Submicroscopic-Void Resonance: The Effect of Internal Roughness on Optical Absorption

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An expression is developed for the optical dielectric constant of a medium containing submicroscopic voids. For an absorbing host medium, voids introduce additional optical structure resembling that due to surface roughness. Void resonance absorption may account for unexplained structure recently reported in the optical constants of amorphous germanium.

The physical properties of thin films of amorphous semiconductors[1,2] are currently subjects of lively interest and controversy. Discrepancies in experimental results reported by different laboratories are widely ascribed to incomplete characterization of samples. Adequate characterization of thin films is notoriously difficult,[3] partly because of the frequent occurrence of microscopic inhomogeneities in the form of compositional fluctuations, granules, or pinholes. Effects due to extremely small structural imperfections may be important: Thus, inhomogeneities with dimensions less than 50 Å have recently been postulated to account for results observed in electron-spin-resonance[4] and electron-diffraction[5] studies of amorphous Si. Optical effects have not been elucidated.

Previous theories of the optical properties of inhomogeneous films have focused attention on the scattering of waves by islands (or microparticles) of solid material[6] whose imperfect fit with one another leaves irregular void spaces in the sample. As will be shown elsewhere, there is profound computational advantage in treating dense inhomogeneous films from the present alternative point of view, wherein waves are considered to propagate in the solid regions and suffer scattering by the void spaces.

This Letter presents a simple theory for the effect of sharply delimited submicroscopic voids on the optical constants of a material. The theory is entirely classical and assumes a steplike change in local permittivity at each void surface. The results predict that the introduction of voids into an absorbing host leads both to diminution of absorption characteristic of the host *and* to the appearance of new resonance peaks in the imaginary part of the effective dielectric constant. These latter peaks are termed "submicroscopic-void resonances" when caused by internal voids too small to be resolved by radiation of the wavelengths involved.

To facilitate mathematics the highly idealized model shown in Fig. 1 is assumed. The voids are approximated by aligned ellipsoidal vacuum spaces of various sizes having identical shapes and depolarization factors L.[7] They comprise a volume fraction δ of the composite material; the host material occupies a volume fraction $1-\delta$. The host material (between the voids) is assumed to be isotropic with a complex dielectric constant $\kappa \equiv \kappa' + i\kappa''$ which may be a strong function of several variables, including photon energy and sample temperature.

The problem then is to calculate wave propagation through a disordered array of aligned, anisotropically polarizable scatterers. Complete results, including multiple scattering for the case of dipole scatterers, will be presented elsewhere. It can be shown that the effective dielectric constant of the composite medium is a *tensor* with symmetry properties related to those of an individual void. The special case of polarization

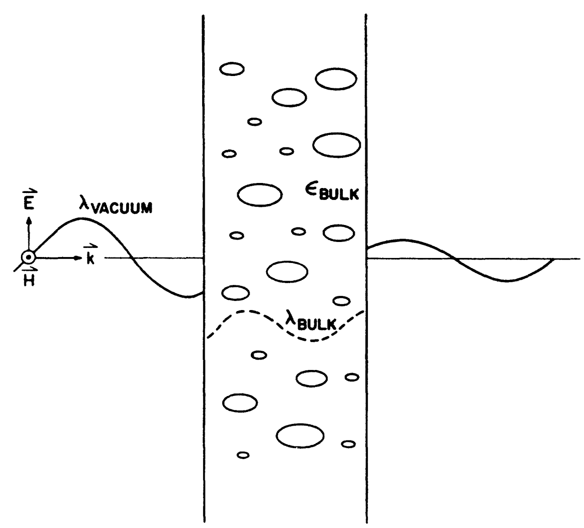

FIG. 1. Idealized model of submicroscopic voids, consisting of oriented ellipsoidal vacuum spaces having different sizes but the same shape. Void dimensions are assumed small, on the scale of the spatial variation of plane waves in vacuum or in the bulk interstitial material.

along a principal axis of a void (assumed in Fig. 1) reduces, for $\delta \ll 1$, to an expression reminiscent of the Clausius-Mossotti equation[8]:

$$\kappa_{\text{eff}} = \kappa(1 + \tfrac{2}{3}\delta\pi_v)/(1 - \tfrac{1}{3}\delta\pi_v), \tag{1}$$

where κ_{eff} is the effective dielectric constant of the composite medium and π_v is the electric polarizability per unit volume of an isolated ellipsoidal void in an unbounded space of the host material. As in the rest of the paper, mks units are used.

The polarizability of an isolated void is calculated in the Rayleigh limit of classical scattering theory,[9] which requires the void to be small compared to the wavelength and decay length of plane waves in the host. As will be shown elsewhere, the principal polarizabilities π of an ellipsoidal void of volume V then become

$$\pi = V\frac{1-\kappa}{L+(1-L)\kappa} \equiv V\pi_v, \tag{2}$$

where L is the depolarization factor for electric fields directed along the principal axis of interest. This result shows that the polarizability per unit volume of the void (π_v) is *independent of the void size* (V) and reflects its shape only through the factor L, which has range $0 \leqslant L \leqslant 1$. Void size consequently does not appear as a parameter in κ_{eff}. For a distribution of void *shapes*, π_v in Eq. (1) is replaced by a weighted average of the expression in (2), covering the values of L involved.

When the effective dielectric constant is evaluated using Eq. (2) in Eq. (1), it is possible to arrange the results in the following way:

$$\kappa_{\text{eff}} = F + H\kappa - FG/(\kappa + G). \tag{3}$$

Here F, G, and H are functions of δ and L only, given by

$$\begin{aligned} F &\equiv \delta/(1 - L + \tfrac{1}{3}\delta), \\ G &\equiv (L - \tfrac{1}{3}\delta)/(1 - L + \tfrac{1}{3}\delta), \\ H &\equiv (1 - L - \tfrac{2}{3}\delta)/(1 - L + \tfrac{1}{3}). \end{aligned} \tag{4}$$

If the host dielectric constant has a peak in its imaginary part (κ''), then the second term of Eq. (3) shows that this peak will also appear in κ''_{eff}, reduced in strength as the volume fraction of voids increases ($H \leqslant 1$). The third term of Eq. (3) accounts for void resonance, which will occur approximately[10] when the real part of the host dielectric constant (κ') passes through the value $-G$. This resonance will have strength $\simeq FG/\kappa''$, evaluated at resonance.[10]

These effects are illustrated in Fig. 2 where the dashed line corresponds to Eq. (3) evaluated for a 15% volume fraction of spherical voids ($L = \frac{1}{3}$) in a hypothetical Lorentzian host dielectric shown by the solid line. Fixing attention on the imaginary part (in the lower half of the figure) one sees the reduction in strength of the host resonance (expected because there is a reduced number of host oscillators per unit volume of sample). Note the nonlinearity associated with void interaction through multiple scattering: The 15% concentration of voids causes a 21% reduction in host strength ($H = 0.79$). One further observes the additional *void resonance* line at $X \simeq -4.1$, occurring near the condition $\kappa' = -0.4$ (note $G \simeq 0.4$). At the void resonance the absorptive part of κ_{eff} is nearly double that of the host without voids ($FG/\kappa'' \simeq 0.7\kappa''$). The additional absorption is associated with energy lost into the *host* material through the dipole fields scattered by each void. A twofold increase in κ'' can result in remarkably prominent effects in transmission or reflection.

Equation (3) can also be applied to films having both electric and magnetic response. Effective waves then have complex propagation constants given by

$$k_{\text{eff}}^2 = k_0^2 \kappa_{\text{eff}}^e \kappa_{\text{eff}}^m, \tag{5}$$

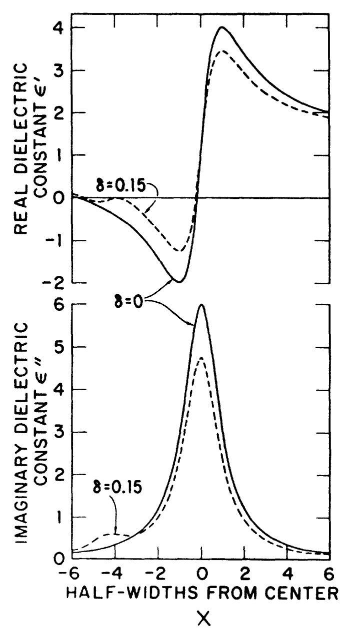

FIG. 2. Theoretical effect of spherical voids on the complex dielectric constant of a hypothetical Lorentzian medium, illustrating Eq. (3). The solid line represents the host material, while the dashed line corresponds to the composite medium containing a 15% volume fraction of voids.

where k_0 is the free space propagation constant, while the superscripts e and m refer, respectively, to electric and magnetic dipole contributions to void scattering. The effective *permittivity* ratio $\kappa_{\rm eff}{}^e$ is evaluated using Eq. (3) with κ given by $\kappa^e \equiv \epsilon/\epsilon_0$, where ϵ is the bulk permittivity of the solid material and ϵ_0 that of vacuum. Similarly, the effective *permeability* ratio $\kappa_{\rm eff}{}^m$ is also given by Eq. (3) with κ replaced by the permeability ratio of the host, $\kappa^m \equiv \mu/\mu_0$.

The foregoing expressions describe the coherent component[11] of the waves transmitted through a randomly scattering sample. Void resonance absorption in these waves can be directly related to a peak in the forward scattering cross section of an isolated void. In this sense, measurement of the effective dielectric constant probes very small-angle scattering.

Void resonance can be viewed as a bulk analog of surface-roughness–induced plasmon absorption.[12] In a normal-incidence experiment, surface roughness induces surface wave absorption approximately proportional to $\mathrm{Im}[1/(\kappa+1)]$.[13] Void losses are induced by roughness *in the bulk* and for sparse distributions of *spherical* voids vary like $\mathrm{Im}[1/(\kappa+\frac{1}{2})]$. The resonance conditions for the two phenomena are very similar, $\kappa' = -1$ and $\kappa' = -\frac{1}{2}$, respectively. Internal roughness may often physically go hand in hand with surface roughness, and both will contribute neighboring or overlapping structure to dielectric constants determined by standard experimental techniques. However, unlike surface-roughness absorption, the total absorption due to voids will increase with sample thickness.

As we have seen, voids can significantly alter the optical properties of an absorbing film even though they are much too small to be resolved by visible light. Since Eq. (3) should hold for voids only tens of angstroms in dimension, void resonance may reveal defects irresolvable by electron microscopy on films of normal thickness (> 500 Å).

In a forthcoming paper it will be shown that void resonance provides a likely explanation for the anomalous structure recently reported by Donovan, Spicer, Bennett, and Ashley[14] in the dielectric constants of amorphous germanium. The strength and position of the secondary peak they observe at photon energies near 8 eV is consistent with a 5% volume fraction of voids having average depolarization factor $L = 0.8$. Void resonance may also partially explain absorption structure reported in optical studies of evaporated metal films,[15] often ascribed entirely to surface-roughness–induced plasmon absorption.

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