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RHEED observation of the growth of chalcopyrite-type $MnGeP_2$ on GaAs(0 0 1) substrate using Ge–buffer layer

K. Minami*, J. Jogo, Y. Morishita, T. Ishibashi, K. Sato

Graduate School of Engineering, Tokyo University of Agriculture and Technology, 2-24-16 Nakacho, Koganei, Tokyo 184-8588, Japan

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Abstract

Epitaxial growth of a novel chalcopyrite-type $MnGeP_2$ has been investigated using an MBE technique. In order to improve the surface morphology of the films, an effect of introduction of a Ge buffer layer was investigated. This results in dramatic change of the RHEED pattern from spotty to streaky ones. Improvement of surface morphology was confirmed by SEM observation. We attribute the improvement to the crystallographic affinity of Ge with II–IV–V_2 compounds and atomically flat surface of the buffer layer.

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1. Introduction

Mn-containing chalcopyrite semiconductors have been intensively investigated due to their ferromagnetism revealing at room temperature [1,2]. In the course of this study we have found that transition elements are more easily incorporated into II–IV–V_2 compounds than III–V materials. In situ XPS observation during Mn deposition on $ZnGeP_2$ suggested a complete substitution of Zn element by the Mn at the surface [3]. Therefore, we have been challenging a growth of a novel ternary material $MnGeP_2$ by using molecular beam epitaxy (MBE). Recently, we have successfully obtained $MnGeP_2$ thin films on InP(0 0 1) and GaAs(0 0 1) substrates [4]. However, an in situ reflection high energy electron diffraction (RHEED) observation revealed that $MnGeP_2$ grows three-dimennsionally on InP substrates.

In order to achieve two-dimensional (2D) growth of the $MnGeP_2$ thin films, we introduced a Ge buffer layer from the following reasons: It has been known that II–Ge–V_2 chalcopyrites tend to form a solid solution with Ge [5,6], and the lattice constant of Ge (5.657 Å) is close to both lattice constants of GaAs (5.653 Å) and $MnGeP_2$ [7,8].

*Corresponding author. Tel./fax: +81 42 388 7432.
E-mail address: minami_5@cc.tuat.ac.jp (K. Minami).

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2. Experiments

Mn and Ge were supplied from solid sources using K-cells with the beam flux of Mn and Ge around 6×10^{-9} Torr, while P_2 was supplied by decomposing tertiary butyl phosphine (TBP) gas with flow rate of 2.0 sccm using a cracking cell whose temperature was 835 °C. Chemical composition of Mn and Ge was adjusted to be 1:1 by controlling the beam fluxes. GaAs(0 0 1) wafers were employed as substrates, which were etched using a $H_2O+H_2O_2+NH_3$ solution followed by a thermal cleaning process at 580 °C without using As to remove the native oxide layer in a main chamber.

Sample #1 was directly grown on GaAs(0 0 1), while sample #2 was grown on a Ge buffer layer, the latter having been grown on the GaAs substrate at 380 °C. Growth temperature of $MnGeP_2$ was 435 °C in both experiments.

RHEED observation was performed during the growth of Ge buffer layers and $MnGeP_2$ films. The surface morphology of grown films was observed by scanning electron microscopy (SEM) and chemical compositions were measured by energy dispersive X-ray analysis (EDX).

3. Results and discussion

Fig. 1(a) shows a RHEED pattern of a GaAs substrate before growth and Fig. 1(b) that of $MnGeP_2$ film (sample #1; 1.0 nm in thickness) directly grown on the GaAs substrate. The incidence of electron beam was along the [1 1 0] azimuth of the substrate. A spotty pattern observed in Fig. 1(a) indicates that the thermal cleaning without supplying As made the surface of GaAs substrate rough. Many spots appearing at the beginning of the growth indicate a formation of polycrystalline MnP. No RHEED pattern from $MnGeP_2$ was observed [4]. Nevertheless we believe that $MnGeP_2$ should have been grown on the substrate, from the reciprocal lattice mapping of X-ray diffraction.

Fig. 2 shows RHEED patterns of sample #2 taken during the growth. The direction of incident electron beam is along the [1 1 0] azimuth of the substrate. Fig. 2(a) shows a streak pattern with 2×2 surface reconstruction, indicating that the Ge buffer layer improves the surface flatness from that of the GaAs substrate shown in Fig. 1(a). During the growth of $MnGeP_2$, the 2×2 streak pattern was observed until thickness reached 15 nm as shown in Figs. 2(b) and (c). We attribute the 2×2 surface reconstruction to phosphorous-dimmers in $MnGeP_2$ by analogy of the group V dimmers

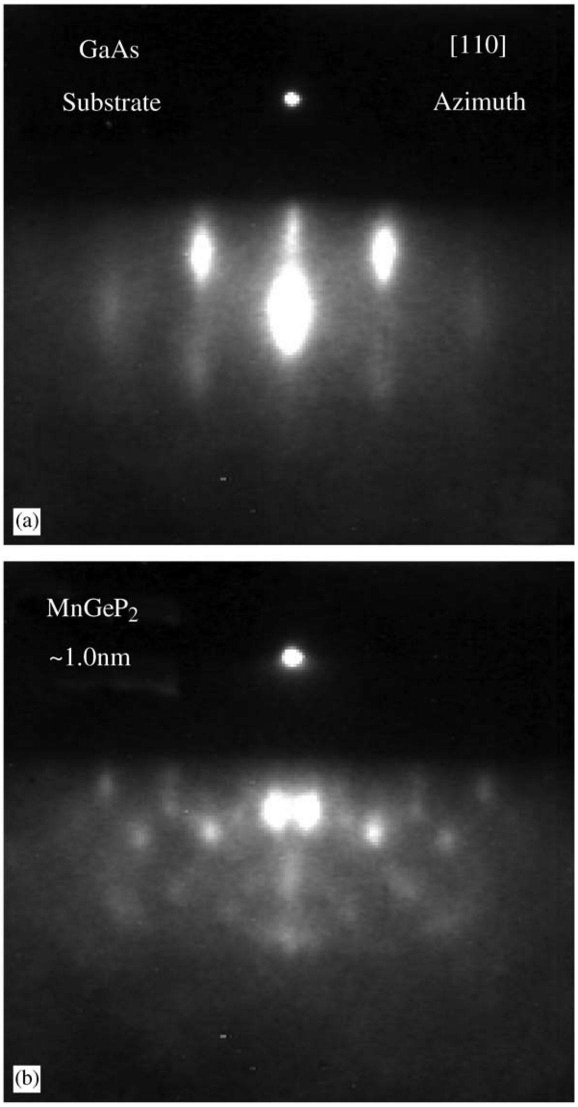

Fig. 1. (a) RHEED patterns of a GaAs substrate, and (b) $MnGeP_2$ film directly grown on a substrate. Azimuth is GaAs [1 1 0].

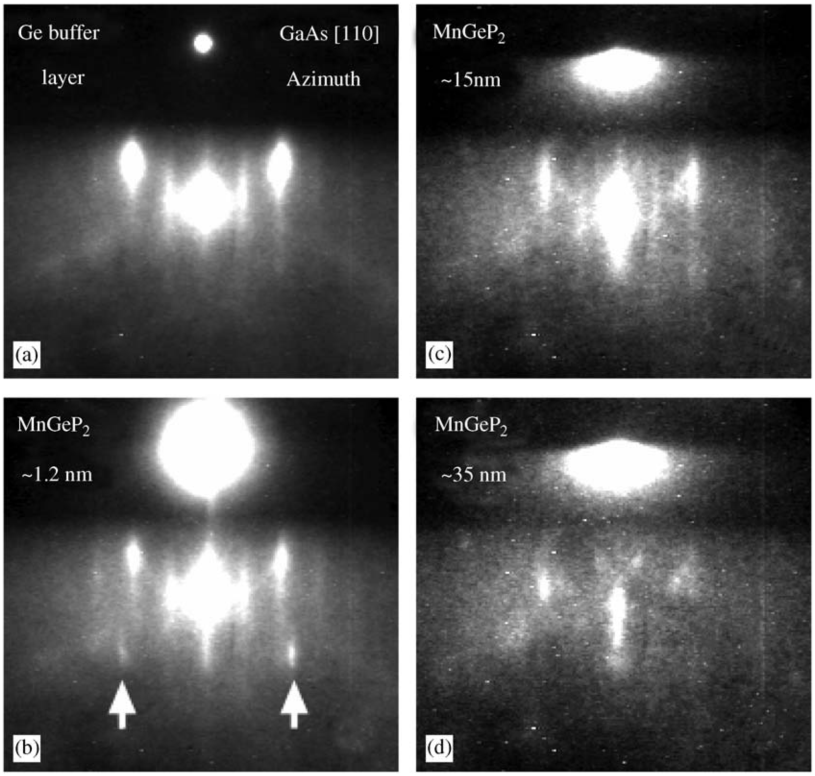

Fig. 2. (a) RHEED patterns of Ge buffer layer grown on a GaAs, and (b)–(d) $MnGeP_2$ film grown on a Ge buffer layer. Azimuth is GaAs[1 1 0].

in III–V compounds, which are crystallographic analogues of II–IV–V_2 compounds.

However, the MnP was confirmed in Fig. 2(b) as pointed by arrows, suggesting that a little amount of MnP was also grown. For the thickness above 35 nm, the surface reconstruction disappeared and some spots related to secondary phases appeared as shown in Fig. 2(d).

Figs. 3(a) and (b) show SEM images of a surface of sample #1 ($MnGeP_2$/GaAs) and sample #2 ($MnGeP_2$/Ge/GaAs), respectively. The sample #1 shows a rough surface morphology with 3D grains. We believe that the grains with a flat surface pointed by arrows may be assigned to $MnGeP_2$ and the other small grains to extraneous phases such as MnP. On the other hand, the surface morphology of $MnGeP_2$ grown on the Ge buffer layer is entirely flat, although a little amount of the segregation of MnP seems to have occurred. Epitaxial relationship and interface properties may be clearly witnessed by transmission electron microscope (TEM) observation, which is under investigation and will be published in later publications.

The 2D growth of $MnGeP_2$ may be explained by an enhanced migration of Mn and Ge atoms due to improved flatness of the surface by introduction of the Ge buffer layer. In addition, we consider that the crystallographic affinity [5,6] between $MnGeP_2$ and Ge may further assist the crystal growth. This consideration is also supported by our preliminary study in which extremely low growth rate is required to obtain $MnGeP_2$ and to suppress other phases [4].

As stated above, our films suffer segregation of secondary phase (MnP) even though the film composition was nearly stoichiometric. In order to obtain single-phase $MnGeP_2$ crystal, Kanagawa et al., performed the thermodynamic calculation in MnP–GeP system. A preliminary result suggests

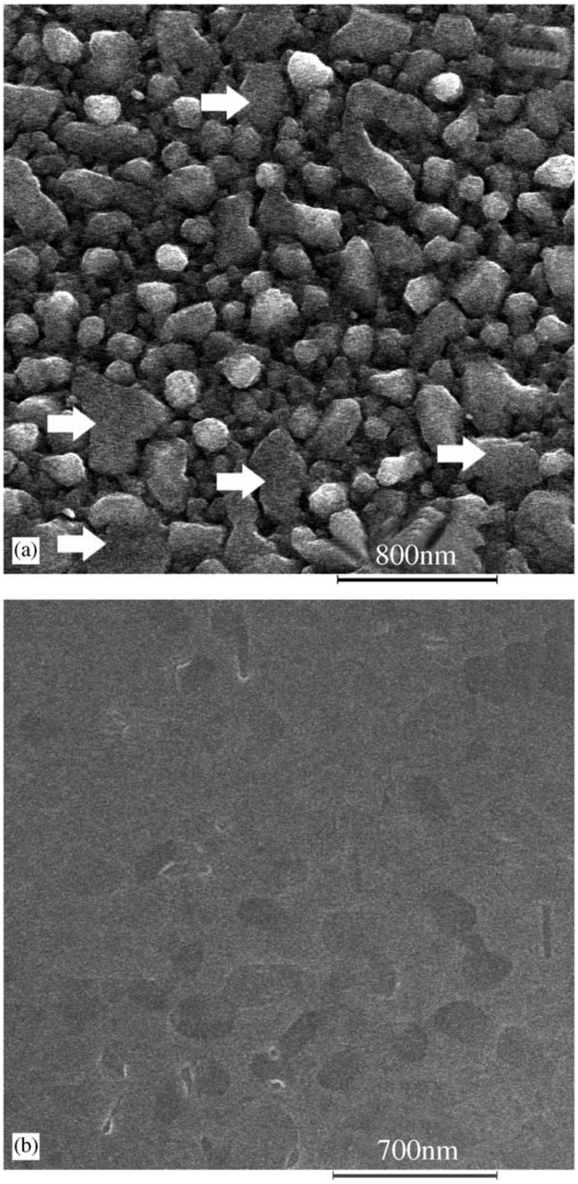

Fig. 3. (a) SEM images of a surface of $MnGeP_2$ film directly grown on a GaAs substrate, and (b) a surface of $MnGeP_2$ film grown on a Ge buffer layer on a GaAs substrate.

that growth temperature above 700 °C favors formation of $MnGeP_2$ suppressing other phases [9]. Experimental studies to obtain an optimal growth condition are underway.

4. Conclusions

We have studied the growth of ternary $MnGeP_2$ films on GaAs (0 0 1) substrate with and without a Ge buffer layer. 2D growth of $MnGeP_2$ thin films was achieved by using the Ge buffer layer. We attributed the improvement to an enhanced migration of Mn and Ge atoms due to flatness of the surface by introduction of the buffer. We have thus found that an introduction of the Ge buffer layer is effective for an improvement of crystallinity of $MnGeP_2$.

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