Mn$_x$Ge$_{1-x}$ dilute magnetic semiconductor studied by XAFS

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Abstract. Fluorescence X-ray absorption fine structure (XAFS) technique was used to investigate the local structures of the doped Mn in the Mn$_x$Ge$_{1-x}$ dilute magnetic semiconductors (DMSs) with different Mn content ($x=0.07, 0.25, 0.36$) prepared by magnetron cosputtering method. The results indicate that for the sample with low Mn content ($x=0.07$), the Mn atoms are mainly incorporated into the lattice of Ge, and locate at the substitutional sites of Ge atoms with the ratio of 75%. With the Mn content increasing to 0.25 or higher, only part of Mn atoms enter the lattice of Ge and the others exist in the form of the Mn$_2$Ge$_3$ phase whose content increases with the doped Mn concentration. It is found that, in the Mn$_{0.07}$Ge$_{0.93}$ the bond length of the first (Mn-Ge) shell is $R_{\text{Mn-Ge}}=2.50$ Å, which is bigger than the first (Ge-Ge) shell distance in Ge by about 0.05 Å. These results imply that local structure expansion is induced by dilute Mn substituting into Ge sites.

1. Introduction

Dilute magnetic semiconductors (DMSs) have attracted great fundamental and technological interest since the discovery of ferromagnetism in GaMnAs with Curie temperature $T_c=110$ K [1]. Especially, group-IV Mn$_x$Ge$_{1-x}$ DMSs have received remarkable attention both in experiment and theory in recent years due to its full compatibility with the main-stream silicon technology [2, 3]. The evidence of a ferromagnetic order in an epitaxial layer of Mn-doped Ge was first reported in 2002 by Park et al. [4]. They reported on the epitaxial growth of Mn$_x$Ge$_{1-x}$ by molecular beam epitaxy (MBE), and found that the Curie temperature of Mn$_x$Ge$_{1-x}$ increased linearly from 25 to 116 K with the increment of the Mn concentration. Following this initial report, some groups observed quite high ferromagnetic ordering temperatures in (Ge, Mn) films [5-9]. However, the origin of magnetism of Mn$_x$Ge$_{1-x}$ is still on the debate. For example, the magnetic response of most of the Mn$_x$Ge$_{1-x}$ alloys realized so far is due to Mn-rich separated phases [5, 10], and only few are indicative of an efficient dilution [4, 6]. It has been known that the magnetic and electronic properties of the DMS strongly depend on the concentration of the magnetic atoms in the host structure and the existence of secondary phases [11, 12], therefore, the investigation of the local structure of the Mn atoms in the germanium matrix is necessary to clarify the origin of the ferromagnetism in the Mn$_x$Ge$_{1-x}$ DMS.

In this work, fluorescence x-ray absorption fine structure (XAFS) was used to investigate the atomic structure in Mn$_x$Ge$_{1-x}$ thin films fabricated by magnetron cosputtering deposition. With the advantage of the sensitivity of the XAFS spectroscopy to the local structure around Mn atoms, in conjunction with the theoretical calculations, we aim to reveal the local structure of the Mn atoms into Ge host lattice. Our findings indicate that the the existence phases of Mn atoms in the Mn$_x$Ge$_{1-x}$ strongly depends on the Mn content.
2. Experimental
The Mn$_x$Ge$_{1-x}$ DMS thin films, with Mn contents of 7, 25, and 36 wt%, respectively, were grown on Si(100) substrate by the magnetron cosputtering method [13]. The sizes of the high-purity (>99.99%) Mn and Ge targets for sputtering are 76 mm, and the distance between the targets and the substrate is 5 cm with an angle of 45º. All films were grown at 900 K in Ar ambient pressure of 0.5 Pa for 3 hours. The growth rate of Mn$_x$Ge$_{1-x}$ films is about 1.5 nm/min, and the thickness of the films was approximately 300 nm.

The Mn K-edge XAFS spectra of Mn$_x$Ge$_{1-x}$ DMS samples were measured at the beamline BL-13B1 of Photon Factory, High Energy Accelerator Research Organization (PF, KEK), Japan and the U7C beamline of National Synchrotron Radiation Laboratory of China. The monochromator is Si (111) double crystals. The XAFS spectra of the samples were collected in fluorescence mode using a 100-element high purity Ge solid state detector. XAFS data were analyzed by UWXAFS3.0 [14] and USTCXAFS3.0 [15] software packages. The XAFS data of Mn$_5$Ge$_3$ were taken from Ottaviano et al. [16] for reference.

3. Results and Discussion
Figure 1 displays the Mn K-edge XANES spectra for the Mn$_5$Ge$_3$ compound, Mn$_x$Ge$_{1-x}$ thin films with different Mn contents, and a theoretical XANES spectrum for substitutional site model GeMn calculated by Feff 8.2 code [17]. First of all, the shapes of the XANES spectra for Mn$_5$Ge$_3$ and GeMn are significantly different. The spectrum of Mn$_5$Ge$_3$ shows four absorption peaks: A, B, C, and D in the post-edge; In contrast, the spectrum of GeMn demonstrates only three absorption peaks with a sharp white line peak at A location. It can be found that Mn$_{0.07}$Ge$_{0.93}$ thin film has a white line peak at A location as shown in Fig. 1, similar to that of GeMn, and its XANES shape is almost identical to that of GeMn. With Mn concentration in the Mn$_x$Ge$_{1-x}$ increasing, the intensity of peak A decreases while those of peaks B, C, and D are enhanced. When Mn content reaches 36 wt%, the XANES shape is very close to that of the Mn$_5$Ge$_3$ compound. Therefore, it is suggested that there are two existence phases of Mn atoms in the Mn$_x$Ge$_{1-x}$ thin films with different Mn contents. In the Mn$_x$Ge$_{1-x}$ thin films with low Mn content (7 wt%), most of Mn atoms are incorporated into the Ge lattice and substitute the Ge...
atoms; With the Mn content increasing to 25 wt% or higher, only part of Mn atoms enter the lattice of Ge, and the rest form Mn$_5$Ge$_3$ phase.

To more clearly illustrate the local structure change for the Mn$_x$Ge$_{1-x}$ thin films with different Mn contents, the radial structure functions (RSFs) of the Mn sites were obtained by Fourier transformation of the $k^3$-weighted EXAFS functions as shown in Figure 2. It is clear that the RSF of c-Ge is remarkably different from that of Mn$_5$Ge$_3$. In RSF of c-Ge, the coordination peaks at 2.2, 3.7, and 4.4 Å correspond to the first three coordination shells of Ge-Ge, respectively; while for Mn$_5$Ge$_3$, there is a double-peak structure located at 2.2 and 2.6 Å, corresponding to the first shell of Mn-Ge and the second shell of Mn-Mn, respectively. From Fig. 2, it can be seen that the RSFs for all the Mn$_x$Ge$_{1-x}$ thin films with different Mn contents show the first peak at 2.2 Å, which corresponds to the first shell of Mn-Ge, and the peak intensity is enhanced with the Mn content increasing. This signifies a notable increment of the Mn$_5$Ge$_3$ phase in the Mn$_x$Ge$_{1-x}$ films with high Mn content, consistent with the XANES analyses. To obtain the structure parameters of Mn$_x$Ge$_{1-x}$ thin films, least-squares curve fits were performed using the UWXAFS3.0 code. The theoretical amplitude functions and phase shifts were calculated by Feff 8.2. Two paths were used in the fitting. The Mn-Ge bond was used in the model with Mn substituting for Ge in the Ge lattice. The fitting results are summarized in Table I.

Table I. Structure parameters around Mn atoms in Mn$_x$Ge$_{1-x}$ thin films

| Sample         | Bond type | N    | R (Å)  | $\sigma^2$ ($10^3$ Å$^2$) |
|----------------|-----------|------|--------|--------------------------|
| Mn$_{0.07}$Ge$_{0.93}$ | Mn-Ge     | 4.0±0.4 | 2.50±0.01 | 8.0±0.9     |
|                 | Mn-Mn     | 1.2±0.2 | 3.01±0.01 | 14.1±1.2   |
| Mn$_{0.25}$Ge$_{0.75}$ | Mn-Ge     | 4.3±0.4 | 2.52±0.01 | 8.8±1.0     |
|                 | Mn-Mn     | 3.9±0.5 | 3.03±0.02 | 17.0±1.3    |
| Mn$_{0.36}$Ge$_{0.64}$ | Mn-Ge     | 4.4±0.5 | 2.52±0.01 | 9.2±1.0     |
|                 | Mn-Mn     | 4.1±0.5 | 3.05±0.02 | 23.3±1.4    |
| Mn$_0$Ge$_3$    | Mn-Ge     | 4.4±0.3 | 2.52±0.01 | 4.0±0.6     |
|                 | Mn-Mn     | 4.9±0.3 | 3.05±0.01 | 5.0±0.8     |
| c-Ge           | Ge-Ge     | 4.0±0.2 | 2.45±0.01 | 3.0±0.5     |

As seen from Table I, the coordination numbers N of the first-nearest and second-nearest shells change from 4.0 to 4.4 and 1.2 to 4.1, respectively, as the Mn content rises from 7 to 36 wt%, owing to the increase of Mn$_5$Ge$_3$ amount. Based on the proportion of Mn-Mn coordination to all the Mn nearest coordinations, we calculated the contents of Mn$_5$Ge$_3$ phase in the Mn$_x$Ge$_{1-x}$ thin films with different Mn contents are 25±(5)%, 80±(10)%, and 85±(10)% for Mn$_{0.07}$Ge$_{0.93}$, Mn$_{0.25}$Ge$_{0.75}$, and Mn$_{0.36}$Ge$_{0.64}$, respectively. Considering that there are two existence phases of Mn atoms in the Mn$_x$Ge$_{1-x}$ thin films, we can deduce that the proportions of the Mn atoms at substitutional sites are 75±(5)%, 20±(10)%, and 15±(10)%, respectively. These indicate that in the Mn$_x$Ge$_{1-x}$ thin films with high Mn content, most of Mn atoms form Mn$_5$Ge$_3$ phase, and only part of Mn atoms enter the lattice of Ge. While for the Mn$_x$Ge$_{1-x}$ thin films with low Mn content, about 75% of Mn atoms are incorporated into the Ge lattice and substitute the Ge atoms, but there is still some amounts of Mn$_5$Ge$_3$ existing in Mn$_{0.07}$Ge$_{0.93}$. This means the solid solubility limit of Mn in Ge for the Mn$_x$Ge$_{1-x}$ thin films fabricated by the magnetron cosputtering method is about 5%, in agreement with the Ref. [18]. The low solubility of Mn in Ge-based DMS films may be related to the growth direction [19]. Here, we used the Si(111) as substrate to fabricate Mn$_x$Ge$_{1-x}$ thin films. The tensile strain of MnGe/Si(111) interface actives the segregation of the intermetallic Mn compounds [19], so as to lower the solubility of Mn in Ge host significantly.

Finally, it is instructive to clarify the homogeneity and structural distortion of the films. It has been reported that the transition of the Mn$_x$Ge$_{1-x}$ alloy to a Mn-rich phase occurs around the 473 K [19]. Thus, the inhomogeneity of Mn in our films might be related to the high growth temperature of 900 K, which extensively exceeds the temperature limit and favors to precipitate the secondary magnetic phases [19]. Another detail to be mentioned is that the intensities of the peak at 2.6 Å in the FT spectra of the high Mn content samples are significantly reduced. From Table I, it can be observed that the disorder factors $\sigma^2$ for these samples are quite large, reflecting a high structural distortion around the
Mn ion. Accordingly, this structural distortion weakens the multiple-scattering of the surrounding atoms of Mn, and thus reduces the corresponding peak intensity in the FT spectra.

4. Conclusion
In summary, the Mn$_x$Ge$_{1-x}$ DMS thin films prepared by magnetron cosputtering method were studied by using fluorescence XAFS. It is found that for the sample with low Mn content ($x=0.07$), the Mn atoms are mainly incorporated into the lattice of Ge, and locate at the substitutional sites of Ge atoms with the ratio of 75%. With the Mn content increasing to 0.25 or higher, only part of Mn atoms enter the lattice of Ge and the others exist in the form of the Mn$_3$Ge$_3$ phase whose content increases with the increment of the doped Mn concentration. The fitting results indicate that the local structure expansion is induced by dilute Mn substituting into Ge sites.

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