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Nanocrystalline silicon as a photovoltaic material

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bstract Nanocrystalline silicon thin films have been developed by Plasma Enhanced Chemical Vapour Deposition technique (PECVD) using vel plasma power and pressure regime. The optoelectronic and structural properties of these films have been studied The optical gap of the nc-Si ms varies from 1.8 eV to 2.09 eV depending upon the deposition conditions The size of the crystallites varies from 7 nm to 10 nm as observed from insmission electron micrographs Degradations of these films under exposure of light have been investigated Solar cells have been fabricated with ese nc Si as absorber layers and the efficiencies of 8.7% have been achieved

eywords PECVD, nc-Si, TEM, Raman spectra

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Introduction

luch effort has been devoted to the study of low dimensional :on systems *i.e* nanocrystalline silicon (nc-Si:H) thin films as is a promising material for many devices including flat panel splay application [1]. This new generation semiconductor aterial also raised the attention of scientific community in the eld of Solar Photovoltaics as it combines the best properties of norphous silicon (a-Si:H) *i.e* remarkable optoelectronic operties with some of the best properties of microcrystalline licon, *i.e* these films are much stable during light soaking than norphous silicon [2]. In these films, nano order size crystals e embedded in an amorphous matrix. This is generally obtained sing a hydrogen rich plasma by various methods *e.g* plasma ihanced chemical vapour deposition (CVD) method and active sputtering. The growth mechanism of these materials is matter of debate [3,4] through the 'etching', 'chemical mealing' and 'surface diffusion' model [4]. To meet the quirement of both high deposition rate and low processing mperature for industrial purpose, some novel deposition rameters have been chosen for PECVD process. A common ature of this material is the quantum confinement due to the esence of nanoscale particle. Role of hydrogen in the growth nc Si:H, is important especially when prepared by plasma anced chemical vapour deposition (PECVD) from SiH_4 diluted ith H_2. The hydrogen content in microcrystalline silicon film usually decreases as the crystalline volume fraction increases but in nc-Si:H it is almost the same as that in a-Si:H. It is well known that the role of hydrogen is important in the formation of nc-Si:H films, however, have not yet been properly understood.

To produce silicon thin films with different structural quality or composition such as microcrystalline, nanocrystalline or amorphous silicon, plasma enhanced chemical vapour deposition of silicon-hydrogen mixture is most popular. The structure of these silicon films, related to their particular deposition conditions, is clearly identified by structural measurements such as Raman spectroscopy, X-ray diffraction, SEM, TEM *etc*. The nanocrystalline silicon film thus developed has some novel properties which make the material suitable for fabrication of stable photovoltaic devices.

2. Experimental details

Hydrogenated silicon thin films were deposited using 13.56 MHz plasma enhanced chemical vapour deposition technique. The process gases used here are silane and hydrogen. One set of samples have been deposited with 15 mW/ cm^2 power density, 1.8 Torr pressure and varying the substrate temperature from 200°C to 250°C. Another set were deposited at 200°C using high rf power 400 mW/ cm^2 and varying the chamber pressure (P_r) from 2.0 Torr to 6.0 Torr.

For optoelectronic and structural studies samples were deposited on 7059 corning glass. The thicknesses of the films

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were maintained between 700 nm to 800 nm and were measured by a stylus type profilometer (Planar Product, UK). Carbon coated copper grids were used for Transmission Electron Microscopy study. Optical absorption and reflection data in the UV-VIS range of photon energy were taken using UV-VIS-NIR double beam spectrophotometer and the optical gap of the films were determined by Tauc's method. The electrical conductivities (dark and photoconducties) were measured in a cryostat after annealing the samples at 150°C under vacuum (~ 10^{-6} Torr) in a gap cell configuration. The photoconductivity measurements were done under white light of intensity 100 mW/ cm^2 using a tungsten halogen lamp. X-ray diffraction pattern were taken using CuK_α radiation ($\lambda = 1.5418$ Å). Silicon-hydrogen bonding configurations in the films have been studied by Fourier Transform Infrared vibrational spectroscopy The Raman spectra of the films were obtained at room temperature using 785nm light from a Diode NIR laser in a micro Raman spectrometer (Renishaw Raman System RM 1000 B).

3. Results and discussions

3.1 Optoelectronic properties :

The dark and photoconductivities, bandgap of the silicon films deposited at different power, pressure, substrate temperature and hydrogen dilution have been shown in Table 1. The bonded hydrogen content in the films as calculated from wagging mode of infrared vibrational spectra are also shown in Table 1. Figure 1 shows the absorption coefficient (α) *vs* photon energy ($h\nu$) plots of films prepared under different chamber pressure. The α *vs* hv plot of Si thin films shifts to higher energy sides as chamber pressure increases from 2 Torr to 5 Torr. This implies that with increase of chamber pressure optical gap of the film decreases. This decrease of optical gap is also shown in Table 1, set B, which is due to increase in crystallinity and decrease of bonded hydrogen content in the films. At higher pressure *i.e* at 6 Torr, the absorption increases again as the crystallinity decreases. This is shown later in structural studies. Table 1 shows that the optical bandgap of these materials varies from 1.8 eV to 2.09 eV depending upon the deposition conditions. These optical gaps are higher than those of the amorphous silicon films (1.7 eV) deposited by plasma enhanced deposition technique. Thus, we may call this as wide bandgap material compared to amorphous silicon. We know that for macroparticles the energy states *i.e* conduction band and valence bands are continuous. When light falls on the materials electron-hole pairs *i.e* excitons are generated. If we make the size of the particle less than the first Bohr radius of the exciton then the energy states of valence and conduction bands remain no longer continuous but becomes discrete *i.e* quantised. In other word we can say that the de Broglie wave associated with the electron becomes confined within the boundaries of the particle whose dimension is less than the first Bohr radius of the exciton. This is known as 'Quantum Confinement Effect' and this effect is prominent when the particle size becomes less than 30 nm. The most striking property of semiconductor nanocrystals are the massive change in optical properties as a function of size. This enhancement of optical gap can be explained by a simple model developed by the nanosize crystallites which behaves as a quantum dot Confinement of an electron or hole with effective mass m^* in a three–dimensional spherical well with diameter D, results a shifting of the energy levels of the electrons or holes to their

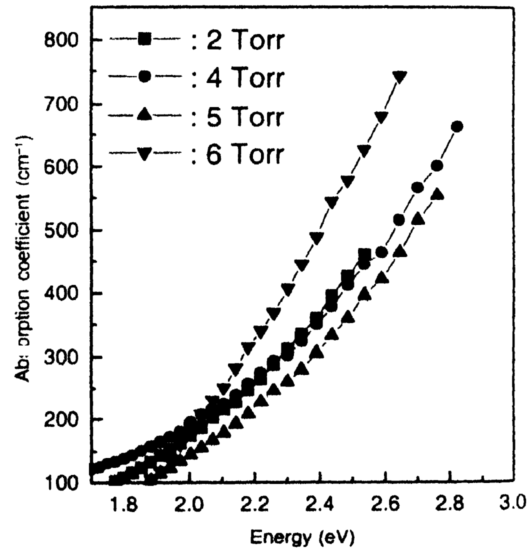

Figure 1. Absorption coefficient *vs.* Photon energy plots for the deposited at different chamber pressure.

Table 1. Optoelectronic properties and bonded hydrogen content of the nc-Si films.

	Sample no.	Optical gap (E_{opt}) (eV)	Dark conductivity (σ_D) (Scm^{-1})	Photoconductivity (σ_{ph}) (Scm^{-1})	σ_{ph}/σ_D	Bonded hydrogen content (C_H)	Size of the Quantum dot (from calculations)
Set A	H1	1.8	9.21×10^{-12}	1.56×10^{-12}	1.7×10^{6}	8.2	3.02
	H2	1.89	3.58×10^{-12}	7.36×10^{-12}	2.06×10^{6}	7.0	2 58
	H3	1.92	$8\ 66\times10^{-12}$	$3\ 58\times10^{-12}$	$4\ 13\times10^{6}$	5.2	2.47
Set B	HP1	1.99	1.95×10^{-6}	1.5×10^{-5}	7.69	9.4	2.26
	HP2	1.92	8.9×10^{-6}	4.69×10^{-5}	5.27	9.2	2.47
	HP3	1.85	2.8×10^{-5}	7.29×10^{-5}	2 6	5.35	2.75
	HP4	2.09	2.85×10^{-8}	3.1×10^{-5}	1.09×10^{3}	11 86	2.04

igher energy states [5]. $\Delta E = (2\hbar n^2\pi^2)/(m^* D^2)$, where n is n integer. So the quantum confinement of charge carriers nhances the separation between conduction band and valence and, *i.e.* optical gap of Si films. Again this increase of optical ap depends upon the crystalline volume fraction of the silicon in films. It was observed that the bandgap of the materials icreases with the decrease in the size of the quantum dots. ptical bandgap (E_g) may be related to size of the quantum dot ollowing the relation $E_g(\mathrm{eV}) = 1.56 + 2.2/d^2$, where d (in nm) is e size of the dot [6]. This is shown in table 1.

Electronic property of these mixed phase materials can be cplained by the proportion of crystalline volume fraction and at of amorphous fraction. Dark conductivity σ_D of nc-Si:H lm can be expressed as [7] $(\sigma_D - \sigma_a)/(\sigma_D + 2\sigma_a) = (\sigma_c - \sigma_a)/(\sigma_c + 2\sigma_a)$, where σ_a and σ_c are the onductivities of amorphous and crystalline phase respectively, here f_c is the crystalline volume fraction of the material. In one pe of nc-Si films, the neighboring nanocrystallites are separated a distance of 2 to 3 atomic spacing and the volume fraction of ystallinity is high (60 – 80%)[8]. Since crystalline volume action is high *i.e* greater than 60%, σ_c dominates in σ_D and nce conductivity is high > 10^{-5} Scm^{-1}. But in case of another t of samples since the crystalline volume fraction is less *i.e* e nanocrystallites are widely separated by amorphous tissue | So the charge carriers are transferred between the ighboring crystallites by tunneling through the thin norphous tissue. As a result, the dark conductivity of these ms (H1, H2 and H3) are similar to that of amorphous silicon. ourier Transform infrared spectra of all the nc-Si films are ominated by silicon monohydride [9]. So it can be concluded at microstructural defects of all these films are less *i.e* norphous phase is more ordered. At high chamber pressure th high hydrogen dilution, the average energy of electrons creases and large amount of nascent hydrogen is generated the plasma [10]. These energetic hydrogen atoms can supply ge amount of energy to the growing surface and thus formed tructurally relaxed amorphous matrix.

2 *Structural studies :*

ansmission electron micrographs for the films deposited at ferent chamber pressure are shown in Figure 2. In Figure 2(a) erage crystallites size varies from 7 nm. to 10 nm whereas erage crystallite size in Figure 2(b) is 7 nm. The transmission ctron micrographs (TEM) for the set A films have been shown our previous work [11]. Crystalline volume fraction was culated from Raman spectroscopy measurement. Crystalline lume fraction for set B films are also shown in Figure 3. To imate the crystalline volume fraction of the films, all the Raman ectra has been deconvoluted into three spectra. Crystalline lume fraction has been calculated from the simplified empirical ation $X_c = (I_c + I_b)/(I_c + I_b + I_a)$, where I_c, I_b, I_a are the integrated ensities of crystalline, grain boundary and amorphous mponent respectively.

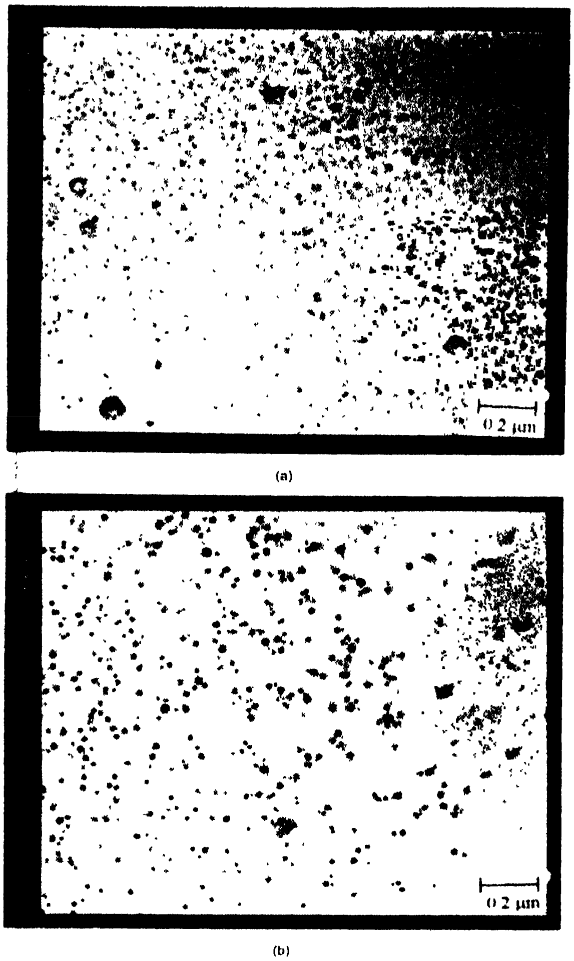

Figure 2. Transmission electron micrographs of nc-Si films deposited at (a) P_r = 2 Torr, (b) P_r = 5 Torr and at a plasma power of 400 mW/ cm^2

3.3 *Degradation studies :*

For application in photovoltaic devices not only the optical and electronic properties but also the stability of these material under prolonged intense light illumination are important. So all these films have been kept under the light of intensity 100 mW/cm^2 for 1000 hours. The light induced degradations of two

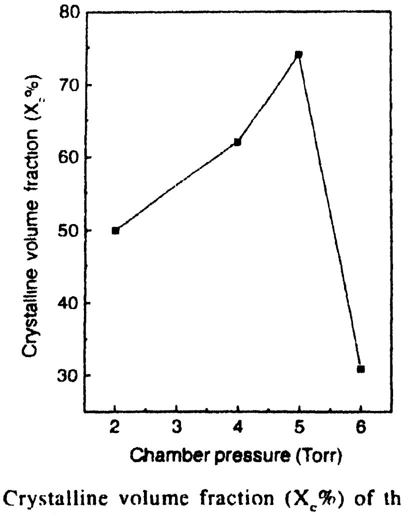

Figure 3. Crystalline volume fraction (X_c%) of the silicon thin films deposited at different pressure.

nanocrystalline Si films have deposited under different pressure and having different crystallinity (X_c) are shown in Figure 4. Degradation of the films deposited at 6 Torr is faster compared to the film prepared at 5 Torr. But both the films stabilises after 10 hours of light soaking. The crystalline volume fraction of the first film is 31% whereas that for the later is 74%. This shows that light induced degradation is dependent on degree of crystallinity. Degradation studies for set A films are shown in our previous paper [12]. It may be mentioned here that amorphous silicon thin films degrades upto 1000 hours of light soaking.

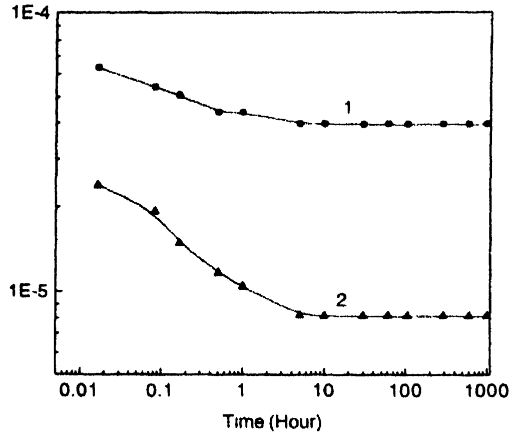

Figure 4. Degradation of photoconductivity with light soaking time for the nanocrystalline silicon films with different crystallinity (1) X_c = 74% and (2) 31%.

3.4 Application in solar cells :

The nanocrystalline silicon thin films have been used as intrinsic layer of single junction thin film solar cell. Structure is simple p-Si/ i-nc-Si/ n-Si deposited one after another on a textured SnO_2:F coated glass substrate. On the structure, Al is deposited as one of the electrodes where as transparent conducting tin oxide serves as another electrode. The current voltage characteristic (I-V) of one of the cells is shown in Figure 5. The nanocrystalline silicon layer acts as the absorber of solar radiation. In one type of cell the low conductivity nc-Si mater [12] was used and in another cell higher conductivity nc material was used. The corresponding open circuit voltage (V short circuit current (I_{sc}), fill factor (*FF*) and efficiency (η), shown in Table 2. In case of the wide bandgap silicon film w low crystalline volume fraction the high V_{oc} has been achiev whereas using highly crystalline silicon material as absor layer low V_{oc} has been realised. Highest efficiency achieve 8.7% for single junction cell and this wide bandg nanocrystalline Si can be used in top cell of double juncti thin film solar cell (nc-Si/ a-Si) to achieve higher efficiency (14%) in near future. The two different bandgaps of nc-Si an Si will help to absorb solar radiation of different wavelen regions and the tandem structure of double junction cell w reduce the light induced degradation.

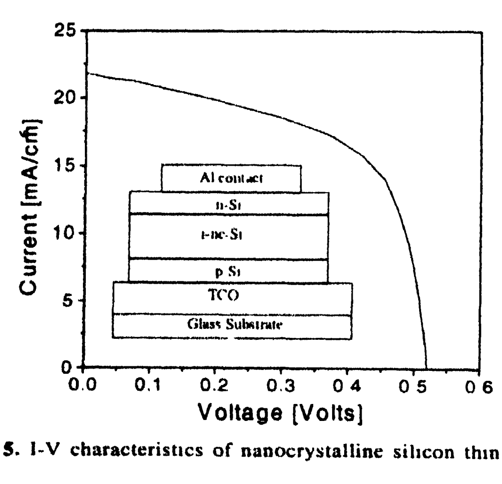

Figure 5. I-V characteristics of nanocrystalline silicon thin film solar cell.

Table 2. Cell performances of single junction solar cells having deposited at different conditions

Sample no.	V_{oc}	I_{sc}	FF	Efficienc
H2	0.93	14.0	0.65	8.7
HP3	0.52	21.8	0.58	6.62

4. Conclusions

Nanocrystalline silicon (nc-Si) thin films have been develo by plasma enhanced chemical vapour deposition at differ parametric conditions. Optical gaps of these nc-Si films va from 1.8 eV to 2.09 eV depending upon the deposition conditio The grain sizes of these materials as observed from TEM stud varies from 7 to 10 nm. Degradation studies of these films h shown that the material is much stable compared to amorph silicon. Performances of single junction solar cell having th Si as absorber layer shows the feasibility of the materials application in photovoltaic devices. It is expected to achi high efficiency using the high bandgap nc-Si one of the cell multijunction thin film solar cell.

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