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Local structures of dilute impurities in Si crystal studied by fluorescence XAFS

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Local structures of dilute isovalent and heterovalent impurity atoms in Si crystal (Si:X, X=Ga, Ge, As) have been studied by fluorescence XAFS. The results indicate that the local lattice deformation is strongly dependent on the electronic configuration of impurity atoms. The As-Si bond length is 0.244 nm while both Ge-Si and Ga-Si bond lengths are 0.238 nm. We find an anomalous expansion (0.009 nm) along the [111] direction for donor (As) atoms but much smaller magnitude (0.003 nm) for isovalent (Ge) atoms and acceptor (Ga) atoms. An electronic charge density is piled up to screen the ion core is a dominant factor for anomalous lattice expansion.

Keyword: fluorescence XAFS; dilute impurity; Si crystal

1. Introduction

The doping of crystalline Si (both thin films and bulk crystals) has numerous applications for the fabrication of advanced semiconductor devices (Shlimak *et al.*, 1997; Oyanagi *et al.*, 1988) which requires the state-of-the art tailoring of a band gap. In order to understand the nature of doping-induced electronic states, it is essential to study the local structures around impurities in the doped Si semiconductors. Furthermore, the information on the local distortion around heterovalent impurities would be helpful to understand the electron states of impurities from first principle calculations.

In this paper, fluorescence XAFS has been used to study the local structures of dilute acceptor (Ga) atoms, isoelectronic (Ge) atoms and donor (As) atoms doped in Si crystal. Recent advances in fluorescence detectors have allowed access to impurity levels of the order of $10^{18}/\text{cm}^3$ on a second generation synchrotron radiation source with a multipole wiggler (Oyanagi *et al.*, 1995; Murphy *et al.*, 1995). The bond lengths of impurity atoms can be obtained within the precision of 0.001 nm.

2. Experimental

The Si:X (X= Ge, Ga, As) samples were prepared by either molecular beam epitaxy or chemical vapor deposition. For Si:Ge, the 2000 nm thick heteroepitaxial $\text{Si}_{1-x}\text{Ge}_x$ (X=0.006) thin films were deposited on the substrate Si(001) surface at 673K in an molecular beam epitaxy growth chamber with a base pressure of 1×10^{-10} Torr. The Si:Ga sample is a Ga-doped 1050 nm thick Si epitaxial film with the doping concentration of $6.2 \times 10^{18} \text{ cm}^{-3}$. The Si:As sample is an epitaxial wafer which consists of As-

doped 9600 nm thick top layer with the doping concentration of $4.6 \times 10^{16} \text{ cm}^{-3}$ and As-doped 5400 nm thick second layer with the doping concentration of $2.6 \times 10^{18} \text{ cm}^{-3}$.

The fluorescence yield spectra of Si:X (X=Ga, Ge, As) samples were measured at the BL-13B of National Laboratory for High Energy Physics (PF, KEK). The electron beam energy was 2.5 GeV and the maximum stored current was 400 mA. A 27-pole wiggler with the maximum magnetic field B_0 of 1.5 T inserted in the straight section of the storage ring was used. XAFS data were collected using a fixed-exit double-crystal Si(111) monochromator. The first crystal is a water-cooled flat Si(111) crystal (Oyanagi *et al.*, 1995) while the second crystal is a sagittally bent Si(111) crystal which can focus the horizontal beam over ~ 2 mrad. A 7-element Si(Li) solid-state detector array was used to collect the fluorescence signal (Oyanagi & Owen *et al.*, 1995). The detector element is a planar-type Si(Li) crystal (16 mm in diameter and 4.6 mm deep). These elements were arranged to focus the sample position 100 mm away from the Be window with the element-to-window distance of 5 mm. The average energy resolution of each Si(Li) element with an active area of 200 mm^2 was 240 eV at 5.9 keV, using a shaping time of 6 μsecond . The elastic scattering peak are eliminated by using the thin Zn, Ga and GeO_2 X-ray filters for the Ga, Ge and As K-edge, respectively.

3. Results

Figure 1 compares the normalized K-edge EXAFS oscillations $k^2\chi(k)$ in the k range of 20–180 nm^{-1} . It can be readily seen that

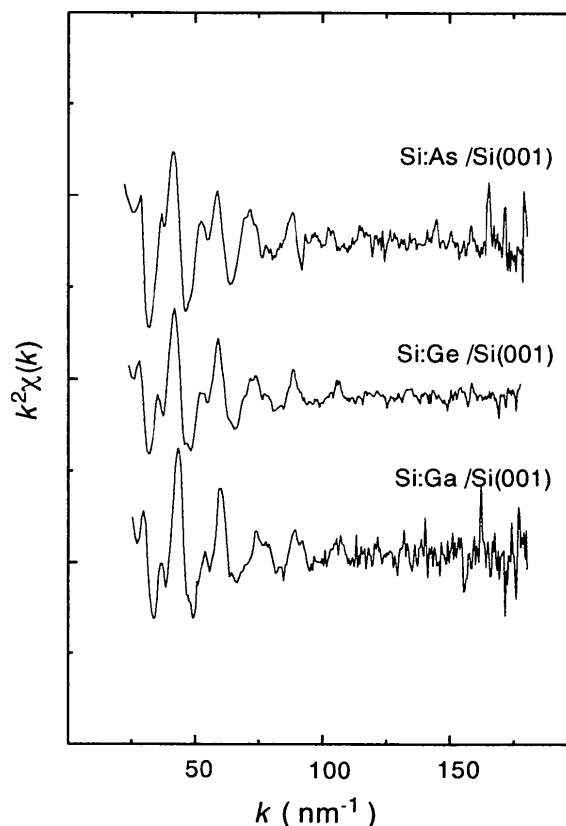


Figure 1
EXAFS oscillation functions $\chi(k)$ with k^2 weighting for Si:Ga/Si(001), Si:Ge/Si(001) and Si:As/Si(001).

their EXAFS features are similar and the prominent oscillations appear in the low k region of 30–80 nm⁻¹. The magnitude of oscillations decreases as an increase in k showing negligible magnitude beyond 100 nm⁻¹.

The results of Fourier transform (FT) of EXAFS oscillations $k\chi(k)$ for Si:X representing the radial distribution functions (RDF) are shown in Figure 2. The features of the RDF are similar to those of crystalline Ge and Si_{0.95}Ge_{0.05}/Si(001) (Oyanagi *et al.*, 1996). Prominent peaks at ~0.20 nm and 0.3~0.4 nm are due to the first nearest neighbors and second and third nearest neighbors, respectively. The presence of the second and third shells indicates that impurity atoms take substitutional sites without degrading the medium range order. However, that the tetrahedral arrangement of silicon atoms is still preserved around impurity atoms.

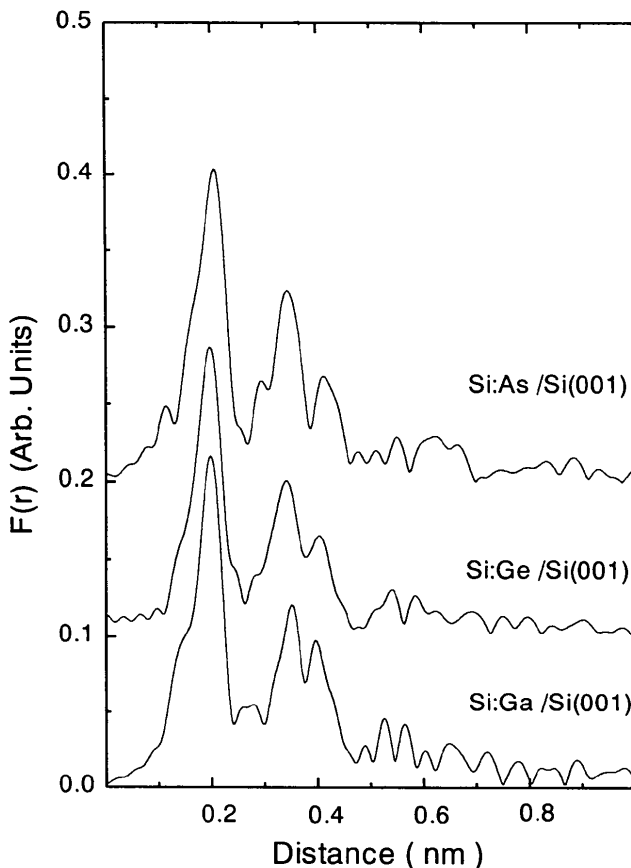


Figure 2

Radial distribution functions obtained by Fourier transform of EXAFS oscillation function $k\chi(k)$ for Si:Ga/Si(001), Si:Ge/Si(001) and Si:As/Si(001).

In order to obtain the structural parameters of nearest neighbor coordination of Ga, Ge and As impurities, the radial distribution function of Si:Ga/Si(001), Si:Ge/Si(001) and Si:As/Si(001) samples in figure 2 were inversely transformed to isolate the first nearest neighbor shell EXAFS contribution. The theoretical amplitude function $|f_j(k, \pi)|$ and phase shift function $\phi_j(k)$ were obtained by FEFF6 (Rehr *et al.*, 1992). The curve fitting results are summarized in table 1.

Table 1

Structural parameters obtained from fitting the EXAFS data for Si:Ga/Si(001), Si:Ge/Si(001) and Si:As/Si(001)

sample	K-edge	coordination type	R(nm)	N	$\sigma(10^3\text{nm})$
Si:Ga	Ga	Ga-Si	0.238±0.001	4.2±0.5	6.4±0.2
Si:Ge	Ge	Ge-Si	0.238±0.001	3.8±0.5	6.3±0.2
Si:As	As	As-Si	0.244±0.001	4.5±0.5	7.0±0.2
c-Si		Si-Si	2.35	4	

4. Discussion

The local structures around Ga and As isoelectronic impurities doped in InP crystals have been studied by Oyanagi *et al.* (1995). They found that the Ga-P and In-As bond lengths of impurities in InP were close to those in pure binary compounds GaP and InAs ($R_{\text{Ga-P}}=0.236$ nm, $R_{\text{In-As}}=0.2623$ nm), deviating from the interatomic distance of InP host lattice ($R_{\text{In-P}}=0.2541$ nm). Such deviation from the average lattice along the [111] direction gives rise to the local expansion or compression around impurities. Mikkelsen *et al.* (1983) have demonstrated that, in case of pseudo binary alloys such as In_{1-x}Ga_xAs, the positions of isoivalent atoms (In, Ga) significantly deviate from the average lattice of a VCA crystal.

The behavior of the heterovalent impurities, i.e., whether they introduce not only a simple atomic size effect but also a new source of lattice distortion because of a stronger interaction with host atoms is an interesting problem. Thus it is necessary to systematically investigate the dependence of valency. The RDF in Figure 2 suggests that the coordination geometry of Si atoms. According to Pauling's rule (Phillips, 1973) the tetrahedral covalent radii of Si, Ga, Ge and As atoms are 0.1173, 0.1260, 0.1225 and 0.1180 nm, respectively. Their covalent bond lengths are $R_{\text{Si-Si}}=0.235$ nm, $R_{\text{Ga-Si}}=0.243$ nm, $R_{\text{Ge-Si}}=0.240$ nm, $R_{\text{As-Si}}=0.236$ nm. The bond lengths are in the following order: $R_{\text{Ga-Si}} > R_{\text{Ge-Si}} > R_{\text{As-Si}} > R_{\text{Si-Si}}$. On the contrary, we find an anomalous behavior; although the Si lattice is expected to expand toward the [111] direction in going from As to Ga, the results show that the $R_{\text{Ga-Si}}$ and $R_{\text{Ge-Si}}$ have the same value (0.238 nm) which are 0.002 nm shorter than the covalent bond lengths $R=0.240$ nm while $R_{\text{As-Si}}$ is 0.244 nm which is 0.004 nm longer than the sum of $R_{\text{Ge-Si}}$ covalent radii.

When the As atom replaces Si sites, its ion core is positively charged. In order to screen this charge, some electrons are transferred from the bond charge and pile up between the ion core and the bond charge. Since the interaction for both the core-core and electron-electron interactions are repulsive, nearest Si atoms are shifted away from the As impurity. In our calculation, the σ_s disorder factors are 0.0064, 0.0063 and 0.0070 nm for Ga-Si, Ge-Si and As-Si covalent bonds, respectively. The σ_s value for Si:As/Si(001) is about 0.0006 nm greater than that of both Si:Ga/Si(001) and Si:Ge/Si(001). This indicates that there is slightly larger disorder in the first shell around impurity sites in case of Si:As/Si(001). Since the charge pile up to screen the ion core would weaken the bond strength, the increased relative displacement is consistent with the conclusion that the repulsion between the extra charge pile up and bond charge is a dominant

factor of the local lattice distortion. If the ion core charge plays an important role, we should observe at least the effect of the negative charge for Si:Ga/Si(001) but we see no such effect. Theoretical calculations are necessary to further clarify the detailed mechanism of lattice expansion around impurity atoms.

5. Conclusion

We have determined the magnitude of the local lattice distortion around dilute impurity atoms along the [111] direction for isovalent (Ge) and heterovalent (Ga, As) atoms in Si crystal with fluorescence XAFS. Contrary to the systematic variation $R_{\text{Ga-Si}} > R_{\text{Ge-Si}} > R_{\text{As-Si}}$ predicted by the sum of covalent radii, the As-Si bond length is unusually long (0.244 nm) indicating that the local lattice expands by 0.009 nm. The results suggest that the local lattice distortion is not dependent on the ion-core repulsion only. Instead, the present results suggest that the Si nearest neighbor atoms move away due to the repulsive interaction of a charge pile up to screen the positive charge and the bond charge.

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