ELECTRONIC DIELECTRIC CONSTANT OF AMORPHOUS SEMICONDUCTORS

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We calculate the electronic dielectric constants for amorphous semiconductors from their short-range structural data. The agreement with measured values supports the contention in Phillips' spectroscopic theory of bonding that it is the chemical bond which is of primary importance in determining the electronic dielectric constants.

In this report we extend the recently developed Phillips spectroscopic theory[1,2] of chemical bonding in crystals to interpret the electronic dielectric constant ϵ_0 of amorphous semiconductors in terms of their short-range structure. Two classes of amorphous semiconductors are considered: (1) those with different short-range order in their crystalline and amorphous forms, such as GeTe, and (2) those with essentially the same short-range order in their cyrstalline and amorphous forms, such as Si and Ge.

We account for the dramatic changes in ϵ_0 between the crystalline and amorphous forms of the first class by a straightforward application of the extension[3] of Phillips's theory[1,2] to average valence V materials. More subtle changes are exhibited by the second class of amorphous semiconductors. We incorporate the essential aspects of disorder-induced density variations, dangling bonds, and voids into the framework of the spectroscopic theory. This allows one to calculate the observed magnitude of ϵ_0 as well as its dependence on annealing. To our knowledge, no other theory is presently available to calculate ϵ_0 in amorphous semiconductors. The success of these applications not only shows the usefulness of the Phillips theory but also lends support to Phillips's underlying concept of the importance of the short-range bonding in determining the dielectric properties of solids.

The spectroscopic theory of chemical bonding in crystals is based on an isotropic, single-gap, two-band model.[4] In the theory the zero-frequency electronic dielectric constant ϵ_0 is expressed in terms of a single effective energy gap E_g by the relation

$$\epsilon_0 = 1 + (\hbar\omega_p)^2/E_g^2, \tag{1}$$

where $\omega_p^2 = 4\pi Ne^2/m$ is the plasma frequency of the N valence electrons (of mass m and charge e) per unit volume. Note that the Kramers-Kronig relation

$$\epsilon_0 - 1 = (2/\pi)\int_0^\infty (\epsilon_2/\omega)d\omega \tag{2}$$

and the sum rule

$$\omega_p^2 = (2/\pi)\int_0^\infty \omega\epsilon_2 d\omega \tag{3}$$

relate the parameters of Eq. (1) to ϵ_2, the imaginary part of the dielectric constant. Thus the theory seems particularly appropriate for the many crystals where ϵ_2 is dominated by a large narrow peak. However, the usefulness of defining an average optical gap in this way is not restricted to a particular form of ϵ_2 as is demonstrated by the successful application of the theory to a wide variety of physical problems.[1,2,5] As the model is based on an average spherical potential it should be particularly suitable for amorphous semiconductors[4] which do not have much detail in their optical spectra.

According to Phillips's theory the effective gap E_g which is evaluated by Eq. (1) has a covalent component E_h and an ionic component C, related by

$$E_g^2 = E_h^2 + C^2. \tag{4}$$

E_h is assumed to depend only on the nearest-neighbor distance d, as

$$E_h \propto d^{-5/2} \tag{5}$$

for the $A^M B^{8-M}$ crystals. C is then found from Eq. (4). Ionic gaps determined in this way closely fit

$$C = b\left(\frac{Z_\alpha}{r_\alpha} - \frac{Z_\beta}{r_\beta}\right)\exp\left[-k_s\frac{r_\alpha + r_\beta}{2}\right], \tag{6}$$

where Z_α and Z_β are the number of valence electrons of atoms α and β, r_α and r_β are the covalent radii of the group-IV crystals on the same rows of the periodic table as atoms α and β, k_s is the Thomas-Fermi screening factor, and b is an experimentally determined constant of order unity.[2]

Amorphous GeTe has an ϵ_0 55 to 70% less than crystalline GeTe.[6,7] As we will show, the large decrease in ϵ_0 results from a change in short-range order from weakly bound nearest neighbors in the crystal to more strongly bound nearest neighbors in the amorphous phase. Because the difference is so large, our analysis for GeTe will consider only those factors that produce large changes and leave to the treatment of Si and Ge below those corrections of the order of a few percent. Further we do not explicitly include the effects of d electrons, but since we treat the parameters by scaling, any change in the results due to d-electron effects should be very small.

Crystalline GeTe at room temperature exists in a slightly distorted rock-salt structure. The deviation from coordination 6 with a nearest-neighbor distance of 2.99 Å is so small as to be negligible for the discussion below. We calculate the effective energy gap for the crystal from ϵ_0 and the crystal structure. We find E_h from an approximate radial dependence of $d^{-5/2}$ inferred from the group V semimetals[3] for average valence V crystals just as Phillips[1] inferred from the group-IV semiconductors for the average valence-IV crystals. From E_h and E_g we then determine C from Eq. (4) (see Table I).

Dove et al.[8] and Betts, Bienenstock, and Ovshinsky[9] have studied the radial distribution function (rdf) of amorphous GeTe. They obtain a peak in the rdf at 2.65 Å. The amorphous film density is measured as 5.6 ± 0.5 g/cm^3,[8] and is used to calculate ω_p and k_s. At this point we apply the concept that it is the chemical bond which determines the electronic dielectric properties. The strength and the character of the chemical bond (E_h, C) are determined by nearest-neighbor distances and densities, according to Eqs. (5) and (6). Hence we obtain the amorphous homopolar gap E_h^{amor} from the crystalline homopolar gap E_h^{cryst} by

$$E_h^{\text{amor}} = E_h^{\text{cryst}}(d^{\text{cryst}}/d^{\text{amor}})^{5/2}. \tag{7}$$

In scaling C according to Eq. (6), we assume that r_α and r_β are proportional to d, and obtain

$$C^{\text{amor}} = C^{\text{cryst}}(d^{\text{cryst}}/d^{\text{amor}}) \times \exp[-2(k_s^{\text{amor}}d^{\text{amor}} - k_s^{\text{cryst}}d^{\text{cryst}})]. \tag{8}$$

Scaling the gaps in this way results in a value for ϵ_0 for amorphous GeTe of 14, a decrease of 60% from the crystalline value as compared with the observed 55 to 70% (see Table I).

Table I. Parameters measured and calculated for crystalline and amorphous GeTe, with labels defined in the text.

	ϵ_0 (meas)	ϵ_0 (calc)	E_g (eV)	E_h (eV)	C (eV)	d (Å)
Crystalline	36	···	2.7	1.7	2.1	2.99
Amorphous	11	14	4.4	2.2	3.7	2.65

To test the assumptions which led us to the prediction of the dielectric constant of amorphous GeTe, we proceed to study the case of GeSe. Here the crystal structure is also only slightly different from rock salt and has three nearest neighbors at 2.58 Å and three at 3.34 Å. The crystal[10] and amorphous[11] dielectric constants are known so that we predict, assuming the amorphous form is similar in coordination to amorphous GeTe,[12] that the peak in the rdf is at 2.46 Å. Measurements are in progress to test this prediction.

While amorphous GeTe has a different short-range order than its crystalline form, amorphous Si and Ge both have about the same nearest- and second-nearest-neighbor environment as their respective crystals. The experimental observations of ϵ_0 indicate about the same values in both crystalline and amorphous forms with ϵ_0 having a small dependence on the thermal history of the amorphous samples. The densities of amorphous films of Si and Ge are generally observed to be less than the densities of the corresponding single crystals. The studies of Moss and Graczyk,[13] Polk,[14] and Brodsky and Title[15] indicate there are two different origins of the observed deficiencies. A real amorphous film is composed of disordered atoms interspersed with voids. The regions with disordered atoms have a local density which we call the microscopic amorphous density ρ^{amor}.[16] The density of the filled regions is less than crystalline density because of the inefficient filling of space due to the disorder. Polk[14] has estimated this density deficiency to be small, ~3%, for "idealized" amorphous Si or Ge. The rest of the density deficiency of a real film arises from voids either within an "idealized" amorphous medium or between clusters of "idealized" amorphous material, although for our purposes it does not matter where the voids are located. The significant point is that in a real film on which one measures ϵ_0, about 10% of the film volume is occupied by voids and 90% by "idealized" amorphous material with about 97% of crystalline density. Such a distribution of atoms is in agreement with the x-ray observations of density by Moss and Graczyk[13] on amorphous Si films as well as the bulk density measurements of Donovan, Spicer, and Bennett[17] and Chopra and Bahl[18] on amorphous Ge, and Mogab and Block[19] on amorphous

Si. There is one other structural effect to consider, namely, the large number of dangling bonds that is observable on internal surfaces in both amorphous Si and Ge films.[15] Both the dielectric constant and the number of dangling bonds decrease with annealing.[20] Because each atom at the surface of a void has a broken or otherwise weakened bond, there must be a decrease in E_h, the measure of the average bond strength, proportional to the fraction s of atoms lying on the surface. That is,

$$E_h(s) = (1-s)E_h(0). \tag{9}$$

We now can write Eq. (1) for amorphous Si or Ge as

$$\epsilon^{\mathrm{amor}} - 1 = \frac{[h\omega_p^{\mathrm{cryst}}(\rho^{\mathrm{amor}}/\rho^{\mathrm{cryst}})^{1/2}]^2}{[E_h^{\mathrm{cryst}}(d^{\mathrm{cryst}}/d^{\mathrm{amor}})^{5/2}(1-s)]^2}, \tag{10}$$

where $\epsilon_0^{\mathrm{amor}}$ is the dielectric constant of the "idealized" amorphous material with its surfaces taken into account. To account for the volume effect of the voids we note that the susceptibility $(\epsilon_0 - 1)/4\pi$ should scale with the occupied volume for a material containing submacroscopic voids of random shapes. Combining Eqs. (1) and (10) with the scaled susceptibilities gives the final result for the measured $\epsilon_0^{\mathrm{film}}$ of a real amorphous film in terms of $\epsilon_0^{\mathrm{cryst}}$ as

$$\frac{\epsilon_0^{\mathrm{film}} - 1}{\epsilon_0^{\mathrm{cryst}} - 1} = \frac{\rho^{\mathrm{film}}}{\rho^{\mathrm{cryst}}} \frac{(d^{\mathrm{amor}}/d^{\mathrm{cryst}})^5}{(1-s)^2}. \tag{11}$$

Note that $\epsilon_0^{\mathrm{film}}$ is very sensitive to the relative magnitudes of the three effects: density, bond length, and surface atoms. Any detailed comparison would require all three parameters to be measured on the same sample. Light and Wagner[21] and Moss and Graczyk[13] cite no change in d, the first peak in the rdf in crystalline and amorphous Si, while Grigorovici[22] in his review quotes a d^{amor} larger than d^{cryst}. Similar variations exist in density measurements. Information on all three parameters on a single sample is not readily available, but we still can make a comparison with a meaningful experiment by varying one of the parameters while keeping the others constant. The change in the number of dangling bonds with annealing is such an experiment. Moss and Graczyk[13] report that d^{amor} in amorphous Si does not change with annealing and a re-examination of the data of Brodsky et al.[20] indicates that ϵ_0 and the number of dangling bonds both decrease with annealing while the film thickness (and therefore the density) remains the same. The observed change in ϵ_0 due to the annealing out of dangling bonds and surface atoms is well accounted for by Eq. (11) (see Table II).

Table II. Comparison of the calculated and measured changes in ϵ_0 with annealing for an amorphous Si film. The initial fraction s_i of surface atoms [(number of surface atoms per unit volume)/(number of atoms per unit volume)] was for a room-temperature annealed film while s_f was measured after 400°C anneal. The ϵ_0's were measured under the same conditions on the same film.

s_i before anneal	4×10^{-2}[a]
s_f after anneal	10^{-2}[b]
$\Delta s = s_f - s_i$	-3×10^{-2}
$\Delta\epsilon_0/\epsilon_0 = 2\Delta s/(1-s_i)$	-0.06
$\Delta\epsilon_0/\epsilon_0$ (meas)	-0.06[b]

[a] Ref. 15. [b] Ref. 20.

In summary, the comparison of our calculated values and those determined experimentally lends support to the underlying contention that the electronic dielectric constant is strongly influenced by the short-range structural parameters of amorphous films. We can account for the magnitudes as well as the changes in ϵ_0 in amorphous films due to annealing.

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REFLECTION SPECTRUM OF SOLID NITROGEN IN THE VACUUM ULTRAVIOLET

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The reflection spectrum of solid N_2 at 4.2°K has been measured over the wavelength range 550-1550 Å for the first time. These data reveal that Rydberg states thought to perturb excited vibrational levels of the $b\,^1\Pi_u$ state are present though not directly observable in the solid.

The study of the absorption spectra of solidified gases has usually been limited to energies less than the transmission limit of LiF at 11.8 eV. This has prevented many of the strong valence and Rydberg transitions of the common gases from being observed either in the pure solid or when isolated in an inert matrix. The perturbations introduced by the crystalline lattice often aid in confirming the classification of the gas-phase energy levels, particularly when these levels are perturbed by close-lying Rydberg states. The large size of Rydberg orbitals makes them particularly susceptible to modification in the solid, so that perturbations due to Rydberg states in the gas phase can be reduced or even eliminated in the solid-state spectra. For example, when NO is isolated in a rare-gas matrix,[1] the Rydberg series fail to appear in the spectrum, and the spacing of the $B^2\Pi$ and $B'^2\Delta$ valence-state vibrational levels becomes perfectly regular, in contrast to the gas phase.

The absorption spectrum of N_2 has been examined for $E < 11.8$ eV in both the pure solid[1-4] and in a rare-gas matrix.[1] The two weak gas-phase transitions, $a^1\Pi_g \leftarrow X^1\Sigma_g^+$ and $w^1\Delta_u \leftarrow X^1\Sigma_g^+$, are observed in both spectra, but as the energies of the strong gas-phase valence and Rydberg transitions exceed 11.8 eV, they have not yet been observed in the solid. Although the bands arising from these transitions were first discovered almost thirty years ago,[5] only recently has a consistent classification for them been proposed.[6,7] This scheme formally groups the twelve or more "states" previously believed to exist into two valence and three Rydberg states. These states interact strongly in the gas phase. In particular, the lowest level of the $c^1\Pi_u$ Rydberg state, $c_3(0)$, severely perturbs the $v' = 5$ level of the $b^1\Pi_u$ valence state. Smaller perturbations are produced in neighboring vibrational levels, resulting in a highly irregular spacing in the b state.

We have obtained for the first time the reflection spectrum of solid α-N_2 from 8 to 22 eV. Spectroscopically pure N_2 was condensed from the gas as a film at least 1000 Å thick onto a polished copper substrate maintained at 4.2°K. Collimated Lyman continuum radiation produced by a Garton flash tube[8,9] illuminated the sample directly at an angle of incidence of 45°, and the beam was reflected specularly into a 3-m normal-incidence vacuum spectrograph with a dispersion of 5.5 Å/mm. A slit width of 300 μm ensured adequate density on Kodak 101-01 film for 50-100 flashes of the source. Photographic photometry was used to separate the continuous features of the nitrogen spectrum from the wavelength dependence of the source intensity. To this end, the spectrum of the source reflected off the bare substrate was photographed on each film in a set of calibration exposures prior to cooling the substrate. Numerical data of the film density $D(\lambda)$ versus the number of source flashes N were