Visible—near-uv optical spectra of a-Ge$_x$Se$_{1-x}$

H. J. Trodahl[*] and L. Viña

Max-Planck-Institut für Festkörperforschung, Heisenbergstrasse 1,
D-7000 Stuttgart 80, Federal Republic of Germany
(Received 30 December 1982)

Dielectric function spectra from 2 to 5 eV are reported for a series of a-Ge$_x$Se$_{1-x}$ films in the compositional range $0.20 \leq x \leq 0.52$. The spectra show two broad absorption features which shift systematically with changes in composition. From these shifts we determine the compositional changes in the lone-pair to antibonding band gap and in the bonding to antibonding band gap. The results are compared with theoretically predicted band-center and bandwidth changes.

I. INTRODUCTION

Thin films of the amorphous semiconducting alloy system Ge$_x$Se$_{1-x}$ can be prepared for the entire range of compositions. For $x \lesssim 0.4$ it is quite clear that the short-range order is described by a model in which fourfold coordinated Ge atoms and twofold coordinated Se atoms form a random network, subject only to the restriction that heteropolar bonds are favored over either Ge—Ge or Se—Se bonds.[1-3] For $x > 0.4$ there appears to be an alternative structure based on a chemically ordered 3:3 fold coordinated network in which each Ge (Se) atom is bonded to three Se (Ge) atoms.[4-6] These alloys thus provide an opportunity to study the behavior of electronic states in a system with varying, but reasonably well characterized, numbers of homopolar bonds. With this in mind we have performed ellipsometric measurements of the visible and near uv optical constants a-Ge$_x$Se$_{1-x}$ films with $0.2 \leq x \leq 0.52$.

Earlier optical work on this alloy system has concentrated primarily on defining the compositional dependence of the fundamental abosorption edge near 2 eV and measuring the absorption coefficient just below the edge.[7-10] Optical studies extending to energies substantially above the gap include ellipsometry on a-GeSe$_2$ (Ref. 11) $(x = \frac{1}{3})$ and reflectivity measurements on a series of alloys with $x \leq \frac{1}{3}$.[12] Both of these earlier studies showed a second absorption feature near 4—5 eV. Such structure above the edge is unusual in amorphous semiconductors, and appears to be characteristic of lone-pair materials.[11] Our systematic measurements have led to a firm identification of the electronic transition responsible for this second edge and to a determination of the compositional dependence of the relative energies of the bonding, the lone-pair, and the antibonding states.

II. EXPERIMENTAL

The samples were prepared by coevaporation of Ge and Se in a vacuum system with a base pressure of less than 10^{-8} torr. Deposition rates of near 10 Å/sec were monitored and controlled by two separate quartz-crystal microbalances. The films were typically 1 μm thick. Compositions were measured using x-ray flourescence. More details concerning their preparation and characterization can be found elsewhere.[13]

Dielectric function spectra $\epsilon(\omega) = \epsilon_1(\omega) + i\epsilon_2(\omega)$ were measured at room temperature between 2 and 5 eV with an automatic rotating analyzer ellipsometer similar to that described by Aspnes and Studna.[14] In brief, it consists of a light source (75-W Xe short-arc lamp), a $\frac{3}{4}$-m Spex monochromator, Rochon prisms of crystal quartz as polarizing elements, a photomultiplier with an S20 response as detector, and mirror optics for collimating and focusing the light. The output signal of the photomultiplier is digitized and later analyzed with the help of a Hewlett-Packard model 9845B computer. The measurements were made at an angle of incidence of 67.5°.

The samples were mounted in a windowless cell in flowing dry N$_2$ gas to minimize surface contamination. Prior to measurement the samples were rinsed *in situ* with methanol, which was seen to increase the peak in ϵ_2. The treatment was repeated several times, until changes were no longer seen, and the spectra were collected immediately afterward. Pseudodielectric functions were than calculated from the complex reflectance ratios using the two-phase model in which the surface is treated as a simple plane boundary between two homogeneous media, each filling one-half of space. Data from below the fundamental edge have been rejected, for in this region multiple internal reflections render the two-phase model inappropriate.

III. RESULTS AND DISCUSSION

A selection of spectra are shown in Fig. 1. For $x > 0.40$ the absorption edge lies below the energy range measured, but for $0.20 \leq x \leq 0.40$ both the fundamental and the secondary (4—5-eV) edges can
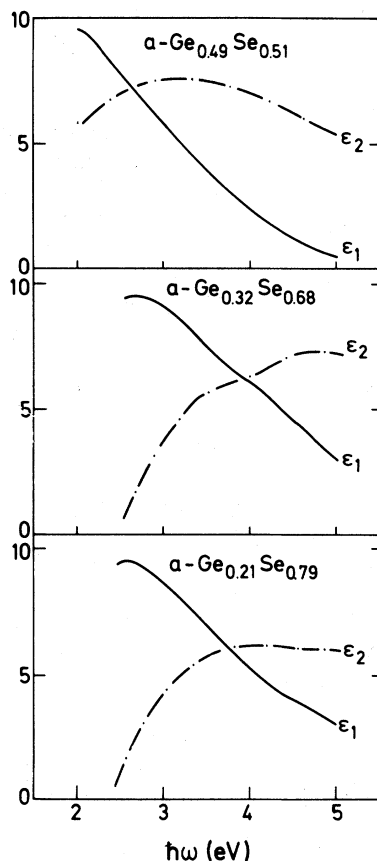
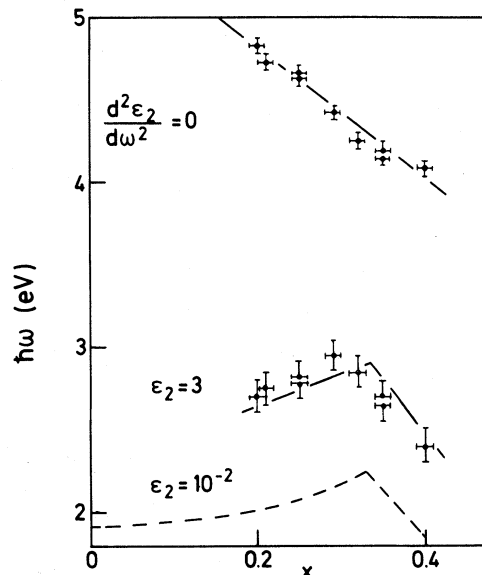FIG. 1. Measured dielectric functions for representative samples.

FIG. 2. Edge positions vs Ge concentration. The data points were determined as described in the text. The solid lines are fits to the data and were used to estimate the rates at which the edges shift. The dashed line represents the edge positions measured by Bensoussan (Ref. 8), defined as the energy at which $\epsilon_2 = 10^{-2}$.

be seen. Both edges shift with changing composition, and in order to clearly define these shifts we require quantitative measurements of the edge positions. The upper edge position is conveniently located as the energy of the maximum slope in ϵ_2, determined by calculating the second derivative ($d^2\epsilon_2/d\omega^2$) and finding the zero. A similar procedure cannot be used for the fundamental edge, so we identify its position as the energy at which ϵ_2 reaches the value 3, approximately one-half of its peak value. A smaller value of ϵ_2 would more accurately identify the energy at which absorption sets in, but the ellipsometric measurement is relatively inaccurate at small values of ϵ_2.

The resulting trends are shown in Fig. 2. Turning first to the fundamental edge, our results can be compared with Bensoussan's measurements[8] of the energy at which $\epsilon_2 = 10^{-2}$. Not surprisingly, Bensoussan's edge positions lie somewhat below ours, but the compositional dependence is similar. Both results show an increase of about 25-meV/at. % Ge for $x < \frac{1}{3}$, followed by a shift of −55-meV/at. % Ge for $x > \frac{1}{3}$.

By contrast, the upper edge shifts −40-meV/at. % Ge toward lower energy over the entire range of concentration. There is a suggestion that the rate of shift slows for $x > \frac{1}{3}$, but errors in the measurement make such a conclusion uncertain.

The interpretation of these data requires an identification of the relavent transitions. Aspnes *et al.*[11] modeled the a-GeSe$_2$ data in terms of a double valence band and a single conduction band. On the other hand, Lannoo and Bensoussan,[12] who saw only weak effects in the reflectivity due to the second, edge, suggested that it was related to structure in both the valence and conduction bands.[12] This proposal was backed up by a simple tight-binding calculation, which gave approximate positions and widths of various features in the electronic spectrum at a few values of $x \leq \frac{1}{3}$. A simplified version of the theoretical state densities for $x = 0$ and $\frac{1}{3}$ is shown in Fig. 3. The Se s band, which takes part in neither the bonding nor the optical properties, is left out of the figure. The remaining bands are arranged as follows:

(i) The bonding states, made up of Ge s and p orbitals and Se p orbitals extend over about 8 eV. It is important to note that the upper edge of this region contains states with predominantly p character about Ge atoms.

(ii) The Se lone-pair (τ) band lies about 1−2 eV above the top of the bonding band. This state narrows rapidly as x changes from 0 to $\frac{1}{3}$.
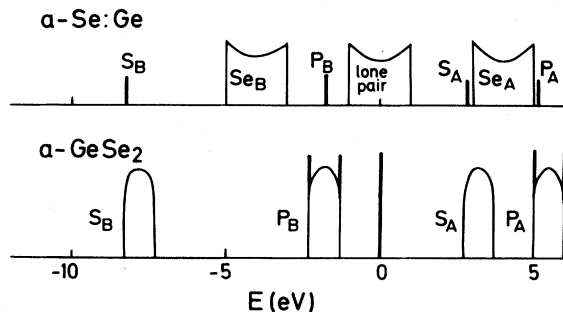
a-Se:Ge

FIG. 3. Simplified energy-band diagrams for a-Se with isolated Ge impurities (upper diagram) and for a-GeSe$_2$ (lower diagram), after Ref. 12. Energies are shown relative to the center of the Se lone-pair band. The δ functions in the upper diagram are from states centered on Ge atoms, and these broaden into bands in a-GeSe$_2$. The character of these states (s or p, bonding or antibonding) is indicated in both diagrams. The Se bonding, lone-pair, and antibonding bands in the upper diagram narrow to a series of δ functions in a-GeSe$_2$ in the simple model of Ref. 12.

(iii) The antibonding bands are found a further 2−8 eV above the τ band. The Se p_A and the Ge s_A bands overlap and lie about 2 eV below the Ge p_A band.

The Fermi energy lies between the lone-pair and the antibonding bands.

The scale of energies in the valence bands of Fig. 3 can be compared with ultraviolet photoelectron spectroscopy (UPS) measurements.[15,16] In these there is clear evidence for three peaks in the valence band of a-GeSe$_2$, with the upper (τ) peak separated from the central (p_B) beak by about 1.5 eV. Very little UPS work has been reported for compositions other than GeSe$_2$, but what meager data exist indicates that the peaks are separated by almost 2 eV for $x = 0.25$, but that they remain separated by 1.5 eV for $x > \frac{1}{3}$.[16] These relative shifts are consistent with Fig. 2 if we assign the fundamental edge to a $\tau \rightarrow$ antibonding band (s_A) transition and the second feature to a bonding band (p_B) $\rightarrow$ antibonding band (s_A) transition. The data of Fig. 2 then show the energy gap

between the bonding and antibonding bands (upper curve, near 4.5 eV) and the position of the lone-pair band relative to the edge of the antibonding band (lower curve, near 2.5 eV).

With these assignments the shifts shown in Fig. 2 are in at least qualitative agreement with the energy levels of Lannoo and Bensoussan.[12] The increase in the $\tau \rightarrow s_A$ edge with increasing x arises from a narrowing of the lone-pair (τ) band as the number of Se—Se bonds decrease, partially offset by a slower increase in the width of the Ge s_A level. The model predicts an increase of about 20-meV/at.% Ge, close to the value (25) found experimentally. The model further predicts a shift of the $p_B \rightarrow s_A$ edge at a rate of −20-meV/at.% Ge, a factor of 2 smaller than the measured shift. The reduction in this gap is primarily a result of the broadening of the p_B and s_A bands as x increases. The model clearly underestiamtes this broadening.

The suggestion[12] that the 4.5-eV edge contains contributions from the $\tau \rightarrow$ Ge p_A transition can be eliminated on the basis of the shifts with x. The model shows this gap to widen at a rate of 30-meV/at.% Ge, a shift opposite in sign to that measured.

In summary, we have presented ellipsometric measurements of the visible—near uv optical constants of a-Ge$_x$Se$_{1-x}$ alloys in the compositional range $0.20 \leq x \leq 0.52$. From these we determine that the lone-pair antibonding band gap is near 2.5 eV and that the bonding-antibonding band gap is near 4.5 eV. These gaps change with composition at rates of 25- and −40-meV/at.% Ge, respectively, for $x < \frac{1}{3}$. The corresponding shifts for $x > \frac{1}{3}$ are −55- and −40-meV/at.% Ge. These shifts are in qualitative agreement with the band-center and bandwidth changes calculated by Lannoo and Bensoussan.

*Permanent address: Physics Department, Victoria University, Wellington, New Zealand.

[1]P. Tronc, M. Bensoussan, A. Brenac, and C. Sebenne, Phys. Rev. B **8**, 5947 (1973).

[2]P. Tronc, M. Bensoussan, A. Brenac, G. Erradonea, and C. Sebenne, J. Phys. (Paris) **38**, 1493 (1977).

[3]H. Kawamura, M. Matsumura, and S. Ushioda, J. Non-Cryst. Solids **35—36**, 1215 (1980).

[4]P. H. Fuoss, P. Eisenberger, W. K. Warburton, and A. Bienenstock, Phys. Rev. Lett. **46**, 1537 (1981).

[5]E. P. O'Reilly, J. Robertson, and M. J. Kelly, Solid State Commun. **38**, 565 (1981).

[6]H. J. Trodahl, Solid State Commun. **44**, 319 (1982).

[7]T. T. Nang, M. Okuda, T. Matsushita, S. Yokota, and A. Suzuki, Jpn. J. App. Phys. **15**, 849 (1976).

[8]M. Bensoussan, Rev. Phys. Appl. **12**, 753 (1977).

[9]J. Shirafuji, G. I. Kim, and Y. Inuishi, Jpn. J. Appl. Phys. **16**, 67 (1977).

[10]M. Kumeda, M. Ishikawa, M. Suzuki, and T. Shimizu, Solid State Commun. **25**, 933 (1978).

[11]D. E. Aspnes, J. C. Phillips, K. L. Tai, and P. M. Briden-
baugh, Phys. Rev. B 23, 816 (1981).
[12]M. Lannoo and M. Bensoussan, Phys. Rev. B 16, 3546
(1977).
[13]H. J. Trodahl (unpublished).
[14]D. E. Aspnes and A. A. Studna, Appl. Opt. 14, 220

(1975).
[15]S. Hino, T. Takahashi, and Y. Harada, Solid State Com-
mun. 35, 379 (1980).
[16]T. Ueno and A. Odajima, Jpn. J. Appl. Phys. 12, 1382
(1982).