

Nanocrystalline and Amorphous Silicon Semiconductors as Competing Candidates for PV Applications

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Abstract: The optical properties of two Hydrogenated nanocrystalline (nc-Si: H) and amorphous silicon (a-Si: H) thin film samples are investigated using conventional spectrophotometric technique. Both samples were prepared by plasma enhanced chemical vapor deposition technique (PECVD). The nc-Si: H sample prepared with 1% silicon concentration at temperature of 220°C with ~1 Å/s growth rate exhibits optical behavior closer to crystalline Silicon (c-Si) sample than the a-Si: H sample prepared with Helium (He) percentage of the initial gas mixture of 20 at temperature of 80°C with increased growth rate of ~2.8 Å/s. The optical constants, thicknesses and the energy band gap of both samples are obtained from the transmission data only. The values of refractive index within an estimated uncertainty of 1% for both a-Si: H and nc-Si: H samples are found close to those of c-Si sample in the chosen range of wavelengths. Both samples are found to have the same optical energy gap of ~1.7 eV within an uncertainty of ~ 0.03 eV and exhibit absorption features close to those of c-Si sample. The absorption behavior in the visible and near infrared regions of electromagnetic spectrum makes both samples good candidates for photovoltaic (PV) applications.

Keywords: Optical Properties, Nanocrystalline Silicon, Amorphous Silicon, PECVD.

1. INTRODUCTION

Hydrogenated amorphous silicon (a-Si: H) and nanocrystalline silicon (nc-Si: H) have wide spread applications in solar cells and transistors in addition to several other electronic devices. The Plasma Enhanced Chemical Vapor Deposition (PECVD) has become a prominent technique in preparing quality thin films that are used in large-area devices, such as photovoltaic (PV) cells and thin-film transistors (TFT). Monocrystalline cells, which are made of pure silicon surface and a thin structure, are known to have high efficiency (15-20%). They have two different manufacturing technologies - Si (Silicon) and Gallium Arsenide (GaAs). The PV cells with the highest efficiency (20-35%) today are those made of Gallium Arsenide. The amorphous solar cell which has an efficiency of 7-10% becomes widely used in digital calculators because it is the cheapest in its manufacturing technology. However, the most expensive one is the hybrid solar cell which is the one of the newest technologies where organic and chemical substances are used together in its structure. Even though such hybrid solar cell has quite a high rate of energy efficiency (30 – 45%), it is not yet in the industrial manufacturing phase.

The most common available technique that enables us to study the optical properties of thin films is optical transmission spectroscopy. The optical transmission spectroscopy, which is an easy and a nondestructive

technique, provides information about the complex refractive index $n(\lambda) = n(\lambda) + i k(\lambda)$. Here $n(\lambda)$ is the real part of refractive index, and $k(\lambda)$ is the imaginary part of refractive index (the extinction coefficient). Information on the absorption coefficient $\alpha(\lambda) (= 4\pi k/\lambda)$ in addition to film thickness and optical energy gap can also be obtained. Different methods have been employed in the analysis of optical transmission data [1-7]. The simplest commonly used method is that of Swanepoel [5-10].

In this paper optical properties of a-Si: H and nc-Si: H thin film samples prepared by PECVD technique using He-diluted and H₂-diluted SiH₄ gases, respectively, are studied. IR and Raman measurements have been conducted (not shown here) on the samples. The IR study on a-Si: H indicates that this sample is amorphous in its structure while the Raman study conducted on nc-Si: H sample shows that it has a crystalline volume fraction 84%. The transmission data of the samples obtained from optical measurements using JASCO double-beam spectrophotometer have been analyzed using the method of Swanepoel [5]. The optical constants obtained from this analysis indicate that these two samples are good candidates for photovoltaic (PV) applications.

2. EXPERIMENTAL TECHNIQUES

Hydrogenated nanocrystalline and amorphous silicon nc-Si: H, a-Si: H samples, respectively, have been prepared by Plasma Enhanced Chemical Vapor Deposition (PECVD) technique at different preparation conditions. A nanocrystalline silicon sample with silicon

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Table 1: The optical energy gap E_g , Urbach energy E_u , deposition rate, experimental and theoretical values of sample thickness, d , for both nc -Si: H with $X_c = 84\%$ and a -Si: H with He -dilution of 20%, samples. Here, the fitting parameters, A and B , are extracted from fitting the calculated values of refractive index, $n(\lambda)$, using the formula $n(\lambda) = A/\lambda^2 + B$ [5]

| Sample | E_g (eV) | E_u (meV) | Deposition rate ($\text{\AA}/s$) | Thickness (measured) (nm) | Thickness (calculated) (nm) | $A \times 10^5$ (nm^2) | B |
|-------------|-----------------|-------------|------------------------------------|---------------------------|-----------------------------|-----------------------------------|------|
| nc -Si: H | 1.7 ± 0.07 | 480 | 1 | 300 | 316 | 1.67 | 3.1 |
| a -Si: H | 1.74 ± 0.03 | 184 | 2.8 | 540 | 481 | 2.26 | 3.38 |

concentration (SC) of 1.0%, using H_2 -diluted SiH_4 gases, was prepared at standard power and pressure of 25W and 120 Pa, respectively, when the substrate temperature was maintained at $T_s = 220^\circ C$. This sample is deposited on Corning 7059 glass substrate. The sample with He dilution of initial gas mixture ($H_2 + SiH_4$) gases of 20% is deposited at $T_s = 80^\circ C$ on Corning 1737 glass substrate at pressure of 1.4torr and power of 50W. The He dilution is used to reduce the stress resulted from the increasing growth rate. The deposition rate and thickness, together with other extracted physical quantities, for each sample were listed in Table 1.

Optical measurements were conducted using JASCO V-570, UV-VIS-NIR double beam spectrophotometer. Transmission spectra were recorded in the range of wavelengths 400-2500nm. Spectrophotometric measurements for the two samples were performed at room temperature.

3. RESULTS AND ANALYSIS

The transmission data for the thin film samples prepared at different preparation conditions are shown in Figure 1. Both samples exhibit good transparency in the infrared region and this transparency is degraded in the visible region. The spectra show interference pattern with sharp fall off in the transmittance at the band edge, which is an indication of good crystallinity for the samples. The global features of these spectra are found similar to those obtained elsewhere [8-10].

A FORTRAN program has been developed to calculate the values of $n(\lambda)$, $k(\lambda)$ and to estimate the values of thickness of both samples using the appropriate formulas of Ref [5]. Corrections for the initial calculated values of $n(\lambda)$ and thickness have also been performed. The values of thickness d are determined using the relation $l/2 = 2d(n(\lambda)/\lambda) - m$, where integer l has values of 0, 1, 2, 3...etc. and m is the order number of extreme (integer for a maximum or

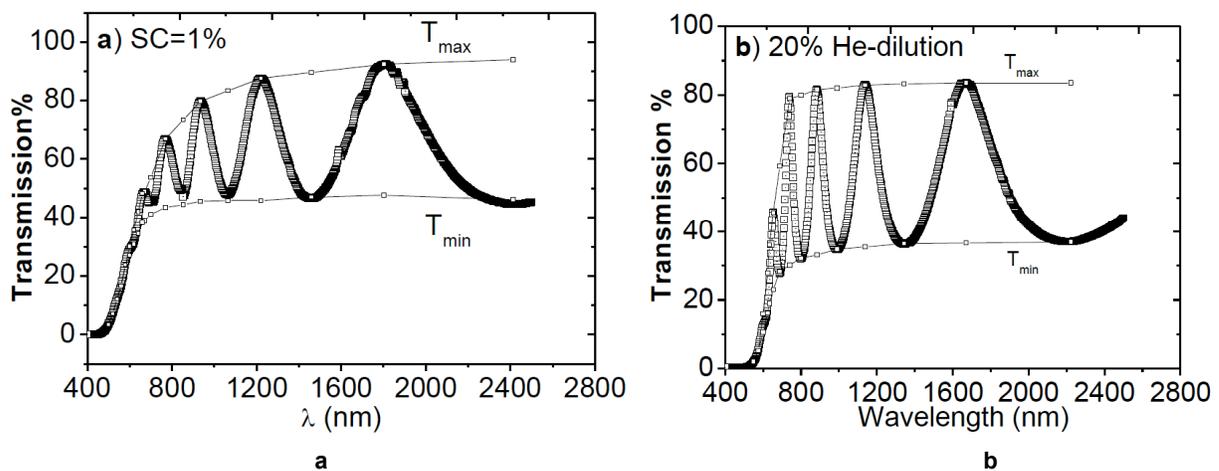


Figure 1: Transmission spectra of **a)** nc -Si: H sample with SC= 1% **b)** a -Si: H sample with He -dilution of 20%, respectively; both prepared using PECVD technique. Optical measurements were conducted using JASCO double beam spectrophotometer at room temperature. T_{max} and T_{min} (lines + symbols) were obtained from the extrema of experimental data of transmission (symbols) [5].

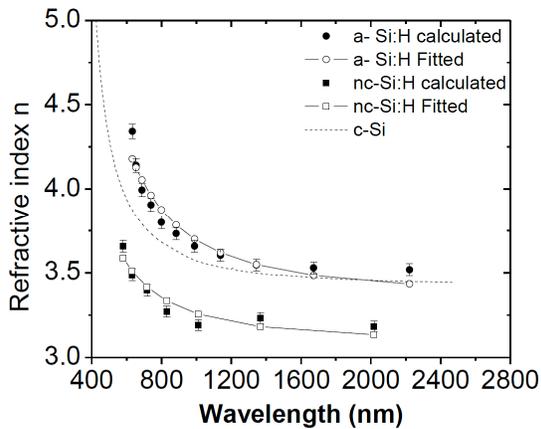


Figure 2: The refractive index, n , versus wavelength (calculated (symbols) and fitted (line + symbols)) for a-Si: H with He dilution of 20% and nc-Si: H prepared with 1% silane concentration, respectively, using PECVD technique. These dispersion curves are compared to that of c-Si (dashed line).

half integer for a minimum). The program makes its iteration to search for the nearest integer (or half integer if the first extreme is a minimum) which gives the best straight line fit to the initial obtained values of n (λ). The value of the thickness is obtained from the slope of the straight line. The formulas of Ref [5] are used to get the corrected values of thickness. Accurate values of n (λ) can be reached by using the obtained accurate values of m and d , and using the relation $2n(\lambda)d = m\lambda$. The relation $n(\lambda) = A/\lambda^2 + B$ is then used to fit the obtained accurate values of n (λ). The best-obtained fitting parameters, A and B , are listed in Table 1. Both the calculated and best-fitted values of n (λ) are plotted against wavelength and shown in Figure 2 for both samples. In this Figure, the error bars indicate the uncertainty in calculated values of n (λ). The a-Si: H sample shows closer values of refractive index to that of c-Si values than those of nc-Si: H sample in the whole range of the spectrum (400-2500nm). The error in refractive index is determined to be about 1% of the corrected value. It is noted that the fitting relation can produce each required transmission spectrum with a reasonable accuracy. Therefore, the values of $\alpha(\lambda)$ and $k(\lambda)$ have been determined using the relevant formulas [5] and the obtained fitted values of n (λ). Figure 3 also presents the variation of extinction coefficient, k (λ), against wavelength. It can be noted that the a-Si: H and nc-Si: H samples show 76% and 58% of reduced absorption, respectively, as λ changes from 680 to 960 nm. The latter behaviour at $\lambda > 680$ nm may be attributed to free-carrier absorption. However, a reduced absorption at smaller wavelengths (< 680 nm) could be attributed to the higher generation of carriers in a-Si: H sample than that of nc-Si: H [11, 12]. Here, the a-Si: H sample exhibits 91% reduction in absorption

as compared to a corresponding reduction of 67% in the nc-Si: H sample as λ changes from 550 to 960 nm. The amount of absorption in the shown range of wavelengths is found comparable to those found by others [8-10] and close to that of the c-Si sample. The trend that has been exhibited for enhanced absorption in the visible and near infrared regions may make these samples good candidates for PV applications.

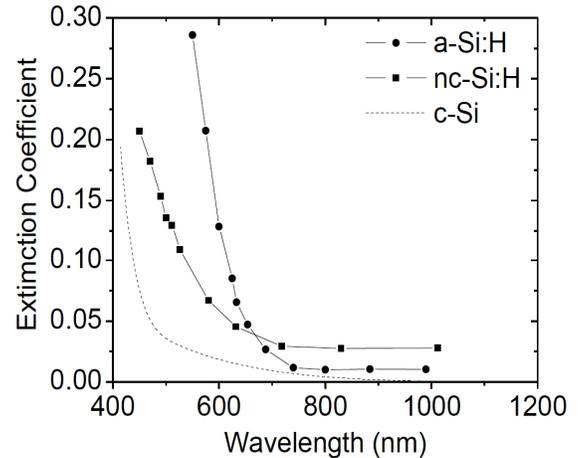


Figure 3: Variation of extinction coefficient, k , versus wavelength for both a-Si: H and nc-Si: H samples as compared to that of c-Si.

The values of the optical energy gap have been obtained from variation of $(\alpha h\nu)^{0.5}$ against photon energy for the samples using the well known Tauc relation $(\alpha h\nu) = C(h\nu - E_g)^2$, where C is the edge width parameter, which is related to the width of the band tails or disorder in the sample and $h\nu$ is the photon energy. The energy gap of nc-Si: H sample is almost similar to that of a-Si: H sample but differs by a mild uncertainty (< 0.04 eV), as seen in Table 1. However, these results may give an indication that not only the amount of the hydrogen content plays a role in reducing the disorder, but also the way that such hydrogen is incorporated into the entire network of the material. Similar values of optical energy gap were also found by others [8-10, 12,13]. The Urbach energy of nc-Si: H sample is higher than that of a-Si: H sample. This may indicate the former sample which contains high degree of crystallinity has more defect density at band tails than the latter sample.

The refractive index n for nc-Si: H sample, at the non-absorbing region (at 1800nm), has lower values than those of c-Si sample while those for the a-Si: H sample have higher values than those of c-Si sample, as shown in Figure 2. The beginning of fall off in n with decreasing SC is consistent with that illustrated by other groups [13]. The error in estimating the value of

thickness increases with larger values of thickness. However, the global estimated error in calculating the thickness is within 15% of the average measured value of thickness.

It was shown that the decrease in SC might lead to a loose structure of *nc*-Si: H sample, which has a lot of defects and disorder. Such increase in defects may allow for oxygen contamination in the samples [14].

The results show that the optical energy gap is not strongly dependent on the hydrogen content but rather on the way it is incorporated into the random network. Concrete explanation to effectiveness of hydrogen in reducing defects and disorder may need more investigation on the bonded-hydrogen content.

CONCLUSION

The hydrogenated nanocrystalline and amorphous silicon samples prepared by PECVD under different deposition conditions have been investigated. The optical parameters have been obtained from the optical transmission data with a reasonable accuracy. In particular, the optical energy gap of the two samples of ~ 1.7 eV around an estimated uncertainty of ~ 0.03 eV is obtained. Moreover, the refractive index is obtained with an estimated error of 1%. The refractive index for the two samples studied in the chosen range of wavelengths exhibits similar features and is found comparable to a standard crystalline silicon sample. The general trend of absorption at wavelength values less than and/or greater than 680nm is consistent with those found by others. The studied hydrogenated nanocrystalline silicon samples may be good competing candidates for photovoltaic applications due to their behavior in visible and near infrared region of electromagnetic spectrum.

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