Si K x-ray-absorption spectra of single-crystal Si and amorphous SiO_2

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Fine structures near the Si K-absorption edges of single-crystal Si and amorphous SiO_2 were measured for well-characterized films by a transmission method with a high-resolution double-crystal spectrometer. The spectrum of single-crystal Si was not affected by the changes of the angle between the polarization vector and the crystal axis. Both single-crystal Si and amorphous SiO_2 showed strong absorption lines near the edges. Energies of the K-absorption edges were determined to be 1840.3 and 1846.1 eV for single-crystal Si and amorphous SiO_2, respectively. The edge structure of single-crystal Si shows features related to the theoretical empty-conduction-band structure of Si. In amorphous SiO_2, the strong absorption line can be interpreted in terms of the excitonic state.

I. INTRODUCTION

The x-ray-absorption fine structure of a solid has been investigated by many investigators in order to get information about electronic states and short-range structures.[1] In the course of an investigation of electronic states and short-range atomic arrangements on the Si surface at the initial stages of oxidation, by using x-ray-absorption near-edge structure (XANES) and extended x-ray-absorption fine-structure (EXAFS) methods, we were faced with the necessity of taking Si K-absorption spectra of single-crystal Si and amorphous SiO_2.

As for single-crystal Si, Comin *et al.*[2] and Bianconi *et al.*[3] have reported the K-absorption spectrum through Auger yield measurements. For SiO_2, Senemaud *et al.*[4] measured the K-absorption spectrum of deposited SiO_2 film, but their spectrum is restricted within the narrow energy range of about 25 eV from the K edge. Hecht *et al.*[5] reported that of amorphous SiO_2 using the Auger yield measurements. Reliable data for these materials by means of the transmission method, however, have not been reported yet, to our knowledge. This might be attributed to the difficulties in making the films of single-crystal Si and amorphous SiO_2 thin enough to measure the transmitted intensity.

Theoretical calculations of density of states (DOS) for the conduction band were carried out for single-crystal Si (Refs. 6–8) and for amorphous SiO_2.[9,10] It is very interesting to compare the experimental XANES with the calculated DOS.

In this study we made the films of single-crystal Si and amorphous SiO_2 and measured the Si K-absorption spectra. The purpose of this paper is to present the data of single-crystal Si and amorphous SiO_2 obtained by the transmission method, and to discuss the XANES obtained from this work compared with the other data published.

II. EXPERIMENT

The single-crystal Si film was made from an epitaxial Si wafer which deposited a few-μm thick nondoped layer on the p-type 0.01 Ω cm (001) or (111) faced Si substrate with a thickness of 300 μm.

A chip of 1×1 cm was cut out from the wafer, the substrate side was grinded to about 30 μm thick, and the chip was sputtered with argon ions on the central portion of the substrate side in an ion etcher (manufactured by Hitachi Science Systems Co.). This method allowed us a uniform single-crystal film of a few μm-thick in the range of about 8 mm in diameter. The sample was carefully etched in a mixture of 48% HF–70% HNO_3 (1:20) to remove the damaged surface layer produced by argon sputtering. Etching time was set so that the layer of about 100 Å from the top surface was removed. The (001) and (111) faced films were prepared.

The starting material for SiO_2 was a high-purity quartz tube with an outer diameter of 5 mm. An end of this

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tube was melted with oxyhydrogen flame. By blowing dry air from the other end, a balloon of a thin SiO_2 film was made. A bit of the balloon with a thickness suitable for the transmission measurement was used as the sample. The film was annealed at 1100 °C in dry air for 5 min and was then confirmed to be amorphous by electron diffraction.

X-ray-absorption measurements were performed at the BL-8 in the Photon Factory (a synchrotron radiation facility in the National Laboratory for High Energy Physics, Japan). The spectrometer was equipped with a $(1,-1)$ position of InSb (111) crystals, which gave a resolution of approximately 0.2 eV at the Si-K edge.[11] The sample was placed in the beam monochromatized through these crystals. The x-ray absorption was measured by simultaneously recording the current from two ion chambers, one of which was mounted in front of the sample, and the other mounted behind the sample. The spectrometer, including the sample, was mounted into a vacuum chamber of 1×10^{-7} Torr.

In order to check whether the angle between the crystal plane of a single-crystal sample and the polarization vector of incident x rays affects the absorption fine structures or not, measurements on the (001) sample were carried out orienting the respective (100) and (110) plane parallel to the x-ray polarization vector $\mathbf{E}$ [denoted by $\mathbf{E}\|(100)$ and $\mathbf{E}\|(110)$, respectively]. Likewise, measurements on the (111) sample were carried out orienting the respective $(1\bar{1}0)$ plane and $(11\bar{2})$ plane parallel to the vector $\mathbf{E}$ [denoted by $\mathbf{E}\|(1\bar{1}0)$ and $\mathbf{E}\|(11\bar{2})$, respectively].

III. RESULTS

Figure 1 shows the EXAFS curves which have been subtracted from the raw experimental data of single-crystal Si (001) and amorphous SiO_2. The background was approximately determined by fitting the preedge absorption curve to Victoreen's empirical function and by extrapolating this function into the post-edge region. In this figure spectrum (a) was obtained from the (001) sample which was placed so that the (100) plane became parallel to the polarization vector of incident x rays [$\mathbf{E}\|(100)$]. The spectrum of $\mathbf{E}\|(110)$, which was obtained by rotating the sample in azimuth by 45° from the position of $\mathbf{E}\|(100)$, agreed well with that of $\mathbf{E}\|(100)$. The measurements on the (111) sample which were carried out on the positions of $\mathbf{E}\|(1\bar{1}0)$ and $\mathbf{E}\|(11\bar{2})$ yielded the same results as those of the (001) sample except that the (111) sample showed a small absorption anomaly at 136 eV above the absorption edge; this anomaly is considered to be caused by Bragg reflection at the normal incidence.[11] It can be concluded that the K-absorption spectrum of single-crystal Si is independent of the angle between the polarization vector and the crystal plane within the experimental error.

Both the Si K-absorption spectra of single-crystal Si and of amorphous SiO_2 yielded the strong absorption lines (white lines) near the edge as seen from Fig. 1. Figures 2 and 3 show the near-edge structures for the single-crystal Si and amorphous SiO_2, respectively. Although the present curves are not corrected for the spectral win-

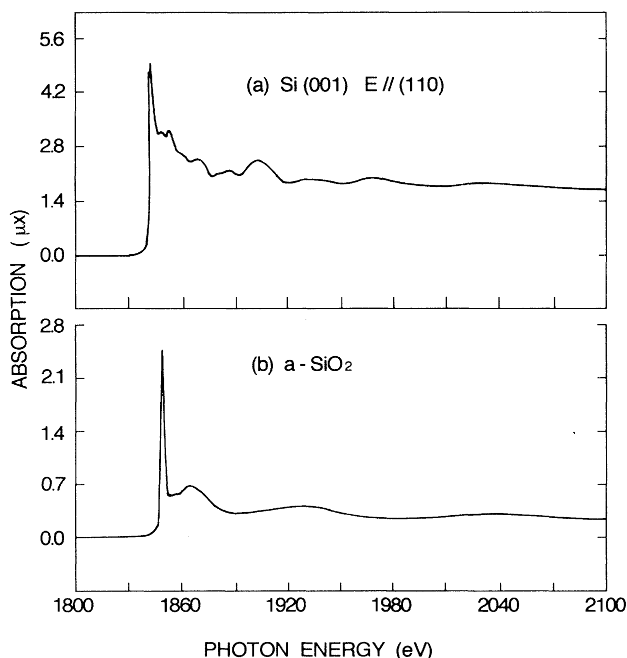

FIG. 1. K x-ray-absorption spectra of single-crystal Si (a) and amorphous SiO_2. (b) μ and x in the ordinate indicate the linear absorption coefficient and the sample thickness, respectively.

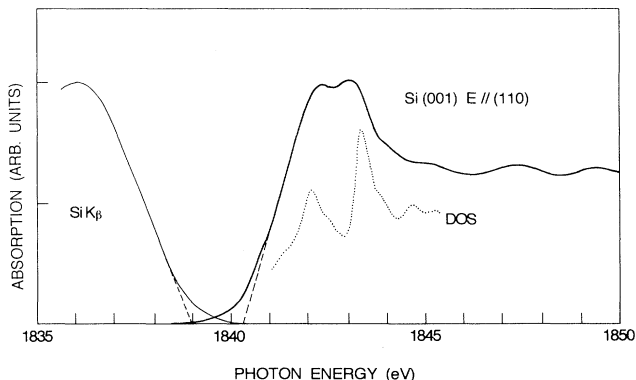

FIG. 2. Structure of the absorption edge of single-crystal Si. The $K\beta$ curve is from Ref. 14 and the DOS curve is from Ref. 8.

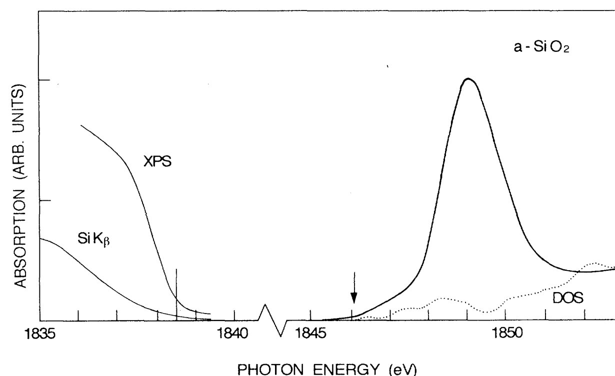

FIG. 3. Structure of the absorption edge of amorphous SiO_2. The XPS curve is from Ref. 16, the $K\beta$ curve is from Ref. 15, and the DOS curve is from Ref. 9.

dow function, the features of fine structure appear clearly because the high-resolution spectrometer was used.

IV. DISCUSSION

The K-absorption spectrum of single-crystal Si obtained from the measurements of transmission agreed well with that obtained from the Auger-electron yield measurements by Comin *et al.*[2] and Bianconi *et al.*[3] The escape depth, or the mean free path of Auger electrons with energy around the K-absorption edge, is about 20 Å. This means the absorption spectrum resulting from the thin layer to 20 Å from the top surface is almost the same as that of Si bulk.

The white line of the single-crystal Si is not a single peak but is rather complicated. The fine structure of the absorption edge obtained in the present study is in good agreement with the data obtained from the KLL Auger yield measurements by Woicik *et al.*[12] In the dipole approximation the K x-ray-absorption coefficient is proportional to the product of transition probability from the 1s state to the final state, and the partial density of unoccupied states of p symmetry at the final-state energy. Above the absorption edge, the K-absorption coefficient is approximately proportional to the partial density of unoccupied states of p symmetry since the matrix elements of transition probability are slowly varying. As data of the partial density of states of p symmetry were unavailable, we have compared our data with the density of states for the conduction band of Si calculated by Chelikowsky *et al.*[8] who used an empirical nonlocal pseudopotential, as shown in Fig. 2 with a dashed line. Even though the theoretical curve is of the total density of states, the agreement between theory and experiment is fairly good with regard to the positions of maxima and minima. Brown and Rustgi[13] have reported that the feature of the L_{111}-absorption spectrum of crystalline Si agreed well with the theoretical conduction-band density.

In the vicinity of the initial rise of single-crystal Si, a small hump was observed. This is probably attributable to excitonic states having small binding energy due to dielectric screening in the solid. The energy position of the absorption onset, which was determined by extrapolating the straight portion of the absorption edge to zero absorption, was determined to be 1840.3 ± 0.15 eV. This value agreed well with the energy of the 1s–to–conduction-band minimum, which was obtained by Woicik *et al.*[12]

The Si $K\beta$ band of Si obtained by Wiech[14] is shown in Fig. 2. The high-energy edge of the band was not clear since there is tailing on the high-energy side of it. We estimated the edge energy to be 1839.0 eV by extrapolating the straight portion of the high-energy side of Wiech's curve to the zero-intensity line. Thus the energy difference between the conduction-band edge, which was obtained from the present study, and the valence-band edge was determined as 1.3 eV, which corresponds to the energy gap of single-crystal Si.

On the other hand, the feature of the absorption edge of amorphous SiO_2 is basically different from that of single-crystal Si. It should be noted that a strong and narrow white line is found at the absorption edge. As seen from Fig. 3, there is a hump on the initial rise of absorption. The energy of absorption onset was determined to be 1846.1 ± 0.15 eV by assuming that is the energy at which the extension of the hump intersects with the base line, as shown with an arrow in Fig. 3. We consider the absorption onset as the bottom of the conduction band with p symmetry.

We will discuss the appropriateness of the energy position of the conduction-band edge obtained in this way, on referring to the valence band which has been published elsewhere. In Fig. 3, we showed the high-energy portions of the Si $K\beta$ band and the XPS valence band of a-SiO_2 obtained by Wiech *et al.*[15] and Fischer *et al.*,[16] respectively. Superimposing these two spectra so that the best fit of peaks was obtained, the valence-band edge which has been marked by Fisher was determined to be 1838.5 eV, as shown with a vertical line in Fig. 3. The energy difference between the absorption onset and the valence-band edge is 7.6 eV, and this corresponds to the energy gap E_g of a-SiO_2. Gupta,[17] who calculated the electronic structure of SiO_2, has reported that the energy gaps were 8.4 eV for α-SiO_2 and 7.2 eV for a-SiO_2. Thus, it is concluded that the energy position of the conduction-band edge obtained in this study is acceptable.

The peak of the white line is at 1849.05 eV. In Fig. 3, the DOS for the conduction band of a-SiO_2 calculated by Ching[18] is shown with a dashed line. Gupta[17] has also calculated the DOS for valence and conduction bands. However, the band model is unable to account for the white line which is located at 10.5 eV from the valence-band edge. Furthermore, the white line is approximately Gaussian in shape.

On the basis of the above considerations, it is concluded that the white line is a p-symmetry excitonic state which results from the formation of the core hole. The reason why the excitonic level is located on the high-energy side of the absorption onset or the conduction-band edge is probably due to localization of the excitonic state in a-SiO_2.

In amorphous SiO_2, the absorption spectrum above the white line shows no remarkable structure and connects smoothly with the EXAFS curve on the higher-energy side.

To summarize our results, the Si K-absorption fine structure of single-crystal Si and amorphous SiO_2 were obtained by a transmission method with a high-resolution double-crystal spectrometer. The edge structure of single-crystal Si can be interpreted in terms of the density of states of the empty conduction band. On the other side, the strong white line at the Si K edge of amorphous SiO_2 may be explained as the excitonic state with p symmetry.

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