Influence of Film Thickness on Optical Properties of Hydrogenated Amorphous Silicon Thin Films

A. M. Bakry

Physics Department, Faculty of Science, Ain-Shams University, Cairo, Egypt 11566.

A detailed study of the dependence of optical constants on thickness for vacuum-deposited hydrogenated amorphous silicon thin films is reported. The thicknesses of the films range from 190 nm to 540 nm. The refractive index $n(\lambda)$, absorption coefficient $\alpha(\lambda)$, extinction coefficient $k(\lambda)$ and consequently the band gap, are determined from the spectrophotometric measurements of the film transmittance in the wavelength range 400-2500 nm. The average gap $E_g$ is calculated as well using Wemple's equations. A comparison between different mechanisms to study the band gap and their correlation to the obtained results is given. The carrier concentration $N/m^*$, static refractive index $n_0$ and the high frequency dielectric constant $\varepsilon_\infty$ were studied.

1. Introduction

Amorphous hydrogenated silicon (a-Si:H) has attracted much attention in the field of electronic devices, particularly for the production of large inexpensive photovoltaic arrays. Many papers have been published on the influence of substrate temperature, hydrogen content, doping and flow rate on the optical properties of a-Si:H films [1-5]. However, the influence of film thickness on optical properties does not appear to have enough investigation.

Amorphous thin films often exhibit inhomogeneities, where the mean grain size at the surface of the films are found to depend on film thickness [6,7]. An inhomogeneous region close to the substrate would play an increasingly important role as the film thickness decreases. It is possible to estimate the effect of inhomogeneities from the knowledge of the measured complex dielectric constant. Therefore the dependence of optical constants on thickness can give information about inhomogeneity in the films.

E-mail: assem_seddy@yahoo.com
Different preparation techniques were used to study the effect of thickness on the optical properties of the a-Si:H films such as magnetron sputtering [8], glow discharge [8,9] plasma-enhanced chemical vapor deposition [10] and vacuum deposition [11]. Reactive magnetron sputtering was used for Nb2O5 films [12]. Hot wall deposition was also used to prepare CdSe thin films [13]. Other researchers used thermal evaporation to prepare (Ge2S3)(Sb2Se3) [14], InSe [15] thin films, Ga0.49As0.51Te46 [16] and As45.2Te46.6In8.2 [17]. A final conclusion could be drawn, that, regardless of the film composition and the preparation technique, film thickness affects significantly the properties of the film.

In the present work, the effect of film thickness on the optical gap, refractive index and carrier concentration for a-Si:H films is studied.

2. Experimental procedures:

The preparation of the films was carried out in Klaushal Ziellerfield Technical University in Germany. The investigated films were prepared on Corning 7059 glass substrates at a temperature 300°C. Silicon was evaporated from an electron beam heated vitreous Carbon crucible at a rate of approximately 3 Å° per second to a thickness of about 5000 Å°. The film thickness was measured by the Tolansky method of multiple beam Fizeau fringes [18]. The base pressure of vacuum was 10^-7 mbar. During the entire evaporation process, atomic hydrogen was blown at the growing film from a radio frequency dissociation system. The resulting hydrogen pressure in the vacuum vessel was 3×10^-5 mbar and the hydrogen flux through the dissociator was about 16 ml N/min. The hydrogen content in all used films was kept fixed at CH=12 at.%. The transmittance, T, and reflectance, R, spectra were carried out between 400 and 2500 nm in steps of 2 nm using a computer-aided double-beam spectrophotometer (Shimadzu 3101 PC UV-VIS-NIR). The relative uncertainty in the transmittance and reflectance is 0.2%. Transmittance scans were performed using a glass substrate in the reference compartment of the same kind that was used for the film deposition. The transmittance and reflectance were measured at the same incidence angle of 5º.

3. Determination of the optical constants

3.1. Film thickness d

The film thickness d was also estimated using the method proposed by Ambrico [19]. If n11 and n12 are the refractive indices at two adjacent maxima (or minima) at λ1 and λ2 then
\[ d_i = \frac{\lambda_1 \lambda_2}{2(\lambda_i n_{12} - \lambda_i n_{11})} \]  

(1)

The \( d_i \) values have been derived at each extremum and averaged \( \langle d_i \rangle \). Then using the equation of interference fringes

\[ 2n_i\langle d_i \rangle = m' \lambda \]  

(2)

where \( m' \) is the order of interference and generally not an integer number. True order numbers \( m \) is calculated by rounding \( m' \) values to integer or half integers. Using values of \( m \) and \( n_i \) in the equation

\[ 2n_i\langle d_2 \rangle = m \lambda \]

\( d_2 \) values at each wavelength and average corrected thickness \( \langle d_2 \rangle \) is determined. Eqn. 2 is used to determine exact integer (for maxima) or half integer (for minima) values of \( m \) for each \( \lambda \). Exact values of \( d \) can be calculated using \( n \) values again. The set of \( m \) that gives the smallest dispersion should be taken. A very good agreement was found between values of film thickness calculated using this method and those measured using Tolansky’s approach.

3.2. Refractive index \( n \)

Away from absorption, the refractive index \( n \) is given by [20]

\[ n = [M + (M^2 - s^2)^{\frac{1}{2}}]^{\frac{1}{2}} \]  

(3)

where

\[ M = \frac{2s}{T_m} - \frac{s^2 + 1}{2} \]

and \( T_m \) is the transmission minimum and \( s \) is the refractive index of the substrate.

In the region of weak and medium absorption, where the absorption coefficient \( \alpha \neq 0 \), the refractive index \( n \) is given by

\[ n = [N + (N^2 - s^2)^{\frac{1}{2}}]^{\frac{1}{2}} \]  

(4)

where

\[ N = 2s \frac{T_m - T_w}{T_m T_m} + \frac{s^2 + 1}{2} \]
and $T_M$ is the transmission maximum. The spectral envelopes of the transmittance, $T_M(\lambda)$ and $T_m(\lambda)$ (which are assumed to be continuous functions of the wavelength) were computed using a polynomial interpolation between extrema. In the region of strong absorption, $n$ can be estimated by extrapolating the values calculated in the other regions of the spectrum.

3.3. Absorption coefficient $\alpha$

The absorption coefficient $\alpha$ can be determined if the absorbance $x$ is calculated from the relation

$$x = \exp(-\alpha d) \quad \text{.......................................................... (5)}$$

In the region of weak and medium absorption, $x$ is given by two different relations. Using the transmission maximum $T_M$, $x$ is given by

$$x = \frac{E_M - \left[ E_M^2 - (n^2 - 1)^3(n^2 - s^4) \right]^{1/2}}{(n - 1)^3(n - s^2)} \quad \text{.............................. (6)}$$

where

$$E_M = \frac{8n^2s}{T_M} + (n^2 - 1)(n^2 - s^2)$$

Using the transmission minimum $T_m$, $x$ is given by

$$x = \frac{E_m - \left[ E_m^2 - (n^2 - 1)^3(n^2 - s^4) \right]^{1/2}}{(n - 1)^3(n - s^2)} \quad \text{.............................. (6)}$$

where

$$E_m = \frac{8n^2s}{T_m} - (n^2 - 1)(n^2 - s^2)$$

3.4. Extinction coefficient $k$

When the absorption coefficient $\alpha$ is known, the extinction coefficient $k$ can be found from the relation

$$k = \frac{\alpha \lambda}{4\pi} \quad \text{................................................................. (7)}$$

The real and imaginary parts of dielectric constants $\varepsilon_1$ and $\varepsilon_2$ can be calculated if the refractive index and extinction coefficient are known using the relations $\varepsilon_1 = (n^2 - k^2)$ and $\varepsilon_2 = 2nk$
3.5. Evaluation of material characteristic energies

An interesting model (single oscillator model) describing the index dispersion behavior was proposed by Wemple and Di Domenico [21, 22]. It accounts for the dispersion curve according to the relation

\[ n^2(\hbar \omega) = 1 + \frac{E_w E_d}{E_w^2 - (\hbar \omega)^2} \]  

(8)

where \( \hbar \omega \) is the photon energy, \( E_w \) and \( E_d \) are two parameters connected to the optical properties of the material and they are known as the single oscillator energy and the oscillator strength, respectively. \( E_w \) defines the average energy gap usually considered as the energy separation between the centers of both the conduction and the valence bands. \( E_d \) is a measure of the average strength of the interband optical transitions. Plotting \((n^2-1)^{-1}\) against \((\hbar \omega)^2\) and fitting it to the straight part of the curve in the high-energy region allows obtaining from the slope and the intercept values of the single oscillator parameters \((E_w \text{ and } E_d)\).

3.6. High frequency dielectric constant and carrier concentration

The real part of the complex dielectric constant could be expressed as [24]

\[ \varepsilon_r = n^2 - k^2 = \varepsilon_\infty - \frac{e^2}{4\pi^2 c^2\varepsilon_0} \frac{N}{m^*} \lambda^2, \]  

(9)

where \( \varepsilon_0 \) is the free space dielectric constant, \( N/m^* \) the ratio of free carrier concentration, \( N \) to the free carrier effective mass, \( m^* \). Plotting of \( \varepsilon_r \) versus \( \lambda^2 \) both the high frequency dielectric constant \( \varepsilon_\infty \) and \( N/m^* \) could be determined.

3.7. Urbach energy and tail of absorption edge

It is well known that the shape of the fundamental absorption edge in the exponential (Urbach) region yields information on the disorder effects [25]. With incident photon energy less than the band gap, the increase in absorption coefficient is followed with an exponential decay of density of states of the localized into the gap [26] and the absorption edge is known as Urbach edge. The lack of crystalline long-range order in amorphous/glassy materials is associated with a tailing of density of states [26]. At lower values of the absorption coefficient \((1 \text{ cm}^{-1} < \alpha < 10^4 \text{ cm}^{-1})\), the extent of the exponential tail of the absorption edge characterized by the Urbach energy is given by [27]

\[ \alpha(hv) = \beta \exp(hv/E_U) \]  

(10)
where $\beta$ is a constant, $E_U$ is the Urbach energy which indicates the width of the band tails of the localized states. The optical absorption coefficient just below the absorption edge shows exponential variation with photon energy indicating the presence of Urbach’s tail. Plotting $\ln(\alpha)$ vs. $h\nu$ and taking the reciprocals of the slopes of the linear portion in the lower photon energy of these curves, $E_U$ could be obtained

3.8. Analysis of energy gap

An expression for the absorption coefficient, $\alpha(h\nu)$, as a function of photon energy ($h\nu$) for direct and indirect optical transitions is given by the following expression [28].

$$\alpha(\nu) = \frac{A(h\nu - E_{g}^{opt})^m}{h\nu}$$

(11)

where the exponent $m = 1/2$ for allowed direct transition, while $m = 2$ for allowed indirect transition. $E_{g}^{opt}$ is optical band gap energy (Tauc gap) and $A$ is a constant related to the extent of the band tailing. Plotting $(\alpha h\nu)^{1/2}$ against photon energy ($h\nu$) gives a straight line with intercept equal to the optical energy band gap for indirect ($E_{g}^{opt}$) transitions. The optical gap can also be found from the imaginary part $\varepsilon_2$ of the dielectric constant [8]. Plotting $(\varepsilon_2)^{1/2}$ versus Photon energy defines the optical gap $E_{g}^{opt}$ from the extrapolated intercept.

4. Results and discussion

The dispersion of the refractive index $n$ for different samples is shown in Fig. (1). The figure shows a normal dispersion behaviour (where $dn/d\lambda$ is negative). From figure, the dispersion curves show an increase with increasing the thickness. Similar observation was previously reported for sputtered samples [8] and those grown by glow discharge [9]. The same behavior was also reported for other amorphous thin films [12, 13]. Values for the refractive index at $\lambda = 850$ nm (comparable to $\lambda$ infinity) is given in Table (1) (error in $n$ is 0.007). It can be seen that, for thickness higher than 490 nm the opposite behavior starts to show, in which a decrease in the refractive index is obtained with the further increase in the film thickness. A similar behavior was reported for sputter deposited Nb$_2$O$_3$ films [12]. Figure (2) shows for the Si-1 sample a proof of a direct band gap transition at low energy values. The value for this gap was calculated and found to be 0.52 eV.
Fig. (1): Variation of the normal dispersion curve of refractive index \( n \) with film thickness

Table (1): Calculated values of the Tauc optical gap \( E_{g}^{\text{opt}} \), the optical gap calculated using imaginary part of dielectric constant \( E_{g}' \), Urbach parameter \( E_{u} \), average gap \( E_{w} \), oscillator strength \( E_{d} \), carrier concentration \( N/m^* \), refractive index \( n \), high frequency dielectric constant \( \varepsilon_\infty \), and static refractive index \( n_0 \).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Thickness (nm)</th>
<th>( E_{g}^{\text{opt}} ) (eV)</th>
<th>( E_{g}' ) (eV)</th>
<th>( E_{d} ) (eV)</th>
<th>( E_{w} ) (eV)</th>
<th>( N/m^* \times 10^{21} ) (cm(^{-3}))</th>
<th>( n ) (850 nm)</th>
<th>( \varepsilon_\infty )</th>
<th>( n_0 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si 1</td>
<td>190</td>
<td>1.8</td>
<td>1.68</td>
<td>265</td>
<td>2.59</td>
<td>12.02</td>
<td>4.42</td>
<td>2.94</td>
<td>8.45</td>
</tr>
<tr>
<td>Si 2</td>
<td>405</td>
<td>1.73</td>
<td>1.65</td>
<td>128</td>
<td>2.61</td>
<td>16.66</td>
<td>9.37</td>
<td>3.14</td>
<td>9.81</td>
</tr>
<tr>
<td>Si 3</td>
<td>490</td>
<td>1.53</td>
<td>1.62</td>
<td>125</td>
<td>2.24</td>
<td>7.88</td>
<td>31.2</td>
<td>3.34</td>
<td>10.84</td>
</tr>
<tr>
<td>Si 4</td>
<td>540</td>
<td>1.56</td>
<td>1.68</td>
<td>176</td>
<td>2.21</td>
<td>9.91</td>
<td>71.0</td>
<td>3.32</td>
<td>10.21</td>
</tr>
</tbody>
</table>
The absorption coefficient is plotted for different thickness and energy and shown in Fig. (2). It is seen that $\alpha$ is higher for thinner films showing little dependence for thicker films. The absorption edge shifts also to smaller values of energy with increase in thickness. As for thickness greater than 490 nm, it showed similar opposite behavior as in case of refractive index.

![Graph showing absorption coefficient vs. film thickness](image)

**Fig. (2):** The change of the absorption coefficient $\alpha$ with film thickness.

The variation of $E_{g}^{\text{opt}}$ and $E_{g}'$ with thickness is shown in Figs. (3 and 4). Values of $E_{g}^{\text{opt}}$ and $E_{g}'$ are given in Table 1 (error is 0.01). It can be seen that $E_{g}^{\text{opt}}$ decreases with increasing thickness (same as reported by Demichelis et al. [8] and Talukder et al. [11]), reaching a saturation value for thickness 490 nm. The opposite behavior was previously reported [9] but with critical thickness of 0.9 \(\mu\)m. The decrease of $E_{g}^{\text{opt}}$ with thickness was interpreted by Talukder et al. [11] as due to the fact that the surface layers of the film can vary in a fundamental way from the bulk layer. This is owing to an unintentional grading of the constituents of the material. However, values of $E_{g}'$ showed no significant change with thickness. Demichelis et al. [8] and Cody et al. [29] reported the same conclusion and related this behavior to the non-direct type of optical transitions in amorphous materials. In non-direct optical transitions the electron momentum is no longer a good quantum number, so that the
assumption of a constant momentum matrix element, leading to $E_g^\text{opt}$, seems to be incorrect. The assumption of a constant dipole matrix element, which is more general and free of momentum constraints, leads to $E_g$.

**Fig. (3):** Plots of the optical gap as calculated from Tauc's equation for different film thicknesses.

**Fig. (4):** Plots of the optical gap as calculated from using the imaginary part of dielectric constant for different film thicknesses.
Values of the Urbach parameter $E_u$ are listed in Table (1). As shown in table, $E_u$ decreased with increase in film thickness for values less than 490 nm. As the Urbach parameter is a measure of the degree of disorder, the assumption of the presence of defects in the thinly amorphous film seems to be valid in our case. During the deposition of amorphous film, unsaturated bonds are produced as a result of insufficient number of atoms. The unsaturated bonds are responsible for the formation of some defects in the film. Such defects produce localized states. In the case of thicker films, greater deposition builds up a more homogeneous network. Calculated values of $E_u$ and $E_d$ are given in Table (1). The results show that values of the average gap agreed in behavior with the calculated Tauc gap ($E_{opt}^\alpha$), i.e., decreased with increasing film thickness.

The change in the carrier concentration is calculated and given in Table (1). The data in table shows that the carrier concentration increases with increasing film thickness, such increase could be explained as follows [9]. Tetrahedral amorphous semiconductor thin films exhibit inhomogeneities. For thicker films, longer deposition time builds up better homogeneity with better compensation of dangling bonds. Poor compensation of dangling bonds and inhomogeneities which are predominant at the substrate-film interface dominates over the bulk since the surface to volume ratio is higher for thinner films. Since thicker films are more homogeneous, and also the surface to volume ratio is lower than that of thinner films, the influence of the interface and surface to bulk becomes less crucial. Hence, the disorder induced tailing decreases for thicker films. This decrease is due to the lower density of defects and better homogeneity which reduces the density of localized states near the mobility edges, and thereby reducing the extent of tailing. So the donor type defect states, below $E_f$, which otherwise had been occupied in the thinner films, becomes neutral, releasing electrons. These electrons can be accepted by the acceptor type defect states above the Fermi level and go to the conduction band. When it is accepted by the defect states above the Fermi level, the defect state is negatively charged and hence has to be below the Fermi level. Hence the Fermi level rises, and when it reaching the conduction band, the carrier concentration increases.

Values of the static refractive index $n_0$ are calculated and given in Table (1). $n_0$ increased with increasing thickness. The static refractive index $n_0$ is the lower limit of refractive index and it represents the response of the material to DC electric field and it is proportional to the carrier concentration $N$. It is given by [28],

$$n_0^2 \propto \frac{N\epsilon^2}{\epsilon_m \omega_0^2}$$  \hspace{1cm} (12)
From the above equation it is clear that \( n_o \) depends on the carrier concentration, \( N \), where \( e \) and \( m \) are the charge and mass of the electron, respectively. \( \varepsilon_o \) is the permittivity of vacuum and \( \omega_o \) is the oscillator natural frequency. Consequently, with the increase carrier concentration \( N \), \( n_o \) shows an increase as listed in Table (1).

The calculated values for the high frequency dielectric constant \( \varepsilon_\infty \) are listed in Table (1). As could be seen that \( \varepsilon_\infty \) increased with film thickness up to 490 nm, \( i.e., \) increased with increasing saturation of dangling bonds. Beyond this thickness, \( \varepsilon_\infty \) started to decrease.

5. Conclusion

Investigations of the dependence of optical constants on film thickness of vacuum-deposited hydrogenated amorphous silicon thin films are reported in the present study. The refractive index dispersion curves shifted to higher values with increasing the thickness. The absorption coefficient \( \alpha \) is higher for thinner films and showed little dependence for thicker films. The optical gap \( E_g^{opt} \) (Tauc gap) decreases with increasing thickness, reaching a saturation value for thickness 490 nm. Values of optical gap calculated using imaginary part of dielectric constant \( E_g' \) showed no significant change with thickness. Values of the Urbach parameter \( E_u \) decreased with the increase in film thickness for values less than 490 nm. Values of the average gap, calculated using Wemple's equation, \( E_w \) agreed in behavior with that calculated using Tauc's equation, \( i.e., \) decreased with increasing film thickness. The carrier concentration increased with film thickness. Values of the static refractive index \( n_o \) increased with increasing thickness. The high frequency dielectric constant \( \varepsilon_\infty \) increased with thickness up to 490 nm. Beyond this thickness, \( \varepsilon_\infty \) started to decrease.

References