Photoionization spectra of deep centers in semiconductors showing a narrow peak near the threshold

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A class of deep centers in semiconductors is identified by their photoionization spectra, which have a narrow peak near the threshold energy and a broader peak at higher energy. The *M* center in ZnSe is an example. An explanation of the spectral shape is given in terms of a wave function with a radial node. Such wave functions can occur when a substantial contribution to the function comes from nearest-neighbor atoms.

There are now many published experimental spectra of the photoionization of deep centers in semiconductors. There are also many theoretical models. Usually it is found that the photoionization cross section rises smoothly from a threshold energy $h\nu=E_{\rm th}$ to a broad peak at $h\nu\sim 2E_{\rm th}$ and decreases gradually thereafter. Often the higher-energy parts of the spectrum are masked by absorption from the valence to conduction bands. The spectra are more or less broadened by phonon interactions. For some combinations of deep center and host the spectrum is quite different and consists of a lower-energy peak a few tenths of an electron volt wide followed by a broader peak at higher energies. As examples, Chantre, Vincent, and Bois[1] show such peaked spectra for a number of centers of unknown identity in GaAs and Suda, Matsuzaki, and Kurita[2] for a center in ZnS:Ag. A particularly striking example is the so-called *M* center in ZnSe. Photocapacitance studies by Grimmeiss, Ovrén, and Allen[3] of transitions of electrons from the valence band to the center (i.e., photoionization of holes) gave a spectrum with a threshold at 0.68 eV, rising to a peak at about 0.85 eV, followed by a broad peak at about 1.35 eV. Zheng and Allen[4] have discussed the nature of the center: it is likely to be a lattice defect. It was not clear in the earlier work whether the 0.85- and 1.35-eV peaks were associated with the same center. Using ZnSe of better quality, grown by metallo-organic chemical vapor deposition (MOCVD) at 280 °C under atmospheric pressure on GaAs substrates, we have obtained the spectrum shown in Fig. 1. Details of the measurements will be published elsewhere. We have shown that the two peaks are associated with a single center. Earlier published spectra of the *M* center were strongly affected by another center which produces a broad peak overlying the second peak in Fig. 1. Measurements over the range 80–180 K show that only a small fraction of the width is due to phonon interactions.

The general form of the usual photoionization spectrum is easily explained. The cross section $\sigma(h\nu)$ is proportional to the transition probability T_{if} given by the golden rule

$$T_{if}=\frac{2\pi}{\hbar}|\langle i|\bar{o}|f\rangle|^2\rho(E)\ , \tag{1}$$

where the energy of the final state E is measured from the band edge, i.e., $E=h\nu-h\nu_{\rm th}$. In the simplest model, phonon interaction is ignored, the final state $|f\rangle$ is taken as a plane wave $\exp(i\mathbf{k}\cdot\mathbf{r})$, the density of states is taken to be that of a parabolic band so $\rho(E)\propto E^{1/2}$, the operator for the dipole transition $\bar{o}$ is taken as proportional to $\pi\cdot\nabla$ where π is a unit vector in the polarization direction and the initial state $|i\rangle$ has spherical symmetry. One then has

$$\sigma\propto(h\nu)^{-1}k^2|\langle i|e^{i\mathbf{k}\cdot\mathbf{r}}\rangle|^2E^{1/2} \tag{2}$$

$$\propto(h\nu)^{-1}(h\nu-h\nu_{\rm th})^{3/2}|F(k)|^2\ , \tag{3}$$

where $F(k)$ is the three-dimensional Fourier transform of $|i\rangle$. For example, if $|i\rangle\propto r^{-1}e^{-\alpha r}$, which might be an appropriate approximation if the main contribution to σ comes from outside the core region, then $F(k)\propto(\alpha^2+k^2)^{-1}$ and

$$\sigma\propto(E+E_{\rm th})^{-1}E^{3/2}(E_\alpha+E)^{-2}\ , \tag{4}$$

where $E_\alpha\equiv\hbar^2\alpha^2/(2m^*)$. Lucovsky[5] obtained his well-known formula, illustrated in Fig. 2, by setting $E_\alpha=E_{\rm th}$ which is equivalent to extrapolating the $E=\hbar^2k^2/(2m^*)$ dispersion relation into the energy gap. A more complicated situation occurs when the dipole transition is allowed at the band edge, instead of forbidden by parity as in the above example. However if $|i\rangle$ can be approximated by $G(\mathbf{r})u(0,\mathbf{r})$, where $G(\mathbf{r})$ is an envelope function and $u(0,\mathbf{r})$ is a band-edge Bloch function for a band different from $|f\rangle$ then, with the usual approximations, (3) becomes

$$\sigma\propto(h\nu)^{-1}(h\nu-h\nu_{\rm th})^{1/2}|F(k)|^2\ , \tag{5}$$

where $F(k)$ is now the Fourier transform of $G(r)$. With $G(r)\propto r^{-1}e^{-\alpha r}$ the equivalent of (4) is now

$$\sigma\propto(E+E_{\rm th})^{-1}E^{1/2}(E_\alpha+E)^{-2}\ . \tag{6}$$

Many of the published theories of the spectral form of σ are variants of these simple continuum models with more elaborate initial- and final-state functions and with some convolution with a phonon broadening term. The essential features of forms such as (4) are that σ increases from

threshold approximately as a power law, reaches a peak, and then decreases again as another power law.

Spectra of the second type, with a sharp peak near threshold, could arise from initial- or final-state effects. An excited final state, near or resonant with the band states, would give such a spectrum and systems for which this is an explanation exist, as, for example, GaP:Ni.[6] It is unlikely that this explanation is a general one, since that would imply that several systems have an excited state lying within 0.2 eV of the band edge but very few with a higher energy. Some attempts have been made, for example, by Chantre, Vincent, and Bois,[1] to fit (6) or a similar equation to the photoionization peak taking the spread α^{-1} of the initial state to be a few angstroms. Then E_α is a few tenths of an eV and the calculated spectrum of σ has a peak of width the same order of magnitude. This is illustrated in Fig. 2. Such fittings fail to give a good account of the high-energy side of the peak and, without additional assumptions, do not explain the second peak.

Cooper[7] has pointed out, in connection with photoionization of atoms, that if the initial state has a radial node the spectrum of σ can consist of a threshold peak and a second higher-energy peak. In terms of the argument given above, if $|i\rangle$ changes sign at some value of r then under suitable circumstances $F(k)$ can change sign at some value of k and thus σ, which is proportional to $|F(k)|^2$, is zero at the corresponding energy. As a simple illustrative example, if $|i\rangle$ has the hydrogen $2s$ form

$$|i\rangle \propto (1-\alpha r)e^{-\alpha r}, \tag{7}$$

then

$$F(k) \propto (k^2-\alpha^2)(k^2+\alpha^2)^{-3} \tag{8}$$

and σ has a zero at $E=\hbar^2\alpha^2/(2m^*)$. In a slight generalization, if

$$|i\rangle \propto [1-(r/a)]e^{-\alpha r}, \tag{9}$$

then

$$F(k) \propto \frac{k^2-\alpha^2(3-\alpha a)(1+\alpha a)^{-1}}{(\alpha^2+k^2)^3}. \tag{10}$$

In Fig. 2 we show a plot of the spectrum of σ according to (3) with $F(k)$ according to (10). The values of α and a are chosen to reproduce the width of the first peak and the ratio of the heights of the first and second peaks in the M-center spectrum. Even such a simple model gives a fair representation of the main features of the spectrum. The experimental spectrum does not go to zero between the peaks, as it would if $F(k)$ goes through a zero and if thermal broadening is absent. However, if $F(k)$ has a

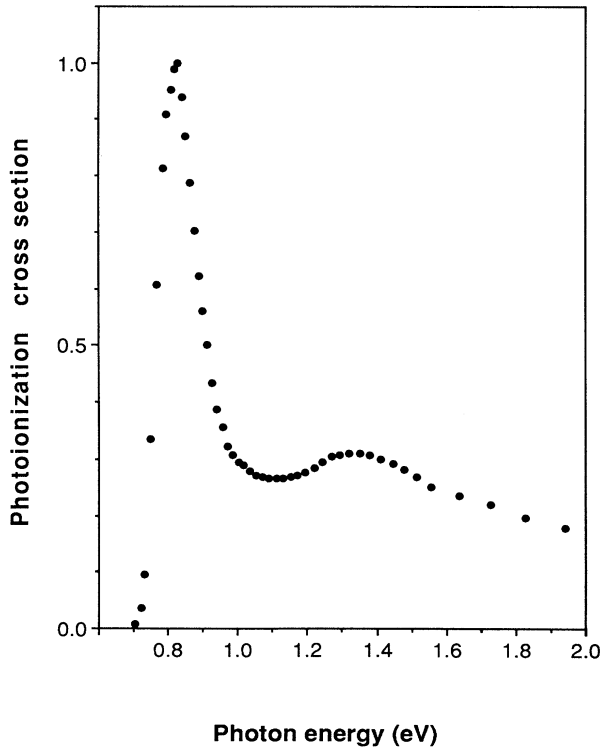

FIG. 1. The photoionization spectrum for transitions of holes from the M center in ZnSe to the valence band at 80 K. The spectrum was measured by the double-light-source photocapacitance method with MOCVD ZnSe and is normalized to unity peak height.

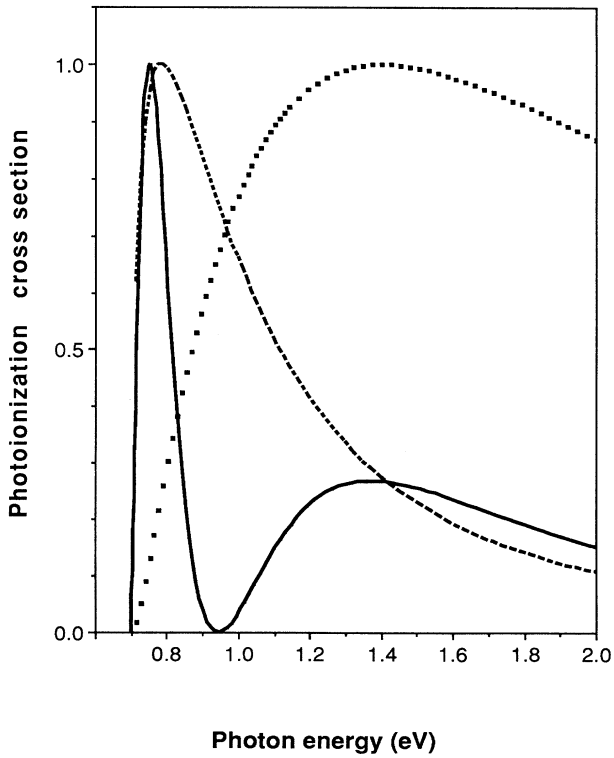

FIG. 2. Calculated photoionization spectra for different models. — — —, the Lucovsky formula. —·—·—·, Eq. (6) with $E_\alpha/E_{\rm th}=0.5$. ——, Eq. (3) combined with Eq. (10) with $\alpha^{-1}=3.0$ Å and $a=3.6$ Å. The spectra are normalized to unity peak height and the threshold energy is taken as 0.7 eV.

small imaginary part and it is the real part which goes through zero, then $|F(k)|^2$ and hence σ will not fall to zero. Also if $|i\rangle$ is not spherically symmetrical, $F(k)$ will go to zero at different values of k in different directions and this can result in σ not going to zero.

From the fit to the M-center spectrum we find the radial node to lie at roughly 3.6 Å. This distance is near the Zn-Se interatomic spacing of 2.5 Å. Often in treatments of photoionization one considers the deep-center wave function to have an atomiclike core region and an extended "tail" region. A dimension of a few angstroms is too large for a core contribution and too small for a tail represented by Bloch functions modulated by an envelope function. It is possible, therefore, that the deep center has a wave function largely composed of orbitals located on atoms adjacent to a central site. As an illustrative example, one could have a lattice defect or impurity at a zinc site with a potential which raises a p orbital on each of the four nearest-neighbor selenium atoms from the valence band into the gap. If each p orbital is aligned along a bond direction, then the A_1 state has a radial node which, although not spherically symmetric as in (9), is approximately at the interatomic distance. A similar model is that of the As_{Ga} antisite defect in GaAs described by Baraff[8] in which antibonding orbitals between As_{Ga} and nearest-neighbor arsenic atoms have a node at about half the bond-length distance.

We conclude that there is a class of deep centers in semiconductors characterized by a distinctive form of their photoionization spectrum to the conduction or valence bands. The spectrum rises from a threshold to a peak only a few tenths of an electron volt wide, i.e., the width is much less than the threshold energy. This initial peak is followed by a broader peak at higher energy. The M center in ZnSe is an excellent example. An explanation for the shape of the photoionization spectrum can be given in terms of an initial-state wave function with a radial node. Under appropriate conditions this produces a surface in $\mathbf{k}$ space at which the real part of the Fourier transform $F(\mathbf{k})$ of the wave function changes sign. As a result, the photoionization spectrum as a function of energy goes through a minimum separating two peaks. From the position of the minimum it is found that the radial node is at a distance of the order of a bond length. This leads to the conclusion that for this class of centers a substantial contribution to the deep-center wave function comes from orbitals on atoms neighboring a central site. For a given position of the radial node, the initial peak is narrower (and therefore more prominent) the greater the effective mass in the band states.

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