THE EFFECT OF HYDROGEN CONCENTRATION ON REFRACTIVE INDEX AND OPTICAL GAP IN HYDROGENATED AMORPHOUS SILICON

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Abstract

The optical properties of a-Si:H have been measured by several workers but there has been no suitable model to explain these results. A quantitative model for the incorporation of hydrogen in a-Si:H network to introduce hydrogen dependency of the optical properties has been developed. The concept of bond polarizabilities has been used to compute refractive index of a-Si:H as a function of hydrogen concentration. The results obtained have been compared with recent experimental results and the discrepancy has been explained. It has been found that the optical gap (E_g) increases with the increase of hydrogen concentration (C_H). The results have been found to be consistent with the recent experimental results. Other results have also been compared and a theoretical relation $E_g = 1.5 + 1.2 \, C_H$ is thus obtained which corresponds reasonably well with the experimental results.

1. Introduction

Due to exciting opto-elecronic properties the hydrogenated amorphous silicon (a-Si:H) has been widely used to fabricate low cost large area solar cells. a-Si:H exhibits continuously adjustable band gap, a suitable carrier lifetime and can be deposited on foreign substrates without much difficulty as thin films. But the performance of a-Si:H solar cells is seriously limited [1] by the light-induced degradation. It has been found [2] that with the pulsed light illumination a-Si:H solar cells degrade at a much faster rate. It has been reported [3] that the minority carrier diffusion length of polycrystalline silicon wafers is considerably improved when annealed in hydrogen at temperatures greater than 1000°C. Due to the presence of hydrogen and other reactive impurities in a-Si:H its optical properties are modified [4,5]. For reaching the goal of a high quality electronic material, the knowledge of the bonding of hydrogen to the host material and of thermal stability of the hydrogen incorporation is of particular interest. Hence it is extremely important to investigate the role of hydrogen in a-Si:H which may be very useful in improving the performance of a-Si:H solar cells. The optical properties of a-Si:H have been measured by several workers [6-8] but there has been no suitable model to explain these results. In the present paper quantitative

model for the incorporation of hydrogen in the a-Si:H network to introduce the hydrogen dependency of the optical properties has been developed. The concept of bond polarizabilities has been used to compute refractive index of a-Si:H for various values of hydrogen concentration. Using harmonic oscillator approximation the optical gap of a-Si:H has been calculated as a function of hydrogen content. The results thus obtained have been compared with the recent experimental results. The theoretical results have been found to be consistent with experimental results.

1- Theory

The behaviour of a solid to electromagnetic radiation of angular frequency ω can be determined by the complex dielectric constant.

$$\bar{\in}(\omega) = \in_1(\omega) - i \in_2(\omega) \qquad \dots \dots \quad (1)$$

The refractive index $n(\omega)$ and the extinction coefficient $k(\omega)$ obtained from optical reflection and transmission measurements can be used to obtain $\bar{\in}(\omega)$

$$\in_1 = n^2 - k^2 \text{ and } \in_2 = 2nk \qquad \dots \dots \quad (2)$$

The absorption coefficient $\alpha(\omega)$ is given by

$$\alpha(\omega) = \frac{4\pi}{\lambda} k(\omega) \quad = \frac{\omega}{nc} \in_2(\omega)$$

where λ is the wavelength of radiation and c is the speed of light in vacuum. The response of a solid to electromagnetic radiation in the harmonic oscillator model can be approximated by a number of oscillators of the same type. The polarizability [9] of the harmonic oscillator is given by

$$\bar{\alpha}_p(\omega) = \frac{q^2}{n\left(\omega_0^2 - \omega^2 + i\gamma\omega\right)} \qquad \dots \dots \quad (3)$$

where q is the electronic charge, ω_0 is the natural frequency of the oscillator, m is the mass of electron and γ is the damping factor. The dielectric constant is obtained from the polarizability with the Clausius-Mossotti relation

$$\frac{\bar{\in}(\omega) - 1}{\bar{\in}(\omega) + 2} = \frac{4\pi}{3} N_{os} \bar{\alpha}_p(\omega) \qquad \dots \dots \quad (4)$$

where N_{os} is the number of oscillators per unit volume. The dielectric constant is now proportional to the sum of polarizabilities because of the local field correction [10]. The electric field felt by the oscillator is not the applied field because of the other oscillators. The

surrounding oscillators modify the applied field which results in a different electric field at the place of the oscillator. This field is called the local field. The dielectric constant obtained from eqn. (3) and (4) is given by

$$\bar{\in}(\omega) = 1 + \frac{\omega_p^2}{\omega_1^2 - \omega^2 + i\gamma\omega} \qquad \ldots \ldots \quad (5)$$

where $\omega_1^2 = \omega_0^2 - \frac{\omega_p^2}{3}$ and $\omega_p^2 = 4\pi N_{os}\frac{\upsilon^2}{m}$

The replacement of ω_0^2 by ω_1^2 is the consequence of the local field correction. The above equation does not accurately describe the data but it can be used to determine ω_1 and ω_p both of which have physical significance. The plasma frequency ω_p is used to obtain the Penn gap $\bar{h}\omega_g$ using [11]

$$n_\infty^2 = 1 + \frac{2}{3}\frac{\omega_p^2}{\omega_g^2} \qquad \ldots \ldots \quad (6)$$

where n_∞ is the refractive index at long wave lengths. The Penn gap is based on a simple two band model for an isotropic semiconductor with a spherical Brillouin zone [12]. The Penn gap $\bar{h}\omega_g$ represents an average separation between valence and conduction bands and is a measure of the covalent bond strength [13, 14].

(A) The effect of hydrogen concentration on the refractive index:

The refractive index at long wave-lengths n_∞ can be written in terms of individual oscillators with polarizability α_p using Lorentz-Lorenz equation [15, 16]

$$\frac{n_\infty^2 - 1}{n_\infty^2 + 2} = \frac{4\pi}{3} Nos\ \alpha_p \qquad \ldots \ldots \quad (7)$$

In a-Si:H these oscillators are the Si-Si bond and the Si-H bond because the electrons are located in a covalent bond between the atoms, we use the concept of bond polarizability. For an ionic compound the concept of ion polarizability has to be used.

The bond polarizability of the Si-Si bond is obtained from the refractive index of a-Si:H with a low hydrogen content. The refractive index of a-Si:H with a low hydrogen content is slightly higher than that of crystalline silicon, which is 3.42, because the average Si-Si bond strength is smaller [17,18] for a-Si:H. Taking for a-Si:H refractive index of 3.6

and an atomic density of 5×10^{22} atoms/cm^3 (the density of C-Si) we get from eqn. (7) the polarizability of the Si-Si bond in a-Si:H,

$$\alpha_{si-si} = 1.91 \times 10^{-24} \text{cm}^3 \qquad \text{… …} \quad (8)$$

The bond polarizability of the Si-H bond has been taken from the polarizability of SiH$_4$ molecule which is [19].

$$\alpha_{SiH_4} = 5.44 \times 10^{-24} \text{cm}^3 \text{ which gives}$$

$$\alpha_{Si-H} = 1.36 \times 10^{-24} \text{cm}^3 \qquad \text{… …} \quad (9)$$

Thus eqn. (7) becomes

$$\frac{n_\infty^2 - 1}{n_\infty^2 + 2} = \frac{4\pi}{3} \left[N_{Si-Si} \alpha_{Si-Si} + N_{Si-H} \alpha_{Si-H} \right] \qquad \text{… …} \quad (10)$$

where N_{Si-Si} is the number of Si-Si bonds per unit volume and N_{Si-H} is the number of Si–H bonds per unit volume.

The refractive index depends on the hydrogen content because Si–Si bonds are broken and replaced by Si–H bonds. Incorporation of hydrogen in the a–Si:H leads to cluster I where for every hydrogen atom one Si–Si bond is broken and replaced by one Si–H bond. When more hydrogen is added two hydrogen atoms can break three Si–Si bonds which are replaced by three Si–H bonds thus forming cluster II. It means that the total polarizability decreases at a faster rate for the forming of cluster II than for the forming of cluster I.

Using eqn. (10) for the forming of cluster I, the refractive index can be calculated as a function or hydrogen concentration. The hydrogen concentration in atomic fraction is given by

$$C_H = \frac{N_H}{N_{Si} + N_H} \qquad \text{… …} \quad (11)$$

using $N_{Si} = N_{C-Si} - [1/4] N_H$ eqn. (11) reduces to

$$C_H = \frac{N_H}{N_{C-Si} + \frac{3}{4} N_H} \qquad \text{… …} \quad (12)$$

where N_H and N_{Si} are the number of hydrogen and silicon atoms per unit volume in the a–Si:H layer and $N_{c–Si}$ is the number of Si atoms per unit volume in crystalline silicon. Thus eqn. (12) gives the number of hydrogen atoms per unit volume as a function of hydrogen concentration as

$$N_H = \frac{C_H N_{C-Si}}{1 - \frac{3}{4}C_H} \cong N_{C-Si}\left(C_H + \frac{3}{4}C_H^2\right) \qquad \ldots \ldots \quad (13)$$

The number of Si–Si and Si–H bonds per unit volume is given by

$$N_{Si-Si} = 2N_{C-Si} - N_H \cong N_{C-Si}\left(2 - C_H - 3/4\,C_H^2\right) \ldots \ldots (14)$$

and $\qquad N_{Si-H} = N_H \cong N_{C-Si}\left(C_H + 3/4\,C_H^2\right) \qquad \ldots \ldots \quad (15)$
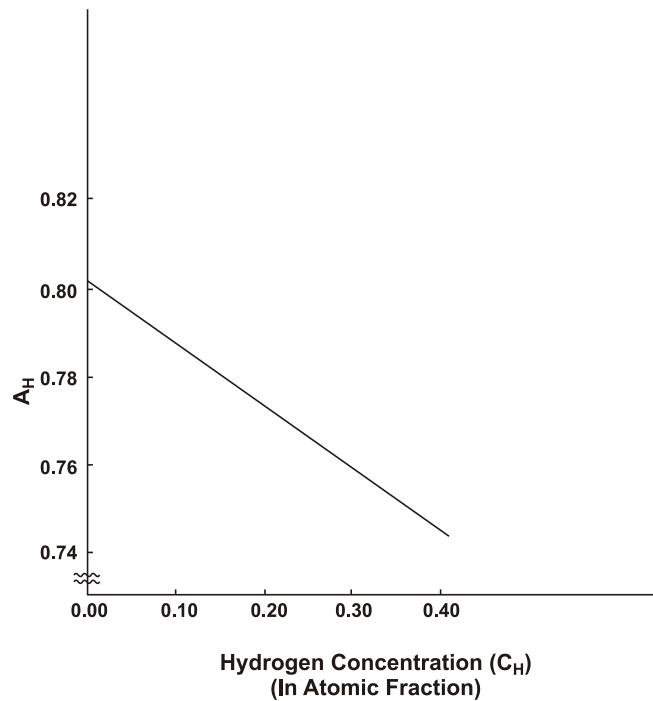
Using the number of Si–Si and Si–H bonds given by eqns. (14) and (15) the referactive index can be calculated from eqn. (10) as a function of hydrogen concentration.

Thus the relation between refractive index at long wave length and hydrogen concentration is given by
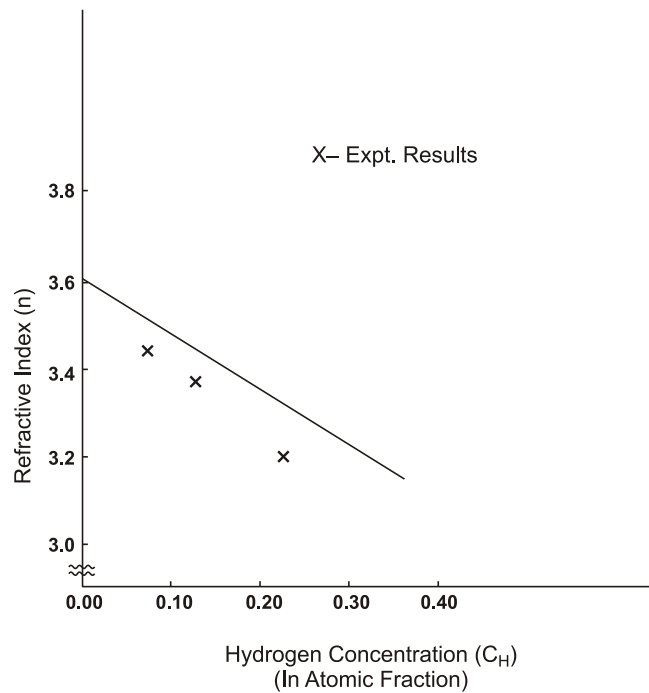
$$n_\infty = \left[\frac{(1 + 2A_H)}{(1 - A_H)}\right]^{1/2} \qquad \ldots \ldots \quad (16)$$

where

$$A_H = \frac{4\pi}{3}N_{C-Si}\left[\left(2 - C_H - \frac{3}{4}C_H^2\right)\alpha_{Si-Si} + \left(C_H + \frac{3}{4}C_H^2\right)\alpha_{Si-H}\right] \ldots (17)$$

Fig. 1 Variation of A_H with hydrogen concentration (C_H) in atomic fraction

Fig. 2 . Variation of refractive index (n) at 900 nm with hydrogen concentration (C_H) in atomic fraction. The line indicates the theoretical results and the points (X) indicate experimental data.

B. The effect of Hydrogen Concentration on the Optical gap:

The harmonic oscillator model has been used to obtain the relation between the optical gap and the hydrogen concentration. Assuming the optical gap is the gap that is obtained from $\alpha(\omega)$ with the Tauc relation. The complex dielectric constant is given by eqn. (5). The polarizability of a single oscillator is given by eqn. (3) and for low frequencies it is given by

$$\alpha_p = \frac{q^2}{m\omega_0^2} \qquad \ldots \ldots \quad (18)$$

The plasma frequency ω_p given by eqn (5) can be expressed in terms of ω_0 and refractive index n_∞. Using α_p and eqn (7) we get

$$\omega_p^2 = 4\pi Nos \frac{q^2}{m} = \frac{4\pi}{3} Nos\,\alpha_p\,3\omega_0^2$$

$$= \frac{n_\infty^2 - 1}{n_\infty^2 + 2} 3\,\omega_0^2 \qquad \ldots \ldots \quad (19)$$

If n_∞ increase from 3.0 to 3.6 the value of ω_p increase from $1.477\,\omega_0$ to $1.5486754\,\omega_0$. This is a small relative increase compared to the shift in ω_1 from $0.519\,\omega_0$ to $0.446\,\omega_0$ for the same increase in the refractive index. It means that shift in ω_1 will dominate the optical properties as a function of the hydrogen concentration.

The optical gap will be described in terms of $\bar{h}\omega_1$. We will use the approximation that the shift in $\bar{h}\omega_1$ is the same as the shift in the optical gap.

$\Delta E_g = \Delta\bar{h}\omega_1$ which leads to

$$E_g = \bar{h}\omega_1 + E_s \qquad \ldots\ldots \quad (20)$$

Where E_s is a constant. The relation between E_g and C_H is obtained from the relation between n_∞ and $\bar{h}\omega_1$. The relation between n_∞ and $\bar{h}\omega_1$ is obtained from eqn (5) and (19) and is given by–

$$\bar{h}\omega_1 = \bar{h}\omega_0\left[1 - \frac{\left(n_\infty^2 - 1\right)}{\left(n_\infty^2 + 2\right)}\right]^{1/2} \qquad \ldots\ldots \quad (21)$$

The relation between $\bar{h}\omega_1$ and hydrogen concentration is obtained from the eqn. (21) by applying the Lorentz-Lorenz eqn. and using eqn. (16)

$$\bar{h}\omega_1 = \bar{h}\omega_0\left[1 - A_H\right]^{1/2} \qquad \ldots\ldots \quad (22)$$

The larger hydrogen clusters are formed. For larger hydrogen clusters more Si–Si bonds are broken per incorporated hydrogen atom. Therefore, the total polarizability which consists of the polarizabilities of Si–Si and Si–H bonds is decreased faster with increasing hydrogen concentration as compared to the situation with the formation of small clusters.

Using the computed values of A_H the optical gap is obtained from eqn (23) as a function of hydrogen concentration C_H. The results have been represented in Fig. 3. It is obvious from this figure that the optical gap (Eg.) increases with the increase of hydrogen concentration. The experimental results [24] for the variation of optical gap with the hydrogen concentration have also been shown in figure.
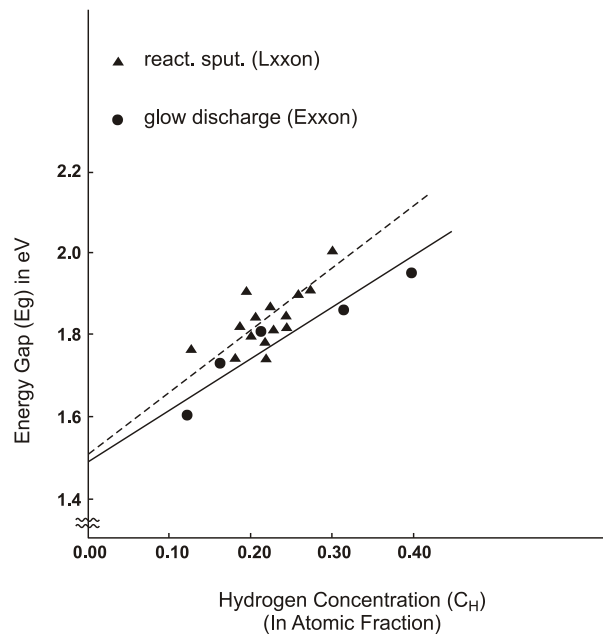
Fig. 3 Variation of Optical gap (Eg) with hydrogen concentration (C_H) in atomic fraction. The continuous line indicates the theoretical results, the dashed line indicates the relation Eg = 1.5 + 1.5 C_H. The points • and ▲ indicate experimental data.

It may also be seen from the figure that the slope of Eg–C_H curve of theoretical results is smaller than the slope or Eg–C_H curve of experimental result. The difference in the slope of Eg–C_H curve can be explained by assuming that the large hydrogen clusters are formed.

The results obtained are in complete agreement with the recent results [25]. It has been found that increase of hydrogen concentration widens the band gap and reduces the density of defect states. The phenomenological results reported by various research groups [17, 26-28] have been investigated and a theoretical relation between Eg and C_H is thus obtained which is given by

$$Eg = 1.5 + 1.2 C_H \qquad\qquad \dots \dots \quad (24)$$

The results obtained on the basis of eqn. (24) have been found to be in good agreement with the experimental results.

3. Conclusion:

Using the concept of bond polarizabilities a quantitative model for the incorporation of hydrogen in a-Si:H network has been developed which describes the relation between optical gap, refractive index and hydrogen concentration. The results obtained for the variation of refractive index with hydrogen concentration have been compared with experimental results and the discrepancy has been explained on the basis of this model. The

optical gap has been found to increase with the hydrogen concentration which is in good agreement with the recent experimental results. The relation Eg = 1.5 + 1.2 C_H corresponds reasonably well with the experimental results.

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