RHEED observation of the growth of chalcopyrite-type MnGeP$_2$ on GaAs(001) 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

Available online 3 February 2005

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.

© 2005 Elsevier B.V. All rights reserved.

PACS: 75.50.Pp; 81.15.Hi

Keywords: A1. Reflection high energy electron diffraction; A3. Molecular beam epitaxy; B1. Phosphides; B2. Magnetic materials

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(001) and GaAs(001) substrates [4]. However, an in situ reflection high energy electron diffraction (RHEED) observation revealed that MnGeP$_2$ grows three-dimensionally 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].
2. Experiments

Mn and Ge were supplied from solid sources using K-cells with the beam flux of Mn and Ge around \(6 \times 10^{-9}\) 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(001) 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(001), 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 [110] 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 \(\times\) 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 \(\times\) 2 streak pattern was observed until thickness reached 15 nm as shown in Figs. 2(b) and (c). We attribute the 2 \(\times\) 2 surface reconstruction to phosphorous-dimmers in MnGeP\(_2\) by analogy of the group V dimmers.
in III–V compounds, which are crystallographic analogues of II–IV–V₂ 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 (MnGeP₂/GaAs) and sample #2 (MnGeP₂/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 MnGeP₂ and the other small grains to extraneous phases such as MnP. On the other hand, the surface morphology of MnGeP₂ 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 MnGeP₂ 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 MnGeP₂ 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 MnGeP₂ 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 MnGeP₂ crystal, Kanagawa et al., performed the thermodynamic calculation in MnP–GeP system. A preliminary result suggests
that growth temperature above 700°C favors formation of MnGeP₂ suppressing other phases [9]. Experimental studies to obtain an optimal growth condition are underway.

4. Conclusions

We have studied the growth of ternary MnGeP₂ films on GaAs (0 0 1) substrate with and without a Ge buffer layer. 2D growth of MnGeP₂ 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 MnGeP₂.

Acknowledgment

This work has been carried out under the 21st Century COE program on “Future Nano-Materials” of TUAT and supported in part by the Grant-in-Aid for Scientific Research (A). The authors are thankful to Sumitomo Electric Industries Ltd., for supplying GaAs substrates.

References