Local structures around Mn atoms in Mn$_x$Si$_{1-x}$ thin films probed by fluorescence XAFS

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Abstract. The local structure of the doped Mn in the Mn$_x$Si$_{1-x}$ dilute magnetic semiconductors (DMSs) fabricated by magnetron cosputtering method are studied by fluorescence X-ray absorption fine structure (XAFS) at Mn K-edge. It is found that the occupation of Mn atoms in the Mn$_x$Si$_{1-x}$ DMS strongly depends on the Mn content. The Mn K-edge XAFS results indicate that for the sample with low Mn content (x=0.03~0.08), the Mn atoms are incorporated into the lattice of Si, and substitute part of the Si sites. As the Mn content reaches 0.15, Mn atoms mainly form the phase of Mn$_5$Si$_3$ compound.

1. Introduction

Dilute magnetic semiconductors (DMSs) have attracted intense interest due to their potential for “spintronic” applications [1,2]. Most activities are focused on the Mn-doped III-V or II-VI DMS materials, for which high quality epitaxial films with room temperature ferromagnetism (RT-FM) have been grown [3]. However, since the theoretical prediction of high Curie temperature [4,5] in 5% Mn doped Si, more research interest has been devoted to the realization of ferromagnetism in Mn-doped group IV, owing to their potential compatibility with current Si-based processing technology [6].

Despite the considerable work which reported the RT-FM in Mn-doped IV group DMS, the occupation nature of Mn ions in the host matrix is quite controversial nowadays [7,8]. Dalpian et al. [9] have theoretically predicted that the substitutional site Mn can stably exist in the Si matrix, and suggest that it might be possible to grow Mn$_5$Si$_3$ samples with a high enough concentration of substitutional Mn. Kim and Kown et al. [10,11] have indicated that their prepared Mn$_5$Si$_3$ samples were characterized to be Mn-Si compounds. Considering 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 [12], the investigation of the local structure of the Mn atoms in the silicon matrix is necessary to clarify the origin of the ferromagnetism in the Mn$_5$Si$_3$ DMS.

In this work, fluorescence x-ray absorption fine structure (XAFS) was used to investigate the atomic structure in Mn$_5$Si$_3$ thin films with diamond structure fabricated by magnetron cosputtering deposition at a low temperature. 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 Si host lattice. Our findings indicate that the occupation of Mn atoms in the Mn$_x$Si$_{1-x}$ DMS strongly depends on the Mn content.

2. Experimental

The Mn$_x$Si$_{1-x}$ DMS thin films, with Mn contents 3, 5, 8, and 15 wt%, respectively, were grown on Si(100) substrate by the magnetron cosputtering method [13]. The sizes of the high-purity (>99.99%) Mn and Si targets for sputtering are 76 mm, and the distance between the targets and the substrate is 5 cm with an angle of 45°. To increase the homogeneity of Mn ions distributed into the samples [14], all films were grown at 550 K in Ar ambient pressure of 0.5 Pa for 3 hours. The growth rate of Mn$_x$Si$_{1-x}$ films is about 1.5 nm/min, and the thickness of the films was approximately 300 nm. As reference, we prepared a Mn$_{1}$Si$_{1}$ compound thin film at 973 K by magnetron cosputtering method.

The Mn $K$-edge XAFS spectra of Mn$_x$Si$_{1-x}$ 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 [15] and USTCXAFS3.0 [16] software packages.

3. Results and Discussion

Figures 1 and 2 display the Mn $K$-edge extended XAFS $k^3 \chi(k)$ functions and their Fourier transform (FT) for Mn metal, Mn$_1$Si$_1$ and the Mn$_x$Si$_{1-x}$ thin films with different manganese concentrations. A Si

![Figure 1](image1.png)  
**Figure 1.** Experimental EXAFS $k^3 \chi(k)$ functions of Mn metal, Mn$_1$Si$_1$ and the Mn$_x$Si$_{1-x}$ thin films with different manganese concentrations along with the calculated spectrum for Si.

![Figure 2](image2.png)  
**Figure 2.** Experimental Fourier transform (FT) curves of Mn metal, Mn$_1$Si$_1$ and the Mn$_x$Si$_{1-x}$ thin films with different manganese concentrations, and the calculated FT curve for the models of Mn$_{si}$, Mn$_{It}$, and Mn$_{B}$. $K$-edge functions of theoretical calculation amorphous Si is also plotted in Fig. 1 as reference. First of all, the existence of metallic Mn atoms in Mn$_x$Si$_{1-x}$ thin films can be easily excluded, since the $k^3 \chi(k)$ feature and FT shape of the first peak at 2.28 Å corresponding to the first Mn-Mn coordination shell of
metallic Mn, are significantly different from those of Mn$_{x}$Si$_{1-x}$ thin films. From Fig. 1, the oscillatory function of Mn$_{0.15}$Si$_{0.85}$ thin film is very close to that of Mn$_{1}$Si$_{1}$ compound. Mn$_{x}$Si$_{1-x}$ thin films with low Mn content (3, 5, and 8 wt%) exhibit almost identical curves with a simple and smooth oscillation, which have the strong oscillation in the low $k$ region around $k=4.4$ Å$^{-1}$ and decrease gradually with the increase of $k$. Although the oscillation shape of $k^3 \chi(k)$ of Mn$_{x}$Si$_{1-x}$ thin films with low Mn content is similar to that of the Mn$_{0.15}$Si$_{0.85}$ thin film in the low $k$ region, they are evidently different in the high $k$ region. The oscillation curve of the Mn$_{0.15}$Si$_{0.85}$ thin film indicates that the presence of XAFS signals is mainly produced by higher coordination shells. This means that there is a different local environment around Mn atoms between Mn$_{x}$Si$_{1-x}$ thin films ($x=0.03, 0.05, 0.08$) and Mn$_{0.15}$Si$_{0.85}$ thin film. Moreover, as shown in Fig. 2, one can see that the FTs of Mn$_{0.15}$Si$_{0.85}$ thin film is similar to that of Mn$_{1}$Si$_{1}$ thin film, and presents two peaks at about 1.9 and 2.4 Å corresponding to the first coordination Mn-Si shell and second Mn-Mn shell, respectively. However, there is only one strong peak of the first Mn-Si shell at about 1.90 Å and no other peak of the higher shells of Mn-Mn or Mn-Si coordination in the Mn$_{x}$Si$_{1-x}$ thin films with $x=0.03, 0.05, 0.08$. It is worth noting that the $k^3 \chi(k)$ function features of Mn$_{x}$Si$_{1-x}$ thin films with low Mn content are close to those of the theoretic calculation amorphous Si as shown in Fig. 1. Therefore, these results indicate that in the Mn$_{x}$Si$_{1-x}$ thin films with $x=0.03, 0.05, 0.08$ the local structure of the Mn atoms is the same as that of Si atoms in the Si matrix, and the Mn atoms are incorporated into the lattice of Si host and no Mn-related secondary phases exist; When Mn content increases to 15 wt%, Mn atoms mainly form the phase of Mn$_{1}$Si$_{1}$ compound.

We have attempted to calculate the XAFS spectra for the substitutional (Mn$_{Si}$), tetrahedral interstitial (Mn$_{It}$), and hexagonal interstitial (Mn$_{Ih}$) sites. The calculations were performed with the Feff 8.2 code [17] at the Mn K-edge, and the calculation results are shown in Fig. 2. First of all, the presence of Mn$_{It}$ and Mn$_{Ih}$ can be safely excluded, since the FT shapes of Mn$_{It}$ and Mn$_{Ih}$ are quite different from those of Mn$_{Si}$, films. For the theoretical substitutional Mn atoms in Mn$_{Si}$ DMS, the first peak of the Mn-Si shell is at 1.90 Å. It can be clearly found that the experimental spectra with a strong peak (1.9 Å) in the Mn$_{Si}$ thin films with low Mn content are well reproduced by the calculated spectrum for substitutional Mn$_{Si}$. Hence, we can deduce that most of Mn atoms in Mn$_{Si}$ thin films with $x=0.03, 0.05, 0.08$ occupy the substitutional positions of the Si sites in Mn$_{Si}$ thin films. Table I summarizes the fitting structural parameters for the prepared Mn$_{Si}$ samples. The Mn-Si coordination number and distances in the theoretical substitutional site is also listed. The coordination number N$_{Mn-Si}$ of the Mn$_{0.15}$Si$_{0.85}$ thin film is about 7, similar to that of the Mn$_{1}$Si$_{1}$, which are consistent with Ref. 18. Different from these values, the coordination number N$_{Mn-Si}$=4.1 and bond length R$_{Mn-Si}$=2.35 Å of the first shell Mn-Si for the Mn$_{Si}$ thin films are correspondingly close to those N$_{Mn-Si}$ (4.0) and R$_{Mn-Si}$ (2.35 Å) of the substitutional Mn$_{Si}$ model structure. All these results indicate that Mn atoms in the Mn$_{Si}$ thin films with low Mn content are substitutionally doped into the Si host in the Mn$_{Si}$ thin films.

Table I. Structure parameters around Mn atoms for Mn$_{x}$Si$_{1-x}$ thin films, and for the model of Mn$_{Si}$ and Mn$_{1}$Si$_{1}$.

| Sample          | Bond type | N  | $R$ (Å)   | $\sigma^2$ (10$^{-3}$ Å$^2$) |
|-----------------|-----------|----|-----------|-----------------------------|
| Mn$_{0.03}$Si$_{0.97}$ | Mn-Si     | 4.1±0.4 | 2.35±0.01 | 8.8±0.1                    |
| Mn$_{0.08}$Si$_{0.92}$ | Mn-Si     | 4.2±0.3 | 2.36±0.01 | 10.2±0.2                   |
| Mn$_{0.15}$Si$_{0.85}$ | Mn-Si     | 6.9±0.3 | 2.36±0.01 | 13.7±0.1                   |
| Mn$_{Si}$ model  | Mn-Si     | 6.1±0.2 | 2.80±0.01 | 8.3±0.2                    |
| Mn$_{1}$Si$_{1}$ calculation | Mn-Si | 4.0 | 2.35 |                |
|                 | Mn-Si     | 1.0 | 2.31 |                |
|                 | Mn-Si     | 3.0 | 2.40 |                |
|                 | Mn-Si     | 3.0 | 2.54 |                |
|                 | Mn-Mn     | 6.0 | 2.80 |                |
It has been known that the crystallization temperature of silicon is 923K [19]. When the growth temperature of Mn\textsubscript{x}Si\textsubscript{1-x} thin films is under this critical temperature during the magnetron cosputtering (550K), the structure of the Si base approaches to be amorphous with large disorder [19]. When the doped Mn content is low, they tend to homogeneously separate into Si matrix, and randomly substitute the host atoms in the Si network on the substrate, close to those of Gd-doped Si with amorphous structure [20]. As the Mn content reaches 0.15 wt%, the doped Mn atoms are prone to aggregate and react with the Si atoms around them and finally form the energetically more favorable Mn-Si compounds.

4. Conclusions

In summary, the Mn\textsubscript{x}Si\textsubscript{1-x} DMS thin films prepared by low-temperature magnetron cosputtering method were studied by using fluorescence XAFS. It was found that the occupation of Mn atoms in the Mn\textsubscript{x}Si\textsubscript{1-x} DMS strongly depends on the Mn content. The comparison between the experimental and the theoretical XAFS spectra indicates that most of Mn atoms in Mn\textsubscript{x}Si\textsubscript{1-x} DMS thin films with low Mn content (x=0.03~0.08) locate at Si substitutional sites in the Si matrix. As the Mn content reaches 0.15, Mn atoms mainly form the phase of Mn\textsubscript{1}Si\textsubscript{1} compound.

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