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Exponential absorption edge and disorder in Column IV amorphous semiconductors

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We discuss the likely origin of the exponential absorption tail, or Urbach edge, of fourfold coordinated amorphous (*a*-)semiconductors. The present analysis is based on a compilation of a considerable amount of experimental data originating from a great variety of samples, alloys, and authors, and obtained with quite different spectroscopic techniques. An attempt is made to correlate the measured Urbach edge with the structural and optical properties of the samples. The present analysis indicates that the Urbach edge may not only reflect the shape of the joint density of states of the valence and conduction band tails, but may also have important contributions from short-range order potential fluctuations produced by charged defects or impurities. © 1998 American Institute of Physics. [S0021-8979(98)02921-1]

I. INTRODUCTION

In 1953, Urbach reported that photographic emulsions have a fundamental absorption edge displaying an exponential dependence on photon energy.¹ Since then, the effect has been observed in a large collection of other dielectric materials. As this particular behavior is so widely observed, efforts have been made to establish its origin on a single universal mechanism. In spite of past extensive experimental²⁻⁷ and theoretical⁸⁻³² investigations, the microscopic origin of the absorption tail continues to be a matter of research. In crystalline lattices the characteristic energy of the exponential absorption tail (E_U) originates from: (i) a temperature-induced structural disorder, reflecting the thermal occupancy of phonon states;^{7,8} and (ii) the contribution of electric fields, originating from charged impurities or due to strong ionic bonds.^{9,33} All amorphous (*a*-)semiconductors display an exponential absorption edge,

$$\alpha(\hbar\omega) = \alpha_0 \exp[(E_0 - \hbar\omega)/E_U], \quad (1)$$

where E_0 and α_0 are constants associated to thermal and static disorder.³³ In *a*-semiconductors the static disorder (bond-angle and bond-length variations) leads to the appearance of localized electron states in the pseudogap near the conduction-band (CB) and valence-band (VB) extrema. The density of these localized states falls off exponentially with energy into the pseudogap and determines the overall optoelectronic properties.

The energy region probed by photons around the absorption edge corresponds to band-to-band and band-to-tail (tail-to-band) electronic transitions in which the probability of a photon with energy $\hbar\omega$ being absorbed is proportional to the

product of initial (VB) and final (CB) state densities separated by that energy. This is the joint density of states defined as

$$\text{JDOS}(\hbar\omega) = \int N_V(E) N_C(E + \hbar\omega) dE, \quad (2)$$

where N_V and N_C are the density of states of VB and CB, respectively. The initial and final states, however, have a wave nature, and transitions between them are possible only to the extent that the corresponding wave functions overlap. The matrix element for optical transitions between any two such states is the dipole matrix element \mathbf{R} . The imaginary part of the dielectric constant and, consequently, the absorption coefficient depend on both the joint density of states JDOS and the transition matrix element \mathbf{R} :

$$\epsilon_2(\hbar\omega) \propto \mathbf{R}^2(\hbar\omega) (\text{JDOS}) \quad \text{and} \quad \alpha(\hbar\omega) \propto \epsilon_2(\hbar\omega)/n, \quad (3)$$

where $\mathbf{R}^2(\hbar\omega)$ is the squared normalized dipole matrix element averaged over all transitions separated by $\hbar\omega$, and n is the index of refraction. Jackson *et al.*³⁴ have reported measurements on *a*-Si:H indicating that $\mathbf{R}^2(\hbar\omega) \sim 10 \text{ \AA}^2$ over the photon energy range $1.5 < \hbar\omega < 3.0 \text{ eV}$, and slightly greater for $0.6 < \hbar\omega < 1.5 \text{ eV}$.

Impurities in fourfold coordinated *a*-semiconductors may influence the material's properties in a number of ways. Hydrogen atoms, for example, passivate dangling bonds and induce the widening of the pseudogap, a consequence of the recession of the top of the valence band.³⁵ At small concentrations (typically below 1 at. %), Column III and Column V elements provoke important changes in the electronic properties of fourfold coordinated *a*-semiconductors.^{35,36} Larger impurity concentrations correspond to the alloy regime, the samples possessing very different electronic, structural and optical properties. Potential fluctuations produced by impu-

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urities having a very different electronegativity than the atoms of the host network, like N in *a*-Si:H or *a*-Ge:H, may induce an increased absorption via changes of the dipole moment of localized tail electrons or holes. Strictly speaking, in the sub-gap region $R^2(\hbar\omega)$ should depend on the nature of defects and, in particular, on the distribution of charge around it, which modifies the dipole moment of the bound electron. So the constancy of $R^2(\hbar\omega)$ measured in the extended and band-tail states energy range of intrinsic *a*-Si:H is not expected to hold in the last case, for instance, when different impurities are added or defects of a new kind created.³⁴

It is accepted today that the Urbach energy E_U in *a*-semiconductors, normally measured by photothermal deflection spectroscopy (PDS), roughly represents the tailing off of the valence-band density of states (DOS), broader than the conduction-band tail.²⁷ Nevertheless, the above picture suggests that the Urbach slope changes measured in singly doped samples may have contributions from both a broadening of the JDOS due to an augmented topological disorder and from changes of the $R^2(\hbar\omega)$ of transitions induced by charged impurities—there being still no definite conclusion.

Most reports on Urbach energy in *a*-semiconductors correlate E_U variations to just a single structural, electrical, or optical macroscopic parameter. To the present authors' knowledge, a compilation of experimental data involving different disorder-induced parameters, and their relationship to E_U , has not yet been published. This is the main objective of this contribution. We present and discuss such compilation of data referring to intrinsic and doped *a*-Si:H, *a*-Ge:H, and their alloys.³⁷ Based on data extracted from the literature and from our own results we discuss in this article: (i) The influence of the void microstructure on E_U ; (ii) the structural disorder probed by Raman scattering and its correlation with E_U ; (iii) the dependence of E_U on alloying and composition; as well as (iv) the role of deep defects and impurities on E_U variations. Finally, the conclusions suggested by the available experimental evidence are presented.

II. ANALYSIS AND DISCUSSION OF EXPERIMENTAL DATA

A. Analysis of structural data

1. Hydrogenation, microstructure and Urbach edge

In hydrogenated *a*-semiconductors, the peak energy of the infrared (IR) stretching vibration mode of the Si–H (Ge–H) bond indicate two different hydrogen bonding configurations. One corresponds to hydrogen bonded to Si (Ge) in voids having the size of a vacancy [bulk-like Si–H (Ge–H) mode]. The other, with a slightly higher vibration frequency, corresponds to either polyhydride groups SiH_{*n*} (GeH_{*n*}), or to Si–H (Ge–H) bonds inside large size voids [surface-like Si–H (Ge–H) mode].³⁸ The microstructure parameter M is given by the ratio of the integrated areas A of the absorption band of the surface-like IR vibration and the whole Si–H (Ge–H) stretching absorption band:

$$M = A_{\text{surface}} / (A_{\text{bulk}} + A_{\text{surface}}). \quad (4)$$

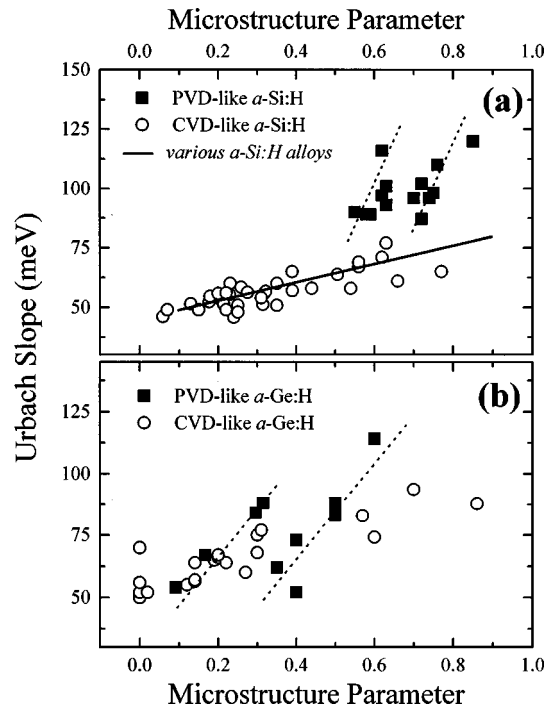


FIG. 1. Urbach slope as a function of the microstructure parameter, as determined from infrared absorption data (see Refs. 40–44, 49–52). The figure indicates a correlation between E_U and M . PVD- and CVD-like methods stand for physical and chemical vapor deposition techniques, respectively. The two dashed lines associated to PVD *a*-Si:H and *a*-Ge:H in (a) and (b) correspond to two different deposition systems. The data of various *a*-Si:H alloys have been taken from the literature (see Ref. 41) and correspond to different *a*-Si:H, *a*-SiGe:H, and *a*-SiC:H samples deposited by the glow discharge technique.

Note that large M 's may correspond to either a less homogeneous hydrogen distribution or to a void rich structure, or both.³⁹

Figures 1(a) and 1(b) show the dependence of E_U on M for *a*-Si:H and *a*-Ge:H alloys, respectively. It is found that E_U always increases with increasing M . Figure 1(a) displays two sets of data corresponding to *a*-Si:H samples deposited by the rf sputtering (physical vapor deposition: PVD-like)⁴⁰ and by the rf glow discharge (chemical vapor deposition: CVD-like)^{41–44} of SiH₄ techniques. It is apparent from the figure that different deposition methods induce different microstructures. The Urbach energy and the corresponding M of PVD-like *a*-Si:H samples are always larger than those of CVD-like *a*-Si:H, an indication that energetic processes deteriorate the compactness of *a*-Si:H films. On the contrary, the density of *a*-Ge:H films increases with some particle bombardment during growth.⁴⁵ Up to the moment, hydrogenated *a*-Ge films of improved quality have been prepared either by sputtering⁴⁶ or by cathodic^{47,48} glow discharge. The data of Fig. 1(b) show that both PVD-like^{49,50} and cathodic CVD-like^{51,52} *a*-Ge:H samples display a dependence of E_U on M similar to that of *a*-Si:H.

Summarizing, the existing experimental data indicate that the broadness of the absorption tail always correlates with the void microstructure, the effect being more important in PVD-like samples. The increased E_U may originate from electric field discontinuities at the edges of the voids which

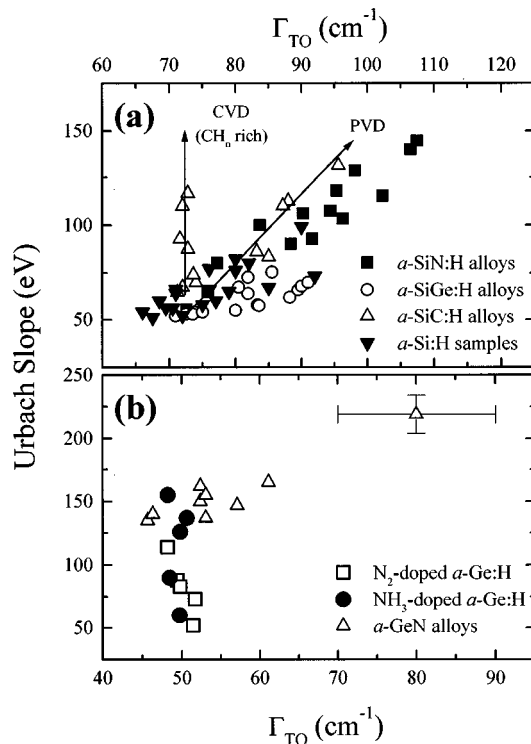


FIG. 2. Urbach slope as a function of the full width at half maximum (FWHM) height of the TO vibration mode, as probed through Raman scattering (Γ_{TO}). The amount of foreign impurities in the samples increases with increasing E_U and Γ_{TO} (see Refs. 40 and 56–58). It may be seen from the figure that small impurity concentrations and/or the presence of polyhydride groups do not induce measurable changes of Γ_{TO} . Notwithstanding the absence of any detectable structural modification at small impurity concentrations E_U variations are always measured. Note that, depending on the method used to deposit the samples [CVD-like methods (rich of CH_n groups) or PVD-like methods (giving a low CH_n concentration)] α -SiC:H alloys show a different dependence of E_U on Γ_{TO} . N_2 -doped and NH_3 -doped α -Ge:H stand for N-doped α -Ge:H samples using nitrogen and ammonia as doping source gases, respectively.

can cause sizable local potential variations in, at least, several atomic layers surrounding the edges. The voids may also induce some additional local disorder at the discontinuity edge resulting from possible reconstruction of their internal surfaces.

2. Raman scattering and Urbach edge

The full width at half maximum (FWHM) height of the Raman transverse optical-like vibration mode (Γ_{TO}) of α -semiconductors depends on the structural disorder.⁵³ Changes of Γ_{TO} correspond to modifications of the short-range order (SRO), particularly of the bond-angle distribution.⁵⁴ Structural disorder in these materials can also be correlated with shifts of the Raman peak frequency which, as those of Γ_{TO} , result from the anharmonic decay of optical phonons due to ionicity, to different atomic masses, or to the interaction of phonons with free carriers.⁵⁵

Figure 2 shows experimental data on E_U and Γ_{TO} of different group IV α -semiconductor alloy samples.^{40,56–58} A clear correspondence between E_U and Γ_{TO} can only be detected in the high impurity concentration, or alloying range. In N-doped α -Ge:H, important E_U changes are measured

without a concomitant Γ_{TO} broadening [Fig. 2(b)]. A similar situation occurs for some Si–C alloys [Fig. 2(a), CVD samples]. CVD α -SiC:H alloys are deposited from the rf decomposition of carbon hydrides and contain a considerable density of CH_n fragments, which are not present in PVD samples. The electronic disorder induced by carbon in the α -Si:H network is always important but, for similar carbon contents, the structural disorder (as measured by Γ_{TO}) in PVD samples appears to be larger than in CVD samples.

Consider now the incorporation of Ge in the α -Si:H network: α -SiGe:H samples display a somewhat opposite behavior. Figure 2(a) shows that α -SiGe:H samples with relatively high Ge concentrations³⁷ display a reasonable degree of structural disorder, as evidenced by an important broadening of Γ_{TO} (more than 20 cm^{-1}), but without a concomitant large increase of the Urbach energy [open circles in Fig. 2(a)]. This experimental finding suggests that Ge may provoke in α -Si:H more structural than electronic disorder, E_U being more sensitive to the latter than to the former. This may stem from the fact that Si and Ge atoms have similar valence structure and chemical properties, their main difference being just their size. This would not be the case for tetrahedrally bonded carbon which, in spite of an electron valence structure similar to Si, possess not only a very different size, but also an electronegativity different from that of Si. The differences should induce both, a structural and an electronic disorder. Carbon atoms, on the other hand, can form complexes with hydrogen giving rise to sp , sp^2 , and sp^3 skeletal configurations. The different configuration of carbon induce a different relaxation of the overconstrained α -Si network. As a consequence, it is expected that the presence of CH_n radicals may help to reduce the structural disorder (network relaxation). Figure 2(a) indicates that this is the case for CVD produced samples. The electronic disorder, however, determined by charge transfer in Si–C bonds is present in all cases and an increased E_U should be always measured, in agreement with experimental results.

Despite the above discussion, it should be noted that Γ_{TO} in α -semiconductors is much larger than in crystalline lattices (α - $\Gamma_{TO} \sim 40 \text{ cm}^{-1}$, c - $\Gamma_{TO} \sim 4 \text{ cm}^{-1}$). As a consequence, Raman scattering does not detect structural changes induced by a small addition of localized states in the α -matrix, although these few additional states may cause a sizable electronic disorder.⁵⁹ In other words, Raman scattering cannot be a very sensitive probe to quantify small structural changes of the α -network. In this sense, the data relating Γ_{TO} with disorder in α -semiconductors have to be considered with some caution. The methods providing structural information about α -alloys, e.g., IR spectroscopy, Raman scattering, small angle x-ray scattering (SAXS), small angle neutron scattering (SANS), extended x-ray absorption fine structure (EXAFS), etc., are much less sensitive (or possess a smaller dynamical detection range) than optical absorption [E_U changes induced by doping or alloying easily measured by (PDS) remain unnoticed in Raman spectra]. In spite of the above, the available experimental data presented in Sec. II A suggest that, in some cases, the structural and the electronic disorder may influence differently E_U changes. In the next section we discuss the optical data.

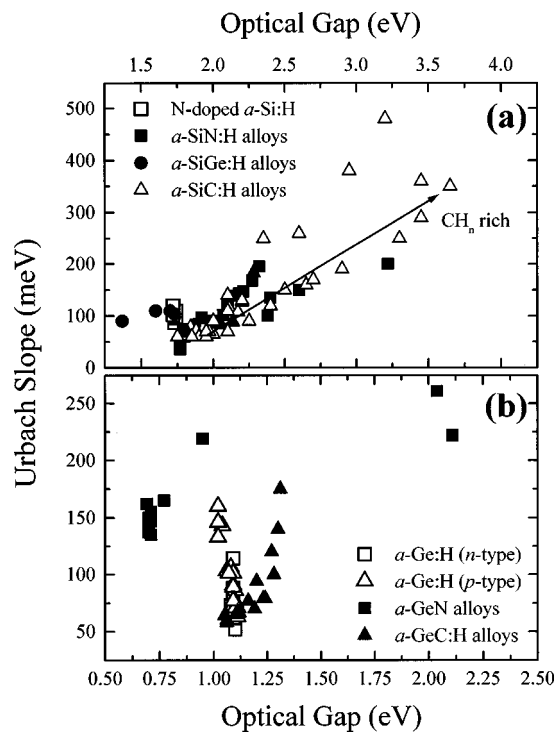


FIG. 3. Urbach slope as a function of the optical gap E_{Tauc} for various different (a) a -Si (see Refs. 40 and 61–67) and (b) a -Ge (see Refs. 67–72) based compounds. A large concentration of impurities leads to an increase of both, E_U and E_{Tauc} .

B. Analysis of optical data

1. Optical gap and Urbach edge

Using the random-phase approximation (complete relaxation of the \mathbf{k} selection rule), the constancy of the momentum matrix operator with energy, and assuming parabolic valence and conduction bands, Tauc *et al.*⁶⁰ defined an optical gap (E_{Tauc}) that has been widely used by experimentalists when reporting on the optical properties of fourfold coordinated a -semiconductors:

$$(\alpha \hbar \omega)^{1/2} = B^{1/2}(\hbar \omega - E_{Tauc}), \quad (5)$$

where $B^{1/2}$ includes information on the convolution of the valence and conduction band states, and on the momentum matrix element for optical transitions, which reflects the relaxed \mathbf{k} selection rule and the disorder-induced spatial correlation of optical transitions between the VB and CB states. Formally, $B^{1/2}$ depends on the product of the oscillator strength for optical transition, the deformation potential and the mean deviation of the atomic coordinates.

Figure 3(a) shows E_U as a function of E_{Tauc} for some a -Si based alloys.^{40,61–67} While E_U increases with the introduction of foreign species in the host matrix both in the doping and in the alloy regime, E_{Tauc} changes are only detectable in the latter case. The same phenomenon is observed in hydrogenated and H-free a -Ge based alloys, shown in Fig. 3(b).^{68–72} In the specific case of nitrogen, an impurity having coordination number and electronegativity different from the host element, doping ($[N] \leq 1$ at. %) gives rise to a large increase of E_U , without affecting E_{Tauc} . In the alloy regime, however, an increase of both E_U and E_{Tauc} is measured. The

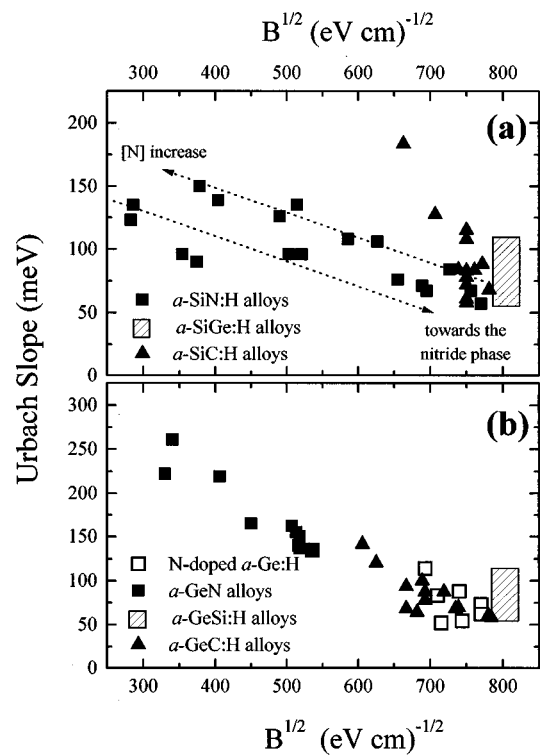


FIG. 4. Urbach slope as a function of the Tauc's $B^{1/2}$ parameter (see Refs. 63, 65, 72, 74, and 75). The figure indicates that the presence of impurities always causes an increase of E_U . There is no general correlation between E_U and $B^{1/2}$, except in the alloy regime, in which the increased Urbach energy stems from structural disorder provoked by a large density of atoms having a different coordination. Note that no clear correlation is found for SiGe alloys. The changes of $B^{1/2}$ in N-containing alloys derive from a change in the character of the electronic orbitals at the VB top, as measured by photoemission techniques.

optical gap widening mechanism in a -GeN alloys is similar to that of a -SiN alloys, in which the VB maximum, dominated by Si 3p states in a -Si, recedes with $[N]$, the highest occupied states changing over N 2p at large contents.⁷³ The data in Fig. 3 show again the possible different contributions of structural and electronic disorder to E_U .

2. Tauc's $B^{1/2}$ parameter and Urbach edge

In a recent publication Zanatta and Chambouleyron⁷⁴ studied the relationship between the characteristic energy of the exponential absorption edge E_U and the Tauc's $B^{1/2}$ parameter [Eq. (5)] of a -SiN and a -GeN based alloys (see Fig. 4).^{63,65,72,74,75} No correspondence was experimentally found between $B^{1/2}$ and E_U at small impurity concentrations in the network (less than a few at.%). These small impurity concentrations may, however, provoke a considerable broadening of the Urbach edge.

In the alloy regime E_U and $B^{1/2}$ are clearly correlated, a correlation originating from the dominant bonding character and the electronic states at the top of the VB as the nitrogen concentration $[N]$ is increased. Electron photoemission spectra, much more sensitive than optical techniques though not susceptible to selection rules, indicate that this is the case.^{73,76} $B^{1/2}$ is primarily associated with the symmetry of

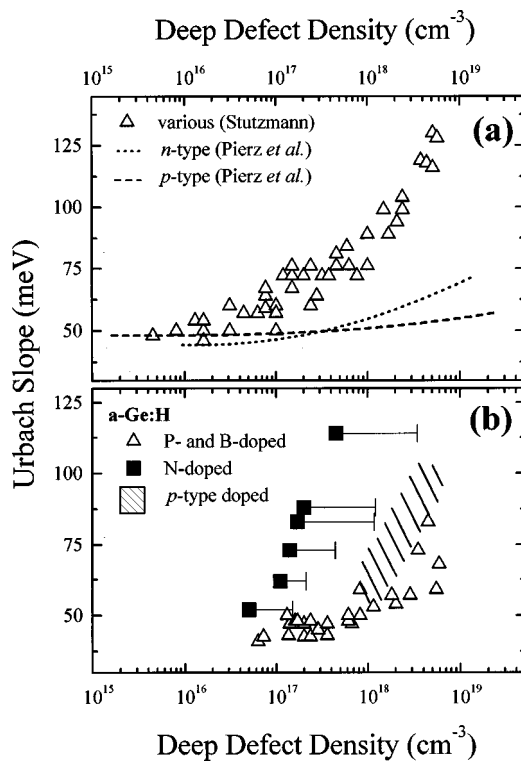


FIG. 5. Urbach slope as a function of the density of dangling bonds for several different *a*-Si (see Refs. 77, 79) and *a*-Ge (see Refs. 68, 71, 80) based compounds. Note the very different dependence of E_U on N_D for P- and B-doped *a*-Ge:H as compared to N-doped samples.

the bonding orbital at the top of the VB (extended states), whereas E_U involves the distribution of localized tail states.

While in the case of *a*-SiGe alloys, no $B^{1/2}$ variation is verified despite a significant E_U increase, in the case of *a*-SiC and *a*-GeC alloys, both $B^{1/2}$ and E_U variations are observed. This is again an indication of different structural and electronic disorder contributions to E_U variations, as previously discussed. Moreover, a connection between E_U and short-range potential fluctuations produced by nitrogen is thus suggested by Fig. 4.

3. Deep defects and Urbach edge

The weak-bond→dangling-bond (DB) conversion model⁷⁷ establishes a relationship between weak bonds (or tail states) and broken bonds. The increase of the structural disorder in *a*-semiconductors leads to an increase of the density of strained bonds. Above a certain threshold, a fraction of these strained bonds “break” giving rise to DBs. In addition to the DB density due to the weak-bond breaking mechanism,⁷⁷ the role of impurities in the process of DB creation must also be considered, once that the chemical doping of *a*-semiconductors is always accompanied by an increased density of DB.⁷⁸ Depending on the position of the Fermi level, the DBs can also be viewed as charged centers inducing potential fluctuations.

Figure 5 shows the relationship between E_U and the DB density (N_D) for *a*-Si:H^{77,79} and *a*-Ge:H^{68–71,80} samples. In spite of the dispersion of the data (most probably a consequence of the method used for the determination of N_D), it is

possible to establish a relationship between these two parameters. Figure 5(a) shows that N_D values higher than $\sim 5 \times 10^{17} \text{ cm}^{-3}$ originate a considerable increase of E_U in *a*-Si:H films. The situation holds for *n*- and *p*-type doped *a*-Ge:H samples as well [Fig. 5(b)]. Note, however, that the dependence of E_U on N_D for N-doped *a*-Ge:H is different from the dependence measured in samples doped with conventional impurities (P, B, As). Although the difference might be fortuitous, it gives support to the considerations done in the previous paragraphs concerning the different contributions to E_U . Nitrogen atoms are more electronegative than any other of the impurities employed and, consequently, may induce considerable changes of $\mathbf{R}^2(\hbar\omega)$ involving weak neighboring Ge–Ge bonds. The available experimental information suggests that a threshold N_D value exists for every impurity above which a significant increase of E_U is detected. In addition, in a recent publication Chambouleyron and Comedi³⁶ have shown that for doped *a*-Ge:H, distinct dopants (B, Al, Ga, In, N, P, and As) lead to the same E_U dependence on the ratio of the density of impurities to the matrix atoms ($N_{\text{imp}}/N_{\text{Ge}}$). This information and the data presented in Fig. 5(b) suggest again the existence of different contributions of structural and electronic disorder to E_U .

In summary, the analysis of the optical data in Sec. II B shows that in intrinsic Column IV *a*-semiconductors, a small amount of foreign impurities (doping regime) leads to an increased density of electronic defects, which also increases the Urbach edge. In this same regime, on the other hand, no variation of the optical parameters associated to structural disorder like E_{Tauc} or $B^{1/2}$ is observed. These latter parameters only correlate with E_U in the alloy regime. Considering the structural (Sec. II A) and optical (Sec. II B) parameters altogether, it can be said that the Urbach edge is determined by both the structural and the electronic disorder. The electronic disorder seems to be the main actor when a small amount of foreign impurities is introduced in the host network, its contribution to E_U being masked when the structural disorder is large. In the *alloy regime* static disorder normally dominates. The latter is the most common reported case, inducing many authors to associate E_U variations with structural disorder only.^{81–85}

III. CONCLUSIONS

This article presents and discusses for the first time a considerable amount of experimental data on the relationship between the exponential absorption tail E_U of Group IV *a*-semiconductors and several disorder-dependent (structural and optical) macroscopic parameters. The available information suggests that the increased absorption measured in *a*-semiconductors may not only originate from changes of the joint density of states, but also from electronic disorder (short-range order potential fluctuations) induced by different chemical species, which may considerably contribute to the broadening of the absorption tails. Contributions from changes of the dipole matrix element for optical transitions deriving from impurities and alloy atoms of very different electronegativity appear to play a role.

Summarizing, besides the broadness of the VB tail, E_U values may be influenced by:

- (1) States localized by long-wavelength potential fluctuations;^{19,20,86,87}
- (2) The variance of the Gaussian potential fluctuations, arising from thermal vibrations, and structural and compositional disorder;⁸⁸
- (3) Potential fluctuations “frozen-in” at the glass transition temperature, or determined by the formation process,^{23,24,89} and
- (4) Long-range electrostatic potentials due to a relatively low concentration of randomly located charged defects.^{6,25,26}

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- ¹F. Urbach, *Phys. Rev.* **92**, 1324 (1953).
- ²T. Tiedje, J. M. Cebulka, D. L. Morel, and B. Abeles, *Phys. Rev. Lett.* **46**, 1425 (1981).
- ³G. D. Cody, T. Tiedje, B. Abeles, B. Brooks, and Y. Goldstein, *Phys. Rev. Lett.* **47**, 1480 (1981). See also, G. D. Cody, in *Semiconductors and Semimetals*, edited by J. I. Pankove (Academic, New York, 1984), Vol. 21B, p. 11.
- ⁴A. H. Mahan, P. Menna, and R. Tsu, *Appl. Phys. Lett.* **51**, 1167 (1987).
- ⁵S. Aljishi, J. D. Cohen, S. Jin, and L. Ley, *Phys. Rev. Lett.* **64**, 2811 (1990).
- ⁶J. A. Howard and R. A. Street, *Phys. Rev. B* **44**, 7935 (1991).
- ⁷M. V. Kurik, *Phys. Status Solidi A* **8**, 9 (1971).
- ⁸D. L. Dexter, *Phys. Rev. Lett.* **19**, 1328 (1967).
- ⁹D. Redfield, *Phys. Rev. B* **130**, 914 (1963); **130**, 916 (1963); **140**, 2056 (1965).
- ¹⁰J. J. Hopfield, *Comments Solid State Phys.* **1**, 16 (1968).
- ¹¹J. D. Dow and D. Redfield, *Phys. Rev. B* **1**, 3358 (1970).
- ¹²H. Sumi and Y. Toyozawa, *J. Phys. Soc. Jpn.* **31**, 342 (1971).
- ¹³J. D. Dow and D. Redfield, *Phys. Rev. B* **5**, 594 (1972).
- ¹⁴J. Skettrup, *Phys. Rev. B* **18**, 2622 (1978).
- ¹⁵S. Abe and Y. Toyozawa, *J. Phys. Soc. Jpn.* **50**, 2185 (1981).
- ¹⁶M. Schreiber and Y. Toyozawa, *J. Phys. Soc. Jpn.* **51**, 1528 (1982); **51**, 1537 (1982); **51**, 1544 (1982).
- ¹⁷J. Singh and A. Madhukar, *Solid State Commun.* **41**, 241 (1982).
- ¹⁸D. Redfield, *Solid State Commun.* **44**, 1347 (1982).
- ¹⁹C. M. Soukoulis, M. H. Cohen, and E. Economou, *Phys. Rev. Lett.* **53**, 616 (1984).
- ²⁰C. M. Soukoulis and M. H. Cohen, *J. Non-Cryst. Solids* **66**, 279 (1984).
- ²¹S. John, C. Soukoulis, M. H. Cohen, and E. N. Economou, *Phys. Rev. Lett.* **57**, 1777 (1986).
- ²²Y. Bar-Yam, D. Adler, and J. D. Joannopoulos, *Phys. Rev. Lett.* **57**, 467 (1986).
- ²³Z. E. Smith and S. Wagner, *Phys. Rev. Lett.* **59**, 688 (1987).
- ²⁴C. T. Chan, S. G. Louie, and J. C. Phillips, *Phys. Rev. B* **35**, 2744 (1987).
- ²⁵M. Silver, L. Pautmeier, and H. Bassler, *Solid State Commun.* **72**, 177 (1989).
- ²⁶M. Silver, G. Winborne, H. Branz, L. Pautmeier, and H. Bassler, *J. Non-Cryst. Solids* **144**, 244 (1989).
- ²⁷S. John and C. H. Grein, *Rev. Solid State Sci.* **4**, 1 (1990).
- ²⁸H. M. Branz and M. Silver, *Phys. Rev. B* **42**, 7420 (1990).
- ²⁹S. D. Baranovskii and M. Silver, *Philos. Mag. Lett.* **61**, 77 (1990).
- ³⁰M. Kemp and M. Silver, *Appl. Phys. Lett.* **62**, 1487 (1993).
- ³¹S. D. Baranovskii, F. Hensel, K. Ruckes, P. Thomas, and G. J. Adriaenssens, *J. Non-Cryst. Solids* **190**, 117 (1995).
- ³²G. Allan, C. Delerue, and M. Lannoo, *Phys. Rev. B* **57**, 6933 (1998).
- ³³N. Mott and E. A. Davis, *Electronic Processes in Non-Crystalline Materials*, 2nd ed. (Oxford University Press, Oxford, 1979).
- ³⁴W. B. Jackson, S. M. Kelso, C. C. Tsai, J. W. Allen, and S. J. Oh, *Phys. Rev. B* **31**, 5187 (1985).
- ³⁵See, for instance, R. A. Street, *Hydrogenated Amorphous Silicon* (Cambridge University Press, Cambridge, 1991), Chaps. 2 and 3.
- ³⁶I. Chambouleyron and D. Comedi, *J. Non-Cryst. Solids* **227–230**, 411 (1998).
- ³⁷In this contribution we separate the samples in two groups: doped samples—the ones with impurities concentration below 1 at. % and; alloy samples—above this limit. We are not interested in the exact composition of the samples for the present discussion. For this specific information the reader should see the original articles. For a simple guide to the figures, it should be noted that the increased amount of foreign species in the original material leads also to an increase of the Urbach edge.
- ³⁸See, for instance, H. Shanks, C. J. Fang, L. Ley, M. Cardona, F. J. Demond, and S. Kalbitzer, *Phys. Status Solidi B* **100**, 43 (1980); M. Cardona, *ibid.* **118**, 463 (1983).
- ³⁹M. K. Cheung and M. A. Petrich, *J. Appl. Phys.* **73**, 3237 (1993).
- ⁴⁰A. R. Zanatta and I. Chambouleyron (unpublished).
- ⁴¹A. H. Mahan, A. Mascarenhas, D. L. Williamson, and R. S. Crandall, *Mater. Res. Soc. Symp. Proc.* **118**, 641 (1988).
- ⁴²J. H. Yoon, X. Xu, M. Kotharay, and S. Wagner, *Mater. Res. Soc. Symp. Proc.* **219**, 93 (1991).
- ⁴³U. Kroll, F. Finger, J. Dutta, H. Keppner, A. Shah, A. Howling, J. L. Dorier, and C. Hollenstein, *Mater. Res. Soc. Symp. Proc.* **258**, 135 (1992).
- ⁴⁴D. Caputo, G. DeCesare, F. Irrera, G. Masini, F. Palma, M. C. Rossi, G. Conte, G. Nobile, and E. Terzini, *Mater. Res. Soc. Symp. Proc.* **297**, 583 (1993).
- ⁴⁵A. M. Antoine, B. Drevillon, and P. Roca, *J. Non-Cryst. Solids* **77&78**, 769 (1985).
- ⁴⁶F. C. Marques and I. Chambouleyron, in *Proceedings of the 9th European Photovoltaic Solar Energy Conference*, edited by W. Palz, G. T. Wrixon, and P. Helm (Kluwer, Dordrecht, 1989), p. 1042.
- ⁴⁷F. H. Karg, H. Böhm, and K. Pierz, *J. Non-Cryst. Solids* **114**, 477 (1989).
- ⁴⁸W. A. Turner *et al.*, *J. Appl. Phys.* **67**, 7430 (1990).
- ⁴⁹A. R. Zanatta and I. Chambouleyron, *Phys. Rev. B* **46**, 2119 (1992).
- ⁵⁰F. H. Karg, B. Hirschauer, W. Kasper, and K. Pierz, *Sol. Energy Mater.* **22**, 169 (1991).
- ⁵¹L. Zanzig, W. Bayer, and H. Wagner, *Appl. Phys. Lett.* **67**, 1567 (1995).
- ⁵²M. Heintze, K. Eberhardt, F. Kessler, and G. H. Bauer, *Proceedings of the 10th European Photovoltaic Solar Energy Conference*, edited by A. Luque, G. Sala, W. Palz, G. dos Santos, and P. Helm (Harwood, Brussels, 1991), p. 1075.
- ⁵³J. E. Smith, Jr., M. H. Brodsky, B. L. Crowder, M. I. Nathan, and A. Pinczuk, *Phys. Rev. Lett.* **26**, 642 (1971).
- ⁵⁴M. H. Brodsky, in *Light Scattering in Solids*, edited by M. Cardona, *Top. Appl. Phys.* Vol. **8** (Springer, Berlin, 1975), p. 208.
- ⁵⁵J. S. Lannin, *J. Non-Cryst. Solids* **97&98**, 39 (1987).
- ⁵⁶E. Bustarret and E. Morgado, *Solid State Commun.* **63**, 581 (1987); E. Bustarret, F. Vaillant, and B. Hepp, *Mater. Res. Soc. Symp. Proc.* **118**, 123 (1988).
- ⁵⁷M. B. Schubert, H. D. Mohring, E. Lotter, and G. H. Bauer, *IEEE Trans. Electron Devices* **36**, 2863 (1989).
- ⁵⁸A. R. Zanatta, I. Chambouleyron, and P. V. Santos, *J. Appl. Phys.* **79**, 433 (1996).
- ⁵⁹Even in the case of a dilute alloy, the impurity may not have the same size as the atom it replaces, so that the lattice in the neighborhood may be somewhat distorted. This can also induce a new distribution of electrons in the neighborhood, e.g., the substitutional impurity could be a point defect of the lattice, such as a vacancy. The effects may also depend upon the nature of the atoms on neighboring sites.
- ⁶⁰J. Tauc, R. Grigorocivi, and A. Vancu, *Phys. Status Solidi* **15**, 627 (1966).
- ⁶¹S. Hasegawa, M. Matsuda, and Y. Kurata, *Appl. Phys. Lett.* **58**, 741 (1991).
- ⁶²J. M. Shen, C. Palsule, S. Gangopadhyay, H. A. Naseem, S. Kizzar, and F. H. C. Goh, *J. Appl. Phys.* **76**, 1055 (1994).
- ⁶³A. Skumanich, A. Fropa, and N. M. Amer, *Solid State Commun.* **54**, 597 (1985).
- ⁶⁴L. R. Tessler and I. Solomon, *Phys. Rev. B* **52**, 10962 (1995).
- ⁶⁵S. Nonomura, S. Sakata, T. Kamada, H. Kida, D. Kruangam, H. Okamoto, and Y. Hamakawa, *J. Non-Cryst. Solids* **77&78**, 865 (1985).
- ⁶⁶F. Boulitrop, J. Bullo, M. Gauthier, M. P. Schmidt, and Y. Catherine, *Solid State Commun.* **54**, 107 (1985).

- ⁶⁷J. Sotiropoulos and G. Weiser, *J. Non-Cryst. Solids* **92**, 95 (1987).
- ⁶⁸I. Chambouleyron and A. R. Zanatta, *Appl. Phys. Lett.* **62**, 58 (1993).
- ⁶⁹A. R. Zanatta and I. Chambouleyron, *Phys. Rev. B* **48**, 4560 (1993).
- ⁷⁰F. Fajardo and I. Chambouleyron, *Phys. Rev. B* **52**, 4965 (1995).
- ⁷¹D. Comedi, F. Fajardo, and I. Chambouleyron, *Phys. Rev. B* **52**, 4974 (1995).
- ⁷²T. P. Druessedau, A. Annen, B. Schroeder, and H. Freistedt, *Philos. Mag. B* **69**, 1 (1994).
- ⁷³R. Kärcher, L. Ley, and R. Johnson, *Phys. Rev. B* **30**, 1896 (1984).
- ⁷⁴A. R. Zanatta and I. Chambouleyron, *Phys. Rev. B* **53**, 3833 (1996).
- ⁷⁵S. Hasegawa, M. Mutuura, and Y. Kurata, *Appl. Phys. Lett.* **49**, 1272 (1986).
- ⁷⁶D. Comedi, A. R. Zanatta, F. Alvarez, and I. Chambouleyron, *J. Non-Cryst. Solids* **198–200**, 136 (1996).
- ⁷⁷M. Stutzmann, *Philos. Mag. B* **60**, 531 (1989).
- ⁷⁸Reference 35, Chap. 5.
- ⁷⁹K. Pierz, W. Fuhs, and H. Mell, *Philos. Mag. B* **63**, 123 (1991).
- ⁸⁰B. Ebersberger, W. Kruehler, and W. Fuhs, *Proceedings of the 11th European Photovoltaic Solar Energy Conference*, edited by L. Guimarães, W. Palz, C. de Reyff, H. Kiess, and P. Helm (Harwood, Academic, Chur, Switzerland, 1993), p. 598.
- ⁸¹S. K. O'Leary, S. Zukotynski, and J. M. Perz, *Phys. Rev. B* **51**, 4143 (1995).
- ⁸²S. K. O'Leary, S. Zukotynski, and J. M. Perz, *Phys. Rev. B* **52**, 7795 (1995).
- ⁸³S. K. O'Leary, S. Zukotynski, and J. M. Perz, *J. Non-Cryst. Solids* **210**, 249 (1997).
- ⁸⁴S. K. O'Leary and P. K. Lim, *Solid State Commun.* **104**, 17 (1997).
- ⁸⁵S. K. O'Leary, *Appl. Phys. Lett.* **72**, 1332 (1998).
- ⁸⁶B. I. Halperin and M. Lax, *Phys. Rev.* **148**, 722 (1966); *ibid.* **153**, 802 (1967).
- ⁸⁷D. J. Thouless, *Phys. Rev. Lett.* **39**, 1167 (1977).
- ⁸⁸J. Bullot and M. P. Schmidt, *Phys. Status Solidi B* **143**, 345 (1987).
- ⁸⁹S. R. Elliott, *Physics of Amorphous Materials* (Longmans, Green, New York, 1990), Chap. 6, p. 380.