Analysis for Positions of Sn Atoms in Epitaxial $\text{Ge}_{1-x}\text{Sn}_x$ Film in Low Temperature Depositions

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Abstract

We investigated the position of Sn atoms in $\text{Ge}_{1-x}\text{Sn}_x$ film grown at a low temperature by using the Extended X-ray Absorption Fine Structure (EXAFS) method. Vacancies had been expected to be introduced near the growing surface vicinity of a Sn atom and located at a split-vacancy position due to the binding nature between a Sn atom and a vacancy, which was predicted by the calculation for a bulk model in the literature. However, the EXAFS showed almost all Sn atoms were located at the substitutional position and did not form a split-vacancy.

Keywords: $\text{Ge}_{1-x}\text{Sn}_x$, vacancy, tin, crystal growth, surface, Extended X-ray Absorption Fine Structure

1. Introduction

High-mobility germanium (Ge)-based channels are attractive candidates for driving a higher current in p-type **metal-oxide-semiconductor field-effect-transistors**. Strained Ge channels for ultimate hole mobility enhancement are of particular interest. A uniaxial compressive channel architecture had been proposed using $\text{Ge}_{1-x}\text{Sn}_x$ alloys as Source/Drain stressors [1] in the same manner as biaxial **$\text{Si}_{1-x}\text{Ge}_x$** stressors. An alternative proposal was the use of strained $\text{Ge}_{1-x}\text{Sn}_x$ quantum well channels on a Ge substrate to take advantage of both mobility enhancement [2] and bandgap reduction [3]. A $\text{Ge}_{1-x}\text{Sn}_x$ film with an Sn content higher than about 5 % was required for these purposes and was achieved beyond the Sn solubility in Ge by lowering growth temperature [4]. Vacancies are expected to be introduced together with Sn atoms because they have a binding energy of 0.61 eV and become a split-vacancy in the bulk calculation [5] [6].

In the present paper, we investigate the structure of incorporated Sn atoms in as-grown $\text{Ge}_{1-x}\text{Sn}_x$ film by the Extended X-ray Absorption Fine Structure (EXAFS) method.

2. Experimental details

The substrates used for $\text{Ge}_{1-x}\text{Sn}_x$ epitaxial film growth were Germanium on insulator (GOI) wafers. This is because the thin film grown on GOI, in which an amorphous insulator layer (SiO_2) is under the analyzing film, has an advantage for detecting the signals by weakening the diffraction lines from the Si substrate in the EXAFS signal. The GOI wafers used in the present work were prepared by a germanium condensation technique, and the details of preparation have been previously reported [7]. The remaining Si content in the GOI layer was estimated to be below 0.5%, which was the detection limit of the Auger electron spectroscopy. After a GOI wafer was chemically cleaned, it was thermally cleaned with annealing at 430 °C in an ultra high vacuum (UHV) chamber. After the cleaning, a $\text{Ge}_{1-x}\text{Sn}_x$ layer was heteroepitaxially grown on the GOI substrate with a **molecular beam epitaxy (MBE)** system in the same UHV chamber. Germanium and Sn were deposited with Knudsen cells. The substrate temperature during the growth was controlled around 170 °C, and the thickness of $\text{Ge}_{1-x}\text{Sn}_x$ layers was 200 nm. The epitaxial layers were deposited as the target Sn contents of 0.00 % (no Sn doped), 1.7 %, and 5.0 %, and we call these samples (a), (b), and (c), respectively. The growth

rates of all epitaxial layers except sample (c) in Fig. 1 were 57 nm/hour, while that of sample (c) was 100 nm/hour. Conventional transmission electron microscope (TEM) observations were carried out using the model name Hitachi H-800 operated at an acceleration voltage of 200 kV as shown in Fig. 1. TEM samples were prepared by mechanical grinding followed by argon-ion milling. Some Sn precipitations were detected by TEM in the $\text{Ge}_{1-x}\text{Sn}_x$ layer of the only sample (c). The $\text{Ge}_{1-x}\text{Sn}_x$ layers of sample (b) and (c) were fully strained, which was confirmed by X-ray diffraction two-dimensional reciprocal space mapping. In this technique, we estimated actual Sn contents as 2.6 % for sample (b) and 1.3% for sample (c). Germanium powder of 99.99% purity, 100-um-thick pure Sn foil, and pure SnO and SnO_2 powder were also measured as references.

The EXAFS spectra were measured at the bendingmagnet beamline BL14B2 of the large-scale synchrotron radiation facility SPring-8 in Hyogo, Japan. The incident X-rays were monochromatized by a silicon (311) double crystal monochromator. The higher harmonics of the incident X-rays were reduced by two Rh-coated mirrors. The spectra were taken in a conversion electron yield method for the Ge K-absorption edges and X-ray fluorescence yield method for the Sn K-absorption edge. The samples were kept at room temperature during the measurements. The extraction of the EXAFS oscillation from the spectra, normalization by edge-jump, and Fourier transformation were performed by a code Athena [8]. The curve-fitting analysis was carried out in R-space by a code Artemis [8], and the quantitative structural parameters were obtained.

3. Results

3. 1 Absorption spectrum

Figs. 2a and 2b show the absorption spectrums near the K edge of Ge atoms and Sn atoms, respectively. The coordination environment of Ge atoms in sample (a) Sn 0 % is similar to Ge since the edge position and the curve shape of sample (a) are almost the same as those of pure Ge sample in Fig. 2a. The coordination environment of Sn atoms in sample (b) Sn 1.7 % and (c) Sn 5.0 % also seems to be similar to that of pure Sn, judging from the curve shape in Fig. 2b, especially the height at the peak of the curves. Although the edge positions of sample (c) Sn 5.0 % somehow deviated from that of pure Sn, this deviation was due to the mixing of Ge atoms in the Sn precipitates of these samples.

3. 2 EXAFS oscillations and their Fourier transforms

Figures 3 depict the k^3 -weighted EXAFS oscillations patterns extracted from the absorption spectra (not shown here) and the absolute values of their Fourier transforms (FTs). The position of peak A of sample (a) Sn 0 % in Fig. 3a, the origin of which is the interference between a Ge atom and its nearest neighbor atoms, agreed well with that of pure Ge. The positions of peaks B / C, the origins of which are speculated to be the interferences between a Ge atom and its next nearest neighbor atoms / its third nearest atoms, also agreed well. In Fig. 3b, the position of peak A originating from the interference between an Sn atom and its nearest neighbor atoms in sample (b) Sn 1.7 % agreed fairly well with that of peak A originating from that of a Ge atom and its nearest neighbor atoms in sample (a) Sn 0 %. These facts mean that most Sn atoms in the sample (b) are located at the substitutional positions of Ge atoms. The shifts of the positions of peaks B and C were most probably due to the structural relaxation of the Ge atoms surrounding an Sn atom in sample (b). In Fig. 3c, the curve shape originating from the interference between an Sn atom and its neighbor atoms in sample (c) Sn 5.0 %, however, was considerably different from that originating from that of an Ge atom and its neighbor atoms in sample (a) Sn 0 %, but it was rather similar with that originating from that of an Sn atom and its neighbor atoms in pure Sn. These results correspond with the detection of Sn precipitations in sample (c) by TEM as mentioned above and mean that almost all Sn exists in these precipitations.

3. 3 Curve-fitting analysis

To obtain the quantitative structural parameters (interatomic distances r and coordination numbers N) around the core-excited atoms, fine analysis by curve-fitting techniques was carried out. The curve-fitting results for Figs. 3 are summarized in Table I. These fitting results will provide models in which almost all Sn atoms are located at the substitutional position in sample (b) and in which most Sn atoms are in the precipitations of Sn metals and the remaining Sn atoms are located at the substitutional position in sample (c), although the R-factor of sample (b) is somehow larger than those of other samples.

4. Discussion

The lower detection limit of EXAFS measurements is generally estimated as several percent for Sn atoms at split-vacancy positions in $\text{Ge}_{1-x}\text{Sn}_x$ film. It has been proved that the Sn positions in as-grown $\text{Ge}_{1-x}\text{Sn}_x$ film by MBE at low temperature were mainly not split-vacancy positions but substitutional positions, contrary to the results obtained by ab initio calculation mentioned in the introduction section. No one can claim that no contents of Sn atoms are at split-vacancy positions. More than several percent of Sn atoms introduced by ion implantation has unquestionably been detected at split-vacancy positions by emission channeling experiments [9]. This is because ion implantations always introduce many vacancies near the introduced species from the Ge surface, so they can easily combine together and form a split-vacancy. In the MBE growth in lower temperature, the introduction of vacancies to the growing film is expected but it will be a much lower concentration. This can be explained by the formation energy of a pair of a vacancy and a Sn atom. The formation energies for a vacancy in a Ge crystal and an independent substitutional Sn in the crystal are estimated as 1.9~2.9eV [10] and 0.19eV [9], respectively. Taking the energy gain in binding a vacancy and a Sn atom into consideration, the formation energy of these pair must be 1.5~2.5 eV. From these differences of the formation energies for between the pair and a substitutional Sn, the concentration of a vacancy is estimated as at least several orders lower than that of a Sn atom at the growth temperature and much lower than the lower detection limit of EXAFS measurements. The binding nature between a Sn atom and a vacancy in a Ge crystal definitely introduces vacancies during a $\text{Ge}_{1-x}\text{Sn}_x$ crystal growth of Sn atom content. This increase in vacancies is too small to detect by EXAFS when introducing Sn atoms in Ge based crystal even if they all form a split-vacancy. However, this increase will be possible to detect by using positron annihilation spectroscopy (PAS). The PAS measurement of these samples is now in progress.

5. Conclusions

We investigated the position of Sn atoms in as-grown $\text{Ge}_{1-x}\text{Sn}_x$ film growth at a lower temperature by using the EXAFS method. The experimental results showed that almost all Sn atoms were located at the substitutional position and did not form a split-vacancy.

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Figure Captions

Fig. 1 Cross sectional TEM images of $\text{Ge}_{1-x}\text{Sn}_x$ (Ge) film; (a) no intended Sn doping, (b) Sn 1.7 %, (c) Sn 5.0 %. The parts indicated by “#” in the films of a GOI structure are grown by MBE.

Fig. 2 Absorption spectrums near K edge of a) Ge atoms and b) Sn atoms.

Fig. 3 Comparisons of Fourier transforms (FTs) of k^3 -weighted EXAFS oscillations patterns extracted from absorption spectra (Fig. 2).

Table I Results of curve-fitting analysis. Interatomic distances r and coordination numbers N obtained by analysis are listed.

Parameter [Unit]	Sn 0%	Sn 1.7%	Sn 5.0%	Sn 5.0%	Sn 5.0%	Pure Ge	Pure Sn	Pure Sn
	Ge-Ge	Sn-Ge	Sn-Ge	Sn-Sn (1 st nn)	Sn-Sn (2 nd nn)	Ge-Ge	Sn-Sn (1 st nn)	Sn-Sn (2 nd nn)
r [Å]	2.46	2.55	2.58	3.01	3.17	2.46	3.00	3.16
N	4.3	4.5	1.5	2.8	1.4	4.3	3.9	2.0
R -factor	0.0043	0.0952	0.0206			0.0005	0.0079

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Fig. 2 Kamiyama et al

Fig.3a,b Kamiyama et al

Fig. 3c, d Kamiyama et al