

## Structural, Electrical, and Optical Properties of Amorphous Germanium Films

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Measurements of the ac and dc resistivity in the temperature range of 77–750°K and of the optical transmission and reflectance have been made on amorphous Ge films of 1000-Å to 7-μ thickness prepared by thermal evaporation. The resistivity of amorphous Ge films at room temperature is ~100 Ω cm, and increases with decreasing temperature. The conduction is thermally activated, with activation energy decreasing continuously from 0.5 eV at 600°K down to 0.069 eV at 77°K. At 450°C, the amorphous → crystalline transformation is observed and is accompanied by an irreversible decrease of resistivity by a factor of ≥20. The ac resistivity of amorphous films is found to decrease with frequency  $\omega$ . At high frequencies, the resistivity varies as  $\omega^{-n}$ , where  $n$  lies between 0.5 and 1, depending on temperature. The resistivity decreases with applied field beyond the Ohmic regime. At 77°K, the current increases exponentially with the square root of the field for fields  $\lesssim 2.5 \times 10^8$  V/cm. The optical absorption coefficient is found to vary as  $\exp(h\nu/0.14 \text{ eV})$ , in the energy range of 0.6–1.24 eV. Below 0.6 eV, the absorption coefficient falls rapidly down to a value of ~60 cm<sup>-1</sup> at 0.53 eV. The dc and ac electrical properties may be understood in terms of a mechanism of conduction by hopping of the carriers in the localized states (near the “fuzzy” band edges) caused by the fluctuation potential in the disordered lattice. The exponential decay of the optical-absorption coefficient with energy near the absorption edge and the presence of a red-shifted absorption edge are consistent with the crystalline energy-band diagram modified by the presence of acceptor states due to vacancies, by tailing, and by localization of states near the band edges due to disorder. The sharpness (which is comparable to that in single-crystal Ge) of the amorphous absorption edge is, however, not compatible with the “tailing” concept.

### I. INTRODUCTION

AMONG many elemental and alloy amorphous semiconductors, amorphous Ge films have been studied most extensively. The primary purpose of these structural,<sup>1–3</sup> optical,<sup>4–8</sup> and electrical<sup>8–13</sup> investigations on amorphous Ge films has been to make a comparative analysis of the nature of the short-range order, energy-band diagram (in particular, the tailing of the band edges and the existence of localized states near the band edges), and the transport mechanisms in amorphous (disordered) versus crystalline Ge lattice. Despite much published literature on the subject, the “amorphous Ge problem” is not satisfactorily understood at present. A brief and critical review of the significant developments in this field is presented in the following in order to emphasize the complexity of the problem to the reader.

<sup>1</sup> H. Richter and G. Breitling, *Z. Naturforsch* **13a**, 988 (1958).

<sup>2</sup> D. B. Dove (private communication).

<sup>3</sup> G. Breitling, *J. Vac. Sci. Technol.* **6**, 628 (1969).

<sup>4</sup> J. Wales, G. J. Lovitt, and R. A. Hill, *Thin Solid Films* **1**, 137 (1967).

<sup>5</sup> T. M. Donovan, W. E. Spicer, and J. M. Bennett, *Phys. Rev. Letters* **22**, 1058 (1969); W. E. Spicer and T. M. Donovan, *J. Non-crystalline Solids* (to be published).

<sup>6</sup> J. Tauc, R. Grigorovici, and A. Vancu, *Phys. Status Solidi* **15**, 627 (1966).

<sup>7</sup> J. Tauc, A. Abraham, L. Pajasová, R. Grigorovici, and A. Vancu, in *Physics of Non-Crystalline Solids*, edited by J. A. Prins (North-Holland Publishing Co., Amsterdam, 1965), p. 606.

<sup>8</sup> A. H. Clark, *Phys. Rev.* **154**, 750 (1967).

<sup>9</sup> P. P. Konorov and O. V. Romanov, *Fiz. Tverd. Tela* **2**, 1869 (1960) [English transl.: *Soviet Phys—Solid State* **2**, 1688 (1960)].

<sup>10</sup> L. Reimer, *Z. Naturforsch* **13a**, 536 (1958).

<sup>11</sup> R. Grigorovici, N. Croitoru, A. Devenyi, and E. Teleman, in *Proceedings of the International Conference on Physics of Semiconductors, Paris, 1964* (Dunod Cie., Paris, 1964), p. 423.

<sup>12</sup> P. A. Walley and A. K. Jonscher, *Thin Solid Films* **1**, 367 (1967).

<sup>13</sup> P. A. Walley, *Thin Solid Films* **2**, 327 (1968).

(1) The radial distribution function of amorphous Ge films as deduced from both x-ray<sup>1</sup> and scanning electron<sup>2</sup> diffraction data reveals that the first nearest neighbor distance and the coordination number (the value of which depends on the assumed value of the density of Ge films) are the same in amorphous and crystalline Ge. Therefore, one may conclude that (a) the short-range order of the crystalline phase is retained in the amorphous state, and (b) the densities of the two states should be equal. Values of the density of amorphous Ge films ranging from 5 to 28% below the crystalline value have been reported in the literature.<sup>5,8,14</sup> It is well known<sup>15</sup> that due to the atom-by-atom condensation process of a film, the “apparent” density of a thin film may be smaller than that of the corresponding bulk. The departure from the bulk value depends on the mobility of the adatoms during condensation, becoming increasingly marked in thin amorphous films where the mobility is nearly zero (i.e., the vapor atoms condense at or very near the point of impingement). Moreover, both the film density value and its accuracy depend strongly on the measurement technique. Measurement by x-ray technique,<sup>14</sup> for example, have yielded the highest (within 5% of the bulk) value of the density of amorphous Ge films. The measured density is not a true microscopic value. It includes the effects of physical voids and the microstructure and is, therefore, an “apparent” value. The low value of the apparent density does not indicate a dilated lattice and thus the energy-band calculations of

<sup>14</sup> T. B. Light, *Phys. Rev. Letters* **22**, 999 (1969).

<sup>15</sup> K. L. Chopra, *Thin Film Phenomena* (McGraw-Hill Book Co., New York, 1969), Chap. 4.

Herman and Van Dyke<sup>16</sup> are not applicable. Note these calculations predict an increased conductivity for the dilated lattice in disagreement with the observed behavior.

(2) Although systematic electron microscope investigations of the amorphous state and the amorphous  $\rightarrow$  crystalline transformation have not been made, it is clear from the electron micrographs that amorphous Ge films show no microcrystallites of dimension greater than  $\sim 20$  Å. On the basis of annealing and aging effects on the resistivity, it has been suggested<sup>12,17</sup> that amorphous Ge may consist of a mixture of amorphous and microcrystallite regions. (There are, however, alternative explanation of these effects.) A similar conclusion has been drawn by Brodsky and Title<sup>18</sup> from their electron-spin-resonance (ESR) studies. If the observed high density of uncoupled spins is due to dangling bonds, then the film must consist of discrete microcrystallites or "microamorphosites" separated by voids or large vacancy clusters. The interpretation of the ESR data is generally difficult and it may not be unique in this case. It is interesting to point out that ESR data yield nearly (within experimental error) the same value (approximately equal to that of a free electron) of the  $g$  factor for both amorphous and crystalline states of Si, SiC,<sup>18</sup> and Se.<sup>19</sup> The significance of this result is not clear at present.

(3) The temperature dependence of the resistivity of amorphous Ge films has been measured by various workers. Grigorovici *et al.*,<sup>11</sup> and Croitoru and Marinescu<sup>20</sup> obtained an activation energy  $\sim 0.55$  eV at high temperatures and  $\sim 0.2$  eV at low temperatures. The two values of the activation energy of conduction have been speculatively interpreted (in the absence of data on carrier concentration and mobility) in terms of intrinsic (band-to-band) and extrinsic (in the localized states caused by the disorder) conduction, respectively. On the other hand, the data of Clark,<sup>8</sup> Walley,<sup>13</sup> and Walley and Jonscher<sup>12</sup> show an activation energy decreasing monotonically from 0.65 to 0.02 eV as the temperature decreases from 700 to 25°K. The results at low temperatures have been interpreted (see Sec. IV for further discussion of this interpretation) in terms of conduction by hopping of the carriers in the localized states (caused by the disorder in the lattice) in the vicinity of the "fuzzy" valence band edge.

The interpretation of the conduction behavior of high-resistivity amorphous semiconductors is made difficult by the fact that it is not possible to measure the Hall coefficient with any confidence. Clark<sup>8</sup> made a very crude measurement of the Hall effect in amorphous Ge

films and showed them to be  $n$ -type with a carrier density  $\sim 10^{18}$  cm<sup>-3</sup>. On the other hand, using the bias dependence of the barrier capacitance of amorphous Ge- $n$ -type crystalline Ge junction, Grigorovici *et al.*<sup>11</sup> established amorphous Ge films to be  $p$  type with a carrier concentration  $\sim 10^{17}$  cm<sup>-3</sup>. We may note that polycrystalline Ge films prepared under high vacuum conditions invariably yield  $p$ -type<sup>15</sup> Hall effect (presumably due to acceptorlike vacancies) irrespective of the conductivity type of the starting bulk material.

(4) Thermoelectric power studies of Grigorovici *et al.*<sup>21</sup> show amorphous Ge to be  $p$  type with reversal to  $n$  type below 280°K. Both the reversal of sign and the high magnitude of the thermopower are unusual effects and need to be confirmed.

(5) If the band edges are "fuzzy" and the states in the vicinity of the crystalline state edges are localized due to lattice disorder (this point is discussed later in Sec. IV), then "hopping" conduction is expected to take place in the localized states. Conduction by hopping is expected to exhibit frequency dependence. No such dependence has been observed by Walley<sup>13</sup> at frequencies up to 20 kc. This does not, however, rule out frequency-dependent conduction, since this frequency may be smaller than that for the trap-to-trap transition process.

(6) A direct measurement of the band parameters by the tunnel-spectroscopy technique reported by Nowachuku and Kuhn<sup>22</sup> showed that the position and separation of band edges of the amorphous films was similar to that for the crystalline Ge. Unfortunately, the same authors have not been able to subsequently reproduce their results (unpublished) and thus, in effect, their conclusions remain questionable.

(7) Comprehensive studies of the optical-absorption spectrum (from infrared to ultraviolet) of amorphous versus crystalline Ge by Tauc *et al.*<sup>6,7</sup> and their interpretation have suggested that (a) although the bands in the amorphous films are broadened, both the conduction and valence bands are not much changed by the transition from crystalline into the amorphous state, (b) the density-of-states functions in the valence and conduction bands are essentially the same in both states, (c) the fundamental absorption edge is nearly the same in both cases, (d) the transition corresponding to the fundamental edge in the amorphous state is indirect (only energy conserved), and (e) the  $\mathbf{k}$  vector is sufficiently well defined and conserved so as to yield the infrared absorption peaks (corresponding to the transitions between the subbands in the valence band) at nearly the same photon energy in both states.

Optical-absorption studies on amorphous Ge films in the vicinity of the fundamental edge by Clark,<sup>8</sup> and by Wales *et al.*<sup>4</sup> show an exponential decay of the absorp-

<sup>16</sup> F. Herman and J. P. Van Dyke, Phys. Rev. Letters **21**, 1575 (1968).

<sup>17</sup> N. F. Mott, Advan. Phys. **16**, 49 (1967).

<sup>18</sup> M. H. Brodsky and R. S. Title, Phys. Rev. Letters **23**, 581 (1969).

<sup>19</sup> P. I. Sampath, J. Chem. Phys. **45**, 3519 (1966).

<sup>20</sup> N. Croitoru and N. Marinescu, Phys. Rev. (Bucharest) **9**, 202 (1964).

<sup>21</sup> R. Grigorovici, N. Croitoru, and A. DeVenyi, Phys. Status Solidi **16**, K143 (1966).

<sup>22</sup> A. Nowachuku and M. Kuhn, Appl. Phys. Letters **12**, 163 (1968).

tion coefficient  $\alpha$ , i.e.,  $\alpha \propto \exp(h\nu/\Delta)$ , where  $\Delta=0.14$  eV. The absolute values of  $\alpha$  obtained by Wales *et al.* are  $\sim 2.5$  times lower than that of Clark. The exponential decay of  $\alpha$  has been interpreted to suggest an exponential tailing of the density of states in the valence band of the amorphous state.

In sharp contrast to the results cited above, photoemission studies of Donovan and Spicer<sup>23</sup> on amorphous Ge have revealed that (a) the structure in the density of states in the conduction band of the crystalline state disappears in the amorphous state; (b) the peak of the density of states in the valence band is shifted 1.5 eV to higher energy with respect to the crystalline density of states, and detailed structure associated with crystal symmetry points is absent; and (c)  $k$  conservation is not an important selection rule for the amorphous state. Further, precise measurements of the absorption coefficient of amorphous Ge films (deposited on supersmooth substrates) by Donovan *et al.*<sup>5</sup> showed that (a) the functional dependence of the decrease of  $\alpha$  with decreasing energy in the vicinity of the optical edge differs considerably from that of Clark,<sup>8</sup> and Wales *et al.*<sup>4</sup> although in some samples a similar exponential decay is observed, (b) a rapid fall of  $\alpha$  is observed at  $\sim 0.5$ – $0.6$  eV (the range depending on the sample preparation), the fall being just as sharp as observed<sup>24</sup> in single-crystal Ge samples, (c) the absolute value of  $\alpha$  drops to  $\sim 6$  cm<sup>-1</sup> at  $\sim 0.55$  eV, which corresponds to a small ( $<10^{18}$ ) optical density of states. These results and their interpretation suggest that the band edges in the amorphous state retain the sharpness found in the crystalline state, and further, that the optical density of states in the "modified" forbidden gap is negligible.

Electroreflectance studies by Piller *et al.*<sup>25</sup> show that the fundamental edge of amorphous Ge is only slightly ( $\sim 0.1$  eV) shifted from the crystalline value. All other electronic structures in the valence band associated with the crystal symmetry disappear in the amorphous state. A second weak and broad electroreflectance peak at  $\sim 0.2$  eV below the fundamental edge has been observed. Piller *et al.* have speculated that the observed two peaks may be due to the strong  $p$ -type character of amorphous films with transitions from heavy- and light-hole states in the valence band. This interpretation would clearly require well defined subbands in the valence band of the amorphous state.

The preceding discussion makes it clear that various basic aspects of the amorphous Ge problem are not understood, and further that there exist serious discrepancies in the results reported by different workers. Structure-sensitive properties of thin films are notoriously dependent on numerous poorly understood deposition conditions. This fact may explain to some extent

differences in behavior of Ge films reported by different workers using ill-defined deposition conditions. It is generally recognized by thin-film workers that, in order to obtain meaningful data, different types of measurements should be done on the same films. We have, therefore, carried out structural, optical, and electrical studies of the same amorphous Ge films and the results are reported here.

## II. EXPERIMENTAL DETAILS

Amorphous Ge films of thickness ranging from 300 Å– $7\ \mu$  were prepared by thermal evaporation of high-purity Ge from a tungsten basket (or a graphite boat for thick films) in an ion pump system maintained at  $\sim 10^{-7}$  Torr during deposition. Films were deposited on water-cooled  $15 \times 14$ -mm<sup>2</sup> substrates of ultrasonically cleaned glass, freshly cleaved single-crystal rocksalt and mica, rocksalt polished with water and rinsed with alcohol, and commercially available optical smooth quartz. Films were deposited simultaneously on several substrates at a typical rate  $\sim 10$  Å/sec. A large ( $\sim 30$ -cm) distance between the vapor source and the substrates was used to ensure the uniformity of the film thickness over the substrate surface and also to minimize radiation heating of the substrate from the vapor source.

The thickness of the films was measured gravimetrically (with a microbalance) and interferometrically. The interferometric values were in good agreement with those obtained from the spectrophotometric data using bulk values of the optical constants. The accuracy of the film thickness increased with the thickness and it ranged from a fraction of a percent for thick films to several percent for thin films. Electron microscopy and reflection and transmission electron diffraction studies were carried out in Hitachi HU-11A to examine the structural order and microstructure of films. For transmission studies, thin films (with a support layer of carbon for ultrathin films) were floated off rocksalt.

Optical reflectance and transmittance measurements were made at 300°K on films deposited on all substrates using a double-beam spectrophotometer (Perkin Elmer 137G). Both the accuracy and reproducibility of these measurements were about 1%.

The dependence of the electrical resistance on temperature over the range 750–77°K, on frequency up to 10<sup>6</sup> cps, and on applied electric field was studied along the plane of the films deposited on glass substrates across a 64- $\mu$ -wide specimen. The specimens were obtained by masking the film with a 44 B&S gauge copper wire during the vapor deposition of the electrodes of In, Au, or Al films.

## III. RESULTS AND DISCUSSION

*Structure.* Thin Ge films evaporated onto any substrate at  $\sim 25^\circ\text{C}$  over a considerable range of deposition

<sup>23</sup> T. M. Donovan and W. E. Spicer, Phys. Rev. Letters **21**, 1572 (1968).

<sup>24</sup> W. E. Dash and R. Newman, Phys. Rev. **99**, 1151 (1955).

<sup>25</sup> H. Piller, B. O. Seraphin, K. Markel, and J. E. Fischer, Phys. Rev. Letters **23**, 775 (1969).

conditions exhibit a diffuse electron diffraction pattern of the type shown in Fig. 1(a). Diffuse diffraction patterns may be associated with a small ( $<50 \text{ \AA}$ ) crystallite size or a disordered structure. Above a certain value of the deposition temperature, Ge films yield a sharp diffraction pattern [Fig. 1(b)] characteristic of a crystalline material. The deposition temperature above which a crystalline pattern is obtained is determined<sup>15</sup> by the adatom mobility during condensation and as such depends on the vacuum (in particular, the partial pressure of reactive gases, e.g., oxygen), rate of deposition, the binding energy and the activation energy for surface diffusion of adatoms on the substrate surface, surface temperature during deposition, kinetic energy of the impinging atoms, etc. The range of values from  $350\text{--}120^\circ\text{C}$  reported in the literature<sup>26,27</sup> are clearly a consequence of these variables being different in different cases. An observation of significance to studies on thick amorphous Ge films is illustrated by the reflection patterns [Fig. 1(c)] of  $7\text{-}\mu$ -thick film prepared near the room temperature. It is clear that with increasing thickness, the clean and smooth film surface (the temperature<sup>15</sup> of which can be significantly higher than that indicated by the thermocouple attached to the substrate due to heating by radiation from the vapor source and due to the heat of condensation) can provide sufficient adatom mobility to yield a partially oriented crystalline film superimposed on an initially amorphous film. It is, therefore, important to keep the substrate temperature at or below  $25^\circ\text{C}$  in order to obtain thick ( $\geq 1 \mu$ ) homogeneously amorphous films.

Electron micrographs of thin ( $\leq 2000 \text{ \AA}$ ) Ge films

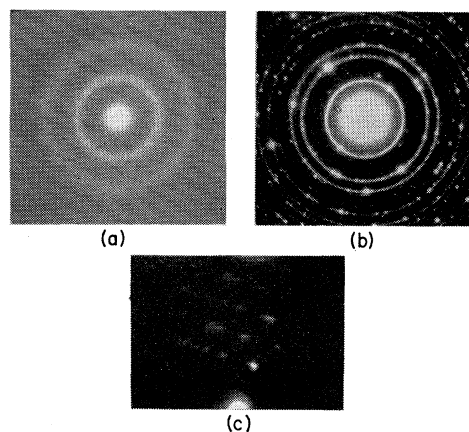


FIG. 1. Transmission electron diffraction patterns of  $\sim 600\text{-}\text{\AA}$ -thick Ge film evaporated onto cleaved NaCl. (a) Amorphous film deposited at room temperature; (b) polycrystalline film deposited at  $350^\circ\text{C}$ ; (c) reflection electron diffraction pattern of  $\sim 7\text{-}\mu$ -thick Ge film deposited on glass substrate at  $25^\circ\text{C}$  from a graphite boat at a rate  $\sim 10 \text{ \AA}/\text{sec}$ .

<sup>26</sup> R. F. Adamsky, K. H. Behrnt, and W. T. Brogen, *J. Vac. Sci. Technol.* **6**, 542 (1969); R. F. Adamsky, *J. Appl. Phys.* **40**, 4301 (1969).

<sup>27</sup> E. Krikorian and R. J. Sneed, *J. Appl. Phys.* **37**, 3665 (1966).

deposited on rocksalt at  $\sim 25^\circ\text{C}$  reveal no discernible microstructure that can be associated with microcrystallites. If microcrystallites exist, their size must be smaller than the resolution of the microscope used, that is  $\sim 10 \text{ \AA}$ . That these films are indeed amorphous can be verified by studying structural changes in the film. We define an amorphous phase as one which exhibits diffuse diffraction patterns and which transforms spontaneously to the crystalline phase at a well-defined temperature via random nucleation centers and is attended by the release of heat of transformation ( $\sim$ fraction of the heat of fusion). Germanium films satisfy these criteria as verified by the observed kinetics of the amorphous  $\rightarrow$  crystalline transformation in the heating stage of the electron microscope. Owing to higher temperature at the boundaries of the wire grid (which supports the electron-microscope specimen), the transformation is initiated at the grid corners and then it propagates inward. The transformation initiates rapidly via randomly distributed nucleation centers as shown in Fig. 2(a). Owing to strong Bragg diffraction, the crystalline regions appear bright on a uniformly dark background of the amorphous matrix. After the initial rapid nucleation, the crystalline regions grow slowly. With a further increase in temperature, the crystalline regions grow in number and size as shown in the micrograph of Fig. 2(b). It is noteworthy that microregions of crystalline and amorphous phases can and do coexist as a mixture in a stable intermediate phase. If the size of the crystalline regions is small, the electron diffraction patterns will continue to remain diffuse. Thus, it is clear that the observation of diffuse electron diffraction patterns is a necessary but by no means sufficient condition for the existence of a completely amorphous phase. In view of this observation, it is possible that thick films used by some investigators indeed consisted of a mixture of amorphous and crystalline regions.

It should be mentioned that the slow growth of the crystalline phase is not typical of amorphous semiconductors. For example,<sup>28</sup> both the nucleation and growth of the crystalline phase in amorphous GeTe films is very rapid. The difference in behavior of Ge and GeTe is probably due to the difference in the heat of transformations which provides the driving force for growth. Our measurement of the heat of transformation of Ge shows it to be  $<100 \text{ cal/g mole}$  which is about 10 times smaller than that for GeTe. The slow rate of crystallization of the amorphous phase is reflected in gradual changes in the electrical resistance during transformation of the film. The resistance begins to fall at a temperature of  $450^\circ\text{C}$  for Ge films deposited on glass, and the transformation is complete with a temperature increment of  $\sim 25^\circ\text{C}$  (as compared with  $1.5^\circ\text{C}$  for GeTe).<sup>28</sup>

Large thermal and intrinsic stresses  $\sim 10^9 \text{ dyn/cm}^2$

<sup>28</sup> K. L. Chopra and S. K. Bahl, *J. Appl. Phys.* **40**, 4171 (1969).

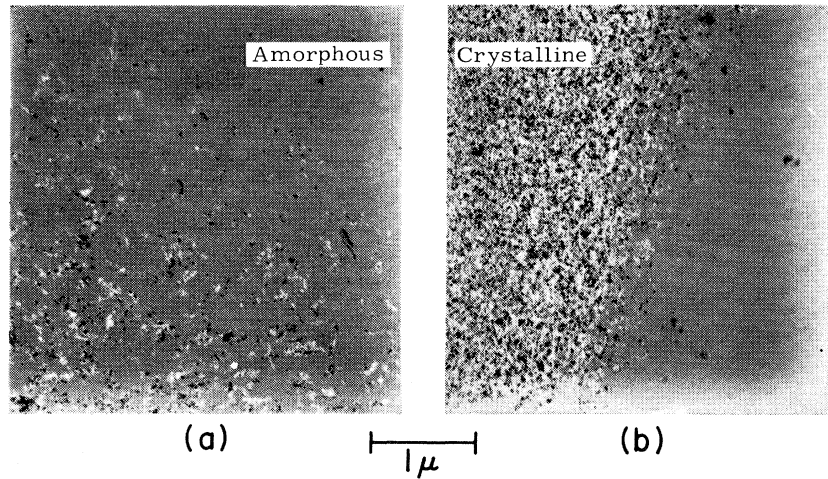


FIG. 2. Electron micrographs of two stages of amorphous  $\rightarrow$  crystalline transformation of a 600-Å-thick Ge film supported on a microscope stainless-steel grid and heated in the microscope heating stage. The micrograph (a) shows the randomly distributed nucleation centers of the crystalline phase obtained on heating of the amorphous film to a temperature of 350°C. The growth of the crystalline phase at higher temperatures is shown in (b).

are known<sup>29</sup> to exist in vapor-deposited films of all types of materials. As a result of these large stresses (more detailed explanation is not known at present), films crack, peel off the substrate, and, in some cases, show oscillatory buckle waves. Thick amorphous films develop long rectangular cracks (easily visible with magnifications  $\sim 10$ –50) and also tend to peel off the substrates. By carefully selecting suitable substrates and other deposition conditions on primarily an empirical basis, it is possible to get frequently crack-free adherent amorphous films as thick as  $\sim 10 \mu$ . It is clear, therefore, that all films must be examined in the microscope before the properties are measured.

The density of our amorphous Ge films was determined from the film weight and interferometrically determined film thickness. The value for a 2- $\mu$ -thick film was found to be  $4.7 \pm 0.2 \text{ g cm}^{-3}$ . This value is about 11% smaller than the bulk value. As emphasized already in Sec. I, this is an "apparent" value which increases with the film thickness, which can be changed by several percent by changing the rate of deposition or substrate temperature.

**Electrical properties.** The electrical resistivity of amorphous Ge films of different thicknesses at 300°K is  $\sim 100 \Omega \text{ cm}$  (with small deviations depending on deposition conditions) as compared with a value of  $\sim 0.2 \Omega \text{ cm}$  for crystallized (transformed) films. The resistivity of crystalline films decreases with increase of temperature corresponding to an activation energy  $\sim 0.1 \text{ eV}$  in the temperature range of 25–400°C. The inverse temperature dependence of the resistivity of an amorphous film is shown in Fig. 3. The observation of the monotonic variation of the resistivity and the absence of a discrete activation energy is similar to that reported by Clark,<sup>8</sup> and Walley and Jonscher (WJ).<sup>12</sup> Our values of the activation energy at and below 300°K as calculated from the slopes of the curve (Fig. 3) are comparable to those of WJ. The maximum value of the

activation energy near the transformation temperature is  $\sim 0.5 \text{ eV}$  (as compared with 0.65 eV reported by WJ). At the amorphous  $\rightarrow$  crystalline transformation temperature ( $\sim 720^\circ\text{K}$ ), the resistivity falls rapidly. The

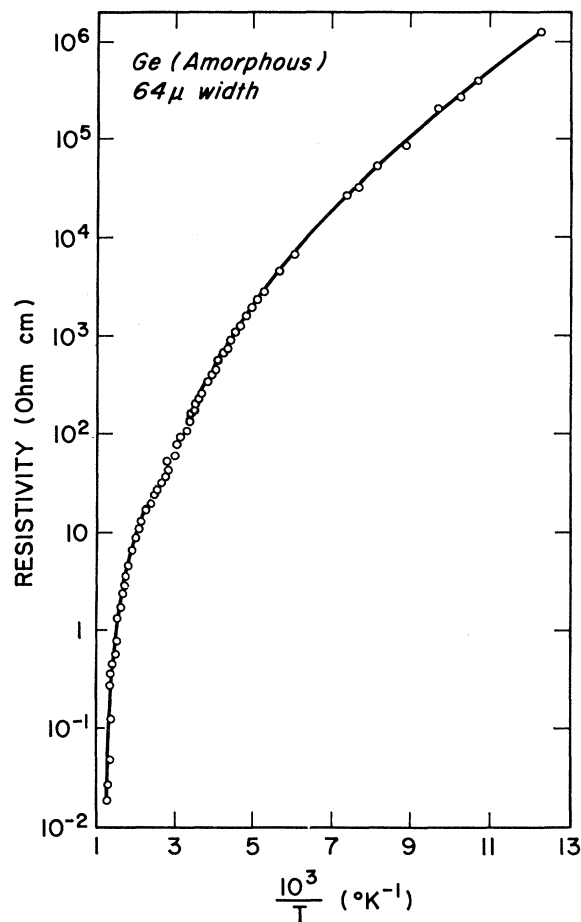


FIG. 3. The inverse temperature dependence of the  $\log_{10}$  of the electrical resistivity of 1.5- $\mu$ -thick and 64- $\mu$ -wide amorphous Ge film deposited on glass at room temperature.

<sup>29</sup> See Ref. 15, Chap. V.

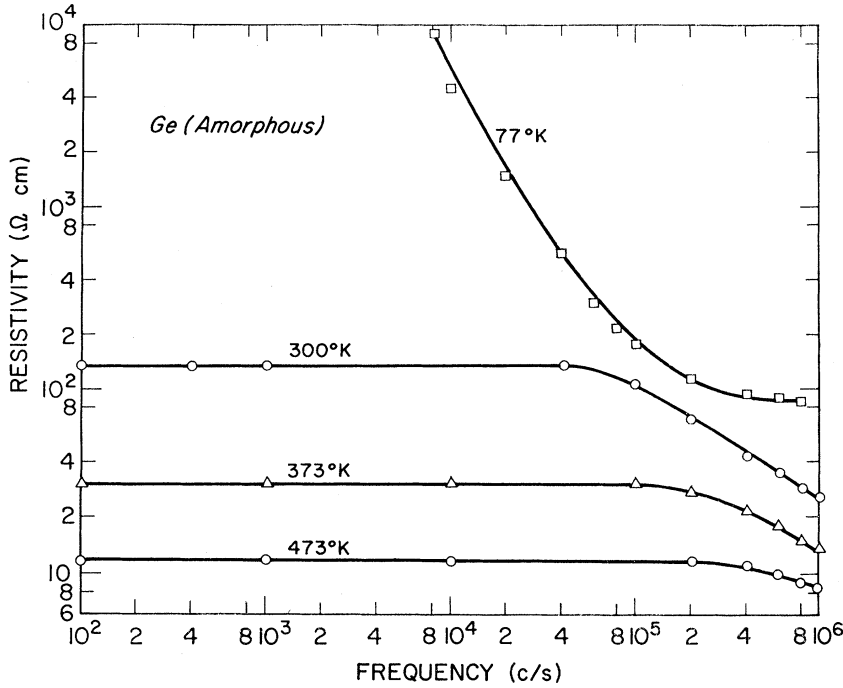


FIG. 4.  $\text{Log}_{10}$  resistivity versus  $\text{log}_{10}$  frequency measured at different temperatures for a  $64\text{-}\mu$ -wide amorphous Ge film ( $1.5\text{-}\mu$ -thick) deposited on glass at room temperature.

corresponding high value ( $\sim 1.5$  eV) of the activation energy is obviously not a physically significant parameter for a conduction process.

In contrast to little or no frequency dependence of the ac resistivity of crystalline Ge films, the amorphous films exhibit marked dependence as shown in Fig. 4.

The data show that the ac resistivity decreases with frequency  $\omega$  as  $\omega^{-n}$  above a minimum frequency. The value of  $n$  increases with decreasing temperature and lies between 0.5 and 1.0. The minimum frequency above which frequency dependence is observed is higher at higher temperatures.

Amorphous films exhibit Ohmic and nonlinear (non-Ohmic) dependence of the current  $I$  on field  $F$  at high fields as shown in Fig. 5. The lower the temperature, the lower is the minimum field above which non-Ohmic behavior is observed. The current in the non-Ohmic region generally follows an  $F^n$  dependence. At intermediate fields, the value of  $n$  at  $77^\circ\text{K}$  is 3.5. With further increase in the field,  $n$  increases rapidly until thermal breakdown of the film occurs. An alternative representation of the data on the field dependence of current is shown in Fig. 6. It is seen that the data at high fields (from  $\sim 2.5 \times 10^3$  to  $10^5$   $\text{V/cm}$  at  $77^\circ\text{K}$ ) follow

$$I \propto \exp(\beta F^{1/2})$$

dependence. The value of  $\beta$  at  $77^\circ\text{K}$  is 0.026.

A further discussion and interpretation of the electrical data is presented in Sec. IV.

**Thermoelectric power.** Preliminary measurements of the thermoelectric power of amorphous Ge films against gold-film electrode show the thermopower to be small at or below room temperature. The sign below room temperature appears to be negative. At higher temperatures, the thermopower rises rapidly from  $\sim 1 \mu\text{V}/^\circ\text{C}$  at  $\sim 40^\circ\text{C}$  to  $600 \mu\text{V}/^\circ\text{C}$  at  $\sim 140^\circ\text{C}$ , and the sign corresponds definitely to  $p$ -type conduction. Results of these

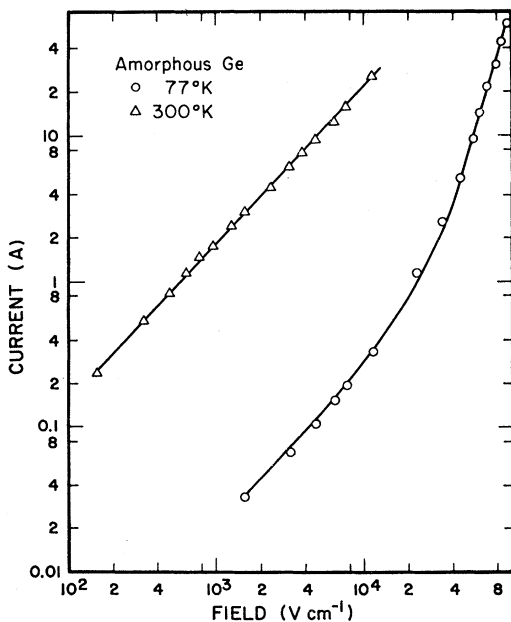


FIG. 5.  $\text{Log}_{10}\text{-log}_{10}$  variation of current ( $I$ ) with field ( $F$ ) for a  $64\text{-}\mu$ -wide,  $1.5\text{-}\mu$ -thick amorphous Ge film at 300 and  $77^\circ\text{K}$ . At  $77^\circ\text{K}$ , the  $I \propto F$  changes to  $I \propto F^{3.5}$  at fields above  $2 \times 10^4$   $\text{V/cm}$ .

studies on Ge (and GeTe films) will be published separately.

*Optical properties.* The dependence of the absorption coefficient  $\alpha$  of amorphous films on the photon energy  $h\nu$  is shown in Fig. 7. In view of the importance of these data, several comments are in order here. (a) The results shown in Fig. 7 are a partial representation of the large number of overlapping data on films of different thicknesses deposited on polished rocksalt, smooth quartz, and glass substrates. (b) The absorption coefficient was calculated from the observed reflectance  $R$  and transmittance  $T$  of the films using the well-known approximate relation  $T = (1-R)^2 e^{-\alpha t} / 1 - R^2 e^{-2\alpha t}$  in the interference-free region. Here,  $t$  is the interferometrically determined film thickness. Measurements in the overlapping interference-free regions throughout the desired range of photon energy were made possible by using a large range (1000 Å to 7  $\mu$ ) of film thicknesses. (c) Most, but not all, films prepared under the best possible and reasonably reproducible deposition conditions yielded similar values of  $R$  and  $T$ , irrespective of the substrate. (d) The small values of  $\alpha$  were measured with as thick and adherent films as were possible to obtain free of cracks. The accuracy of the calculated  $\alpha$  is a few percent at high values ( $\geq 100$ ) but is very poor at lower values of  $\alpha$  due to the dominant effect of the errors in the measurement of  $R$ . We estimate that the values of  $\alpha$  below 100  $\text{cm}^{-1}$  may be in error by a factor of up to 2.

The spectral dependence (Fig. 7) shows that in the

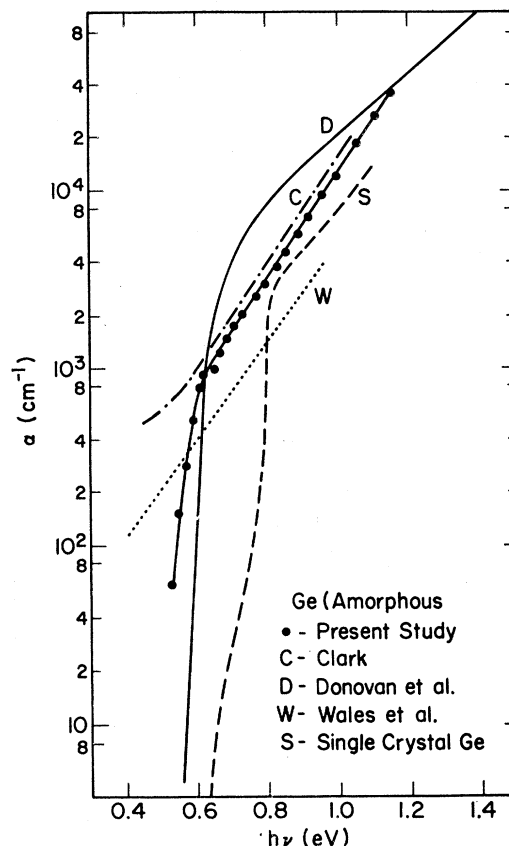


FIG. 7. Comparison of the photon-energy dependence of the absorption coefficient  $\alpha$  of amorphous Ge films obtained by different workers. Results of Dash and Newman (Ref. 24) on single-crystal Ge are also shown.

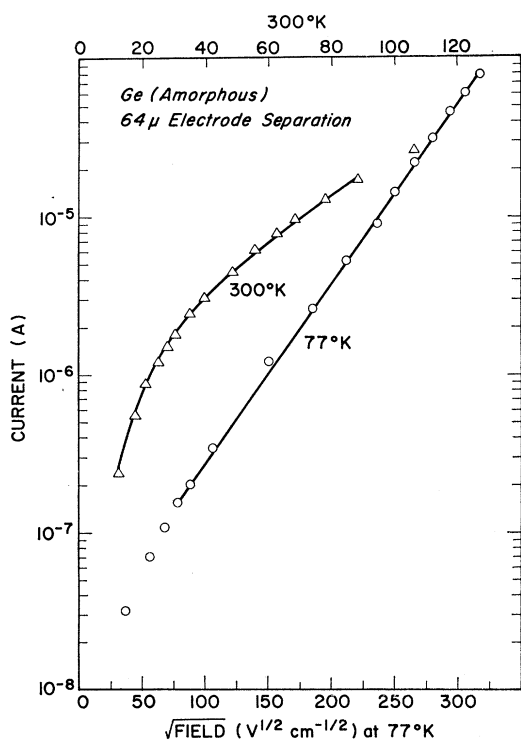


FIG. 6. Replot of the data of Fig. 5 in the form  $\log_{10} I$  versus  $\sqrt{F}$ .

range 0.6–1.2 eV,  $\alpha$  varies as  $\exp(h\nu/\Delta)$  where the inverse slope  $\Delta = 0.14$  eV. This value of  $\Delta$  is the same as that calculated from the results of Clark,<sup>8</sup> and Wales et al.<sup>4</sup> (also shown in Fig. 7 for comparison). Donovan et al.<sup>5</sup> have reported that the functional form of the energy dependence of  $\alpha$  above 0.6 eV is generally different from exponential and is influenced strongly by the substrate on which film is deposited. In some cases, these authors also observed exponential dependence similar to that reported by other workers. The absolute values of  $\alpha$  obtained by different workers differ considerably from each other. This discrepancy is certainly due to the variations in the optical quality of films prepared under different deposition conditions used by different workers. In the light of this observation, the significance of the absolute value of  $\alpha$  should be considered with prudence.

Below 0.6 eV, a definite change in the slope of  $\alpha$ -versus- $h\nu$  curve takes place, and  $\alpha$  falls rapidly in a way qualitatively similar to that reported by Donovan et al.<sup>5</sup> and also similar to the behavior of single-crystal Ge (see Fig. 7). The lowest value of  $\alpha$  observed by us at 0.53 eV is 60  $\text{cm}^{-1}$  (which may be in error by a factor

of up to 2) compared with  $\sim 6 \text{ cm}^{-1}$  at 0.55 eV reported by Donovan *et al.* Thus, although a rapid fall of  $\alpha$  is indicated by our data, the lowest value of  $\alpha$  is still an order of magnitude higher than that reported by Donovan *et al.* Further discussion of these results is presented in the following section.

#### IV. INTERPRETATION OF DATA

In order to interpret the electrical and optical data, we must assume an energy-band diagram for amorphous Ge. The band theory of solids has been developed on the basis of the existence of the translational symmetry (that is, long-range order) and the resulting periodic potential throughout a crystalline solid. The theoretical extension<sup>17,30-33</sup> of these concepts to both one- and three-dimensional disordered lattices concludes that as long as the short-range order is maintained, the essential features of the crystalline lattice band structure are retained with the following two significant modifications. Due to the fluctuations in the value of the distance between neighboring atoms, the periodic potential shows fluctuations of two types: (a) The maxima and minima of the periodic potential shift in a random fashion and thereby produce "tailing" (also called "smearing" or "fuzziness") of the band edges. (b) The heights of the maxima and minima of the periodic potential fluctuate randomly. As a result, some band (allowed) states which are represented by wave (Bloch) functions extending throughout the lattice become localized in the disordered lattice. Localization means that the wave function has the probability amplitude decreasing exponentially with distance from the center of localization. The average conductivity is zero at  $T=0$  in localized states.

It is not possible to calculate the degree of tailing of band edges without a detailed knowledge of the fluctuation potential. It is clear, however, that the larger the fluctuation, the larger the tailing is. Thus, the effective band gap becomes narrower in the disordered lattice. Tailing may extend deep into the forbidden zone and may even result in the overlapping of the conduction and valence bands. The localization of states has been discussed and reviewed by Mott.<sup>17,31</sup> On the basis of a speculative criterion, he has concluded that the localized and nonlocalized states are separated by a critical electron energy at which the electron mean free path and the electron wavelength are comparable. How sharply defined this energy is not yet clear.

Since the short-range order is known<sup>1,2</sup> to be the same in crystalline and amorphous Ge, it is reasonable to expect that the energy-band diagram of amorphous Ge

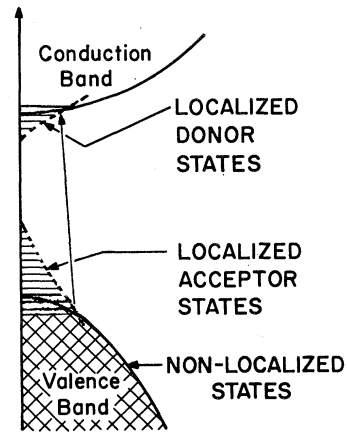


Fig. 8. Schematic representation of a proposed energy-band diagram of amorphous Ge. The band edges of the crystalline Ge lattice are shown by the solid curve while those of amorphous Ge are shown by the dotted curve. The shaded regions correspond to localized states. The cross-hatched regions of the valence band and the unmarked regions of the conduction band correspond to allowed or nonlocalized states. The asymmetry of localized regions is due to the presence of acceptor type of defects.

is essentially the same as that of crystalline Ge, except that the presence of acceptor states due to large concentration of vacancies, tailing of bands, and localization of states in the vicinity of the band edges must be taken into account. A plausible energy-band diagram is shown schematically in Fig. 8. We should emphasize that the diagram is only of qualitative significance. Further, due to the lack of knowledge we have assumed that the acceptor states form a smeared-out band in the valence band tail. To explain the observed<sup>21</sup> reversal of the sign of thermopower of amorphous Ge at low temperatures, Mott<sup>17</sup> proposed an acceptor band above the valence band. In view of the questionable nature of the thermopower data of Grigorovici *et al.*,<sup>21</sup> such a band has not been shown in Fig. 8.

Mott<sup>31</sup> has discussed the carrier mobility in localized and nonlocalized states near the critical energy. He has shown that the mobility due to conduction by hopping in the localized states is considerably ( $\sim 100$  times) smaller than that in the nonlocalized states. This conclusion results from the fact that the phonon frequency is  $\sim 10^2$  smaller than the electron collision frequency to which the respective mobilities are proportional to.

An electron in the localized state is effectively trapped by the polarized and/or distorted lattice and it can move from one localized state (or trapping center) to another only by "hopping." The low-mobility hopping process of conduction in a disordered lattice thus yields an apparent energy gap in which mobility is negligible, and therefore the dc conductivity is zero at low temperatures. This energy gap has been named<sup>34</sup> as "mobility gap" in contrast with the conventional

<sup>30</sup> A. I. Gubanov, *Quantum Electron Theory of Amorphous Conductors* (Consultants Bureau Enterprises, Inc., New York, 1965).

<sup>31</sup> N. F. Mott, *Phil. Mag.* **19**, 835 (1969); *J. Non-Cryst. Solids* **1**, 1 (1968); *Phil. Mag.* **17**, 1259 (1968); *Contemp. Phys.* **10**, 125 (1969).

<sup>32</sup> L. Banyai, in Ref. 11, p. 417.

<sup>33</sup> K. Moorjani and C. Feldman, *Rev. Mod. Phys.* **36**, 1042 (1964).

<sup>34</sup> M. H. Cohen, H. Fritzsche, and S. R. Ovshinsky, *Phys. Rev. Letters* **22**, 1065 (1969).



crystalline semiconductor "band gap" in which the density of states is zero.

dc *Conduction*. In the proposed energy-band model (Fig. 8), electrical conduction can take place by two parallel processes: (a) by intrinsic excitation across the mobility gap, and (b) by hopping process in the localized states in the valence band. The dc resistivity in the first case will vary as

$$\rho_1 \propto e^{E_g/2kT}, \quad (1)$$

where  $E_g$  is the amorphous energy gap equal to the crystalline gap plus localized regions  $\delta E_v$  and  $\delta E_c$  in the valence and conduction bands, respectively, and  $k$  is the Boltzmann constant.

In the second process, hopping conduction occurs by thermal activation and/or under the influence of an ac field. If the states are localized, the mobility for thermally activated hopping (for a nondegenerate case) is given by<sup>31</sup>

$$\mu = (e\nu_{ph}a^2\phi/kT) \exp(-W/kT), \quad (2)$$

where  $W$  is the hopping energy,  $\nu_{ph}$  a phonon frequency ( $\sim 10^{13}$  sec<sup>-1</sup>), and  $1/a^3$  corresponds to the number of electrons per unit volume. The parameter  $\phi$  depends on the overlap between localized states and is of the order of unity for considerable overlap. For small overlap,  $\phi$  contains a factor  $e^{-2\gamma R}$ , where  $\gamma$  is defined as the rate at which the atomic wave function falls off with distance, and  $R$  is the average distance between nearest neighbors.

Note that although the localized states form a continuum of trapping energy levels, transport of current by tunneling between these states without an activation energy cannot take place. Mott<sup>31</sup> has shown that if states are close enough energetically for tunneling, they split into two states which do not have the same energy. Thus, dc conduction in localized states is thermally activated.

Since only electrons or holes with energies  $\sim kT$  below the Fermi level have a significant probability of hopping, the resistivity is given by<sup>31</sup>

$$\rho_2 = \frac{1}{eN(E_f)kT\mu} = \frac{1}{N(E_f)\phi e^2 a^2 \nu_{ph}} \exp\left(\frac{W}{kT}\right), \quad (3)$$

where  $N(E_f)$  is the density of states. Therefore, we note that this process also yields an exponential temperature dependence. It differs from intrinsic conduction in that  $W$  is of the order of  $kT$ , and it should decrease to zero at low temperatures, and, furthermore,  $W$  is not a unique value since it also depends on the hopping distance.

If conduction takes place by both processes, the resistivity  $\rho$  should be given by  $1/\rho = 1/\rho_1 + 1/\rho_2$ . Since processes (1) and (2) are expected to dominate conductivity at high and low temperatures, respectively, it is clear that the "apparent" activation energy of  $\rho$

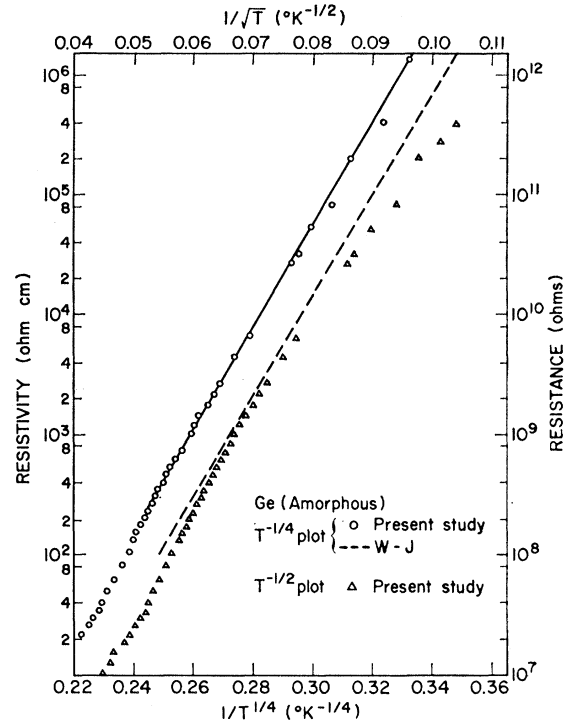


FIG. 9. Replots of the data of Fig. 3 in the forms:  $\log_{10}$  resistivity versus  $1/T^{1/4}$  and  $1/\sqrt{T}$ . Also plotted are the data of Walley and Jonscher [(W-J), Ref. 12] as  $\log_{10}$  resistance versus  $1/T^{1/4}$  for comparison.

will change monotonically from  $\frac{1}{2}E_g$  to  $W$  with decreasing temperature. This prediction is in agreement with the observed variation. However, further data are required to verify that  $W \rightarrow 0$  as  $T \rightarrow 0$ . If we assume the high-temperature activation energy  $\sim 0.5$  eV corresponds to the intrinsic process, then  $E_g \sim 1.0$  eV. Since the band gap of crystalline Ge is  $\sim 0.8$  eV, this value of  $E_g$  suggests that  $(\delta E_v + \delta E_c) \sim 0.2$  eV.

Mott<sup>31</sup> has interpreted the low-temperature resistivity data of Walley and Jonscher<sup>12</sup> on the basis that, in a system with strongly localized states ( $\gamma R > 1$ ), the most probable hop will not be to the nearest neighbors but to a more distant site for which the energy difference is smaller. Thus,  $\rho_2$  [Eq. (3)] will be minimum when  $2\gamma R = W/kT$ . Since the number of states in the range  $dE$  is  $\frac{4}{3}\pi R^3 N(E)dE$ , the average spacing between energies is  $W = 3/4\pi R^3 N(E)$ . Therefore, at low temperatures,  $\rho_2$  should behave like

$$\ln \rho_2 = A + BT^{-1/4}, \quad (4)$$

where  $A$  and  $B$  are constants. A replot of our data of Fig. 3 in the form  $\log \rho$  versus  $1/T^{1/4}$  is shown in Fig. 9 and is compared with the resistance (resistivity is not given by these authors) data of Walley and Jonscher. It is clear that our data yield an excellent fit to the  $T^{-1/4}$  relation below 300°K, and a reasonable fit up to 500°K. The validity of the  $T^{-1/4}$  relation in such a

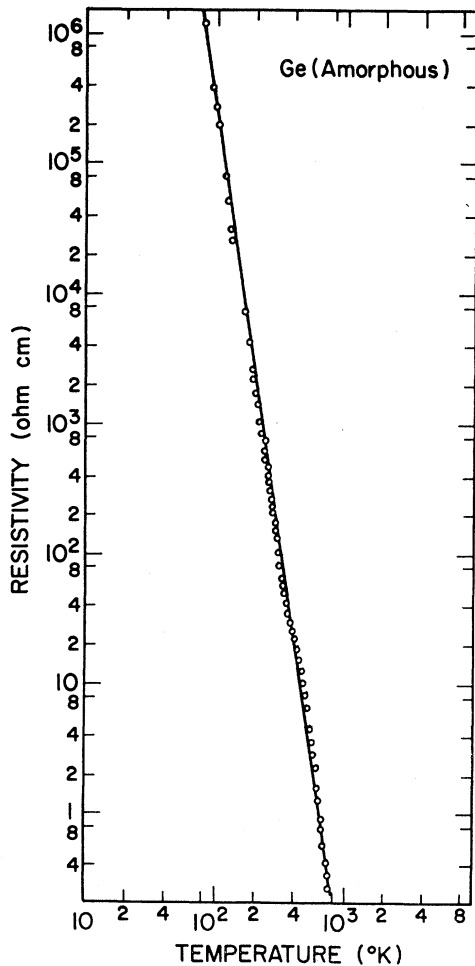


Fig. 10. Replot of the data of Fig. 3 in the form of a  $\log_{10}$ - $\log_{10}$  plot of the resistivity versus temperature.

large temperature range indicates that the relation may not be unique. That this is most probably the case is seen by the replots of our data in two other arbitrary forms, e.g.,  $\log_{10}\rho$  versus  $T^{-1/2}$  (Fig. 9), and  $\log_{10}\rho$  versus  $\log_{10}T$  (Fig. 10). Although  $T^{-1/2}$  relation is only a fair fit,  $\rho \propto T^{-7}$  provides an excellent fit for six decades of the variation of  $\rho$  over the temperature range 77–740°K. The significance of the  $T^{-7}$  law is not clear.

**ac Conduction.** Although dc conduction by hopping in the trapping (localized) states is negligible, hopping under an ac field yields high conductivity. The statistical rate at which an electron (or hole) hops between two states depends on the energy difference of the two states which is altered by the applied field. An applied ac field of sufficiently high frequency may produce a net polarization (of the lattice in the vicinity of the trapped charge), which will lag behind the field, since the tunneling transition rates are finite. The part of the polarization which is out of phase with the field yields ac conductivity or dielectric loss. The ac conductivity should appear at frequencies greater than that at which

traps are filled or emptied. With increasing lag at higher frequencies, the ac conductivity is expected to increase and then saturate at high enough frequencies comparable to the natural frequency of hopping between two centers. According to the analysis of ac conduction by Pollak and Geballe<sup>35</sup> (also see Argall and Jonscher,<sup>36</sup> the resistivity  $\rho_2$  at frequency  $\omega$  for hopping between pairs of identical hopping centers is given by

$$\rho_{ac} \propto (\omega^2 + \Omega^2)/\omega^2, \quad (5)$$

where  $\Omega$  is the characteristic hopping frequency between the pair. Thus, for  $\Omega \gg \omega$ ,  $\rho_{ac} \propto 1/\omega^2$ ; and for  $\Omega \ll \omega$ ,  $\rho_{ac} = \text{const.}$

In the presence of a random distribution of hopping centers (which is physically more significant in amorphous materials) it is necessary to average conductivity over all hopping distances and activation energies for all pairs of occupied and empty centers. This averaging process yields (for  $\Omega \gg \omega$ ) for single or multiple hops

$$\rho_{ac} \propto \omega^{-n}, \quad (6)$$

where  $n$  decreases from 1.0 for single hops to 0.5 for multiple hops. This relation is in reasonable agreement with the observations; the increase of  $n$  at low temperatures is due to the predominance of single hops. Since no saturation of  $\rho_{ac}$  at high frequencies has been observed, a value of  $\Omega > 10^6$  cps is indicated for amorphous Ge films.

The preceding discussion of ac conduction suggests that as the frequency increases the activation energy should decrease from the dc value down to a small value characteristic of thermally activated hopping. Since the conduction by intrinsic excitation and by hopping are parallel processes, the total ac resistivity will be given by the equation

$$(1/\rho)_{ac} = 1/\rho_1 + (A/\omega^n)e^{-W(T,\omega)/kT} \quad (\Omega \gg \omega). \quad (7)$$

Here,  $A$  is a constant, and the activation energy  $W$  for hopping is a function of both the temperature and the frequency. The frequency dependence arises, since  $W$  depends on the hopping path which will vary with the frequency.

We would like to point out that the observed frequency dependence of the resistivity can also be explained alternatively in terms of intergranular or interfacial barriers due to the well-known Maxwell-Wagner polarization<sup>37,38</sup> mechanism. In principle, if a material can be described as consisting of high- and low-resistivity regions, a circuit configuration of resistor and capacitor components can always be synthesized to

<sup>35</sup> M. Pollak and T. H. Geballe, *Phys. Rev.* **122**, 1742 (1961); in *Proceedings of the International Conference on Semiconductors, Prague, 1960* (Publishing House of the Czechoslovak Academy of Sciences, Prague, 1961), p. 212.

<sup>36</sup> F. Argall and A. K. Jonscher, *Thin Solid Films* **2**, 185 (1968).

<sup>37</sup> R. W. Sillars, *J. Inst. Electron. Eng.* **80**, 378 (1937).

<sup>38</sup> L. K. H. Van Beek, in *Progress in Dielectrics*, edited by J. B. Birks and J. Hart (Heywood and Company, Ltd., London, 1967), Vol. 7, p. 69.

produce any frequency behavior. Indeed, the explanation offered above for the frequency dependence is essentially based on the same physical process of charging and discharging of traps acting as microcapacitors. However, one theory is microscopic and the other is macroscopic in description. Despite this physical similarity, we can reject an explanation in terms of intergranular barriers on the basis of the following reasons. (a) High-magnification and high-resolution electron micrographs of amorphous films do not reveal any microstructure of dimensions down to the resolution ( $\sim 10 \text{ \AA}$ ) of the microscope. (b) The observed activation energy for dc conduction (at higher temperatures) is too high to be explained by an intergranular barrier height. (c) The decrease of the activation energy to zero value at high frequencies and low temperatures is not compatible with the model of structural barriers. (d) All electrical properties are the same along the length as well as across the thickness of the films, indicating the homogeneous nature of the film material. A film consisting of micropolycrystallites should exhibit quite different microstructure along the thickness than along the film length.

*Field dependence.* Now we will attempt to understand the observed dc field dependence of current (or conductivity). Electron transport through thin insulators has been studied by numerous workers and several reviews<sup>39-43</sup> of the subject have been published in the literature. At very low voltages applied to any material, current due to thermally excited carriers is proportional to voltage (Ohmic behavior). With increasing field,  $F$ , the large density of traps, and continuous distribution of many different sets of traps, which are expected to be characteristic of all amorphous insulators, play a dominant role in the transport of current through amorphous insulators. The effect of traps on current through crystalline insulators has been analyzed in detail by Rose<sup>42</sup> and Lampert.<sup>43</sup> In the absence of any theory of electron transport through amorphous materials, we may apply the theories and concepts developed for crystalline materials in terms of the energy-band diagram of Fig. 8. Since the observed  $I$ - $F$  characteristics are similar for thin and thick films and do not depend on the electrode material (e.g., Au, Ag, Al, In, etc.), we can rule out tunneling and Schottky effect as transport mechanism. Bulk controlled transport may be attributed to space-charge-limited current (SCLC) flow and/or Poole-Frenkel (PF) effect.<sup>44,45</sup> The  $I$ - $F$  characteristic for SCLC flow depends on the density and energy distribution of traps. If traps are uniformly distributed in energy, current is expected to depend

exponentially on the voltage. Different sets of traps, each having a Gaussian distribution, may, on the other hand, be represented by an exponential distribution. Such a distribution would yield  $I \propto F^{1+\Delta/kT}$ , where  $\Delta$  is the inverse of the slope of the exponential trap distribution. Thus, power law or exponential dependence can be explained in terms of trap modified SCLC flow. Physically,<sup>43</sup> the rapid rise of current with voltage at high fields is due to the rapid filling of traps above a certain voltage. The observed  $I \propto F^{3.5}$  dependence following the Ohmic region yields  $\Delta = 2.5kT$ . It is interesting to note that approximately similar values have been observed in amorphous Se<sup>46</sup> and GeTe<sup>47</sup> films.

At sufficiently high fields ( $> 2.5 \times 10^3 \text{ V/cm}$ ), the Coulombic barrier around a trap is lowered by the field to enable thermally assisted field emission of the trap in a way analogous to the thermally assisted field emission from electrodes bounding an insulator. The former effect is called PF,<sup>44</sup> while the latter is the Schottky effect. The current in either case is given by

$$I = AsT^2 \exp(\beta\sqrt{F} - e\Phi/kT), \quad (8)$$

where  $A$  is the well-known Richardson-Dushman constant,  $s$  is the active area,  $\beta = \beta_S$  (Schottky) =  $\frac{1}{2}\beta_{PF}$  (Poole-Frenkel) =  $(e^3/\epsilon)^{1/2}/kT$  with  $e$  as unit charge in esu and  $\epsilon$  as the high-frequency dielectric constant,  $\Phi$  is the appropriate barrier height, and  $F = V/t$  is the field due to voltage  $V$  applied across insulator thickness  $t$ . Thus, a plot of  $\log I$  versus  $\sqrt{F}$  or  $\sqrt{V}$  should yield a straight line.

The experimental data (Fig. 6) yield a value of  $\beta = 0.026$ . This value is 0.9 times the theoretical value of  $\beta_{PF}$  calculated by using<sup>4</sup> high-frequency dielectric constant value of  $\epsilon$  as 15. This may be considered as a reasonable agreement, particularly in view of the uncertainty of the proper value of  $\epsilon$  to be used as well as the validity of the PF theory to such a system.<sup>40,45</sup> It should be emphasized that the value of  $\beta$  is not reliable and accurate enough to allow a distinction between Schottky or PF emission.

It is noteworthy that thin films of numerous amorphous insulators<sup>48-53</sup> and semiconductors<sup>12,13,46,54,55</sup> exhibit similar power-law or exponential dependence of current on the field. Further, it is remarkable that the observed field dependence can be understood, at least qualitatively, in terms of trap controlled SCLC flow

<sup>46</sup> H. P. D. Lanyon, Phys. Rev. **130**, 134 (1963).

<sup>47</sup> S. K. Bahl and K. L. Chopra, J. Applied Phys. (to be published).

<sup>48</sup> C. A. Mead, Phys. Rev. **128**, 2088 (1962).

<sup>49</sup> S. R. Pollack, J. Appl. Phys. **34**, 877 (1963).

<sup>50</sup> H. Hirose and Y. Wada, Japan. J. Appl. Phys. **4**, 639 (1965).

<sup>51</sup> K. L. Chopra, J. Appl. Phys. **36**, 184 (1965).

<sup>52</sup> T. E. Hartman, J. C. Blair, and R. Bauer, J. Appl. Phys. **37**, 2468 (1966).

<sup>53</sup> A. Servini and A. K. Jonscher, Thin Solid Films **3**, 341 (1969).

<sup>54</sup> T. E. Hartman, J. C. Blair, and C. A. Mead, Thin Solid Films **2**, 79 (1968).

<sup>55</sup> N. Croitoru and L. Vesan, Thin Solid Films **3**, 269 (1969).

<sup>39</sup> See Ref. 15, Chap. 8.

<sup>40</sup> A. K. Jonscher, Thin Solid Films **1**, 213 (1967).

<sup>41</sup> R. M. Hill, Thin Solid Films **1**, 39 (1967).

<sup>42</sup> A. Rose, RCA Rev. **12**, 362 (1951).

<sup>43</sup> M. A. Lampert, Rept. Progr. Phys. **27**, 329 (1964).

<sup>44</sup> J. Frenkel, Phys. Rev. **54**, 647 (1938).

<sup>45</sup> J. G. Simmons, Phys. Rev. **155**, 657 (1967).

and/or PF emission theories which have been developed for crystalline materials with a small density of traps.

*Optical absorption.* On the basis of the energy-band diagram (Fig. 8), we should expect the absorption coefficient  $\alpha$  to decrease gradually (in the vicinity of the energy separating localized states from nonlocalized states) to a negligible value at an energy equal to the crystalline band gap minus the tails of the conduction and valence bands extending into the crystalline-forbidden gap. By assuming exponential tailing of the valence band [that is, density of states falling as  $\exp(-E/\Delta)$ ], and the magnitude of tailing inside the forbidden gap  $\sim 0.2$  eV, we can understand the observed exponential decay<sup>46</sup> [that is,  $\exp(h\nu/\Delta)$ ] of  $\alpha$  and the amorphous optical edge at  $\sim 0.6$  eV. However, the observed sharpness of the optical edge at  $\sim 0.6$  eV is not compatible with the exponential decay of the density-of-states hypothesis, unless we speculate further that the exponential decay is truncated at some value or else the states below a certain level are made ineffective for optical absorption.

An exponential tail of the absorption edge is a common characteristic of a number of materials such as amorphous Se<sup>46</sup> and GeTe<sup>56</sup> films, and intrinsic bulk materials of ZnS,<sup>57</sup> CdS,<sup>58,59</sup> CdSe,<sup>60</sup> AgBr<sup>57,61</sup> etc. A remarkable feature of the  $\alpha \propto \exp(h\nu/\Delta)$  variation is that  $\Delta$  in all these cases is  $\sim 3kT$ . Although no satisfactory theory has yet been given<sup>62</sup> for this phenomenon, it is generally agreed that the explanation must be sought in the decay of the optical density-of-states function. Our results (as well as those of Clark<sup>8</sup> and of Wales *et al.*<sup>4</sup>) show exponential decay of  $\alpha$  for amorphous Ge films. However, the value of  $\Delta$  is 0.14 eV  $\sim 5.5kT$ . In sharp contrast, the field dependence of current through amorphous Ge films yields  $\Delta \sim 2.5kT$  (which is a similar value to that observed<sup>46,56</sup> in amorphous films of other materials). In view of this result and the preceding discussion, the physical significance of  $\Delta$  is uncertain.

The observed sharp absorption edge at  $\sim 0.6$  eV, therefore, is difficult to understand, as already empha-

sized by Donovan *et al.*<sup>5</sup> A kink in the absorption curve of crystalline Ge at  $\sim 0.6$  eV is known<sup>63</sup> to occur and has been explained in terms of transitions from spin-orbit split valence to conduction band. In view of the disappearance or at least smearing of the electronic symmetry structure of the crystalline lattice in the disordered lattice, it is unlikely that the substructure of the valence band of amorphous Ge is sufficiently defined to produce a sharp absorption edge.

## V. CONCLUSIONS

We conclude from our structural studies that Ge films can be prepared in an amorphous (continuously random rather than micropolycrystalline) form with a judicious choice of deposition conditions. In the case of thick ( $\sim 1\text{-}\mu$ ) films, if the deposition temperature rises above 25°C, a mixture of amorphous and micropolycrystalline regions is likely to occur. Our studies strongly recommend that films must be examined in the optical as well as electron microscope before measurements are made.

The dc and ac conductivity behavior of amorphous Ge films and the field dependence of current through such films can be understood on the basis of the energy-band diagram of crystalline Ge modified by the tailing and localization of states near the band edges caused by the disorder. The extension of the concepts and theories of electron transport in crystalline materials to disordered materials predicts results remarkably similar to those observed.

The exponential decay of the optical-absorption coefficient near the absorption edge and a shift in the crystalline absorption edge in the amorphous state are consistent with the proposed energy-band diagram. But the sharpness of the absorption edge remains a mystery. Measurements of optical absorption in the far infrared are required to throw more light on the existence and/or ineffectiveness of the localized states in the crystalline forbidden gap.

## ACKNOWLEDGMENTS

The technical assistance of M. R. Randlett in the preparation of films and of Mary Plumridge in the electron microscopy studies is acknowledged.

<sup>56</sup> S. K. Bahl and K. L. Chopra, *J. Appl. Phys.* **40**, 4940 (1969).

<sup>57</sup> W. W. Piper, *Phys. Rev.* **92**, 23 (1953).

<sup>58</sup> F. Urbach, *Phys. Rev.* **93**, 1324 (1953).

<sup>59</sup> D. L. Dexter, *J. Phys. Chem. Solids* **8**, 473 (1959).

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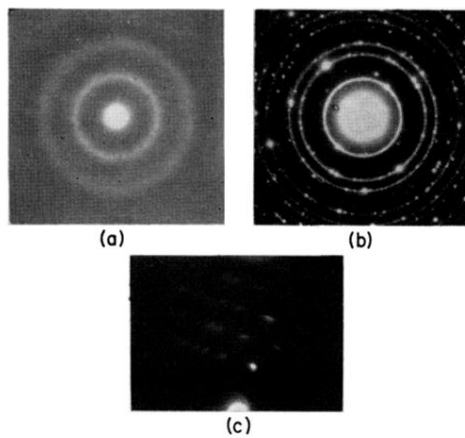


FIG. 1. Transmission electron diffraction patterns of  $\sim 600\text{-\AA}$ -thick Ge film evaporated onto cleaved NaCl. (a) Amorphous film deposited at room temperature; (b) polycrystalline film deposited at  $350^\circ\text{C}$ ; (c) reflection electron diffraction pattern of  $\sim 7\text{-}\mu$ -thick Ge film deposited on glass substrate at  $25^\circ\text{C}$  from a graphite boat at a rate  $\sim 10\text{\AA}/\text{sec}$ .

FIG. 2. Electron micrographs of two stages of amorphous  $\rightarrow$  crystalline transformation of a 600-Å-thick Ge film supported on a microscope stainless-steel grid and heated in the microscope heating stage. The micrograph (a) shows the randomly distributed nucleation centers of the crystalline phase obtained on heating of the amorphous film to a temperature of 350°C. The growth of the crystalline phase at higher temperatures is shown in (b).

