PHYSICAL REVIEW B VOLUME 48, NUMBER 3 15 JULY 1993-I

Band-structure effects in the excitation-energy dependence of Si $L_{2,3}$ x-ray-emission spectra

K. E. Miyano and D. L. Ederer
Tulane University, New Orleans, Louisiana 70118

T. A. Callcott, W. L. O'Brien, J. J. Jia, L. Zhou, and Q.-Y. Dong
University of Tennessee, Knoxville, Tennessee 37996

Y. Ma
University of Washington, Seattle, Washington 98195

J. C. Woicik and D. R. Mueller
National Institute of Standards and Technology, Gaithersburg, Maryland 20899

(Received 26 January 1993; revised manuscript received 1 March 1993)

Si $L_{2,3}$ x-ray emission stimulated with narrow-band synchrotron radiation has been studied as a function of excitation energy. In strong contrast to crystalline silicon, amorphous silicon yields emission spectra that are independent of the excitation energy, thereby demonstrating that long-range order plays a necessary role in the excitation-energy dependence of the crystalline emission.

Investigations of soft-x-ray emission (SXE) as a function of excitation energy, $h\nu_e$, have been actively pursued ever since high-efficiency fluorescence spectrometers were combined with excitation by monochromatized synchrotron radiation. Strong variations in emission spectra have been reported as a function of $h\nu_e$, particularly in the neighborhood of the absorption threshold.[1-4] In some cases the $h\nu_e$-dependent changes involve the appearance of satellites related to additional holes in the valence states.[1,3] These additional holes must be localized to influence the emission process and have presently been reported in transition metals with their valence *d* bands[3] as well as in atomic and molecular systems.[1] Strong $h\nu_e$ dependences have also been observed in emission from light *s-p* bonded materials with *delocalized* valence states.[2,4] This was first observed in crystalline silicon, and it was tentatively suggested that electrons excited to states near the bottom of the conduction band remain sufficiently localized to influence the emission process as spectators.[2] Ma *et al.*[4] recently observed a strong $h\nu_e$ dependence in diamond *K* emission; however, they explained this dependence in terms of an alternative inelastic-scattering description of the absorption and emission processes. Their treatment is unique in that it emphasizes a material's long-range order rather than a localized phenomenon to account for the excitation dependence of emission.

This inelastic-scattering treatment leads to a simple band-structure-based interpretation of $h\nu_e$-dependent emission data when phonon coupling, which may occur between the absorption and emission processes,[5-7] can be neglected. Then, for the negligible photon momenta in the soft-x-ray regime, the following momentum-conservation rule governs the combined absorption and emission processes: the crystal momentum $\mathbf{k}$ of the conduction-band state to which the initial excitation occurs is the same as the $\mathbf{k}$ of the valence state involved in the subsequent emission process, to within a reciprocal-lattice vector. From a related local viewpoint, this treatment assumes that the recoil following electron emission is not taken up by the surrounding lattice before the filling of the hole occurs: this assumption should be valid when the core-hole lifetime is shorter than the phonon relaxation times.[5-7] Ma *et al.* proposed this $\mathbf{k}$-conservation interpretation after they observed that features of the diamond SXE spectra corresponding to certain points in the Brillouin zone are intensified upon selective excitation of electrons to unoccupied states at these same zone points.[4] This interpretation, for which the phonon coupling has been neglected, would have to be modified for the metallic[7] and ionic insulator[8] systems in which such coupling effects have been observed. Phonon coupling is weak in nonpolar, nonmetallic materials such as diamond and silicon.[9] Silicon then represents another system in which the $\mathbf{k}$-conservation framework can be considered.

This paper describes a general test of the role of band structure in the silicon emission variations: measurement of the $h\nu_e$ dependence in *amorphous* silicon (*a*-Si) emission. It is found that emission from an amorphous sample is independent of $h\nu_e$, in contrast to the strong $h\nu_e$ dependence of crystalline silicon (*c*-Si) emission, as measured in this study as well as in Ref. 2. This contrast is a direct confirmation of the role of band structure in the *c*-Si emission variations. Detailed implications of the difference between the amorphous and crystalline data will be discussed below.

SXE spectra were collected using a grazing incidence Rowland circle spectrometer[10] with the entrance slit set to yield an emitted photon energy resolution of 0.25 eV. The spectra were excited using monochromatized synchrotron radiation from Beamline U10A of the National Synchrotron Light Source, where the previous *c*-Si study of Ref. 2 was also conducted. Since the preceding study the monochromator has been modified from a transmission grating to a variable line space grating design,[11] yielding a tenfold improvement in resolution as well as suppressing the white light background. The resolution of the exciting photon energy at 100 eV was 0.37 eV in the present experiment. This improved resolution is useful for the *selective* excitation of electrons to points in the Brillouin zone. All excitation photon energies $h\nu_e$ as well as the monochromator resolution were directly established at the time of each emission measurement by recording the elastically scattered photon peak with the spectrometer. Thus all photon energies quoted in this paper, both for excitation and emission, correspond to the calibration of this same spectrometer. In the measurement of *c*-Si, a piece of polished (100)-oriented wafer was used, while the *a*-Si consisted of a 1000-Å film sputtered onto a 1500-Å tungsten interlayer, which in turn was deposited on a polished Si substrate. Both samples were etched in HF and then loaded into vacuum within a few minutes.

Figure 1 demonstrates the contrast in $h\nu_e$ dependence between the amorphous and crystalline samples. The *a*-Si emission spectra are nearly indistinguishable for all values of $h\nu_e$ studied, as well as for excitation with a 3-keV electron beam. This point is emphasized in Fig. 2(a), in which four of the *a*-Si emission spectra are superimposed. The absence of $h\nu_e$ dependence in the amorphous data shows that band structure necessarily plays a role in the strong variations of the single-crystal emission. In amorphous material **k** is no longer a meaningful quantum number, to be conserved in transitions. Hence this absence of $h\nu_e$ dependence in the *a*-Si is anticipated in the **k**-conservation description outlined above. On the other hand, the amorphous data rule out the localized-excitation explanation for the *c*-Si emission variation.[2] If excitation to localized states near the bottom of the conduction band is the reason for these variations, analogous effects are expected to persist in the amorphous material. The 2*p* core exciton in both *c*-Si and *a*-Si has been a controversial topic, in terms of its existence as well as the specific binding energy. However, recent experimental studies have suggested that the exciton exists in *both* Si forms and that the binding energy is greater in the amorphous material.[12,13]

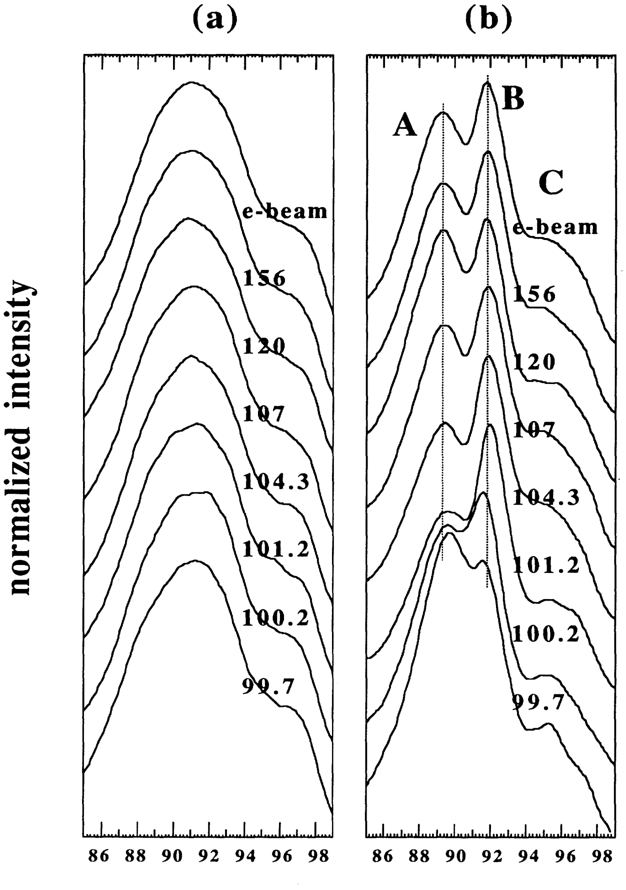

FIG. 1. Si $L_{2,3}$ soft-x-ray emission spectra are plotted for (a) amorphous and (b) crystalline silicon samples with $h\nu_e$ (in eV) as a parameter. The spectra labeled *e*-beam were stimulated with a 3-keV electron beam. The *a*-Si data are normalized to equal area, while the *c*-Si data are normalized to the intensity of the central peak, *B*. The data sets are offset along the ordinate for clarity.

In contrast to the *a*-Si case, emission from *c*-Si exhibits a strong variation with excitation energy. The $h\nu_e$ dependence of the *c*-Si emission shown in Figs. 1(b) and 2(b) is consistent with the major findings of Ref. 2 if the narrower excitation band of the present measurements is taken into account. First, the spectra always consist of three major features that are labeled *A*, *B*, and *C* in Fig.

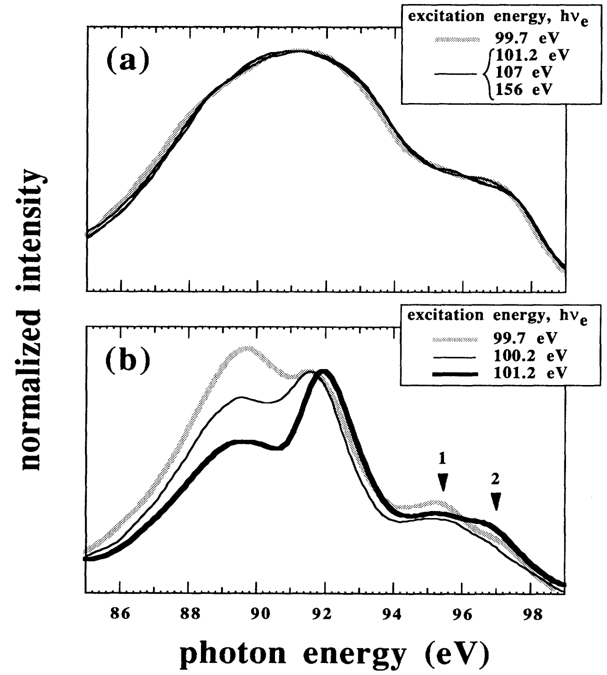

FIG. 2. The emission spectra for (a) amorphous and (b) crystalline silicon taken at selected values of $h\nu_e$ are superimposed on one another for the purposes of comparison. The *a*-Si data are normalized to equal area, while the *c*-Si data are normalized to the intensity of the central peak, *B*.

1(b). This three-peaked line shape agrees qualitatively with the Si $L_{2,3}$ emission spectrum calculated by Klíma,[14] who performed his calculation with no restrictions on $\mathbf{k}$ for emission transitions. Second, relative intensity variations between these features occur for values of $h\nu_e$ up to 30 eV above threshold; beyond this excitation level the spectra approach a line shape in agreement with the electron-stimulated data.

Close to the $L_{2,3}$ absorption threshold, where the emission line shape changes most rapidly as a function of $h\nu_e$, the difference in excitation bandwidth between the present measurement and that of Ref. 2 comes into play. For 99.7-eV excitation, as shown in Fig. 2(b), the intensity of peak A exceeds that of peak B, while peak C is also enhanced with respect to B due to strong emission at 95.5 eV (arrow 1). Peak A is not only intensified at $h\nu_e=99.7$ eV but is also broadened on its high-energy edge so that its centroid is shifted to higher energy by 0.4 eV. This shift is made clear by reference to the dotted lines drawn through the high-$h\nu_e$ positions of peaks A and B in Fig. 1(b).

One complication in analyzing the $h\nu_e$ dependence of Si $L_{2,3}$ emission is the spin-orbit splitting of the $2p$ core level. Transitions from the $2p_{3/2}$ level have an onset at around $h\nu_e=99.6$ eV, and at this $h\nu_e$ only emission due to the filling of this $2p_{3/2}$ level is present in the SXE spectrum. Transitions from the $2p_{1/2}$ level begin at 0.6 eV higher $h\nu_e$, where 0.6 eV is the Si $2p$ spin-orbit splitting. Thus the corresponding $2p_{1/2}$ emission component, lying at 0.6 eV higher *emitted* energy, has its onset at around $h\nu_e=100.2$ eV. In Figs. 1(b) and 2(b), the shift of peak B to higher energy between $h\nu_e$ of 99.7 and 101.2 eV is a manifestation the $2p_{1/2}$ emission onset, and a similar shift is seen between the 99.7-eV and higher-$h\nu_e$ data for a-Si. Note that the centroid shift of peak A *to lower energies* as $h\nu_e$ is increased above threshold is partially masked by this L_2 onset. Unfortunately, no simple separation of the $2p_{3/2}$ and $2p_{1/2}$ components can be performed on the c-Si emission data. These two components can have quite different line shapes near threshold because the spin-orbit-split $2p$ electrons are excited to different levels in the conduction band.

Certain changes in the c-Si emission as a function of $h\nu_e$ may be interpreted within the framework of the $\mathbf{k}$-conservation model discussed above. For example, the region of peak C near 95.5 eV that is enhanced at $h\nu_e=99.7$ eV [arrow 1 in Fig. 2(b)] is associated with the X point in the Brillouin zone, and this intensity increase coincides with excitations to the conduction-band minimum near X.[15,16] Similarly, the enhancement of the high-energy edge of peak A at this excitation energy may be attributed to increased emission from states neighboring the X point in this part of the valence-band density of states.[15] When $h\nu_e$ is raised to 101.2 eV, excitations to the L point take place, and the region of peak C near 97 eV, which is associated with this same critical point, is intensified [arrow 2 in Fig. 2(b)].[15,16] The variations in feature C are analogous to those reported for diamond K emission,[4] in which the intensity of the p-density-of-states feature is dominant. For sufficiently large $h\nu_e$ the density of available unoccupied states becomes high, and a given excitation band can access any point in the Brillouin zone. At these energies the emission spectra are predicted to resemble their electron-stimulated counterpart.

Quantitative evaluation of the $\mathbf{k}$-conservation model for c-Si awaits detailed calculations which take into account the full band structure rather than isolated symmetry points. Preliminary results[17] reproduce specific variations in the c-Si data of Figs. 1(b) and 2(b), including those mentioned above. For the present the role of band structure and long-range order in Si $L_{2,3}$ soft-x-ray emission is dramatized by the contrast between the strong $h\nu_e$ dependence of c-Si to the $h\nu_e$ insensitivity of a-Si.

The authors thank Dr. Rupert C. C. Perera for providing the amorphous Si sample. This research was supported by National Science Foundation Grant No. DMR-8715430 and by a Science Alliance Center for Excellence Grant from the University of Tennessee.

---

[1] P. L. Cowan, Phys. Scr. T **31**, 112 (1990), and references therein.

[2] J.-E. Rubensson, D. Mueller, R. Shuker, D. L. Ederer, C. H. Zhang, J. Jia, and T. A. Callcott, Phys. Rev. Lett. **64**, 1047 (1990).

[3] N. Wassdahl, P. Bleckert, G. Bray, P. Glans, N. Mårtensson, J. Nordgren, J.-E. Rubensson, R. Nyholm, and S. Cramm, in *X-ray and Inner Shell Processes,* edited by T. A. Carlson, M. O. Krause, and S. T. Manson (American Institute of Physics, New York, 1990), p. 451, and references therein.

[4] Y. Ma, N. Wassdahl, P. Skytt, J. Guo, J. Nordgren, P. D. Johnson, J.-E. Rubensson, T. Boske, W. Eberhardt, and S. D. Kevan, Phys. Rev. Lett. **69**, 2598 (1992).

[5] G. D. Mahan, Phys. Rev. B **15**, 4587 (1977).

[6] C.-O. Almbladh, Phys. Rev. B **16**, 4343 (1977).

[7] T. A. Callcott, E. T. Arakawa, and D. L. Ederer, Phys. Rev. B **16**, 5185 (1977).

[8] W. L. O'Brien, J. Jia, Q.-Y. Dong, T. A. Callcott, K. E. Miyano, D. L. Ederer, D. R. Mueller, and C.-C. Kao, Phys. Rev. B **47**, 140 (1993).

[9] R. D. Carson and S. E. Schnatterly, Phys. Rev. B **39**, 1659 (1989).

[10] T. A. Callcott, K. L. Tsang, C. H. Zhang, D. L. Ederer, and E. T. Arakawa, Rev. Sci. Instrum. **57**, 2680 (1986).

[11] T. A. Callcott, W. L. O'Brien, J. J. Jia, Q. Y. Dong, D. L. Ederer, R. N. Watts, and D. R. Mueller, Nucl. Instrum. Methods Phys. Res. A **319**, 128 (1992).

[12] F. Evangelisti, F. Patella, R. A. Riedel, G. Margaritondo, P. Fiorini, P. Perfetti, and C. Quaresima, Phys. Rev. Lett. **53**, 2504 (1984).

[13] R. Carson and S. E. Schnatterly, Phys. Rev. Lett. **59**, 319 (1987).

[14] J. Klíma, J. Phys. C **3**, 70 (1970).

[15] J. R. Chelikowsky and M. L. Cohen, Phys. Rev. B **10**, 5095 (1974).

[16] A. Bianconi, R. Del Sole, A. Selloni, P. Chiaradia, M. Fanfoni, and I. Davoli, Solid State Commun. **64**, 1313 (1987).

[17] P. D. Johnson (private communication).