MnGeP₂ Thin Films Grown by Molecular Beam Epitaxy

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Growth conditions for MnGeP₂ thin films have been investigated by using molecular beam epitaxy (MBE) method. Mn and Ge were evaporated by K-cells, and P₂ was supplied by decomposing tertialybutylphosphine (TBP). GaAs (001) and InP (001) single crystals were used as substrates. An X-ray diffraction peak, which can be assigned to (008) peak of MnGeP₂, was observed at nearly the same position as the (004) peak of GaAs. The lattice constant of the MnGeP₂ thin film was determined to be 1.13 nm assuming its crystal structure is a c-axis oriented chalcopyrite type structure. Secondary phases such as GeP, MnGe, and MnP were observed for beam fluxes of Mn and Ge as high as 1×10^{-8} Torr.

KEY WORDS: MnGeP₂; molecular beam epitaxy; MnP; GeP; chalcopyrite.

1. INTRODUCTION

Doping of 3d transition metals into various semiconductors has been attracting attention because of the possibility to make semiconductors ferromagnetic. We reported that Mn-doped II–IV–V₂ type chalcopyrite crystals, CdGeP₂ and ZnGeP₂, have shown a room temperature ferromagnetism [1,2]. Compared with III–V materials (e.g., GaAs, InP, etc.), II–IV–V₂ crystals were found to be easier to incorporate 3d transition metals, the fact suggesting a possibility of complete substitution of the II-site by 3d transition metals. In fact, MnGeP₂ seems to be formed at the surface when Mn is deposited on a ZnGeP₂ crystal heated at 400 C. It was found by an *in situ* X-ray photoemission spectroscopy (XPS) measurement that the top surface of the Mn-deposited crystal consisted of Mn, Ge and P. It was also suggested from *in situ* reflection high-energy diffraction (RHEED) observation during deposition that the crystal structure was maintained during the Mn-deposition process [3,4].

For detailed study of the MnGeP₂ material, preparation of high quality thin films is strongly required since the samples obtained in the previous work have a gradation in Mn concentration due to the Mn diffusion procedure. Therefore, we have started a study of a preparation of thin films by using molecular beam epitaxy (MBE) technique. In this paper, we report on a preparation and X-ray characterization of MnGeP₂ thin films on GaAs (001) and InP (001).

2. EXPERIMENTS

A schematic drawing of the MBE equipment used in this study is shown in Fig. 1, in which Mn and Ge are evaporated from conventional Knudsen cells (K-cells), while P₂ is supplied by decomposing tertiary butyl phosphine (TBP) using a cracking cell, the flow rate of which is controlled by a mass flow controller. TBP is known to be less toxic and easier to control than the popular phosphorous source PH₃. The structure of cracking cell, which consists of a pyrolytic boron nitride (PBN) tube packed with Ta shots, was designed following the structure reported by Sai *et al.* [5]. The cracking procedure is required for the substrate temperature lower than 700 C. The temperature of the cracking cell is kept at 810 ∼ 835 C to assure an efficient decomposition of TPB into P₂ during the MBE growth [6].

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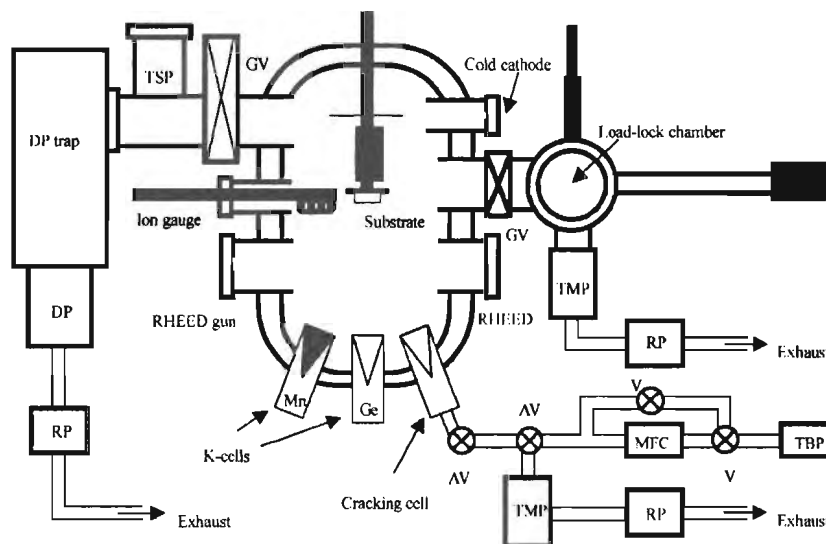[2] Ioffe Physico-Technical Institute, St Petersburg 194021, Russia.

Fig. 1. A schematic drawing of our molecular beam epitaxy equipment.

MnGeP$_2$ thin films were prepared on GaAs(001) and InP(001) substrates by a co-evaporation technique. The growth process of MnGeP$_2$ was monitored using an *in situ* RHEED measurement. Chemical compositions were measured using an energy dispersion type X-ray spectroscopy (EDX) attached to the SEM apparatus. The crystallinity was analyzed by X-ray diffraction (XRD) technique using a Philips type X'Pert X-ray diffractometer.

3. RESULTS AND DISCUSSION

Growth conditions of thin films prepared in this experiment and those chemical compositions measured by EDX are listed in Tables I and II. GaAs(001) substrates were used for samples #1 to #4 shown in Table I, and InP(001) for samples #5 to #8 shown in Table II. The beam flux of both Mn and Ge

was varied between 6.4×10^{-9} and 9.0×10^{-9} Torr and the TBP flow rate between 1.6 and 2.0 sccm. Substrate temperatures of 342–541 °C were used and deposition time was 90–180 min. The composition ration Mn/Ge was deviated from 1 because of an error in measuring the low beam fluxes of 10^{-9}–10^{-8} Torr. In all cases, therefore, a re-evaporation of Mn was not confirmed within an experimental error. We could not determine an exact value of the partial pressure of P$_2$, in our MBE system, but it should be several orders of magnitude higher than Mn and Ge, taking into account a total pressure that reaches as high as 10^{-4} Torr during growth.

Figures 2 and 3 show XRD patterns measured in the samples shown in Tables I and II, respectively. It is found that zinc-blend (ZB) type GeP [7] and MnGe$_x$ are observed in the samples #1 and #2 which were prepared with high growth rate above 1.8×10^{-8} Torr for both Mn and Ge. In contrast, GeP

Table I. Growth Conditions for Thin Films on GaAs(001) Substrates

Sample	Mn flux (Torr)	Ge flux (Torr)	TBP flow rate (sccm)	T_{sub} (°C)	Depo. time (min)	Composition Mn:Ge:P
#1	1.8×10^{-8}	1.8×10^{-8}	1.6	541	90	0.81 : 1 : 1.11
#2	2.4×10^{-8}	2.1×10^{-8}	1.6	414	180	1.72 : 1 : 2.99
#3	1.1×10^{-8}	1.1×10^{-8}	2.0	400	240	1.37 : 1 : 2.59
#4	6.5×10^{-9}	9.0×10^{-9}	2.0	400	180	0.95 : 1 : 2.14

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Table II. Growth Conditions for Thin Films on InP(001) Substrates

Sample	Mn flux (Torr)	Ge flux (Torr)	TBP flow rate (sccm)	T_{sub} (C)	Depo. time (min)	Composition Mn:Ge:P
#5	9.0×10^{-9}	9.0×10^{-9}	2.0	435	180	1.92·1:–
#6	1.0×10^{-8}	1.0×10^{-8}	2.0	342	180	1.29:1:–
#7	6.5×10^{-9}	9.0×10^{-9}	2.0	342	100	0.95:1:–
#8	6.4×10^{-9}	6.4×10^{-9}	2.0	435	180	1.40:1:–

can not be detected by XRD measurement when the beam fluxes of Mn and Ge is lower than 1.1×10^{-8} Torr. A similar feature is observed for MnP. Although it is quite difficult to completely suppress a segregation of MnP, it is suppressed for thin films prepared on InP substrates using beam fluxes less than 1×10^{-8} Torr. Suppression of these secondary phases has a crucial importance for magnetic studies of MnGeP₂, because MnP and Mn₅Ge₃ are known to show ferromagnetism at room temperature.

On the other hand, a diffraction peak from MnGeP₂ is found at 66.04 , which is labeled as (008) assuming that the chalcopyrite MnGeP₂ is grown with a c-axis perpendicular to the substrate surface. The position of the peak is so close to the (002) peak

position of GaAs that it can only be discriminated in films prepared on InP substrates, whose lattice constant is much larger than GaAs. Therefore, we believe that thin films with the same lattice constant as observed in the films prepared on InP substrates are grown on the GaAs substrates. Segregation of secondary phases seems considerably suppressed compared with those prepared on GaAs substrates, in spite of a larger lattice mismatch of MnGeP₂ with InP than with GaAs. The reason may be that the surface morphology of the InP substrate is better than that of the GaAs substrate and beam fluxes of Mn and Ge are lower than that for GaAs. In fact, RHEED patterns of InP substrates after thermal cleaning is better than that of GaAs, because epi-ready InP
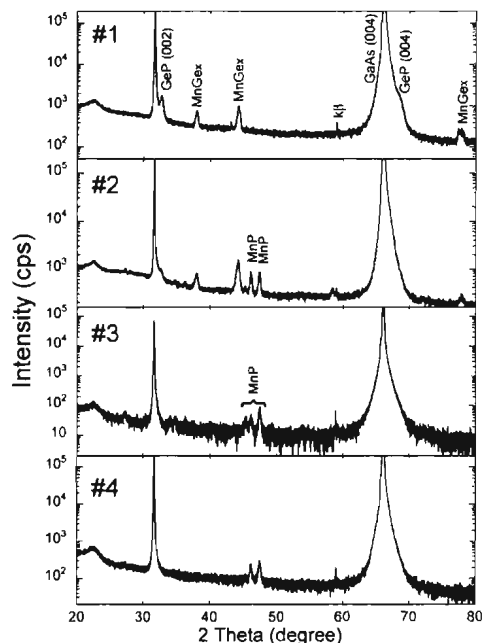

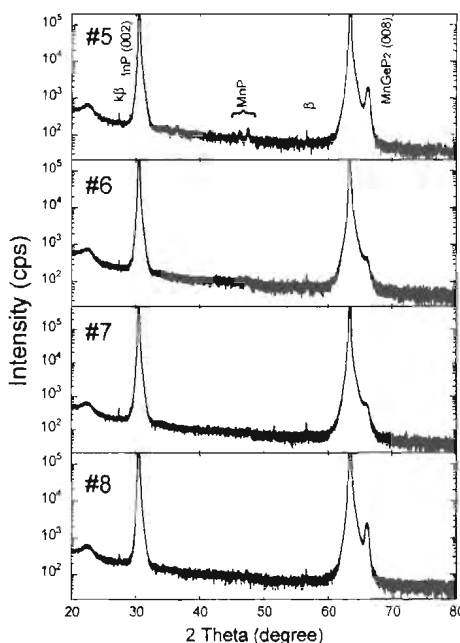**Fig. 2.** XRD patterns of thin films prepared on GaAs (001) substrates shown in Table I.

Fig. 3. XRD patterns of thin films prepared on InP (001) substrates shown in Table II.

substrates were used while GaAs substrates were non-epi-ready. Therefore, the buffer layer is strongly required. We consider that Ge is a good candidate as a buffer layer, because Ge is congenial to II-Ge-IV_2 chalcopyrite materials, and a Ge buffer layer can easily be used in our system compared to buffer layers of GaAs or InP.

The lattice constant of $MnGeP_2$ is determined to be $c = 1.130$ nm assuming the peak observed in Fig. 3 is the (008) diffraction line. This value is quite close to that of polycrystalline $MnGeP_2$, $c = 1.127$ nm, reported by Cho et al. [8]. but it is not close to that of $MnGeP_2$, $c = 1.0716$ nm, predicted theoretically by a calculation reported by Zhao et al. [9]. The difference between these data may be due to the difference in a degree of ordering in the crystal structure. Although a perfectly ordered chalcopyrite structure is assumed in the calculation, it is difficult to consider that these samples obtained experimentally have a perfectly ordered structure. The structure, ordered or disordered structure, can be revealed by a reciprocal lattice mapping and a transmission electron microscope, and they are under investigation.

4. SUMMARY

We have successfully obtained oriented $MnGeP_2$ thin films on InP (001) and GaAs (001) substrates by MBE method. The lattice constant of $MnGeP_2$ was determined to be $c = 1.130$ nm, assuming the c-axis oriented chalcopyrite structure. It is found that extremely low beam fluxes of Mn and

Ge less than 1×10^{-8} Torr are required to suppress secondary phases such as GeP, $MnGe_x$ and MnP.

REFERENCES

1. K. Sato. in *Japanese Reseach for Pioneering Ternary and Multinary Compounds in the 21st Century*, T. Matsumoto. T. Takizawa. S. Shirakata. T. Wada. and N. Yamamoto. eds.. (IPAP. Tokyo. 2001) 228–243.
2. G. A. Medvedkin, T. Ishibashi, T. Nishi, K. Hayata, Y. Hasegawa, and K. Sato, *Jpn. J. Appl. Phys.* **39,** Part 2 [10] L949–L951 (2000).
3. G. A. Medvedkin, K. Hirose, T Ishibashi, T. Nishi, V. G. Voevodin. and K. Sato. *J. Cryst. Growth* **236,** 609–612 (2002).
4. Y. Ishida, D. D. Sarma, K. Okazaki, J. Okabayashi, J. I. Hwang. H. Ott, A. Fujimori, G. A. Medvedkin, T. Ishibashi, and K. Sato, *Phys. Rev. Lett.* **91,** 107202 (2003).
5. H. Sai, H. Fujikura, and H. Hasegawa. *Jpn. J. Appl. Phys.* **38,** Part1 [1A] L151–L158 (1999).
6. E. A. Beam III, T. S. Henderson, A. C. Seabaugh, and J. Y Yang, *J. Crystal. Growth.* **116,** 436–446 (1992).
7. J. Osugi, R. Namikawa, and Y. Tanaka, *Rev. Phys. Chem. Jpn.* **37,** (1967) 81–93; [JCPDS-ICDD No. 210353].
8. S. Cho, S. Choi, G. B. Cha, S. C. Hong, Y. Kim. A. J. Freeman, J. B. Ketterson, Y. Park, and H. M. Park, *Soli. Stat. Commun.* **129,** 609–613 (2004).
9. Y. Zhao W. T. Geng, A. J. Freeman, and T. Oguchi. *Phys. Rev. B.* **63,** 201202–201201 (2001).