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# مجلة أريد الدولية للعلوم والتكنولوجيا

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## Investigation of the Effect of Disorder on the Tauc Edge of Hydrogenated Amorphous Silicon Using Dunstan's Bandgap Fluctuations Model

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استقصاء تأثير اللاانتظام على حافة تاوس للسليكون العشوائي المهدرج باستخدام نموذج دونستان لفجوة الطاقة المتعاقبة

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**ABSTRACT**

The optical absorption edge in both Urbach and Tauc regions are analyzed for hydrogenated amorphous silicon optical data of Cody et al and Viturro and Weiser. Dunstan's model, introduces disorder into the band-band absorption through a linear exponential distribution of local energy gaps. This model has a simple mathematical form and has a clear physical meaning in comparison to the somewhat similar models of O'Leary and Guerra, yet Dunstan's model is unjustly neglected in literature.

The most important physical parameter of the model is the energy gap parameter-  $E_o$ , which represents the separation between the valence and conduction band edges, it can be considered as the mobility gap of the material. Dunstan's model is found successful in capturing the optical data of Cody et al and, Viturro and Weiser. A plot of the energy parameters of the Dunstan and Cody models,  $E_o$  against  $E_{opt}$  respectively, was proposed here to separate the masking contribution of tail-related absorption from the real change of the band gap, and was found fruitful for this purpose. This is because  $E_o$  is a function only of the separation between valence and conduction band edges, while the meaning of the optical energy  $E_{opt}$  is ambiguous because it is also a function of absorption due to tail-related absorption that results from disorder. This simple plot of  $E_o$  vs.  $E_{opt}$ , through the slope  $\Delta E_o/\Delta E_{opt}$  of the fitting straight line, was capable of distinguishing the different relative contributions of disorder between Cody et al and Viturro and Weiser optical data,  $E_o$  value was found less sensitive to hydrogen content variation for Viturro and Weiser data which is interpreted due to their better control of the thin film deposition process.

**Keywords:** optical energy gap, absorption coefficient, amorphous semiconductor, mobility gap.

### المخلص

تم تحليل منطقتي اورباخ وتاوس للبيانات البصرية للسليكون العشوائي المهدرج لكودي وجماعته وفيتوررو وفايزر. نموذج دونستان يستقدم اللانتظام إلى الامتصاص بين الحزم من خلال توزيع أسّي خطّي لفجوات الطاقة الموضوعية. هذا النموذج يمتلك صيغة رياضية بسيطة ومعنى فيزيائي أوضح بالمقابلة مع نماذج أخرى قريبة لاوليري وكويررا، لكن نموذج دونستان تم إهماله في الأدبيات بشكل غير منصف. أهم معلم فيزيائي لهذا النموذج هو معلم فجوة الطاقة  $E_0$  الذي يمثل الفسحة بين حافتي حزمة التكافؤ والتوصيل، ويمكن اعتباره يمثل فجوة التحركية للمادة. وجد نموذج دونستان ناجحا في موائمة البيانات البصرية لكودي وجماعته وفيتوررو وفايزر. تم اقتراح رسما بيانيا بين معلم الطاقة لنموذجي دونستان وكودي،  $E_0$  مقابل  $E_{opt}$  وذلك لفصل الإضافة الحاجبة للامتصاص المتعلق بالذيول عن التغير الحقيقي في فجوة الطاقة. وقد وجد هذا الأمر مثمرا لهذا الغرض وذلك بسبب كون  $E_0$  هي دالة للفسحة بين حافتي حزمة التكافؤ والتوصيل فقط، بينما معنى فجوة الطاقة البصرية  $E_{opt}$  هو ملتبس لأنها دالة للامتصاص المتعلق بالذيول الناتج عن اللانتظام أيضا. هذا الرسم البياني بين  $E_0$  و  $E_{opt}$  من خلال الميل  $\Delta E_{opt}/\Delta E_0$  الناتج عن موائمة الخط المستقيم يتمكن من تمييز المساهمات النسبية للانتظام بين البيانات البصرية لكودي وجماعته وفيتوررو وفايزر، ووجد أن قيمة  $E_0$  هي أقل حساسية لتغير منسوب الهيدروجين لبيانات فيتوررو وفايزر الأمر الذي عزي إلى السيطرة الأفضل على عملية ترسيب الأغشية.

**الكلمات المفتاحية:** فجوة الطاقة البصرية، معامل الامتصاص، شبه الموصل العشوائي، فجوة التحركية.

## 1. Introduction:

One of the most important parameters that can be deduced from the analysis of the experimental absorption spectrum of a semiconductor is the optical energy gap  $E_{opt}$ . It is for example, a crucial physical parameter for the modeling of optoelectronic semiconductor devices especially solar cells. Its physical meaning is well established in crystalline semiconductors because they have a real and definite energy gap between their conduction band (CB) and valence band (VB) band edges.

In amorphous semiconductors, disorder obscures the physical meaning of the experimental optical gap because there is no real energy gap in their density of states (DOS) diagram due the encroachment of the VB and CB states towards the pseudo-gap region in the form of localized states [1].

Due to the ambiguities in the interpretation of the Tauc edge of semiconductors and especially amorphous semiconductors (mainly because of the complex nature of their density of states), some researchers, including one of the authors of this article, suggested alternative methods to analyze optical absorption data in the Tauc region such as the inverse logarithmic derivative method to obtain  $E_{opt}$  and the optical transition matrix element index [2,3]; yet another method was suggested by Zanatta [4], he used a unified formalism based on the Sigmoid (Boltzmann) model that he found appropriate to fit optical absorption edge data and to obtain the energy gap parameter of semiconductors including amorphous ones.

Still, the usual Tauc plot by virtue of its simplicity in defining an effective optical gap is predominately used in amorphous semiconductor literature [5]. However, one main deficiency of the Tauc model is in its neglect of the absorption due to band tail related optical transitions, it is basically a model of optical transitions between valence band extended states and conduction

band extended states. Therefore, it neglects the effect of disorder on the high absorption edge region ( $\alpha \geq 10^4 \text{ cm}^{-1}$ , where  $\alpha$  is the absorption coefficient) [6]. Disorder effect is usually considered to appear mainly in the Urbach tail of amorphous semiconductors, just below the Tauc edge, this Urbach region of the optical absorption edge is most frequently attributed to tail states related optical transitions [7,8,9].

One of the early attempts by us to include the disorder contribution to the Tauc edge of amorphous semiconductors was by employing the full Davis-Mott model formulation which includes the width of localized states  $\Delta E$  in the optical absorption formula of the Tauc region [10], yet the parameter  $\Delta E$  is not available experimentally, usually the available parameter is the Urbach energy  $E_u$  which is an important marker of disorder [7].

Realistic optical absorption data in the Tauc region of the absorption edge, is not due only to extended to extended state optical transitions, but is also due to optical transitions from valence band localized (extended) states to conduction band extended (localized) states to a lesser extent. The neglect of tail related transitions in the Tauc region impedes us from a more correct interpretation of optical absorption data especially from attaining a reasonable physical meaning for the optical energy gap  $E_{opt}$  obtained from optical absorption experimental data [6]. Therefore there is an ambiguity in interpreting the variation of optical band gap  $E_{opt}$  with deposition parameters whether it is due to a real change in the mobility gap  $E_\mu$  or it is due to an indirect effect of disorder [11].

Thus, further development of the Tauc model is needed to take into account the effect of the tail-related transitions in addition to extended-extended transitions. This was achieved by a small number of researchers in a long time span beginning with Dunstan 1982 [12] and Frova et al 1985 [11], through O'Leary and various collaborators [13,14,15,16] and finally the task was

undertaken by Guerra and collaborators [17,18,19]. As tail-related transitions are due to the influence of disorder, these models combine the Urbach region with the Tauc region in one theoretical model, thus the Urbach parameter  $E_u$  which is a marker of disorder should also contribute to the Tauc region, as was found in these models.

These models were successful in fitting both the Urbach and Tauc regions of the optical absorption edge and gave new insight to the optical gap interpretation, yet the older model due to Dunstan [12,20] which accounted for disorder through the Urbach edge is the simplest one whether in its mathematical form or its direct physical interpretation compared to the more detailed O'Leary model [14,15] and the polylogarithm model of Guerra [18]. Dunstan claimed and showed that his model accounted successfully for most amorphous semiconductor optical data he analyzed [12]. However, this simple and successful Dunstan model was unjustly neglected in literature with the exception of the analogous Frova et al model [11], and it is also mentioned by Ley and Guerra et al [21, 18].

In a previous joint work by one of the authors [ 6], Dunstan's model was used to analyze and model optical data of a-Si:H due to Jackson et al [22] and Maurer et al [23] in both the Urbach and Tauc regions, and this model excellently fitted those data. The Cody constant dipole matrix element approximation [24] was employed which is more suitable for a-Si:H thin films than the constant momentum matrix element approximation of the Tauc model as was validated by Jackson et al experimental work [22]. The most important fitting parameter of the Dunstan model is  $E_0$ , which is the energy gap parameter of this model, is a marker of the separation between the valence band and conduction band edges thus it avoids the above mentioned ambiguities of the interpretation of the conventional Tauc optical gap  $E_{opt}$ .

This paper is organized in the following manner. In section 2, the 3-parameter Dunstan model is presented, then its importance and physical implications are given in section 3, describing the two contributions of extended states absorption and tail-related absorption to the Tauc region, an application of the Dunstan model to Jackson et al [22] optical data of a-Si:H is included, and a density of states diagram is presented to clarify the meaning of some important energy gap parameters. Section 4, is the results and discussion section, Dunstan's model is used to fit the important Cody et al [25] and Viturro and Weiser [26] a-Si:H optical data sets which cover both the Urbach and Tauc regions, this gives us the opportunity to analyze these data in order to investigate the effect of disorder especially on the Tauc edge by taking advantage of the different physical interpretations of the Dunstan energy gap  $E_0$  and the conventional optical gap parameter  $E_{opt}$ , through a suggested plot between these the two parameters. Finally, the conclusions are given in section 5.

## **2. The Description of Dunstan's Model:**

Dunstan built his model on the band-gap fluctuations model of Skettrup (1972) [27] originally proposed as an alternative interpretation of the Urbach edge of crystalline semiconductors [28]. In the Skettrup model, a band gap is defined locally within small cells about the size of phonon coherence length. This local band gap is reduced in proportion to the number of thermal phonons present, thus this local band gap fluctuates spatially and temporally with a linear exponential distribution of values. Disorder in Skettrup's model is due to the thermal disorder caused by phonon excitations. Dunstan extended this model to the amorphous case, he considered the static (time-independent) disorder in the amorphous semiconductor as a fictive phonon disorder i.e. structural disorder is considered due to frozen-in phonons, a proposal introduced earlier by Cody et al [25]. Dunstan assumed that the absorption above the gap is given in the general form [ 20]:

$$\alpha(E) = f(E - E_{oG}) \dots \dots \dots (1)$$

where  $E_{oG}$  is the local fluctuating band gap that is assumed to take a distribution of values

$E_o - \varepsilon$ ,  $\varepsilon$  has a linear exponential probability distribution  $P(\varepsilon)$  with a slope  $\beta$ :

$$P(\varepsilon) = \beta e^{-\beta\varepsilon} \quad \text{for } \varepsilon \geq 0 \dots \dots \dots (2)$$

The absorption spectrum is obtained by integrating the band-to-band absorption eq. (1) of overall values of  $E_{oG}$ :

$$\alpha(E) = \int_0^{\infty} P(\varepsilon) f(E - E_o + \varepsilon) d\varepsilon \dots \dots \dots (3)$$

The solution of eq. (3) depends on the mathematical form of the function  $f(E)$ .

Fortunately, for the special case in which  $f(E-E_o)$  obeys a Tauc-law form, the integration eq. (3) can be solved analytically to give the following simple form formulas [20]:

$$\alpha(E) = \frac{2\alpha_o}{E\beta^2} e^{-\beta(E_o - E)} \quad E \leq E_o \dots \dots \dots (4-a)$$

$$\alpha(E) = \frac{\alpha_o}{E} \left\{ (E - E_o)^2 + \frac{2}{\beta}(E - E_o) + \frac{2}{\beta^2} \right\} \quad E \geq E_o \dots \dots (4-b)$$

Dunstan considered the parameter  $\beta$  to be the inverse of the Urbach energy, i.e.,  $\beta=1/E_u$ ,  $E_u$  is the Urbach energy parameter.

Dunstan claimed that his model described accurately the absorption spectrum in every amorphous semiconductor he tested, it did give an exponential tail and gave the correct strength of absorption in the Urbach tail and the correct form of the spectrum at the transition (around)  $E_o$  from the tail to the intrinsic (Tauc-region) absorption. Dunstan assumed that  $E_o$  in the absence of any chemical modification is a constant of the material which can be interpreted



as the energy gap in the absence of disorder. The only researchers on optical data using Dunstan mathematical expressions are Frova & Selloni 1985 [11], they neglected conduction band exponential tails because it is well known that in a-Si:H related films, the dominant contribution to the Urbach tail is due to transitions from valence band tail states to conduction band extended states. They assumed an exponential broadening of the valence band extended states into localized states which results from disorder (the parameter in Dunstan model), they applied the model to a-Si:H and a-SiC:H optical data with reasonable success.

### 3. The importance and physical implications of Dunstan's model:

In Tauc or Cody models, the so-called optical energy gap  $E_{opt}$  is obtained from the optical absorption data through the Tauc or Cody plots. In the Tauc plot  $(\alpha E)^{1/2}$  (or  $(E^2 \epsilon_2)^{1/2}$ ,  $\epsilon_2$  is the imaginary part of the dielectric function  $\epsilon(\omega)$ ) is plotted versus photon energy  $E$ , whereas in the Cody plot  $(\alpha/E)^{1/2}$  (or  $\epsilon_2^{1/2}$ ) is plotted against photon energy  $E$  [5,24]. In Tauc theoretical model,  $E_{opt}$  is interpreted as an extrapolation of the parabolic valence band and conduction band extended states to the zero of the density of states in the pseudo-gap [29].

Tauc and Cody models consider only the optical transitions between parabolic extended band states, transitions due to localized states are not considered. This makes the extrapolated  $E_{opt}$  value obtained from, the Tauc plot equation:

$$(\alpha E)^{1/2} = B_{Tauc} (E - E_{opt}^{Tauc}) \dots\dots\dots(5)$$

Or from the Cody plot equation:

$$(\alpha/E)^{1/2} = C_{Cody} (E - E_{opt}^{Cody}) \dots\dots\dots(6)$$

lower than the theoretical optical energy gap proposed by these models [30]. In fact, with increasing structural or/and thermal disorder this discrepancy between theory and experiment

should increase due to the larger contribution from tail related optical transitions to the Tauc region of the absorption edge [11]. Therefore, more realistically, optical transitions that contribute to the Tauc region of the absorption edge ( $\alpha \gtrsim 10^4 \text{ cm}^{-1}$ ) are not only extended-extended transitions, but also localized (extended) - extended (localized) transitions [14,15].

Here comes the necessity for such models as Dunstan's model and similar models like O'Leary's and Guerra's models [15, 18]. These models take into account exponential tail states related transitions, and thus it is expected to obtain from them a more realistic value of the energy gap of an amorphous semiconductor. In this case, both the Urbach and Tauc regions data must be available from experiment. As the Urbach energy is a measure of disorder, a more explicit and physically meaningful explanation of the role of disorder on the absorption edge of amorphous semiconductors can be obtained.

Dunstan's equation in the Tauc region (eq.4-b) can be re-written in the following more informative form:

$$\alpha(E) = f(E) + \Delta(E) \quad E > E_0 \dots \dots \dots (7-a)$$

Where:

$$f(E) = \frac{\alpha_0}{E} (E - E_0)^2 \dots \dots \dots (7-b)$$

gives exclusively the contribution of extended band to band transitions to the Tauc edge.

and,

$$\Delta(E) = \frac{\alpha_0}{E} [2E_u(E - E_0) + 2E_u^2] \dots \dots \dots (7-c)$$

is the contribution of localized-extended transitions to the Tauc edge.

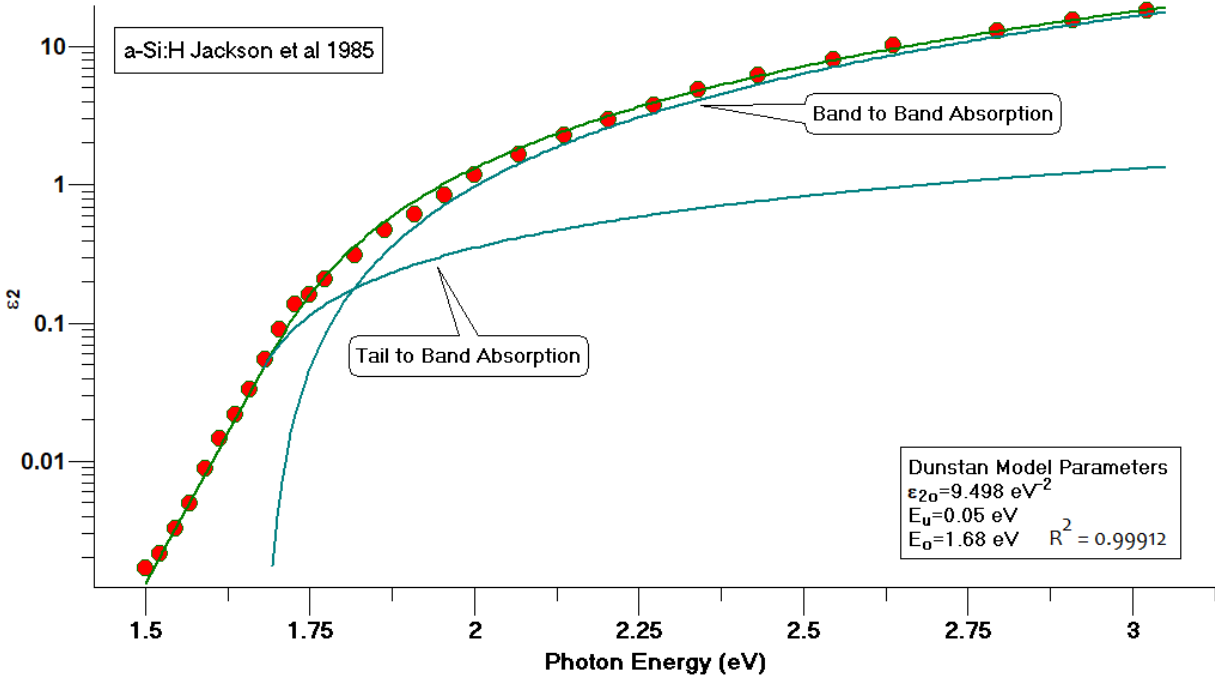
Notice that the Urbach edge parameter  $E_u$  is already included in the expression eq. (7-c) indicating the effect of disorder on the Tauc edge. Notice also that with increasing disorder through increasing Urbach edge parameter the  $\Delta(E)$  contribution increases, and thus increasingly lowering the obtained value of the experimental Tauc optical gap [11]. The Urbach edge contribution to the Dunstan model (eq.4-a) can be re-written in terms of  $E_u$  as:

$$\alpha(E) = 2\alpha_0 E_u^2 \exp\left(-\frac{E - E_0}{E_u}\right) \dots\dots\dots(8)$$

Notice from inspecting eqs. (7) & (8) that,  $\alpha(E)$  and its first derivative  $d\alpha/dE$  are continuous at the threshold energy  $E_0$ .

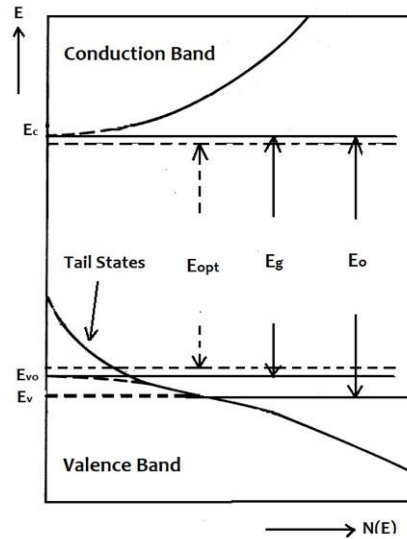
To show how the simple Dunstan model fits well the optical data in a wide photon energy range, and gives the relative contributions of tail-related and band-related absorption, Fig.1 shows Jackson et al [22]  $\epsilon_2(E)$  vs. photon energy a-Si:H data, fitted in a previous work [6] to Dunstan's model; a good fit was obtained for the parameter values,  $E_u=0.05\text{eV}$ ,  $E_0=1.68\text{ eV}$  and  $\epsilon_{20}=9.498\text{ eV}^{-2}$  (where  $\epsilon_{20}$  is the counterpart of  $\alpha_0$  in terms of the imaginary part of the dielectric function  $\epsilon_2$ ) in the very wide energy range (1.5 - 3 eV) covering both the Urbach and the Tauc regions of the absorption edge; the constant dipole transition matrix element approximation was used. These results compare very well with O'Leary's model analysis [14]. The relative contributions of tail-related transitions and band-related transitions are depicted in the figure, notice how the relative contributions of  $f(E)$  (band to band absorption) and  $\Delta(E)$  (tail to band absorption) vary with photon energy, the band-related absorption starts at the threshold energy  $E_0=1.68\text{ eV}$ , then beyond the intersection point at  $E\sim 1.82\text{ eV}$ , band-related absorption starts to gradually dominate over tail-related absorption. It is important to mention

that the optical energy gap of these samples as fitted to the Cody plot in the wide photon energy range (1.7 - 3 eV) is  $\sim 1.63$  eV, is lower  $\sim 0.05$  eV than  $E_0$  value for these Jackson et al high-quality a-Si:H samples.



**Figure(1):** Dunstan's model fitting to Jackson et al a-Si:H data in the photon energy range (1.5-3)eV [6].

In fig. (2), an appropriate density of states diagram is shown to explain the main energy gap parameters relevant to the absorption edge of an amorphous semiconductor [ 6 ].



**Figure (2):** Amorphous density of states diagram that depict the main energy gap parameters,  $E_{opt}$ ,  $E_g$  and  $E_o$  .

In this figure, conduction band tails are neglected, this assumption is suitable for a-Si:H and related films, where the valence band tail region is significantly broader than the conduction band tails [11].  $E_g$  in the figure is the extrapolated band gap to the zero density of states; in the limit that the effect of disorder can be neglected  $E_g \approx E_{opt}$  as predicted by the Tauc or Cody theoretical models. It is also the important energy gap parameter of the O'Leary model before the introduction of disorder [14]. Due to the contribution of localized states related transitions,  $E_{opt}$  determined experimentally is smaller than  $E_g$ , and it is in fact a fictitious band gap in the pseudo-gap as depicted in the figure, the difference between  $E_g$  and  $E_{opt}$  increases with increasing disorder i.e. with increasing Urbach energy  $E_u$ .  $E_o$ , which is the energy gap of both Dunstan and Guerra models [18,20] and the threshold energy of the O'Leary model, is the energy gap between the band edges ( $E_o = E_c - E_v$ ), only if  $E_v$  is the critical energy separation between valence band extended states and the valence band localized tail states, then  $E_o$  can be considered to be the mobility gap  $E_\mu$  of the material, which is a parameter very difficult to extract experimentally [31]. An important point should be

mentioned here about the significance of  $E_0$  compared to  $E_{opt}$ .  $E_{opt}$  physical meaning is ambiguous because it is a function of both the masking contribution of disorder through tail-related absorption, in addition to the separation between the valence band and conduction band edges which is equal to  $E_0$  and is more of chemical origin.  $E_0$  is very important energy parameter because it signifies the energy separation between the valence band and conduction band, band edges, then its variation with preparation conditions of the sample should be due to a real change in the separation between the band edges, hopefully it could be equal to the mobility gap [32].

#### **4. Results and Discussion:**

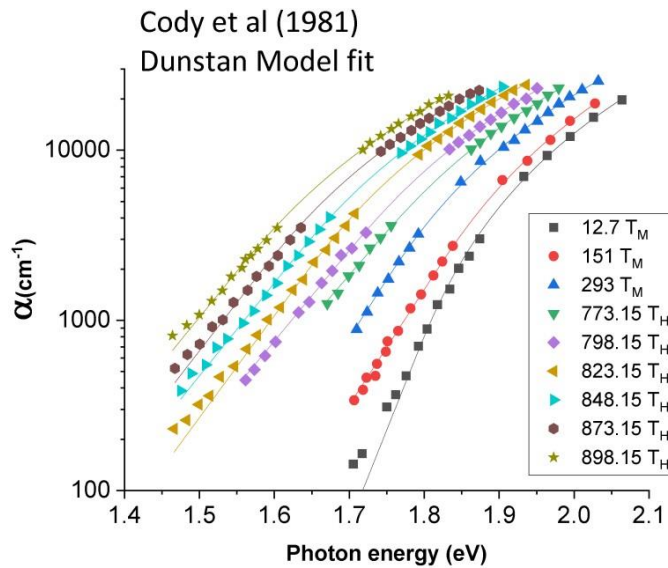
We analyzed optical data sets of a-Si:H thin films due to Cody et al [25] and Viturro and Weiser [26]. These optical data was fitted to Dunstan's model using nonlinear Levenberg-Marquardt fitting algorithm [33].

##### **4.a- Cody et al (1981) [25] optical data analysis:**

Cody et al a-Si:H samples were prepared by PECVD onto anodic substrates held at elevated temperatures. They performed an important study of the effects of both thermal and static disorder on the optical absorption edge of a-Si:H. They investigated the relationship between the  $T_{auc}$  optical gap and the Urbach energy, they introduced structural disorder through thermal evolution of hydrogen. They found that their results are compatible with the idea of additive thermal and structural disorder. They suggested that relaxed network disorder rather than hydrogen content is responsible for the dependence of optical energy gap of a-Si:H on hydrogen content. Their results indicated an inverse linear relationship between  $T_{auc}$  optical gap and Urbach energy.

Fig. (3) shows Dunstan's model nonlinear fits to Cody et al a-Si:H data.  $T_M=12.7\text{K}$ ,  $151\text{K}$  and  $293\text{K}$  are different measurement temperatures for an as-prepared film of composition

a-Si:H<sub>0.13</sub>,  $T_H$  is the isochronal heating temperature of the  $T_M=293\text{K}$  film at  $25^\circ\text{C}$  intervals from  $500^\circ\text{C}$  ( $773\text{K}$ ) to  $625^\circ\text{C}$  ( $898\text{K}$ ). This heating procedure was intended to induce varying out-diffusion of hydrogen from the films. The fitting parameters; of the Cody plot ( $E_{\text{Cody}}$  and  $B_{\text{Cody}}$  in the Cody model linearized equation,  $\varepsilon_2 = B_{\text{Cody}} (E - E_{\text{Cody}})$  and, of Dunstan's model  $E_u=1/\beta$ ,  $\alpha_o$ , and  $E_o$  in eqs.4-a and 4-b) are given in table (1).



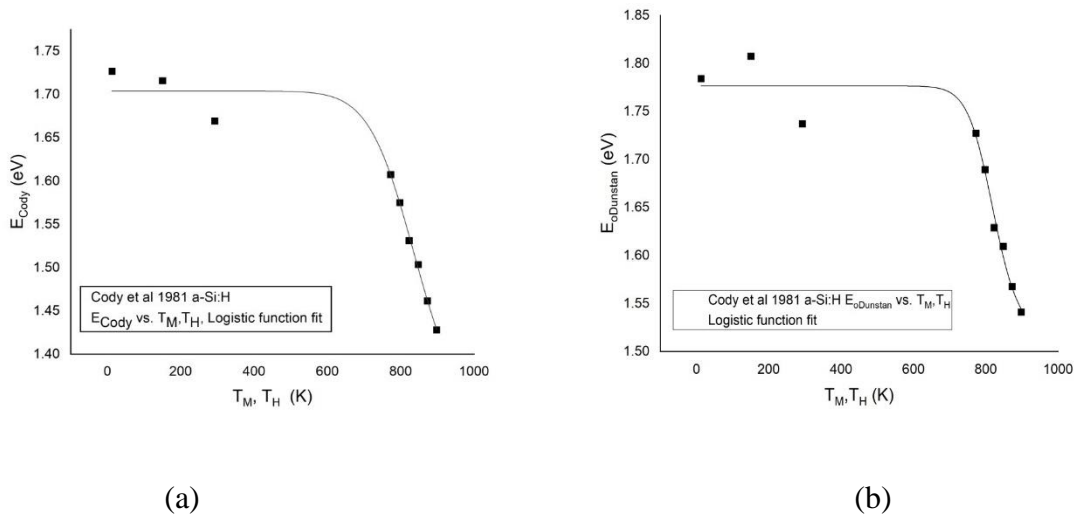
**Figure(3):** Nonlinear fitting plots of Cody et al data to Dunstan's model, fitting parameters are listed in table 1.

It is easily noted from table 1, the inverse proportion between both  $E_{\text{Cody}}$  and  $E_o$ , and the Urbach energy  $E_u$ , which means that increasing disorder through increasing  $E_u$  decreases both energy gap parameters  $E_{\text{Cody}}$  and  $E_o$ . The behavior of  $E_{\text{Cody}}$  versus  $E_u$  was already accounted for by Cody et al through the well-known Cody model of disorder [ 25]. However, the

decrease of  $E_o$  with increasing disorder through increasing  $E_u$  seems to mean that disorder really affects the mobility gap.

**Table (1):** Cody and Dunstan model fitting parameters for Cody et al a-Si:H data.

Temperature	$E_u$ (eV)	$E_{Cody}$ (eV)	$B_{Cody}$ ( $cm^{-1}eV^{-3}$ )	$E_o$ (eV)	$\alpha_o$ ( $cm^{-1}eV^{-3}$ )
12.7 K	0.0402	1.727	84701.2322	1.7839	93353.78
151 K	0.0664	1.716	94403.256	1.8074	106900.60
293 K	0.0659	1.669	96734.957	1.7369	93757.64
773.15 K	0.0892	1.607	83100.4843	1.7273	92796.62
798.15 K	0.0859	1.575	81919.4709	1.6894	90691.59
823.15 K	0.0761	1.531	77566.7904	1.6281	83136.63
848.15 K	0.0838	1.503	77523.765	1.6095	82779.405
873.15 K	0.0806	1.46156	71,854.6808	1.5676	78549.68
898.15 K	0.085	1.42805	70769.4856	1.541	77931.203

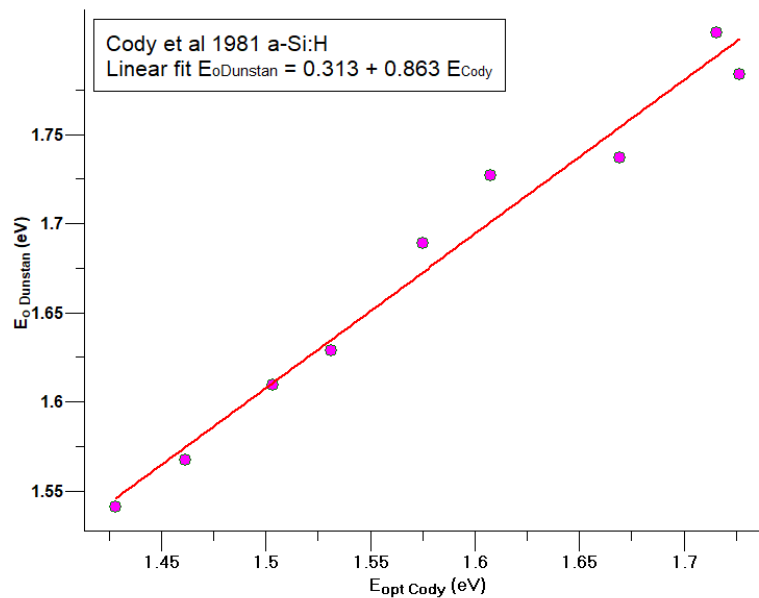


**Figure (4):** (a)  $E_{Cody}$  vs.  $T_M, T_H$  plot for Cody et al a-Si:H samples (b)  $E_{oDunstan}$  vs.  $T_M, T_H$  plot for Cody et al a-Si:H samples; both data are fitted to a logistic function.

Fig.(4-a) shows  $E_{Cody}$  vs.  $T_M, T_H$  plot for Cody et al a-Si:H samples. Here a logistic function fit [  $y = a / \{1 + \exp(b - cx)\}$  a, b and, c are constants] is performed as it is found capable to capture the main trend of the data variation. It is seen that  $E_{Cody}$  does not change appreciably with  $T_M$ , but decreases systematically with increasing  $T_H$  which means that hydrogen evolution affects the optical energy gap as already known in literature. The variation of  $E_o$  Dunstan with  $T_M, T_H$  shows similar behavior to the variation of  $E_{Cody}$  with  $T_M, T_H$ ,



this is shown in figure (4-b). This means that the evolution of hydrogen changes the band to band gap significantly, i.e. this seems to imply that hydrogen evolution from the films changes the mobility gap appreciably. We expect then that for Cody et al a-Si:H samples, the contribution of tail to band optical transitions which is accounted for by Dunstan's model is relatively insignificant compared to the real change in the mobility gap, i.e. the band to band threshold energy  $E_o$ . To check for this in a more quantitative way,  $E_{o\text{ Dunstan}}$  in figure (5) is plotted against  $E_{\text{Cody}}$  for Cody et al a-Si:H samples. A least squares straight line fitting gives a slope value of 0.863 which is closer significantly to 1 than zero, thus Dunstan's model accounts only ~15% for the apparent change of the optical gap, while ~85% is a real change in the separation between the valence band and conduction band band edges. We consider here that a zero slope ( $\Delta E_{o\text{ Dunstan}}/\Delta E_{\text{Cody}} = 0$ ) means that  $E_{o\text{ Dunstan}}$  is independent of  $E_{\text{Cody}}$ , while a unity slope means a perfect correspondence between  $E_{o\text{ Dunstan}}$  and  $E_{\text{Cody}}$ .



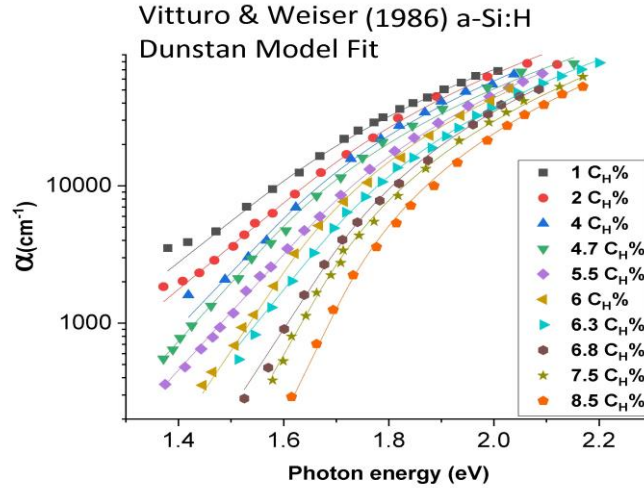
**Figure (5):**  $E_{o\text{ Dunstan}}$  vs.  $E_{\text{optCody}}$ , plot for Cody et al a-Si:H samples. Each pair of  $E_{o\text{ Dunstan}}$  and  $E_{\text{optCody}}$  values is taken at a definite  $T_M$  or  $T_H$  value in table 1.

Thus, for Cody et al a-Si:H optical data set, the main contributor to the change of the optical gap  $E_{\text{Cody}}$  is a real change in the mobility gap. What is the reason for this change? This is a longstanding controversial problem, and opinions were mainly divided between two well-known ones, the shift of the valence band edge or the indirect effect of disorder on the a-Si:H network [ 34]. Cody et al [ 25] adopted the second view in that hydrogenation is the primary reason for  $E_{\text{opt}}$  variation through its indirect network relaxing effect of the random network, and not through the recession of the valence band edge. We see here through Dunstan's model analysis and the inspection of Table I, that although  $E_o$  is always larger than  $E_{\text{opt}}$  because of the subtraction of the masking effect of tail-related absorption, it also changes with hydrogen evolution ( Note however, Cody et al did not give measurements results for the hydrogen content of their samples after isochronal heating). This means that there a real shift in the band edges separation, but the source of this change still cannot be decided here whether it is chemical or through disorder or due to both causes . According to theoretical work of Teate and Hadler, the mobility gap of a-Si:H decreases with increasing disorder according to localization theory [ 35], thus in view of the above-mentioned work, disorder not only creates band tails but can also shifts the mobility edges. It is also necessary to mention here a recent result by Steffens et al [36] that  $E_{\text{opt}}$  of a-Si:H correlates well with monohydride bond density of a-Si:H rather than either hydrogen concentration or structural disorder, which is an important result that needs to be further exploited. Another point to be mentioned is that  $E_o$  is not the same as the Urbach focus energy  $E_F$  concept, this issue is well discussed by Guerra in relation to his band-fluctuations model [ 19],  $E_F$  is the energy gap in the absence of any disorder whether thermal or structural disorder or even due to zero-point energy, i.e., for an ideal random network at zero Kelvin. However,  $E_{o\text{Dunstan}}$  is the band gap between valence and

conduction band edges at ambient conditions similar to  $E_o$  of Guerra's model [ 18] and the threshold energy gap of O'Leary's model [ 15] and not an extrapolated gap to the ideal case of the absence of any kind of disorder, that is the Urbach focus of Cody's model of disorder [ 25]. The most important point that should be clarified here, is that Dunstan's gap  $E_{oDunstan}$  (the band edges separation) is masked by the contribution of tail-related absorption to the Tauc edge, therefore only by subtracting this contribution,  $E_o$ , the real threshold energy to the onset of the band to band optical transitions, can be determined by any appropriate model such as Dunstan, O'Leary or Guerra models , Dunstan's model is the simplest one beyond the Tauc model.

#### **4-b Viturro and Weiser(1986) [26] Optical Data Analysis:**

Vitturo and Weiser [26] used a direct synthesis method for producing a-Si:H in which atomic hydrogen and silicon react on a substrate at ultrahigh vacuum to produce material with good properties. They argued that Cody et al [25] employed hydrogen evolution to produce static disorder, but they claimed that Cody et al procedure might cause other changes in the material in addition to the loss of hydrogen. Thus Vitturo and Weiser varied the hydrogen concentration systematically at the same deposition conditions, in order to reach more decisive results concerning the relation between the optical gap  $E_{opt}$ , the Urbach energy  $E_u$ , and hydrogen concentration  $C_{H\%}$ .



**Figure (6):** Dunstan model nonlinear fitting plots for Vitturo and Weiser a-Si:H data, fitting parameters are listed in Table 2.

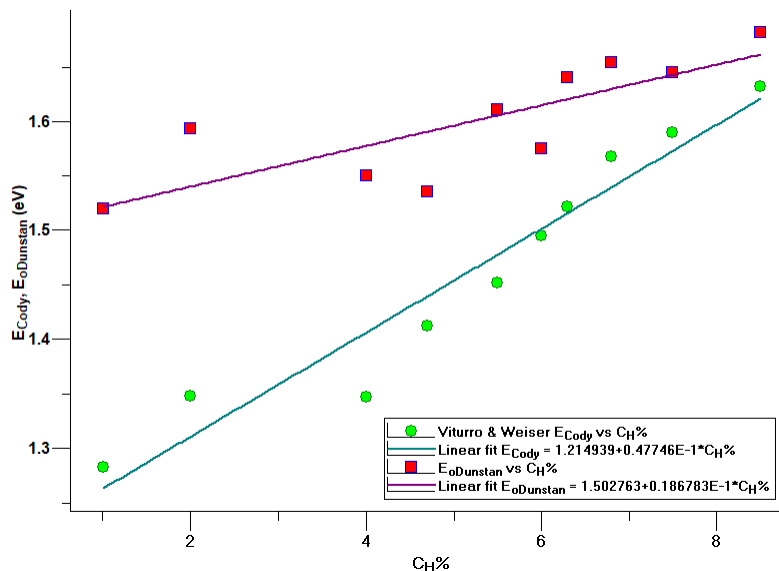
Fig.(6) shows Dunstan’s model nonlinear fits to Vitturo and Weiser a-Si:H optical data set for various percentage hydrogen concentrations  $C_H\%$  from 1% to 8.5%. These nonlinear fitting results successfully capture Vitturo and Weiser data, confirming the capability of Dunstan model to explain optical data covering Urbach and Tauc regions of the optical absorption edge. All the fitting parameters are given in Table 2.

**Table (2):** Cody and Dunstan models fitting parameters for Vitturo and Weiser a-Si:H data.

$C_H\%$	$E_u$ (eV)	$E_{Cody}$ (eV)	$B_{Cody}$ ( $cm^{-1}eV^{-3}$ )	$E_s$ (eV)	$\alpha_s$ ( $cm^{-1}eV^{-3}$ )
1	0.1606	1.341882	67992.455	1.52	80766.83
2	0.152	1.421464	75742.1910	1.593	96850.9
4	0.117	1.422799	67395.596	1.55	86830.33
4.7	0.11	1.463586	81123.4114	1.535	74147.23
5.5	0.111	1.501475	77677.329	1.6105	87806.23
6	0.08	1.54260	85774.3172	1.575	83469.8
6.3	0.098	1.55189	76535.5267	1.64	85297.12
6.8	0.0776	1.590196	88912.1728	1.654	93777.83
7.5	0.0666	1.60931	83544.18159	1.645	81137.97
8.5	0.0571	1.658137	86524.26294	1.682	83534.25

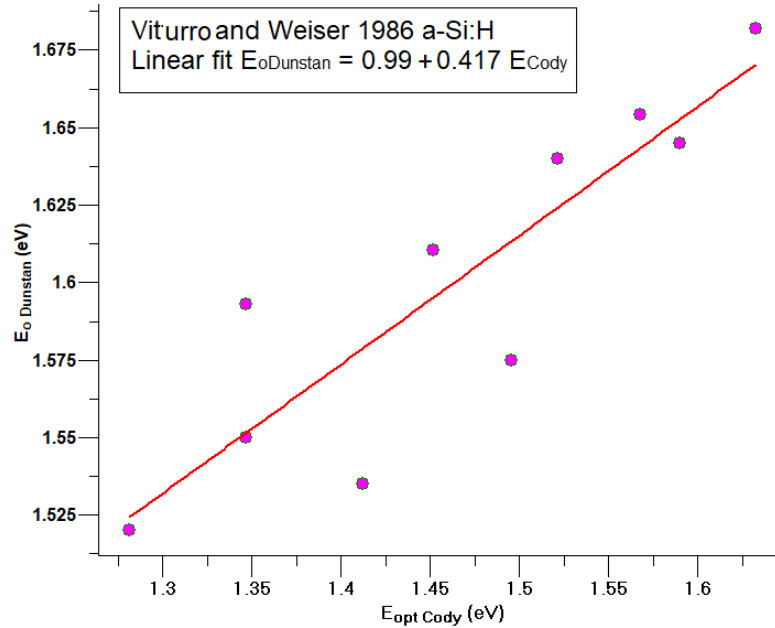
It can easily be seen from Table (2) that increasing the hydrogen concentration  $C_{H\%}$  (1% - 8.5% range) of Viturro and Weiser samples decreases the disorder through decreasing the Urbach parameter  $E_u$ .

To show the effect of varying  $C_{H\%}$  on the energy gap parameters  $E_{Cody}$  and  $E_{oDunstan}$ , figure. (7) is a combined plot of  $E_{Cody}$  and  $E_{oDunstan}$  vs.  $C_{H\%}$ . Both  $E_{Cody}$  and  $E_{oDunstan}$  increase with hydrogen concentration, but it is observed that  $E_o$  increase is significantly slower than  $E_{Cody}$  increase, as seen from the magnitudes of the slopes of the fitting straight lines ;  $0.477 \cdot 10^{-1}$  for  $E_{Cody}$  vs.  $C_{H\%}$  and  $0.187 \cdot 10^{-1}$  for  $E_{oDunstan}$  vs.  $C_{H\%}$ . The ratio between the slope of  $E_{oDunstan}$  vs.  $C_{H\%}$  and the slope of  $E_{Cody}$  vs.  $C_{H\%}$   $\sim 0.4$  or 40%. This means that  $\sim 60\%$  of the variation of the optical energy gap is explained by Dunstan's model while the remaining variation  $\sim 40\%$  is due to a real change in the band edge to band energy gap.



**Figure (7):** Comparative plots for  $E_{oDunstan}$  and  $E_{Cody}$  vs.  $C_{H\%}$  for Viturro and Weiser a-Si:H samples.

This behavior can be shown also from figure. (8) which depicts a plot of  $E_{ODunstan}$  vs.  $E_{Cody}$  for Vitturo and Weiser a-Si:H samples. The slope of the fitting straight line  $\Delta E_{ODunstan}/\Delta E_{Cody}$  is 0.417, this means that hydrogen causes a real variation in the mobility gap about 40% of the change of  $E_{opt}$  with hydrogen, while the other 60% is the due enhanced masking effect of absorption in the Tauc region due to tail related transitions. Thus, in contrast to the results of the analysis of Cody et al a-Si:H optical absorption data through the Dunstan's model which showed a dominating behavior due to mobility gap variation, Vitturo and Weiser a-Si:H data analysis shows a significantly slower mobility gap behavior. This obviously reveals that the more systematic control of hydrogen incorporation in a-Si:H films in Vitturo and Weiser work as compared to Cody et al work was fruitful through lowering the effect of disorder on the mobility gap. This kind of conclusion cannot be reached from the Tauc plot analysis alone. The subtraction of tail-related contribution to the Tauc edge through Dunstan's model is found here necessary to extract more useful physical information that explains the change of  $E_{opt}$  with deposition variables, i.e. only 40% of the change in  $E_{opt}$  is due to a real change in the separation between the valence and conduction band edges for Vitturo and Weiser a-Si:H samples, the other 60% change is not due to a real band gap change, but due to the masking effect of the tail-related optical transitions contribution to the Tauc edge. Here, one of the important ambiguities in the interpretation of  $E_{opt}$  as deduced from the Cody (or Tauc) plot is explicitly revealed, which demands a model that accounts for the effect of disorder on the Tauc edge such as Dunstan's model, but of course, the Urbach region data should also be available to the experimenter to reach such conclusions that are beyond the Tauc model.



**Figure (8):**  $E_{oDunstan}$  vs.  $E_{optCody}$  plot for Viturro and Weiser a-Si:H samples. Each pair of  $E_{oDunstan}$  and  $E_{optCody}$  values is at a definite  $C_H\%$  value in Table 2.

## 5. Conclusion:

In conclusion, Dunstan's model was found successful in capturing the optical absorption data covering both Urbach and Tauc regions for Cody et al and Viturro and Weiser a-Si:H optical data sets. Aside from this success, this work concentrates on what kind of new physical information can be extracted from the simple Dunstan model beyond the conventional Tauc model through the comparison between the main energy gap parameters of these model;  $E_{opt}$ , the optical energy gap and,  $E_o$ , the energy gap between the valence and conduction band edges its value is masked by the contribution of the tail-related absorption to the Tauc edge. It was found that the different behavior trends of  $E_o$  and  $E_{opt}$  are fruitful in differentiating between the masking effect of disorder through tail-related absorption in the Tauc region, and the real change in the band gap of a-Si:H samples. This differentiation was made apparent by adopting the slope ( $\Delta E_o / \Delta E_{opt}$ ) of the straight line fit to the relation between  $E_o$  and  $E_{opt}$ , assuming

that it as an indicator of the effect of disorder on the Tauc edge of a-Si:H, which is a simple approach not attempted before in previous literature according to our knowledge. Using this approach, we found that there is a larger relative change in  $E_{ODunstan}$  of Cody et al a-Si:H samples compared to Viturro and Weiser samples due to varying hydrogen content, and this is attributed to the better control of hydrogen incorporation process of Viturro and Weiser samples, which caused a lower shift in the band edges. Dunstan's model with its simple analytic formulas can easily be implemented in any suitable software such as Origin or Mathematica. It should also be mentioned that Dunstan's original convolution integral (eq.3) can also be applied to crystalline semiconductors and nano- materials optical data by inserting the appropriate form of the function  $f(E - E_{oG})$  of eq.1 inside the integral and solving it numerically.



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