Growth temperature dependence on local structures of Fe_{0.05}Si_{0.95} diluted magnetic semiconductors studied by X-ray absorption near-edge structure

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Abstract. X-ray absorption near-edge structure (XANES) spectroscopy was used to investigate the local structures of Fe_{0.05}Si_{0.95} diluted magnetic semiconductors (DMSs) thin film deposited by radio-frequency (RF) reactive magnetron co-sputtering device at temperatures of room-temperature (RT), 473 K and 573 K. Using the ab initio self-consistent real-space multiple-scattering approach, the experimental XANES spectra can be well reproduced by the theoretical calculation curves. The results indicate that the majority of Fe atoms are located at Si substitutional sites Fe\_Si in Fe_{0.05}Si_{0.95} at the room temperature. Upon increasing the temperature to 473 and 573 K, the majority of Fe atoms tend to form the FeSi\_2 compound.

1. Introduction

Since the discovery of carrier-induced ferromagnetism in GaMnAs diluted magnetic semiconductors (DMSs), a number of studied have been paid on III-V, IV, and II-VI DMSs for their potential applications in “spintronic” devices [1-3]. In particular, the Si-based DMS, including Fe\_Si\_x and Mn\_Si\_1-x, which is compatible with the mature microelectronics technologies, attracted considerable research interests recently [4, 5]. Despite the considerable work which reported the room temperature ferromagnetism in Si-based DMSs, the ferromagnetism origin of Fe-doped Si DMS is quite controversial nowadays. For instance, some believe the magnetism of Fe\_Si\_x originates from the presence of metal clusters, while others treat the ferromagnetism as intrinsic [4-7]. Considering that the magnetic properties of DMS strongly depend on the occupation of the magnetic atoms in the host and the existence of secondary phases [8-10], the investigation of the local structure of the Fe atoms in the silicon matrix is necessary to clarify the origin of the ferromagnetism in Fe\_Si\_x DMSs.

In this work, XANES is used to characterize the local structure around Fe atoms in Fe_{0.05}Si_{0.95} DMS thin films grown by reactive magnetron co-sputtering device at temperatures of room-temperature (RT), 473 K and 573 K. We find that for the RT Fe_{0.05}Si_{0.95} film, most of the Fe atoms are located at the substitutional sites. Upon increasing the temperature to 473 K and 573 K, the majority of Fe atoms tend to form the FeSi\_2 compound.
2. Experimental

Fe$_{0.05}$Si$_{0.95}$ DMSs films with a thickness of about 300 nm were deposited by radio-frequency (RF) reactive magnetron co-sputtering device on the Si(111) substrates at three different temperatures of RT, 473 K and 573 K. The sizes of Fe and Si targets for sputtering are 76 mm, and the growth rate of Fe$_{0.05}$Si$_{0.95}$ films is 1.0 nm/min. The content of the metal Fe component was determined by the sputtering power and was evaluated using the X-ray photoelectron spectroscopy (XPS).

The Fe K-edge XANES spectra of Fe$_{0.05}$Si$_{0.95}$ thin films were measured at the beamline 13B1 of Photon Factory of High Energy Accelerator Research Organization of Japan and the U7C beamline of National Synchrotron Radiation Laboratory of China. The monochrotron is Si(111) plane double crystals.

3. Results and discussion

Figure 1 shows the Fe K-edge XANES spectra of Fe$_{0.05}$Si$_{0.95}$ thin films of RT, 473 K and 573 K. First of all, it can be observed that the XANES spectra of 473 K film and 573 K film have quite similar XANES features with three characteristic peaks: A$_1$ (10.8 eV), B$_1$ (27.1 eV) and C$_1$ (73 eV). This implies that the local structure of 473 K film is similar with that of 573 K film. In contrast, the shape of the XANES spectrum for RT Fe$_{0.05}$Si$_{0.95}$ film is obviously different from those of the spectra for the 473 K and 573 K films. It is clear that the peaks A (12.9 eV) and B (27.1 eV) in the spectrum of RT film are broad and almost in equal intensity. While for the spectra of the 473 K and 573 K films, the intensity of the sharp peak B$_1$ is significantly stronger than that of peak A$_1$. Thus, we consider that the local structures of Fe$_{0.05}$Si$_{0.95}$ thin films are strongly affected by the growth temperature.

![Figure 1](image1.png)

**Figure 1.** Fe K-edge XANES spectra of the Fe$_{0.05}$Si$_{0.95}$, along with the calculated spectra for four model structures: FeSi, V$_t$, V$_h$ and FeSi$_2$. The red, the cyan and the magenta ones are our experimental spectra.

![Figure 2](image2.png)

**Figure 2.** The four model structures of Fe atoms in Si lattice (a) the substitutional FeSi; (b) the tetrahedral interstitial V$_t$; (c) the hexagonal interstitial V$_h$; (d) FeSi$_2$ compound.
In order to investigate the occupation of Fe atoms in Si lattice, we attempted to model four representative Fe$_{Si1-x}$ clusters which are shown in Figure 2 for the XANES calculations [11], such as the substitutional Fe$_{Si}$, the tetrahedral interstitial V$_t$, the hexagonal interstitial V$_h$, and the compound FeSi$_2$. The initial structural parameters of the Fe$_{Si1-x}$ cluster with 123 atoms based on the crystalline cubic Si and optimization of total energy are used to calculate the theoretical Fe K-edge XANES spectra of Fe$_{Si1-x}$. The XANES calculations were carried out using the ab initio self-consistent real-space multiple-scattering approach.

Figure 1 shows the Fe K-edge XANES spectra for the models shown in Figure 2. For the substitutional Fe$_{Si}$, it can be observed that there are two broad peaks A (12.9 eV) and B (27.1 eV) and one sharp peak C (73 eV) in the postedge region of Fe K-edge for the Fe$_{Si1-x}$. The XANES spectrum for the tetrahedral interstitial model V$_t$ also presents three peaks A2, B2, and C2 in the postedge region. However, the spectral shape and the peak positions for the spectrum of model V$_t$ are completely different from those of the model Fe$_{Si}$. This situation is similar to that of the hexagonal interstitial model V$_h$. In the substitutional Fe sites, Fe atoms are coordinated by four Si neighbors in the first shell and twelve Si neighbors in the second shell. While for the tetrahedral interstitial Fe sites, although Fe atoms are coordinated by four Si neighbors in the first shell, the next-nearest neighbors of central Fe are six Si atoms. As for the hexagonal interstitial Fe sites, Fe atoms are coordinated by six Si neighbors in the first shell and eight Si neighbors in the second shell. The difference between the substitutional and interstitial Fe sites in their coordination environments consequently produces the different multiple-scattering contributions that are attributed to the distinct features in their XANES spectra. It can be observed that the experimental spectrum of Fe$_{0.05Si0.95}$ thin films fabricated at the room temperature can only be reproduced by the calculated XANES spectrum of model Fe$_{Si}$. Hence, we can deduce that most of Fe atoms occupy at the substitutional Si sites for the RT-prepared thin films. For the calculated XANES spectrum of FeSi$_2$ compound, three peaks A1 (10.8 eV), B1 (27.1 eV) and C1 (73 eV) are also observed. Compared with the experimental spectra for the films of 473 K and 573 K, they all have three similar peaks A1, B1 and C1, in terms of intensity ratios as well as energy positions. It is obvious that the calculated XANES spectrum of FeSi$_2$ compound reproduces the experimental spectra of 473 K and 573 K films. And thus we can deduce that the nearly all the Fe atoms reacted with Si atoms forming the FeSi$_2$ compound at the elevated temperature.

In practice, when Fe atoms are incorporated into the Si lattice, the doped Fe atoms probably substitute simultaneously more than one position. Thus, the kinds of complex cases should be considered in principle. However, this concern appears very complicated and beyond the present study, we can not discuss them in detail. In fact, seeing from Figure 2, we can find a large structural difference between various Fe occupation sites in Si lattice, and the occurrence of the complexes consequently produces distinct features in the XANES spectra. Our experimental XANES spectra can only be reproduced by the calculated curves for the model structures of Fe substitutional or FeSi$_2$ compound. Thus, we consider that the quantity of Fe atoms which simultaneously occupy more than one site in the Si lattice is in a small amount. So we simplify the structural models and do not take into account these complex cases (including Fe atoms located at two sites in a sample) when we construct the theoretical models in this work.

Based on above XANES analyses, it can be inferred that the local structures of the Fe$_{Si1-x}$ thin films are dependent on the growth temperature. This can be rationalized by the crystallization of the Si based structures [12]. When the growth temperature of Fe$_{Si1-x}$ thin films is low, such as at the room temperature, the structure of the Si base approaches to be amorphous with large disorder [12]. Therefore, the doped Fe atoms are prone to randomly substitute the host atoms in the Si network on the substrate. However, the environment around the substitutional Fe ion doped into the Fe$_{Si1-x}$ films is under a metastable state. Consequently, when the growth temperature gets elevated, the substitutional Fe atoms would more actively react with the Si atoms around them and finally form the energetically more favorable Fe-Si compounds, making the process of the phase transformation approach a thermodynamic equilibrium [13]. In fact, a similar phenomenon has already been observed during the preparation of the Mn-doped Si samples grown by molecular beam epitaxy method [14, 15].
Put the above together, the results suggest that the Fe occupations in Fe$_x$Si$_{1-x}$ are significantly influenced by the preparation temperature. Hence, for practical spintronic applications, further investigations, particular studies on the structural order in the samples associated with appropriate preparation temperature are essentially required.

4. Conclusions

In summary, the local structures of Fe$_{0.05}$Si$_{0.95}$ films were studied by using X-ray absorption near edge spectra. The results show the location of Fe atoms in Si lattice depends on the growth temperature. For the Fe$_x$Si$_{1-x}$ film fabricated at room temperature, the majority of Fe atoms are located at Si substitutional sites FeSi. Upon increasing the temperature to 473 K and 573 K, the majority of Fe atoms tend to form the FeSi$_2$ compound with Si atoms.

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