CHANGES IN THE DENSITY OF STATES OF GERMANIUM ON DISORDERING AS OBSERVED BY PHOTOEMISSION*

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An optical density of states in amorphous Ge derived from photoemission measurements shows that the maximum in the valence-band density of states is shifted 1.5 eV to higher energy with respect to the crystalline density of states. No structure is observed in the conduction-band density of states for the amorphous material, whereas strong structure is present in the crysalline density of states. Changes observed in the optical properties of Ge on disordering can be explained using these results.

In this Letter we present some results of a study of the effect of long-range order on photoemission from Ge, results which we believe account for the observed changes in the optical properties as one goes from crystalline Ge to a disordered or amorphous Ge film. The imaginary part of the dielectric constant, ϵ_2, for crystalline and amorphous Ge has been derived by Kramers-Kronig analyses of the respective reflectivity data.$^{1-4}$ The highest maximum in ϵ_2 for the crystal is at about 4.3 eV. The detailed structure has been interpreted in terms of direct transitions occurring at symmetry points or along symmetry directions in the Brillouin zone. In the amorphous-film result, the maximum in ϵ_2 has shifted to lower energies (2.6 eV) and the detailed structure apparent in the crystal results is not present (see insert in Fig. 3).

The photoemission results show that this change in the optical properties on disordering can be understood by assuming that $\vec{k}$ conservation, in the usual one-particle sense, is not an important selection rule for the disordered system and by a shift to higher energies of the maximum in the valence-band density of states from the crystalline case. That is, the crystal photoemission results presented here are consistant with calculated energy-band structures[5,6] assuming direct optical transitions, i.e., that $\vec{k}$ conservation is an important selection rule, a conclusion in agreement with the previous interpretation of the optical and previous lower-energy photoemission[7] results. The amorphous-film results, on the other hand, can be understood assuming constant matrix elements and that $\vec{k}$ conservation is not an important selection rule. Furthermore, the photoemission data show directly that the maximum in the valence-band density of states for the amorphous system has shifted to higher energies than its calculated position for the crystalline system. Using these results, an imaginary dielectric constant in rather good agreement, as to shape, with experiment can be calculated.

Photoelectronic quantum-yield and energy-distribution measurements have been made throughout the spectral range $1.8 \leq h\nu \leq 11.8$ eV on crystalline samples cleaved in a vacuum of 10^{-9} Torr and Ge films vacuum deposited on substrates which have been mechanically polished and which have been heat cleaned (450°C at 10^{-8} Torr for 15 min). The substrate is held at room temperature during evaporation. Figure 1 shows energy distribution curves for photon energies of 7.4, 8.6, and 10.4 eV for cleaved single-crystal surfaces and of 8.8, 9.8, and 10.8 eV for amorphous Ge films. All measurements were made in a vacuum of at least 10^{-9} Torr. The energy distribution curves were obtained using an ac-modulated retarding-potential method that has been described by Spicer and Berglund.[8] The distributions have been normalized to the quantum yield, and the energy is given relative to the maximum in the filled states.

More information about the electronic structure is available from the energy distribution curves than is available from the optical data. For example, structural detail related to the electronic structure is apparent in the data of Fig. 1 while the reflectivity or imaginary part of the dielectric constant in this spectral range shows no detail at all. This can be understood if one considers that the number of electrons at a given final energy in a distribution is proportional at a given photon energy to the transition probability from a given initial state, while the dielectric constant ϵ_2 at a given photon energy is proportional to the integral of the transition probabilities from all possible initial or to all possible final states. It follows that the optical experiments determine only the energy difference between quantum levels. Photoemission

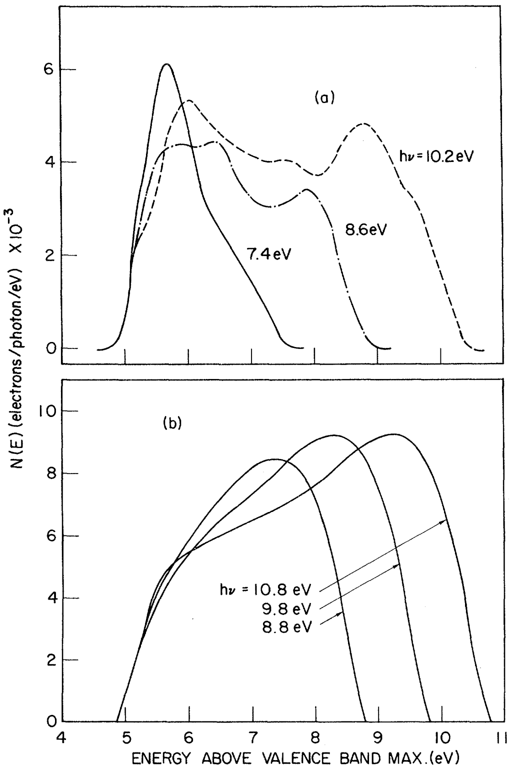

FIG. 1. Photoelectron energy distributions for Ge surfaces. (a) Cleaved, intrinsic, single crystal. (b) Amorphous film. The vertical axis gives the number of electrons per absorbed photon per eV. The horizontal axis gives the electron energy relative to the maximum in the valence band. The sharp structure in (a) is due to direct transitions in specific regions of the zone. The single broad peak in (b) is due to a peak in the valence-band optical density of states.

measurements, on the other hand, determine the absolute energies of the levels involved in an electronic transition.

A detailed analysis of data for both cleaved and amorphous samples over a photon energy range of 1.8 to 11.8 eV (results for photon energies less than about 6 eV are obtained by applying cesium to the surfaces to lower the semiconductor work function) will be published at a later date. For the present purposes we will point out certain features in the data of Fig. 1 that have led us to our conclusion that the crystal results are consistent with a direct transition model and the disordered film results are consistent with a nondirect, constant matrix-element model.

In Fig. 1(a), there is a broad shoulder seen at the high-energy edge of the distribution for a photon energy of 7.4 eV. Since the shoulder appears near the maximum energy, it is due to transitions from initial states near the valence-band maximum which, in the case of Ge, occurs at Γ. The threshold for this transition, as determined by the photoemission experiment, is at about 7.0 eV in good agreement with the value predicted by Herman[4] for the $\Gamma_{25'}$-Γ_1 separation. Thus, we have associated this shoulder with vertical transitions between the $\Gamma_{25'}$ valence-band maximum and the Γ_1 conduction-band minimum. The peak that develops from this shoulder at higher photon energies moves to higher final energies in increments of energy somewhat different than increments in photon energy which again implies direct transitions, since for direct transitions the initial energy is a function of the photon energy. The sharp peak seen on the lower edge of the 10.4-eV distribution first appears at a photon energy of about 10.0 eV and is seen over a 2-eV range in these data. Subtracting the exciting photon energy from the final energy of this peak as one moves to higher photon energies makes it apparent that this particular structure originates from a flat, high density-of-states region 4.2 eV below the top of the upper valence band. By examination of energy-band calculations,[4,5] this structure can only be associated with transitions from the high density-of-states region, along Σ, near *K*. The location of this high density-of-states region 4.2 eV below the valence-band maximum is in good agreement with the value of 4.0 eV predicted by Herman's[4] band calculation.

The low-energy peak which dominates the distribution for 7.4 eV is seen over a wide range of photon energies, in both the clean and cesiated data, and is associated with transitions between bands along the Δ and Σ directions going from Γ out to *X*. This interpretation involves the consideration of structure plots of the type used by Spicer and Eden[9] in the interpretation of their GaAs data. This peak disappears between stronger structures at the higher photon energies. Its movement with photon energy and disappearance at higher energies as seen here are both consistent with a direct-transition interpretation.

Figure 1(b) shows normalized energy distribution curves for an amorphous Ge film at various photon energies. The structural detail present in the crystal results is absent here, particularly at the lower energy end of the distributions. This lack of structural detail at the lower energies has been confirmed by results from films where the vacuum level has been reduced by a surface monolayer of cesium. These data show that the lower energy portion of the curves of

Fig. 1(b) are not being limited by a reduced (over the crystal case) electron escape probability. The position of the maximum in the distributions moves to higher energies when the photon energy is increased, in increments equal to the increments in photon energy. Such movement of structure with photon energy over as wide a range of photon energies as seen here implies that the structure originates in the filled density of states and that the direct conservation of $\vec{k}$ is not an important selection rule. Indeed, it is found that all the amorphous-film data are consistent with the nondirect, constant-matrix-element model.[10] Using the nondirect matrix-element analysis,[10] an optical density of states has been derived for the valence band and the conduction band for amorphous Ge and this result is shown in Fig. 2. Here the optical density of states obtained from the amorphous-film data is compared with the density of states of crystalline Ge calculated by Herman and Shay.[11] There is no evidence of conduction-band structure in the photoemission data. The step in the conduction-band density of states near the conduction-band minimum was chosen so that the imaginary part of the dielectric constant, calculated assuming this optical density of states and the nondirect, constant-matrix-element model, would be consistent in both leading-edge and peak position with the experimental ϵ_2 (this assumption is necessary since conduction-band states lying below the vacuum level are inaccessible to the photoemission experiment). The result of this calculation is shown in Fig. 3 in comparison with the experimentally derived results. The coincidence of the leading-edge and peak positions is apparent. In our results, the appearance of scattered electrons in the distributions has not been considered; but it is felt that the effect of correcting the distributions for these electrons would be to decrease the optical density of states at low energy and, thus, to increase the dielectric constant in the region of the maximum and decrease it at higher energeis, or, in other words, to bring the two results into closer agreement. A similar calculation using the crystal density of states and assuming constant matrix elements gives a maximum in ϵ_2 at about 4.5 eV or about 2 eV higher in energy than what is observed experimentally. The insert in Fig. 3 shows for comparison purposes the imaginary part of the dielectric constant ϵ_2 for (1) crystalline and (2) amorphous Ge as derived by Kramers-Kronig analyses of the respective reflectivity data.[1]

From these results then, we conclude that the valence-band and conduction-band densities of states are strongly affected on going from ordered to disordered Ge. Crystalline Ge has strong structure in the conduction-band density of states, whereas amorphous Ge has no such structure. The maximum in the valence-band density of states is shifted by 1.5 eV to higher energies from the crystalline case and detailed

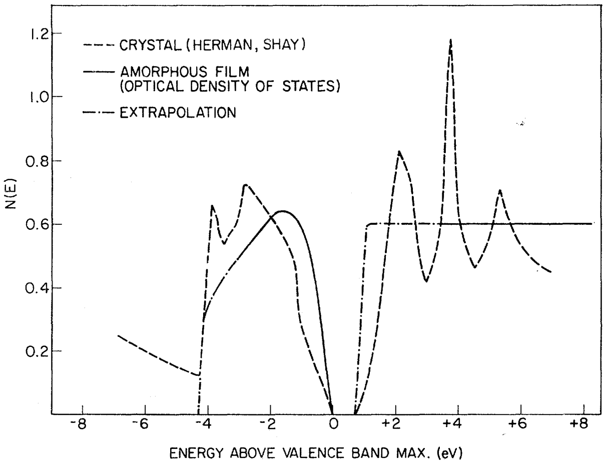

FIG. 2. Optical density of states for amorphous Ge as determined by photoemission compared with the electronic density of states for crystalline Ge calculated by Herman and Shay (Ref. 11). The vertical axis is in units of states per eV per atom for the crystal density of states and in arbitrary units for the optical density of states. The energy zero in both cases is taken at the maximum of the valence band.

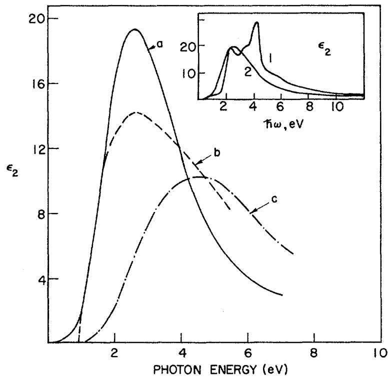

FIG. 3. The imaginary part of the dielectric constant, ϵ_2: *a*, as determined by Kramers-Kronig analysis of reflectivity data (Ref. 1); *b*, calculated from the optical density of states assuming nondirect transitions and constant matrix elements; *c*, calculated from the crystalline density of states assuming nondirect transitions and constant matrix elements. The insert shows for comparison ϵ_2 for (1) crystal Ge as determined by Philipp and Ehrenreich (Ref. 4) and (2) amorphous Ge as determined by Tauc (Ref. 1).

structure in the density of states associated with symmetry points on the surface of the Brillouin zone is absent in the amorphous-film results. Using the above results—the change in the valence- and conduction-band density of states and the change in optical selection rules—one can account for the observed changes in the optical properties as one goes from crystalline to amorphous germanium.

In the following Letter Herman and Van Dyke examine through a band calculation the effect of changing the Ge lattice constant from that of crystalline Ge to the average value of amorphous Ge. Combining this with the photoemission results, some insight can be obtained into the separate effects of lattice spacing and disorder.

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NEW INTERPRETATION OF THE ELECTRONIC STRUCTURE AND OPTICAL SPECTRUM OF AMORPHOUS GERMANIUM*

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The electronic density of states of amorphous germanium is simulated by that of a dilated germanium crystal having the same density as amorphous germanium (3.9 g/cm^3). This simulated density of states accounts quite nicely for some recent experimental results obtained by optical and photoemission techniques. The band structure and density of states of a suitable dilated germanium crystal may well be a better starting point for a more sophisticated analysis of the electronic structure of amorphous germanium than their counterparts in normal crystalline germanium.

Donovan and Spicer[1] have recently investigated the electronic structure of amorphous films of germanium using the highly successful photoemission technique.[2] Their experimental results indicate that the valence- and conduction-band density of states is considerably different in amorphous and crystalline germanium. These experimental findings stand in sharp contrast to earlier theoretical discussions of amorphous semiconductors,[3,4] in which the density of states of a disordered crystalline material is usually regarded as merely a slightly perturbed version of the density of states of the corresponding ordered crystalline material. Although these theoretical discussions emphasize the role played by the atomic disorder in fuzzing out the electronic density of states, particularly in the neighborhood of the band edges (band tailing effects), they usually ignore the important changes in electronic structure that can be produced by disorder-induced changes in the average atomic density (average number of atoms per unit volume).

In this Letter we will introduce a simple model