

Resonant Photoemission from Si

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Anomalous evolution of the silicon valence-band photoemission spectra is observed in the photon energy region from the $2p$ core-excitation threshold to about 3 eV above the threshold. The $3p$ -like topmost emission band shows a Fano-type resonance, and stronger intensity enhancement is observed in the deeper binding-energy region around 7.6 eV. The present results show the existence of a decaying localized core exciton at the $2p$ core-excitation threshold.

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Correlation effects in solids under high-energy excitation by photons have been attracting interest during the past few years. In materials with a narrow valence band, where strong electron correlation is expected, the decay process of the inner-shell excitations greatly influences the photoionization cross sections of the valence-band states. These phenomena have been, to some extent, successfully interpreted with an atomic picture.¹

In this Letter, we report the first observation of anomalous photoemission enhancement in the vicinity of the $2p$ -core excitation threshold in Si, a typical wide-valence-band material. The observation shows the existence of a localized decaying core exciton² and clarifies the mechanism of the absorption edge anomaly at the $2p$ -core threshold.

Measurements were performed in the photon energy region from 30 to 130 eV with the photoemission facility at BL-2 of the SOR-Ring in the Synchrotron Radiation Laboratory of the Institute for Solid State Physics at the University of Tokyo. Most of the measurements were carried out with a monochromator resolution of 0.7 eV at around $h\nu = 100$ eV, with an analyzer resolution of 0.5 eV. In order to reduce the uncertainty in the photon energy caused by backlash of the grating movement, the photon energy was varied in one direction from low to high energy during each series of measurements. Photon energy reproducibility was within 0.1 eV. The pressure in the analyzer chamber was lower than 5×10^{-10} Torr during measurements.

Figure 1 shows the photoemission spectra of a Si(111) cleaved surface at various energies in the photon energy region of interest. Spectra below

the $2p$ -core excitation threshold at 99.7 eV show three band structures at binding energies of 3, 7, and 11 eV. These are assigned to come from the $3p$ -, $3p3s$ -, and $3s$ -like bands in the Si valence-band density of states.³ When the photon energy is increased above the $2p$ threshold, the spectra show anomalous evolution: First, the topmost band shows a slight intensity enhancement with

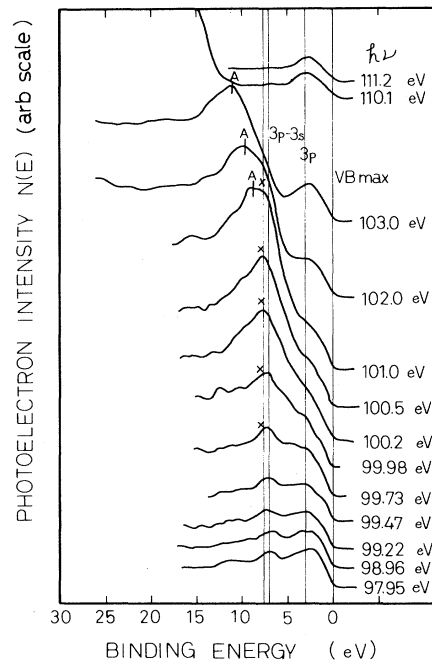


FIG. 1. Photoemission spectra of a Si(111) cleaved surface at various photon energies. Vertical solid lines show the position of the valence-band maximum, $3p$ -band peak, $3p3s$ -band peak, and the peak position of X, which arises in the vicinity of the $2p$ -core excitation threshold.

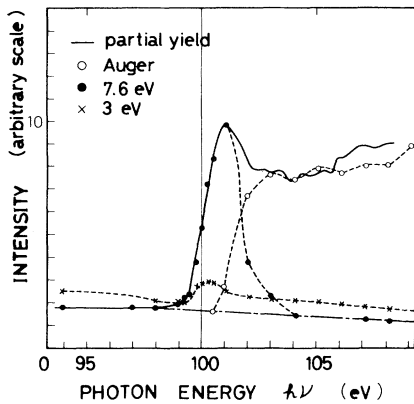


FIG. 2. Photon energy dependence of the $3p$ -band (crosses), X (filled circles), and the Auger (open circles) peak intensities. The solid curve shows a partial yield spectrum measured with a final-state energy of 4 eV.

increasing photon energy, and becomes structureless. Secondly, a new broad structure, denoted by X , arises. This structure peaks at a binding energy of 7.6 eV, about 0.6 eV larger than the 7-eV $3p3s$ -band peak. The X structure intensity increases with photon energy, while keeping the same absolute binding-energy position. At $h\nu=101.0$ eV, another structure denoted by A appears at slightly higher binding energy than X . The X feature disappears in the spectra at higher photon energies, while A shifts linearly towards the higher binding-energy region with increased photon energy. When the photon energy exceeds 110 eV, the A feature, which is identified as an $L_{2,3}VV$ Auger structure, disappears from the valence-band region, and the X feature fades out. The $3p3s$ band again peaks at a binding energy of 7 eV in these high-photon-energy spectra.

The peak heights in the spectra at A and X and the $3p$ structures are plotted as functions of photon energy in Fig. 2. The A and X features are separated by assuming that their line shapes do not change in the region where both structures are superposed. The solid curve in the same figure shows the yield of photoelectrons with a kinetic energy of 4 eV as a function of photon energy. As is well known,⁴ the spectral behavior of this type of partial yield reproduces that of an optical absorption coefficient. The X feature arises just at the $2p$ absorption edge, and falls at about 2–3 eV above the edge. The onset of the Auger feature A coincides with the fall of X . The sum of the intensities of A and X is proportional to the partial yield spectrum, within experimental error. This

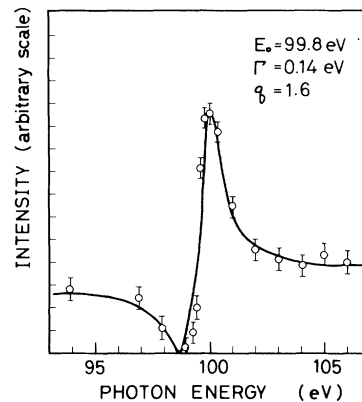


FIG. 3. Fano line-shape fitting for $3p$ -band emission intensity.

suggests that the anomalous enhancement of the absorption coefficient in the vicinity of the $2p$ -core absorption edge is mainly caused by the same mechanism that causes resonance enhancement of X .

The topmost band intensity shows a dip just below the edge and an enhancement in the narrow region above the edge. After subtraction of the monotonic background, the $3p$ -band intensity was replotted as a function of photon energy in Fig. 3. The asymmetric distribution of the data points strongly suggests the occurrence of a Fano effect,⁵ i.e., interference between continuous and discrete excitations.

Figure 4 shows diagrams of possible photoelectron excitation processes in the $2p$ -core excitation region. ϵ , v , c , and $2p$ represent an emitted electron, a valence hole, an electron bound to a $2p$ -core hole, and the $2p$ -core hole, respectively. The dashed line indicates a Coulomb interaction. Figures 4(a), 4(b), and 4(c) show processes that leave a single valence hole in the final states.

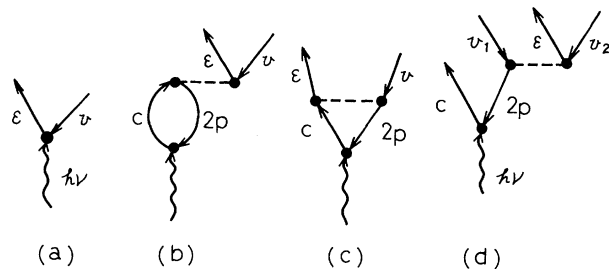


FIG. 4. Diagrams of the $2p$ -core exciton decay processes. (a) Direct emission, (b) emission due to direct recombination of core exciton, (c) counterpart of (b), and (d) Auger-type process.

Figure 4(a) corresponds to direct emission, which has a continuous excitation spectrum. Figure 4(b) is a so-called direct recombination process. One photon is annihilated and a conduction-electron- $2p$ -core-hole pair is created. This electron-hole pair recombines with transfer of energy to a valence excitation through the Coulomb interaction. Consequently a free electron and a valence hole are created. Figure 4(c) shows the counterpart of 4(b). A valence electron recombines with the core hole reexciting the photoexcited electron into a free-electron state. Provided that the photoelectron in the conduction band is bound to the core hole, Figs. 4(b) and 4(c) are discrete excitations. Fano interference takes place between the continuous excitation [Fig. 4(a)] and discrete excitations [Figs. 4(b) and 4(c)]. The Fano line-shape function⁵ is fitted to the experimental data as shown by the solid line in Fig. 3.

In this line-shape fitting, we superposed $2p_{3/2}$ and $2p_{1/2}$ components with the intensity ratio of 2 to 1 and spin-orbit splitting of 0.6 eV. We also convoluted the monochromator resolution of 0.7 eV. The best fit was obtained with resonance energy $E_0 = 99.8 \pm 0.2$ eV, exciton width $\Gamma = 0.14 \pm 0.02$ eV, and $q = 1.6 \pm 0.1$. The value obtained here is astonishingly large as it is comparable to the best binding-energy value of 0.3 eV recently reported by Margaritondo *et al.*⁶ However, this large value is not unreasonable, since it is still smaller than the broadening of 280 meV for the L_3 absorption edge of the bulk Si determined by Eberhardt *et al.*⁷

Margaritondo *et al.*⁶ have carried out careful measurement of photoemission and partial yield spectra to obtain core exciton binding energies. They have obtained an excitation energy of 99.96 eV from the $2p_{3/2}$ core level to the bottom of the conduction band. They also determined the L_3 edge of the partial yield spectrum to be 99.68 eV. From the difference between these values they have deduced a $2p$ -core exciton binding energy of $0.3^{+0.15}_0$ eV. Subtracting the resonance energy of 99.8 ± 0.2 eV, obtained from the Fano line-shape fit, from the $2p$ -core excitation energy of 99.96 eV, we obtained an exciton binding energy of 0.16 ± 0.2 eV. The discrepancy between this value and that of Margaritondo *et al.* is smaller than the experimental uncertainty.

Hjalmarson, Büttner, and Dow⁸ showed that the central-cell potential experienced by the exciton's electron can be strong enough to produce a small Frenkel exciton. They found that the Si $2p$ -core

exciton is on the verge of transition from the Wannier to the Frenkel type. Because of the large uncertainty, the size of the experimentally determined binding energy seems not to be conclusive evidence for identifying the type of the core exciton. However, the occurrence of the Fano resonance suggests that the Si $2p$ -core exciton has a strongly localized nature, which can reasonably be expected of a Frenkel-type exciton.

The observed variations in the binding-energy positions and the intensities of the A and X features suggest that these features are due to competing processes with similar origins. We propose that an Auger-type two-final-hole decay of the core exciton is the origin of X . A diagram of this process is shown in Fig. 4(d). A photon is annihilated and an electron-core-hole pair which forms a bound state of finite lifetime is created. The core hole recombines with a valence electron and transfers energy to another valence excitation. When the lifetime of this electron-core-hole bound state is comparable to, or longer than, the inverse of probability of this process, energy is conserved between the initial (ground state plus one photon) and final (one emitted electron plus one conduction electron plus two valence holes) states. Thus the kinetic energy of the emitted electron is estimated to be $E_k = h\nu + E_c - E_{v1} - E_{v2} - \phi$, with E_c , E_{v1} , E_{v2} , and ϕ the energies of the conduction-band edge, the two valence holes measured from the Fermi level, and the analyzer work function, respectively. If we assume that the $3p$ valence-band states dominantly contribute to this process, as is the case in the normal Auger process, this predicts the position of the X peak to be at around 7 eV binding energy. This value is very close to the observed X peak position.

The discrete state of the core exciton decays into a two-hole continuum through the $L_{2,3}VV$ Auger-type process as discussed above. Enhancement of the X -feature intensity near the $2p$ excitation threshold is interpreted as resonance due to this decay. The mechanism is analogous to that proposed by Davis and Feldkamp⁹ to explain resonance in Cu. In the case of Cu, resonance takes place as a result of decay of $3p^5 3d^{10}(4s-4p)^{n+1}$ to $3p^6 3d^8(4s-4p)^n$ through an $M_{2,3}M_{4,5}M_{4,5}$ super-Coster-Kronig transition. Generally, strong resonances observed in such materials as $3d$ transition metals and $4f$ rare earths are thought to be due to a strong configuration interaction of the super-Coster-Kronig type. In the case of the Si resonance, however, the configur-

ation interaction involved is not a Coster-Kronig type. In spite of this fact, the two-final-hole resonance in Si is as prominent as that in Cu. This may be due to the large oscillator strength of the $2p$ -core excitation due to the strongly localized nature of the core excitation. Another difference between the Cu and Si resonances is that in the case of Si, the Coulomb interaction of the two final valence holes is negligible. Very recently Strinati has proposed a new theory of core excitons. He predicted narrowing of the core exciton linewidth as compared to the photoemission spectral linewidth of the $2p$ core, which is measured well above the $2p$ -core excitation threshold. This is due to the presence of an electron orbiting about the hole which hinders the Auger filling of the hole by the remaining electrons. The core exciton linewidth of 0.13–0.15 eV estimated in the present study is apparently smaller than the $2p$ -core level spectral linewidth of 0.2 to 0.22 eV.^{7,10} In spite of the inadequate resolution of the experimental apparatus, the difference of 50–90 meV between these two widths is surprisingly close to Strinati's estimation of 58 meV for a core exciton binding energy of 0.186 eV.

In conclusion, an anomalous intensity enhancement, with a strong line-shape distortion, of the valence-band photoemission spectra was observed in the vicinity of the $2p$ -core excitation threshold of Si. The observed phenomena are evidence of the existence of a strongly localized core exciton which decays into single-hole and two-hole final

states. The latter, Auger-type decay gives the dominant contribution to the decay of the core exciton.

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