XAFS studies of diluted magnetic semiconductor Mn-doped ZnSnAs$_2$ thin films on InP substrates

H. Oomae$^1$, H. Toyota$^1$, S. Emura$^2$, H. Asahi$^2$, and N. Uchitomi$^{1,a}$

$^1$Department of Electrical Engineering, Nagaoka University of Technology, Niigata, Japan
$^2$The Institute of Scientific and Industrial Research, Osaka University, Osaka, Japan

Abstract. Mn-doped ZnSnAs$_2$ (ZnSnAs$_2$:Mn) thin films with 5.0 and 6.5% Mn composition were epitaxially grown by molecular beam epitaxy on InP (001) substrates. These films had a Curie temperature of 334 K, corresponding to room-temperature ferromagnetism. The local structures around Mn atoms in ZnSnAs$_2$:Mn were studied by analysis of the X-ray absorption fine-structure spectra. It was found that the Mn atoms substitute into Zn or Sn cation sites, and the Mn–As bond length is 2.50 Å, which is slightly smaller than the value of 2.53 Å in a sphalerite (zinc-blende) ZnSnAs$_2$ bulk crystal. The Mn–As bond length in ZnSnAs$_2$:Mn is consistent with the value obtained from GaMnAs, and has a smaller value than that obtained from the zinc-blend MnAs thin films grown on a InP substrate.

1 Introduction

Over the last two decades, III-V based diluted magnetic semiconductors (DMSs), as well as recently developed ferromagnetic metals such as half-metallic materials, have attracted much attention for use in spintronic devices and as candidates for beyond-CMOS technology. In particular, GaMnAs has been extensively studied from experimental and theoretical points of view, because it is well lattice-matched with GaAs substrates and shows a relatively high Curie temperature of more than 100 K [1-4]. Therefore, it has been considered to be a promising candidate for producing semiconductor spintronic devices.

As the alternative ferromagnetic semiconductors, II-IV-V$_2$ chalcopyrite semiconductors such as CdGeP$_2$[5], CdGeAs$_2$[6] and ZnSnAs$_2$[7-8] have been shown to become ferromagnetic by Mn doping, and have Curie temperatures higher than 300 K. A bulk-type ZnSnAs$_2$ crystal doped with Mn has been experimentally shown to be ferromagnetic at a high Curie temperature [7]. The magnetic ion Mn, which occupies the cation IV site in host chalcopyrite or zinc-blende ( sphalerite) structures, has a local spin and at the same time acts as an acceptor. Very recently, ZnSnAs$_2$:Mn thin films have been epitaxially grown on InP (001) without any secondary phases, and have shown room-temperature ferromagnetism [8-10]. Both experimentally and theoretically, ZnSnAs$_2$ is probably regarded as a “vertical GaAs” to some extent, consisting of two interposing zinc-blende lattices, while permitting a high degree of Mn incorporation because Mn$^{2+}$ ions may easily substitute on the group II Zn sites. The ZnSnAs$_2$ thin films grown by molecular beam epitaxy (MBE) tend to show zinc-blende structure rather than chalcopyrite structure, which is analogous to the GaAs zinc-blende structure with Ga atoms being randomly replaced with either a Zn or Sn atom. Therefore, the ternary compound ZnSnAs$_2$ grown by MBE is referred to as zinc-blend ZnSnAs$_2$. On the basis of the present results, this material has the potential to produce InP-based spintronic devices, for which the lattice-matched III-V semiconductors InGaAs and InAlAs are expected to make possible magnetic quantum-well structures. However, the state of research and development of ferromagnetic II-IV-V$_2$ chalcopyrite semiconductors is still at the very early stage, and basic information is still not available on the parameters needed for spintronic device application.

X-ray absorption fine structure (XAFS) is a powerful tool for the study of the local structure around a specific component like Mn atoms in Mn-doped DMSs. This method offers important information on bond lengths and coordination numbers around the central atom, and helps us know which site the specific component occupies in the host material. Therefore, XAFS analysis has been effectively used for clarifying the physical properties of III-V based DMSs such as InMnAs [11], GaMnAs [12] and GaCrN [13]. In the case of the GaMnAs, it has been reported that the Mn atoms are substituted into the Ga sites and the Mn–As bond (0.249–0.250 nm) is slightly elongated from the Ga–As bond of the GaAs lattice. In contrast to the systematic investigation of III-V based DMS thin films, there have been few opportunities to study the structural properties of II-IV-V$_2$ based DMS thin films until now.

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In this paper, we report on the local structure around the Mn atoms in the ZnSnAs$_2$:Mn thin films grown epitaxially on InP substrates using Mn K-edge XAFS.

2 Experimental procedure

ZnSnAs$_2$ films doped with 5.0% and 6.5% Mn content were mainly employed for this experiment. The ZnSnAs$_2$:Mn films were grown on semi-insulating InP (001) substrates in a MBE chamber using solid elemental sources. Using the optimum substrate temperature of 300 °C and a Zn:Sn:As beam equivalent pressure (BEP) ratio of 24:1:52, we grew a 100-nm-thick ZnSnAs$_2$ epitaxial film doped with 5.0% or 6.5% Mn on a 16-nm ZnSnAs$_2$ buffer layer. The detailed growth procedure of ZnSnAs$_2$:Mn films on InP (001) has been published [9-10]. High-resolution X-ray diffraction (HR-XRD) measurements were performed to determine the lattice constant of the samples. Superconducting quantum interference device (SQUID) magnetometry was used to investigate the magnetic properties of the ZnSnAs$_2$:Mn thin films.

X-ray absorption spectroscopic measurements of the XAFS spectra were performed at a beamline BL9A in PF, KEK. The beamline BL9A was installed with a Si (111) double-crystal monochromator and a pseudo-conical shape mirror for collimation of incident X-rays. The XAFS spectra at the Mn K-edge from ZnSnAs$_2$:Mn thin films were recorded in fluorescence mode in an almost total reflection configuration, using a solid-state detector (SSD, Ge:Li) with 19 elements. A high-purity (99.95%) aluminum pipe was set just before the sample to block the detector reception of elastic and inelastic scattering by air in the X-ray path to the sample. The incident X-ray energy was calibrated at the pre-edge of the Cu foil (12.7185 degrees). The typical sample size was 5 mm in width and 10 mm in length. All measurements were run at room temperature. The observed XAFS spectra were analyzed by the code REX2000.

3. Results and discussion

Figure 1 shows the high-resolution XRD profiles close to the InP (004) reflection observed for 5.0% and 6.5% Mn-doped ZnSnAs$_2$ thin films. As seen from the patterns, the reflection peaks from Mn-doped and buffer ZnSnAs$_2$ thin films, respectively, are clearly separated into 62.76° and 63.07°, suggesting that these samples were successfully prepared. The diffraction patterns showed no traces of the other phase or Mn precipitates. A diffraction peak from the ZnSnAs$_2$ buffer layer was also observed for the 5.0% Mn-doped ZnSnAs$_2$ thin film.

Figures 2(a) and (b) show the magnetization values $M$ as a function of the magnetic field $H$ for 5.0 and 6.5% Mn-doped ZnSnAs$_2$ thin films observed at 300 K, respectively. It should be mentioned that the $M$-$H$ curves shown here were generated by subtracting the diamagnetic response of the underlying InP substrates. The hysteresis loops of both Mn-doped ZnSnAs$_2$ thin films were clearly observed even at 300 K. The $M$-$T$ curves (not shown here) were measured from 5 to 400 K, and showed ferromagnetism with a Curie temperature of 334 K.

The XAFS oscillations $\chi(k)$ were extracted by the code REX2000 from the observed spectra, and weighted by $k^3$ in order to compensate for the damping of the XAFS amplitude with increasing $k$, where $k$ is the wave-number of the excited electron in the free space. Figures 3 (a) and (b) show the XAFS oscillations weighted with $k^3$ for

![Figure 1. High-resolution XRD profiles of Mn-doped ZnSnAs$_2$ thin films with Mn concentrations of 5.0% and 6.5% on InP (001) substrates.](image)

![Figure 2. Magnetization as a function of applied field for (a) 5.0% and (b) 6.5% Mn-doped ZnSnAs$_2$ thin films at 300 K.](image)
ZnSnAs$_2$ thin films doped with 5.0 and 6.5 % Mn, respectively. The $k^2\chi(k)$ oscillations were Fourier-transformed within $k = 2 \sim 15$ Å$^{-1}$ to obtain a radial distribution function (RDF) as shown in Figs. 4 (a) and (b). The RDF shows an apparent peak at around 2.2 Å, which corresponds to the scattering of photoelectrons due to the nearest neighbor atom, As. In contrast, although the smaller peaks from the second-nearest neighbor atoms are expected to appear at around 3.8–3.9 Å, they are not well defined. The curve-fitting process for the dominant peak at 2.2 Å was run to search the exact local structural quantities of the first-nearest neighbor. Figures 5 (a) and (b) show both spectra of the reverse Fourier transformation of the dominant first peak and the best-fitted oscillation. The agreement is excellent as indicated by the very low values of the reliability factor (R-factor) given in Table 1. Here, it is assumed that the nearest neighbor atom is As. From this result, the second-nearest neighbor atoms might vary in terms of the positions of Zn and Sn because of their disordering. This result was supported from local three-dimensional structure analysis of ZnSnAs$_2$–Mn thin films by X-ray fluorescence holography [14]. The local structural quantities around the Mn atom in the Mn-doped ZnSnAs$_2$ thin films obtained from the curve-fitting process are listed in Table 1. The average distance of four arsenic atoms surrounding the central Mn atom was determined to be 2.50 Å. The bond lengths of both Mn$_2$Zn–As and Mn$_2$Sn–As in these ZnSnAs$_2$:Mn films were found to be elongated, which might be ascribed to the large atomic radius of Mn compared with Zn.

The growth of zinc-blende (zb) type MnAs thin films on InP (001) substrates has been reported [15]. The zb-type MnAs thin films are pseudomorphically lattice-matched with InP (001) substrates. The free-standing lattice constant of zb-type MnAs was obtained as 6.068 Å or 6.060 Å by high-resolution X-ray diffraction. The Mn–As bond length was estimated to be 2.63 or 2.62 Å. The expected Mn–As bond length of the zb-type MnAs was reported to be 2.55 Å since the lattice constant of zb-MnAs predicted from the linear extrapolation of the experimental lattice constant of Ga$_{1-x}$Mn$_x$As for $x \to 1$ was 5.89 Å [16].

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bond length. The Mn–As bond length of zb-type MnAs grown on InP is larger than that of zb-type MnAs grown on GaAs. In contrast, the Mn–As bond length in ZnSnAs$_2$:Mn is well consistent with the value obtained from GaMnAs.

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<th>Table 1. Summary of curve fitting results</th>
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4. Conclusion

ZnSnAs$_2$:Mn thin films with 5.0% and 6.5% Mn composition were epitaxially grown by molecular beam epitaxy on InP (001) substrates. These films had a Curie temperature of 334 K, corresponding to room-temperature ferromagnetism. The local structures around Mn atoms in the ZnSnAs$_2$:Mn were studied by XAFS measurements. It was found that the Mn atoms were substituted into Zn or Sn cation sites, and the Mn–As bond length was 2.50 Å, which is slightly smaller than the value of 2.53 Å in sphalerite (zinc-blende) ZnSnAs$_2$ bulk crystal.

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References