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## Optical Evidence for a Network of Cracklike Voids in Amorphous Germanium

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The electrodynamic phenomenon of void resonance is used to interpret anomalous structure reported by Donovan and co-workers in the uv dielectric constants of evaporated amorphous germanium. The resulting void parameters are consistent with the existence of a connected network of microcracks perhaps 6 Å in width, separating much larger islands of void-free material. The origin and consequences of these fissures are discussed, including the expectation that several film properties are anisotropic.

The possible existence of voids in amorphous materials was discussed years ago in connection with attempts at microcrystalline explanations of x-ray diffraction by glasses.<sup>1</sup> These ideas were recently revived<sup>2</sup> upon discovery that amorphous germanium (*a*-Ge) and amorphous silicon (*a*-Si) can be as much as 30% less dense than their crystalline counterparts.<sup>3,4</sup> Moss and Graczyk<sup>5</sup> have noted an excess of low-angle scattering in their electron diffraction studies of *a*-Si and attributed this to the existence of void spaces or density-deficient regions <10 Å in diameter. No one has been able to observe voids directly in these materials.<sup>6,7</sup> In this Letter, void-resonance theory<sup>8,9</sup> is used to interpret the measured dielectric constants of evaporated *a*-Ge,<sup>10</sup> revealing the presence of oriented disklike voids.<sup>9</sup> These voids are probably connected together into a network of microcracks, with far-reaching consequences for other physical properties.

It was previously shown<sup>8,9</sup> that

$$\kappa_{\text{eff}} = F + HK - FG / (\kappa + G) \quad (1)$$

gives the effective dielectric constant of a medium consisting of a spatially random array of aligned, submicroscopic, ellipsoidal voids embedded in a host material having complex dielectric constant  $\kappa \equiv \kappa' + i\kappa''$ . The coefficients,<sup>11</sup>  $F \equiv \delta / (1 - L + \frac{1}{3}\delta)^2$ ,  $G \equiv (L - \frac{1}{3}\delta) / (1 - L + \frac{1}{3}\delta)$ , and  $H \equiv (1 - L - \frac{2}{3}\delta) / (1 - L + \frac{1}{3}\delta)$ , are functions only of the volume fraction of voids,  $\delta$ , and their (identical) depolarization factors,  $L$ .<sup>12</sup>

Void resonance is able to explain the anomalous

structure recently reported by Donovan, Spicer, Bennett, and Ashley (DSBA)<sup>10</sup> in the uv dielectric constant of *a*-Ge. The heavy curve marked  $\delta = 0$  in Fig. 1 shows the experimental values of optical transition strength  $\omega^2\kappa''$  in which DSBA noted the secondary structure at about 8 eV. A solitary peak might have been expected.<sup>13</sup> When the bump at 8 eV is assumed to arise entirely from void resonance, physically reasonable values for  $\delta$ ,  $L$ , and  $\kappa$  are extracted from the data. To accomplish this, Eq. (1) is first solved for the unknown host dielectric constant in terms of the composite

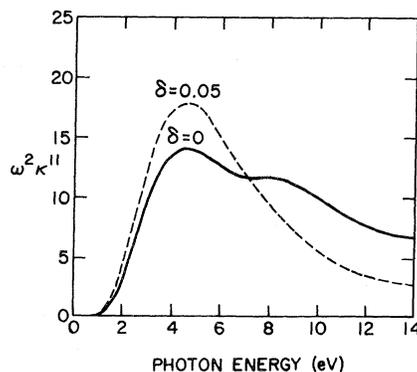


FIG. 1. Optical transition strength  $\omega^2\kappa''$  of *a*-Ge in arbitrary units. The heavy curve is the experimental result obtained by DSBA (Ref. 9); in this paper, the secondary structure near 8 eV is ascribed entirely to void resonance. The light curve represents void-free *a*-Ge and is determined by finding the set of void parameters ( $\delta = 0.05$  and  $L = 0.8$ ) that best removes the void-resonance bump from the DSBA data.

value  $\kappa_{\text{eff}}$ :

$$\kappa = \frac{1}{(2H)^{-1}} \{ (\kappa_{\text{eff}} - F - GH) \pm [(\kappa_{\text{eff}} - F - GH)^2 + 4HG]^{1/2} \}. \quad (2)$$

Then, using the DSBA values for  $\kappa_{\text{eff}}$ , it is a simple matter to search for pairs of parameters ( $0 \leq \delta \leq 1$ ;  $0 \leq L \leq 1$ ) which remove the anomalous bump and leave a single peak in the  $\omega^2 \kappa''$  of the host material, presumed to be void-free *a*-Ge. The dashed line of Fig. 1 is the best result obtained, and corresponds to the removal of a 5% volume fraction of voids having depolarization factor 0.8. A complete search over all  $\delta, L$  pairs leads to a remarkably narrow range of values:  $\delta = 0.05 \pm 0.02$  and  $L = 0.8 \pm 0.1$ . This volume fraction of voids is consistent with the observation that DSBA samples are  $\sim 10\%$  less dense than the higher density form of *a*-Ge reported by Donovan, Ashley, and Spicer (DAS).<sup>4</sup> The large depolarization factor violates no facts known about the samples and will later be shown to have special significance.

Small concentrations of these voids have large effects on the dielectric constants of *a*-Ge, as illustrated in Fig. 2. The heavy curves were deduced by the procedure just described and repre-

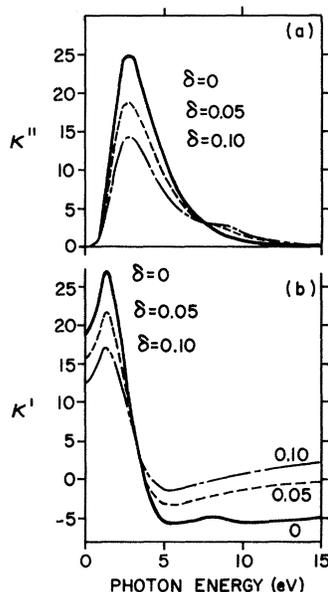


FIG. 2. Theoretical variation of the room-temperature dielectric constant of *a*-Ge with increasing volume fraction  $\delta$  of cracklike voids having depolarization factor  $L=0.8$ . Here  $\delta=0$  indicates void-free material. Similar trends with the deposition substrate temperature  $T_s$  have been reported at low photon energies, as noted in the text.

sent void-free *a*-Ge (here labeled  $\delta=0$ ),<sup>14</sup> while the lighter ones are generated from the heavy curves using Eq. (1) and  $L=0.8$ . The  $\delta=0.05$  case reproduces the DSBA data, as it should. Clearly, a necessary step for accurate experimental determination of the dielectric constant of "ideal" *a*-Ge is the elimination of voids, or correction for their existence.<sup>14</sup> It appears that void concentration is reduced by the procedures DAS employed to obtain their dense form of *a*-Ge: These included slow deposition at high vacuum onto substrates held at temperatures just below the crystallization regime.<sup>4,10</sup>

Note in Fig. 2(a) that void removal from the DSBA samples corresponds to increasing the amount of host material by 5%, but occasions a much larger increase ( $\sim 30\%$ ) in the peak value of  $\kappa''$ . This swift rise is a result of the high value of  $L$ . Swift increases are also expected in the real part of the dielectric constant  $\kappa'$  at photon energies below 2.5 eV, as shown in Fig. 2(b).

These last two effects suggest a reinterpretation of the data recently reported by Jungk<sup>15</sup> who measured the dielectric constant of *a*-Ge as a function of deposition substrate temperature  $T_s$ , in the narrow photon energy range 2–4 eV. When  $T_s$  was raised from 20 to 200°C he observed a large ( $\sim 25\%$ ) increase in the peak value of  $\kappa''$ , with negligible energy shift, and a large increase ( $\sim 16\%$ ) in the value of  $\kappa'$  at 2.0 eV. The absolute values of Jungk's data at 20 and 200°C correspond rather well to the cases  $\delta=0.10$  and  $\delta=0.05$ , respectively, plotted in Fig. 2. This fact and the swift rises observed by Jungk tend to confirm the large depolarization factor previously deduced from the DSBA data. In addition to this confirmation, Bauer, Galeener, and Spicer<sup>16</sup> have observed similar trends with  $T_s$  in independent measurements of the dielectric constants of *a*-Ge.

The high experimental value  $L=0.8$  is interpreted by relating selected values of  $L$  to specific void shapes and orientations relative to  $\vec{E}$ .<sup>12</sup> Spheres have  $L = \frac{1}{3}$  and needles have  $L \leq \frac{1}{2}$ , so neither can suffice. The largest possible value of  $L$  is 1, corresponding to a very thin disk with  $\vec{E}$  normal to its plane. Since an amorphous sample containing "disks" all aligned perpendicular to the incident field is unreasonable, we are led to interpret  $L=0.8$  as corresponding to a distribution of disks with their normals randomly oriented in the plane of the film. Other shapes (and normals significantly out of the plane) are disfavored because they correspond to appreciably lower values of average  $L$ .

This system of partially aligned nonspherical voids indicates that several physical properties should prove to be different when measured parallel ( $\parallel$ ) to the perpendicular ( $\perp$ ) to the plane of the film. The films must be optically uniaxial, with the  $\parallel$  and  $\perp$  dielectric constants estimated using  $L=0.8$  and  $L=0$ , respectively, in Eq. (1). Similar asymmetry should appear, for example, in electrical conductivity, pressure response, and the low-angle x-ray and electron diffraction intensities<sup>5</sup> expected from voids.

The thickness  $t$  of the disks can be estimated using the value reported by Brodsky and Title<sup>17</sup> for the density of free spins in their unannealed  $a$ -Ge films ( $n_s = 1 \times 10^{20} \text{ cm}^{-3}$ ) and assuming that all spins are due to dangling bonds on the internal surfaces of the voids. Using  $n = 4.4 \times 10^{20} \text{ cm}^{-3}$  as the density of Ge atoms in the host material and  $\delta = 0.05$ , and estimating  $n_a = 10$  as the number of surface atoms per free spin,<sup>18</sup> one obtains  $t = 2n^{2/3}\delta/n_s n_a = 12 \text{ \AA}$ . This value is probably an upper limit, as argued under Ref. 18.

There is a compellingly reasonable interpretation of these slitlike voids. They correspond to a network of very fine cracks, which may arise during deposition as follows. The low substrate temperatures used to form amorphous material lead to adatom mobilities on the substrate which are small, but not zero. Hence, atoms do not directly stick (as often seems to be assumed), but film growth proceeds by a nucleation process similar to that known to produce crystalline thin films.<sup>19</sup> There is, however, at least one important difference: As the islands of "ideal" amorphous material depicted in Fig. 3(a) grow, they encroach on each other, but are unable to coalesce, as illustrated in Fig. 3(b). Coalescence is inhibited because it is energetically unfavorable for atoms to fill the last one or two atomic

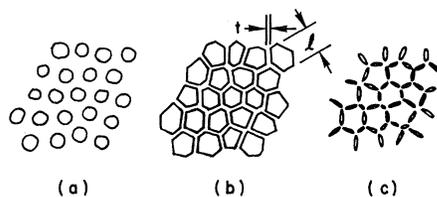


FIG. 3. Evolution of cracklike voids in  $a$ -Ge. It is assumed that islands of amorphous material growing in the plane of the film, as depicted in (a), are unable to coalesce, for reasons given in the text. The result is a connected network of cracks (b) with estimated  $t = 6 \text{ \AA}$ . Quantitative treatment using Eq. (1) assumes isolated voids as in (c), which is clearly a reasonable approximation to the connected system (b).

"layers" separating the islands, bonds being required at angles and distances too different from the ideal tetrahedral bonding conditions.<sup>20</sup> Since the nearest neighbor (nn) distance in  $a$ -Ge is about  $2.5 \text{ \AA}$ , the mean of one or two missing layers suggests that  $t \sim 6 \text{ \AA}$ , or less, is probably a better estimate of average microcrack thickness than the  $12 \text{ \AA}$  calculated above.<sup>18</sup> Whether these cracks propagate all the way upward through the thickness of the film as it grows, or are occasionally bridged over and new networks formed, is difficult to answer at present. Figure 3(c) shows that the connected network in Fig. 3(b) is quite naturally approximated by a distribution of isolated thin ellipsoidal disks having their normals randomly distributed in the plane of the film.

One can estimate the linear dimension  $l$  of the amorphous islands, since the ratio of crack area to the associated island area should give the volume fraction of voids. Assuming regular hexagonal islands, as an idealization suggested by Fig. 3(b), the distance across the flats is  $l = t/\delta \approx 120 \text{ \AA}$ . Notice that  $l$  also measures the average separation of nucleation centers that lead to mature islands.

The qualitative dependence of island film density on deposition rate  $D$  and substrate temperature  $T_s$  is easily predicted on the assumption that nucleation sites are determined by the chance collision of adatoms to form nuclei above a critical size. When  $D$  is increased at constant  $T_s$  the rate of adatom collision rises, as does the rate of formation of supracritical nuclei and, therefore, the number of mature islands per square centimeter. It follows that island size  $l$  is reduced. Since  $t$  is fixed by the nn distance,  $\delta = t/l$  increases. This corresponds to the experimental fact that higher  $D$  leads to less dense films. When  $T_s$  is raised at constant  $D$  the rate of adatom collisions is unchanged; however, the loss of small nuclei by collision and evaporation increases. As a result, the rate of formation of supracritical nuclei diminishes, as does the number of mature islands per square centimeter. Island size therefore is enhanced, the value of  $\delta = t/l$  diminishes, and the film density increases, as indicated by the DAS results<sup>4</sup> and our analysis of Jungk's data.<sup>15</sup> Other mechanisms may be involved in determining void density, especially in those circumstances where isolated defects or voids are formed.

Void structure may indirectly affect the position of the optical absorption edge  $E_g$ . For low void densities ( $0 \leq \delta \leq 0.2$ ), Eq. (1) predicts negligible

shifts and therefore does not account for the 0.13-eV reduction in  $E_g$  that Donovan and co-workers<sup>4,10</sup> observed when they decreased  $T_s$  from 300 to 20°C. This downward shift with decreasing  $T_s$  may instead be due to dilation of the amorphous material with diminishing island size, associated with the enhanced proximity of all atoms to surfaces of the islands. Using pressure data for crystalline Ge,<sup>21</sup> the 0.13-eV downshift corresponds to a 1.3% increase in the nn distance. This adds a density deficiency of ~4% to the 5% assigned to voids and yields a total deficiency of ~9%, in good agreement with that measured directly by DAS.<sup>4</sup>

Films formed under different conditions of substrate temperature, atom flux, and gaseous contamination will perforce have differing void structures. Moreover, the voids existent after annealing at a temperature  $T_a > T_s$  may not have the same character as those obtained by direct growth on a substrate at temperature  $T_a$ . Connected networks of submicroscopic cracks will strongly affect many other physical properties, as will be discussed elsewhere.

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<sup>1</sup>See, e.g., B. E. Warren, *J. Appl. Phys.* **8**, 645 (1937).

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<sup>7</sup>M. H. Brodsky, R. S. Title, K. Weiser, and G. D. Pettit, *Phys. Rev. B* **1**, 2632 (1970).

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<sup>11</sup>The coefficients  $F$  and  $H$  were incorrectly printed in the original Letter of Ref. 8, as noted in the Erratum.

<sup>12</sup>We use mks values of  $L$ , where  $L_{\text{Gaussian}} = 4\pi L_{\text{mks}}$ . See, e.g., C. Kittel, *Introduction to Solid State Physics* (Wiley, New York, 1966), 3rd ed., p. 378.

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<sup>14</sup>If the voids are connected as described later in the text, improvements on Eq. (1) may be required for accurate numerical treatment of optical effects.

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<sup>16</sup>R. S. Bauer, F. L. Galeener, and W. E. Spicer, in *Proceedings of the Fourth International Conference on Amorphous and Liquid Semiconductors*, Ann Arbor, Michigan, August 1971 (to be published).

<sup>17</sup>M. H. Brodsky and R. S. Title, *Phys. Rev. Lett.* **23**, 581 (1969).

<sup>18</sup>This is the value of  $n_a$  determined for freshly cleaved (111) surfaces of *crystalline* Si by D. Haneman, *Phys. Rev.* **170**, 705 (1968), and applied to *a*-Ge in Brodsky and Stiles, Ref. 13, and to *a*-Si in Ref. 7. The present author believes this number will *increase* as a second surface is brought close to the first, since it must become infinite when the surfaces join. Accordingly, the result in Eq. (3) is probably an overestimate of  $t$ .

<sup>19</sup>See the Frenkel theory, as described in O. S. Heavens, *Optical Properties of Thin Solid Films* (Dover, New York, 1966), p. 18 ff.

<sup>20</sup>See the structural model for ideal *a*-Ge developed by D. E. Polk, *J. Non-Cryst. Solids* **5**, 365 (1971).

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## Percolation Theory and Electrical Conductivity

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We report the results of an experiment to determine the bulk conductivity of a sheet of colloidal graphite paper with holes randomly punched in it. The behavior of the conductivity is found to be quite different from that of the percolation probability.

It has been argued by Ziman<sup>1</sup> that the mobility of an electron in a disordered semiconductor should be given by a solution of the classical percolation problem. This idea has been explored by a number of workers, and Eggarter and Cohen<sup>2</sup> in particular have assumed that the mobility

should be proportional to the percolation probability  $P(p)$ .<sup>3</sup> Percolation theory has also been used for the theory of hopping conductivity in semiconductors,<sup>4</sup> and for a model of switching in amorphous semiconductors.<sup>5</sup> There is, however, no theory of the electrical conductivity of a class-