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# Resonant Auger-decay process in solid $SiO_2$ at the Si 1*s* edge

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The Auger-decay processes in solid $SiO_2$ after resonant and off-resonant excitations around the Si 1*s* edge have been investigated using synchrotron radiation. It was found that the Si $KL_{2,3}L_{2,3}$ Auger line splits into two peaks when the photon energy is close to that of the Si $1s\rightarrow3p$ resonance. These two peaks are ascribed to the normal and resonant Auger-decay processes. It was also observed that the resonant Auger peak is shifted to higher energy in proportion to the photon energy. The resonant Auger peak is attributed to the spectator Auger decay following the Si $1s\rightarrow3p$ excitation. The energy shift of the resonant Auger electron is interpreted in terms of the energy transfer from the excited electron in the conduction band to the Auger electron in the course of the Auger-decay process.

The resonant excitation from core to unoccupied valence orbitals is followed by an Auger-decay process, which is different from a normal Auger-decay process after core ionization. The most remarkable difference is observed in the energy of the Auger electrons. This is interpreted in terms of the difference in the final electronic configuration between resonant excitation and core ionization.[1] Namely, resonant Auger decay (normally called autoionization) results in final electronic states of +1 positive ions while a normal Auger decay ends in +2 positive ions, which leads to differences in the screening effects (relaxation energies) on the Auger-electron emission.

Auger-decay processes after resonant excitation have been extensively investigated for isolated atoms and molecules in the gas phase.[1-8] When Auger electrons are emitted from a solid, it is assumed that the resonant Auger-decay process is different from that in the gas phase, because the screening effect in a solid is considerably larger. Resonant Auger-decay processes other than in the gas phase have been recently examined for transition metals,[9,10] metallic lanthanides,[11-14] ionic solids,[15] and some adsorbed layers.[16-18] In the Auger transitions measured in these works, one or two valence electrons participate in the Auger process, leading to complex Auger spectral patterns.

In this paper, we report the *KLL* resonant Auger decay process in solid $SiO_2$ at the Si 1*s* edge. All three orbitals involved in this Auger transition are in the core region, and a sharp Auger peak is expected. As a result, we found a clear energy split of the Si$KL_{2,3}L_{2,3}$ Auger peak when the incident photon energy is close to that of the Si $1s\rightarrow3p$ resonance. Also we observed that the energy of the resonant Auger electrons shifts with the photon energy. These phenomena are discussed in relation to the electronic structures of unoccupied orbitals in the valence-band region and the relaxation processes of the core holes.

The experiments were performed at the BL-27A station of the Photon Factory in the National Laboratory for High-Energy Physics (KEK-PF), using two single crystals of InSb(111) as a monochromator.

The $SiO_2$ sample was prepared by thermal oxidation of a Si(100) single crystal at 1000 °C for 12 h in atmosphere. The sample was annealed in an ultrahigh vacuum until surface contaminants were completely removed.

The x-ray-absorption near-edge structure (XANES) was measured by recording the intensity of secondary electrons at a fixed energy (partial electron yield mode) as a function of the photon energy. The kinetic energy ($E_k$) of the secondary electrons was adjusted to be 1000 eV, which was far below the energy of the Si $KL_{2,3}L_{2,3}$ Auger electron, because the $E_k$ of the Si $KL_{2,3}L_{2,3}$ Auger peak changed around the energy of resonance excitation. The partial electron yield (PEY) was normalized by the photon intensity which was monitored by a copper mesh located in front of the sample.

The Auger electron spectra were measured in an ultrahigh vacuum chamber (base pressure: $2\times10^{-8}$ Pa) using a hemispherical electron energy analyzer. The polar angle of the electric vector of the incident x rays was 45°, and the takeoff direction of Auger electrons was surface normal.

Figure 1 shows the PEY from $SiO_2$ around the Si 1*s* edge as a function of photon energy (hereafter we call this curve the XANES spectrum). The spectral shape is in good agreement with that previously reported.[19,20] Based on the dipole-selection rules, and its highly *p*-like charac-

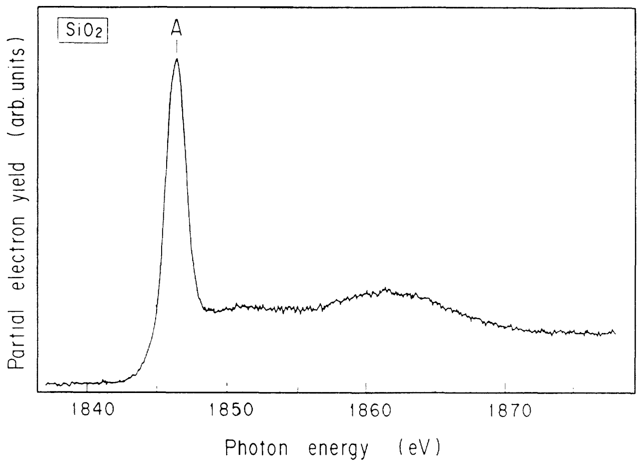

FIG. 1. Partial electron yield as a function of photon energy (XANES spectrum) for $SiO_2$.

ter, the sharp peak at 1846.6 eV (peak A) is attributed to the resonance from Si 1*s* to Si 3*p*–dominant unoccupied orbital. If we adopt the one-electron transition approximation, peak A represents the electronic structure of the main components of the conduction band.

The Si $KL_{2,3}L_{2,3}$ Auger decay spectra taken at various photon energies around the Si 1*s* absorption edge are presented in Fig. 2. The 2023.3-eV spectrum corresponds to the normal Auger decay after Si 1*s* ionization.

When the photon energy is between 1845.7 and 1850.2 eV, two peaks are observed. The lower-energy peak (peak A) apparently originates from the normal Auger decay after core ionization. Regarding the higher-energy peak (peak B), the following two features are noticed.

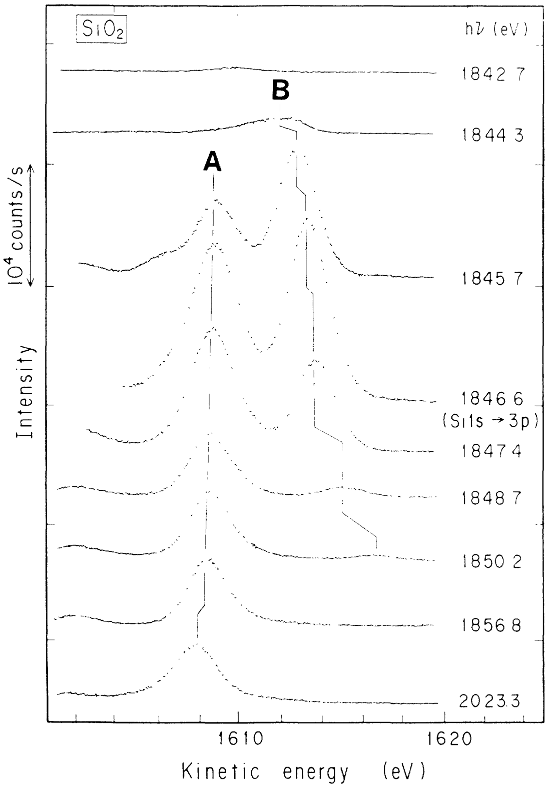

FIG. 2. Auger decay spectra of $SiO_2$ around Si 1*s* edge excited by various photon energies. The photon energy is indicated in each spectrum.

First, the energy of peak B becomes higher with the increase in photon energy. Second, the intensity of peak B is maximum at 1846.6 eV (Si $1s \rightarrow 3p$ resonance), but it rapidly decreases and almost disappears at 1850.2 eV. The latter feature resembles the XANES spectrum (Fig. 1), thus it is deduced that peak B originates from the Auger-decay process after Si $1s \rightarrow 3p$ resonant excitation. The energies of both peaks are plotted in Fig. 3 as a function of the photon energy.

Now we will concentrate on the origin of the gradual energy gain of the resonant Auger peak. For the normal Auger process, the kinetic energy of the Si $KL_{2,3}L_{2,3}$ Auger electron ($E_{KLL}$) is given as follows:[21]

$$E_{KLL}=E_b(1s)-E_b(2p)-E_b(2p)-U_{\text{eff}}(2p,2p)+R(2p,2p)\ , \qquad (1)$$

where $E_b$ is the binding energy of the indicated orbital, $U_{\text{eff}}$ is the energy of two-hole interaction, and $R$ is the relaxation energy. Note that $E_b$ is measured from the Fermi level.

It has been established that the Auger decay following the resonant excitation from the core to the valence unoccupied orbital is classified into two processes.[22] First is the participant Auger decay, in which the excited electron itself decays into the core hole and the other electron is emitted as an Auger electron. Second is the spectator Auger decay, in which the excited electron remains in the excited state as a spectator, another electron decays into the core hole, and finally a second electron is emitted as an Auger electron. In the present system, if the participant Auger decay happens, the energy of the Auger electron is displayed as

$$E_{KLL}=E_b(1s)+E_b(\text{un})+\Delta E_b(\text{un})-E_b(2p)+R(2p)\ , \qquad (2)$$

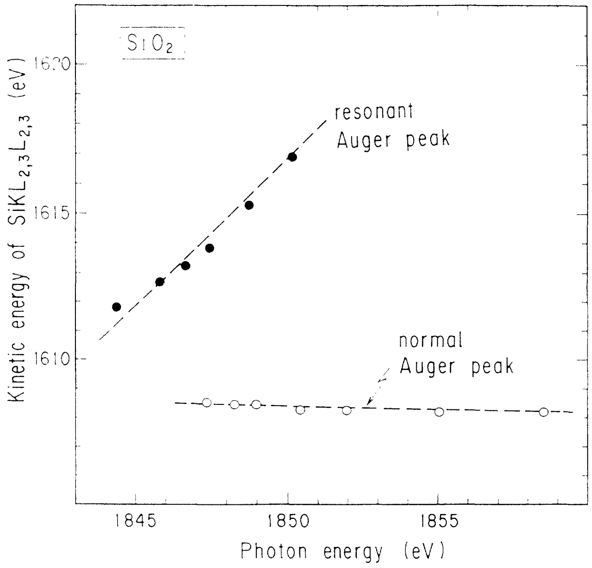

FIG. 3. Kinetic energies of the Si $KL_{2,3}L_{2,3}$ Auger peak as a function of photon energy.

where $E_b(\text{un})$ is the energy of the bottom of the conduction band. The $E_b(\text{un})+\Delta E_b(\text{un})$ is the energy level of the unoccupied orbital into which the Si 1*s* electron is excited. The final electronic state of this process is nearly identical to that of the Si 2*p* photoemission process. Actually, we observed enhancement of the intensity of the Si 2*p* photoelectron peak at the photon energy of the Si $1s \rightarrow 3p$ resonance excitation. But the energy of the Si 2*p* photoelectron is far above that of the Si $KL_{2,3}L_{2,3}$ Auger peak, thus this process cannot explain the origin of peak B. On the other hand, if spectator Auger decay takes place, the energy of the Auger electron is expressed as

$$E_{KLL}=E_b(1s)+E_b(\text{un})+\Delta E_b(\text{un})-E_b(2p)-E_b(2p)-U_{\text{eff}}(2p,2p)+R'(2p,2p) . \quad (3)$$

In this case, the relaxation energy is slightly reduced compared to the normal Auger process due to the presence of the spectator electron. Thus the energy difference ($\Delta E_{KLL}$) between normal and resonant Auger electrons is simply estimated from Eqs. (1) and (3) as

$$\Delta E_{KLL}=E_b(\text{un})+\Delta E_b(\text{un})+R'(2p,2p)-R(2p,2p) . \quad (4)$$

Considering that the amount of relaxation energy is at most a few eV (the reduction of the relaxation energy due to the presence of the spectator electron is small), it is considered that the $\Delta E_{KLL}$ is mainly caused by the $E_b(\text{un})+\Delta E_b(\text{un})$ value. The gradual energy gain of the resonant Auger peak is interpreted as the increase in the $\Delta E_b(\text{un})$ value with the photon energy. The width of the unoccupied orbitals in the solid is generally larger than that in the gas phase. Actually, the width of the conduction band of $SiO_2$ amounts to a few eV, based on band calculations[23] and optical reflectivity measurements.[24] We consider that an electron excited from the Si 1*s* orbital into the $E_b(\text{un})+\Delta E_b(\text{un})$ level decays into the $E_b(\text{un})$ level in the course of the Auger transition, and the excess energy $[\Delta E_b(\text{un})]$ is transferred to the emitting Auger electron. This means that the Auger decay cannot be treated as an independent process.

We have observed similar energy shifts of the Si *KLL* resonant Auger peaks in $Si_3N_4$,[25] but not in Si or SiC.[26] It is deduced that excited electrons are highly localized in $SiO_2$ and $Si_3N_4$ due to the wide band gap. In contrast, in the case of Si and SiC, the core holes are immediately screened by the conduction electrons due to their high mobility, and the charge is delocalized before the core-hole decay happens. This is the reason why the energy split of the Auger peak is not observed in these materials. Further experiments are now in progress to clarify these points.

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