Absorption edge, band tails, and disorder of amorphous semiconductors

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In this work the relationship between the characteristic energy of the Urbach edge E_0 and the parameter $B^{1/2}$ of the Tauc's representation of the absorption coefficient of a-SiN– and a-GeN–based alloys is presented and discussed. No correspondence has been experimentally found between $B^{1/2}$ and the topological disorder induced by small impurity concentrations in the network (less than a few at. %), which provokes a broadening of the Urbach tail. In the alloy regime, nevertheless, E_0 and $B^{1/2}$ present a linear correspondence. This fact is discussed in terms of the structural changes induced by atoms of different atomic coordination, i.e., on the base of the dominant bonding character (which changes from purely covalent to partially ionic) and the electronic states at the top of the valence band, as the nitrogen content is increased. The effects of hydrogen, carbon, and silicon in the a-Si and a-Ge networks are also discussed in terms of the Tauc slope $B^{1/2}$ parameter.

I. INTRODUCTION

Despite the similarity of the gross features of the electronic density of states of crystalline semiconductors and their amorphous (a) parents, important differences appear between their optical properties in the fundamental absorption edge region. The break down of the electron **k** wavevector selection rule in the amorphous case entails an optical response which is free of fine features, like van Hove singularities and sharp and well-defined band edges. Moreover, with disorder the abrupt band edges of crystals broaden into tails of localized states extending into the pseudogap. These localized states originate from weak bonds, corresponding to deviations from ideal bond length and bond angle, a characteristic of the topological disorder of the a network. The width of the tails depends on the degree of disorder, and on the bonding character of the master states.

The subgap absorption involves transitions from or to localized states, and has an exponential-like dependence on photon energy. The tailing of the band edges is characterized by a parameter called the Urbach edge E_0,[1] usually determined from photothermal deflection spectroscopy (PDS) data.[2] E_0 is the characteristic energy of the exponential part of the optical-absorption edge which corresponds to absorption coefficients α in the $10 \text{ cm}^{-1} \leqslant \alpha \leqslant 10^4 \text{ cm}^{-1}$ range, and roughly represents the tailing of the valence-band density of states (VB DOS), which is broader than the conduction-band (CB) tail.

In the high-photon-energy range, the so-called intrinsic region involving transitions between extended electron states, the optical absorption of a semiconductors is essentially determined by the convolution of the density of states of the VB and CB, and by the matrix element for optical transitions, normally assumed to be independent of energy.

Because of the presence of localized states at energies between valence and conduction bands, the optical gap is an ill-defined parameter in a semiconductors. Several ways are currently in use to define optical gaps E_g in a semiconductors. The simplest one is to consider E_g as the energy corresponding to an absorption coefficient of 10^3 cm^{-1} (E_{03}) or 10^4 cm^{-1} (E_{04}). Another usual definition of the optical gap

in a semiconductors is the so-called Tauc's gap.[3]

Using the random-phase approximation (complete relaxation of the **k** selection rule) and assuming parabolic valence and conduction bands, Tauc, Grigorocivi, and Vancu[3] defined an optical gap (E_{Tauc}) that is widely used by experimentalists reporting on the optical properties of tetrahedrally bonded a semiconductors:

$$(\alpha h\nu)^{1/2} = B^{1/2}(h\nu - E_{\text{Tauc}}). \quad (1)$$

$B^{1/2}$ includes information on the convolution of the VB and CB states, and on the matrix element of optical transitions, which reflects not only the relaxed **k** selection rule but also the disorder-induced spatial correlation of optical transitions between the valence and conduction bands. Formally, $B^{1/2}$ depends on the product of the oscillator strength of the optical transition, the deformation potential, and the mean deviation of the atomic coordinates.[4] In a perfect crystal, this deviation is characterized by phonons, whereas in a semiconductors it is characterized by the mean bond angle distribution.

In the case of a-Si (or a-Ge) alloys, a decreasing $B^{1/2}$ has been associated with the erosion of the band edges (above the tails) due to a decrease of the Si-Si (or Ge-Ge) bond density.[5] At the energy levels where the Tauc model is used, i.e., for photon energies corresponding to $\alpha \gtrsim 10^4 \text{ cm}^{-1}$, the joint DOS does not include tail states. In spite of this, efforts have been made to associate the Tauc parameter $B^{1/2}$ with the topological disorder and with the band-edge modifications.[5–7] The likely relationship between both parameters, as well its possible interpretation, are the main subject of the present contribution.

II. ANALYSIS OF EXPERIMENTAL DATA

In order to explore the relationship between $B^{1/2}$ and topological disorder, we have analyzed a series of a-Ge– and a-Si–based alloys. Figure 1 shows the E_{04} and E_{Tauc} optical gaps, the Urbach edge E_0, and the full width at half maximum height (FWHM) of the TO-like Raman mode of a series of a-GeN alloy samples, as a function of the nitrogen content (determined from nuclear reaction data[8]). The a-GeN
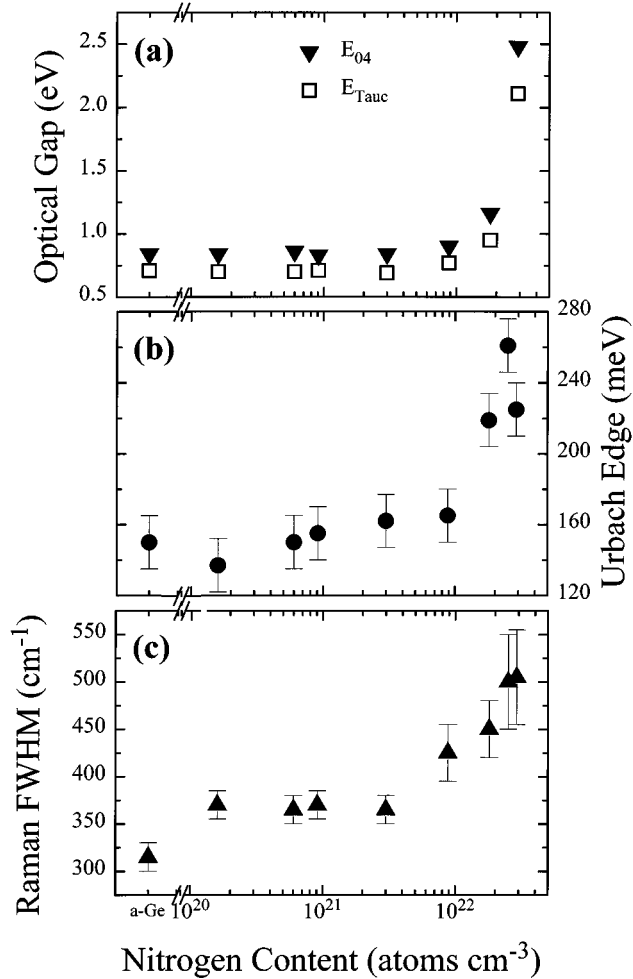
FIG. 1. E_{04} and E_{Tauc} optical gaps (a), characteristic energy of the Urbach edge E_0 (b), and full width at half maximum height (FWHM) of the Raman TO-like mode signal (c) as a function of the nitrogen concentration in the a-GeN alloy sample series. Small nitrogen concentrations (up to $\approx 10^{22}$ atoms cm^{-3}) induce a small increase of the topological disorder. The large N content induces important changes in the structural parameters and in the character of the bonding orbitals.

samples were prepared by rf *sputtering* a pure c-Ge target in an Ar+(N$_2$) atmosphere. With the exception of the nitrogen partial pressure in the chamber during growth, all samples were deposited under the same conditions. Detailed information concerning deposition conditions and the optical, electronic, and structural characterizations of the samples can be found in Refs. 8 and 9. For the series under consideration, the nitrogen concentration in the samples varied from 0 to $\approx 3 \times 10^{22}$ atoms cm^{-3}. Figure 1 shows that the optical properties of the alloys depend on the nitrogen content, a characteristic feature of a alloys involving the bonding of atoms with different coordination.

It is well known that the Urbach edge and the full width at half maximum height (FWHM) of the Raman signal are useful parameters to evaluate the degree of topological disorder.[10] Figures 1(a)–1(c) indicate that at relatively small nitrogen concentrations (up to $N \approx 10^{22}$ atoms cm^{-3}) no significative changes occur, neither of E_{04} and E_{Tauc} gaps, nor of the E_0 Urbach edge and Raman FWHM parameters. Con-
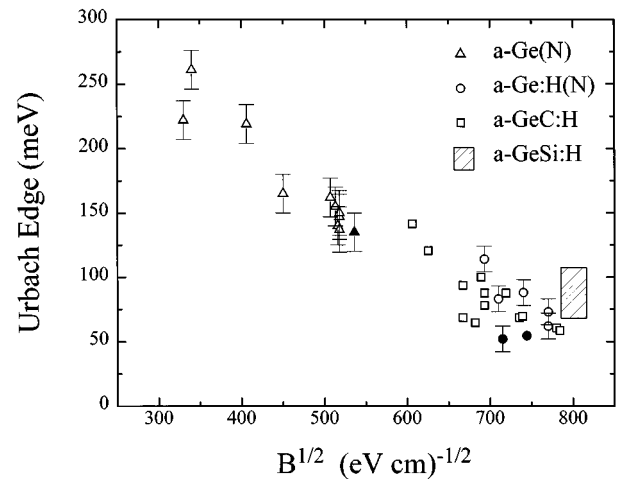

FIG. 2. Urbach edge E_0 vs Tauc's $B^{1/2}$ parameter as measured in different a-Ge-based alloys. Note that, in a-GeN alloys (open triangles), a well-defined trend between both parameters appears only at high nitrogen contents, whereas small N concentrations (N-doped a-Ge:H samples, open circles) produce a collection of scattered values around the parameters of a-Ge:H (filled circles). Alloying with elements which bond with a coordination similar to the host (a-SiGe:H, shaded area) produces also dispersed data around the values corresponding to a-Ge:H. Referring to GeC alloys (open squares), increasing amounts of carbon induce effects similar to those detected for large [N]. These effects are believed to originate from carbon atoms in a *graphiticlike* coordination.

versely, nitrogen concentrations larger than $\approx 10^{22}$ atoms cm^{-3}, induce abrupt changes of all these parameters. In addition to modifications of the optical properties, both IR (Ref. 8) and Raman[9] data indicate that at this specific nitrogen content important structural changes are taking place in the a-Ge network. At small nitrogen concentrations the Ge host network just incorporates a certain amount of impurities having a different size and atomic coordination, which produce a slight increase of topological disorder. Nitrogen concentrations higher than $\approx 10^{22}$ atoms cm^{-3} mean important changes in the electronic structure of the material. At these N concentrations the predominant bonding character slowly changes from covalent to partially ionic, as a result of the combination of sp^3 and sp^2 (or p) hybrid orbitals.[11] This is the main reason for the band-gap widening for a-SiN and a-GeN alloys, the largest values of the gap energies corresponding to the stoichiometric composition ([N]≈ 57 at. %).

III. DISCUSSION

Figure 2 displays the topological disorder (Urbach edge E_0) as a function of $B^{1/2}$ for several a-Ge–based compounds: a-Ge:H,[12] N-doped a-Ge:H [a-Ge:H(N)],[12] a-Ge[8], a-GeN,[8] a-GeC:H,[13] and a-GeSi:H (Ref. 14) alloys. According to Fig. 2, we have the following.

(i) Hydrogenated amorphous germanium (a-Ge:H) samples possess a small Urbach energy, $E_0 \approx 50$ meV, and a $B^{1/2}$ Tauc coefficient in the 700–800 (eV cm)$^{-1/2}$ range. Let us remember that these values closely resemble those found in a-Si:H films. (ii) The doping of a-Ge:H with nitrogen ([N]<1 at %) increases the topological disorder ($50 < E_0 < 120$ meV), but does not significantly alter $B^{1/2}$,

which stays around 750 $(eV\ cm)^{-1/2}$. (iii) E_0 and $B^{1/2}$ for hydrogenated silicon-germanium alloys (shaded rectangle in Fig. 2) remain almost constant through the whole composition range. Note that both elements have the same tetrahedral bonding configuration given by the sp^3 hybridization. (iv) Hydrogenated amorphous germanium-carbon alloys, on the contrary, display scattered values of E_0 and $B^{1/2}$, which may be the consequence of the fact that C atoms can enter the network with tetrahedral and trigonal bonding configuration. (v) Nonhydrogenated germanium (a-Ge) samples possess larger values of $E_0(\approx 140$ meV) and a small $B^{1/2}$ [≈ 550 $(eV\ cm)^{-1/2}$]. (vi) Finally, the introduction of nitrogen into the nonhydrogenated amorphous germanium network, in the 1 at. %$<$[N]$<$35 at. % concentration range, favors the tendency of a decreasing $B^{1/2}$ and an increasing E_0 (see Fig. 2, open triangles). It is only in this case that a clear correlation appears between the Urbach energy and the $B^{1/2}$ parameter.

Big differences emerge between the structures of hydrogenated and nonhydrogenated a semiconductors. The inclusion of hydrogen atoms into the amorphous network of Ge (of the order of 5 at. %), for example, relaxes the structure, producing a less disordered network. The band gap widens, and thermally activated transport dominates. The density of Ge-Ge, and of Ge dangling bonds, decreases and changes in the top of valence-band states occur.[15,10] As a consequence, the absorption edge becomes steeper and $B^{1/2}$ presents a high value.[16,17] However, $B^{1/2}$ is not very sensitive to H concentrations higher than a few percent as the local atomic order is not appreciably altered. The situation resembles that of N doping of a-Si:H and a-Ge:H networks represented in Figs. 2 and 3, in which the electronic states at the top of the valence band (VBM) have not suffered significant modifications. Conversely, the analysis of a-GeC:H alloys indicate that, depending on the deposition conditions and on the C and H concentrations (sometimes involving CH_n complexes), very different $B^{1/2}$ values can be found, without clear trends in most cases. The possibility of simultaneous *graphiticlike* and *diamondlike* bonding configurations prevents us from finding a good correlation between $B^{1/2}$ and disorder (at high-C concentrations).

The existing reported data on disorder induced by nitrogen in a-Si and a-Ge networks have been plotted in Figs. 3(a) and 3(b), which display the relationship between E_0 and $B^{1/2}$ for samples having quite different nitrogen contents. Figure 3(a) reproduces some of the data shown in Fig. 2. Let us note that referring to the alloy phase, Fig. 3(a) shows data corresponding to nonhydrogenated samples, whereas Fig. 3(b) corresponds to hydrogenated alloys of silicon and nitrogen. In spite of the difference, the trends appear to be the same.

Let us now consider Fig. 3(b). The full line represents data of samples in which [N] increases from the nitrogen-free a-Si:H material up to ≈ 50 at. %.[5] As in the case of a-Ge:H, a significant reduction of $B^{1/2}$ and a concomitant augmented E_0 appear only at N concentrations indicative of the SiN alloy phase. However, for even larger nitrogen concentrations, at which the alloy is frankly approaching the nitride phase (phenacite structure,[11] wide optical band gap, high resistivity, etc.[5,8]), the structure again becomes ordered: $B^{1/2}$ increases and E_0 decreases [dashed line, samples indicated by arrows in Fig. 3(b)]. This is an indication that $B^{1/2}$ is
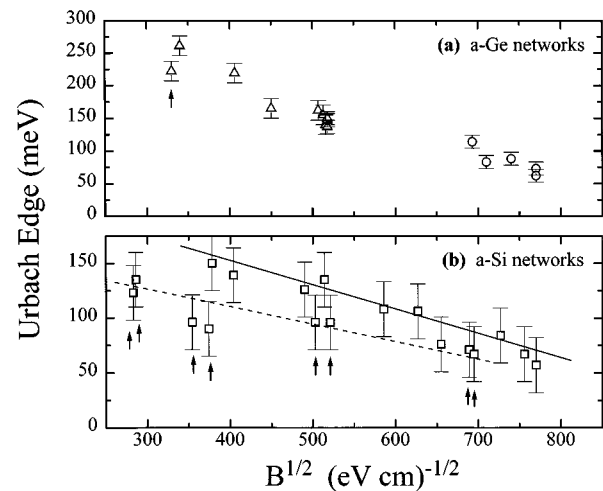

FIG. 3. Urbach energy E_0 vs the Tauc $B^{1/2}$ parameter for a-Ge and a-Si networks containing varying amounts of nitrogen. (a) Some of the experimental data of Fig. 2 referring to a-Ge have been reproduced for comparison with the a-Si case. Note that large $B^{1/2}$ values are associated with less disordered materials. They correspond to N-doped a-Ge:H samples. A well-defined trend between E_0 and $B^{1/2}$ appears at large N concentrations in a-Ge:N samples. (b) Nitrogen in the a-Si:H network: (i) The continuous line represents the variation of structural parameters with increasing [N], from a-Si:H up to [N] 30 at. %. (ii) The dashed line corresponds to E_0 and $B^{1/2}$ values for still larger amounts of nitrogen. Note that the material becomes more ordered as the structure evolves toward the nitride phase [phenacite (Ref. 11)]. The arrows indicate samples possessing a prominent nitride structure. The data on a-SiN:H samples are from S. Hasegawa, M. Matuura, and Y. Kurata, Appl. Phys. Lett. **49**, 1272 (1986). For these samples the E_0 values were calculated from the density of spins using the model proposed by M. Stutzmann, Philos. Mag. **60**, 531 (1989).

sensitive to topological disorder only when electronic structural changes are occurring. The topological disorder (like the one induced by chemical doping), which does not imply a concomitant important modification of the bonding structure and electronic states at the VBM (and/or bonding character) of the network, does not appreciably affect the $B^{1/2}$ values. Note that the same trend seems to be triggered in Fig. 3(a), corresponding to a-GeN samples. The sample indicated by an arrow in Fig. 3(a) is the one having the largest nitrogen concentration.

Taking into account that the samples of Fig. 3 present important changes of $B^{1/2}$ and, simultaneously, present large variations of the optical gap value, it is convenient to investigate any possible connection between both parameters. The analysis of the sample series leads us to conclude that this is not the case. The $B^{1/2}$ parameter appears to be exclusively related to the electronic states at the VBM (and to the elements of the transition matrix which are sensitive to the symmetry of the wave functions[18]), and does not depend on the absolute value of the optical gap. To illustrate the point let us simply remember that for both a-Si:H and a-Ge:H ($E_{04} \approx 1.8$ and 1.2 eV, respectively), $B^{1/2}$ stays around 750 $(eV\ cm)^{-1/2}$. a-GeC:H alloys,[13] a-Ge:H ($E_{04} \approx 1.2$ eV) and a-GeC$_{40\%}$:H ($E_{04} \approx 1.5$ eV) possess $B^{1/2} \approx 700$ $(eV\ cm)^{-1/2}$. a-GeSi:H alloys[14] a-GeSi$_{90\%}$:H ($E_{04} \approx 1.9$

eV) and a-GeSi$_{40\%}$:H ($E_{04} \approx 1.4$ eV) have $B^{1/2} \approx 800$ (eV cm)$^{-1/2}$.

As mentioned in Sec. I, several attempts have been made to associate the $B^{1/2}$ parameter to disorder (Urbach tail).[5–7,13] Most of them are based on a model proposed by Mott and Davis in which[16]

$$B \propto [N(E_C)]^2/(n_0 \Delta E_C), \qquad (2)$$

where $N(E_C)$, n_0, and ΔE_C represent the DOS at the CB edge, the index of refraction and the width of the CB tail, respectively. The above relationship is found assuming that the matrix elements for the electronic transitions are constant over the range of photon energies of interest, the **k**-conservation selection rule is relaxed, and that the DOS at the band tails are linear functions of energy. Reasonable values of $B^{1/2}$ are found by taking $\Delta E_C \approx 0.2$ eV. Experimental data of $B^{1/2}$ and E_0 for a-Ge:H, a-Si:H and a-SiGe:H films, like the ones shown in Fig. 2, do not show the clear correlation implied by the above equation. This may stem from the fact that the photon energy ranges into which $B^{1/2}$ and E_0 are measured are quite distinct, and involve transitions between different electron states.

The present contribution discusses only tetrahedrally coordinated amorphous semiconductors. It is expected that similar considerations between disorder and the Tauc $B^{1/2}$ parameter apply to other classes of amorphous materials like, for example, chalcogenide glasses. The data available in the literature, however, do not allow us to draw definite conclusions on the point.

IV. CONCLUSIONS

The present work indicates that both the Urbach edge E_0 and the $B^{1/2}$ Tauc's parameter give information about the distribution of electronic states in the absorption edge region. The former is exclusively associated with topological (or compositional) disorder at the exponential band tails. The latter (corresponding to extended states above and below the band edges) is highly dependent on the character of the bonding orbitals. In this sense, $B^{1/2}$ can be considered as a probe of topological disorder just in the case of large modifications of the valence-band extreme, which is the case of nitrogen alloys of Si and Ge. Carbon (with the exception of *graphiticlike* bonding) and silicon (germanium) alloying of elemental tetrahedrally coordinated a semiconductors do not produce such important changes in $B^{1/2}$ values, since no important changes in the bonding character and/or network structure occur.

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