

EFFECTS OF ANNEALING ON THE ELECTRO-OPTICAL PROPERTIES OF a-Si:H THIN FILMS DEPOSITED BY D.C. AND PULSED PECVD

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ABSTRACT

Hydrogenated amorphous silicon thin films studied in this work were prepared by d.c. and pulsed PECVD technique at a fixed silane flow-rates of 10 sccm and 40 sccm. The deposition temperature, pressure and power were fixed at 200°C, 0.45 mbar and 1.4 W respectively. The pulsed PECVD system was developed from a modification of the existing d.c. PECVD system with a modulation frequency of 10 kHz. The ON-time and OFF-time was set at 30 seconds. In this work, the effects of annealing on the electro-optical properties of films prepared by both techniques at these flow-rates were investigated. These films were analyzed using optical absorption spectroscopy technique. The results showed that annealing had significant effects on electro-optical properties of these films at annealing temperatures above 300°C mainly due the evolution of hydrogen. The silane flow-rate and the deposition technique also influenced the effects of annealing on the electro-optical properties of these films.

INTRODUCTION

Thin films of hydrogenated amorphous silicon (a-Si:H) have a wide range of practical applications, such as photovoltaic modules [1], thin film transistors in flat-panel displays[2], and 3-colour detectors in imaging systems [3]. Pulsed Plasma Enhanced Chemical Vapour Deposition (PECVD) Technique has been shown to increase the deposition rate and suppress dust formation which is a prerequisite in obtaining a high yield production. In this work, the a-Si:H films studied are prepared by pulsed PECVD technique with an objective of producing multilayers of nanometer thickness consisting of alternating layers of two materials with different energy gaps using the pulsating voltage applied across two PECVD electrodes. Quantum confinement effect in our a-Si:H films prepared by this technique has been reported earlier.

Hydrogen incorporation during growth of a-Si:H films saturates silicon dangling bonds leading to the decrease in the mid-gap density of defects and reduces structural disorder which results in the narrowing of the band tail states. Effective incorporation of hydrogen is determined by the preparation technique and preparation parameters during deposition. Low temperature annealing in a-Si:H films has been diagnosed as a tool to reduce the defects but high temperature annealing result in the removal of hydrogen atoms from the structure thus distorting the silicon matrix due to formation of dangling bonds. This brings a change in the electro-optical properties of the films. In this work, a comparison on the effects of annealing

on the electro-optical properties of a-Si:H prepared by d.c. PECVD and pulsed PECVD are investigated.

EXPERIMENTAL DETAILS

Two different sets of a-Si:H films on soda glass substrates were prepared using Silane flow-rates of 10 and 40 sccm using both the pulsed and d.c. PECVD technique. The pulsed PECVD a-Si:H films studied in this work were prepared using a pulsed power supply which delivers a positive d. c. voltage over a discharge time of 30 seconds and zero voltage over a post-discharge time of 30 seconds. The 30 seconds discharge time was accomplished using a pulsed voltage with a modulation frequency of 10 KHz. The deposition pressure and temperature were maintained at 0.45 mbar and 200°C respectively throughout the deposition. The deposition time for the d.c. and pulsed PECVD samples were fixed at one and three hours respectively. The discharge current, discharge voltage and power were maintained at 14 mA, 900 V and 12.6 W respectively during the deposition of the d.c. PECVD a-Si:H films. As for the pulsed PECVD a-Si:H films, the discharge current, discharge voltage and power were maintained at 20 mA, 700 V and 14 W respectively during the deposition. The films were annealed in a temperature controlled quartz tube furnace from 100°C to 500°C in steps of 100°C under a steady flow of ambient nitrogen to prevent oxidation of the film. Anneals were performed for a duration of 30 minutes and were cooled to room temperature under a steady flow of ambient nitrogen.

The optical transmission spectra were scanned within a scanning range of 250 nm to 2500 nm wavelength using the Jasco V570 UV-VIS-NIR spectrophotometer. The refractive index and film thickness were derived from interference fringes in the high transmission region using techniques proposed by J. C. Manifacier [4] and E. A. Davies [5]. The optical energy gap, E_g was determined by Tauc formula [6]

$$(\alpha E)^{1/2} = B^{1/2}(E - E_g) \dots\dots\dots (1)$$

where α is the absorption coefficient, E is the energy of incident light quanta and B is a constant indicating the steepness of the absorption edge. The non-silicon atom percentage in this work is determined from the relationship

$$I\% = \frac{1}{3} \frac{n_v}{n_s} \left(4 - \sqrt{\frac{E_d}{2.8}} \right) \times 100 \dots\dots\dots (2)$$

where the density of valence electrons, n_v is obtained from the model by C. Ance et al [8]

$$n_v = 0.0143 \frac{E_d^2}{(\epsilon(0) - 1)} \dots\dots\dots (3)$$

and the dispersion energy, E_d is determined from the Wemple and Domenico equation[9].

$$(n^2 - 1) = \frac{E_o E_d}{E_d^2 - e} \dots\dots\dots (4)$$

The dielectric constant, $\epsilon(0)$ is taken as the square of the saturated refractive index in the long wavelength region. E_o is the single oscillator energy and n_s is the density of valence electrons in crystal silicon which is taken to be $2 \times 10^{23} \text{ cm}^{-3}$.

RESULTS AND DISCUSSIONS

The results of the effects of annealing temperatures on the electro-optical properties of the a-Si:H films are presented in this section. The pulsed PECVD a-Si:H films are labeled as p10 and p40 for the films prepared at silane flow-rate of 10 and 40 sccm respectively. Similarly, the d.c. PECVD films are labeled as dc10 and dc40 for the films prepared at silane flow-rates of 10 and 40 sccm respectively.

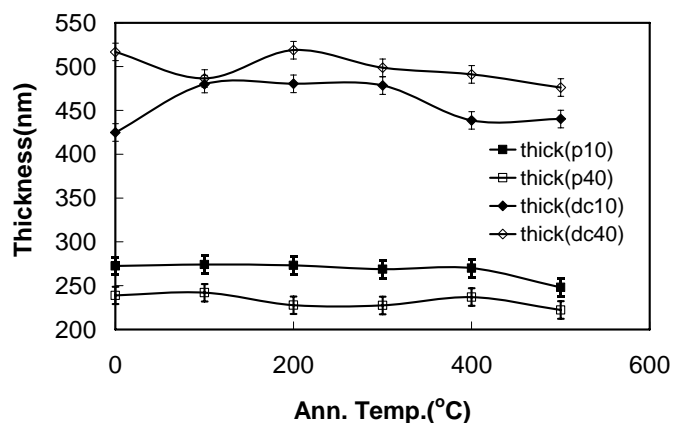


Figure 1: Variation of a-Si:H film thickness with annealing temperature

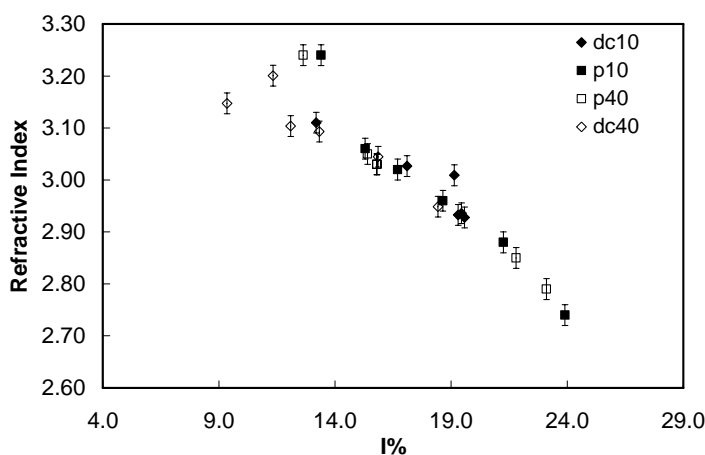


Figure 2: Variation of refractive index of a-Si:H films with percentage of non-silicon atom in the film.

Figure 1 shows the variation of the film thickness with annealing temperature. Variation in the film thickness when the d.c. PECVD a-Si:H films are annealed at temperatures between 100°C to 500°C indicates structural reordering of the film structure due to removal of defects, bond switching and monohydride clustering. The film thickness appears to be stable for the pulsed PECVD film prepared at silane flow-rate of 10sccm when annealed up to 400°C while a slight decrease in film thickness is observed for the film prepared at silane flow-rate of assuming uniform deposition. Thus isolated multilayers are formed on the substrate in clustered form. Movement of hydrogen atoms is more probable in this film as atoms can move where the layers are not properly formed. Movement of atoms is confined within layers

that are well formed and is of one atomic thickness or larger as in the 10 sccm silane flow-rate film which explains the stability of this film thickness with annealing at temperatures below 500°C.

The dependence of refractive indices of the annealed a-Si:H films on the percentage of non-silicon atom present in the film is shown in figure 2. In these films I% is dominated by hydrogen atoms while oxygen atoms could also be included as possible contamination in the film structure. Consistently, increase in I% results in the decrease in the film refractive index showing that refractive index of these amorphous films are strongly related to the film density, more non-silicon atoms will result in lower density films. Figure 3 shows the variation of film refractive index with annealing temperature. These plots show that hydrogen evolution is more significant in the pulsed PECVD films when annealed at 500°C.

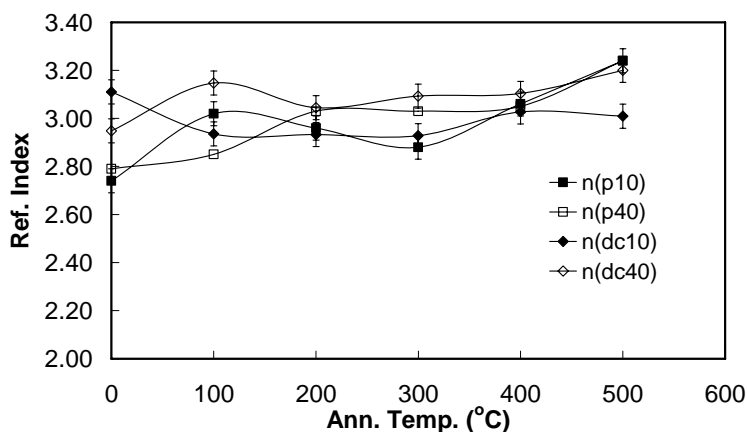


Figure 3: Variation of refractive index of a-Si:H films with annealing temperature.

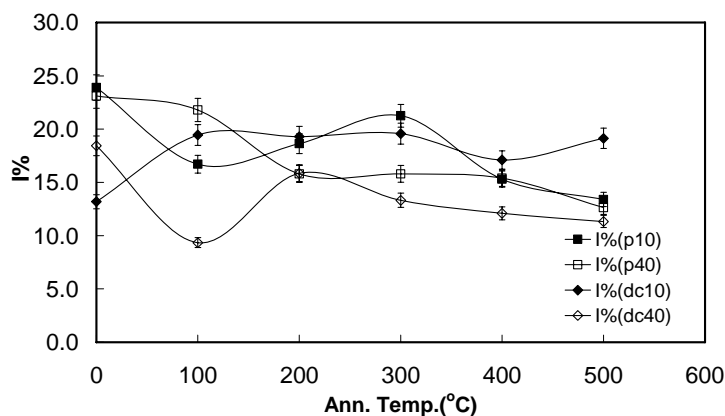


Figure 4: Variation of non-silicon atom percentage in a-Si:H film with annealing temperature.

Figures 5 and 6 present the variation of optical energy gap, E_g and $B^{1/2}$ with annealing temperature respectively. Evidence of quantum confinement is usually reported by in many papers by a blue shift in the optical energy gap and the increase in $B^{1/2}$ value [13]. A blue shift of the optical energy gap is observed for all pulsed PECVD films as-prepared and annealed at temperatures below 500°C as compared to the E_g value of the d.c. PECVD films prepared at the same silane flow-rate. The increase in the optical energy gap is not associated

with the increase in non-silicon atom percentage in the film, since no direct relationship is observed between E_g and $I\%$ values as seen in figures 4 and 5. The $B^{1/2}$ value is observed to be equal or higher than the d.c. PECVD films only for the pulsed PECVD film prepared at silane flow-rate of 40 sccm as-prepared and when annealed at temperatures below 500°C. For the 10sccm silane flow-rate film, $B^{1/2}$ value is observed to be equal or higher than the d.c. PECVD film prepared at the same silane flow-rate only when the film is annealed at temperatures above 200°C, however the $B^{1/2}$ value is comparatively much higher as-prepared and when annealed at temperatures below 300°C than the $B^{1/2}$ value obtained for the 40 sccm silane flow-rate film. Thus, evidence of quantum confinement effect is observed in both the pulsed PECVD film as-prepared and when annealed at temperatures below 500°C. Hydrogen evolution from the film structure is

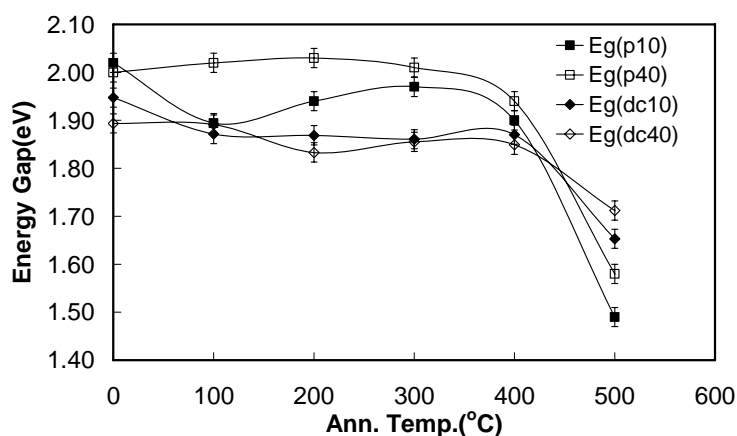


Figure 5: Variation of the optical energy gap, E_g of a-Si:H films with annealing temperature

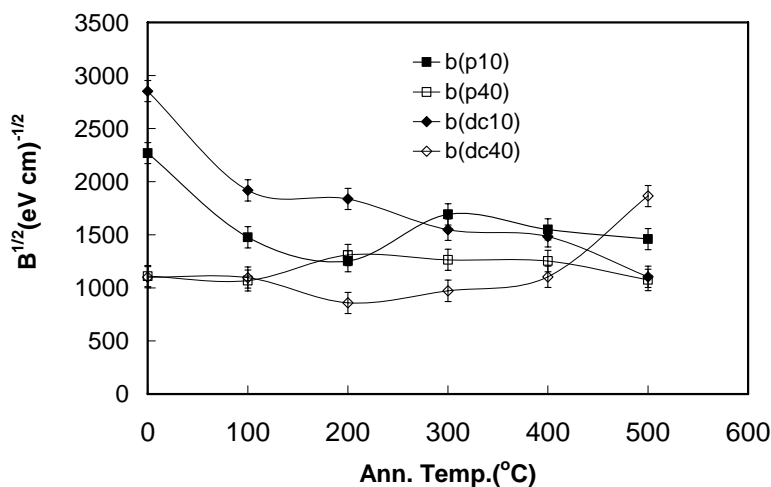


Figure 6: Variation of the $B^{1/2}$ of a-Si:H films with annealing temperature.

observed to be most evident when the film is annealed at 500°C as observed in figure 4. This contributes to the significant decrease in the optical energy gap. Quantum confinement effect

in this film disappears as a result of evolution of hydrogen from the film structure as the optical energy gap of this film is significantly lower than the optical energy gap of the d.c. PECVD film prepared at the same silane flow-rate.

CONCLUSIONS

Evidence of quantum confinement effect is observed in the pulsed PECVD a-Si:H films. This effect is thermally stable up to annealing temperature of 400°C. High temperature annealing at temperatures above 400°C removes evidence of quantum confinement effect as a result of the collapse of the multilayered structure as hydrogen are evolved from the film structure. Evolution of hydrogen may have destroyed the barrier layers of this multilayered structure.

REFERENCES

- [1] S. Guha, J. Yang, A. Banerjee and S. Sugiyama, in *Amorphous and Microcrystalline Silicon Technology-1998*, edited by R. Schropp, H. M. Branz, M. Hack, I. Shimizu and S. Wagner, MRS Symposium Proceedings, **Vol. 507** (Materials Research Society, Warrendale, Pennsylvania, 1998), 99.
- [2] J.T. Rahn, F. Lemmi, P. Mei, J.P. Lu, J.B. Boyce, R.A. Street, R.B. Apte, S.E. Ready, K.F. Van Schuylenbergh, P. Nylén, J. Ho, R.T. Fulks, R. Lau, R.L. Weisfields, in *Amorphous and Heterogeneous Silicon Thin Films: Fundamentals to Devices-1999*, edited by H. M. Branz, R.W. Collins, H. Okamoto, S. Guha and R. Schropp, MRS Symposium Proceedings, **Vol. 557** (Materials Research Society, Warrendale, Pennsylvania, 1999), 809.
- [3] H. Stiebig, B. Stannowski, D. Knipp and H. Wagner, in *Amorphous and Heterogeneous Silicon Thin Films: Fundamentals to Devices-1999*, edited by H. M. Branz, R.W. Collins, H. Okamoto, S. Guha and R. Schropp, MRS Symposium Proceedings, **Vol. 557** (Materials Research Society, Warrendale, Pennsylvania, 1999), 833.
- [4] J.C. Manifacier, J.P. Fillard, J.M. Bind, *Thin Solid Films*, **77** (1981), 77.
- [5] E.A. Davies, N. Piggins, S.C. Bayliss, 1987, *J. Phys. C : Solid State Phys.*, **20** (1987), 4415.
- [6] J. Tauc, *Amorphous and Liquid Semiconductors*, Plenum Press, New York (1974) 173.
- [7] C. Ance, J.P. Ferraton, J.M. Berger and F. De Chelle, *Phys. Stat. Sol., (B)* **113** (1982) 105.
- [8] S.H. Wemple and M. Di Domenico Jr., *Phys. Rev.*, **B3** (1971) 1338.
- [9] S. Miyazaki, K. Yamada, M. Hirose, *J. Non-Cryst. Sols.*, **137 and 138**(1991) 1111.