Electronic Structure and Optical Properties of Amorphous Ge and Si[†]

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The amorphous density of states for an assembly of atoms with short-range order has been obtained from a phenomenological model in which the density of states of the corresponding crystal with different nearest-neighbor distances ($\pm$ 5% of crystalline value, r_0) are averaged by introducing a suitable weighting function of the form $\exp[-(1/2\sigma^2)(r_0 - r)^2]$, σ being the Gaussian spread. The pseudopotential formalism is employed in the calculation. The nondirect transition model of Tauc and energy-dependent matrix elements have been used to evaluate the imaginary part of the dielectric constant, $\epsilon_2(\omega)$. The density of states and $\epsilon_2(\omega)$ of amorphous Ge and Si are reported in this paper.

I. INTRODUCTION

In the last two decades, there has been a tremendous activity in the electron theory of solids. However, until very recently, most of the work in the subject has been dealing with crystalline solids. Experimental and theoretical investigations have been extended since then to liquid and noncrystalline materials. Many recent experiments[1-7] have been geared to compare observations on structural and electronic properties of crystalline and amorphous forms of the same material to understand the effects of disorder. Despite a substantial level of research activity in the past few years, the structure[1,3,8,9] of amorphous semiconductors remains a controversial topic. In particular, the exact definition of the short-range order needs careful examination.

The existence of band structure is essentially a consequence of short-range order.[10] The nature and extent of the long-range order is responsible for the finer details in the density of states.[11,12] The preservation of a band structure for a certain degree of disorder has been shown theoretically by Gubanov[13] and Cohen[14] for models in which disorder is imposed on a basic periodic system. Based on the tight-binding method, Wearie[11] proposed a model Hamiltonian representing a nonperiodic network that predicted rigorous bounds for the density of electronic states in a "topologically" disordered system of elemental (group-IV) and compound (III-V) semiconductors. The electronic behavior of amorphous conductors has also been considered from the point of view of nearly free electrons which are multiply scattered by atomic centers in a disordered array.[10,15] Brodsky and Stiles[16] have used the Phillips spectroscopic theory of chemical bonding[17] to calculate electronic dielectric constants in amorphous semiconductors. Other authors[1,4,18] have pointed out that the covalent-bond

energies might be appearing in spectral observations.[19] It is also possible to use a modified Penn model[20] to calculate the optical properties of amorphous structures.

Bulk of the above investigations have been more or less concerned with the band-edge region, the occurrence of band gap, and the tailing of states into the gap. After the successful photoemission studies on Ge[7] and Si,[21] various workers[22-26] have theoretically calculated the fundamental absorption bands in amorphous semiconductors. Herman and Van Dyke[22] and Brust[23] have used a virtual-crystal approach which produces full energy bands and Bloch functions. Using a nondirect-transition (NDT) constant-matrix-element model[2] Herman and Van Dyke[22] have simulated the electronic density of states of amorphous Ge[7] by that of a dilated (an over-all expansion of the lattice constant by 10%) Ge crystal having the same density as amorphous Ge. Their procedure suffers from (a) an overestimate of density difference ($\sim$ 30%) between crystal and amorphous Ge and (b) completely closing the energy gap, making it a semimetal. Brust[23] showed that the gross features of the density of states can be related to umklapp scattering effects associated with the short-range order in the disordered phase. Starting with some diagrammatic expansions of configurationally averaged one-electron Green's function and using partial summations and approximations for n-body correlation functions, Kramer and co-workers[24] have followed the pseudopotential formalism in their method of complex-band-structure (CBS) calculation of density of states for amorphous Se, Ge, Si, and other III-V compounds. The ϵ_2 spectrum obtained from the CBS method as well as the NDT model with energy-dependent "amorphous" matrix elements[25(a)] have been compared.[26] In contrast to Brust's[23] work on amorphous Ge, which is otherwise very similar to that of Kramer and his associates,[25(b)] the matrix elements are not

taken as constant, and the energy and the wave-vector dependence of lifetimes is not treated as an adjustable parameter.

In this paper, we present a model calculation based on the assumption that the amorphous density of states for an assembly of atoms with short-range order can be obtained by statistical averaging of the density of states of corresponding crystal with different nearest-neighbor distances. Our phenomenological model is supported by the experimental observations[1,3,8] on the radial distribution functions of amorphous Ge and Si, which literally suggest a statistical distribution[1] of nearest-neighbor distances centering around the crystalline value. The imaginary part of the dielectric constant of amorphous Ge and Si have been obtained from these density of states using the NDT model[2] with energy-dependent matrix elements.[25(a)]

II. METHOD OF CALCULATION

In the present work, the "statistical" point of view as discussed by Grigorovici[1] was adopted, in which the structural parameters (such as bond length, bond angle, etc.) of an amorphous solid are regarded as having statistical distributions about some normal values. The energy spectrum of the amorphous semiconductors is then assumed to be the statistical (configurational) average of the distribution. The works of Gubanov,[27] Fletcher,[28] and Kramer[24] are typical examples based on this general point of view.

Current pictures of amorphous Si and Ge suggest the existence of short-range order, similar to that of the crystalline solids. The nearest-neighbor distance, however, is slightly different, as evidenced from the radial distribution function (RDF). In this work we assume that these solids are composed of microcrystallites, in which the nearest-neighbor distance between atoms has a statistical distribution given by the first peak of the RDF. The amorphous density of states has been calculated from the weighted average of the crystalline density of states corresponding to various nearest-neighbor distances. The weighting function has the form of $\exp[-(r_0 - r)^2/2\sigma^2]$. The band structures of the crystal corresponding to nearest-neighbor distances slightly varied from that of the crystalline one is calculated by the following procedure: At first, the band structure at crystalline nearest-neighbor distance r_0 is calculated using the empirical pseudopotential method.[29]

The pseudopotential form factors of Cohen and Bergstresser[29] were used. To calculate the band structure for slightly different nearest-neighbor distance, one notes that the pseudopotential form factor depends on the lattice constant through the primitive cell volume, the reciprocal-lattice vector, and probably the crystal pseudopotential $V(\vec{r})$.

We assume, however, the "rigid-ion" model is valid, i. e., $V(\vec{r})$ remains unchanged for slightly varied lattice constant. A similar assumption has been made to calculate the dilation contribution to the temperature coefficient of the energy gap in PbTe,[30] and also the band structures of strained crystals.[31] Specifically, we obtained the form factors for a dilated crystal by first interpolating a smooth curve through the crystalline form factors, reading off the corresponding values required for the dilated lattice, and then scaling each of them by the ratio of the unit-cell volume of the normal lattice to that of the dilated lattice. We found the above procedure sufficiently adequate for our purpose.

The density of states are obtained by calculating the eigenvalues of the Hamiltonian at 74 evenly distributed points of the irreducible part of the first Brillouin zone. This corresponds to approximately 1500 points in the whole Brillouin zone. We found that this number of sampling points yields density of states which compares reasonably well with that given by Kramer[24] where a larger number of sam-
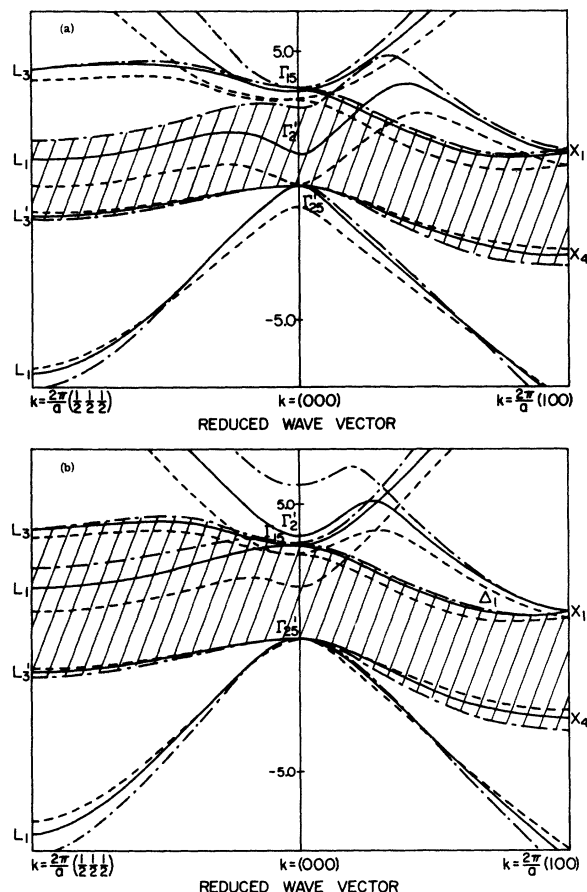

FIG. 1. E-vs-k diagram: solid line, crystalline nearest-neighbor distance r_0; dotted line, 1.05 r_0; dash-dotted line, 0.95 r_0. (a) Germanium, (b) silicon.

pling points were used.

The imaginary part of the dielectric constant $\epsilon_2(\omega)$ in the one-electron approximation may be written[2]

$$\epsilon_2(\omega) \sim \frac{1}{\omega^2} |M(\omega)|^2 \sum_{i,f} \delta(E_f - E_i - \hbar\omega) , \qquad (1)$$

where the summation is performed over all initial and final states i, f, over the volume of the unit cell. $|M(\omega)|^2$ is defined as the arithmatical average probability of dipole transitions[25] for a given photon energy ω.

In the crystalline case both momentum and energy are conserved. We may write

$$\epsilon_2(\omega) \sim (1/\omega^2) |M(\omega)|^2_{cryst} n_j(\omega) , \qquad (2)$$

where $n_j(\omega)$ is the joint density of states which contains the essential informtaion of crystalline band structure.

In an amorphous solid, the $\vec{k}$ selection rule breaks down, and only energy is conserved. Assuming the NDT model of Tauc[2] and considering energy dependent matrix elements[25] for the dipole transitions, one may similarly write

$$\epsilon_2(\omega) \sim (1/\omega^2) |M(\omega)|^2_{amorph} n_c(\omega) , \qquad (3)$$

where $|M(\omega)|^2_{amorph}$ are the amorphous matrix elements. It is apparent that $\epsilon_2(\omega)$ is determined mainly by the convoluted densities of states $n_c(\omega)$ of the valence and conduction bands for which the energy is conserved. Sharp structures[25] in $|M(\omega)|^2_{cryst}$, which originate from localized transitions[32] in the Brillouin zone (umklapp enhanced), are smoothed out to give $|M(\omega)|^2_{amorph}$. Equation (3) then yields $\epsilon_2(\omega)$ for amorphous semiconductors.

III. RESULTS AND DISCUSSION

For carrying out the calculation as described above, it is necessary to select specific values of the parameter σ in the Gaussian representing the RDF.

Most amorphous Si and Ge films which have been studied electrically and optically have density deficiencies of about 10–15%[1,12] compared with their crystalline forms.[1,12] The analysis[1,8] of the position and shape of the first maximum of the radial distribution curve of amorphous Si and Ge shows existence of fluctuations in the nearest-neighbor distance with a standard deviation of ± 0.19 Å. In our calculations, we have considered $\pm 5\%$ range of nearest-neighbor distance and a Gaussian spread σ of 0.06 Å, compatible with the available experimental data.

The E-$\vec{k}$ relations are plotted in Figs. 1(a) and 1(b) for Ge and Si, respectively, along the [100] and [111] directions for three values of nearest-neighbor distances, viz., r_0, the crystalline value, $0.95r_0$, and $1.05r_0$. In general, the conduction-

band levels change considerably more with the nearest-neighbor distance than the valence-band levels. From Fig. 1(a) we observe that the forbidden band ceases to exist at about $r/r_0 \simeq 1.05$, when the lowest conduction-band level (Γ_2') coincides with the highest valence-band level (Γ_{25}'). However, beyond $r/r_0 < 0.98$, the X_1 level becomes the lowest conduction-band level. Herman, et al.[33] have observed a similar behavior in the extreme pressure studies of crystalline Ge. From Fig. 1(b) for Si, we observe a similar behavior except that (i) there is no switching of conduction-band edges (Δ_1 level is the lowest conduction-band level throughout the range of r/r_0 considered in this paper) and (ii) there is always a band gap ($X_1 - \Gamma_{25}'$ changes from 0.85 to 0.60 eV as r/r_0 increases from 1.0 to 1.05). Careful examination of the energy-band diagrams of Figs. 1(a) and 1(b) indicates that our model is in gross agreement with the amorphous band structures calculated by CBS method[24] rather than that obtained by simple dilation.[22]

The density of states $n(E)$ of amorphous Ge and Si [Figs. 2(a) and 2(b)] as calculated in this paper compare well with the CBS results.[24] Through disorder, there is substantial tailing of energy states into the region of crystal band gap. The crystalline peaks are somewhat broadened. The conduction-band features, in particular, are strongly relaxed. This is consistent with the conduction-band density of states deduced experimentally by Spicer and Donovan.[7] Our calculated valence-band density of
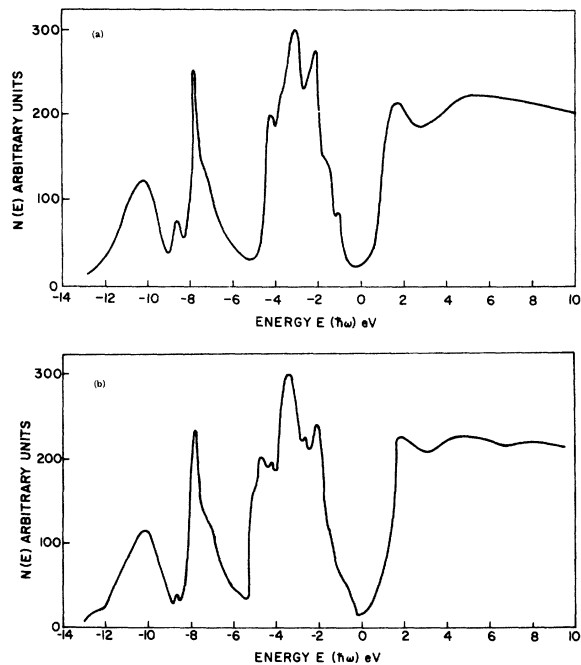

FIG. 2. Density of states. (a) Amorphous germanium; (b) amorphous silicon.

states (VBDS), however, are rather similar to that found in the normal crystals, implying that, at least, they are much less disturbed by disorder, such as change in nearest-neighbor distance from its normal value. This is supported to some extent by the experimental data on secondary electron emission of Ge[6], which strongly suggests that some fine structures in the VBDS might be preserved in the amorphous solids. However, the existence of the two peaks at ~ 8 and ~ 10 eV below the top of valence band predicted by our model is in contrast to the experimental findings of Ley et al.[34] There it was shown that, in going from crystalline to amorphous forms, the two lower energy peaks, somehow, are merged into a single big hump. From calculations of band structures and $\epsilon_2(\omega)$ of various polytypes of Ge and Si, Joannopoulos and Cohen[35] and Henderson and Ortenburger,[36] found that the density of states of GeIII and SiIII (poly-type containing 12 atoms per unit cell, having five-fold rings) are most similar to those of amorphous structures. Joannopoulos and Cohen[35] further argued that the existence of fivefold rings in the polytype, in fact, would introduce eigenstates with energies between the two peaks, thus resulting in their apparent mixing. Except for this, the VBDS are rather similar to that of the crystalline ones, as can be seen from the results[35,36] for other poly-types in which the fivefold rings do not exist. Granting this to be the case, then the difference between the lower-energy regime of our VBDS and the experimental ones, would be the result of the lack of fivefold rings in our model. Although, the argument based on the fivefold rings might not be contended, we feel it is highly possible that other distortions, such as slightly unequal bond length and bond angles, in the basic tetrahedral unit,

FIG. 4. $\epsilon_2(\omega)$ vs photon energy for amorphous Si. Curve 1: experimental (Ref. 5); curve 2: CBS calculation by Kramer (Ref. 24); curve 3: with constant matrix elements; curve 4: calculated in this paper.

might also produce states in between the two lower-energy peaks in VBDS. We would like to point out that although GeIII was regarded as a reasonable model for amorphous Ge, its density is about 10% higher than that of the latter. Slight scatter in density of various amorphous samples is possible due to differences in deposition parameters. A 10% deviation is yet to be realized even in the best annealed amorphous Ge. The fact that GeIII is too much denser is also reflected in its RDF, which is less satisfactory at larger R, as compared with that of the amorphous counterpart.

In passing, it is of interest to note that the x-ray photoemission data of Shevchick et al.[37] showed that the VBDS for both crystalline and amorphous GeTe are essentially the same even though their respec-
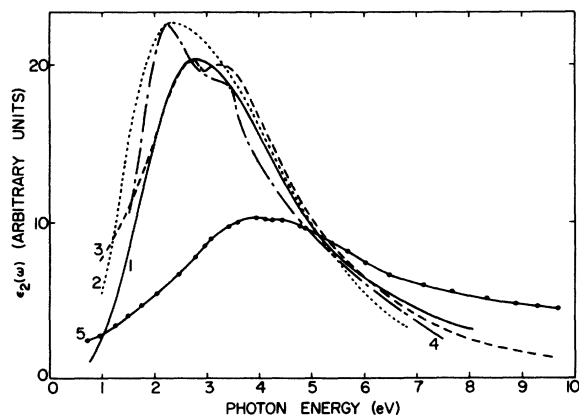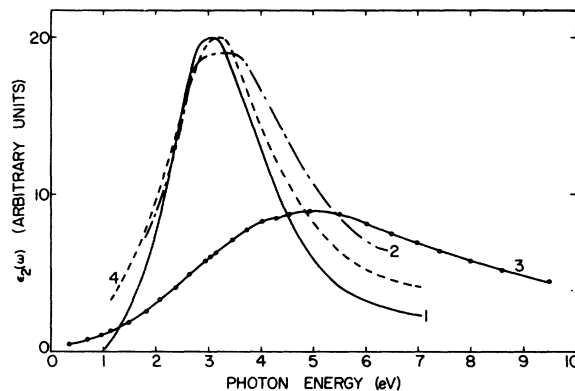

FIG. 3. $\epsilon_2(\omega)$ vs photon energy for amorphous Ge. Curve 1: experimental (Ref. 7); curve 2: calculated by Brust (Ref. 23); curve 3: calculated in this paper; curve 4: calculation of Kramer (Ref. 24); curve 5: with constant matrix elements.
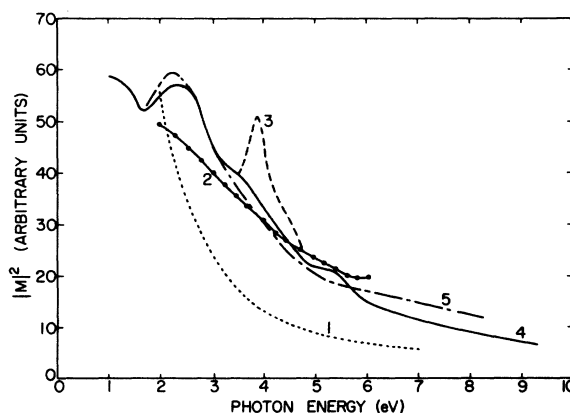

FIG. 5. Matrix transitions elements for germanium. Curve 1: calculated with crystalline density of states; curve 2: calculated with experimental amorphous density of states (Ref. 7); curve 3: crystalline Ge matrix elements; curve 4: amorphous matrix elements as used in this paper for energy-dependent NDT model absorption calculation; curve 5: calculated with theoretical amorphous density of states as obtained in this paper.
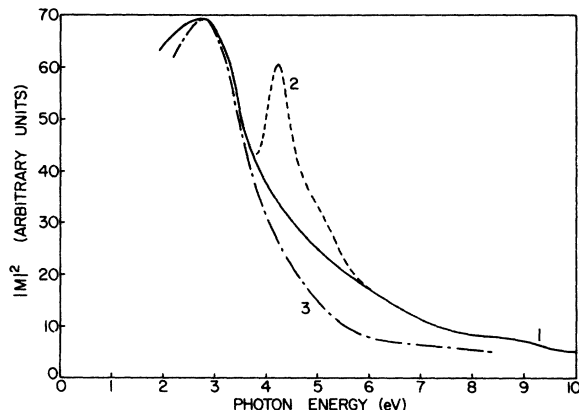
FIG. 6. Matrix transition elements for silicon. Curve 1: amorphous matrix elements as used in this paper for energy-dependent NDT-model absorption calculation; curve 2: crystalline Si matrix elements; curve 3: calculated with theoretical amorphous density of states as obtained in this paper.

tive nearest-neighbor environments are very different. It was concluded[37] that it may be the atomic orbitals only that mainly determine the VBDS in solids.

The imaginary part of the dielectric constant $\epsilon_2(\omega)$ for amorphous Ge and Si are shown in Figs. 3 and 4, respectively. Our results are compared with those of Brust[23] and Kramer[24] and experimental observations.[3,7,19] In order to obtain a better agreement, the energy dependence of the matrix elements has to be considered. The crystalline and amorphous matrix elements for Ge and Si, respectively, are shown in Figs. 5 and 6. Amorphous matrix elements as used in this paper have been obtained from the respective crystalline matrix elements by smoothing out umklapp-enhanced transitions and retaining as much energy dependence of crystalline case as possible. These figures also include the ideal $|M(\omega)|^2$ necessary to get an exact fit to experimental $\epsilon_2(\omega)$, assuming our density of states to be reasonable for the disordered struc-

ture. Ideal $|M(\omega)|^2$ thus calculated agrees quite well with the amorphous $|M(\omega)|^2$ except in the high-energy side beyond 5 eV. This is plausible because of the excessive band tailing of the states. In contrast to the small kinks in CBS calculated $\epsilon_2(\omega)$ curves of amorphous Ge, near 3–4 eV, we observe a small dip near 3 eV. Kramer ascribed the small kinks in the CBS calculation to the residue of the E_2 and E_1' peaks of the crystalline spectra. Whereas in our case, the dip is so small (less than 3.5% of the maximum) that this is well within the limits of experimental accuracy.

The over-all agreement of the fundamental absorption band is quite satisfactory except near the band edges and the higher-energy values beyond 5 eV. This is mainly due to the large tailing of the band states and partly due to the choice of the energy dependence of the matrix elements $|M(\omega)|^2$.

The pronounced shift of the bulk of $\epsilon_2(\omega)$ in going from crystalline to amorphous phase may be understood in terms of breakdown of the momentum conservation rule in amorphous state. Selective changes in ϵ_2 curves of Ge are due to the varying influence of disorder in different directions. Energy states correlated to the [111] direction are less influenced by disorder than in the [100] direction. This is also evident from the temperature coefficient of the absorption edge of Ge.[38]

IV. CONCLUSION

In conclusion, we have shown that the present model in which the amorphous solid is considered as an aggregate of microcrystallites with slightly different nearest-neighbor distance can produce density of states as well as $\epsilon_2(\omega)$, in reasonable agreement with other theoretical calculations (CBS calculation) and experimental data. The existence of two distinct peaks in the lower-energy regime of VBDS, might possibly be ascribed to the lack of fivefold rings in the present model. However, other distortions of the tetrahedral basic unit might also be of comparable importance in this respect.

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