

## Far Infrared Absorption by Tetrahedrally Bonded Amorphous Semiconductors\*

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### *Abstract*

A discussion of the electronic structure of amorphous semiconductors is given and the ideas are developed for the case of the tetrahedrally bonded elements silicon and germanium. This background is used to interpret far infrared conductivity data taken in our laboratory. The results suggest that the void structure in these materials plays a central role in the photon–vibration coupling, particularly at low frequencies.

### **Introduction**

Over the last 10 years the study of amorphous semiconductors has become so popular that it is now impossible to follow all of the literature in any detail. Consequently there are numerous review papers on various aspects of amorphous semiconductor research (e.g. Connell 1975; Paul 1976; Beeman and Alben 1977; Spear 1977; Anderson 1978; Mott 1978; Wilson *et al.* 1978), though most of these are written at a specialist level. In this short paper I shall restrict my general comments to topics that set the scene for a description of our own research, emphasizing the arguments that may be unfamiliar to crystalline phase physicists.

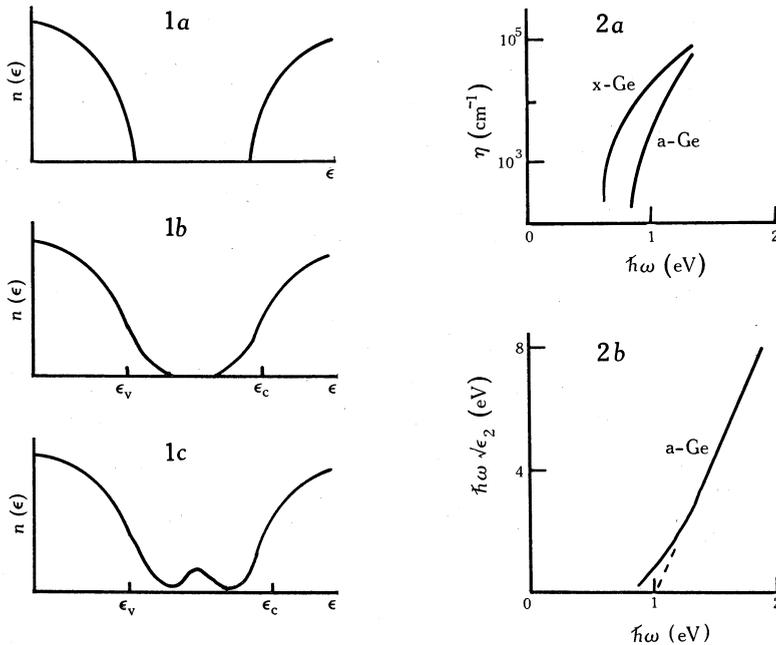
### **Amorphous Semiconductors**

Most solid state physics texts leave the impression that the presence of band gaps in the electronic state densities of solids are a consequence of the perfectly periodic potential in which the electrons move. If that were the case then only crystalline materials could show insulating or semiconducting behaviour, for which relatively large band gaps are required. However, one of the most common solids, namely glass, is an amorphous material whose useful characteristic of transparency is that of an insulator. It is clear that the theories of the crystalline phase cannot be applied simply to the amorphous phase.

The absence of long-range order in amorphous materials prevents the use of the pseudo-wavevector  $k$  as a good quantum number, so there is little point in trying to construct a band structure for amorphous solids. However, it is still possible to define  $n(\epsilon)$ , the volume density of states per unit energy interval. For a crystalline semiconductor this function would look as shown in Fig. 1*a*. The removal of long-range order alters this function surprisingly little; the gross features remain but there is a slight tailing of states into the gap, with the density of states remaining zero or

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near zero across the centre of the gap (Weaire and Thorpe 1971; Thorpe and Weaire 1971) (see Fig. 1*b*). This interesting theoretical model does not accurately represent any real semiconductor, however, for it has not yet been possible to prepare a material which lacks long-range order without simultaneously introducing severe local defects (e.g. 'dangling bonds') which leave states throughout the gap. Thus our picture of the state density in an amorphous material is as shown in Fig. 1*c*, with the rigorous gap of the crystalline material retained as a 'pseudogap', across which there is a substantial reduction in  $n(\epsilon)$  below the values found in the valence and conduction bands.



**Fig. 1 (left).** Schematic density of electron states  $n(\epsilon)$  versus energy  $\epsilon$  for (a) a crystalline semiconductor, (b) an amorphous semiconductor with short-range (nearest neighbour) order retained, and (c) a real amorphous semiconductor. The states between  $\epsilon_v$  and  $\epsilon_c$  are localized states.

**Fig. 2 (right).** Fundamental absorption edge in germanium: (a) a comparison of the absorption coefficient  $\eta$  in the crystalline and amorphous phases; (b) a plot of  $\hbar\omega\sqrt{\epsilon_2}$  versus  $\hbar\omega$  for the amorphous phase ( $\epsilon_2$  is the imaginary part of the dielectric constant). The departure from a straight line at low energies in (b) is due to transitions whose initial or final states are localized. The amorphous samples used to obtain the data shown in both diagrams have been annealed to temperatures near 350°C.

Evidence for the existence of a pseudogap is found, for example, in the optical absorption edge in amorphous germanium (a-Ge) (Theye 1976), which is compared with that in the crystalline phase (x-Ge) in Fig. 2. The data show an edge with a slightly larger optical gap than in crystalline germanium, but with a tailing at lower energies due to states inside the gap. It is not expected that the conductivity ( $\propto \epsilon_2$ ) is simply related to the density of states, for the matrix element describing excitation from a localized state to an extended state is likely to differ from that appropriate for two

extended states. The probability of a transition between two localized states is presumably smaller.

The state density in the gap is still large enough that one might expect at least semimetallic behaviour. The reason that this does not occur is that there are definite boundaries ( $\epsilon_v$  and  $\epsilon_c$  in Fig. 1) between which the electron states are localized; the wavefunctions describing these states fall off approximately exponentially with distance from a defect centre or a minimum in the average potential. The possible existence of such localized states was first recognized by Anderson (1958) and they have been discussed by many authors (see e.g. Kimball 1978 and references therein).

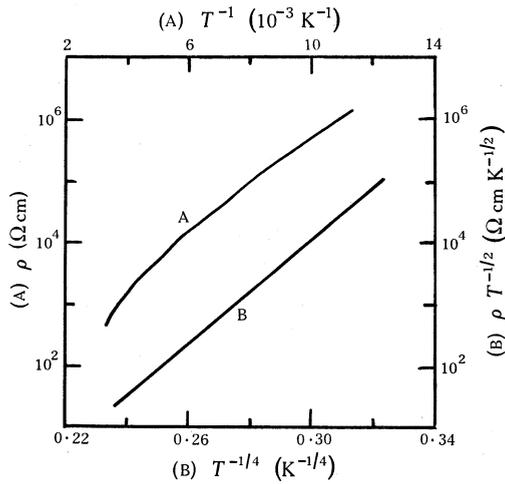


Fig. 3. Resistivity of a-Ge. Curve A is a plot of  $\log \rho$  versus  $T^{-1}$ , appropriate for conductivity by excitation to extended states, while curve B is a plot of  $\log(\rho T^{-1/2})$  versus  $T^{-1/4}$ . The straight line for curve B is predicted for variable range hopping, though its validity is suspect at such high temperatures as these.

The most commonly quoted evidence that the states in the gap are localized is the characteristic thermally activated conductivity (Mott 1969). At a finite temperature an electron can be excited from one localized state to another within a few  $k_B T$  of its energy, the excess energy  $\Delta\epsilon$  being supplied by some thermal excitation (e.g. a vibrational excitation). The typical distance  $R$  to the nearest state of the appropriate energy is related to  $\Delta\epsilon$  by the state density:

$$n(\epsilon) = \{(\Delta\epsilon) \times \frac{4}{3}\pi R^3\}^{-1}. \tag{1}$$

The probability of a hop over energy  $\Delta\epsilon$  and distance  $R$  should be proportional to the product of the matrix element squared,

$$|\langle 1 | V_{\text{vib}} | 2 \rangle|^2 \propto \exp(-2\alpha R),$$

and the probability  $\exp(-\Delta\epsilon/k_B T)$  that the appropriate vibration is present. Thus at a given temperature the probability  $P$  of a hop to a site at distance  $R$  is just

$$P \propto \exp\{-2\alpha R - 3/4\pi n(\epsilon) R^3 k_B T\}. \tag{2}$$

Equation (2) represents a fairly sharp probability function, so it is not unreasonable to assume that the most probable hopping length dominates the conduction process.

The maximum probability of equation (2) is

$$P_{\max} \propto \exp\{-(T_0/T)^{\frac{1}{2}}\}, \quad \text{with} \quad T_0 \approx 18\alpha^3/n(\epsilon_p)k_B.$$

If the conduction is caused by this 'thermally activated diffusion' we expect a conductivity of

$$\sigma(T) = \sigma_0(T) \exp\{-(T_0/T)^{\frac{1}{2}}\},$$

where  $\sigma_0$  is a slowly varying function of  $T$  whose value and temperature dependence are still somewhat uncertain. This, along with other difficulties with the derivation and application of the ' $T^{-\frac{1}{2}}$ ' law are discussed by Paul (1976). Fig. 3 shows data, taken by R. Buckley in our laboratory, which appear to follow the law rather well.

### Amorphous Silicon and Germanium

The elements silicon and germanium can be formed into amorphous networks by simply depositing them on a cool ( $T_s < 500^\circ\text{C}$ ) substrate, using any one of a number of deposition techniques. Early interest in these materials was stimulated by the hope that elemental amorphous semiconductors would be simpler than those involving more than one constituent. This expectation has been only partially realized, for the properties of a-Si and a-Ge depend critically on the sample preparation conditions.

These materials form an amorphous network in which the short-range order is nearly as perfect as that in the crystalline phase: almost every atom has four nearest neighbours at a well-defined distance and arranged in nearly tetrahedral symmetry. Those atoms without the required number of nearest neighbours represent a severe local defect (dangling bond) and provide a centre of formation for a localized state with an energy near the centre of the gap. In addition to single defects, these materials are permeated with a large number of voids with diameters as large as 20 or 30 Å ( $1 \text{ \AA} = 10^{-10} \text{ m}$ ), on the surface of which there are numerous dangling bonds. The void size and density are strong functions of the preparation conditions so that the density of states in the gap can vary over many orders of magnitude upon change of, for example, the substrate temperature during deposition. Furthermore, the incorporation of hydrogen apparently removes the dangling bond states from the gap (Lewis 1976; Moustakas and Paul 1977) (presumably by completing the dangling bonds and pulling the states into the valence band), and the presence of hydrogen is essential to at least one deposition technique (decomposition of silane ( $\text{SiH}_4$ ) or germane ( $\text{GeH}_4$ )).

Since the amorphous forms of silicon and germanium are rather cheaper to prepare than the crystalline forms, there is a considerable industrial interest in the possibility of making electronic components, most importantly solar cells, from the amorphous phase. The development of such devices has been inhibited by difficulties encountered in changing the conduction characteristics by doping. A large number of gap states act as a source or sink of electrons when doping with an acceptor or donor, thus pinning the Fermi level to the centre of the gap. This leads to the curious situation that the room temperature conductivity of the pure materials is higher in the amorphous phase than in the crystalline phase, due to hopping conduction in localized states, while in dilute alloys the crystalline phase conductivity, via band

states, is larger. Successful doping (Spear 1977) and the construction of solar cells of more than 5% efficiency have finally been achieved over the last few years by reducing the density of gap states with the introduction of hydrogen (Carlson and Wronski 1976; Wilson *et al.* 1978).

### Far Infrared Absorption

For some years there has been a research interest in amorphous semiconductors at Victoria University (Sutton 1975; Bringans and Sutton 1976; Buckley and Trodahl 1978), with our most recent work being measurement of the far infrared ( $10\text{--}500\text{ cm}^{-1}$ ) absorbing properties of vacuum deposited a-Si, a-Ge, and a-Ge-Ga alloys. I will concentrate on these measurements and the implications of our results.

Absorption of radiation in the far infrared spectral region arises primarily from coupling between photons and vibrational excitations, a process which is forbidden in the presence of the long-range order found in crystalline silicon and germanium. The relevant selection rules are relaxed in the amorphous phase, and in principle it is possible to obtain vibrational state densities from absorption spectra. In practice this has not been possible, for the frequency (or mode) dependence of the photon-vibration matrix element is not known, and indeed early measurements (Stimets *et al.* 1973; Brodsky and Lurio 1974; Taylor *et al.* 1976) showed that this matrix element depends critically on sample preparation.

Previous far infrared work on a-Si and a-Ge has been inhibited by the fact that bulk samples (thicker than about  $10\text{ }\mu\text{m}$ ) cannot be prepared. The films that can be prepared are either too thin for significant absorption to take place or are so thick that severe thin-film interference partially masks the expected absorption-related structure. We have avoided these problems by using thin ( $<0.5\text{ }\mu\text{m}$ ) weakly absorbing samples and placing them in a nonresonant cavity. Radiation enters the cavity through one hole and escapes to the detector through another, sampling the film many times in the process. Spectral measurements of the radiation entering and leaving the cavity then serve to give a determination of the sample's absorption and of its conductivity or inverse attenuation length  $\eta$  (Buckley and Trodahl 1978). The results for a-Si, a-Ge and an a-Ge-Ga alloy are shown in Fig. 4.

We find that the low frequency conductivity in a-Si is well represented by a term proportional to the square of the frequency, implying that the absorption, by acoustic excitations at these frequencies, is proportional to the density of vibrational states. The same seems to be true of a-Ge and the alloys, though in these samples the structure lies at lower frequencies so that we observe the  $\nu^2$  behaviour over a relatively small range. Thus our data agree with microwave experiments (Taylor *et al.* 1976) which have shown that the photon-vibration matrix element approaches a finite constant at low frequencies, rather than the  $\nu^2$  dependence predicted theoretically for small deviations from tetrahedral order (Alben *et al.* 1975). We feel that it is likely that the coupling at these frequencies is enhanced by charged local defects, a proposal that is strengthened by our alloy results.

Turning next to the germanium alloys, we see that the high frequency ( $\nu > 100\text{ cm}^{-1}$ ) conductivity is nearly independent of gallium concentration and even the low frequency peak grows without shifting as gallium is introduced. We interpret this as indicating that the vibrational density of states (and thus the structure

and force constants) remains nearly unaltered with as much as 15% gallium, and that the rise in the low frequency peak is caused by an increase in the phonon–vibration coupling strength. Such an enhancement could arise from a cluster of charge, which provides strong coupling to any vibrational excitation with a wavelength (or correlation length) larger than the cluster diameter. The strengthened coupling at low frequencies and its concentration dependence are consistent with a model in which at least 10% of the gallium atoms ionize states on the surface of 10–20 Å diameter voids (Buckley and Trodahl 1978).

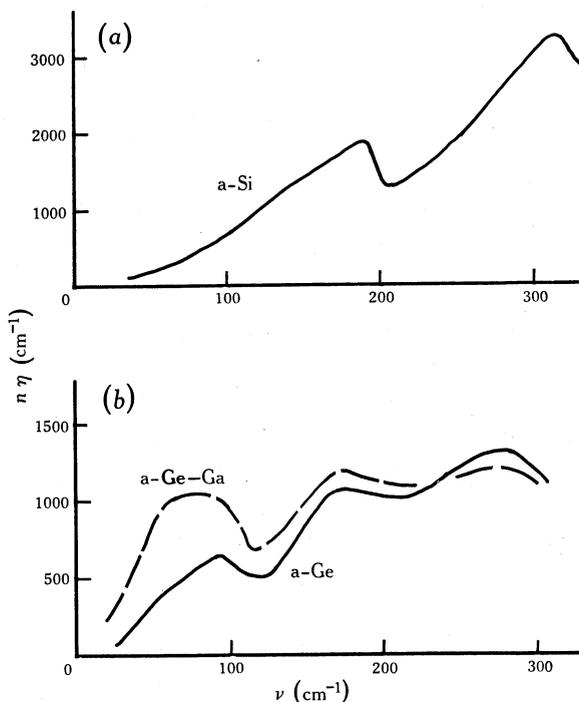


Fig. 4. Product of the absorption coefficient  $\eta$  and the refractive index  $n$  for (a) a-Si and (b) a-Ge and a-Ge-Ga(5%) in the far infrared region.

We believe that the recognition of the role played by voids in the low frequency phonon–photon coupling brings the observed vibrational absorption spectra into line with those calculated numerically (Alben *et al.* 1975; Beeman and Alben 1977) using void-free ‘random’ networks thought to represent the atomic positions in a-Ge. These calculations approximately reproduce the observed structure above about  $100\text{ cm}^{-1}$ , but below this frequency the calculations predict negligible absorption. We believe that the low frequency absorption is enhanced by voids, which carry a residual charge even in the absence of impurity atoms.

An interesting incidental implication of our model is that many, if not most, of the gallium atoms form acceptor states by bonding with fourfold coordination. This is at odds with the simple chemical argument that gallium (valence 3) might enter with threefold coordination thus allowing for a reduction in the strain energy of the amorphous phase.

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