

The silicon L-edge photoabsorption spectrum of silicon carbide

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1989 J. Phys.: Condens. Matter 1 6755

(<http://iopscience.iop.org/0953-8984/1/37/021>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.96

The article was downloaded on 10/05/2010 at 20:05

Please note that [terms and conditions apply](#).

The silicon L-edge photoabsorption spectrum of silicon carbide

I Waki and Y Hirai

Advanced Research Laboratory, Hitachi Ltd, Kokubunji, Tokyo 185, Japan

Received 10 February 1989

Abstract. This paper presents the x-ray absorption spectrum of the Si L-edge of SiC in the energy region 90–180 eV. To obtain the absorption spectrum, we have measured reflectivity spectra at several incidence angles using synchrotron radiation. The absorption coefficient for each photon energy has been deduced from the angular dependence of the reflectivity. The spectrum of the index of refraction is obtained as well. We find that the near-edge structure of the absorption spectrum of SiC is consistent with effective potential barriers formed by electronegative carbon atoms that surround silicon atoms tetrahedrally.

1. Introduction

Absorption spectra of L-edge of silicon and its compounds are among the most-often studied of XANES (x-ray absorption near-edge structure). In many silicon compounds, silicon atoms are surrounded tetrahedrally by other elements, or ligands. The tetrahedral symmetry enables molecular-orbital (MO) interpretation of XANES of the Si L-edge (Dehmer 1972). The observed XANES features are interpreted in terms of resonances localised within effective potential barriers formed by the tetrahedrally arranged ligands which are electronegative. Silicon compounds whose absorption spectra have been reported in the energy region from the Si L-edge (located near 100 eV) to 100 eV above the threshold include crystalline Si (Ershov and Lukirskii 1967, Gäwiller and Brown 1970, Brown *et al* 1977), amorphous SiO₂ (Ershov *et al* 1966, Brown *et al* 1977, Bianconi and Bauer 1980), amorphous Si₃N₄ (Brown *et al* 1977), solid and gaseous SiF₄ (Dehmer 1972, Sonntag 1978), and gaseous SiCl₄ (Dehmer 1972). Thus, addition of absorption spectrum data of SiC will give further information on the understanding of XANES of these tetrahedral silicon compounds.

Si L-edge spectra of secondary electron yield of SiC has been obtained by Zhukova *et al* (1968) in the energy region 100–120 eV. Since it is not possible to make thin films of SiC suitable for transmission experiment, they used secondary electron yield method to obtain the absorption spectrum. The energy range was not wide enough to compare the XANES with other silicon compounds. Instead of using secondary electron yield, Vinogradov *et al* (1983) measured reflectivity at 86° incidence in the energy region 80–180 eV. They compared the near-edge structure in the reflectivity spectrum with those of other silicon compounds.

Another method for obtaining absorption coefficient in the soft x-ray range is to use the angular dependence of reflectivity at grazing incidence at each photon energy

(Parratt 1954, Hendrick 1957, Ershov *et al* 1966, Andre *et al* 1982, Blau *et al* 1983). One can obtain the absorption coefficient from the angular dependence of the reflectivity, since the smaller the absorption coefficient, the sharper the cut-off curve of angular dependence of total reflection. Rife and Osantowski (1981) and Yanagihara *et al* (1986) have used this angular-dependence method to obtain optical constants—index of refraction and absorption coefficient—of SiC near the Si L-edge at discrete photon energies at intervals of 20–50 eV.

In this paper, we present a continuous absorption spectrum of Si L-edge of SiC measured at much finer energy intervals (0.3–1.0 eV) in the energy region 90–180 eV, obtained using the angular-dependence method. We compare the near-edge structure of the spectrum with those of other silicon compounds in which silicon atoms are tetrahedrally surrounded by other atoms.

2. Experiment

We measured the reflectivity spectra on the soft x-ray beamline BL-11A of the Photon Factory, KEK. This beamline is equipped with a 2-m Grasshopper monochromator with 2400-grooves/mm grating that provides soft x-rays in the energy range 90–1200 eV (Yanagihara *et al* 1984). During our measurement, the output beam of the monochromator above 180 eV was contaminated with stray light, so that we were able to measure reliable reflectivity only between 90–180 eV. We have used no filters for the elimination of stray light.

The soft x-ray reflectometer used is described by Yanagihara *et al* (1986). The pressure of the reflectometer was 1×10^{-5} Pa during the measurement. We used a windowless photo-electron multiplier with CuI photo-cathode to detect the reflected light. The time fluctuation of the incidence beam was monitored by photo-current from CuI evaporated on a copper plate partly intervening the incoming beam at upstream of the reflectometer. The spectrum of the incident beam was measured by displacing the sample holder. The incident beam was s-polarised.

We measured the reflectivity by scanning the monochromator at fixed incidence angles with energy resolution of 0.2–0.3 eV. We measured the reflectivity at 270 different photon energies between 90 and 220 eV. Energy interval of measurement increased from 0.3 eV at 90 eV to 1.0 eV at 220 eV. At each energy, photo-current was integrated for 2 seconds. The spectra were taken at incidence angles of 89°, 87°, 83°, 75°, and 65°.

The measured sample was ceramics of α -SiC. The sample was prepared as follows. Fine powder of α -SiC was mixed with 2 wt. % of sintering aid, AlN powder. The mixture was hot pressed and sintered at 2050 °C and 30 MPa for 1 h. The crystal structure of SiC thus obtained was mostly 6H polytype with a small amount of 4H and 15R. The density of the SiC ceramics was 3.18 g cm^{-3} , 99% of the theoretical value calculated from measured values of lattice constants. The surface of the sample was diamond lapped to RMS roughness of better than 2 nm as measured with a Talystep profilometer using a stylus with 1 μm lateral resolution. The size of the sample was 40 mm square and 10 mm thick.

3. Data analysis

Figure 1 shows the reflectivity spectra for s-polarised light measured between 90–220 eV at incidence angles designated in the figure. From these data we deduced the optical constants at each energy as follows. We express the complex refractive index \hat{n} as

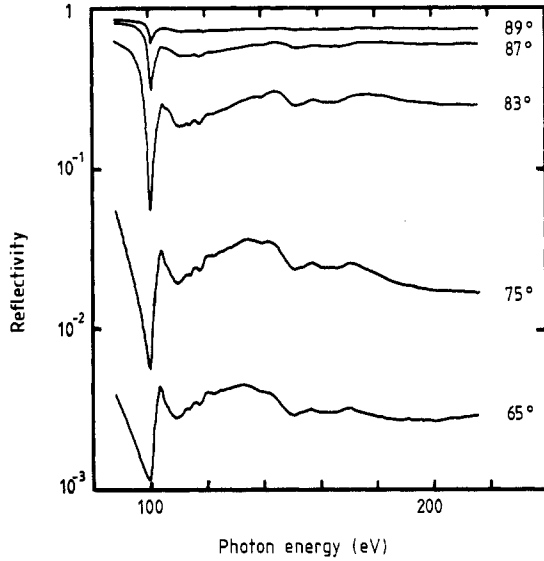


Figure 1. Reflectivity spectra of Si L-edge of SiC at incidence angles of 89°, 87°, 83°, 75° and 65°.

$$\hat{n} = 1 - \delta - i\beta \quad (1)$$

where δ and β are real numbers smaller than unity. The absorption coefficient μ is obtained by

$$\mu = \frac{4\pi\beta}{\lambda} \quad (2)$$

where λ is the wavelength of the incident photon.

The rigorous expression of reflectivity for s-polarised light at an interface between the vacuum and an absorbing medium is given by the Fresnel formula,

$$R_F = \left| \frac{(\cos \varphi - \hat{n} \cos \hat{\psi})}{(\cos \varphi + \hat{n} \cos \hat{\psi})} \right|^2 \quad (3)$$

where φ is the angle of incidence and $\hat{\psi}$ is the complex angle of refraction given by

$$\sin \hat{\psi} = \frac{\sin \varphi}{\hat{n}} \quad (4)$$

(Born and Wolf 1965). Instead of equation (3), we used the expression given by Henke (1972) equivalent to equation (3) but more suitable for the case of reflection of soft x-rays,

$$R_0 = \frac{\rho^2(\cos \varphi - \rho)^2 + \beta^2}{\rho^2(\cos \varphi + \rho)^2 + \beta^2} \quad (5)$$

where

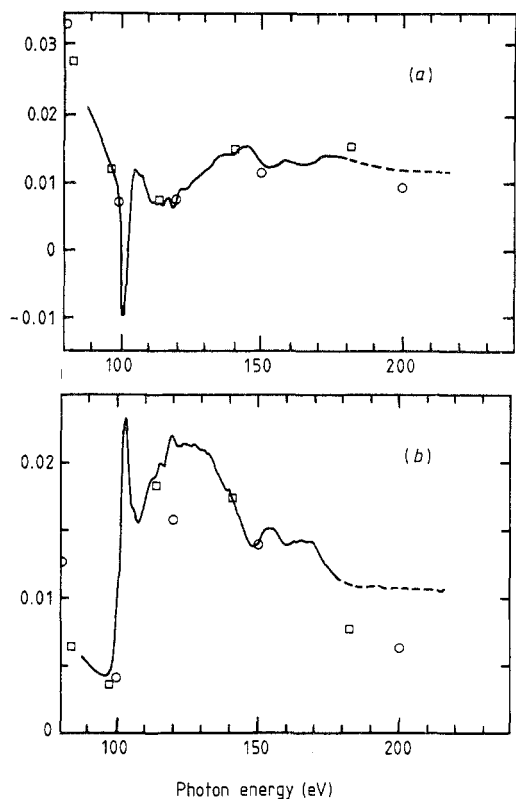


Figure 2. Spectra of optical constants deduced from the reflectivity spectra shown in figure 1. (a) shows the real part, δ , of the complex index of refraction, $n = 1 - \delta - i\beta$; (b) shows the imaginary part, β . \square , optical constants obtained by Rife and Osantowski (1981); \circ , optical constants obtained by Yanagihara *et al* (1986).

$$\rho^2 = \frac{\cos^2 \varphi}{2} - \delta + \left[\left(\frac{\cos^2 \varphi}{2} - \delta \right)^2 + \beta^2 \right]^{1/2} \quad (6)$$

The reduction of the intensity of the reflected beam due to surface roughness is approximated by the factor,

$$r = \exp \left[- \left(\frac{4\pi\sigma \cos \varphi}{\lambda} \right)^2 \right] \quad (7)$$

where σ is the RMS surface roughness of the sample (Bennett and Porteus 1961).

At each photon energy, we have fitted the angular dependence of the observed reflectivity to the calculated reflectivity

$$R_{\text{calc}} = ArR_0 \quad (8)$$

where A is the normalisation factor. The free parameters of the fit were A , δ , and β . Since inclusion of the roughness σ as a free parameter did not improve the goodness of the fit, we fixed it to 0.5 nm. In the fit, the sum of $(R_{\text{obs}} - R_{\text{calc}})^2 / R_{\text{obs}}^2$ was minimised (Yanagihara *et al* 1986). We used the data of incidence angles 89° , 87° , 83° , and 75° for the fitting.

Figure 2 shows the spectra of the best-fit optical constants. Also plotted in the figure are the discrete values given by Rife and Osantowski (1981) and by Yanagihara *et al* (1986). The present spectra are consistent with the published discrete values. Above

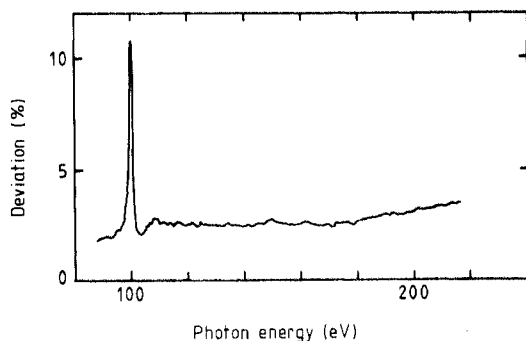


Figure 3. Root-mean-square deviation of the best-fit curve from the measured curve of angular dependence of reflectivity.

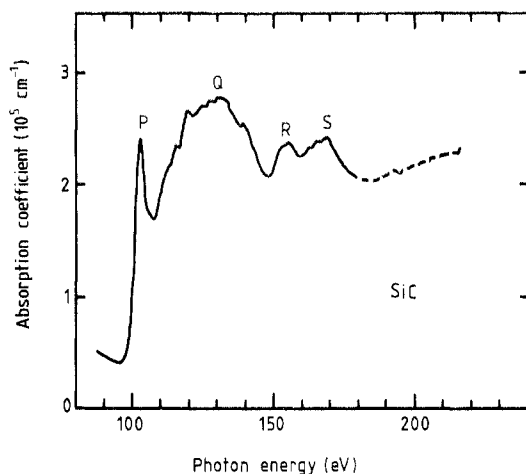


Figure 4. Absorption spectrum of SiC obtained from the spectrum of β shown in figure 2.

180 eV, the data are contaminated with stray light, resulting in the discrepancy with the published values.

In figure 3, we show the energy dependence of mean deviation of the best-fit curve from the observed curve of angular dependence of the reflectivity. We have plotted the root-mean-square of the relative deviation $(R_{\text{obs}} - R_{\text{calc}})/R_{\text{obs}}$ averaged over the angles of incidence at each energy. We see that the deviation of the observed data from the best-fit calculation is about 3% for most of the energy range. The sharp increase of the deviation at 100 ± 2 eV corresponds to the absorption edge of Si $L_{2,3}$. Here, the optical constants change so drastically that the present band pass of the monochromator (0.2–0.3 eV) is too broad to express the observed data with equation (8). The gradual increase of the deviation above 180 eV corresponds to the increase of the stray light in the incident beam. The best-fit value of the normalisation A was within 0.90 ± 0.03 for the energy range 90–220 eV.

4. Photoabsorption spectrum

In figure 4, we present the spectrum of the photoabsorption coefficient obtained from the spectrum of β using equation (2). The spectrum consists of 4 major peaks (or bands), P , Q , R , and S , which are located respectively at 103 eV, 130 eV, 155 eV, and 170 eV.

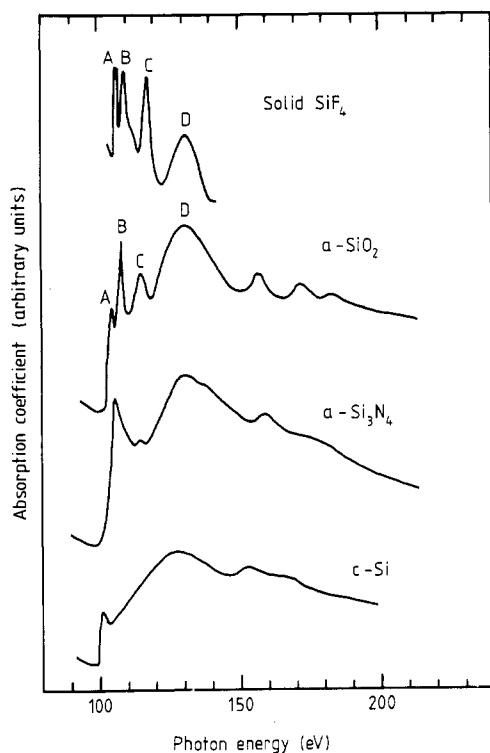


Figure 5. Si L-edge absorption spectra of solid SiF_4 (Sonntag 1978), amorphous SiO_2 (Brown *et al* 1977), amorphous Si_3N_4 (Brown *et al* 1977) and crystalline Si (Brown *et al* 1977).

The rise of the peaks *P* and *R* occur at 100 ± 1 eV and at 150 ± 1 eV, corresponding to Si $L_{2,3}$ and L_1 edges. Since the absorption edges of crystalline Si are at 100 eV and 149 eV (Bearden and Burr 1967), our data are consistent with chemical shift value 1.1 eV of Si 2p obtained from XPS measurement (Fellenberg *et al* 1982).

Our data, however, are inconsistent with the secondary electron yield spectra of SiC measured between 100 eV and 120 eV by Zhukova *et al* (1968). In their spectra, Si $L_{2,3}$ threshold is above 103 eV and two major peaks appear at 108 eV and 116 eV. The inconsistency may arise from the difference in the depth from the surface that is probed. In the secondary electron yield method, the probed depth is in the order of 10 nm from the surface, whereas in the reflectivity method, the penetration depth is in the order of several 100 nm.

Apart from the major peaks, a couple of fine features appear in our spectra which we infer to be artifacts. The small peak at 119 eV, which coincides with Al L_1 edge, is probably due to Al contained in the sample. The shoulder at 140 eV is most likely due to the second harmonics of the carbon K-edge at 284 eV.

We interpret the major spectral bands *P* and *Q* of SiC by comparing them with the spectra of other solid silicon compounds in which silicon atoms are surrounded tetrahedrally by ligands. In figure 5, we have plotted the published spectra of solid SiF_4 (Sonntag 1978), amorphous SiO_2 (Brown *et al* 1977), amorphous Si_3N_4 (Brown *et al* 1977), and crystalline Si (Brown *et al* 1977).

In the spectra of SiF_4 and SiO_2 , four peaks appear between 100 eV and 140 eV. Following the designation by Dehmer (1972), we call these peaks A, B, C, and D in the order of increasing energy. Dehmer (1972) assigned these peaks to transitions from the

Si 2p core state to states localised within the potential barriers formed by tetrahedrally arranged electronegative atoms surrounding silicon; i.e., peaks A, B, C, and D are assigned to transitions to molecular orbitals corresponding to irreducible representations of T_d symmetry: a_1 , t_2 (p-like), e, and t_2 (d-like), respectively. All these four transitions are electric-dipole-allowed under T_d symmetry. Peak D is often referred to as p-to-d transition (Sagawa *et al* 1966), occurring more generally regardless of tetrahedral coordination.

The effect of the tetrahedral field correlates with the electro-negativity of the surrounding atoms (Dehmer 1972), since the greater the electronegativity, the greater the potential barrier. Pauling's electronegativity of F, O, N, C, and Si are as follows (Allred 1961):

Element:	F	O	N	C	Si
Electronegativity:	3.98	3.44	3.04	2.55	1.90

When we compare our present spectra of SiC with the spectra of other solid silicon compounds shown in figure 5, we find that the spectral features of SiC indeed can be interpreted in terms of the above sequence of the electronegativity, fitting in between Si_3N_4 and crystalline Si.

First, the broad peak *Q* in the spectrum of SiC obviously corresponds to the t_2 (d-like) orbital, or peak D in the spectra of SiF_4 and SiO_2 . According to Dehmer (1972), the width of the t_2 (d-like) peak increases as the electronegativity of the ligands decreases. We see that this is the case in SiC as well, by comparing the width of this peak measured by the separation of the two local minima that are located just below and just above of the peak:

Material:	SiF_4	SiO_2	Si_3N_4	SiC	Si
Width of t_2 (d-like) [eV]:	20	30	35	40	44

Second, we look at the e orbital, or peak C in figure 5. This is most distinguished in SiF_4 , and becomes weaker in SiO_2 . It still appears faintly in the spectrum of Si_3N_4 at 115 eV. In our spectrum of SiC, a shoulder near 115 eV is a possible candidate for this orbital. In crystalline Si, it is completely absorbed in the broad peak of t_2 (d-like).

Third, we turn our attention to the two orbitals a_1 and t_2 (p-like). The peak of a_1 has the same tendency as the orbital e: it is most distinguished in SiF_4 , weaker in SiO_2 , and disappears or merges with the peak of orbital t_2 (p-like) in Si_3N_4 , SiC, and c-Si. As the electronegativity of the ligands decrease from N to C and Si, the width and the height of the merged peak of a_1 and t_2 (p-like) continue to decrease. That is, we attribute peak P of SiC to a combination of orbitals a_1 and t_2 (p-like).

Finally, peak S is also seen in the spectra of SiO_2 , Si_3N_4 , and c-Si. (For SiF_4 , no data are available.) This peak is most distinguished in SiC, which would not be expected if the peak were a transition to a state localised within effective potential barriers as discussed above. Thus, we interpret this peak as a part of EXAFS oscillations, as suggested by Brown *et al* (1977).

In summary, we have obtained a continuous spectrum of SiC absorption coefficient in the energy range 90–180 eV. We have qualitatively interpreted the major absorption bands as deriving from the states localised within the tetrahedral potential cage formed by electronegative carbon atoms. The spectral features of SiC are well explained as belonging to the gradual progression of spectral features of tetrahedral Si compounds as the electronegativity of ligands decrease in the order F, O, N, C and Si.

Acknowledgments

We would like to thank Dr M Yanagihara of Tohoku University and Dr A Yagishita of the Photon Factory for guiding us in the manipulation of the Grasshopper monochromator and the soft x-ray reflectometer. We are also grateful to Dr K Maeda and Dr K Usami of the Hitachi Research Laboratory for preparing the SiC ceramics.

References

- Allred A L 1961 *J. Inorg. Nucl. Chem.* **17** 215
Andre J M, Maquet A and Barchewitz R 1982 *Phys. Rev. B* **25** 5671
Bearden J A and Burr A F 1967 *Rev. Mod. Phys.* **39** 125
Bennett H E and Porteus J O 1961 *J. Opt. Soc. Am.* **51** 123
Bianconi A and Bauer R S 1980 *Surf. Sci.* **99** 76
Blau W, Gluskin E S, Lyssenko A P, Kulipanov G N and Hübner 1983 *Nucl. Instrum. Methods* **208** 605
Born M and Wolf E 1965 *Principles of Optics* (Oxford: Pergamon)
Brown F C, Bachrach R Z and Skibowski M 1977 *Phys. Rev. B* **15** 4781
Dehmer J L 1972 *J. Chem. Phys.* **56** 4496
Ershov O A, Goganov D A and Lukirskii A P 1966 *Sov. Phys.–Solid State* **7** 1903
Ershov O A and Lukirskii A P 1967 *Sov. Phys.–Solid State* **8** 1699
Fellenberg R, Streubel P and Meisel A 1982 *Phys. Status Solidi b* **112** 55
Gäwiller C and Brown F C 1970 *Phys. Rev.* **2** 1918
Hendrick R W 1957 *J. Opt. Soc. Am.* **47** 165
Henke B L 1972 *Phys. Rev. A* **6** 94
Parratt L G 1954 *Phys. Rev.* **95** 359
Rife J C and Osantowski J F 1981 *Proc. Soc. Photo-Opt. Instrum. Eng.* **315** 103
Sagawa T, Iguchi Y, Sasanuma M, Ejiri A, Fujiwara S, Yokota M, Yamaguchi S, Nakamura and Sasaki T 1966 *J. Phys. Soc. Japan* **21** 2602
Sonntag B 1978 *J. Physique* **39** C4 9
Vinogradov A S, Filatova E O and Zimkina T M 1983 *Sov. Phys.–Solid State* **25** 643
Yanagihara M, Maezawa H, Sasaki T, Suzuki Y and Iguchi Y 1984 *Performance Tests of a 2-meter Grasshopper Monochromator* KEK Report **84-17**
Yanagihara M, Niwano M, Koide T, Sato S, Miyahara T, Iguchi Y, Yamaguchi S and Sasaki T 1986 *Appl. Opt.* **25** 4586
Zhukova I I, Fomichev V A, Vinogradov A S and Zimkina T M 1968 *Sov. Phys.–Solid State* **10** 1097