

Analytical Study of near Mobility Edge Density of States of Hydrogenated Amorphous Silicon

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Abstract:

Experimental results for the density of states of hydrogenated amorphous silicon due to Jackson et al near the valence and conduction band edges were analyzed using Levenberg-Marquardt nonlinear fitting method. It is found that the density of states of the valence band and the conduction band can be fitted to a simple power law, with a power index 0.60 near the valence band edge, and 0.55 near the conduction band edge. These results indicate a modest but noticeable deviation from the square root law (power index=0.5) which is found in crystalline semiconductors. Analysis of Jackson et al density of states integral $J(E)$ data over about (1.4 eV) of photon energy range, showed a significant fit to a simple power law with a power index of 2.11 close to that predicted from the density of states fitting results 2.15

Key words: density of states, mobility edge, nonlinear fitting, amorphous semiconductors.

Introduction:

Amorphous silicon remains at the center of attention of amorphous solid state community for two main reasons. First the applied technological side especially in cheap and relatively efficient large area solar cell

technology, and second the theoretical and computational side because being an elemental semiconductor it is one of the simplest disordered semiconductors to test new theoretical and simulation methods [1].

In amorphous semiconductor research there is still a controversy concerning the correct functional dependence of the density of states (DOS) distribution close to each of the valence band (VB) and conduction band (CB) mobility edges, its knowledge is crucial for optical properties and electronic device modeling [2].

For crystalline semiconductors this problem does not exist due to the periodic symmetry of the system which facilitated the establishment of robust band structure calculation techniques

[3]. Thus it is well established experimentally and theoretically that the DOS distribution near each of VB and CB edges obeys a simple power square root law, the nearly free electron model through the effective mass approximation is sufficient to account for this behavior [4].

The roots of the amorphous case controversy is due to two main reasons; **first** the lack of sufficient experimental work that spans both VB and CB DOS distributions close to the band edges for the same sample, and the **second** is the theoretical problem as disorder introduces great complexity into calculation efforts [5].

There is a substantial progress in recent years in simulation studies of structural, vibrational and electronic properties of amorphous semiconductors due to the enormous increase in the computational power of modern computers. Important advances were achieved through creating powerful software based on ab initio

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i.e. first principles many-body computational techniques such as density functional theory (DFT), and some satisfactory results are beginning to emerge [5,6].

The experimental side is still lacking somewhat, however the pioneering experimental work of Jackson et al [7] in which a nearly complete DOS diagram for a-Si:H prepared by plasma enhanced chemical vapor deposition (PECVD) determined with reasonable accuracy using various sophisticated experimental techniques, still represents almost a unique achievement in this genre.

In this paper, the density of states results of Jackson et al [7], were analyzed close the CB and VB edges using numerical Levenberg-Marquardt nonlinear least squares fitting method [8], in order to investigate the functional dependence of the experimental DOS near each of VB and CB edges of a-Si:H. The results were compared with the crystalline case and relevant theoretical work, and some of their implications were discussed.

Theory: In crystalline semiconductors, band edges separate occupied band states and unoccupied gap states, and there is a forbidden energy gap between the valence and conduction bands. In amorphous semiconductors, mobility edges separate occupied band states (of delocalized nature similar to crystals) and occupied localized states, and there is instead a pseudo-gap called the mobility gap. Periodic symmetry of the three dimensional crystal potential ensures that the DOS near each of the VB and CB edges is a parabolic function of energy similar to that in free space but with different effective mass [3] :

$$N(E') = (1/2\pi^2) (2 m^*/\hbar^2)^{3/2} E'^{1/2} \dots (1)$$

where $N(E')$ is the density of states, E' is the state energy, m^* is the effective mass, and \hbar is the reduced Planck's constant.

In amorphous semiconductors, the band (mobility) edge is smeared out due to localized states encroaching towards the mobility gap. Disorder ensures that there is no periodic potential thus the effective mass approximation based on the k -space concept seems to be invalid, also the potential fluctuations may/or may not have substantial effects on the density of states distribution near the mobility edge [6].

Singh and Shimakawa [4] succeeded in constructing an effective mass theory for electrons and holes in amorphous semiconductors using the coordinate \mathbf{r} -representation instead of the wave vector \mathbf{k} -representation of the quantum mechanical treatment of the problem, by which they got around the k non-conservation problem peculiar to disordered systems. They proved that the effective mass concept can be applied to transform a fully coordinated network to equivalent effective medium of a Fermi free electron gas similar to the way the periodic structure of the crystal can be transformed into a nearly free electron gas. Thereby they derived an equation similar to eq.1 to represent the density of states near the mobility edge. They further argued that due to the complex topology of amorphous structures, the density of states near band edges may be in fractal space thereby allowing for other possible values for the functional dependence of $N(E')$ on state energy E in amorphous semiconductors, other than the square root one (eq.1) . If we assume the VB DOS $N_v(E')$ is of the form $N_v(E') \propto E'^s$, and the CB DOS

$N_c(E')$ is of the form $N_c(E') \propto E'^p$, where the power indices s and p may take any value, then the solution of the

joint density of states integral $J(E)$ (where E is the transition energy), defined by [9] :

$$J(E) = \int N_v(E') N_c(E' + E) dE' \dots (2)$$

may take the following simple form for transitions between near band edge VB and CB extended states across the pseudo-gap E_0 [10] :

$$J(E) = J_0 (E - E_0)^{s+p+1} \dots (3)$$

J_0 is a constant which depends on the CB and VB DOS at the mobility edges. For parabolic CB and VB DOS distributions, $s=p=1/2$, then the power index $(s+p+1)$ will be equal to 2, and it can assume other values including the possibility of fractional non-integer values .

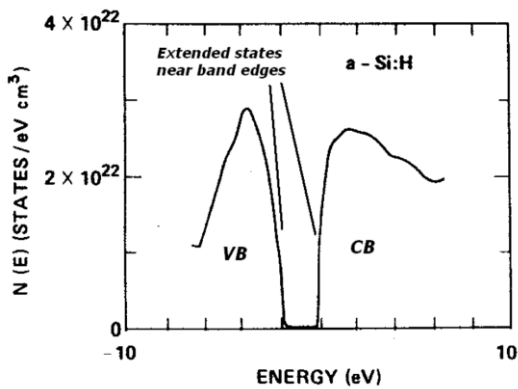


Fig.1: The experimental density of states of Jackson et al [7] with indications on the extended states near VB and CB edges of concern in this study. The

conduction band edge E_c is placed at (0) eV. The mobility gap value is ≈ 1.9 eV.

The availability of Jackson et al [7] experimental DOS results of PECVD a-Si:H shown in fig.1 together with their joint DOS ($J(E)$) results , represents an important opportunity to test the above theoretical predictions consistently.

Results and Discussion:

Fig.2 shows Jackson et al [7] valence band density of states vs. state energy data in the energy range of (2-3.6 eV). The standard Levenberg-Marquardt nonlinear least squares fitting method is used to fit the data near the band edge to a general simple power three parameter equation of the form:

$$y = p_1 (x - p_2)^{p_3} \dots (4)$$

where x is the independent variable (the energy), y is the dependent variable (the density of states), p_1, p_2 and p_3 are three fitting parameters, obviously p_3 represents the fitting parameter of our concern here to obtain the VB DOS power index (s). Good fit was obtained in the energy range (2-2.9 eV) for $p_3 = s = 0.60$ with a standard deviation of 0.012 .

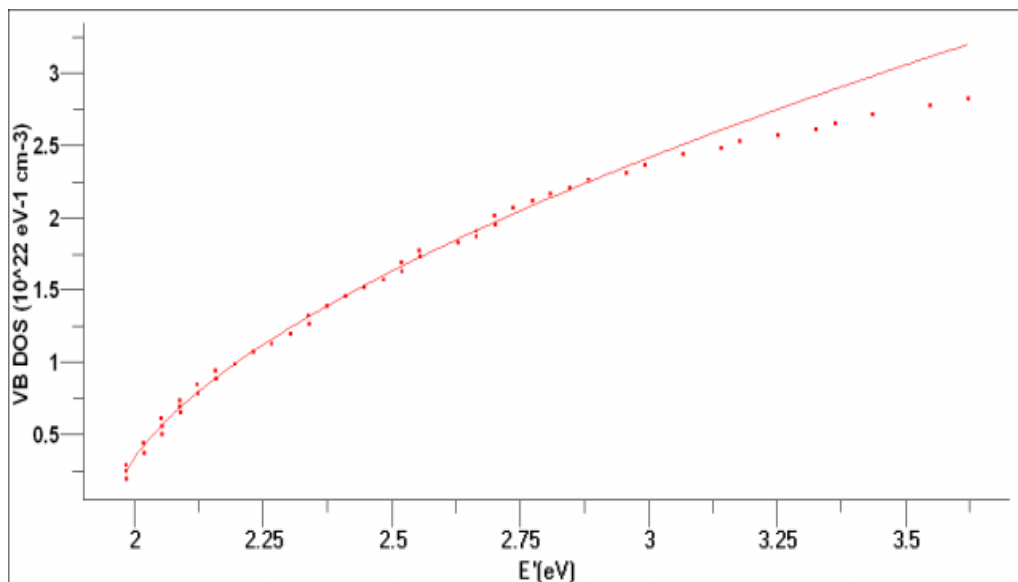


Fig.2: The experimental valence band density of states (VB DOS) of PECVD a-Si:H vs. state energy (E') (data points) fitted to eq.4 in the energy range (2-2.9 eV) (solid curve). The VB edge is at ≈ 1.9 eV, and energy increases positively towards deeper states in the valence band.

Conduction band density of states vs. state energy plot in an energy range (-0.15-1.25 eV) is shown in fig.3. Fitting to eq.4 in the energy range (-0.1-0.6 eV) gives a value of 0.55 for p_3 which is now the conduction band power index p , with a standard deviation of 0.015.

Thus the experimental a-Si:H VB and CB DOS, nonlinearly fitted to eq.4, have been seen that they significantly indicate a simple power law behavior ~ 1 eV from the valence band edge and

~ 0.6 eV from the conduction band edge. The power indices $s=0.60$ for the valence band and $p=0.55$ for the conduction band are still close to the 0.5 value noticed in crystalline semiconductors (eq.1) seemingly justifying the effective mass approach of Singh and Shimakawa [4] to a certain extent. Still, the experimental results of VB & CB fitting showed noticeable deviations from the 0.5 value, valid for three dimensional free electron gas and crystalline semiconductors.

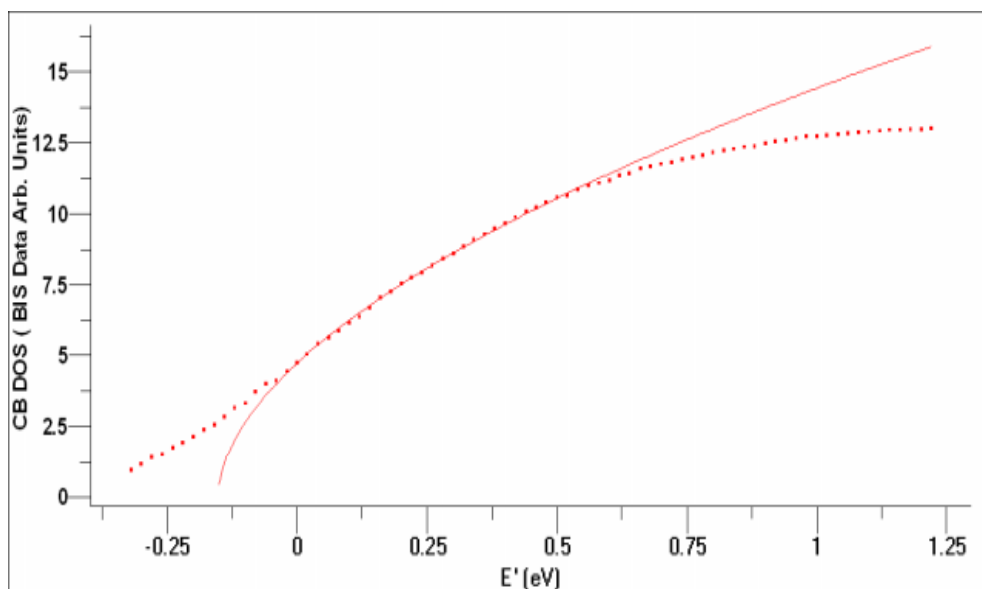


Fig.3: The experimental conduction band density of states (CB DOS) for PECVD a-Si:H {Bremsstrahlung Isochromat Spectroscopy (BIS) data [7]} vs. state energy in the energy range (-0.3-1.25 eV) (data points), fitted to eq.4 in the energy range (0-0.6 eV) (solid curve).The CB edge is at 0 eV.

There is no straightforward explanation for this deviation from the square root behavior of the near band edge DOS in the case of a-Si:H. If we adopt Singh and Shimakawa [4] proposal of DOS in fractal space, we must give a reasonable explanation. For example, these researchers in trying to explain the cubic energy dependence deduced from optical absorption data of multi-component glasses (e.g.,Ge-As-Te-Si) i.e. $s+p+1=3$ $\{s+p+1=(D_v + D_c -2)/2$, where D_v and D_c are the valence and conduction bands dimensionalities [4]}, argued that higher dimensionality

($D_v + D_c = 8$) might be related to branching or cross-linking between tellurium chains by introducing As, Ge, and Si atoms. In a-Si:H, our fitting results imply a dimensionality of ~ 3.15 ($D_v + D_c = 6.3$). There is no obvious source for branching in a-Si:H, there are no chains or layers to cross-link to substantiate the fractal hypothesis [4,11].

For the above fitting results, eq.3 for $J(E)$ predicts a power index value of $(s+p+1=2.15)$ in a wide photon energy range ($\sim 1.9-3.5$ eV) .This can be checked against $J(E)$ results of

Jackson et al [7] using eq.4 with (p_3) which is now equal to ($s+p+1$). We plotted the experimental $J(E)$ vs E data of Jackson et al [7] in the photon energy (1.87-3.3 eV) (Fig.4). Nonlinear fitting was performed to eq.4 on this photon energy range.

The optimized value for p_3 is 2.11 with standard deviation of 0.048. This result is reasonably consistent with our VB & CB DOS fitting results i.e. 2.15, thus justifying in a consistent way the simple power law assumption for the DOS distribution near the mobility edge region of PECVD a-Si:H.

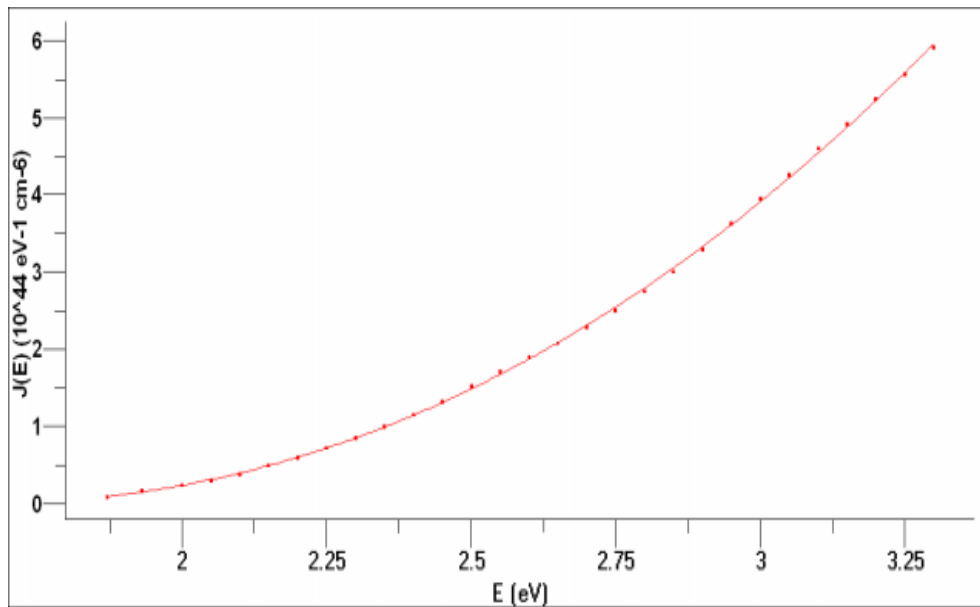


Fig.4: The experimental joint density of states $J(E)$ vs. photon energy E for PECVD a-Si:H due to Jackson et al [7] in the photon energy range (1.87-3.3 eV) (data points), fitted to eq.4 (solid curve). Jackson et al [7] determined $J(E)$ by numerically convolving VB DOS data with CB DOS data.

This modest deviation of the power index ($s+p+1=2.11$) which was found here for a-Si:H, from the crystalline three dimensional value i.e.(2) is more probably a potential fluctuations issue than a fractal dimensionality issue ,especially the valence and conduction bands originate from interacting three dimensional sp^3 tetrahedra in both amorphous silicon and crystalline silicon and there is no possibility for H-H bonding between Si tetrahedral [11], thus there is no reason to believe that the density of states of a-Si:H is in a higher dimensional fractal space other than the three dimensional space. Thus, more reasonably the potential fluctuations near the mobility edge due to slight short range disorder i.e. bond angle and bond length

variations [6], might be the reason for the deviation of the density of states distribution from the nearly free electron behavior. The square root approximation ($N(E) \propto E^{1/2}$) seems to be an acceptable one and do the job in, for example, optical properties analysis and device modeling [9]. However, this point requires more scrutiny.

In fact, the joint DOS function $\{J(E)\}$ is crucial to the analysis of optical absorption data of amorphous semiconductors, because optical absorption is proportional to $J(E)$ together with the squared transition matrix element $M.E^2$ [9].

Thus if the matrix element is constant in the appropriate photon energy range, absorption will be proportional to $J(E)$ only, then the fitting power indices

deduced from the analysis of optical absorption data are expected to be equal to $s+p+1$ including fractional values. There is a number of studies in this respect that support such kind of prediction [4,12,13]. However, more research is needed in this respect, especially one should be careful because the interpretation of optical absorption experimental data might get ambiguous by the possible dependence of the matrix element on photon energy.

Conclusions:

In conclusion, we have analyzed a-Si:H experimental results of Jackson et al [7] near the mobility edge of each of valence band and conduction band density of states. We found that VB DOS and CB DOS obey a simple power law, for some energy range beyond the mobility edge, with noticeable but modest deviation from the square root law $\{N(E') \propto E'^{1/2}\}$ found in crystalline semiconductors and usually used as an empirical model for the density of states in optical properties and device modeling of amorphous semiconductors. Analysis of experimental $J(E)$ results supported the density of states fitting results for a substantial photon energy range beyond the mobility gap value. We suggest that the analysis of optical absorption data in the high energy region of the optical absorption edge of amorphous semiconductors should be checked for such deviations from the square root behavior, with careful attention on the matrix element effect. All this might have a significant effect on the value of the optical energy gap determined from the analysis of optical absorption data.

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دراسة تحليلية لكثافة الحالات للسليكون العشوائي المهدرج قرب حافة التحركية

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الخلاصة:

تم تحليل النتائج التجريبية لكثافة الحالات للسليكون العشوائي المهدرج لجاكسون وجماعته قرب حافتي التكافؤ و التوصيل باستخدام طريقة ليفينبرك وماركوارد للموائمة غير الخطية. لقد وجد ان توزيع كثافة الحالات قرب حافتي حزمة التكافؤ والتوصيل يتواءم مع قانون قوى بسيط بمعامل قوى 0.60 لحزمة التكافؤ و 0.55 لحزمة التوصيل. هذه النتائج تشير الى انحراف معتدل لكن ملحوظ عن قانون الجذر التربيعي (معامل قوى 0.5) الذي ينطبق في اشباه الموصلات البلورية. تم تحليل بيانات جاكسون وجماعته لتكامل كثافة الحالات $J(E)$ في مدى يغطي 1.4 eV من طاقة الفوتون وقد اظهرت النتائج توائما جيدا مع قانون قوى بسيط بمعامل قوى 2.11 قريبا من ذلك المتوقع من نتائج الموائمة مع بيانات كثافة الحالات 2.15.