Shallow-Deep Core-Exciton Instability in Si_xGe_{1-x} Alloys

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Transmission and electron-yield measurements of the Si $L_{2,3}$ edge as a function of alloy composition x in Si_xGe_{1-x} alloys reveal anomalous spectra for $x \approx 0.15$, the composition of the crossover of the conduction-band minima from L in the Brillouin zone (for $x < 0.15$) to Δ (for $x > 0.15$). We interpret this as evidence for a sudden change of the ground state of the exciton from an extended effective-mass Wannier-type state for $x < 0.1$, to a deep localized state near $x = 0.15$, and back to an extended state for $x > 0.2$.

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In this Letter, we report transmission and electron-yield measurements of the Si $L_{2,3}$ edge in a series of crystalline substitutional Si_xGe_{1-x} alloys. These studies were undertaken to test a recent theoretical prediction[1] that the ground state of the Si $2p$ core exciton should change in character from an extended effective-mass state, for compositions $x < 0.1$ and $x > 0.2$, to a deep state near $x = 0.15$, the composition at which the virtual-crystal conduction-band minima switch from being near the $(a_L/2)(1,1,1)$ L point in the Brillouin zone (for Ge-rich compositions) to being on the $(1,0,0)$ Δ line (for Si-rich alloys).[2]

Our samples were evaporated films of ≈ 500- and ≈ 2000-Å thickness for transmission and electron-yield measurements, respectively. Substrate temperatures during the evaporations ranged from 600 to 900 °C, with the higher temperatures for larger x. Crystallite sizes as determined by x-ray diffraction were greater than 300 Å. The alloy composition of the thin films was determined by (i) an electron microprobe, (ii) x-ray diffraction determination of the lattice constant and the use of Vegard's law, and (iii) in the case of the transmission measurements, comparison of the increase in x-ray absorption at the Si $L_{2,3}$ edge and the sample thickness, as determined with a surface profiler.

The measurements utilized synchrotron radiation from the Tantalus electron storage ring at Stoughton, Wisconsin. The electron-yield measurements were made with use of a toroidal-grating monochromator[3] with ≈ 0.4-eV energy resolution at the Si $L_{2,3}$ edge. Both Auger electrons and low-energy (less than about 10 eV) secondary electrons were detected, giving, except for the noise level, the same spectra—an indication that surface effects are insignificant. The transmission spectra were measured by means of a "grasshopper" monochromator[4] with ≈ 0.08-eV energy resolution at the Si $L_{2,3}$ edge. Figure 1 shows the absorption and electron-yield edge spectra[5]; both the L_3 and the L_2 edges, which are spin-orbit split by about 0.6 eV, contribute to the edge structure.

The most significant feature of the spectra is the emergence of a resolvable spin-orbit splitting for alloy compositions near $x \approx 0.15$. This feature is not present in the alloy data for $x < 0.1$ or $x > 0.2$, but it does appear for $x \approx 0.15$ in the high-resolution absorption spectra and the lower-resolution electron-yield spectra (even though different samples were used for absorption and yield measurements, and different spots on the samples gave similar spectra[6]). The emergence of the discernible spin-orbit splitting is highlighted by differentiation of the spectra with respect to photon energy, $d\mu/dE$, as shown in Fig. 2. By normalizing the maximum derivative to the "edge step"—the absorption (or yield) increase at the $L_{2,3}$ edge—samples of different composition or thickness may be directly compared. In Fig. 3 we plot $(\Delta\mu)^{-1}(d\mu/dE)_{\max}$, where $(d\mu/dE)_{\max}$ is the maximum value of $d\mu/dE$ and $\Delta\mu$ is the edge step. *Clearly, an anomaly is observed at the $L_{2,3}$ edge in Si_xGe_{1-x} for $x \approx 0.15$.*

The absorption coefficient $\mu(E)$ is proportional to the square of a dipole matrix element and a density of states, and is subject to alloy broadening. Therefore, there are only three likely candidates for the dramatic sharpening of the Si $L_{2,3}$ edge at $x \approx 0.15$: (i) The wave function of the exciton (and hence the dipole matrix element) changes suddenly at $x \approx 0.15$; (ii) the density of states changes dramatically at $x \approx 0.15$; or (iii) the alloy

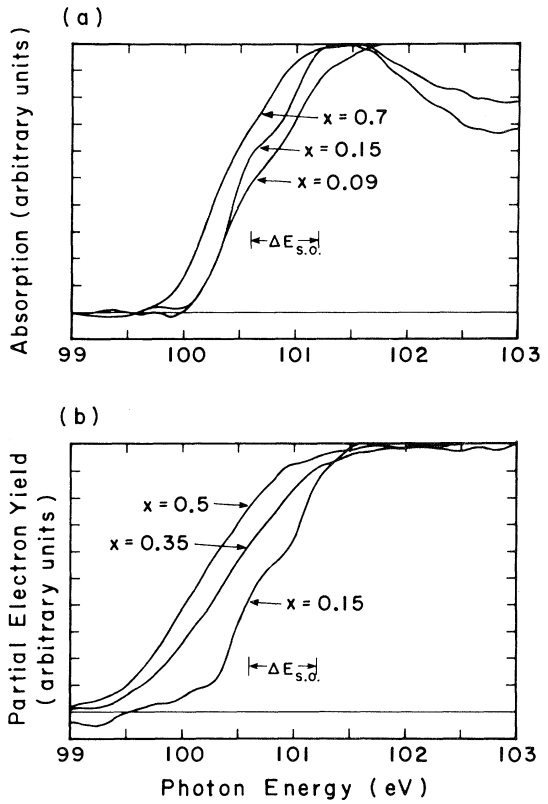

FIG. 1. Absorption coefficient μ as a function of x-ray energy for several of the Si_xGe_{1-x} alloys as determined in (a) transmission, and (b) electron yield. Data smoothing is described in Ref. 5. The spin-orbit splitting of the $L_{2,3}$ edge is indicated as $\Delta E_{s.o.}$. Note the prominent shoulder evident for $x = 0.15$ but not for other values of x. The different spectra have been plotted with different vertical scales.

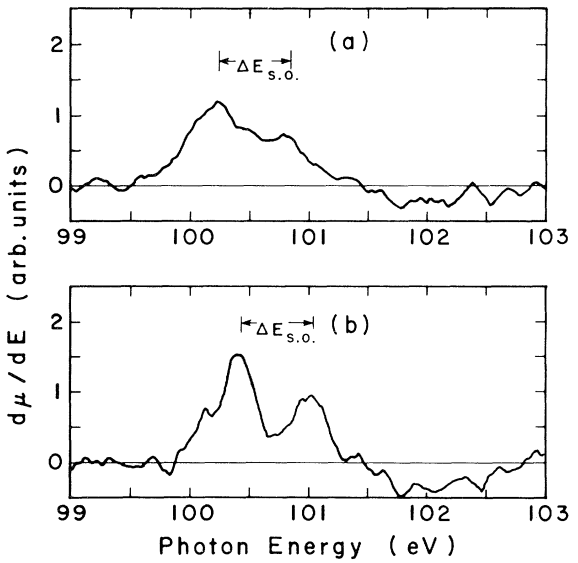

FIG. 2. The derivative of the normalized absorption coefficient $d\mu/dE$ as a function of x-ray energy for (a) $Si_{0.7}Ge_{0.3}$ and (b) $Si_{0.15}Ge_{0.85}$, determined in transmission. The spin-orbit splitting of the $L_{2,3}$ edge is indicated as $\Delta E_{s.o.}$. The different spectra have been plotted with different vertical scales.

broadening is suddenly reduced at $x \approx 0.15$.

The least plausible of these explanations is (iii), a sudden reduction in alloy broadening. In the absence of an ordering transition, alloy or disorder broadening is typically a relatively smooth function of composition, e.g., $x(1-x)$.[7] X-ray diffraction and preliminary extended x-ray-absorption fine structure (EXAFS) measurements show no evidence of ordering in samples near $x \approx 0.15$. In the absence of a more exotic mechanism for alloy broadening, this explanation does not seem viable.

It is more difficult to rule out the possibility that changes of the density of final states as a function of composition are responsible for the observed anomaly. Although both experimental and theoretical studies indicate that the virtual-crystal approximation, which predicts that the density of states changes smoothly with x, should be reasonable for Si_xGe_{1-x},[2,8] there is no conclusive proof that the density of states must be free from singularities as a function of x near $x = 0.15$. However, we cannot imagine any mechanism for producing such a singularity, other than intervalley mixing of the nearly degenerate conduction-band minima at the L-Δ crossing. To the best of our knowledge, no calculations have been made of the effects of intervalley interactions on the density of states for the case of inequivalent conduction-band minima, and no one has demonstrated that the intervalley coupling can produce the drastic change in the density of states for $x \approx 0.15$ needed to explain our data. We cannot totally rule out this explanation, but in the absence of more theoretical work, we give this mechanism no further consideration.

The potential explanation of the data, (i), is quite plausible: The excitonic final state is qualitatively different for $x \approx 0.15$, because near this alloy composition the ground state of the exciton is a "deep," localized state, while for other compositions the ground state is a "shallow" effective-mass state. Such a shallow-deep transition has been discussed by theorists for some time.[9] Our data can be explained if the ground state of the exciton is localized for $x \approx 0.15$ (leading to a resolvable spin-orbit splitting) but not for the other alloy compositions that we have measured.

One theoretical approach to the shallow-deep

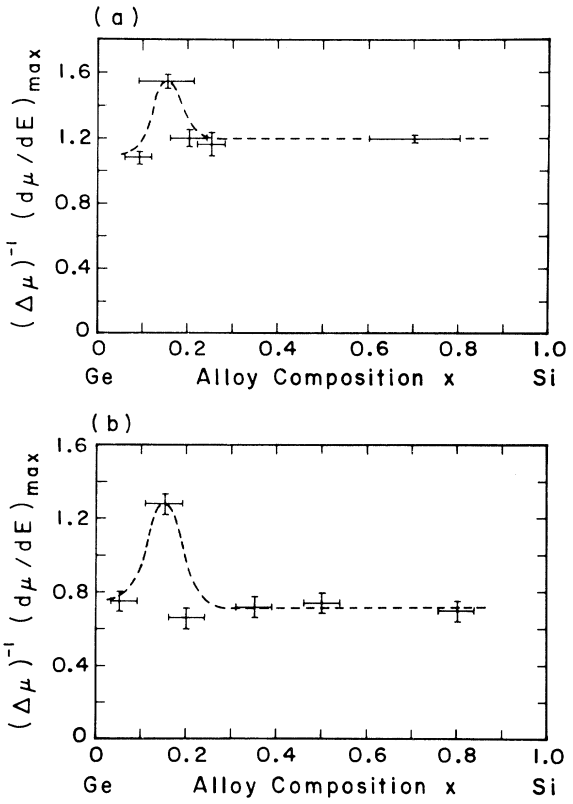

FIG. 3. Maximum normalized slope of the edge $(\Delta\mu)^{-1}(d\mu/dE)_{max}$—the maximum energy derivative of the absorption at the L_3 edge, divided by the absorption increase at the edge—as a function of alloy composition x, for (a) the transmission measurements, and (b) the electron-yield measurements. Note that different samples were used for the two types of measurements. The dashed line is a guide to the eye.

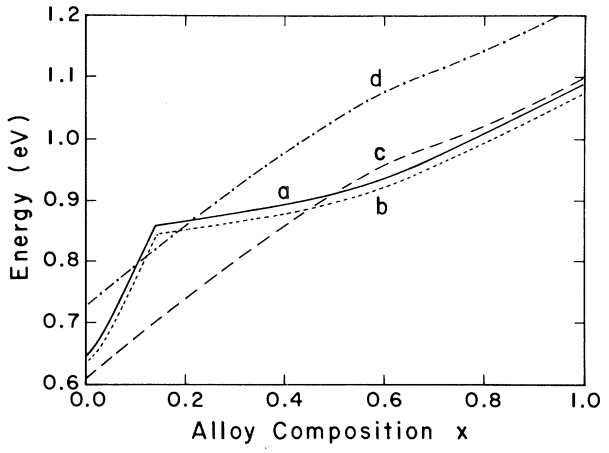

FIG. 4. A schematic diagram of the energies relative to the valence-band maximum of, curve a, the conduction-band edge (from Ref. 2), solid line; curve b, shallow Wannier-Mott excitons which are associated with the band edge, short-dashed line; curve c, Hjalmarson-Frenkel core excitons (from Ref. 1), long dashed line; and curve d, our conjecture for the actual energy of the core exciton, dash-dotted line; all as a function of composition x. The ground state of the exciton is the lower of b and d. When the Hjalmarson-Frenkel core exciton (c) lies above the conduction-band edge (a), it is resonant (having a significant width proportional to the conduction-band density of states) and may not be experimentally resolvable.

transition has shown that the core-exciton binding energies can be increased[10] by intervalley mixing of states associated with the various different conduction-band relative minima in an indirect-gap semiconductor. To our knowledge, no calculations for Si_xGe_{1-x} alloys have been reported,[11] but it is conceivable that the intervalley mixing effect could be especially important for alloy compositions such that the L and Δ minima are nearly degenerate.

Another theoretical approach[12] argues that in general *two* qualitatively different types of core excitons normally coexist in semiconductors: "shallow," delocalized effective-mass, Wannier-Mott excitons, and "deep," quasilocalized, Hjalmarson-Frenkel excitons. The shallow states are produced by the long-ranged screened Coulomb tail of the electron-hole interaction. The deep states are associated with the central-cell potential of the core hole and may lie *above* the conduction-band edge as broad resonances. In this picture, the shallow-deep transition occurs when the energies of the shallow and deep states cross: The ground state of the core exciton changes from the extended Wannier-Mott state to the localized Hjalmarson-Frenkel state. A recent calculation has predicted that this should occur near the L-Δ crossing at $x \approx 0.15$ in Si_xGe_{1-x} alloys. (An electron in the "shallow" state has an energy that is "attached" to the conduction-band edge, and moves up with that edge as a function of alloy composition, until for $x \approx 0.15$ it passes above the "deep" state—which is a resonance in the conduction band for $x = 0$ or $x = 1$.) The theoretical predictions[1] based on this model are given as curve c in Fig. 4.

With a slight modification (a composition-independent shift of the theoretically predicted exciton energy by ≈ 0.13 eV), this prediction agrees with our results. It should be noted that a shift of this size is not unexpected[1] and that the calculation was made for Si_xGe_{1-x} alloys at 4 K, while our data were all obtained at 300 K. The calculational results from Ref. 1 and our speculation about the exciton levels and the conduction-band minima relative to the valence-band maximum are shown in

Fig. 4. We place the exciton energies higher than in Ref. 1 to explain the sensitivity of the effect to alloy composition.

We again stress that the interpretation of Fig. 4, curve *d*, is based on the assumption of coexisting extended and localized exciton states. Presumably, there may exist other models of the core exciton that are not ruled out by our data. In this regard, effective-mass calculations for the Si_xGe_{1-x} system that explicitly include intervalley mixing are needed.

We also note that these results are consistent with measurements[13] that showed the binding energy of the Si $2p$ core exciton to be surface dependent, with a large binding energy when near the surface. Recent theoretical work[14] predicts that the Si $2p$ deep bulk state (uncovered in Si_xGe_{1-x} alloys at $x \approx 0.15$) descends into the gap at the surface and has an energy that depends on its proximity to the surface.

In summary, we find an anomaly in the x-ray absorption spectra at the $L_{2,3}$ edge in Si_xGe_{1-x} alloys for x near 0.15, the composition where the conduction-band minima cross from near L in the Brillouin zone to the Δ line. This anomaly is evidence for a transformation of the core-exciton ground state from a shallow, delocalized state to a deep, localized state near the crossing. Our results are in agreement with a recent calculation of Hjalmarson-Frenkel core excitons in Si_xGe_{1-x} alloys.

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[1]K. E. Newman and J. D. Dow, Solid State Commun. **50**, 587 (1984).

[2]R. Braunstein, A. Moore, and F. Herman, Phys. Rev. **109**, 695 (1958).

[3]B. P. Tonner, Nucl. Instrum. Methods **172**, 133 (1980).

[4]F. C. Brown, R. Z. Bachrach, and N. Lien, Nucl. Instrum. Methods **152**, 173 (1978).

[5]These data were obtained with an energy spacing much smaller than the monochromator resolution. To minimize the noise level, the data shown in Figs. 1–3 have been smoothed with a triangular window of 0.15-eV full width at half maximum.

[6]In the fabrication of these samples, the composition x could only be controlled to within about ± 0.2; the quoted compositions were determined in later characterization, using, for example, the electron microprobe.

[7]Although more complicated dependences of alloy broadening have been observed, no evidence has been presented for the singular behavior needed to explain our results. See, for example, D. J. Wolford, W. Y. Hsu, J. D. Dow, and B. G. Streetman, J. Lumin. **18/19**, 863 (1979).

[8]Y. Onodera and Y. Toyozawa, J. Phys. Soc. Jpn. **24**, 341 (1968); D. Stroud and H. Ehrenreich, Phys. Rev. B **2**, 3197 (1970).

[9]For a review of the theories of core excitons, see F. Bassani, Appl. Opt. **19**, 4093 (1980), and references therein; more recent developments include M. Altarelli, Phys. Rev. Lett. **46**, 205 (1981); and G. Strinati, Phys. Rev. Lett. **49**, 1519 (1982). A survey of core excitons in a number of semiconductors is given in A. Quattropani, F. Bassani, G. Margaritondo, and G. Tinivella, Nuovo Cimento **B51**, 335 (1979).

[10]M. Altarelli and W. Y. Hsu, Phys. Rev. Lett. **43**, 1346 (1979); L. Resca and R. Resta, Phys. Rev. Lett. **44**, 1340 (1980).

[11]A simple model calculation has been performed for the $GaAs_xP_{1-x}$ alloy system, which also exhibits a crossing of conduction-band minima: S. M. Kelso, D. E. Aspnes, C. G. Olsen, D. W. Lynch, and D. Finn, Phys. Rev. Lett. **45**, 1032 (1980).

[12]H. P. Hjalmarson, H. B. Büttner, and J. D. Dow, Phys. Rev. B **24**, 6010 (1981).

[13]F. J. Himpsel, P. Heimann, T.-C. Chiang, and D. E. Eastman, Phys. Rev. Lett. **45**, 1112 (1980); G. Margaritondo, A. Franciosi, N. C. Stoffel, and H. S. Edelman, Solid State Commun. **36**, 297 (1980).

[14]Marshall A. Bowen, Roland E. Allen, and John D. Dow, Phys. Rev. B **30**, 4617 (1984).