



MBE growth of MnGeP_2 thin films

K. Minami^{a,*}, V.M. Smirnov^{a,b}, H. Yuasa^a, J. Jogo^a,
T. Nagatsuka^a, T. Ishibashi^a, K. Sato^a

^a*Faculty of Technology, Tokyo University of Agriculture and Technology, Tokyo 184-8588, Japan*

^b*Ioffe Physico-Technical Institute, St Petersburg 194021, Russia*

Available online 24 December 2004

Abstract

Novel ternary compound MnGeP_2 thin films have been prepared on $\text{InP}(001)$ substrates by molecular beam epitaxy (MBE), in which Mn and Ge were supplied from solid sources using Knudsen cells and P_2 from a gas source by decomposing tertiary butyl phosphine (TBP). From an X-ray analysis the crystal structure was determined to be tetragonal with lattice constants $a = 0.569$ nm and $c = 1.130$ nm, with the c -axis perpendicular to the $\text{InP}(001)$ plane. Optimal conditions to suppress GeP and MnP extraneous phases are discussed.

© 2004 Elsevier B.V. All rights reserved.

PACS: 75.50.Pp; 81.15.Hi

Keywords: A1. Crystal structure; A1. X-ray diffraction; A3. Molecular beam epitaxy; B1. Phosphides; B2. Magnetic materials

1. Introduction

Magnetic semiconductors have been attracting much interest as “spintronic” materials. Although diluted magnetic semiconductors such as III–V binary compounds doped with transition atoms (TA) have been extensively studied by many researchers, these materials demonstrate ferromagnetism only at low temperatures. In a course of basic research on chalcopyrite-type semiconductors doped with TA [1], we occasionally found that

TA can more easily be incorporated into II–IV– V_2 chalcopyrite-type crystals than III–V crystals. We succeeded in doping high concentration of Mn atoms into the surface region of II–IV– V_2 bulk single crystals, and discovered ferromagnetism above room temperature in both CdGeP_2 and ZnGeP_2 [2,3]. However, since these magnetic semiconductor layers were prepared by thermal diffusion of Mn into the semiconductor host matrix, they suffer non-uniform depth-profile of Mn concentration which makes it difficult to evaluate accurately electrical and magnetic properties. Therefore, preparation of high quality single-crystalline thin films of $\text{II}_{1-x}\text{Mn}_x\text{GeP}_2$ is required

*Corresponding author.

E-mail address: minami_5@cc.tuat.ac.jp (K. Minami).

for characterization of these properties. For this purpose a study of the end material ($x = 1$) in the $\text{II}_{1-x}\text{Mn}_x\text{GeP}_2$ series is useful. Indeed, the existence of MnGeP_2 phase has been predicted by ab initio energy band calculations by Zhao et al. [4]. We present evidence for the existence of chalcopyrite-type MnGeP_2 , from our experimental results. First, the in situ reflection high-energy electron diffraction (RHEED) observation during Mn-deposition on ZnGeP_2 at 400°C shows that the chalcopyrite pattern was continuously observed from the beginning to the end of deposition. Second, the X-ray photoelectron spectroscopy (XPS) measurements during sputter-etching of Mn-deposited ZnGeP_2 show that the top surface region consists of Mn, Ge and P, among which Mn is gradually replaced by Zn with increasing depth [5]. If the surface region of $\text{II-GeP}_2\text{:Mn}$ is dominated by the MnGeP_2 compound, the physical properties of the new material should be elucidated to understand the origin of ferromagnetism in chalcopyrite-type magnetic semiconductors. We therefore started to grow the novel MnGeP_2 crystal.

In the present paper, we describe the growth of the MnGeP_2 thin films by molecular beam epitaxy (MBE) technique and characterization of the crystallographic properties.

2. Experiments

Crystal growth experiments were carried out using MBE apparatus shown in Fig. 1. Solid sources of Mn and Ge were evaporated using conventional Knudsen cells, while P_2 was supplied by decomposing tertiary butyl phosphine (TBP) gas using a cracking cell. The TBP flow rate was adjusted using a mass flow controller (MFC). The cracking cell consists of a pyrolytic boron nitride (PBN) tube, Ta shot and TA mesh using the same method reported by H. Sai et al. [6]. TBP is decomposed by the catalysis with the Ta shot in the PBN tube at $810\text{--}835^\circ\text{C}$. It has been shown that a major component of the decomposed gas is P_2 above the cell temperature of 800°C [7]. Use of the cracking cell is indispensable for decomposition of TBP, since no deposition occurred on

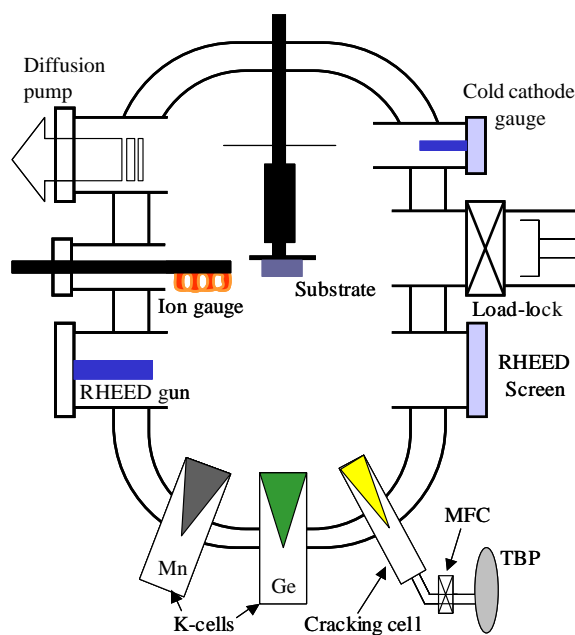


Fig. 1. Illustration of the MBE apparatus.

substrates without the use of the cracking cell. An $\text{InP}(001)$ epi-ready wafer was used as the substrate. The substrate was heated in the load-lock chamber at 300°C . The growth process of MnGeP_2 was monitored using in situ RHEED observation. After the growth, the surface morphology of the films was observed using scanning electron microscopy (SEM), and the composition was determined using an energy-dispersive analysis (EDX) attached to the SEM apparatus. The atomic ratio was normalized to the Ge composition. The crystal structure and lattice constants were determined by reciprocal lattice mapping (RLM) from the X-ray diffraction (XRD) using a Philips X'Pert-MRD X-ray diffractometer.

3. Results and discussion

Growth conditions of MnGeP_2 on the $\text{InP}(001)$ substrate are summarized in Table 1. Beam flux of both Mn and Ge was varied between 6.4×10^{-9} and 9.0×10^{-9} Torr and TBP flow rate was fixed at 2.0 sccm. Growth temperature and growth time were fixed at 435°C and 180 min, respectively.

Table 1
Growth conditions of thin films grown on InP(001)

Sample	Mn flux (Torr)	Ge flux (Torr)	TBP flow (sccm)	Growth Temp. (°C)	Growth Time (min)	Mn:Ge:P
#1	9.0×10^{-9}	9.0×10^{-9}	2.0	435	180	1.92:1.00:---
#2	6.4×10^{-9}	6.4×10^{-9}	2.0	435	180	1.40:1.00:---

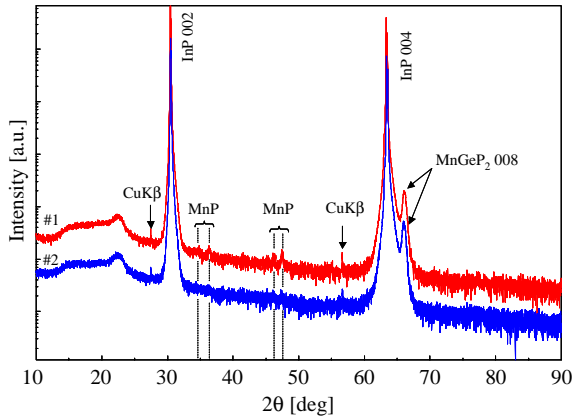


Fig. 2. 2θ - θ XRD curves of thin films grown on InP(001).

Preliminary experiments suggested that GeP tends to be precipitated in the films when the substrate temperature is high, Mn and Ge beam flux is relatively high ($\sim 2 \times 10^{-8}$ Torr), and TBP flow rate is as low as 1.6 sccm. Therefore, beam flux of both Mn and Ge was reduced below 1×10^{-8} Torr, while the TBP flow rate was kept as high as 2.0 sccm. Flux intensity of sample #2 was kept 1.4 times smaller than that of sample #1, while other parameters remained the same. In the table, the ratio of P could not be determined precisely since P is contained in the substrate.

Fig. 2 illustrates the XRD patterns of the films obtained. At $2\theta = 66.04^\circ$, which is approximately the same position as 004 diffraction of GaAs, a diffraction peak is clearly resolved from the 004 diffraction line of InP(001) substrate in both samples. Assuming that c -axis of the chalcopyrite structure grows perpendicular to the (001) plane of the substrate, we can assign $\sim 66.04^\circ$ peak to the 008 diffraction of MnGeP₂. Concerning the 004 diffraction of chalcopyrite structure no trace of peak is found close to the 002 line of InP. This is

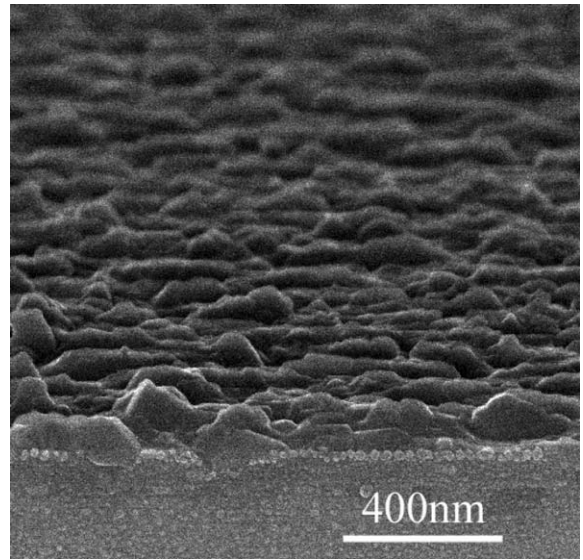


Fig. 3. SEM image of sample #2 taken by tilting the substrate.

reasonable taking into consideration that peak intensity of 004 diffraction of MnGeP₂ is less than $\frac{1}{5}$ of that of 008 by the calculation.

In the case of sample #1, diffraction peaks of MnP were observed in addition to the 008 reflection of MnGeP₂. Subsequently, sample #2 was prepared with parameters other than beam flux of both Mn and Ge fixed. Despite the fact that the thickness of sample #2 is thinner than #1, it shows almost the same 008 diffraction intensity of MnGeP₂ whereas the MnP phase was hardly observed. Excess Mn atoms in both samples would be segregated as MnP. We consider that an equal amount supply of Mn and Ge under excess P₂ partial pressure and extremely low growth rate are required to obtain MnGeP₂ thin film suppressing the deposition of MnP.

In order to determine the crystal structure of sample #2, we carried out the X-ray RLM

analysis, from which it is found that this film has a chalcopyrite-like structure. Assuming chalcopyrite structure with the tetragonal crystal system, we can determine the lattice constants as $a = 0.569$ nm and $c = 1.130$ nm, which is consistent with theoretical calculation [4] and those of polycrystalline MnGeP_2 reported recently by Cho et al. [8].

In addition, streaky RHEED patterns from InP substrate before the growth of MnGeP_2 changed to spotty immediately after the starting of the growth. It is consistent with SEM image as shown in Fig. 3.

4. Conclusion

We have successfully obtained c -axis-oriented chalcopyrite-like MnGeP_2 thin films by MBE technique on InP(001) substrates at $\sim 435^\circ\text{C}$. The crystal structure and lattice constants were determined by X-ray analyses as tetragonal with $a = 0.569$ nm, and $c = 1.130$ nm. In order to suppress the deposition of GeP and MnP it is required that MnGeP_2 should be grown with extremely low growth rate under excess P_2 partial pressure relative to beam flux of both Mn and Ge.

Acknowledgments

This work has been carried out under the 21st COE Project “Future Nano Materials” of TUAT and supported in part by the Grant-in-Aid for Scientific Research (Category no. 13305003) from Japan Society for the Promotion of Science.

References

- [1] K. Sato, T. Matsumoto, T. Takizawa, S. Shirakata, T. Wada, N. Yamamoto (Eds.), Japanese Research for Pioneering Ternary and Multinary Compounds in the 21st Century, vol. 12, IPAP, Tokyo, 2001, pp. 228.
- [2] G.A. Medvedkin, T. Ishibashi, T. Nishi, K. Hayata, Y. Hasegawa, K. Sato, Jpn. J. Appl. Phys. 39 (Part 2) (2000) L949.
- [3] G.A. Medvedkin, K. Hirose, T. Ishibashi, T. Nishi, K. Sato, V.G. Voevodin, J. Crystal Growth 236 (2002) 609.
- [4] Y.-J. Zhao, W.T. Geng, A.J. Freeman, T. Oguchi, Phys. Rev. B. 63 (2001) 201202-1.
- [5] Y. Ishida, D.D. Sarma, K. Okazaki, J. Okabayashi, J.L. Hwang, H. Ott, A. Fujimori, G.A. Medvedkin, T. Ishibashi, K. Sato, Phys. Rev. Lett. 91 (2003) 107202-1.
- [6] H. Sai, H. Fujikura, H. Hasegawa, Jpn. J. Appl. Phys. 38 (Part 1) (1999) L151.
- [7] E.A. Beam III, T.S. Henderson, A.C. Seabaugh, J.Y. Yang, J. Crystal Growth 116 (1992) 436.
- [8] S. Cho, S. Choi, G.-B. Cha, S.C. Hong, Y. Kim, A.J. Freeman, J.B. Ketterson, Y. Park, H.-M. Park, Solid State Commun. 129 (2004) 609.