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Growth of $MnGeP_2$ Thin Films by Molecular Beam Epitaxy

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Epitaxial growth of the Mn-containing novel ternary compound $MnGeP_2$ has been investigated. Prior to the growth experiments, theoretical studies using an *ab initio* calculation were carried out, on the basis of which the stable existence of $MnGeP_2$ with a chalcopyrite structure was predicted. Growth experiments of Mn-Ge-P were performed on GaAs(001) and InP(001) substrates using a molecular beam epitaxy (MBE) technique, in which Mn and Ge were supplied from solid sources and P from a tertiary butyl phosphine (TBP) gas source. The optimum growth condition has been estimated on the basis of X-ray diffraction studies. Oriented overgrowth of $MnGeP_2$ was confirmed from a reciprocal lattice mapping (RLM) on X-ray diffraction (XRD) analyses, and lattice constants have been determined to be $a = 0.569$ nm and $c = 1.13$ nm based on the assumption that the material has a tetragonal crystal structure. [DOI: 10.1143/JJAP.44.L265]

KEYWORDS: molecular beam epitaxy, *ab initio* calculation, novel material, chalcopyrite, X-ray diffraction

We have been working with novel room-temperature ferromagnetic semiconductors based on heavily Mn-doped bulk single crystals of II-IV-V_2 chalcopyrites.[1,2] The most important feature of this study is the fact that the Mn substitution is much easier in II-IV-V_2 compounds than in III-V compounds. Reflection high-energy electron diffraction (RHEED) studies have revealed that a chalcopyrite-like structure was maintained during Mn deposition on $ZnGeP_2$,[1] and *in situ* X-ray photoelectron spectroscopy (XPS) measurements have indicated that the composition of the surface is dominated by Mn, Ge and P, with no trace of Zn.[3] On the basis of these results, we concluded that 100% Mn substitution could be realized in II-IV-V_2 materials, and therefore we have started an investigation on $MnGeP_2$ crystals. During the course of this study, we found that Cho *et al.* have recently reported on the preparation of $MnGeP_2$ bulk crystals and thin film.[4] However, they did not provide detailed descriptions on the growth conditions or on the crystalline properties of their films. The preparation of a well-defined film with a good crystallinity is crucially important for a detailed discussion of magnetic properties in thin films. In the present study, we concentrate on establishing the details of the molecular beam epitaxy (MBE) growth of $MnGeP_2$ films and their X-ray diffraction (XRD) analysis.

Prior to experimental studies, we examined the possibility of the formation of $MnGeP_2$ theoretically using $DMOL^3$ code, i.e., the density functional theory (DFT) for molecules and three-dimensional periodic solids.[5] $DMOL^3$ has been successfully applied for the band-structure calculations of insulating and metallic solids[5] and the complex structure of the $BaTiO_3$ grain boundary.[6] In this work, localized numerical orbitals were used as basis set, where a double set of numerical valence functions with a local basis cut-off of $R_c = 4.7$ Å was used. The relativistic treatments for the atoms are performed via a pseudopotential[7] acting on all electrons, including the core, to obtain the scalar relativistic corrections for the relevant valence orbitals. The generalized gradient approximation (GGA) functional of Perdew-Burke-Ernzerhof[8] is used to illustrate the dependence of our theoretical predictions on the functional treatments. We estimated an enthalpy of mixing as a function of the solid composition x of Mn in $Mn_xGe_{1-x}P$. In this calculation, MnP and GeP (i.e., the cases of $x = 1.0$ and 0.0, respectively) are assumed to have a zincblende (ZB) structure, although actual MnP exhibits a monoclinic structure. This assumption may be justified since the ZB phase transition metal compounds such as CrAs[9] and MnAs[10] have been known to grow on a GaAs substrate. The calculated results shown in Fig. 1 suggest that the chalcopyrite phase with $x = 0.5$ is the most stable state and can be expected to exist, although the lattice constraint from the substrates should be taken into account in order to allow prediction of the detailed thermodynamic properties of thin films.

Using the above-mentioned prediction as a basis, we started growth experiments on $MnGeP_2$. We employed an MBE apparatus in which Mn and Ge were supplied from solid sources using conventional Knudsen cells, while P_2 was supplied by decomposing a tertiary butyl phosphine (TBP) gas source using a cracking cell.[11] The cracking cell was designed following a report by Sai *et al.*[12] in which

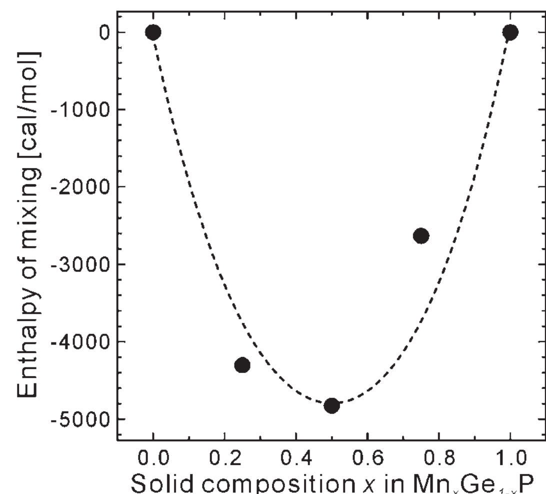

Fig. 1. Enthalpy of mixing as a function of solid composition x of Mn in $Mn_xGe_{1-x}P$.

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TBP is decomposed by catalysis with Ta shots in the PBN tube at 810–835°C. Use of the cracking cell is indispensable for the decomposition of TBP, since no deposition occurs on substrates without the use of the cell.

GaAs(001) and InP(001) single crystals were used as substrates. The GaAs substrate was treated with a H_2O_2+NH_3+H_2O (1:3:50) mixture solution, while no etching process was applied to the InP epi-ready wafer. Thermal cleaning of GaAs substrates was performed at 580°C in vacuum ($\sim 10^{-8}$ Torr) and that of InP was performed at 480°C in a P_2 flow. The substrate temperature was controlled between 400 and 495°C. The beam fluxes of both Mn and Ge were adjusted between 0.6×10^{-8} and 1.1×10^{-8} Torr using an ion gauge, and were set to be equal at around 0.6×10^{-8}–1.1×10^{-8} Torr. The flow rate of TBP gas was adjusted at 1.6–2.0 sccm by using a mass flow controller (MFC).

In the present paper we refer to four typical samples (samples #1 to #4) with different growth conditions. Samples #1 and #2 were grown on GaAs(001) substrates. The growth temperatures of samples #1 and #2 were 495°C and 400°C, respectively. The growth time was 240 min for both samples. On the other hand, samples #3 and #4 were grown on InP (001) substrates; the growth temperature was 435°C and the growth time was 180 min for both samples.

The resultant Mn:Ge:P ratios of samples #1 and #2, as determined by means of an energy dispersive X-ray analyzer (EDX), were 0.97:1.00:1.37 and 1.37:1.00:2.59, respectively. On the other hand, the Mn:Ge ratios of samples #3 and #4 are 1.92:1.00 and 1.40:1.00, respectively, where P is not shown; the precise determination of the P composition is difficult, since P is a constituent atom of the substrate. Nevertheless, we believe that the ratio may have values between 2.0 and 3.0 as estimated on the basis of the case of the GaAs substrate.

The 2θ-θ X-ray diffraction curves of all of the samples are shown in Fig. 2. The broad amorphous-like pattern at around 24° is a contribution from the glass plate used as a sample holder. The 002 and 004 diffraction lines of the GaAs substrates are located at $2\theta \sim 31.6°$ and $2\theta \sim 66.05°$, respectively. Close to these peaks, diffraction peaks (or shoulders) which may be assigned to the 002 and 004 diffractions of the cubic GeP[13] appeared in sample #1 which was grown with the metal-beam flux of 1.0×10^{-8} Torr and the TBP flow rate of 1.6 sccm. Another impurity phase which may be assigned to the Mn_2P compound was also detected, in addition to the GeP peaks. GeP tends to be formed at low TBP flow rates and high substrate temperatures. This latter contribution is also unfavorable for the growth of $MnGeP_2$ since the re-evaporation of phosphorous occurs easily under this condition. Therefore, an increase in the TBP flow rate relative to the beam flux of metals is necessary for the growth of single phase $MnGeP_2$; the TBP flow rate was increased to 2.0 sccm and the growth temperature was reduced to 400°C (sample #2). The diffraction lines of GeP were completely suppressed in the XRD chart of sample #2 and a number of MnP peaks appeared instead.

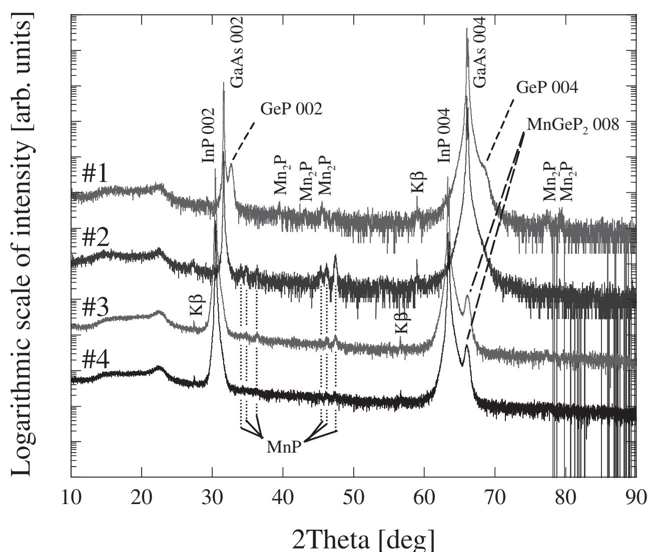

Fig. 2. 2θ-θ XRD curves of Mn-Ge-P films obtained in the present study.

No diffraction peak from the Mn-Ge-P sample could be distinguished in the X-ray chart except for peaks assigned to the GaAs substrate and polycrystalline MnP. We therefore assumed that the diffraction peaks of a ternary compound might be hidden by those of the substrate since such a compound would have a similar lattice constant to that of GaAs. On the basis of assumption, the GaAs(001) substrate was replaced by InP(001) whose lattice constant is unlike that of GaAs.

Sample #3 was grown at the beam flux with 0.9×10^{-8} Torr and the TBP flow rate of 2.0 sccm. As shown in the XRD chart of Fig. 2, a diffraction peak appeared at $2\theta \sim 66.04°$, that was clearly resolved from the 004 diffraction of the InP(001) substrate. The peak position of the newly observed diffraction peak happened to agree with the 004 diffraction of the GaAs(001) substrate, supporting the above assumption. We tentatively assigned the XRD peak to a diffraction line from the (001) plane of the $MnGeP_2$ compound. Assuming that the *c*-axis of the chalcopyrite structure grows perpendicularly to the (001) plane of the substrate, the $2\theta \sim 66.04°$-peak can be assigned to the $MnGeP_2$ 008 diffraction. Concerning the 004 diffraction of the chalcopyrite structure, no trace of a peak is found close to the 002 line of InP. This is consistent with our estimation that the peak intensity of the 004 diffraction of the chalcopyrite-type $MnGeP_2$ is less than 1/5 of that of the 008 diffraction.

Subsequently, we prepare the film with a reduced beam flux of 0.64×10^{-8} Torr (sample #4), fixing the growth temperature at 435°C and the TBP flow rate at around 2.0 sccm. Even though the thickness of sample #4 is smaller than that of sample #3, it exhibits almost the same diffraction intensity for $MnGeP_2$(008) as sample #3.

Figure 3 shows RHEED patterns of sample #4, obtained before and during the growth. The incident electron beam was along the [110] azimuth of InP. Figure 3(a) shows streak patterns from the InP substrate before the growth. The streak patterns completely varied to spotty ones, although they maintained the same spacing as observed immediately after the start of the growth (Fig. 3(b)). This change in the RHEED patterns suggests that this film was grown with a three-dimensional (3D) Volmer-Weber (VW) mode from the initial stage. This consideration was also supported by a scanning electron microscope (SEM) image in which the

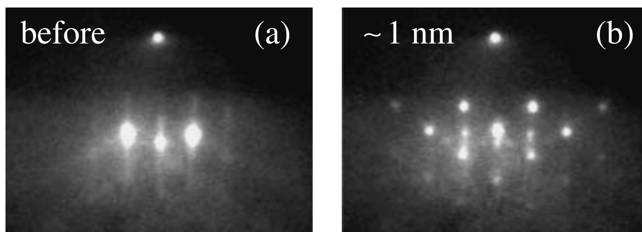

Fig. 3. RHEED patterns of sample #4 before and during deposition. Azimuth was parallel to InP[110]. RHEED patterns (a) from InP substrate before deposition, and (b) from the surface of the film with approximate thickness of 1 nm.

grain growth was observed.

On the basis of our experimental studies, including those mentioned above, it is concluded that the following conditions are required to obtain $MnGeP_2$ thin film and to suppress the deposition of MnP; (1) an excess P_2 partial pressure over the beam equivalent pressure of Mn and Ge fluxes, (2) an extremely low growth rate of around ~0.01 nm/s, and (3) the growth temperature of ~435°C.

In order to determine the crystal structure of the obtained film, X-ray reciprocal lattice mapping (RLM) measurement was carried out. Figure 5 shows the RLM image of sample #4, which is a part of the plane including the InP ⟨001⟩ and ⟨110⟩ directions in the reciprocal lattice space. The horizontal (Q_x) and vertical (Q_y) axes are the reciprocals of the in-plane and out-of-plane lattice constants, respectively. In this map, the 008, 116 and 1110 diffraction spots of $MnGeP_2$ are apparent close to those of InP 004, 113 and 115, respectively. The orientation of each pair of diffraction spots results in the orientation relationships of $MnGeP_2$⟨001⟩//InP⟨001⟩ and $MnGeP_2$⟨110⟩//InP⟨110⟩. This result indicates that the $MnGeP_2$ film obtained possesses a chalcopyrite-like crystal structure and is completely relaxed on the substrate. On the basis of the assumption of a chalcopyrite structure with a tetragonal crystal system, the lattice constants are determined to be $a = 0.569$ nm and $c = 1.13$ nm, and are thus consistent with those determined on the basis of the value obtained from theoretical calculation[14,15] ($a = 5.673$ Å, $c/a = 1.889$) and with those determined experimentally for the polycrystalline $MnGeP_2$ ($a = 5.655$ Å, $c = 11.269$ Å) reported by Cho *et al.*[4] It is considered that the difference in c-axis length between our sample and the calculated one is due to the ordering of cation sites. Therefore, it is necessary to investigate the relationship between the growth condition and the ordering of cation sites by using various methods to obtain the evidences of chalcopyrite-type $MnGeP_2$ which has ordered structure, because this ordering and the point defects are expected to affect the magnetic properties.[16,17]

Further studies to achieve 2D growth are underway, that are employing appropriate buffer layers. We have also investigated the magnetic properties of $MnGeP_2$ films which show ferromagnetism at room temperature. The dtails of these studies will be published in later publications.

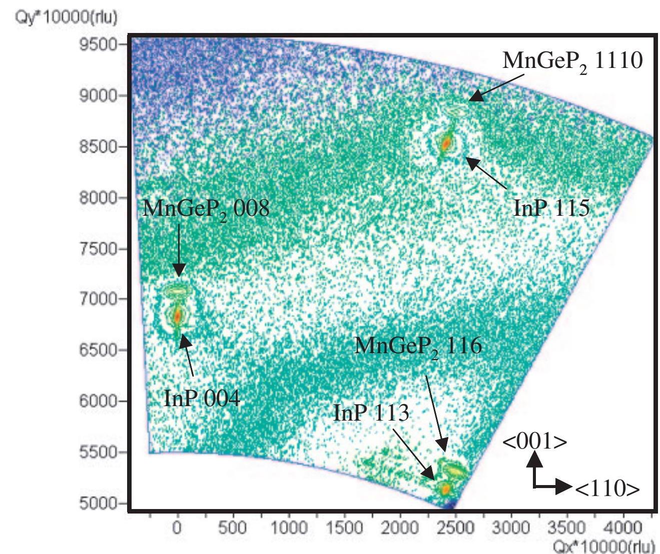

Fig. 4. Reciprocal lattice mapping of sample #4. Q_x and Q_y [shown in rlu (reciprocal lattice units)] are the reciprocals of the in- and out-of-plane lattice constants, respectively.

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