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EVIDENCE FOR A SHARP ABSORPTION EDGE IN AMORPHOUS Ge †

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A sharp optical absorption edge has been found at about 0.5 eV for amorphous Ge on a quartz substrate. The edge is comparable in sharpness with the direct edge of crystalline Ge. No evidence for tailing of the band edges into the forbidden band or for a high density of states in the forbidden band is found by these optical measurements. A new density determination gives a value of 4.54 ± 0.14 g/cm^3.

In an earlier Letter,[1] we described photoemission measurements on amorphous germanium in which the density of states was found to differ from that of crystalline Ge in two important ways. First, the sharp structure in the density of states which characterizes crystalline Ge was completely missing in the amorphous material. Second, the valence band appeared to have narrowed in the amorphous material with a marked increase in the number of states appearing within a volt of the band maximum. In this Letter we extend the earlier work by examining the sharpness of the band edges and density of states in the forbidden gap.

A number of authors[2,3] have discussed the possibility of the loss of any sharply defined band edge in amorphous semiconductors, such as amorphous Ge, and/or suggested that large numbers of states occur in the "forbidden" gap. We looked for evidence of such states in the photoemission energy distribution curves (EDC); however, no evidence was found. In fact, the leading edge of the amorphous EDC was found to be as sharp as that from single Ge crystals.[4] This suggests a relatively sharp edge in the filled density of states and led us to examine the infrared optical absorption for other evidence of a sharp band edge. We report here evidence for such edges. If there were large numbers of empty states lying between the Fermi level and the bottom of the conduction band, this would give rise to significant optical absorption in the infrared; we report here absorption measurements in this spectral range and find no evidence for large numbers of states in the gap. A new determination of the density is also reported.

The density measurements are of importance since theoretical considerations of amorphous Ge often depend on the density. A case in point is the recent calculation by Herman and Van Dyke[5] of the change in density of states of crystalline Ge when the density changes to that determined by Clark[6] for the amorphous material.

While the results of optical studies of amorphous Ge in the infrared and absorption-edge region have been reported by a number of authors,[6-8] in none of these studies has there been any attempt to achieve sensitivity to values of the absorption coefficient of less than 100 cm^{-1}. In order to determine α's in the range of 10 cm^{-1} in the region of the absorption edge, we have used special techniques[9] to deposit films of uniform thickness on extremely smooth (7-Å rms roughness) fused silica blanks as well as on commercially polished KCl substrates. The films were deposited at a rate of 10 Å/sec in a vacuum of 5×10^{-7} to 2×10^{-6} Torr. The vacuum system was let up to an atmosphere of dry argon and the films measured immediately in an atmosphere of dry N_2. Film thickness and uniformity were determined using fringes of equal chromatic order.[10] Average deviations in film thickness measured on random regions of the films have varied from ±4 Å on an 820-Å film to ±28 Å for a 20 654-Å

film. The smoothness of the films and substrates and the uniformity of the films have made possible precision (±0.001) measurements of the reflectance, R, and the transmittance, T, using the absolute reflectometer described by Bennett and Koehler.[11] Electron-transmission and -reflection diffraction and electron microscopy have been used to verify that the films studied optically have actually been amorphous. An iterative computation method[12] was used to determine n and k from the measured values of R, T, and t (film thickness) using an exact theoretical expression for R and T. Multiple reflections in the substrate were taken into account. Further details of the measurement and calculation will be given in a complete article.[9]

Figure 1 shows the absorption coefficient $\alpha = 4\pi k/\lambda$, determined in this work for Ge evaporated on a fused silica substrate[13] (prior results of Clark[6] for amorphous Ge, and Dash and Newman[14] for crystalline Ge are also included in Fig. 1). The striking thing about our results is the sharp absorption edge at about 0.58 eV. Note that the sharpness is comparable with that in crystalline Ge.

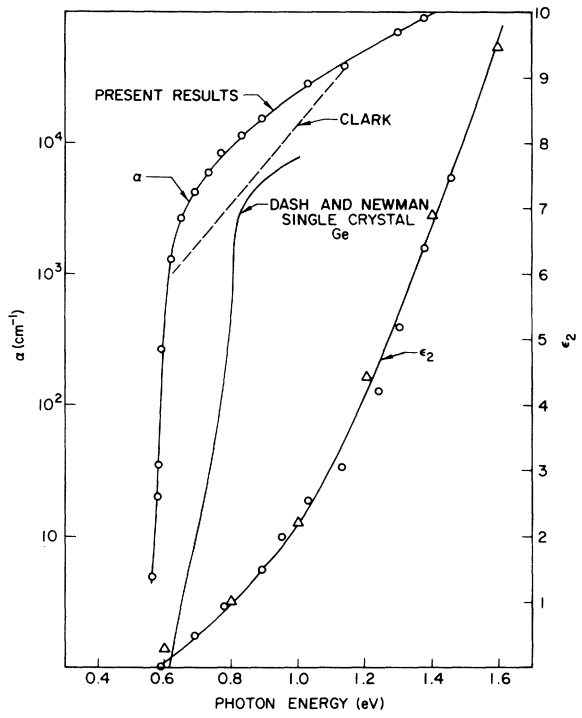

FIG. 1. The absorption coefficient α of amorphous Ge as determined in this study compared with the composite results of Clark (Ref. 6) and the single-crystal results of Dash and Newman (Ref. 14): The absorption edge in amorphous Ge is seen to be about as sharp as the direct edge in crystalline Ge. Also shown is $\epsilon_2 = 2nK$, determined both through the optical absorption and reflection measurements reported here (circles) and by a Kramers-Kronig analysis of the normal-incidence reflectance data (triangles). For $h\nu < 0.57$ eV, the upper limit on α is 10 cm^{-1}.

The measurements were extended to 0.1 eV with films deposited on KCl. Within the limits of the measurement, no absorption was found below 0.56 eV. Realizing the importance of these results, we have made measurements on a series of films of thicknesses 861, 5371, 12 386, and 20 654 Å evaporated on quartz. All of these films showed the sharp edge. With the thickest films studied, the precision of the measurements near 0.56 eV was ±0.001 and sensitivity to the extinction coefficient in the fourth decimal place was obtained giving an upper limit of 10 cm^{-1} to the measurements.

As an independent check on the optical constants determined by film measurements, we have obtained values of the optical constants by applying a Kramers-Kronig analysis to normal-incidence reflectance data. To do this we used the reflectance data taken by Donovan and Ashley[15] from 0.1 to 5.2 eV and the reflectance calculated from the n and k of Marton and Toots[16] from 7.7 to 25.0 eV, with a smooth extrapolation between the two results in the energy interval 5-7.5 eV. The ϵ_2 so determined is presented in Fig. 2. In Fig. 1, ϵ_2 values obtained by both methods are presented. As can be seen, excellent agreement is obtained between the ϵ_2's determined by the two methods in the region of overlap. Both methods of determining the optical constants gave $n = 4.00$ at 0.1 eV. No evidence is found for either the absorption band just below 1.0 eV or the absorption further in the infrared (0.1-0.4 eV) reported by Tauc[7] on films of comparable thickness deposited on KCl.

Using the results of our previous photoemission study, the precise values of ϵ_2 for $0.1 \leq h\nu \leq 1.5$ reported here, and the nondirect, constant-matrix-element model (NDCME),[17] an optical density of states (ODS) has been obtained in the region of the band edges and in the forbidden gap and added to that obtained previously. This is presented in Fig. 3. The valence-band edge was taken to be sharp in agreement with the photoemission results.[18] In addition to the sharp band edges, a "foot" is present below 1.0 eV in the conduction band similar to that which occurs for crystalline Ge. Because of the presence of this foot, ϵ_2 or α rises relatively slowly from the

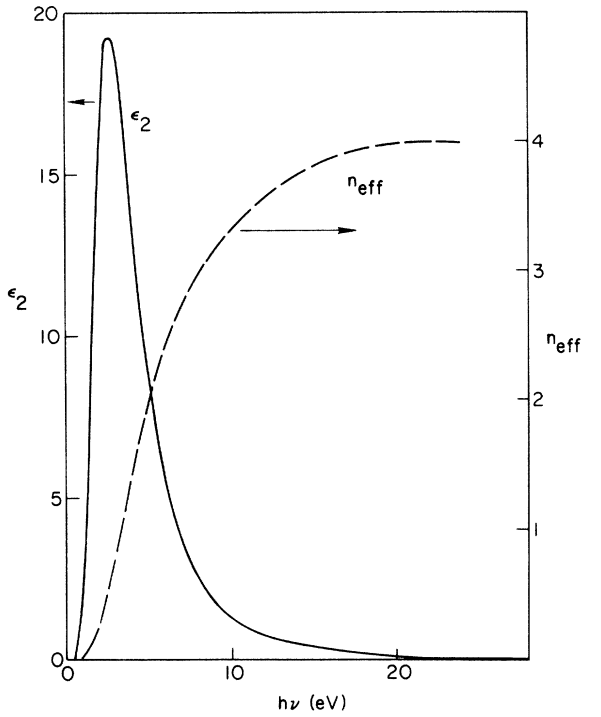

FIG. 2. $\epsilon_2(h\nu)$, the imaginary part of the dielectric constant, and n_{eff}, the effective number of electrons, versus $h\nu$ for amorphous Ge. n_{eff} was calculated from the oscillator-strength sum rule on $\epsilon_2(\omega)$ using the Kramers-Kronig-derived $\epsilon_2(\omega)$ and assuming a density of 4.7 gm/cm^3, which is 11% less than that of crystalline Ge.

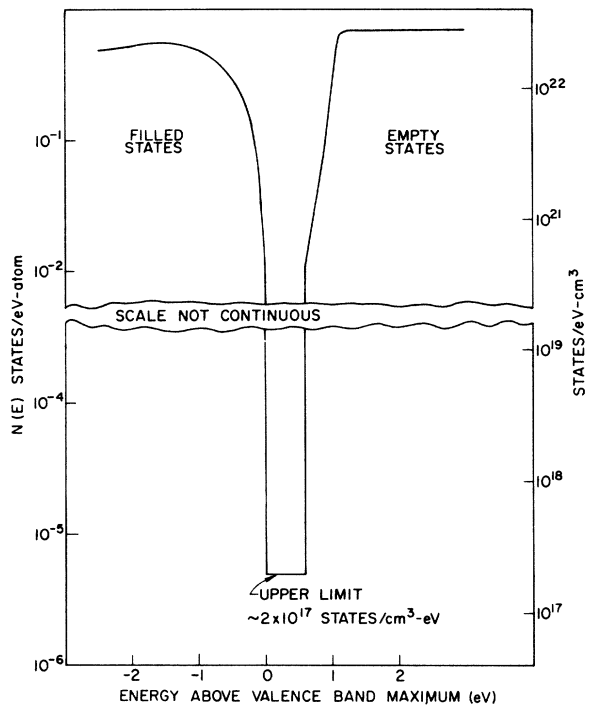

FIG. 3. The optical density of states or amorphous Ge as determined from photoemission data (Ref. 1) and the optical study reported here. The upper limit of 2 $\times 10^{17}$ states/cm^3 in the forbidden region is determined from the lower limit of the optical measurements. The vertical scale is chosen to correspond to 3 electrons per atom in the filled states.

band edge to 1.0 eV. Beyond 1.0 eV ϵ_2 or α rises more rapidly, as does the ODS. In prior work,[7] this slow rise in ϵ_2 or α below 1.0 eV was taken as evidence for "tailing" of states into the forbidden gap despite the fact that the values of α and ϵ_2 were somewhat larger than the intrinsic values for crystalline Ge within 0.5 eV of the crystalline band edge (see Fig. 1). The discovery of the sharp band edges reported in this work should remove any question of the amorphous absorption between 0.5 and 1.0 eV being due to "tailing" of states into the forbidden gap.

The absolute scales on Fig. 3 should be considered as only approximate. Only a relative ODS can be obtained directly from the NDCME analysis. The absolute values for the valence states in Fig. 3 were obtained by placing three electrons per atom[19] in those states. In the analysis all empty states are on the same relative scale, thus the conduction band and states in the forbidden gap fall on the same relative scale. The absolute scale for the states was set by assuming that the number of states below 4 eV was equal to that in crystalline Ge. Obviously, the absolute scales in Fig. 3 are not to be trusted to better than a factor of 2; however, they were included to give a better feel for the numbers involved. The upper limit of about 2×10^{17} states/cm^3 which was obtained for states in the forbidden gap was determined using 10 cm^{-1} as the upper limit for the absorption coefficient. The value of 2×10^{17} states/cm^3 is in reasonable agreement with the number of states determined by Grigorovici[20] from measurements of junction capacitance and by Clark[6] from Hall effect and conductivity measurements on rather thick films.

The density of samples was measured by weighing thin aluminum foils before and after depositing relatively thick (1-μ) films. The thickness of the film was determined interferometrically and the diameter of the circular film measured using an optical microscope. The density of amorphous Ge determined using this technique was 4.54 ± 0.14 g/cm^3 or a decrease of about 15% from crystalline Ge. This is less change than the density of 3.9 ± 0.4 g/cm^3 determined by

Clark by weighing thicker films that had shattered and separated from the substrates. Because of the problems with thick films, which are discussed later, as well as possible problems with included gases, Clark's value is probably too low, due to voids or pinholes.

In order to provide a check to our density determination, we applied the sum rule[21] on $\omega\epsilon_2(\omega)$. As can be seen from Fig. 2, the integral saturates nicely above 20 eV. Assuming a free-electron mass and four electrons per atom, one obtains from the sum rule a density 11% less than that of crystalline Ge, a value slightly less than that obtained by our direct measurements.

In the course of this work, we observed certain peculiarities with Ge amorphous films. The data reported here were obtained carefully so as to minimize any effects due to these peculiarities. With the thicker films (1-2 μ), changes would occur in the optical measurements 2 or 3 days after evaporation. Physically, the films would develop large numbers of pinholes. As films of this thickness tend to shatter, probably changes have also occurred in the microstructure of the films as well. These effects might lead to changes in density. The position of the absorption edge was found to be somewhat sensitive to evaporation conditions and substrates. Effects of this kind have been reported by Wales, Lovitt, and Hill[8] in studies of amorphous Ge. In the present study, absorption edges as low as 0.44-0.48 eV have been obtained on films deposited on KCl (these films were noticeably rougher than the films on fused silica) and on a film deposited on fused silica using an electron-beam gun as source. However, in all cases relatively sharp absorption edges were found with no measurable absorption from the edge to the transmission cutoff of the substrate. It is suspected that the variation of band gap with substrate is due to strain in the amorphous Ge.

An important contribution of this work is the delineation of the density of states near the band edges and the estimate of the upper limit of the density of states in the forbidden region (see Fig. 3). Lack of knowledge of the optical matrix elements makes it impossible to translate this exactly into a true density of states; however, it seems unlikely that important gross features, such as the sharpness of the band edges and the order of magnitude of the rather low upper limit of state density in the forbidden gap, $2.4\times10^{17}/\mathrm{cm}^3$, would be badly distorted by matrix-element effects.

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