Effect of Post-Deposition Annealing on Hydrogenated Amorphous Silicon Thin Films Grown At High Power by Pecvd

Aravind Kumar, Pawan Kumar, Parmender Kumar, Kapil Malik, P. N. Dixit

Abstract- The crystallization of hydrogenated amorphous silicon layers (a-Si:H) [1,2] deposited by plasma enhanced chemical vapor deposition (PECVD) is of great interest. Generally, laser or metals are used to induce crystallization in a-Si:H films. We have found that films deposited at high rf power (> 0.2 W/cm2) by PECVD technique shows some crystallites embedded in a-Si:H matrix and their after its vacuum thermal annealing at 250 and 300 ºC helps to further enhancement of crystallite size. These films were characterized using , UV-VIS spectrometry, Raman Spectra, of these films were measured as a function of temperature in the range of 300 ºC to 250 ºC.
Keyword: Amorphous silicon, Thin Films, Growth PECVD.

I. INTRODUCTOIN

Plasma Enhanced Chemical Vapor Deposition (PECVD) of Silane has evolved as an elegant technique for the deposition of the hydrogenated amorphous silicon (a-Si:H) and related alloys. a-Si:H films have attracted considerable attention because of their outstanding optical properties [3-4]. This material is in use in photovoltaic and large area electronic devices at commercial level. However, low deposition rate and stability are the limitation of this material. Enhancement of the deposition rate should be achieved with maintaining the device quality of the material. Attainment of high rate of deposition could be possible by various approaches, such as (a) containment of the plasma by the use of earth shields so the reactive species do not diffuse out of the Inter-Electrode space & enhancement of the density of ionized species by an increase of power input to the plasma, in a careful way, so that gas phase polymerization reaction are avoided (b) Increase of the plasma excitation frequency (c) use of higher silane radicals. Normally to deposit the device quality a-Si:H films lower power density (less than 20 mW/cm2) is used. In the present investigation we have chosen high power density deposited a-Si:H films for our study.

Aravind Kumar, Department of Physics Kalindi College East Patel Nager New Delhi-110008., India.
Pawan Kumar, Department of Physics Gurukula Kangri Vishwavidyalaya, Haridwar-249404, India.
Parmender Kumar, Department of Physics Gurukula Kangri Vishwavidyalaya, Haridwar-249404, India.
Kapil Malik, Department of Physics Gurukula Kangri Vishwavidyalaya, Haridwar-249404, India.
P.N. Dixit, Plasma Processed Materials Group National Physical LaboratoryDr. K.S. Krishnan Road, New Delhi-110 012

II. EXPERIMENTAL PROCEDURE

It is well known that sustaining plasma by RF excitation is rather easy. It is because electrons in the plasma respond instantaneously to the RF field and absorbs energy from the field via inelastic collision with gas molecules in the bulk, thereby, gaining sufficient energy to ionize the gas. In this section a detailed study of RF plasma (13.56 MHz) produced a-Si:H films by using silane (SiH_4) as the feed gas has been made. For this study a 13.56 MHz source RF plasma Model RF 5S) was used to excite the plasma. Substrates were placed on the anode of the research reactor.

The partial pressure of SiH_4 is adjusted with the help of Mass Flow Controller (MFC). In order to increase the deposition rate (r_d), systematic variation of applied RF Power to the cathode was varied systematically at different pressures. The deposition condition were as follows: (1) Pressure(0.1-1.0 Torr, (2) substrate temperature, 3000 ºC, (3) SiH_4 flow rate, 40.0 sccm, (4) power density varied from 16 to 180 mW cm^{-2}. The thicknesses of the films, was measured by a talystep **(Rank-Taylor Hobson)**, were in the range 1.5 μm. Optical, electrical and structural measurements were carried out on samples as per procedure discussed. We have designated the sample deposited at 1W power as HR-031, and 21W power as HR-022.
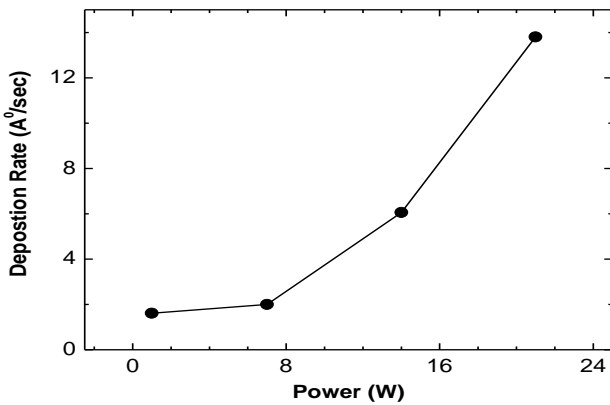
III. DEPOSITION RATE

The deposition rate of the films was calculated from the measured thickness divided by deposition time. Thicknesses of the films were estimated by talystep (Rank-Taylor Hobson) measurement equipment. Variation of deposition rate of a-Si:H films as a function of Power as shown in the Fig (1.1) The variation of deposition rate r_d(A^0/s) with variation of applied power. It is clear that r_d increases monotonically with increase of applied power. Normally to deposit the device quality a-Si:H films low power density (less than 20 mW/cm^2) is preferred. The deposition rate increases from 2.9 to 13 A^0/s with the increases of applied power from 1W to 21W. Increases of the applied power enhance the dissociation and ionization of silane radical and thus resulting increase of the flux of deposition precursors to the substrate surface.

IV. OPTICAL PROPERTIES

Investigations of the optical properties of semiconductors are among the most important sources of information on the band structure, the frequencies of the optical modes of the phonon spectrum and other properties of the semiconductors.

For optical properties absorption and transmission spectra of these films were taken at room temperature with the help of UV-Vis spectrophotometer from Ocean Optics

Fig(1): Shows the variation of deposition rate with applied power.

3.1. Energy band gap

The absorption spectra of the Hydrogenated Amorphous Silicon (a-Si:H) thin film were used to determine the energy band gap in the spectral range 400-1100 nm. It is observed that the absorption coefficient increases sharply below a certain wavelength.

To determine the energy band gap from absorption spectra the Tauc relation [5, 6, 7] is used.

$\alpha h\upsilon = A(h\upsilon - E_g)^n$

where, $h\upsilon$ = Photon energy
α = Absorption coefficient
E_g = Energy band gap
and $n = \frac{1}{2}$, for direct band gap.

To measure the energy band gap from absorption spectra a graph $(\alpha h\upsilon)^{1/2}$ versus $h\upsilon$ is plotted. The extrapolation of the straight line $(\alpha h\upsilon)^{1/2} = 0$ axis gives the, value of the energy band gap. Fig (1.2) shows the plot of $(\alpha h\upsilon)^{1/2}$ versus $h\upsilon$ for the plasma deposited hydrogenated Amorphous Silicon(a-Si:H) thin film. It has been observed that the plot of $(\alpha h\upsilon)^{1/2}$ versus $h\upsilon$ is liner over a wide range of photon energy Indicating the direct type of transitions We know that in semiconductors the band gap decreases with increase in temperature. The same effect is seen here. It is observed that the band gap of the a-Si:H films decreases with increase in the annealing temperature and are tabulated in Table 3.1.
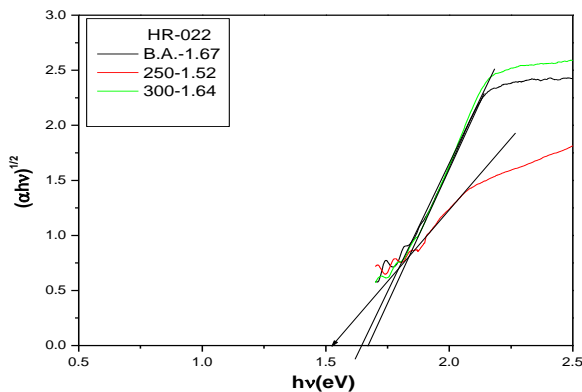

Fig (2): Variation of the $(\alpha h\upsilon)^{1/2}$ versus Photon energy $(h\upsilon)$ of a-Si:H thin films

3.2 Optical Constant

The optical constants especially refractive index (n) of the material of a thin film may be determined from the transmission spectra. The transmission spectra of all samples of a-Si:H thin films in the spectral range 400-1100 nm were used to study the optical constants as shown in below figures. We draw an envelope to the transmittance interference pattern. The refractive index of thin film material at a particular wavelength was calculated using Manifacier's envelope method [4].

$$n = [N + (N^2 + n_0^2 n_1^2)^{1/2}]^{1/2}$$

n_0 and n_1 are the refractive index of air and substrate (glass) respectively. The number N is given by:

$$N = [(n_0^2 + n_1^2)/2] + 2n_0 n_1 [T_{max} - T_{min}]/(T_{max} \times T_{min})$$

T_{max} and T_{min} are the upper extreme point and lower extreme point of the envelope at a particular wavelength.
The extinction coefficient (k) is give by:

$$K = (-\lambda/4 \pi t) \ln p$$

t is the thickness of the film.

$$P = C_1/C_2 [1 - T_{max}/T_{min}]/[1 + T_{max}/T_{min}]$$
$$C_1 = (n+n_0) (n+n_2)$$
$$C_2 = (n-n_0) (n_1-n)$$

The thickness of these films was measured by a Spectrophotometer method using transmission spectra, which are given as:

$$t = M \lambda_1 \lambda_2/2[n(\lambda_1) \lambda_2 - n(\lambda_2) \lambda_1]$$

M is the number of oscillation between the tow extreme in the interference pattern of transmission spectra. λ_1 λ_2 and $n(\lambda_1)$ $n(\lambda_2)$ are the corresponding wave lengths and indices of refraction.

To plot the transmission spectra of a-Si thin films which is deposited on 1W, These films was annealed in vacuum at 20, 250 & 300 ^{0}C for one hour. We were calculat the refractive index and extinction coefficient using Macinfacier's formula [4] are shown in Table (1), Sample are deposited on (7059) glass substrate at 250 ^{0}C temperatures. RF power remains at 1W while the gas flow rate is maintained at 0.5Torr, we were observed that the transmittance is 30% near to the visible region in case of before annealing, while annealing the sample at 250 & 300 ^{0}C temperature the transmittance in same region rises to almost 80 & 90% respectively, The reason for this may be attributed to diffusion of hydrogen to the surface on annealing at higher temperatures which results in increase in the average transmittance. This confirms that the material becomes crystalline from amorphous. Same pattern we was obtain when we have deposited the samples at higher powr ie 7W,14W,19W&22W
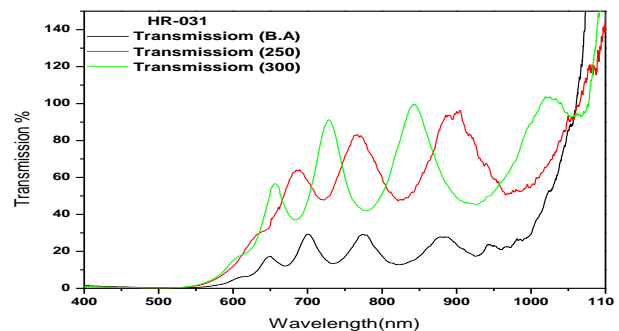

Fig (3): Typical transmission spectra before annealing and after annealing at 250 & 300 ^{0}C of a-Si:H thin film which is deposited on (7059) cornning glass substrate, by Radio Frequency PECVD Technique.
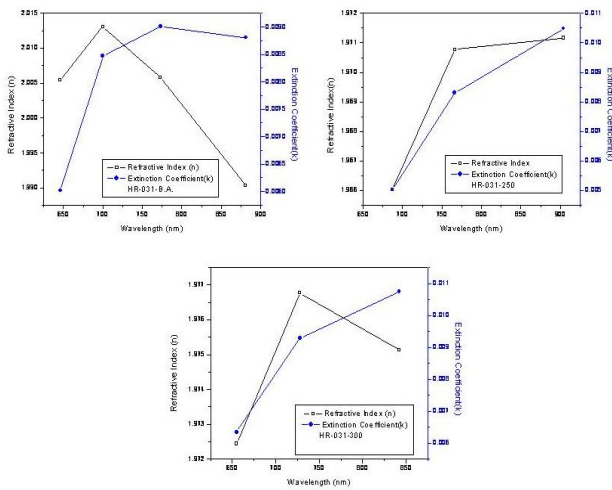
Fig (4): The refractive index and extinction coefficient as a function of wavelength for as deposited and annealed samples.

The Fig (4) shows the graph of refractive index and extinction coefficient as a function of wavelength for the samples deposited at 1W power. It is observed that the behaviour of the refractive index and extinction coefficient are not of the same nature. It depends on the interaction of the sample and the incident wavelength. We have tabulated the values of the refractive index and extinction coefficient for different incident wavelength and are shown in Table (1).

Table (1): n & k Calculation For Before Annealing and Annealing at 250, 300 ^{0}C Temperature.

Temprature (^{0}C)	Wavelength $\square$	T_{Max}	T_{Min}	N	N	K
B.A	646	16.93	10.59	1.731086	2.005404	0.00602
	700	29	13.21	1.748652	2.013086	0.00847
	773	29	14.25	1.732078	2.005838	0.00901
	881	27.68	16.65	1.696799	1.990366	0.00881
250	687	63.79	47.18	1.641557	1.966018	0.00503
	766	82.74	47.18	1.652328	1.970777	0.00831
	904	95.63	50.35	1.653212	1.971167	0.01048
300	655	56.35	35.57	1.656102	1.972443	0.00635
	728	90.82	40.56	1.665932	1.976779	0.00929
	842	99.3	44.51	1.662189	1.975129	0.01074

Table (2): Comparison of the Transmittance values of the samples deposited at different powers.

Annealing Temperature	Transmittance (%) (1W)	Transmittance (%) (21W)
B.A.	30	60
250	50	61
300	90	65

With increase in power, the transmission value is gating decreases from the upper level and increase from the bottom level. And at a power of 21W its attain a constant value.

This is not affected by the annealing Temperature shown in table (2).

V. IR- STUDY

The IR spectra of the sample number HR- 020, deposited on (111) Si substrate at applied power of 14 W of hydrogenated amorphous silicon (a-Si:H) thin films in the range 500-2400 cm^{-1},before annealing and after annealing at 250 ^{o}C are shown in Fig features can be (1.7). These spectra were taken in reflection mode. From the IR spectra some major identified .A broad peek around 621 cm^{-1} and 606 cm^{-1} is due to Si-H. Rocking /waging, in case of before annealing, and annealing at 250 ^{o}C, the band at 630 cm^{-1}(Rock), 862 cm^{-1} (symmetric deformation) originated from SiH$_2$ bonding in case of before and after annealing. This is also observed for all the samples that the shape and intensity of the IR spectra depends on the deposition condition.
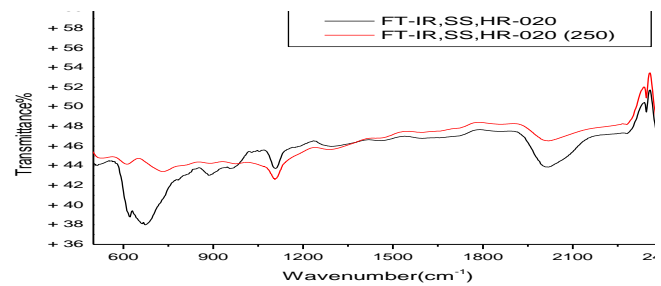

Fig (5): Typical IR transmission Spectrum of a-Si:H, deposited on (111) Si substrate, at 14 W power on 7059 corning Glass Substrate deposited by PECVD technique.

Table (3): Band formation of FT-IR spectra in a-Si:H thin films Deposited at 14W.

Group	Before Anneling		After Anneling	
SiH	2009cm^{-1}	621cm^{-1}	2035cm^{-1}	606 cm^{-1}
	Stretch	Bend	Stretch	Bend
SiH$_2$	880 cm^{-1}	630 cm^{-1}	901 cm^{-1}	862 cm^{-1}
	Band Scissors	Rock	Degnerate deformation	Symmetic deformation

A broad peek around 2009 cm^{-1} and 2035 cm^{-1} is due to Si-H stretch in case of before annealing and annealing at 250 ^{o}C, is due to SiH, SiH$_2$,SiH3 stretching. All bands are strangely broadened indicating amorphous nature of the films with a wide range of bond angle of each mode and strong columbic coupling among the various local structures.

VI. LASER RAMAN RAMAN SPECTROSCOPY

It has been reported [8-11] that the Raman scattering measurement serves as a powerful tool together information about the structural properties of (a-Si:H) and related materials. It is observed that the first order Raman spectra of a-Si consists of features associated with the crystalline phase but broadened by disorder [12]. For the Before Annealing plasma deposited a-Si:H thin film which is deposited at 14 W power, and substrate temperature is maintained at 300 ^{0}C, the most intense mode (TO) shifts from ≈ 460 to ≈ 480 cm^{-1} [13].

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.After annealing at 250 °C & 300 °C the same film most the most intense mode (TO) shifts from ≈ 470 cm^{-1} & 512 cm^{-1} respectively. The shift towards higher frequencies and narrowing of the TO band in consistent with improved short rang order towards the crystalline structure, which exhibits a TO band of width ≈30 cm^{-1} at 512 cm^{-1}. The Raman set up used for this present work consists of a (Perkin Elmer-2000, FT-RAMAN), double monochromator, photon counting electronics, and an argon laser operating at λ=514.5 nm and typically with 120mW cm^{-2} of incident power to the film plane. The measurement were carried out at a room temperature in the air Fig (1.8) shows a typical Raman spectra of a-Si:H. The width of half maximum of the TO-like phonon band, ΔwTo, was used [14], as measure of structural disorder Si-Si binding in a-Si:H. It was found that the TO like band, with the Peek at 475-480 cm^{-1},was asymmetric perhaps due to the presence of the longitudinal-optical (LO) like band with the peak at 410 cm^{-1}. This broadening of TO mode is defined by the parameter Δ_{wTo} and ($\Delta_{wTo=} 2\Gamma(H)$) [15] . Here Γ (H) is the half width of half maximum obtained for higher frequency side of the TO - like band.
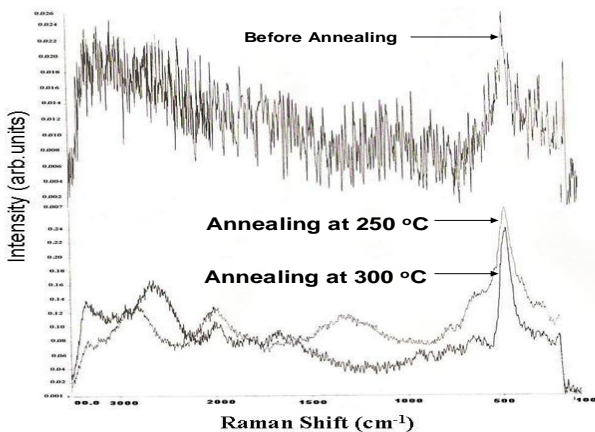

Fig (3.12): Typical Raman spectrum of before annealing and annealing at 250 & 300 °C   a-Si:H thin films.

VII.   CONCLUSIONS

Hydrogenated a-Si thin films grown by using PECVD using the gaseous mixture of SiH$_4$, H$_2$, and Ar. The effect of optical, structural properties was investigated in the range (400-3000 cm^{-1}). Raman Scattering measurement revealed that increasing power fraction in the range (1-21W) favored the enhancement of crystallinity enlargement of crystallites, and relaxation of strained bond. Optical band gap estimated in the higher absorption coefficient region (>10^{4}cm^{-1}) was found in the range(1.5-1.78 ev) are due to a-Si:H. size of the crystallite (Raman=11 nm) was calculated using full-widths at half-maximum (FWHM). Optical constant of a-Si:H was calculated using Manificer formula and tabulated in tabe1. FT-IR spectra were recorded of a-Si:H thin films in the range (600-2400 cm^{-1}), the band formation in a-Si:H thin films which is deposited on 14 W wer tabulated in table 2.

ACKNOWLEDGEMENT

REFRENCES

1. R.A. Street, Hydrogenated amorphous silicon, Cambridge University Press (1991).
2. T. Gruszecki and B. Holmstrom, Solar Energy Materials and solar cells, 31(1993) 227
3. J.C. Manifacier, J. Gasiot, J.P. Fillard, J. Phys. E, 9(1976)1002.
4. M.Hirose, in semiconductor and semimetals 21 ,A ed.j.i. Pankove (academic Press, New Yark(1984).P.9.
5. Tauc J, Ed, Amorphous and Liquid Semiconductor (Plenum Press New York) (1974) 159.
6. T. Moss, Optical Properties of semiconductors (Butter Worths), London.
7. O,S. Heavens optical properties of thin solid films, dover New York (1965).
8. T. Ishidate, K . Inoue, K . Tsuji and S. Minomusa, Solid state Commun. 24. 197 (1982).
9. J .S. Lannin, L. J. Pilione, S. T. Kashiragar, R. Messier and R.C. Ross, Phys . Rev . Lett. 26, 3506 (1982).
10. H.Gleskova, P.I. Hus, Z.Xi, J.C.Sturm, Z.Suo. S. Wagner, Journal of non crystalline solid (338-340) 2004 P 732-735.
11. A. Morimoto, S. Oozora, M. Kumeda and T. Shimizu, Solid State Commun, 47,773 (1983).
12. Ujwal Palanchoke, Viadislav jovanow, Henning Kurz,Philipp obermeyer, Helmnt stiebig and Dietmar Knipp.Optical Express, Vol 20, Issue 6,PP 6340-6347(2012).
13. Y. Hishikawa, K. Watanabe, S. Tsuda, M. Ohnishi and Y. Kuwano, Jpn. J. Appl. Phys. 24, 385 (1985).
14. T. Ishidate, K . Inoue, K . Tsuji and S. Minomusa, Solid state Commun. 24. 197 (1982).
15. Jaran Sritharathikhum, Apichan, moollakorn, Songkiate kittisontirak, Amornrat Limmance, Kobsak Sriprapha, Current Applied Physics Vol-1,PPS17-S20(2010).