Binding Energy and Spectral Width of Si $2p$ Core Excitons in $\mathrm{Si}_x\mathrm{Ge}_{1-x}$ Alloys

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A calculation is presented to explain the anomalous experimental behavior of the Si $2p$ core-exciton binding energy and linewidth in $\mathrm{Si}_x\mathrm{Ge}_{1-x}$ alloys. The observed minimum in the linewidth near $x \simeq 0.15$ can be explained as the result of a competition between intrinsic broadening due to screening and extrinsic alloy broadening. For pure Si, the binding energy is estimated to be 0.15 ± 0.05 eV and the width is shown to be smaller than that observed at $x \simeq 0.15$.

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Until 1984, the Si $2p$ core exciton was believed to have an anomalously large binding energy.[1-10] Later, Newman and Dow[11] proposed a radically different picture in which the Si $2p$ core exciton is in fact a resonance with a negative binding energy. They further predicted that the exciton binding energy remains negative throughout most of the $\mathrm{Si}_x\mathrm{Ge}_{1-x}$ alloy composition range, except near $x \simeq 0.20$ where it becomes positive. In a recent experiment,[12] Bunker *et al.* found an anomalous sharpening of the exciton spectra near $x = 0.15$; the data were interpreted to support the Newman-Dow point of view. Yet the most recent experiment[13] still suggests a positive value for the binding energy E_b^0 in silicon.

In this Letter, we present a calculation that offers a plausible resolution to the above problem. In our theory, the calculated Si $2p$ core-exciton binding energy $E_b(x)$ and the linewidth $\Delta(x)$ in $\mathrm{Si}_x\mathrm{Ge}_{1-x}$ alloys are sensitively dependent on the parameter E_b^0. A comparison of the calculated $\Delta(x)$ with the experiment[12] suggests a positive value 0.15 ± 0.05 for E_b^0. The anomalous experimental spectrum[12] near $x \simeq 0.15$ is explained as a result of a competition between an intrinsic broadening Δ_I due to screening and an extrinsic alloy broadening Δ_A. In the present theory, there is no need to suppose that the exciton suddenly changes its character from an extended effective-mass-like state to a deep localized state.

We need to calculate E_b and $\Delta = \Delta_I + \Delta_A$ as a function of alloy concentration x. The calculations are based on a quantitative coherent-potential-approximation (CPA) band structure. Details of the CPA calculations will be presented elsewhere. Below, we briefly discuss a Green's-function method for calculating E_b and Δ_A.

The one-particle effective Green's function in CPA takes the form

$$G(E) = [E - \overline{H} - \Sigma(E)]^{-1}, \tag{1}$$

where $\overline{H}$ is the virtual-crystal approximation Hamiltonian and $\Sigma(E)$ is the self-energy. The site-diagonal Green's function is denoted as

$$F_\alpha(E) = \langle \phi_\alpha | G(E) | \phi_\alpha \rangle, \tag{2}$$

where ϕ_α is a localized orbital of specified symmetry. Here we only need to consider $\alpha = s$ for A_1 symmetry. The corresponding function in pure Si is denoted as $F_s^0(E)$. Following the theoretical treatment of deep substitutional-impurity levels,[8] the core-exciton level for pure Si is determined by

$$F_s^0(E) = (V - E_s^{\mathrm{Si}})^{-1}, \tag{3}$$

where E_s^{Si} is the site potential seen by an s electron in bulk silicon, and V is a central-potential parameter. For a chosen value of V_b, Eq. (3) can be solved for E, and vice versa. Then $E_b^0 = E_c^0 - E$, where E_c^0 is the conduction-band edge in pure silicon. Because of the uncertainties in the value of experimental E_b^0 and theoretical V, we treat E_b^0 (or V) as a parameter. The binding energy E_b in a $\mathrm{Si}_x\mathrm{Ge}_{1-x}$ alloy can be calculated by solving

$$F_s(E) = [V - \overline{E}_s - \Sigma_s(E)]^{-1}, \tag{4}$$

where

$$\overline{E}_s = x E_s^{\mathrm{Si}} + (1-x) E_s^{\mathrm{Ge}}. \tag{5}$$

Then E_b is given by

$$E_b = E_c - E. \tag{6}$$

The calculated values of the conduction-band edge and the exciton level measured relative to the top of the valence band are plotted in Fig. 1. The band gap increases with x with a slope discontinuity at ≈ 0.15. The dashed lines a, b, and c represent exciton levels obtained with $E_b^0 = 0.1$, 0.15, and 0.30 eV, respectively. The binding energy E_b is also an increasing function of x, with a slope discontinuity near $x \approx 0.15$. The CPA introduces a slight bowing in E_g and E_b.

Strinati[10] has calculated the variation of Δ_I with E_b

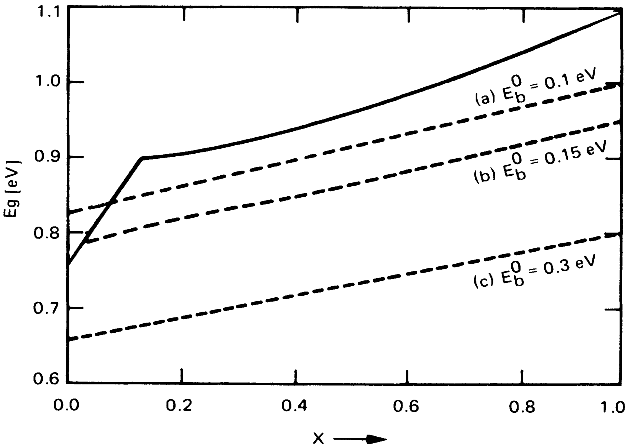

FIG. 1. Variation of the band gap (solid line) and the Si $2p$ core-exciton level with x in $\mathrm{Si}_x\mathrm{Ge}_{1-x}$ alloys. The energy is measured from the top of the valence band. The dashed curves a, b, and c represent exciton levels calculated with $E_b^0 = 0.1$, 0.15, and 0.3 eV, respectively.

by replacing the short-range Coulomb potential with a spherical square well of variable depth and a screened Coulomb tail. Strinati's results can be used to estimate Δ_I corresponding to the calculated E_b. Δ_I decreases rapidly with E_b, then saturates for larger E_b.

The contribution to the natural linewidth from the alloy broadening is calculated by a consideration of the electron part of the exciton wave function, ψ_s. The ψ_s is expanded in a linear combination of the s part of the conduction-band wave functions ϕ_n^s:

$$\psi_s(\mathbf{k}) = \sum_{n,s} C_{ns}\phi_n^s(\mathbf{k}). \tag{7}$$

We found that alloy scattering is only moderate and s scattering is dominant; thus, the alloy broadening $\Delta_A(E)$ is well approximated by

$$\Delta_A(E) \approx x(1-x)\delta_s^2 \operatorname{Im}F_s(E), \tag{8}$$

where δ_s is the difference between E_s^{Si} and E_s^{Ge}. Hence, the alloy-broadening contribution to Δ is related to the alloy broadening of the band states, $\Delta_n(\mathbf{k},\mathbf{E})$:

$$\begin{aligned}\Delta_A &= \frac{1}{N}\sum_{\mathbf{k}} \langle \psi_s(\mathbf{k})|\Delta_A(E)|\psi_s(\mathbf{k})\rangle \\ &\approx \frac{1}{N}\sum_{\mathbf{k}}\sum_{n} C_{n,s}^2\Delta_n(\mathbf{k},E) \\ &= \int \rho_s(E)\Delta_A(E)\,dE \\ &= x(1-x)\delta_s^2\pi\int \rho_s^2(E)\,dE. \end{aligned} \tag{9}$$

The integral in Eq. (9) is evaluated numerically.

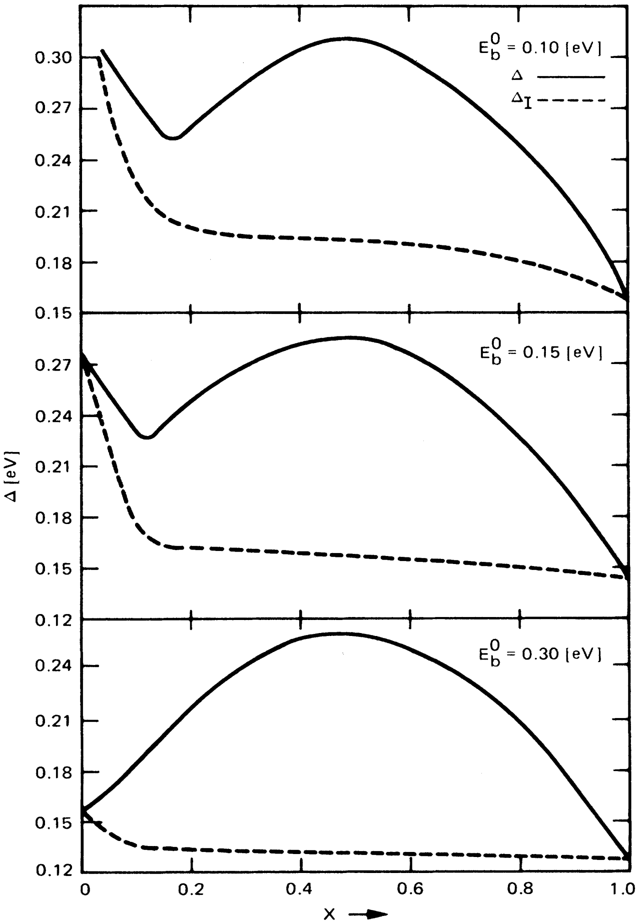

FIG. 2. Variation of Δ (solid lines) and Δ_I (dashed lines) with x for three E_b^0 values.

The calculated Δ, which is the sum of Δ_I and Δ_A, is plotted against x in Fig. 2 for three values of E_b^0. In all three panels, the dashed curve represents Δ_I and the solid line represents Δ. It is seen from Fig. 1 that the exciton level follows the X edge of the conduction band. Hence the binding energy E_b, relative to the conduction band edge, remains almost constant (for a given E_b^0) until the minimum switches from the X edge to the L edge. Because of the change in the slope of E_g, E_b decreases rapidly when L becomes the minimum. Correspondingly, Δ_I varies slowly until the X to L crossover and then increases rapidly. This feature is clearly seen in Fig. 2.

For $E_b^0 = 0.15$, the Δ_I and Δ_A are comparable near $x = 0.50$, and Δ_I dominates for all small x and large x. These two competing mechanisms give a relative minimum near $x \approx 0.15$, a broader maximum near $x \approx 0.50$, and a smaller minimum for pure silicon. As E_b^0 is decreased, the relative minimum is shifted to larger x, e.g., the minimum shifts to $x = 0.20$ for $E_b^0 = 0.10$ eV. For $E_b^0 = 0.15$ eV, the position of the relative minimum is in agreement with the experiment.[12] (By measuring the relative width at $x \approx 0.15$ to that $x=1$, one can make a better estimate of E_b^0.) To correlate the theory with experiment, the calculated $1/\Delta^2$ is compared with the measured[12] $(\Delta\mu)^{-1}(d\mu/dE)_{\max}$ in Fig. 3, where $\Delta\mu$ is the edge step and $(d\mu/dE)_{\max}$ are the maximum values of the derivative of absorption spectra with respect to photon energy. Because the experimental values are given in arbitrary units, the values are normalized to agree at $x=0.5$. The observed anomalous behavior near $x=0.15$ and the qualitative x dependence in that region is clearly replicated by the theory. However, the calculation predicts a larger maximum at $x=1$. It would be interesting to have experiments that cover the entire range of x to further test this prediction.

For larger values of E_b^0, the calculated E_b is also large and hence Δ_I decreases slowly with x. Because the broadening is determined mainly by Δ_A, the linewidth is expected to be small for $x=0$ and $x=1$ only; this occurs for $E_b^0 = 0.30$ eV. For negative values of E_b^0, E_b remains negative for all values of x. Accordingly, the linewidth is broad for all x, and there would be no such anomaly as in Fig. 3.

The calculations presented in this Letter are slightly different from alchemy approximations.[8] We treat the central-cell potential V as a parameter and narrow its range from other considerations. We examine values of $V - E_s^{\mathrm{Si}}$ of −8.49, −7.09, and −6.56 eV, corresponding to E_b^0 values of 0.30, 0.15, and 0.10 eV, respectively. If the strict alchemy approximation were taken, the value of $V - E_s^{\mathrm{Si}}$ would be $E_s^{P} - E_s^{\mathrm{Si}} = -4.59$ eV in the tight-binding approximation, and a negative E_b^0 (~ -0.10 eV) would be obtained. When long-range interactions are included, however, the above resonance state becomes a shallow donor level, which is the experimental situation for a P impurity in Si. Our results suggest that V for core excitons in Si is deeper than those implied by alchemy approximations. However, if we use the alchemy approximation as a means of scaling, the value of V for Ge $3p$ core excitons should be deeper than that for Si $2p$ core excitons. Hence, the curve corresponding to $E_b^0 = 0.30$ in Fig. 2 should be a reasonable estimate for Ge $3p$ core-exciton binding energy in alloys. Therefore, we do not expect to see an anomalous behavior of Δ in alloys for this case.

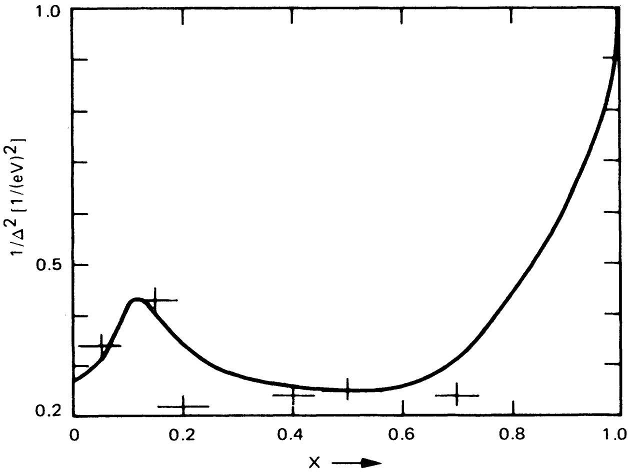

FIG. 3. The calculated $1/\Delta^2$ values (solid line) compared with the experimental results (marks) from Ref. 12. The value of calculated Δ(Si) is 0.127 eV. The experiment is normalized to the theory at $x=0.5$.

In summary, the present calculations of the Si $2p$ core-exciton binding energy and linewidth suggest that the exciton level is about 0.15 ±0.05 eV below the conduction-band edge for pure Si. It follows the X edge for $x > 0.15$ in the $\mathrm{Si}_x\mathrm{Ge}_{1-x}$ alloys, and E_b may eventually reach zero in the dilute limit $x \rightarrow 0$. Our value for E_b^0 represents the lower end of the previous measurements,[1–6] but is in good agreement with a recent experimental[13] value of 0.120 ±0.03 eV. By considering the intrinsic linewidth and the alloy broadening, we can explain the observed relative minimum in the linewidth near $x \simeq 0.15$, without requiring a sudden change of the exciton character. On the basis of this calculation, we expect the corresponding width in pure Si to be even smaller than that observed near $x=0.15$. We further argue that the binding energy of Ge $3p$ core excitons should be larger than that of Si $2p$ core excitons and there should be no anomaly in the Ge $3p$ linewidth in alloys.

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