EXAFS measurements for liquid Ge-Si alloys

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EXAFS measurements around the Ge-K edge have been carried out for liquid Ge-Si alloys for the first time to investigate the local strucure around a Ge atom. To perform the EXAFS measurements for the liquid alloys with high melting temperatures, a new sapphire cell have been developed. The measurements were carried out for the liquid alloys from 10% to 60% of Si and the crystalline ones from 10% to 70% of Si as a reference. EXAFS oscillations, $x(k)$, are observed even at 1480°C for liquid $Ge_{0.4}Si_{0.6}$. The position of the first peak in the radial distribution function obtained from Fourier transform of $x(k)$ is shifted towards smaller distance for liquid and crystalline alloys with increasing Si concentration. The results of a curve-fit analysis in a harmonic approximation show that Ge-Ge and Ge-Si bonds in the liquid alloys become long with increasing Si concentration while those become slightly short in the crystaline ones.

Keywords: local structure; EXAFS measurements at high temperature; liquid Ge-Si alloys.

1. Introduction

Recent electronics is greatly advanced by utilizing various properties of semiconducting compounds. To research and develope them, structural information at atomic level is quite important. Traditional diffraction measurements give information on the average structure and it is known that the lattice constant of many compounds varies according to Vegard's law. However it is difficult to extract information on partial structure from the diffraction measurements in general. EXAFS spectroscopy has an advantage that it observes the partial structure around a selected atom directly for crystalline and amorphous materials. Since the structural study on random solid solutions of Ga-In-As by Mikkelsen, Jr. and Boyce (1983), many compounds including III-V and II-VI compounds were investigated by means of EXAFS and the results suggest that the covalent bonds in the compound have the lengths almost keeping each atomic radii though the lengths have slight concentration dependence.

Ge and Si are fundamental elements for electronics and their properties are well known. Ge and Si are miscible in the liquid state and the alloys form random solid solutions in the entire concentration region. The lattice constant of the alloys is known to obey Vegard's law (Hansen, 1958). Kajiyama *et al* (1992) measured EXAFS for crystalline Ge-Si alloys about the Ge-K absorption edge to investigate the bond-length relaxation in the solid solution. Their results show little composition dependence of Ge-Ge and Ge-Si bond lengths compared to those in III-V and II-VI compounds. Mousseau and Thorpe (1993) have discussed the EXAFS results based on a topological rigidity model. In the model, when the network of the bonds is floppy, each bond keeps its own natural length. To introduce such extreme case in the alloy, they pointed out the possibility of a large density of planar cracks in the sample of Kajiyama *et al*. EXAFS results carried out by Aldrich *et al* (1994) show a slight composition dependence of the Ge-Ge bond expected by the topological rigidity model.

When Ge and Si are melted, their dc conductivities increase up to $10^4(\Omega\cdot\mathrm{cm})^{-1}$ and undergo semiconductor-metal transition on melting. Recent neutron diffraction measurements for liquid (l-) Ge confirm that the coordination number of about 6 as the nearest neighbors is much smaller than that of typical liquid metals (Salmon, 1988). Ab initio molecular dynamics simulations for l-Si (Štich *et al*, 1991) and l-Ge (Kresse & Hafner, 1994) were carried out to investigate the semiconductor-metal transition on melting. Their results suggest that covalent bonds remain in the liquid and it keeps open structure compared to the closed packing of liquid metals.

EXAFS results of Ge fine droplets in carbon powder up to 1340°C have first reported by Filipponi and Di Cicco (1995). They analyzed the data using the pair distribution function deduced from the diffraction measuremets and obtained information on the local structure of l-Ge. However their sample is not bulky l-Ge. It is interesting to study whether the spectra of bulky sample is the same as their fine droplets. This prompts us to measure EXAFS of l-Ge using our own method. In addition, when Ge and Si are mixed, the covalent bonds are expected to be modified by the effects such as charge transfer, which may be contrasted with the unusual results of crystalline alloys. In this article the first results of EXAFS measurements for l-Ge-Si alloys are presented together with crystalline ones as a reference.

2. Experimental procedure

The EXAFS measurements were carried out using the spectrometer installed at BL10B at Photon Factory. A Si (311) channel-cut monochromator was used for the measurements on Ge-K absorption edges. The X-ray intensities before and after transmission were measured using ionization chambers with flowing N_2 and $N_2$85%Ar15% gases, respectively. Sample cells made of polycrystalline sapphire were newly designed for materials with the melting points higher than 1200°C. Figure 1 shows the cell and the heating assemblys. The sample reservoir is located above the sample space with 40μm in thickness and these are heated by the Mo heater. The temperature is measured by two PtRh6%-PtRh30% thermocouples.

Ge-Si alloys (99.999 %) were prepared by Rare Metallic Co. Ltd. The measurements of l-$Ge_{1-x}Si_x$ were performed from temperatures about 50 degree higher than the melting points to 1480°C at the maximum. Those of the crystalline powder were measured at room temperature as references.

3. Results

Figure 2 shows normalized XAFS oscillations, $\chi(k)$, of l-$Ge_{1-x}Si_x$ alloys near the melting temperatures and at the maximum temperature for each alloy. Clear oscillations are observed even at 1480°C. The spectrum of l-$Ge_{0.5}Si_{0.5}$ is noisy because the sample is about half thinner than the best thickness. With increasing Si concentration, x, the amplitude of the oscillations in smaller k region becomes small up to $x = 0.4$ and becomes large in $x \geq 0.5$. This behavior will show the interference effect between Ge-Ge and Ge-Si bonds and it suggests that Si atoms around a central Ge atom increases with increasing x.

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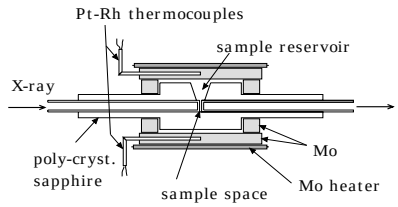

Figure 1
Polycrystalline sapphire cell and heating assembly for EXAFS measurements.

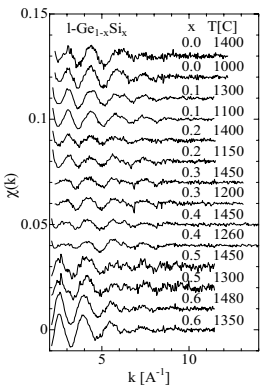

Figure 2
XAFS oscillations, $\chi(k)$, of l-$Ge_{1-x}Si_x$ alloys at temperatures indicated in the figure.

Figure 3 shows the radial distribution functions deduced from Fourier transform of k times $\chi(k)$ shown in Fig. 2. There remains the first peak at around 2.1Å in l-Ge and the position is shifted to smaller r with increasing temperature. The peak position is shifted to smaller r with increasing x. There appears the second peak around 3Å in Ge-rich region. The larger second peak in l-$Ge_{0.5}Si_{0.5}$ will come from the large noise in the $\chi(k)$.

4. Discussion

It is known that the analysis on the assumption of a Gaussian distribution function is not proper for the sysytem with large diorder. However it is not easy to analyze our data taking account of anharmonicity because of binary alloys. To obtain partial structure parameters around a central Ge atom for l–$Ge_{1-x}Si_x$ alloys at the first step, we carried out a curve fit analysis using the following formula based on the Gaussian model.

$$\begin{aligned} k\chi(k) \quad = \quad & N_c \left\{ (1-x)B_1(k_1)\exp(-2r_1/\lambda_1(k_1) - 2\sigma^2 k_1^2) \right. \\ & \times \sin(2k_1 r_1 + \phi_1(k_1))/r_1^2 \\ & + xB_2(k_2)\exp(-2r_2/\lambda_2(k_2) - 2\sigma^2 k_2^2) \\ & \left. \times \sin(2k_2 r_2 + \phi_2(k_2))/r_2^2 \right\} \\ & + n_3 B_3(k_3)\exp(-2r_3/\lambda_2(k_3) - 2\sigma^2 k_3^2) \\ & \times \sin(2k_3 r_3 + \phi_3(k_3))/r_3^2, \end{aligned} \tag{1}$$

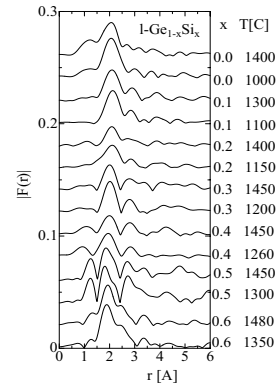

Figure 3
$|F(r)|$ obtained from Fourier transform $k\chi(k)$, of l-$Ge_{1-x}Si_x$ alloys shown in Fig. 2.

$$k_i = \sqrt{k^2 - \Delta E_{0i}/3.81}, \tag{2}$$

where $B_i(k_i)$, $\lambda_i(k_i)$, $\phi_i(k_i)$ are the backscattering amplitude multiplied by a reduction factor, the photoelectron mean free path and the scattering phase shift, respectively, which are given by the FEFF software (Rehr, 1991). Here the suffixes of 1 and 2 denote Ge-Ge and Ge-Si pairs, respectively. ΔE_{0i} is a variable parameter adjusting the experimentally and theoretically determined threshold energy. The total coordination number of a central Ge atom is represented by N_c. We assume that Ge and Si atoms are randomly distributed in the liquid alloys and neighboring Ge and Si atoms around a central Ge atom are coordinated in proportion to $1-x$ and x, respectively. In this analysis the third shell is included for the liquid alloys because the first and second peaks in $|F(r)|$ are not separated well. The parameters of n_3 and r_3 denote the coordination number and the interatomic distance, respectively. As the third shell, we assume a Ge atom for $x \leq 0.5$ and a Si atom for $x = 0.6$. Since the asignment of the third shell is ambiguous, we do not discuss the results. To reduce parameters, we assume common Debye-Waller factor, σ, for the three shells and the constraint of the bond length, $r_2 = 0.98r_1$. The second assumption will be supported by the fact that the bond lengths of the crystalline alloys obtained by a curve fit analysis without the constraint almost keep the condition. ΔE_{01} and ΔE_{02} are fixed to be -13.07eV and 16.15eV, respectively. These are average values of the ones which were obtained from the curve-fitting without the constraint of ΔE_{0i} for liquid alloys. The error of the optimized bond length is ± 0.02 Å. The obtained parameters are listed in Table I.

The obtained bond length of l-Ge is about 0.2Å short compared with the peak position of the pair distribution function obtained from the neutron diffraction measurement by Salmon (1988). The coordination number of about 1 from our EXAFS measurements is also much smaller than about 6 from the diffraction measurements. These facts may suggest that the analysis based on the Gaussian model is not proper. In practice, Filipponi and Di Cicco have succeeded in obtaining a reasonable results from their EXAFS spectra of l-Ge with their own method. However our analysis may give information on the covalent bonds in the liquid alloys. The results of ab initio molecular dynamics computer simulations of l-Si by Štich *et al* (1991), and l-Ge by Kresse and Hafner (1994) suggest the existence of covalent bonds. Štich et al show that the covalent bonds in l-Si almost always form between pairs separated by a distance

less than 2.5Å. Kresse and Hafner show that the percentage of nearest neighbors with 3- and 4-fold coordination is 12.4%. About 17% of atoms in l-Ge is estimated to have covalent bonds from the optimized coordination number of 1 when the average coordination number is assumed to be 6. This rough estimation seems consistent with the ratio of covalent bonds obtained from the simulation.

Table 1
Results of curve fitting for l-$Ge_{1-x}Si_x$. r_{Ge-Si} is fixed to be $0.98r_{Ge-Ge}$ and the error of r_{Ge-Si} is ± 0.02Å.

x	T[°C]	N_c	r_{Ge-Ge}	σ	n_3	r_3
0.0	960	0.858	2.40	0.128		
0.0	1000	0.988	2.39	0.134		
0.0	1050	1.457	2.37	0.156		
0.0	1100	1.021	2.38	0.142		
0.0	1200	1.038	2.37	0.145		
0.0	1300	0.963	2.36	0.146		
0.0	1400	1.107	2.35	0.153		
0.1	1100	0.663	2.41	0.143	0.640	2.91
0.1	1150	0.626	2.40	0.138	0.501	2.90
0.1	1200	0.629	2.39	0.145	0.579	2.91
0.1	1250	0.653	2.38	0.144	0.562	2.89
0.1	1300	0.802	2.39	0.160	0.954	2.90
0.2	1150	0.256	2.44	0.0836	0.0114	3.17
0.2	1200	0.260	2.44	0.0810	0.0115	3.16
0.2	1250	0.207	2.43	0.0797	0.0592	2.94
0.2	1300	0.248	2.42	0.0924	0.0107	2.50
0.2	1350	0.195	2.42	0.0820	0.0733	2.96
0.2	1400	0.173	2.42	0.0820	0.0499	2.95
0.3	1200	0.321	2.44	0.0883	0.159	3.19
0.3	1250	0.297	2.45	0.0819	0.158	3.18
0.3	1300	0.269	2.45	0.0916	0.190	3.18
0.3	1350	0.242	2.45	0.0843	0.176	3.22
0.3	1400	0.246	2.44	0.0961	0.130	3.21
0.3	1450	0.271	2.44	0.0916	0.180	3.19
0.4	1260	0.231	2.47	0.0809	0.142	3.18
0.4	1300	0.223	2.47	0.0884	0.176	3.17
0.4	1350	0.223	2.47	0.0898	0.192	3.17
0.4	1400	0.235	2.45	0.0946	0.165	3.18
0.4	1450	0.226	2.45	0.0938	0.227	3.18
0.5	1300	0.353	2.48	0.100	0.580	3.20
0.5	1350	0.330	2.48	0.100	0.727	3.20
0.5	1400	0.267	2.48	2.62E-05	0.345	3.22
0.5	1450	0.380	2.49	0.107	0.465	3.25
0.6	1350	0.348	2.51	0.0792	0.344	2.71
0.6	1400	0.328	2.50	0.0748	0.345	2.70
0.6	1430	0.348	2.51	0.0804	0.343	2.71
0.6	1480	0.342	2.50	0.0795	0.306	2.71

As shown in Table I, the bonds become short with increasing temperature in $x \leq 0.4$. The variation of the bond length in $x \geq 0.5$ is little due to smaller temperature variation. Such EXAFS results inconsistent with the behavior of thermal expansion are discussed by Crozier and Seary (1980) in solid and liquid zinc with large anharmonicity. Our results can also be explained by increaing anharmonicity with increasing temperature.

Figure 4 shows the obtained Ge-Ge (closed circles) and Ge-Si (closed squares) bond lengths of the liquid alloys shown in Fig.3 as a function of x. Open symbols denote the bond lengths of the crystalline alloys obtained from the curve fitting without the constraint of $r_2 = 0.98r_1$ and with x as a free parameter. For the crystalline alloys, the term of the third shell is deleted and ΔE_{01} and ΔE_{02} are fixed to be 6.73eV and 7.13eV, respectively. The defference in the electronic state between solid and liquid may reflect the different values of ΔE_{0i}. The optimized x's in the crystals are consistent with the Si concentration within ± 0.03. As shown in the figure, the Ge-Ge and Ge-Si bonds of the crystalline alloys becomes slightly short with increasing x. The behavior of the Ge-Ge bond are consistent with the results by Aldrich et al (1994). In addition, our results show that the Ge-Si bond becomes slightly short with increasing x. These concentration dependence are expected by the topological rigidity model for the crystalline alloys. On the other hand, it should be noticed that the bonds in the liquid alloys become long with increasing x and the variation is larger than that of the crystalline bonds. It is difficult to explain this result from the atomic level at the present stage, including the possibility that our model gives misleading results for the liquid alloys. However it may be correlated with the metallic behavior of the liquid alloy. A computer simulation such as ab initio molecular dynamics for liquid Ge-Si alloys will be helpful to understand the EXAFS results.

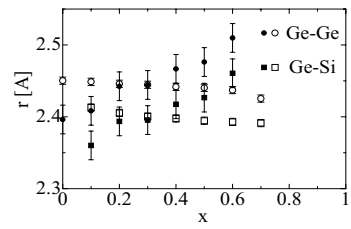

Figure 4
Concentration dependence of Ge-Ge (circles) and Ge-Si (squares) bond length for liquid (closed symbols) and crystalline (open symbols) $Ge_{1-x}Si_x$.

5. Conclusion

We have carried out EXAFS measurements about Ge-K absorption edge for liquid Ge-Si alloys as well as the crystalline alloys. The observed EXAFS spectra are analyzed based on the Gaussian model. The concentration dependence of the Ge-Ge and Ge-Si bond lengths for the crystalline alloys is consistent with that predicted by the topological rigidity model. The bonds in the liquid alloys show the dependence defferent from the crystalline ones.

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