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Cody disorder: Absorption-edge relationships in hydrogenated amorphous silicon

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An analysis of the model of Cody *et al.* explaining the disorder—optical-absorption-edge relationships for hydrogenerated amorphous silicon is presented here. In this analysis, certain disorder-related parameters are defined better in order to facilitate the understanding of the Cody model. Although the present study clarifies some aspects of the model, some questions relating to the topological-disorder—hydrogen-content—thermal-disorder interrelationships remain unanswered. It may be noted here that none of the calculations in the present work are speculative, but are based on well-accepted theories such as the Cody model and their application to hydrogenated amorphous silicon.

I. INTRODUCTION

Exponential absorption edges are a common feature in many crystalline and amorphous materials. These include ionic and covalent materials.[1–8] Thus, generally speaking, disorder in a material does not play a special role as far as these edges are concerned. These edges occur for low absorption coefficients (10^2 to 10^3 cm^{-1}) for amorphous silicon. It is now accepted that excitonic effects coupled with internal electric fields[9] lead to these edges, well known as the Urbach edge.[10] In crystalline semiconductors the width of this edge has been shown[4,11,12] to be proportional to a thermal average $\langle U^2\rangle_T$, like the Debye-Waller factor, which is essentially a measure of the square of the displacement U of the atoms from their original positions. This idea was extended to hydrogenated amorphous silicon by Cody *et al.*[13,14]

Using the idea of equivalence of structural and thermal disorder, Cody *et al.*[13,14] have successfully explained the relationship between the optical gap and the Urbach-edge parameter in hydrogenated amorphous silicon films prepared by rf sputtering. Their studies have shown that the structural and thermal disorders are additive and the disorder rather than the hydrogen content is the fundamental factor in determining the optical band gap.

Earlier studies[15–17] on chemical-vapor-deposited as well as glow-discharge-prepared amorphous silicon have yielded results only in partial accordance with the results of Cody. Recently, Moustakas and co-workers[18] have concluded that in addition to structural and thermal disorder, compositional disorder is also important in determining the optical properties of a-Si;H alloys. Our conclusions[15–17] have been in complete accord with those of Moustakas and co-workers.[18] Adler[19] has attributed a value of 2.4 eV (characteristic of polysilane $[(\text{SiH}_2)_n]$) to the upper limit of the gap of a-Si;H.

The fact that the more homogeneous films have larger gaps for the same amount of hydrogen is consistent with the model of Cody that the gap is related to disorder. In the present study we essentially attempt to reproduce the results of Cody from the point of view of understanding the disorder parameters $\langle U^2\rangle_X$ and $\langle U^2\rangle_T$, representing the structural and thermal disorder parameters, respectively. Hence, all the discussions are based on the present calculations and, wherever relevant, comparisons are made with data in the literature.

II. THEORY, RESULTS, AND DISCUSSION

According to Cody *et al.*,[13,14] the absorption edge characterizing the Urbach-tail parameter is given by

$$E_0(T,X)=\frac{k_B\Theta}{\sigma_0}\left[\frac{1+X}{2}+\frac{1}{\exp(\Theta/T)-1}\right], \tag{1}$$

where k_B is the Boltzmann constant, Θ is a characteristic temperature (like the Debye temperature; $\Theta_D=4\Theta/3$) representing the Einstein model as an approximation to the Debye phonon spectrum, σ_0 an Urbach parameter of order unity, $X=\langle U^2\rangle_X/\langle U^2\rangle_0$ is a measure of the structural disorder normalized to $\langle U^2\rangle_0$, the zero-point uncertainty in the atomic positions, and T is the temperature of measurement in kelvin. For purposes of identifying the pure contributions due to structural and thermal disorder, we write Eq. (1) as

$$\begin{aligned}E_0(T,X)&=\frac{k_B\Theta}{\sigma_0}\left[\frac{1+X}{2}\right]+\frac{k_B\Theta}{\sigma_0}\left[\frac{1}{\exp(\Theta/T)-1}\right]\\&=E_0(X)+E_0(T)\ ,\end{aligned} \tag{2}$$

where, for a-Si;H, $\Theta=400$ K,[13,14] $E_0(X)$ and $E_0(T)$ are the pure structural and thermal disorder contributions to $E_0(T,X)$, respectively. Now, the band gap follows as[13,14]

$$E_G(T,X)=E_G(0,0)-\langle U^2\rangle_0 D\left[\frac{E_0(T,X)}{E_0(0,0)}-1\right], \tag{3}$$

where $E_G(0,0)$ is the upper limit for the band gap of the a-SiH$_x$ family of materials at 0 K ($=2.0$ eV),[13,14] $\langle U^2\rangle_0^{1/2}=0.08$ Å appropriate to an oscillator with frequency $k_B\Theta/h$, D the deformation potential taken to be 30 eV/Å^2 (of the same order of the deformation potentials in crystalline germanium), and $E_0(0,0)=k_B\Theta/2=17.24$ meV. However, noting that the $\ln\alpha$ versus E

TABLE I. Pure structural and thermal disorder contributions to E_0 and E_G. $E_0(X)$ and $E_0(T)$ have been defined in relation (2). Note the following: (i) $X=(\langle U^2\rangle_X/\langle U^2\rangle_0)-1$; $\langle U^2\rangle_0^{1/2}=0.08$ Å. (ii) For $T<\Theta$, $E_0(T)/E_0(0,0)\ll 1$ and so $E_{GT}>E_G(0,0)$. This could be a possible setback for the Cody model. As $T\rightarrow\Theta$ (i.e., 400 K), $E_0(T)\rightarrow E_0(0,0)$ and $E_{GT}\rightarrow E_G(0,0)$. Thus the deformation potential coupled with the term $\langle U^2\rangle_0$ and an extremely slowly varying $E_0(T)$ far less than $E_0(0,0)$ aids increasing $E_G(T)$ beyond the $E_G(0,0)$ limit. (iii) The low-temperature limit value of $E_G(T)$ is very close to the 2.4-eV gap of polysilane [see Adler (Ref. 19)]. (iv) For purposes of showing that $\langle U^2\rangle_{X,T}=\langle U^2\rangle_X+\langle U^2\rangle_T$, the calculated values of these parameters are being quoted without approximating them.

X	$E_0(X)$ (meV)	$E_G(X)$[a] (eV)	$\langle U^2\rangle_X$[b] (Å^2)	T (K)	$E_0(T)$ (meV)	$E_G(T)$[c] (eV)	$\langle U^2\rangle_T$[d] (Å^2)
0	17.24	2.2	0.0064	50	0.012	2.392	0.000 004 5
0.2	20.688	2.162	0.007 68	100	0.64	2.385	0.000 23
0.4	24.136	2.123	0.008 96	150	2.56	2.363	0.000 97
0.6	27.584	2.085	0.010 24	200	5.40	2.332	0.002
0.8	31.032	2.046	0.011 52	250	8.80	2.294	0.0033
1.0	34.48	2.008	0.0128	300	12.40	2.254	0.0046
1.2	37.928	1.970	0.014 08	350	16.20	2.212	0.006
1.4	41.376	1.931	0.015 36	400	20.06	2.169	0.0074
1.6	44.824	1.893	0.016 64				
1.8	48.272	1.854	0.017 92				
2.0	51.72	1.816	0.0192				
2.2	55.168	1.778	0.020 48				
3.0	68.96	1.624	0.0256				

[a] From Eq. (5).
[b] From Eq. (10b).
[c] From Eq. (6).
[d] From Eq. (10a).

focus of Cody *et al.* occurs at 2.2 eV, so that the equation

$$\alpha(E,T)=\alpha_0\exp[(E-E_1)/E_0(T,X)] \tag{4}$$

remains satisfied with $\alpha_0=1.5\times10^6\,\mathrm{cm}^{-1}$ for $2\times10^2\,\mathrm{cm}^{-1}<\alpha<5\times10^3\,\mathrm{cm}^{-1}$ (α is the absorption coefficient), we take $E_G(0,0)=2.2$ eV in our calculations.

Now, looking at the pure contributions,

$$E_G(X)=2.2-0.192X \tag{5}$$

[note that $E_0(X)=E_0(0,0)(1+X)$; see Eq. (2)] and

$$E_G(T)=2.2-0.192\left[\frac{E_0(T)}{17.24}-1\right], \tag{6}$$

where $E_G(T)$ is in eV and $E_0(T)$ in meV. In Table I the results of our calculations are presented. Now, in order to reproduce the results of Cody (as a check on our calculations), we look at the variation of $E_G(2,2,T)$ with $E_0(2.2,T)$ ($X=2.2$). After all, from expressions (3), (5), and (6),

$$E_G(X,T)=E_G(0,0)-D\langle U^2\rangle_0 X$$
$$-D\langle U^2\rangle_0[E_0(T)/E_0(0,0)]$$

or, for this particular case of $E_G(2,2,T)$,

$$E_G(2.2,T)\simeq1.78-0.011E_0(T) \tag{7}$$

with

$$E_0(2.2,T)=55.168+E_0(T)\,. \tag{8}$$

In Fig. 1 $E_G(2.2,T)$ is plotted versus $E_0(2.2,T)$ for T varying from 0 to 400 K. Comparisons have also been made in the figure with the available experimental data corresponding to a constant X and varying T. As can be seen in the figure, the experimental points fall on the line given by Eq. (7), confirming, thereby, the validity of our analysis. Note that in the above expressions (7) and (8), E_G is expressed in eV while E_0 is expressed in meV. In Table II the results of these calculations are presented.

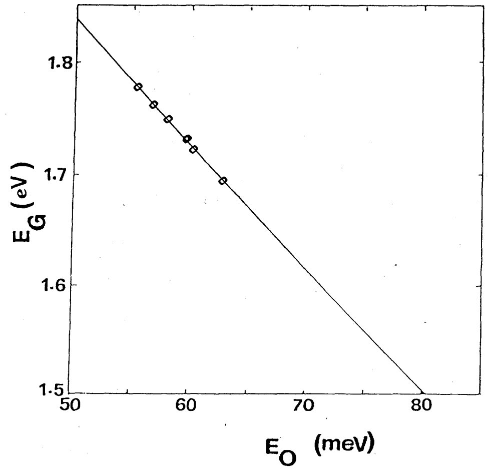

FIG. 1. $E_G(2.2,T)$ vs $E_0(2.2,T)$ evaluated using relations (7) and (8), respectively, in the temperature range 0 to 400 K, compared with experimental points (○) (experimental data taken from Ref. 13).

TABLE II. Values of E_0 and E_G for $X=2.2$ and varying T. From Tables I and II, note that $\langle U^2\rangle_{X,T}=\langle U^2\rangle_X+\langle U^2\rangle_T$ follows, thus verifying relation (11) and hence the additive nature of the disorders.

T (K)	$E_0(2.2,T)$[a] (meV)	$E_G(2.2,T)$[b] (eV)	$\langle U^2\rangle_{X,T}$[c] (Å^2)
50	55.18	1.78	0.0205
100	55.808	1.77	0.0207
150	57.728	1.75	0.0214
200	60.568	1.717	0.0225
250	63.968	1.68	0.024
300	67.568	1.64	0.025
350	71.368	1.597	0.0264
400	75.228	1.554	0.0279

[a] From Eq. (8).
[b] From Eq. (7).
[c] From Eq. (12).

Now, considering that the explicit temperature dependence of the energy gap accounts for most of its total temperature dependence in *a*-Si, Cody *et al.*, utilizing the results for crystalline semiconductors, explain it as

$$E_G(T)=E_G(0)-D(\langle U^2\rangle_T-\langle U^2\rangle_0)\ . \tag{9a}$$

Expression (9a) has been extended also to include the structural effects. Thus,

$$E_G(X)=E_G(0)-D(\langle U^2\rangle_X-\langle U^2\rangle_0)\ . \tag{9b}$$

Expressions (9a) and (9b) permit us to evaluate $\langle U^2\rangle_T$ and $\langle U^2\rangle_X$ separately, since the pure thermal and structural contributions to the optical gap have already been evaluated. Thus,

$$\langle U^2\rangle_T=[2.392-E_G(T)]/30 \tag{10a}$$

and

$$\langle U^2\rangle_X=[2.392-E_G(X)]/30\ . \tag{10b}$$

In Table I we evaluate the contributions of thermal and structural disorder to the mean-square deviation of the atomic positions from a perfectly ordered configuration. Note that unlike Cody's definition of

$$X=(\langle U^2\rangle_X/\langle U^2\rangle_0)\ ,$$

what seems appropriate is

$$X=(\langle U^2\rangle_X/\langle U^2\rangle_0)-1\ ,$$

so that, as $\langle U^2\rangle_X \Longrightarrow \langle U^2\rangle_0$, $X\rightarrow 0$ or the contribution of topological (or structural) disorder is zero. In fact, this definition of X makes Cody's calculations much more self-consistent. Further, $\langle U^2\rangle_{X,T}$ follows easily as

$$\langle U^2\rangle_{X,T}=\langle U^2\rangle_X+\langle U^2\rangle_T\ . \tag{11}$$

The above relation has been tested for $X=2.2$ and T varying from 50 to 300 K (see Tables I and II). This result [relation (11)] is in complete accordance with the result of Cody. However, what remains surprising is the fact that as $T\rightarrow\Theta$, $\langle U^2\rangle_T\rightarrow\langle U^2\rangle_0$. If a similar parameter characterizing the thermal disorder Y is defined as

$$Y=(\langle U^2\rangle_T/\langle U^2\rangle_0)-1\ ,$$

Y remains negative and attains zero as $T\rightarrow 400$ K. Thus, in the Cody model, Θ seems to have been chosen in such a way as to keep the thermal disorder far inferior to the topological disorder. Further, when the effective $\langle U^2\rangle_{X,T}$ is evaluated for $X=2.2$ and varying T, the contribution due to thermal disorder remains negligibly small (see Tables I and II). Note that in Table II

$$\langle U^2\rangle_{X,T}=[2.392-E_G(X,T)]/30\ . \tag{12}$$

The basic question would remain as to why the topological-disorder contribution should remain high and be independent of the hydrogen concentration. Further, what would be the influence of the thermal disorder on the topological disorder? Since the tailing of the density of states, appropriate to silicon, is not necessarily a result of topological disorder, but may be the result of quantitative disorder[20] which would include variations in bond angles and bond lengths, it would probably be appropriate to include such disorder parameters. Recently, Persans *et al.*[21] have reported their studies of the relationship between bond-angle disorder and the optical gap in *a*-Ge;H. Their studies have shown that increasing hydrogen concentration decreases the bond-angle fluctuations by 2°, increases the optical gap by 0.4 eV, and sharpens the absorption tail by a factor of 2. Tanaka and Tsu[22] have attempted to model the electronic structure of amorphous silicon alloys prepared by glow discharge. Their studies have shown a consistent steepening of the valence-band edge with disorder as has been seen in the photoemission spectra.

At $X=2.2$ and $T=300$ K, $\langle U^2\rangle^{1/2}$ takes a value of 0.158 Å (the contribution of X alone would be 0.143 Å). Considering the first-nearest-neighbor distance in *a*-Si;H to be $\simeq 2.3$ Å,[23] this value of 0.158 Å represents only $\approx 6.8\%$ of the first-nearest-neighbor distance. This seems perfectly logical[24] and is in accord with expectations. Thus, the total contributions of topological and thermal disorder to E_0 give[13,14]

$$E_0(T,X)=K(\langle U^2\rangle_X+\langle U^2\rangle_T)$$

with $K\simeq 2693$ meV/Å^2.

We now evaluate the temperature corresponding to the topological disorder to bring about an equivalent thermal disorder. In Fig. 2 the results of these calculations are presented. Naturally, $X=2.2$ would surpass the amorphous limit ($T=824$ K). Of course, as has been pointed out by Cody, the structural disorder of 2.2 is much larger than the room-temperature thermal disorder of 0.7.

Recent studies[25] have shown that, at least for highly doped silicon (n and p), classical adiabatic approximations do not hold any more and the electronic and the phononic states can no longer be independently treated in degenerate semiconductors or semimetals. Because of a large density of localized states in amorphous materials, such adiabatic approximations may be valid in a limited sense. Further, since the model calculations are quite sensitive to the deformation potential, it would be appropriate to utilize the value of the deformation potential of silicon itself. Although, these values are scattered in the literature,[26,27]

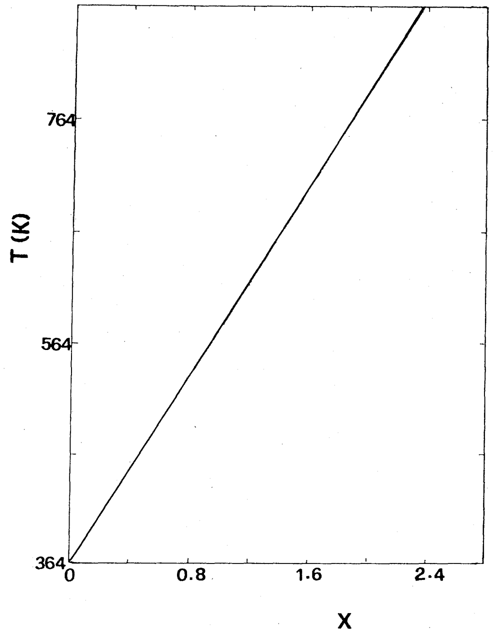

FIG. 2. Temperature T corresponding to structural disorder X to bring about an equivalent thermal disorder. Note that a zero structural disorder would correspond to thermal disorder at $T=364$ K ($\approx\Theta$).

the interband optical deformation potential for silicon is of the order of 30 eV (actually, values quoted vary from 15.4 to 44.8 eV), same as that employed by Cody *et al.*

Above all, what makes the Cody model interesting is the fact that it remains the first systematic approach to study the E_G-E_0 variations. Such studies which were proposed earlier for rf sputter prepared *a*-Si;H films have been extended by Cody *et al.*[28] to include *a*-Si;H films prepared by the glow-discharge decomposition of silane. They[28] again find that

$$E_G(E_0)=E_G(0)-6.2E_0 ,$$

where $E_G(0)=1.94$ eV is the zero-disorder limit of the optical gap of *a*-Si;H. Although the phenomena governing the two parameters E_G and E_0 are so diverse, it is surprising that they should be related in such a simple way. Of course, a slightly different value for $E_G(0)$ now[28] would reflect the role of compositional disorder. Finally, just one last word about the choice of the value of Θ. Accepting that Θ is the highest phonon frequency observed, from Raman studies on *a*-Si;H films, the 480-cm^{-1} peak in the Raman spectra (for chemical-vapor-deposited films)[29] characteristic of the optical phonons in the amorphous silicon structure would correspond to $\Theta=690$ K. The low-temperature-limit Debye temperature of crystalline silicon is $\Theta_D=645$ K.[30] This value for Θ is agreeable since Θ_D is only the cutoff frequency in the Debye model. Thus, the choice of Θ based on the Einstein's approximation in the Cody model would not be representative of the Raman peak in amorphous silicon.

III. CONCLUSIONS

An attempt has been made in the above study to analyze the model of Cody from the point of view of understanding the model and its implications. Corrections have been proposed wherever appropriate in order to bring self-consistency in the Cody model. Limitations on the model have also been discussed. Although the present work goes slightly beyond the original ingenious model of Cody *et al.*, it is interesting from the point of view of understanding (i) the implications of the Cody model, and (ii) the role of topological and thermal disorder in determining the optical gap in amorphous solids.

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