaAs(001) and $(111)_B$ single crystals were used as substrates. In this study, we prepared two kinds of samples. Films were grown at 435 °C on a Ge buffer layer prepared on GaAs(001) and $(111)_B$ substrates. The Ge buffer layer was prepared at 380 °C with the thickness of 25 nm. After growth of the ternary thin film Ge was deposited at RT as cap layer in order to prevent main epitaxial films from oxidation. We also performed MBE growth of the ternary films on GaAs(001) substrate at 485–585 °C without Ge buffer layer. The crystal structure of the thin film was analyzed using RHEED, X-ray diffraction (XRD) and transmission electron microscopy (TEM). The TEM observation was carried out at the Research Laboratory for High Voltage Electron Microscopy, Kyushu University using the FEI type Tecnai-F20 apparatus. Additionally, chemical compositions were analyzed using an energy dispersive X-ray spectroscopy (EDS) attached with the TEM and a scanning electron microscope (SEM). Magnetic field dependences of magnetization of films prepared were investigated using a vibrating sample magnetometer (VSM) at 77 K.

3 Results and discussion

3.1 TEM analyses of ternary thin films

Ternary thin films of 90 nm and 55 nm in thickness were grown at 435 °C on a Ge buffer layer prepared on GaAs(001) and $(111)_B$ substrates. During the growth of both Ge buffer layer and the ternary thin film, RHEED showed streaky patterns due to the zincblendelike phase. In addition, diffraction spots due to a secondary phase assignable to the MnP were observed, an existence of a trace of MnP phase having been confirmed by the 2θ–θ XRD measurement. SEM observations of the $MnGeP_2$ film prepared on the Ge-buffer revealed a drastic improvement of the surface flatness compared with the film prepared without a buffer layer [9]. As described in our previous paper [10], $MnGeP_2$ film exhibited a ferromagnetic behaviour up to 320 K in the M–T curve measured using super conducting quantum interference device (SQUID) magnetometer. Subsequently, the crystal structure and areal distribution of all elements were analyzed using TEM and attached EDS apparatus. Figure 1 shows a diffraction image of the sample grown on the $GaAs(111)_B$. The electron beam was parallel to GaAs$[11\bar{2}]$. Diffraction spots close to those of GaAs substrate (e.g. A–C) indicate an orientational overgrowth of the ternary phase on the substrate. In cross sectional TEM images, it was affirmed that tile-shaped crystals were partially embed-

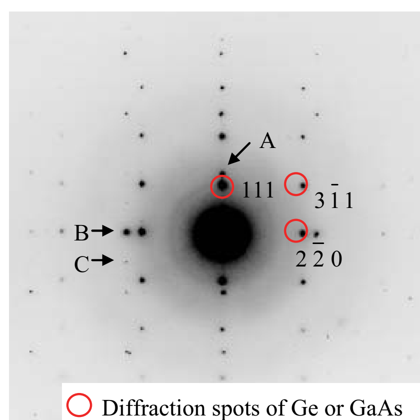

Fig. 1 (online colour at: www.pss-a.com) Diffraction image of the film grown on a $Ge/GaAs(111)_B$. E-beam ∥ GaAs $[11\bar{2}]$.

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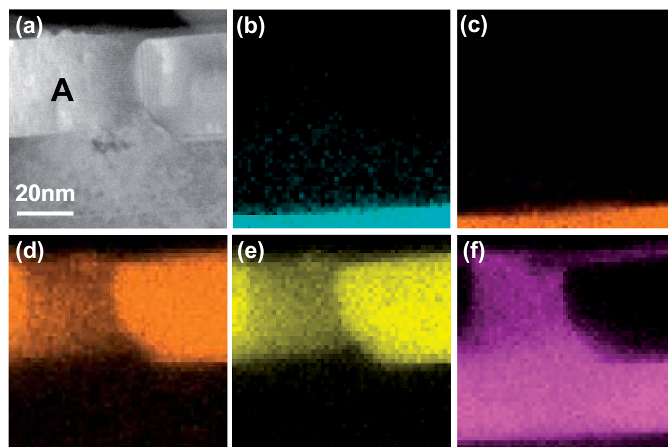

Fig. 2 (online colour at: www.pss-a.com) Dark field image of TEM (a), and distribution maps of all elements; (b) Ga, (c) As, (d) Mn, (e) P and (f) Ge, respectively.

ded into ternary film grown on the Ge buffer layer. Figure 2(a) shows a dark field TEM image of the thin film grown on the GaAs$(111)_B$ substrate. It is clearly observed that tile-shaped crystal grains with thickness of ~50 nm are grown on the Ge buffer layer. Figure 2(b)–(f) show atomic distribution of all elements in the thin film taken at the same area of the dark field TEM image (Fig. 2(a)). The EDS profiles clearly shows the Ge buffer layer is formed on the GaAs substrate with a sharp boundary and on the buffer layer crystalline grains are grown. In the area marked A in the dark-field image all the constituent elements, Mn, Ge and P are found, while in the area B only Mn and P are observed. The ternary Mn–Ge–P and binary Mn–P areas were clearly separated from each other. In the case of GaAs(001) substrate, separation of Mn–P and Mn–Ge–P areas were also observed. Therefore, in order to obtain intrinsic magnetic properties of $MnGeP_2$, single phase film without ferromagnetic secondary phases should be prepared.

3.2 High temperature growth of $MnGeP_2$

As a preliminary investigation to obtain single phase thin films of $MnGeP_2$, we carried out a thermodynamic calculation in MnP–GeP system [11]. This result indicates that MnP should disappear and only $MnGeP_2$ can be grown at an elevated temperature higher than 435 °C. On the basis of theoretical prediction, ternary thin films were grown at 485–585 °C directly on GaAs(001) substrate without buffer layers. Figure 3 shows 2θ–θ XRD profiles of the thin film grown at 585 °C near 002 and 004 diffraction lines of GaAs. Close in the higher angle side of the diffraction peaks of the substrate, strong lines from the thin film were observed and were assigned to 004 and 008 diffractions from $MnGeP_2$. These lines were shifted to slightly higher angle from that observed in our previous works. The estimated lattice constant of *c*-axis of the present film is 11.264 Å, slightly smaller that 11.303 Å obtained in the previous study. Assuming that *a*-axis is not different between two films, the tetragonality is found to be more enhanced in the present film. This difference may be caused by a change of the ordering of cation sites to form stoichiometric $MnGeP_2$ due to high temperature growth. Chemical ratio of the thin film measured using EDS attached SEM apparatus was Mn : Ge : P = 0.7 : 1.0 : 2.7, where atomic ratios were normalized to Ge. It is considered that Mn was poor compared with Ge due to the re-evaporation and GeP was formed by the combination of excess Ge and P. In a wide range 2θ–θ XRD charts, no traces of ferromagnetic secondary phases such as MnP were detected except for $MnGeP_2$ and GeP, the latter being known to be nonmagnetic. Appearance of GeP may be attributed to incomplete adjustment of source elements ratios. In the cases of substrate temperature lower that 585 °C, i.e., at 485 and 535 °C, $MnGeP_2$ diffraction lines could not be discriminated from GaAs 002, 004 lines probably weakness of diffraction due to poor crystallinity of $MnGeP_2$.

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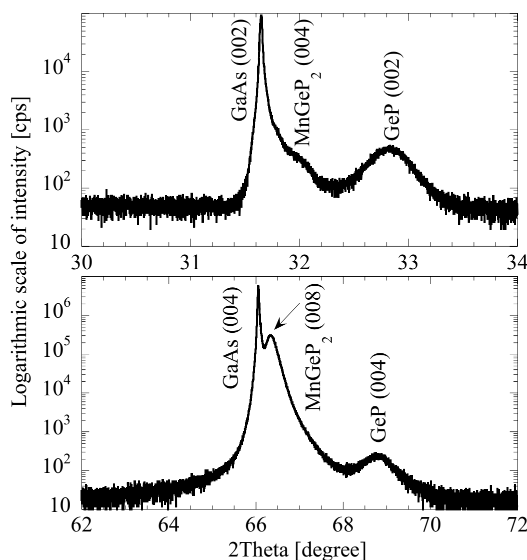

Fig. 3 $2\theta-\theta$ XRD profiles of $MnGeP_2$ thin film gown on a GaAs(001) at 585 °C.

Figure 4 shows magnetization-magnetic field ($M-H$) curve of $MnGeP_2$ thin film grown at 585 °C measured using VSM at 77 K. Magnetic field was applied parallel to the surface of the thin film and ranged from −20 kOe to 20 kOe. No ferromagnetic behaviours were observed in contrast to the ternary thin film grown at lower temperature in previous works [10]. No magnetic signals were detected at RT as well. This result indicates that $MnGeP_2$ thin film grown at 585 °C does not show ferromagnetic behaviour down to 77 K and no ferromagnetic secondary phases with T_c over 77 K exist in the film. Furthermore, it is consistent with the previous photoemission study in which $MnGeP_2$ does not give any magnetic contribution. It should also be noted that in the theoretical work by Zhao et al. [12], they reported that antiferromagnetism is the most stable magnetic phase of chalcopyrite-type $MnGeP_2$.

Here we give a brief discussion on the origin ferromagnetism observed in our previous study $MnGeP_2$ prepared at low substrate temperatures. According to theoretical studies ternary Mn-containing compounds become ferromagnetic when point defects are introduced [13]. There is a possibility of ferromagnetism due to the point defect formation in our $MnGeP_2$, since the XRD results show that $MnGeP_2$ prepared at low temperatures has a less tetragonality suggesting that the material structure is close to zincblende probably due to a randomness of cation distribution. We believe that the ferromagnetism of our film with T_c of the film 320 K is not due to MnP since it is considerably higher than that of MnP single crystal and ferromagnetic-antiferromagnetic phase transition at 47 K is missing.

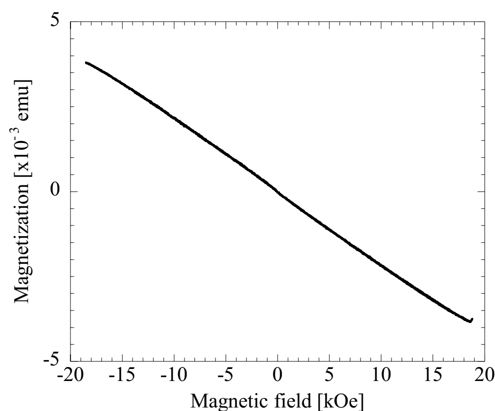

Fig. 4 $M-H$ curve of $MnGeP_2$ thin film at 77 K.

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4 Summary

$MnGeP_2$ thin films were prepared using MBE on GaAs substrates with Ge buffer layers. Tile-shaped crystal grains were observed to grow on the Ge buffer layer at 435 °C in TEM analyses. Atomic distribution map indicates that the film consists of Mn–P and Mn–Ge–P areas clearly separated from each other.

We have found that the films grown at higher substrate temperature of 585 °C show no traces of MnP secondary phases and strong diffraction intensity of chalcopyrite-like $MnGeP_2$ in the XRD profiles. Furthermore, magnetic properties of $MnGeP_2$ prepared at 585 °C are found to be quite different from MnP and do not show ferromagnetism down to 77 K, which is consistent with our previous works and theoretical study by Zhao et al. in which antiferromagnetism should be the most stable phase for stoichiometric chalcopyrite-type $MnGeP_2$.

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