

variation of Conductivity and Optical Energy Gap of Pure and Doped Amorphous Silicon Thin Films Versus Temperature

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ملخص

لقد أجريت دراسة التوصيلية الكهربائية لعدس طبقات الرزازة (a-Si) و (a-Si) كالتن ودرجته
 مول، وكذلك حالة الامتصاص البصرية في مدى طول الموجة (190 - 850) نانومتر لالرس
 السليكون الالرسية (الذراتية Si-H) النقية والسطقة والسيفيرة بطريقة التبخر المرزاري.
 وتم تنظيم اعدسية السليكون بسملة نسب ذرات من موزة البوردون B والبفسور P ، وذلك
 للتحصول على اعدسية نوع p. وكانت اعمل توصيلية وحرية هول في نسب ذرات (P/B) وكلا
 السائتين : البوردون والبفسور.

وتم ايجاد كثافة الحاملات (N) من قياس الترميزية في اعدسية الرزازة منخفضة ، حيث كانت
 الكثافة $4.69 \times 10^{25} \text{ eV}^{-1} \text{ m}^{-3}$ مساوية
 وتم دراسة تأثير الظلمين (T₂) الى درجة 150 كلفن في فوالج اعمل على المرزات القوية
 والكهربائية . كما وجدنا ان حافة الامتصاص القوية ناتجة من الاتصالات غير السليكونية في اعدسية
 ذواتها مشفرة مع درجة حرارة الامساك (T₂) ونسب اظلميم لالرسية نوع p.
 وتبين نتائجنا الممثلة ان السليكون المرزاري المسفر بطريقة التبخر المرزاري يمكن تنظيمه
 بشرط السيطرة على عوامل الترسب.

Abstract

The electrical conductivity in the temperature range 300-650 K and the
 Hall mobility as well as the optical absorption edge in the wavelength range
 190-850 nm of pure and doped amorphous silicon by thermal evaporation is
 reported. Different boron and phosphorus dopant percentages have been
 diffused into silicon to obtain n-and p-type films. The highest conductivity

and Hall mobility were obtained at 3% impurity for both boron
 phosphorous as dopant materials. The density-of-state $N(E_f)$ obtained
 low conductivity measurements for 3% B-a-Si was $4.69 \times 10^{25} \text{ eV}^{-1} \text{ m}^{-3}$
 effect of vacuum annealing and different deposition temperatures up
 K on the electrical and optical properties were investigated. The
 absorption edge was found to be due to non-direct transitions in k-space
 was found to vary with substrate temperature, annealing temperature
 doping percentages for both n- and p-type films. Our experimental data
 that a-Si prepared by thermal evaporation could be doped provided the
 deposition parameters are controlled.

Introduction

Amorphous silicon (a-Si) thin films apparently dominated
 advanced technical fields because of their interesting^(1,2) appli
 optoelectronics, electronics and photovoltaic devices,^(3,5) etc. It is
 fascinating new material. However the optical and electrical prop
 a-Si as a function of annealing and depositing temperature are
 wide investigation in order to explore the possibility of new app

Indeed the pioneer works of Chittick et al,⁽⁶⁾ Le Comber a
 and Carlson and Wronski⁽⁶⁾ in hydrogenated amorphous silicon
 prepared by glow discharge decomposition of SiH₄ opened a w
 investigations in a-Si:H. On the other hand the research into a-S
 prepared by thermal evaporation has slowed down because, exper
 their properties have not yet shown stability and a low density c
 bonds, which is required to allow doping.^(6,7,9)

We have devoted some time in our laboratory to a-Si p
 thermal evaporation to see whether its properties could be contri
 to produce a low dangling bond density so that it would be an
 doping.

In the first attempt, Makadsi and Robac⁽¹¹⁾ showed
 evaporation of predoped silicon yielded doped a-Si, thus they
 in fabricating a p-n junction a-Si solar cell of 3.3% efficiency
 and Haddad⁽¹³⁾ and Haddad⁽¹⁴⁾ tried a large variety of
 temperatures (T₂), substrate temperatures. (T₁) and differ
 percentages and showed that optimum electrical and optical
 appropriate for p-n junction solar cells could be obtained w
 (hereafter all want percentage mentioned in the text are wt%)

n is used as dopant during evaporation. The charge carrier concentrations were about 7×10^{24} and 1×10^{24} m^{-3} and the conductivities were $4.5 \times 10^{-2} \Omega^{-1} m^{-1}$ and $1.2 \times 10^{-2} \Omega^{-1} cm^{-1}$ for n-type and p-type a-Si respectively. The optical energy gap (E_{opt}) was observed to increase with increasing T_s and increase with increasing T_a — the range of variation of E_{opt} was 1.39–1.78 eV with T_s in the range 303–873 K. The mobility of the charge carriers as been studied as well. It has been shown that the mobility of p-type a-Si is temperature dependent, and there was an inflection in the graphs of temperature versus mobility at about 453 K for n-type and at about 423 K for p-type a-Si.

Abbas⁽¹³⁾ followed the same procedure as Haddad⁽¹⁴⁾ but used borophorous as the dopant for n-type and boron as dopant for p-type a-Si, and obtained the highest conductivity for both n- and p-type a-Si at 2.5% purity. The E_{opt} was also increasing with increasing T_s but decreasing with increasing T_a . The interpretation for such results were as follows: on annealing up to ~ 600K (x-ray examination showed that all samples were still amorphous), the degree of amorphousness decreases. Consequently the density of localised states near the edges of the energy gap (tail states) increases hence the maximum absorption shifts toward higher energy photons and E_{opt} appears as if it is increasing. On the other hand the higher E_{opt} increases the density and coordination number with lower (depends on the value of T_s) bond-angle distortions in the As-deposited a-Si thin film structure. Indeed the higher the T_s the nearer the amorphous configuration could be to the crystalline (C) configuration, the E_{opt} of which in general smaller than E_{opt} of the a-state. Thus it may be that E_{opt} decreases as T_s increases. A decrease in E_{opt} against increasing T_s for a-Si has also been reported out by several workers.^(15,16) Our p-n junction solar cells⁽¹³⁾ gave efficiency of about 2.23% for 50 mW/cm² illumination intensity. These results were encouraging, and this has motivated the present research which a nitrogen atmosphere is provided for the evaporation process and different T_s values were investigated. Furthermore low temperature conductivity measurements down to liquid nitrogen (LN) have been investigated and the localised density of states was calculated.

Experimental

Evaporation of Films

Thin films of silicon were prepared by vacuum evaporation from graphite or boron nitride boats in a Balzer's coating unit BA 510 which

is attached BP 100 with mini-computer to control the rate of evaporation (R), power supplied to the boat, substrate temperature (T_s), this and glow discharge time (for cleaning the chamber just before deposition etc). It should be noted that we used to flush the chamber with nitrogen gas in order to have our evaporation in a nitrogen atmosphere. The oxygen contamination, however low, could not be excluded. The pressure was $\sim 10^{-7}$ torr rising to $\sim 10^{-6}$ torr during the thermal evaporation process. Glass slides were used for the substrates and were cleaned in a series of well-known steps before use. Following the procedure in our laboratory, Abbas⁽¹³⁾ found that infrared spectroscopic examination of the As-deposited a-Si thin films showed no an Si-O or Si-H bond. For p- and n-type films, boron and phosphorus were accurately weighed and evaporated on to the pure a-Si thin film molybdenum boat. During this evaporation the temperature of the boat was kept well above 130°C for about 1 hour and this was to ensure homogeneous diffusion of the dopants. It may be worth mentioning the evaporation of both Si and dopants was carried out without the vacuum.

A radiant heater is incorporated into the bell jar assembly for baking out the system and improving the final vacuum, and substrate heating as well as for annealing treatments. The temperature is controlled automatically from outside. The annealing was 30 minutes for all the films.

Electrical and Optical Measurements

For electrical and Hall effect measurements, Al and Ag electrical ohmic contacts and were deposited on to the substrates prior to depositing the silicon films. Substrate temperature ranging from R.T. up to 473 K were used. At $T_s \leq 473$ K it was better to evaporate a-Si films directly on the electrodes. For the electrical measurements, a Kier digital electrometer and Nanovoltmeter 190 were used. The measurements of the fundamental optical absorption edge were taken at room temperature using a Pye-Unicam UV/visible SP 8-200 spectrophotometer.

Although the thicknesses of films were controlled by a microcomputer they were also checked and calibrated with a multi-beam interferometer using Fizeau fringes of equal thickness. X-ray investigation using a Phillips X-ray diffractometer have been carried out for the films that were annealed or prepared at high temperatures to ascertain the amorphous nature of the structure.

Results and Discussion

Electrical Conduction

Figure 1 shows the temperature dependence of dc conductivity σ of pure a-Si thin films and it is in accordance with Stuke's equation⁽²⁰⁾

$$\sigma = \sigma_0 \exp(-E_a/KT) \quad (1)$$

where σ_0 constant, E_a is the activation energy of conduction, k is Boltzmann's constant and T is absolute temperature. This film was deposited at 313 K and annealed at 650 K, and the thickness of the film was 500 nm. We should point out that the graph of Fig. 1 and all the similar graphs in this paper have been plotted according to the obtained data without convoluting the curves, i.e. we did not subtract the low temperature activation energy curve from the points obtained at higher temperatures. This is because the aim of our work is to show how a-Si thin films behave through out the working temperature range. It can be seen from this graph that it is characterised by three stages of conductivity through out the heating temperature range 300–600 K. We believe the three stages of conductivity are not necessarily due to impurities, but most likely due to the fact that the pre-exponential factor σ_0 was not constant throughout our working range of temperature because σ_0 depends on the fluctuations in the potential wells arising from the lack of long range order and because not all the coordination numbers are saturated. Fritzsche⁽²¹⁾ in 1971 stated that σ_0 is strongly influenced by the temperature dependence of the band-edge and the activation energy. Very recently Stuke⁽²²⁾ pointed out that the pre-exponential factor σ_0 is important and unless the defect densities are high, it is a function of the shift in Fermi level on annealing for both evaporated and hydrogenated a-Si. Three different mechanisms of conduction are not unfamiliar in amorphous materials and have been discussed in details by Mott and Davis.⁽²³⁾ The first stage is within the temperature range 300–350 K with E_{a1} equals 0.496 eV the mechanism of this stage may be due to carrier transport to localised states near the band edges. In the temperature range 350–450 K, E_{a2} is 0.563 eV, which may be due to carriers excited into the localised tail states at the edge of the valence band, since our experimental results showed that the charge carriers of our pure a-Si thin films are holes. The third stage, where E_{a3} is 0.633 eV, the conduction is considered to be due to carriers excited into non-localised (extended) states beyond the mobility edge. We speculate from such conduction mechanisms and the values of E_a that there is density of states at the Fermi level extending at both sides of it for about 0.137 eV, similar to what has been suggested by Davis and Mott.⁽²³⁾

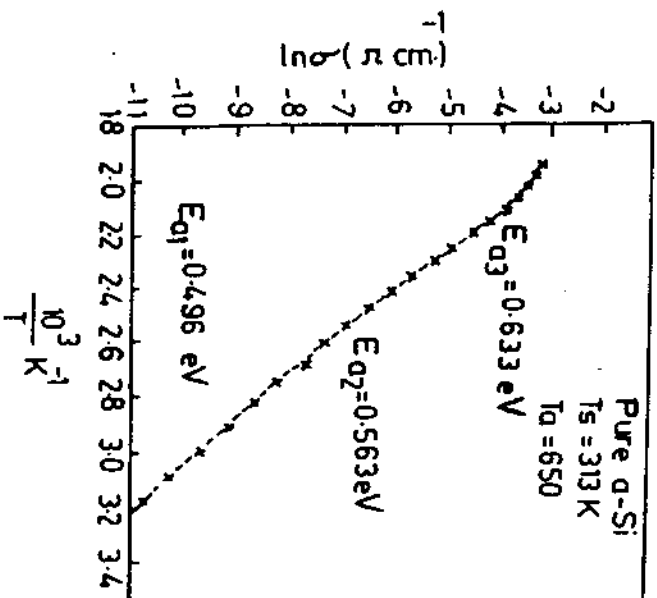


Fig. 1. The temperature dependence of the D.C. conductivity of pure a-silicon thin films deposited at 313 K and annealed at 650 K.

In Fig. 2 we observe also three conduction mechanisms but a-Si doped with boron, and with lower activation energies, namely 0.4 and 0.52 eV. Obviously the Fermi level has moved towards the band on doping by about 0.26 eV, which is the difference between first stages of E_a in Figs. 1 and 2. For the second and third differences between E_a in Figs. 1 and 2 are smaller, namely 0.163 eV respectively. It becomes clear that due to the shift of Fermi doping, E_{a2} and E_{a3} of Fig. 2 could be attributed to deeper trap charge carriers at the top and extended states of the valence respectively. It should be pointed out that the decreasing of E_a a-Si as compared with pure a-Si is a result of decreasing of vacant dangling bonds by the dopant and the formation of an impurity the gap and the associated shift in Fermi level. Although in simple a-Si:H each active donor or acceptor site introduces additional bonds, the doping mechanism in unhydrogenated a-Si may be complex, simply because thermally evaporated a-Si thin film dangling bonds and defects as compared with a-Si:H. The percentages in our work are high compared with the conventional

percentages, ⁽²⁹⁾ thus the assumption here is that most of the impurity atoms may find their way to fill the vacant sites and voids resulting in a considerable reduction in the number of the dangling bonds. It becomes necessary to attribute two roles to the impurity atoms, first annealing out dangling bonds and defects and secondly introducing free charges (as in the conventional doping mechanism) leaving behind each free charge a dangling bond. The resultant is doped a-Si with fewer dangling bonds. More evidence for doping complexes in a-Si is in the work of Spear et al., ⁽²⁹⁾ where they argued that in compensated a-Si the dangling bond density may remain constant. We should also state that our measurements were reproducible to an accepted experimental level.

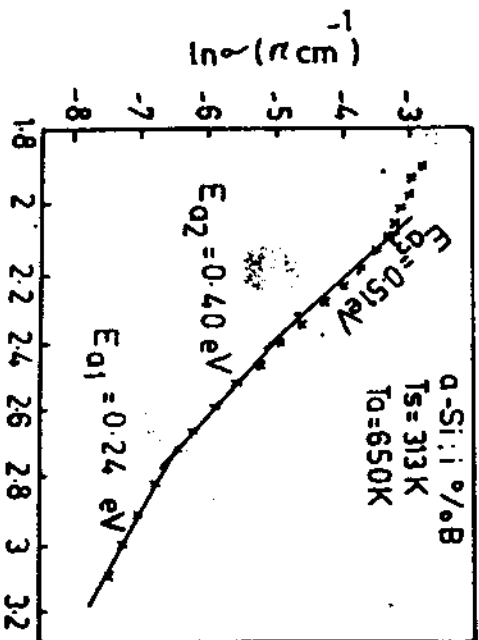


Fig. 2. The D.C. conductivity versus reciprocal temperature of a-Si doped with 1% boron deposited at $T_s = 313$ K and $T_d = 650$ K.

The n-type a-Si is of similar behaviour, as we observe in Fig. 3 for a sample prepared at T_s equals 423 K and annealed at two temperatures, 38 and 650 K. The activation energy is much lower than the pure a-Si. This may be due to its high doping density (2.5% p) and high T_s .

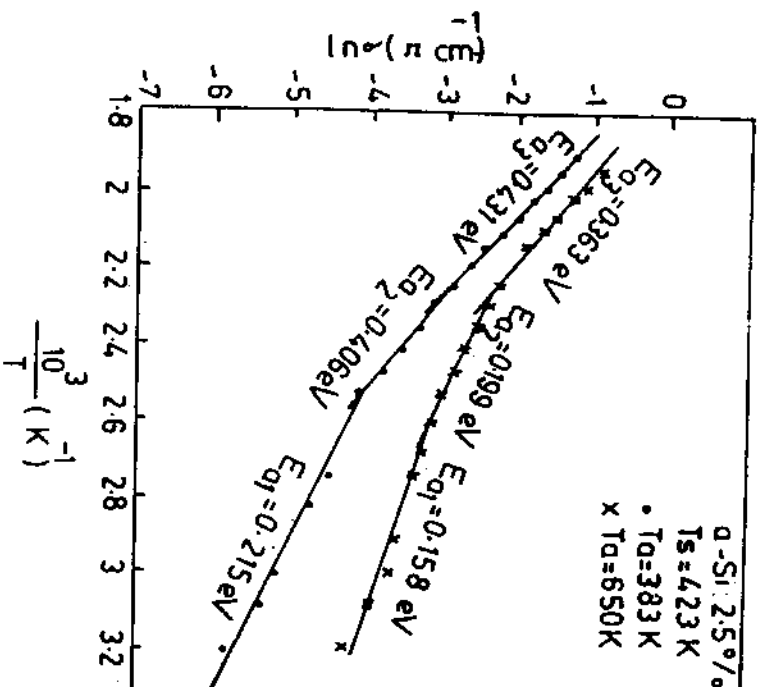


Fig. 3. Showing the effect of annealing temperature on the $\ln \sigma T^{-1}$ plot for a-Si phosphorus deposited at $T_s = 423$ K.

Figs. 4 and 5 and Figs. 6 and 7 show similar graphs for pure a-Si samples prepared at different T_s , but at T_d equals 650 K of which are listed in Table 1. We see that E_a for pure a-Si did considerably in the second and first stages but it did for the temperature quite far from room temperature. This implies the of the thermal history of the a-state. The interesting results p-type a-Si, doped with 1% B, where we observe a continuous E_a with increasing T_s for all three stages. This, we believe, is following: in addition to the fact that some of the impurity incorporated the vacancies, annealing out dangling bonds, the T_s the less dense will be the vacancies that need compensation atoms, thus leading to lower E_a values and higher conductivity the low value of E_a and E_g in Fig. 2 may be due to a hopping process. It is also the standard from Fig. 2

ses by about two orders of magnitude on doping. If we compare the activity values with those obtained by Abbas⁽¹⁵⁾ and Makadsi et al.,⁽²⁷⁾ the present results are in general higher by about two orders of magnitude. This we believe, is due to the role of the difference in the al gases in each case. In the present research it was nitrogen while previous works^(14,27) they were atmospheric gases. Thus it is obvious the presence of oxygen in the residual gases decreases the conductivity. Results are in agreement with the work of Bahl and Bhagat⁽²⁸⁾ who pointed out that the existence of oxygen has lowered the conductivity of films. On the other hand, comparing the present values of conductivity those obtained by Haddad⁽¹⁴⁾ and Makadsi and Haddad⁽¹⁵⁾ who used As as dopants, while we used B and P, we see that our conductivity is by about one order of magnitude, although they have atmospheric gases during deposition. As the other deposition parameters were the same, we can only say at this stage that the difference in conductivity be attributed to the kind of impurity materials. It should also be pointed out that conductivity of our samples is far higher than the conductivity of hydrogenated a-Si, especially pure a-Si;⁽²⁵⁾ the reason could be attributed to the role of hydrogen in compensating the dangling bonds saturating the covalent bonds.

D.C. conductivity vs. reciprocal temperature of pure a-Si thin film prepared at $T_s = 523$ K and $T_a = 650$ K.

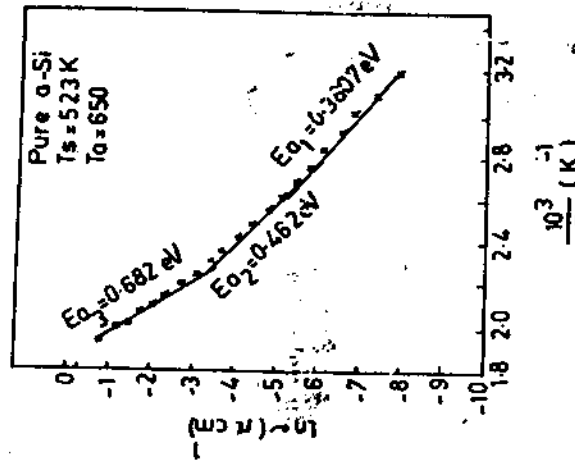


Fig. 6. The D.C. conductivity vs. reciprocal temperature of pure a-Si thin film prepared at $T_s = 523$ K and $T_a = 650$ K.

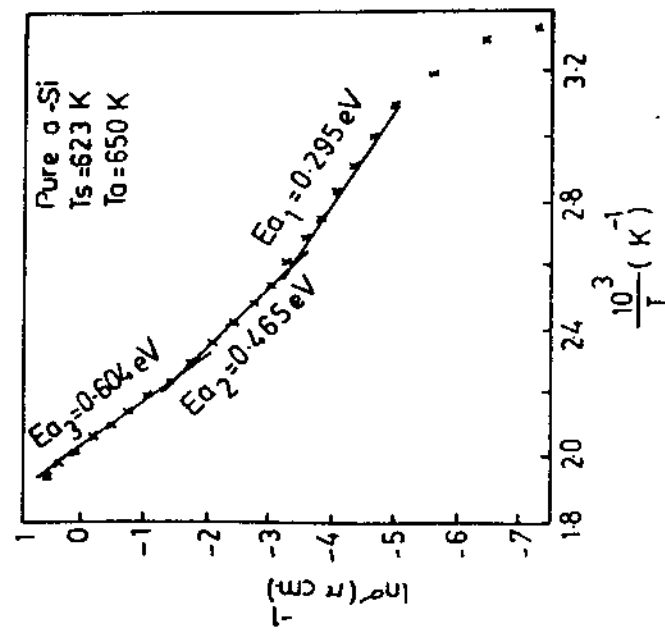


Fig. 5. The D.C. conductivity vs. reciprocal temperature of pure a-Si thin film prepared at $T_s = 623$ K and $T_a = 650$ K.

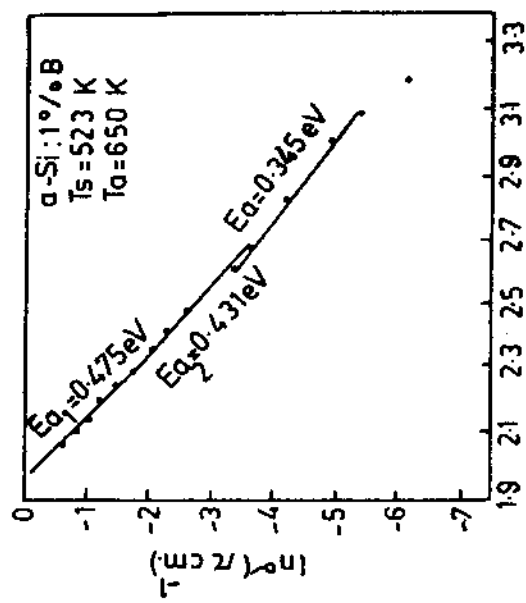
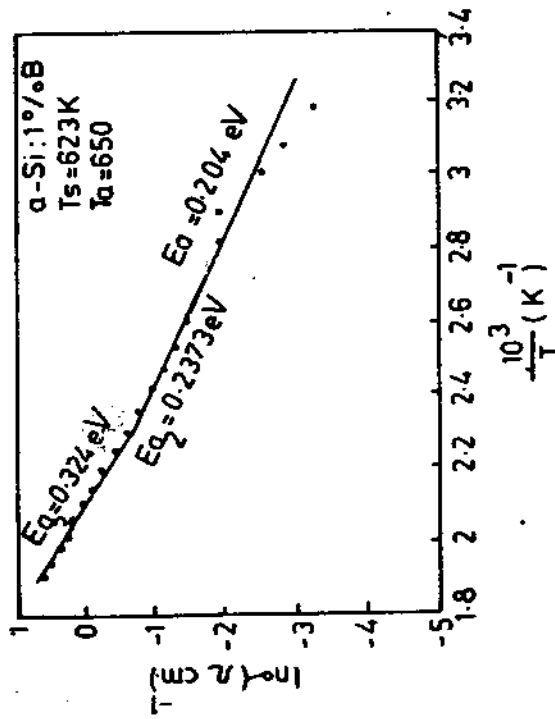


Fig. 6. The D.C. conductivity vs. reciprocal temperature of p-type a-Si thin film prepared at $T_s = 523$ K and $T_a = 650$ K.



D.C. conductivity vs. reciprocal temperature of p-type a-Si thin film prepared at $T_s = 623$ K and $T_0 = 650$ K.

1: Activation energies (eV) of a-Si films thickness (t) ($t = 550 \pm 10$ nm) prepared at different T_s and annealed at $T_0 = 650$ K.

	Pure					1% B				
	E_{g3}	E_{g2}	E_{g1}	E_{g3}	E_{g2}	E_{g1}	E_{g3}	E_{g2}	E_{g1}	
	0.633	0.563	0.496	0.510	0.400	0.240				
	0.682	0.462	0.381	0.475	0.431	0.345				
	0.604	0.465	0.295	0.324	0.237	0.204				

order to understand the conduction mechanism at low temperature the density of states in the gap, $\ln \sigma$ is plotted against $T^{-1/4}$, as shown in Fig. 8 according to the expression:

$$T_0 = \frac{3 \alpha^3}{k N(E_F)}$$

where T_0 is obtained from the slope of the $\ln \sigma$ vs. $T^{-1/4}$ plot and α' is inverse decrease of the length of localised wave functions at the site.

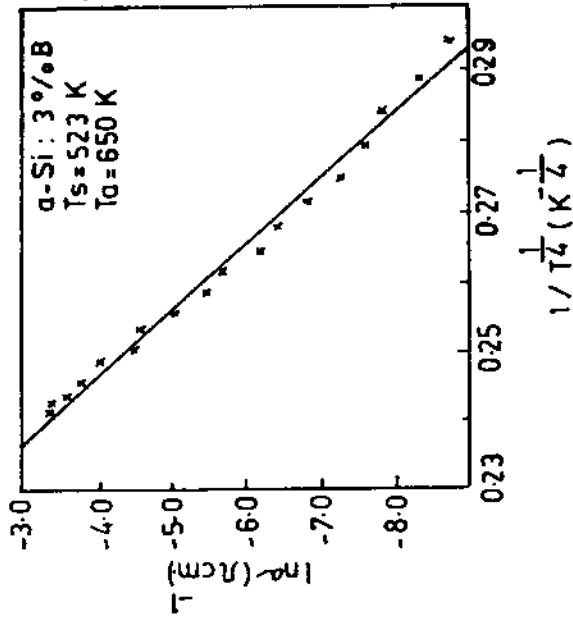


Fig. 8. Showing Mott's relation ($\ln \sigma$ vs. $T^{-1/4}$), plot of 3% boron doped a-Si thin film prepared at $T_s = 523$ K and $T_0 = 650$ K.

$$\sigma = \sigma_0 \exp \left\{ - \left(\frac{T_0}{T} \right)^{1/4} \right\} \quad (2)$$

or

$$\ln \sigma = \ln \sigma_0 - \left(\frac{T_0}{T} \right)^{1/4} \quad (3)$$

which characterises hopping conduction in localised states at the Fermi level or at impurity levels. The linear fit reveals that the conduction is to hopping between localised states. Since the hopping between local states occurs at very low temperature, the density of states at the Fermi level $N(E_F)$ is calculated using the expression⁽²³⁾

Assuming that $(\alpha')^{-1} = 10^8$ angstroms for the region where Mott's relation ($\ln \sigma$ proportional to $T_s^{-1/4}$) is valid, the density of states at the Fermi level $N(E_F)$ can be evaluated. Fig. 8 presents such data for 3% B-doped a-Si film prepared at $T_s = 523$ K and $T_s = 650$ K with $N(E_F) = 4.69 \times 10^{23} \text{ eV}^{-1} \text{ m}^{-3}$. This value, however, is within the values obtained for hydrogenated a-Si films.⁽²³⁾

We now turn our attention to the variation of conductivity of a-Si films vs. B or P as impurities. The results are presented in Figs. 9 and 10 respectively. The highest conductivities for both n- and p-type are obtained at 3% impurities. From the figures, the conductivity of a-Si:B at $T_s = 623$ K was $85 \times 10^{-4} \Omega^{-1} \text{ cm}^{-1}$ which is higher than for a-Si:P, i.e. $16.5 \times 10^{-4} \Omega^{-1} \text{ cm}^{-1}$ at the same T_s .

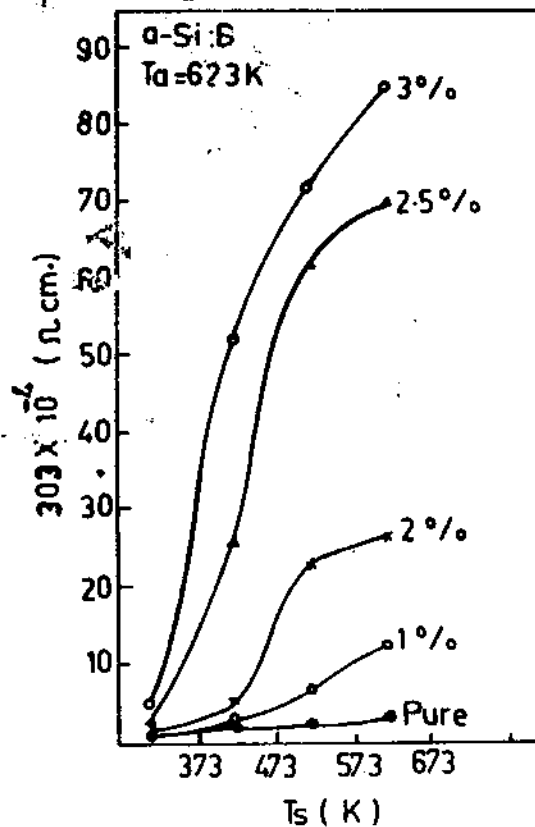


Fig. 9. The variation of conductivity vs. B% as impurities for a-Si thin films prepared at different substrate temperatures and annealed at 623 K.

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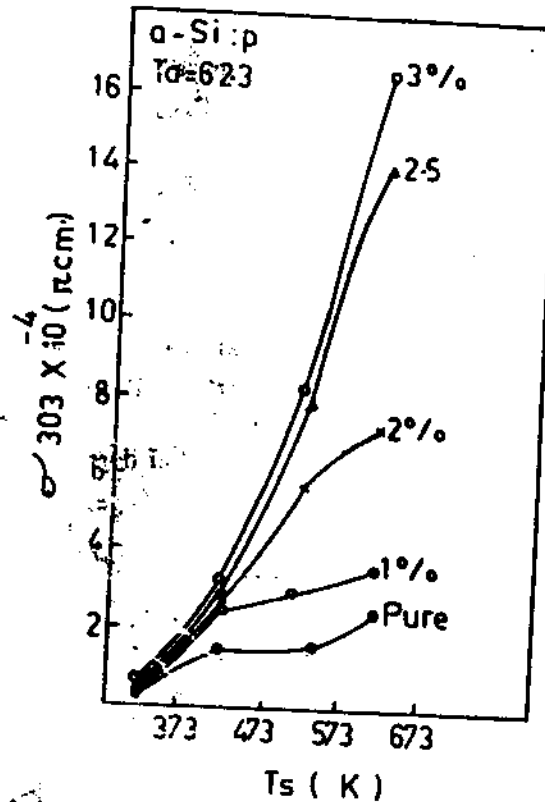


Fig. 10. The variation of conductivity vs. P% as impurities for a-Si thin films prepared at different substrate temperatures and annealed at 623 K.

We believe that the impurities at this level play two roles: first occupying the vacancies (as mentioned above) and secondly being incorporated substitutionally into the random network. At higher percentages the dopant atoms distort the presumably nearly perfect random network structure, which creates a new localisation to become scattering centres. Those results agree qualitatively with those of the As and In doped a-Si films published elsewhere.⁽¹³⁾

Hall Effect Measurements

Hall effect studies are standard tools in understanding the transport properties in conducting materials where the mean free path is sufficiently long; in the case of amorphous semiconductors the mean free path appears to be comparable to the interatomic distances.

The Hall mobility could be a guide to the transport mechanism at the mobility edge or between the localised states.⁽²⁵⁾ Indeed in some amorphous semiconductors the Hall coefficient is found to be negative for both n- and p-type materials, in contrast to thermopower, which shows a positive sign for p-type.^(25,29) However this is not universal, and as Nagel⁽³⁰⁾ pointed out, Hall coefficient measurements have been made on a limited number of amorphous semiconductors due to the high resistivities and the low carrier mobilities. Mott and Davis⁽²⁵⁾ stated that a reverse of sign of Hall coefficient takes place for materials of odd-site configuration while for even-site configuration amorphous semiconductors the coefficient has a normal sign. Thus if the resistivity of amorphous material is not too high on one hand and it has even-site configuration on the other, as is the case with a-Si, the reverse in sign may not occur. However in our works we were very cautious in performing this experiment, and the results were normal sign. In a previous work Makadsi and Hadda⁽¹³⁾ prepared doped a-Si thin films using methods similar to this work, and examined them by Hall experiment. The As-doped a-Si was n-type and the In-doped a-Si was p-type. The confirmation for that was a p-n junction solar cell in accordance to Hall effect measurements.

In this experiment a magnetic field of 0.257 T was applied perpendicular to the current flow and the resulting deflection of the current was observed. The measured quantity was R_H , the Hall coefficient. The Hall mobility μ_H is

$$\mu_H = \sigma R_H \quad (5)$$

Physically the Hall mobility is proportional to the transverse current induced by the Lorentz force.⁽³¹⁾ For free electrons $\mu_H = \mu_c$ where μ_c is the conduction mobility. We have used the Hall effect to investigate the type of carriers as well as calculating its concentration at different substrate temperatures. Pure a-Si thin films are p-type. Doped a-Si films with B are p-type and with P are n-type. By varying the dopant percentages different values of charge carrier concentrations were obtained and are listed in Table 2. From Table 2 we deduce that increasing T_s leads to increasing carrier concentrations. It is not quite as easy to find out the correlation between the change in various defect densities in a-Si with T_s and the charge carrier concentration. We refer to the recent paper of Stuke,⁽²²⁾ who stated that more work is needed to clarify the complicated correlation

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between the density of carriers in the band tails, the dangling band density and the effective donor/acceptor concentration.

However, we suggest the following explanation: the increase in T_s is accompanied by a reduction in the random fields arising from the dangling bonds, voids and bond-angle distortions.⁽²²⁾ Thus the number of trapping centres of the charge carriers decreases. This may lead directly or indirectly to an increase in carrier concentrations. Or alternatively, at least for pure a-Si, we can assume that the electronic density of states for the dangling bond defects, in accordance to Mott's⁽²³⁾ band structure model, consist of two bands of localised states in the gap, donor states (D^+) and acceptor states (D^-). If on increasing T_s the D^+ states decrease more than D^- states then the hole concentration appears, indirectly, as if it were increasing and vice versa.

Table 2: Some values of carrier concentration for pure and doped a-Si films ($t = 550 \pm 10$ nm) deposited at different T_s .

T_s (K)	Pure	%B	%P	$N(m^{-3})$
313	-	-	-	3.59×10^{22}
423	-	-	-	6.64×10^{23}
623	-	-	-	2.72×10^{24}
313	-	1	-	3.69×10^{23}
423	-	2	-	8.86×10^{22}
623	-	2	-	2.55×10^{24}
313	-	-	1	4.85×10^{20}
423	-	-	1	1.51×10^{21}
623	-	-	2	3.55×10^{22}

Several measurements have been carried out of Hall mobility versus temperature for different impurity percentages. These measurements were for sample thicknesses of 550 ± 10 nm deposited at a deposition rate of ~ 3.0 nm sec^{-1} and at $T_s \sim 350$ K. It could be seen from this set of graphs, Fig. 11, that the mobility for both p- and n-type is increasing with impurity

percentage but in general our results indicate that the Hall mobility of holes is higher than that of electrons. Such findings disagree with previous results;^(13,14) this may be due to the anomalous nature of the Hall effect experimental data for amorphous semiconductors.^(23,30) More reliable confirmation for the results is in progress using a thermopower experiment.

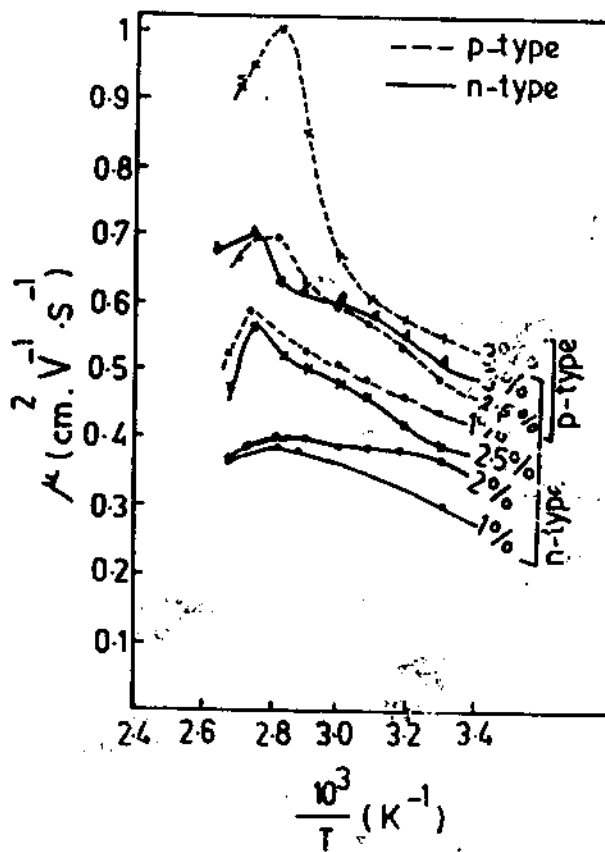


Fig. 11. The Hall mobility vs. reciprocal temperature for different impurity percentages of n- and p-type a-Si films prepared at $T_s = 350$ K.

Optical Absorption Edge

For many amorphous semiconductors an exponential dependence of absorption coefficient $\alpha(\omega)$ at angular frequency of radiation ω on photon energy $\hbar\omega$ is found to hold over several decades and may take^(23,32) the form:

$$\alpha(\omega) = \alpha_0 \exp \frac{\hbar\omega}{E_g} \quad (6)$$

Hall mobility of
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where α_0 is a constant, \hbar is the reduced Planck constant and E_c is an energy which is sometimes interpreted as the width of the tail of localised states in the normally forbidden band gap, which are associated with the amorphous nature of the materials. A relation (equation 6) was first proposed by Urbach⁽³³⁾ to describe the absorption edge in alkali halide crystals at high absorption levels when $\alpha(\omega) \geq 10^4 \text{ cm}^{-1}$. This relation has also been found to hold for many amorphous or glassy materials^(34,35) at the lower range of the absorption edge, while at higher absorption a relationship proposed by Tauc et al.⁽³⁶⁾ and derived in more general form by Davis and Mott⁽²⁴⁾ is found to describe the experimental data:

$$\alpha(\omega) = \frac{B}{\hbar \omega} (\hbar \omega - E_{opt})^r, \quad (7)$$

and to yield values of the optical energy gap E_{opt} where B is a constant and r is an index which can assume values of 1, 2, 3, 1/2 and 3/2 depending on the nature of the electronic transitions responsible for the absorption.

Equation 7 with $r = 2$ is found to represent our experimental results and this case applies to non-direct transitions in a-Si when the electron wave vector k is no longer a good quantum number.

Figures 12 and 13 show the dependence of the room temperature (303 K) optical absorption edge on T_s for 2.5% a-Si:B; a-Si:P from which we observe an Urbach spectrum in accordance with what we may call the spectral Urbach rule arising from the effect of T_s above 313 K. The values of E_c obtained from the exponential part of the curves are found within the expected range (0.05–0.08 eV);⁽³⁷⁾ our E_c values were such that $0.05 < 0.07 \text{ eV}$; E_c does not vary significantly with dopants. The plausible interpretation for the exponential absorption part (linear) of the curves is based on the electronic transitions between localised states in the band-edge tails.^(23,38) Obviously Tauc's model,⁽³⁹⁾ which is based on the assumption that the density of states in the band-edge tails falls off exponentially with energy is highly unlikely in our results, where we observe the linear part of the curves is valid for $\alpha \geq 10^3 \text{ cm}^{-1}$ below which the distribution of states is no longer exponential. Similar results have been pointed out by Mott and Davis,⁽²³⁾ who mentioned that the exponential behaviour is up to $\alpha = 10^2 \text{ cm}^{-1}$ in some materials and upto 10^4 cm^{-1} in others. This means the band-edge tail absorption does not fade exponentially to zero absorption but there are fairly discrete defect states, which are responsible for the

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weak absorption region. The absorption behaviour of our doped a-Si films is not unfamiliar in a-Si thin films. Spear et al.,⁽²⁶⁾ studying the hopping mobility in doped a-Si, deduced that such a transport mechanism could not be explained on a purely exponential tail states distribution, but rather on long-range fluctuations which give rise to an r.m.s. fluctuation amplitude of 0.1 eV.

A convincing interpretation for such band-edge tailing is a lack of long-range order, which gives rise to static spatial fluctuations in the potential in such a way that the state tailing density does not fall off exponentially to zero absorption but rather to a fluctuating weak absorption region, the width of which decreases from 0.2 to 1.6 eV as T_d goes up from 313 to 423 K; but the decrease becomes small when T_d increased to 623 K (see Figs. 12 and 13).

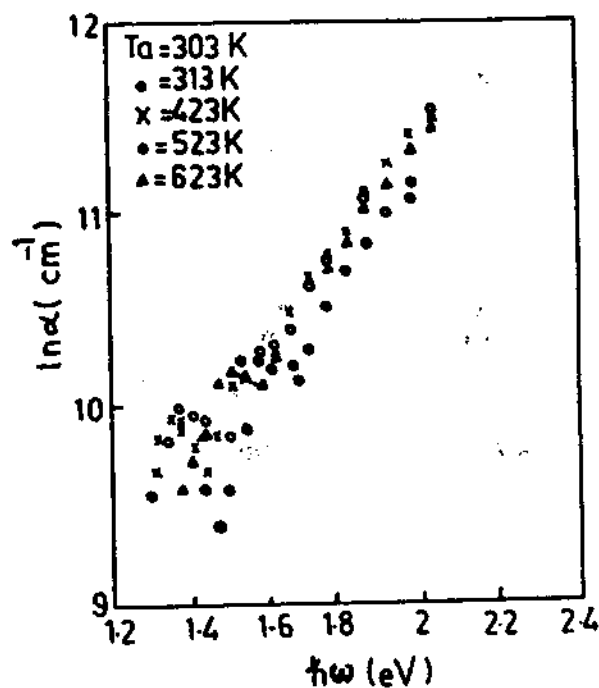


Fig. 12. The Urbach behaviour of the optical absorption data for a-Si:2.5% B films prepared at different T_d and $T_a = 303$ K.

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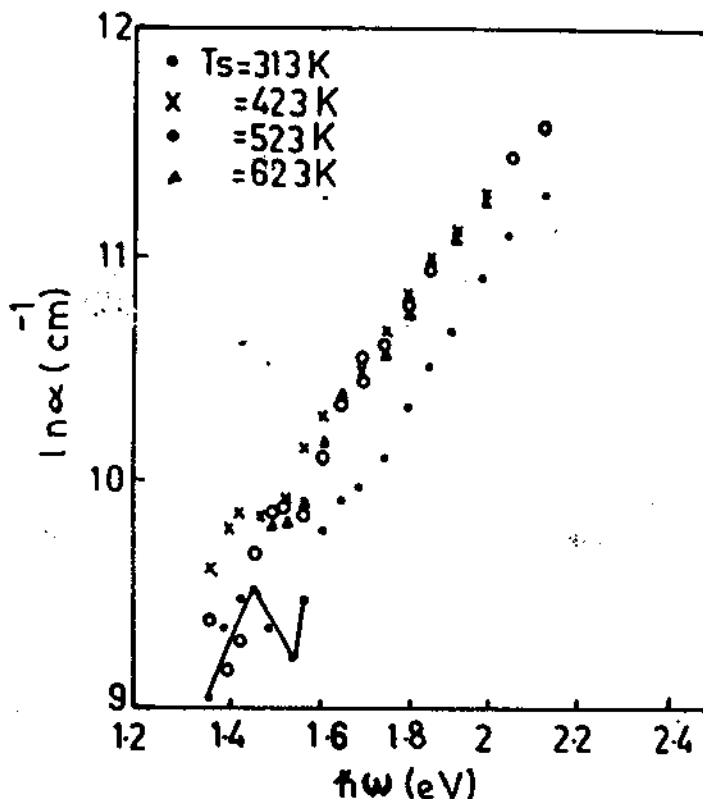


Fig. 13. The Urbach behaviour of the optical absorption $\ln \alpha^{-1}$ for a-Si:2.5% P films prepared at different T_s and $T_d = 303$ K.

The significance of the exponential absorption edge in Figs. 12 and 13 (dependence on T_s) is the displacement towards lower photon energy absorption as T_s increases above room temperature, although not systematic. Thermally evaporated doped a-Si is associated with narrowing E_{opt} , as we can see in figures 14 and 15, which exhibit the variation of $\alpha \hbar \omega^{1/2}$ vs. $\hbar \omega$, in accordance with eq. 7 for a-Si: 2.5% B and a-Si:2.5% P films respectively, deposited at $T_s = 313, 423,$ and 523 K. Obviously the extrapolation of the linear portion to $(\alpha \hbar \omega)^{1/2} = 0$ yields values of E_{opt} .

These results contradict many similar studies; for example, Mass, Flynn and Bauer,⁽⁴⁰⁾ Hasegawa, Yazaki and Shimizu⁽⁴¹⁾ and Mott and Davis⁽²³⁾ and the references cited there. However many studies are in agreement with our results; for example, Makadsi,⁽⁴⁶⁾ Demichelis et al.⁽¹⁷⁾ and Takano et al.⁽¹⁸⁾

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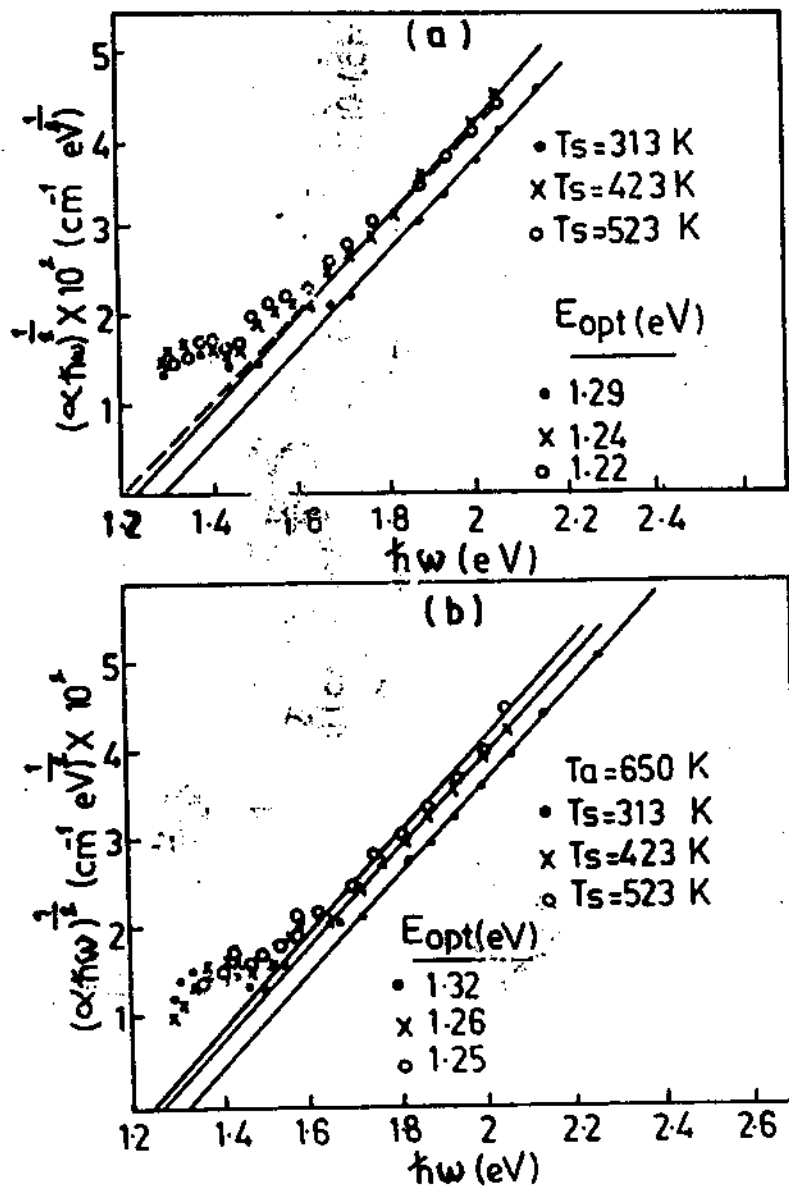


Fig. 14. The Variation of $(\alpha \hbar \omega)^{1/2}$ with $\hbar \omega$ in accordance with the relation of Tauc and of Davis and Mott for n-Si:2.5% B prepared at different T_s :
 (a) Virgin films .
 (b) Annealed films at 650 K.

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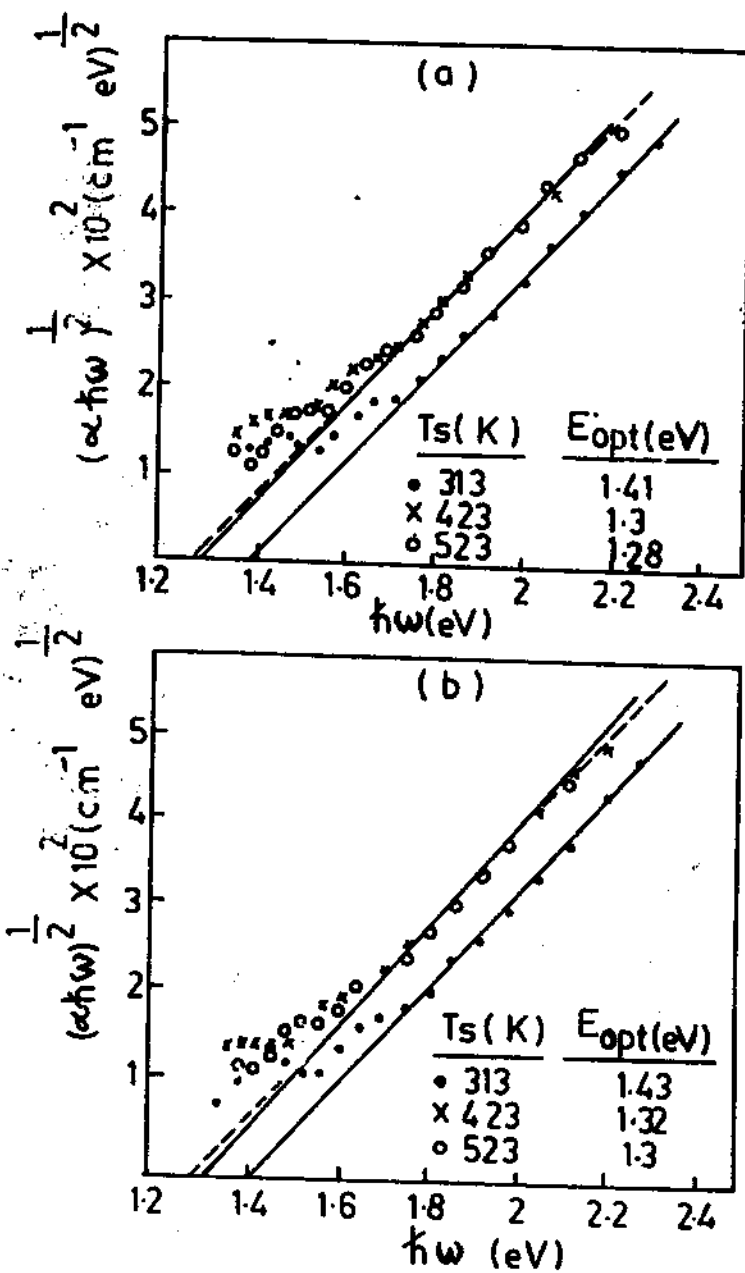


Fig. 15. The Variation of $(\alpha \hbar \omega)^{1/2}$ with $\hbar \omega$ in accordance with the relation of Tauc and of Davis and Mott for n-Si:2.5% P prepared at different T_s :
 (a) Virgin films.
 (b) Annealed films at 650 K.

In fact, there are abundant inconsistencies in the literature concerning the conductivity and optical absorption edge, which is still an outstanding important problem.⁽²²⁾ Thus it would be very useful to review some selected works.

Freeman and Paul⁽⁴²⁾ prepared a-Si:H by rf sputtering at different T_s (298, 427, 523 and 723 K.) They observed a shift in the absorption edge in the opposite way. A significant shift to larger photon energies occurred between $T_s = 298$ K and 473 K, but the edge shifted continuously back to lower energies when T_s further increased to 523 and 723 K. Esquivias et al.⁽⁴³⁾ reported that the absorption coefficient of evaporated a-Si film decreases as T_s increases, saturating towards a curve of higher values than those of crystalline Si. However, our optical results on Urbach edges go to higher values of absorption coefficient as T_s is increased, hence such results are in disagreement with them.

Esquivias et al.⁽⁴³⁾ attributed the changes of optical properties to the increasing density of microcrystallites in the films as T_s increases.

Brodsky et al.⁽⁴⁴⁾ attempted earlier to discuss low conduction and the high annealing process of the optical absorption in a-Si films in terms of the existence of submicrocrystallites in the amorphous structure; the transfer of carriers will be enhanced between the submicrocrystallites by the dangling bonds. The sizes of these submicrocrystallites are in the range 10 to 15 angstroms and their size do not increase beyond 15 angstroms upon annealing.

The same authors state that the optical absorption measurements depend on the surface effects, mostly strains, leading to tailing of these large numbers of submicroscopic surfaces and resulting in a decrease of about 0.4 eV in the onset of the observed optical absorption as compared with other studies.⁽⁴⁵⁾ Upon annealing the strains decrease, leading to a shift of the tail to higher energies. There are many references in the literature (see for example Makadsi⁽⁴⁶⁾ and the references cited there) to the amorphous structure being a random network model of completely bonded atoms, in the ideal state, with no single crystalline unit cell. On the other hand, x-ray analysis of our samples in the range of the temperature under study revealed no any single aggregate of atoms. Thus we exclude in our analysis the submicrocrystallite structure of a-Si.

The work of Cody et al.⁽⁴⁷⁾ on the optical absorption edge of a-Si:H is a good example concerning the contradictions in the results coming from different laboratories. They showed that the absorption edge shifts towards a higher absorption constant as T_a increases. These data are quite inconsistent with the concept that annealing out the dangling bonds on increasing the temperature⁽²²⁾ results in increasing E_{opt} .⁽²³⁾ Their interpretation is based on a model assuming a homogeneous distribution of topological disorder. Abadou et al.⁽⁴⁸⁾ prepared hydrogenated Si films by glow discharge in amorphous and microcrystalline states. They observed that E_{opt} decrease continuously and nearly linearly with increasing T_a throughout the amorphous and microcrystalline states.

Hence there are no consensual experimental data concerning the effect of T_a or T_d on the E_{opt} of a-Si. We should therefore like to suggest an alternative explanation for the decrease of E_{opt} on T_a and to show later on that E_{opt} increases with T_a .

The a-structure is characterised by variation in bond lengths and angles and the existence of dangling bonds, both of which decrease as T_a or T_d increases.^(22,23) Thus we suggest that the "degree of amorphicity" depends on T_a or/and T_d and preparation conditions.

Usually the electron diffraction pattern of the As deposited a-Si at room temperature has a structure which exhibits broad rings (two or three). We say it has a "high degree of amorphicity". These rings become narrower as either T_a or T_d increases. In the following we will explain the role of T_a and later the effect of T_d because their effects in our results are different.

In fact at some elevated T_a ($\sim 700^\circ\text{C}$)⁽⁴⁷⁾, the structure of Si will be polycrystalline. One can conclude that a continuous increase in T_a will lead to a continuous decrease in dangling bonds and bond-angle distortion. This implies the deposited atoms of the film will have more energy to sit in sites of less strain and defects (depends on T_a), leading to a change in the coupling energy between the allowed energy levels of the conduction and valence bands. Presumably the atomic sites are homogeneously distributed and the sites approach saturation (fully occupied) as T_a approaches the crystallisation T_c ($\sim 700^\circ\text{C}$) and consequently higher coordination density.

Thus we could speak of a continuous lowering in the degree of amorphicity as T_a increases, and consequently a continuous decrease in

E_{opt} and tail state density. In fact E_{opt} decreases and tends asymptotically towards some limiting value. At this elevated T_a , the Si film's state will be crystalline which we call of "zero degree of amorphicity". The E_{opt} of the c-Si is 1.1 eV or a bit more if it is polycrystalline.

Support for our argument comes from the work of Loveland et al.⁽⁴⁹⁾ They prepared 13 specimens of a-Si thin films by glow discharge at different T_a and tabled their E_{opt} values, from which one concludes in general E_{opt} decreases with increasing T_a . Very recently Agarwal et al.⁽⁵⁰⁾ pointed out that the energy band gap of most amorphous semiconductors decreases with increasing temperature and hence the associated absorption edge shift.

In Figs. 14b and 15b we observe the absorption behaviour for the specimens of Figs. 14a and 15a after annealing at 650 K. The indicant values of E_{opt} in Figs. 14a,b and 15a,b imply that a shift towards higher E_{opt} occurred on annealing.

Increasing E_{opt} on annealing is apparently universal.⁽²³⁾ However there are some data that do not support this new trend.⁽⁵¹⁾ It is shown that E_{opt} of a-As₂Se₃ decreases on annealing and, as we have mentioned before, recent data of Cody et al.⁽⁴⁷⁾ showed that the absorption constant increases as T_a increases, associated with a decrease in E_{opt} .

Thus we feel ourselves obliged to deduce that there is still neither universal behaviour of the shift in the exponential absorption edge versus temperature nor a unique explanation of its origin.⁽³⁸⁾

In explaining previously similar results of a-Si doped with As and In, Makadsi and Haddad⁽¹³⁾ and Haddad⁽¹⁴⁾ attributed the increase in E_{opt} upon annealing to the decreased density of tail states, while the mobility edges are assumed to be nearly independent of T_a . We assume here, as inferred from Figs. 12 and 13, that the tail width also decreases. Consequently the E_{opt} appears as if increasing. In other words the band edges become sharper and the onset of E_{opt} shifts towards higher photon energies. We can not come to the end of this discussion without referring to the recent work performed by Makadsi and Alias⁽⁵²⁾ on the effect of doping percentages on E_{opt} . They showed that E_{opt} decreases with increasing doping percentages in the range 0–3% for both B and P doped a-Si prepared by thermal evaporation. Thus one may deduce that E_{opt} of evaporated a-Si could be controlled by varying doping percentages and/or T_a .

Conclusions

It has been shown that the electrical and optical properties of a-Si thin films prepared by thermal evaporation depend on substrate temperature and doping percentages. The optical gap tends to saturate at $T_s = 650$ K and the highest conductivities are obtained at 3% boron or phosphorus dopant levels.

We can infer from the discrepancies in the reviewed data on the E_{opt} dependence on T_s or T_a that more experimental and theoretical works are needed to clarify a complex problem.

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