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A Study of a-Si:H Absorption Edge Using Dunstan's Model

Lana F. Sahal* ***Abdullah Al-Numan***

Physics Department, College of Science for Women, University of Baghdad, Baghdad, Iraq.
*Corresponding author: lanasahal24@gmail.com
E-mail addresses: abdullahia_phys@csw.uobaghdad.edu.iq

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Abstract:

The optical absorption data of Hydrogenated Amorphous Silicon was analyzed using a Dunstan model of optical absorption in amorphous semiconductors. This model introduces disorder into the band-band absorption through a linear exponential distribution of local energy gaps, and it accounts for both the Urbach and Tauc regions of the optical absorption edge.Compared to other models of similar bases, such as the O'Leary and Guerra models, it is simpler to understand mathematically and has a physical meaning. The optical absorption data of Jackson et al and Maurer et al were successfully interpreted using Dunstan's model. Useful physical parameters are extracted especially the band to the band energy gap $E_{\circ}$, which is the energy gap in the absence of disorder, that can be interpreted as the mobility gap of the material.

Keywords: Dunstan model, Localized states, Mobility gap, Tauc model, Urbach model.

Introduction:

The use of the Tauc model for optical absorption is the most common in researches to obtain the so-called the energy gap of semiconductors in general, and amorphous semiconductors in particular[1]. It was a successful model in defining an effective optical gap for amorphous semiconductors, although its physical meaning is still somewhat obscure [2-5]. Tauc model virtue is in its simplicity as known to researchers. However the disadvantage of Tauc model is its neglect of absorption due to band tails, it is a model of band to band absorption only, therefore it neglects the effect of disorder on the absorption edge which appears mainly in the Urbach tail of the semiconductors [6]. Many researchers developed more sophisticated models which include the Urbach tail and its effect on the Tauc edge of amorphous semiconductors such as the O'leary with various co-authors [7-10]and Guerra et al [11-13] Their models accounted for both the Urbach and Tauc regions of the absorption edge, these researchers main achievement is that they introduced analytical models that can also be handled numerically to model the absorption edge of amorphous semiconductors to obtain useful model parameters, also they clarified the role of absorption due to tails on the Tauc edge itself. However, there is an older model due to Dunstan [14,15] which accounted for the disorder through the Urbach edge which is simpler in mathematical form than O'Leary and Guerra models, but as claimed and investigated by Dunstan that his model accounted for most optical data he studied. With the exception of Frova and Selloni[16], this simple model seems to remain unexploited in literature although mentioned by Guerra et al [13], who developed a single poly-logarithm equation to fit Urbach and Tauc regions simultaneously which is very useful and is based on the same band fluctuation model of Skettrup [17] adopted by Dunstan. The aim of this work is to use and further exploit Dunstan's model to analyze and model quality optical absorption data of a-Si:H due to Jackson et al [18] and Maurer et al [19], which is in our opinion, a simple modeland clear in its physical meaning, and can account satisfactorily for experimental data. We believe that Dunstan's model is unjustly neglected in literature and deserves further exploitation. We adopted this model because we believe it is the simplest analytical model beyond the Tauc model that can account satisfactorily for the effect of disorder on the absorption edge of amorphous semiconductors, and from which the mobility gap of the material could

be extracted , also further physical insight can be obtained beyond the Tauc approach .

Theoretical Background:

The original Tauc model is a model of the region of high optical absorption ($\alpha \geq 10^4 cm^{-1}$, where α is the absorption coefficient) of the absorption spectrum of amorphous semiconductors is given by the well-known Tauc equation [2,20,21]

$\alpha E = B_{Tauc}(E - E_{Tauc})^2$……..1

Where E, is the photon energy. E_{Tauc} , the Tauc optical gap and B_{Tauc} is a pre-factor.

A more appropriate model to a-Si:H thin films, cody et al[22] adopted Tauc model but with a slight modification, that is the constant dipole matrix element assumption[23]instead of the constant momentum matrix element of Tauc, thus the Cody expression is given by:

$\alpha/E = B_{Cody}\,(E - E_{Cody})^2$……2

Where E_{Cody} is the Cody model optical gap, and B_{Cody} is a pre-factor.

As Tauc and Cody models do not take into account optical transitions due to tail states, they tend to underestimate the energy gap proposed by their models[24]. Dunstan's model[15] is an old and unjustly neglected model which accounts for the effect of tail states on the obtained optical gap. Dunstan considered that static and thermal disorders lead to a distribution of local energy gaps E_g which have the form:

$P(\eta) = \frac{1}{E_u} e^{-\frac{\eta}{E_u}} \eta \geq 0$…….3

Where η is a disorder parameter responsible for taking E_g a distribution of values $E_\circ - \eta$ ($E_\circ$ is the energy gap in the absence of disorder), and E_u is the Urbach energy. If the absorption in the local regions is given by a function of the general form,

$\alpha(E) = f(E - E_g)$……..4

Then the absorption coefficient is expressed by integrating f(E-E_g) which is the local band to band absorption overall values ofE_g, i.e.

$\alpha(E) = \int_\ell^\infty P(\eta) f(E - E_o + \eta) d\eta$……5

Where the lower limit of the integration ℓ is zero for $E \geq E_\circ$ and is $E_\circ - E$for $E \leq E_\circ$. Eq.5 represents the general form of Dunstan's model. For the special case that $f(E - E_g)$ takes the special form of the Tauc law i.e.

$\alpha(E) = \alpha_\circ (E - E_g)^2 / E$……6

Eq.5 can be solved analytically to obtain, 11,12

$\alpha(E) = \frac{2\alpha_\circ {E_u}^2}{E}\, exp\left\{\frac{E - E_\circ}{E_u}\right\}$ $(for\ E < E_\circ)$……..7-a

$\alpha(E) = \frac{\alpha_\circ}{E}\{(E - E_\circ)^2 + 2E_u(E - E_\circ) + 2{E_u}^2\}$ $for\ (E > E_\circ)$……7-b

Dunstan based his model on the Skettrup model[17]. Frova and Selloni[16] neglected conduction band tails which is a suitable approximation for a-Si:H and Si related thin films[8]. In eq.7-b, apart from the common factor, the 1st term concerns the contribution of band to band absorption and the 2nd and 3rd terms concern tail states related absorption.

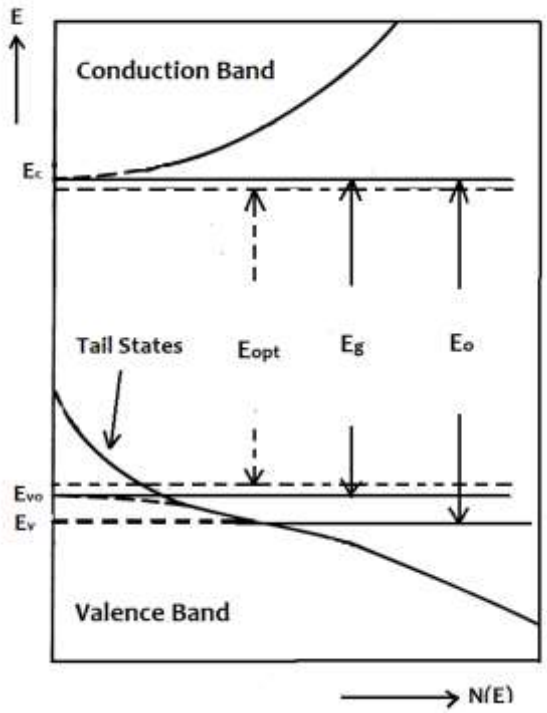

Figure1. A schematic density of states diagram suitable for a-Si:H, which shows the characteristic energy gap parameters E_o, E_g, and E_{opt}.

In Fig.1, we sketch an approximate density of state model suitable for a-Si:H related materials. Here the conduction band tails are neglected; E_g is the extrapolated bandgap to the zero density of states, which is the energy gap proposed by the Tauc model[1], but due to the neglect of optical transitions originating from tail states in this model, the experimentally obtained optical energy gap E_{opt} is smaller than E_g i.e. $E_{opt} < E_g$. $E_g$in fact, is the bandgap extracted from the O'Leary model when conduction band tails are neglected[8]. $E_\circ$is the energy gap between the band edges ($E_\circ = E_c - E_v$) which is the energy gap parameter deduced from Dunstan or Guerra models, it might be interpreted as the mobility gap of the material. Another important result derived by Dunstan[15], is from the inversion of eq.5 without imposing any specific form for the band to band absorption $f(E - E_\circ - \eta)$. He obtained the following result.

$f(E) = \alpha(E) - \acute{\alpha}(E) E_u for\ (E > E_\circ)$……8

Where $\acute{\alpha}(E) = d\alpha/dE$.

Thus by evaluating the numerical derivative of the absorption data in the Tauc region, the band to band absorption function f(E) can be calculated from eq.8.
Thus if f(E) obeys the Tauc power law the plot of $\{Ef(E)\}^{1/2}$ vs .E gives a straight line with an extrapolated gap $E_\circ$, the bandgap in the absence of disorder.

Results and Discussion:

The optical absorptions data of device quality a-Si:H films prepared by Jackson et al[18] which are given in terms of the imaginary part of the dielectric function $\varepsilon_2(E)$ are analyzed here. Fig.2,shows the plots of ${\varepsilon_2}^{1/2}$ and $f^{1/2}(E)$ vs. E in a wide data range (E ~ 1.5-3 eV). Here the Cody model is adopted for the ε_2 data and also to the band to band absorption f(E) extracted using eq.8 $(f(E) = \varepsilon_2(E) - \acute{\varepsilon_2}(E)E_u)E_u$, was obtained from the Urbach plot of Jackson et al data in the Urbach region giving E_u=50 meV, and $\acute{\varepsilon_2} = d\varepsilon_2/d\varepsilon$ were numerically calculated in the photon energy range $(\sim 1.7 - 3\ eV)$. The energy gap parameters obtained are $E_{Cody} = 1.627\ eV$ in the fitting range $(\sim 1.7 - 3\ eV)$and $E_\circ = 1.68\ eV$. It is obvious from the results that ($E_\circ = 1.68\ eV$) is larger by about 0.05 eV than ($E_{opt} \sim 1.63\ eV$). Two points are noticed is (1)$E_\circ \sim E_{Cody} + E_u$ as was originally claimed by Dunstan according to his model, but it should be mentioned that this is true only for low disorder films such as the one by Jackson et al here. For large E_u the relation between $E_\circ$ and E_{Cody} is slightly nonlinear (frova1985), (2) the $E_\circ$ value obtained for Jackson et al[18] a-Si:H sample $(\sim 1.68\ eV)$ is the same as the value obtained by Orapunt et al 2011[25]from the O'Leary model, which they suggested as the value of the mobility gap of Jackson et al a-Si:H samples. The three parameters obtained here for a-Si:H films, $E_u = 0.05\ eV, E_\circ = 1.68\ eV$ and the slope value of $f^{1/2} vs. E$ plot i.e. 3.067 eV^{-1} are substituted in Dunstan eqs.7-a & 7-b but here for the Cody constant dipole matrix element instead of the constant momentum matrix element model of Tauc.

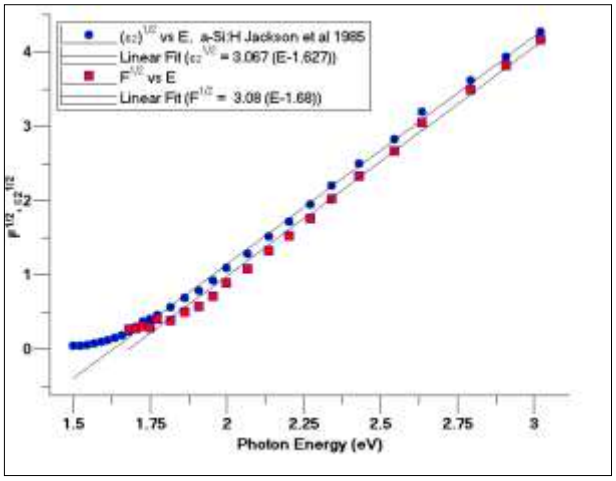

Figure2. Linear fits for $\varepsilon_2^{1/2}$ and $F^{1/2}$ vs. photon energy of Jackson et al[18] a-Si:H samples.

The result is shown in Fig.3. First we see that the Dunstan model fits well the ε_2.data of a-Si:H of Jackson et al in the wide range of photon energy $(\sim 1.5 - 3\ eV)$ using the model parameters deduced from the Cody-like linear fitting of $f^{1/2}(E) vs. E$. Second, the contributions of the band to band absorption and the tail to band absorption are shown. It is seen that the tail to band absorption is dominant in the range $E = E_\circ = 1.68\ eV$ to $E \sim 1.82\ eV$ at the intersection point, then band to band increasingly dominates. This result of the Dunstan model is similar to the O'Leary model prediction illustrated in Fig.3 of ref [8].

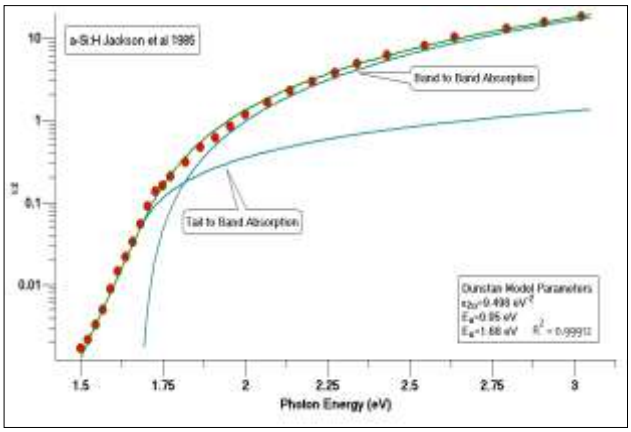

Figure3. Direct Dunstan model fit for Jackson et al[18]a-Si:H samples.

Optical Absorption data prepared by Maurer et al[19] were also analyzed here they used Plasma Enhanced Chemical Vapor Deposition (PECVD) method to prepare their samples. They irradiated them with pulsed laser at $\lambda = 532nm$ in a highly controlled manner to study the effects of controlled hydrogen out-diffusion resulting from laser heating for short times. One of their important results is the determination of the optical absorption

spectra of their samples as a function of the maximum heating temperature Tmax in a wide photon energy range. In our analysis here, the constant dipole matrix element approximation of Cody is used.

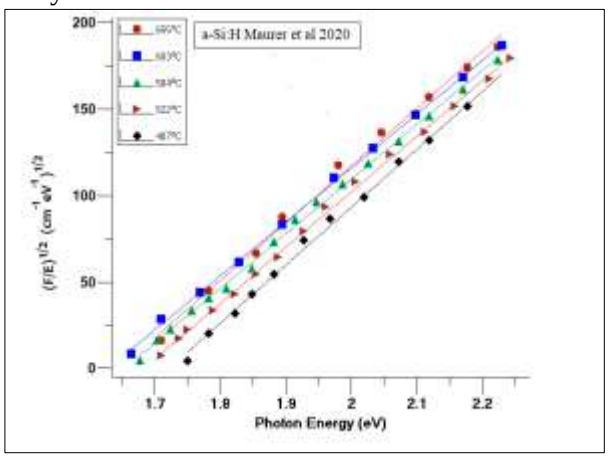

Figure4. Linear fits for $(F/E)^{1/2}$ vs photon energy of Maurer et al[19] a-Si:H samples at five T_{max} values.

Figure.4 shows the plot of $(f(E)/E)^{1/2} vs. E$ for Maurer et al a-Si:H samples for five T_{MAX} values ranging from 407^oC to 655^oC. The data were linearly fitted using the least squares method. The extrapolated E_o values tend to decrease with increasing T_{MAX}. $E_{Cody}$of the samples showed a similar trend as depicted in Table I. The Dunstan model parameters are obtained from the linear fittings of Fig.4. In order to assess the validity of the linear fitting results. The optical data were nonlinearly fitted to the direct Dunstan model equations (i.e. eqs.7-a & 7-b but using the constant dipole model approximation). Fig.5 shows the fitting results. It is obvious that the Dunstan model is capable of capturing the main features of the optical absorption data of a-Si:H samples prepared by Maurer et al[19].

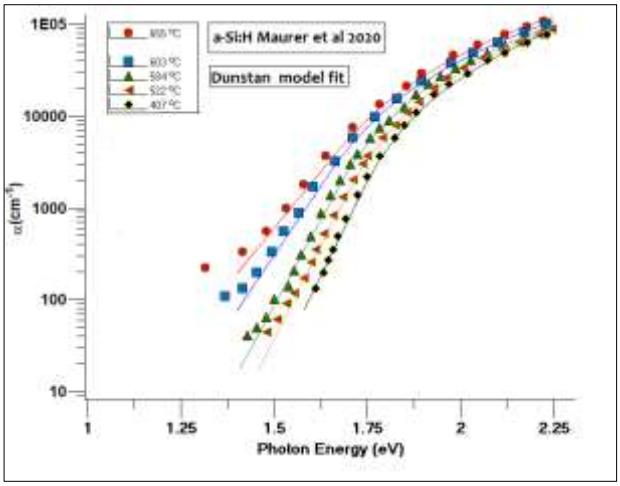

Figure5. Direct Dunstan model fits (eqs. 7a and 7b) for Maurer et al[19] a-Si:H samples using parameters extracted from the Urbach plot (E_u), and $(F/E)^{1/2}$ vs E plots (E_o, $\alpha_o^{1/2}$).

Figure.6 shows a comparative plot of $E_{Cody} vs.T_{max}$ and $E_o vs.T_{max}$ of Maurer et al a-Si:H data. The linear trend of the data is estimated from least squares fitting. Both $E_{Cody} and E_o$ decreases with increasing T_{MAX} indicating the effect of out-diffusion of hydrogen in decreasing the energy gap. $E_o$linear trend is relatively slower than E_{Cody}. This means that part of the dependence of E_{Cody} on Tmax can be attributed to the increase of tail to extended states optical transitions, this interpretation is facilitated by the use of the Dunstan model, while the other part can be attributed to the actual decrease of the mobility gap-related parameter E_o with increasing hydrogen out-diffusion due to increasing Tmax[26,27].Dunstan's model in its general form eq.5 can also be applied to crystalline semiconductors and nanomaterials. [28-33]

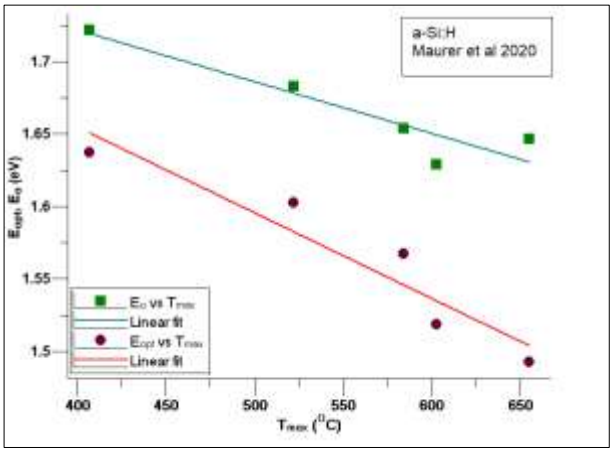

Figure6. Linear fitting trends of E_{opt} and E_o vs T_{max} data points for Maurer et al[19] a-Si:H samples

Conclusion:

In conclusion, in both the Urbach and the Tauc regions, Dunstan model was shown to be successful in fitting and interpreting optical absorption data. More physics can be extracted from the optical data; using this simple model which takes into account tail simultaneouslystates contribution to optical absorption; than the famous Tauc model which neglects these transitions. An important insight is gained because$E_o$in contrast to the optical energy gap obtained from Tauc or Cody plots can be interpreted as the real band to band absorption energy gap, thus its variation with deposition parameters can be interpreted as a variation in the mobility gap E_μ of the amorphous sample with deposition parameters, while the original E_{opt} has the effects of tail states related absorption and band to band absorption intermingled making the meaning of E_{opt} extracted from the Tauc plot ambiguous, especially for samples of relatively high disorder (large Urbach parameter E_u). Also this old and unjustly neglected model due to Dunstan is relatively simpler in form than the important O'Leary and Guerra models, this can assist the experimenter to analyze the optical absorption data of amorphous semiconductors by relatively simple linear or/and nonlinear modeling, and we think it deserves more serious attention, and it should be further studied to assess its validity to wide variety of amorphous materials other than a-Si:H.

Table I. Model parameters obtained in this paper of a-Si:H samples prepared by Maurer et al[19],it includes a comparison between Cody and Dunstan models fitting results.

$T_M{}^\circ C$	$E_u\ (eV)$	$E_{Cody}\ (eV)$	$B_{Cody}(cm^{-1}eV^{-3})$	$E_\circ\ (eV)$	$\alpha_\circ\ (cm^{-1}eV^{-3})$
407	0.054	1.637	100366.7	1.722	112428
522	0.056	1.602	96195.3	1.683	103749.7
584	0.061	1.567	93073.9	1.654	99946.1
603	0.076	1.518	90180.1	1.629	97545.03
655	0.094	1.493	90757.6	1.647	110153.43

Authors' declaration:

- Conflicts of Interest: None.
- We hereby confirm that all the Figures and Tables in the manuscript are mine ours. Besides, the Figures and images, which are not mine ours, have been given the permission for re-publication attached with the manuscript.
- Ethical Clearance: The project was approved by the local ethical committee in University of Baghdad.

Authors' contributions statement:

The first author analyzed the data, and the 2nd author suggested and developed the project. Both authors participated in writing the paper.

References:

1. Tauc J, Grigorovici R, Vancu A. Optical properties and electronic structure of amorphous germanium. Phys status solidi. 1966;15(2): 627–37.
2. Mullerova J, Sutta P. On some ambiguities of the absorption edge and optical band gaps of amorphous and polycrystalline semiconductors. Commun Lett Univ Zilina. 2017; 19(3): 9–15.
3. Pawlak J, Al-Ani SKJ. Inverse logarithmic derivative method for determining the energy gap and the type of electron transitions as an alternative to the Tauc method. Opt Mater (Amst). 2019; 88: 667–73.
4. Makuła P, Pacia M, Macyk W. How to correctly determine the band gap energy of modified semiconductor photocatalysts based on UV–Vis spectra. ACS Publications; 2018.
5. Zanatta AR. Revisiting the optical bandgap of semiconductors and the proposal of a unified methodology to its determination. Sci Rep. 2019; 9(1): 1–12.
6. Studenyak I, Kranjčec M, Kurik M. Urbach rule in solid state physics. Int J Opt Appl. 2014; 4(3): 76–83.
7. O'Leary SK, Johnson SR, Lim PK. The relationship between the distribution of electronic states and the optical absorption spectrum of an amorphous semiconductor: An empirical analysis. J Appl Phys. 1997; 82(7): 3334–40.
8. O'Leary SK, Malik SM. A simplified joint density of states analysis of hydrogenated amorphous silicon. J Appl Phys. 2002; 92(8): 4276–82.
9. O'Leary SK. An analytical density of states and joint density of states analysis of amorphous semiconductors. J Appl Phys. 2004; 96(7): 3680–6.
10. Thevaril JJ, O'Leary SK. A universal feature in the optical absorption spectrum associated with hydrogenated amorphous silicon: A dimensionless joint density of states analysis. J Appl Phys. 2016; 120(13): 135706.
11. Guerra JA, Tejada A, Korte L, Kegelmann L, Töfflinger JA, Albrecht S, et al. Determination of the complex refractive index and optical bandgap of CH3NH3PbI3 thin films. J Appl Phys. 2017; 121(17): 173104.
12. Guerra JA. Optical characterization and thermal activation of Tb doped amorphous SiC, AlN and SiN thin films. Ph. D. dissertation, PUCP, 2017 [Online]. Available: http://hdl.handle.net/20.500.12404/9187.
13. Guerra JA, Tejada A, Töfflinger JA, Grieseler R,

Korte L. Band-fluctuations model for the fundamental absorption of crystalline and amorphous semiconductors: a dimensionless joint density of states analysis. J Phys D Appl Phys. 2019; 52(10): 105303.
14. Dunstan DJ. Evidence for a common origin of the Urbach tails in amorphous and crystalline semiconductors. J Phys C Solid State Phys. 1982; 15(13): L419.
15. Dunstan DJ. New evidence for a fluctuating band-gap in amorphous semiconductors. J Phys C Solid State Phys. 1983; 16(17): L567.
16. Frova A, Selloni A. The Optical Threshold of Hydrogenated Amorphous Silicon. In: Tetrahedrally-Bonded Amorphous Semiconductors. Springer; 1985. p. 271–85.
17. Skettrup T. Urbach's rule derived from thermal fluctuations in the band-gap energy. Phys Rev B. 1978; 18(6): 2622.
18. Jackson WB, Kelso SM, Tsai CC, Allen JW, Oh S-J. Energy dependence of the optical matrix element in hydrogenated amorphous and crystalline silicon. Phys Rev B. 1985; 31(8): 5187.
19. Maurer C, Beyer W, Hülsbeck M, Breuer U, Rau U, Haas S. Impact of Laser Treatment on Hydrogenated Amorphous Silicon Properties. Adv Eng Mater. 2020; 22(6): 1901437.
20. Abbo AI. Analytical Study of near Mobility Edge Density of States of Hydrogenated Amorphous Silicon. Baghdad Sci J. 2014; 11(3).
21. Hussian AC. Analytical study of high absorption region of the absorption edge of a-Si: H using nonlinear regression method. Iraqi J Phys. 2018; 16(37): 88–97.
22. Cody GD, Brooks BG, Abeles B. Optical absorption above the optical gap of amorphous silicon hydride. Sol Energy Mater. 1982; 8(1–3): 231–40.
23. Minar SB, Moghaddam S, O'Leary SK. A re-examination of experimental evidence on the spectral dependence of the optical transition matrix element associated with thin-film silicon. J Mater Sci Mater Electron. 2019; 30(10): 9964–72.
24. Li Z, Lin SH, Qiu GM, Wang JY, Yu YP. A method for determining band parameters from the optical absorption edge of amorphous semiconductor: Application to a-Si: H. J Appl Phys. 2018; 124(2): 25702.
25. Orapunt F, O'Leary SK. Spectral variations in the optical transition matrix element and their impact on the optical properties associated with hydrogenated amorphous silicon. Solid State Commun. 2011; 151(5): 411–4.
26. Steffens J, Rinder J, Hahn G, Terheiden B. Correlation between the optical bandgap and the monohydride bond density of hydrogenated amorphous silicon. J Non-Crystalline Solids X. 2020; 5: 100044.
27. Jafari S, Steffens J, Wendt M, Terheiden B, Meyer S, Lausch D. Occurrence of Sharp Hydrogen Effusion Peaks of Hydrogenated Amorphous Silicon Film and Its Connection to Void Structures. Phys status solidi. 2020; 257(9): 2000097.
28. Schaefer ST, Gao S, Webster PT, Kosireddy RR, Johnson SR. Absorption edge characteristics of GaAs, GaSb, InAs, and InSb. J Appl Phys. 2020; 127(16): 165705.
29. Hakeem HS, Abbas NK. Preparing and Studying Structural and Optical Properties of Pb1-xCdxS Nanoparticles of Solar Cells Applications. Baghdad Sci J. 2021; 18(3): 640.
30. Morigaki K, Ogihara C. Amorphous semiconductors: Structure, optical, and electrical properties. In: Springer Handbook of Electronic and Photonic Materials. Springer; 2nd Ed, 2017. p. 1.
31. Sangiorgi N, Aversa L, Tatti R, Verucchi R, Sanson A. Spectrophotometric method for optical band gap and electronic transitions determination of semiconductor materials. Opt Mater (Amst). 2017; 64: 18–25.
32. Yuan L-D, Deng H-X, Li S-S, Wei S-H, Luo J-W. Unified theory of direct or indirect band-gap nature of conventional semiconductors. Phys Rev B. 2018; 98(24): 245203.
33 Capper P, Willoughby A, Kasap S. Optical Properties of Materials and Their Applications. 2nd EdJohn Wiley & Sons; 2020.

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دراسة حافه الأمتصاص الى a-Si:H باستخدام نموذج دونستان

لنا فاروق سهل **عبد الله النعمان**

قسم الفيزياء، كلية العلوم للبنات، جامعة بغداد، بغداد ، العراق.

الخلاصه:

تم استخدام نموذج الامتصاص البصري في أشباه الموصلات غير المتبلورة المنسوب Dunstan لتحليل بعض بيانات للامتصاص البصري للسيليكون العشوائي المهدرج. يقدم هذا النموذج اضطرابًا في امتصاص حزمه-الى حزمه من خلال التوزيع الأسي الخطي لفجوة الطاقة الموضعيه، والذي يمكن أن يفسر كلا من منطقتيUrbach وTauc من حافه الامتصاص البصري. مقارنة بالنماذج الأخرى ذات الأسس المماثلة، مثل نموذجيO'Learyو Guerra، فهو أبسط في الشكل الرياضي وله معنى فيزيائي مباشر. نموذج دونستان نجح في تفسير بيانات الامتصاص البصري لـ Jackson et al و Maurer et al ، تم استخراج معلمات فيزيائية مهمة خاصة فجوه الطاقه E_0المتعلقه بأنتقالات حزمه-الى حزمه والتي هي فجوة الطاقة في حالة عدم وجود اللانتظام ، والتي يمكن تفسيرها على أنها فجوة التحركيه للماده.

الكلمات الافتتاحية:, نموذج دونستان ,الحالات الموضعيه, فجوه التحركيه , , نموذج تاوس , نموذج اورباخ .