

## Preparation of undoped and phosphorus doped $\mu\text{c-Si:H}$ films : effect of extended period of hydrogen plasma annealing in interrupted growth

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**Abstract** Interrupted growth and H-plasma annealing of stacking layers of Si:H film resulted in a significant improvement in material properties towards microcrystallization. Increase of dark conductivity and reduction of optical absorption due to extended period of hydrogen plasma exposure as noted. An associated improvement in the network structure towards crystallinity was observed by Raman, TEM and XRD studies. Highly conducting ( $\sigma_D \sim 6 \times 10^{-1} \text{ s. cm}^{-1}$ ) undoped  $\mu\text{c-Si:H}$  films have been prepared at significantly low thickness of 650 Å. P-doped  $\mu\text{c-Si:H}$  films having conductivity  $\sim 26.2 \text{ S.cm}^{-1}$  were obtained from very low level of PH<sub>3</sub> dilution. Large number of dopants introduce additional defects at the grain boundary and inhibits the crystallization process.

**Keywords** Interrupted growth, H-plasma annealing, phosphorus doping

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### 1. Introduction

Microcrystalline silicon ( $\mu\text{c-Si:H}$ ) materials processing has become enormously important because of the significant use of the material in the thin film technologies such as solar cells and thin film transistors. Amorphous hydrogenated silicon (a-Si:H) based solar cell technology is now-a-days getting considerable attention for large area, low cost photovoltaic applications. The basic structure is *p-i-n* junction of which *i*-layer is the active layer where photo-carriers are generated. The doped *p*- and *n*-layers act as collector of photo-carriers generated in the *i*-layer. But due to the low carriers mobilities and low doping efficiencies of the a-Si:H material, the conductivities of such amorphous doped layers are relatively poor as compared to their crystalline counterpart. This limits the performance, particularly the open circuit voltage, of purely a-Si based solar cells. Doped microcrystalline silicon, on the other hand, stands as a very effective alternative of its amorphous counterparts because of its much improved optoelectronic properties and its compatibility with the low temperature PECVD process [1-3]. However, very thin layers of  $\mu\text{c-Si}$  films ( $\leq 300 \text{ \AA}$ ) are required for this purpose in order to reduce current loss due to photo-absorption and

carrier recombination in the layers. But the crystallinity in the films, in general, maintains a sharp trade-off relation with its thickness in the lower limit [4]. Proper optimization of deposition parameters for obtaining an improved microcrystallinity at a very low thickness in silicon films is a challenging task.

The most stringent parametric conditions required for the growth of  $\mu\text{c-Si:H}$  films are high hydrogen dilution to SiH<sub>4</sub> and high RF power applied to the electrodes in RF PECVD process [5]. Both the parameters provide an atomic H-rich SiH<sub>4</sub> plasma in RF glow discharge. Thus, the predominant role of atomic H has been well recognized in controlling the microcrystallization in Si-network. Growth interruption and H-plasma exposure on the stacking layers in Layer-by-Layer (LBL) growth scheme is an efficient technique to provide enhanced atomic H reactivity by its presence through an extended period of time at the vicinity of the growing surface [6, 7]. In view of maintaining the crystallinity of Si films within very narrow thickness, the LBL growth process could have its novelty by extending its independent parameter, namely, the dose of H-plasma exposure, compared to other existing process [8]. We, hereby, report the development of highly conducting undoped and doped  $\mu\text{c-Si:H}$  films within a narrow thickness using this LBL growth scheme.

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## 2. Experimental

Films were prepared in a capacitively coupled RF glow discharge single chamber reactor at a microcrystalline-like growth condition. Steady H-plasma was attained from a constant flow of  $H_2$  at an RF power density of  $150 \text{ mW/cm}^2$ . At a substrate temperature of  $200^\circ\text{C}$ , a thin layer of Si:H film was grown by introducing  $SiH_4$  into the plasma, and the growth was interrupted periodically by terminating the  $SiH_4$  flow at regular intervals. During the period of growth interruption, the already grown layer ( $L \text{ \AA}$ ) was allowed to be exposed to continuous and steady H-plasma for a fixed period of time  $t_p$ . For the preparation of P-doped  $\mu\text{-Si:H}$  films, the dopant gas  $PH_3$  was introduced with the same period as the  $SiH_4$  flow. The flow synchronization was maintained with the help of pneumatic valves controlled by electronic timers. The schematic diagram of the gas flow modulation has been presented in Figure 1, where  $t_D$  and  $t_p$  corresponds to the time-period of deposition and plasma exposure respectively during one cycle of LBL growth. The cycle was repeated several times ( $n$ ) to obtain stacked layer films with thickness,  $d = L \times n \text{ \AA}$ . Samples were prepared on Corning 7059 glass substrates for optoelectronic studies and on Si wafers for infrared-absorption, Raman scattering and X-ray diffraction studies in the same deposition run. For electron-transmission and diffraction studies, films were deposited on carbon-coated copper microgrids by separate deposition runs.

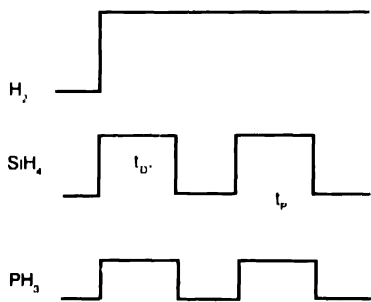


Figure 1. Schematic diagram of gas flow modulation

## 3. Results and discussion

A set of films were prepared by changing the plasma exposure time ( $t_p$ ) keeping the stacking layer thickness ( $L$ ) fixed at around  $20 \text{ \AA}$ , corresponding to one-cycle deposition period ( $t_D$ ) of  $60 \text{ s}$ . Care has been taken to maintain a uniform thickness of the stacked layer films at  $700 \pm 100 \text{ \AA}$ . Figure 2 shows the variation of dark conductivity  $\sigma_D$  and its activation energy  $\Delta E$  with  $t_p$ . The continuously growth film (at  $t_p = 0$ ), had a  $\sigma_D = 2.0 \times 10^{-6} \text{ S.cm}^{-1}$  and corresponding  $\Delta E = 410 \text{ meV}$ . Introduction of growth interruption and extended period of plasma exposure resulted in a continuous increase in  $\sigma_D$  along with corresponding reduction in  $\Delta E$ , which together signifies improvement of crystallinity in the Si-network. At  $t_p = 60 \text{ s}$ , we obtained a thin undoped  $\mu\text{-Si:H}$  film having considerably high  $\sigma_D = 6.0 \times 10^{-3} \text{ S.cm}^{-1}$  and a very low  $\Delta E = 136 \text{ meV}$ . The result demonstrates a significant improvement in the electrical

conductivity, by more than three orders of magnitude over that of continuously deposited films, due to H-plasma exposure on stacking layers.

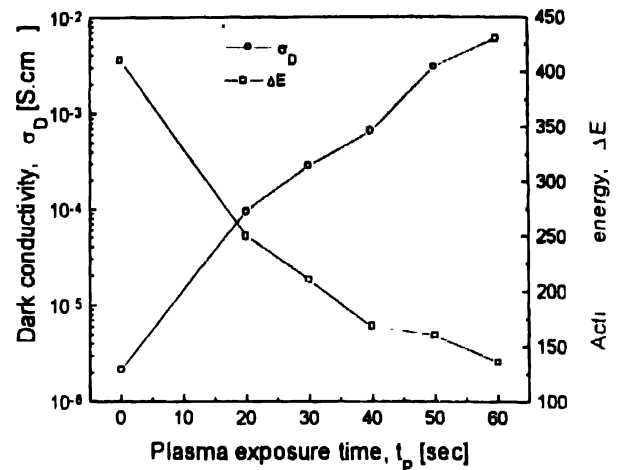


Figure 2. Changes of dark conductivity ( $\sigma_D$ ) and its activation energy ( $\Delta E$ ) of the Si:H films due to extended period of plasma exposure or stacking layers in LBL growth

The optical density data of the samples was obtained from the absorption and reflection measurements in the UV-VIS region by a double beam spectrophotometer. Figure 3 represents the absorption coefficient spectrum of the films prepared at different plasma exposure time ( $t_p$ ). A gradual reduction in the visible absorption ( $\alpha$ ) was pronounced for samples exposed to H-plasma for longer period of time. Such reduction of optical absorption due to extended period of hydrogen plasma annealing is a result of lowering in the volume fraction of amorphous tissue in improved  $\mu\text{-Si:H}$  network. The systematic decrease of amorphous composition, or in other words, increase of microcrystallinity indicated by the lowering of optical absorption resembles the increase of  $\sigma_D$  of the films and that signifies a definite nature of changes in the network structure towards improved microcrystallization at higher  $t_p$ .

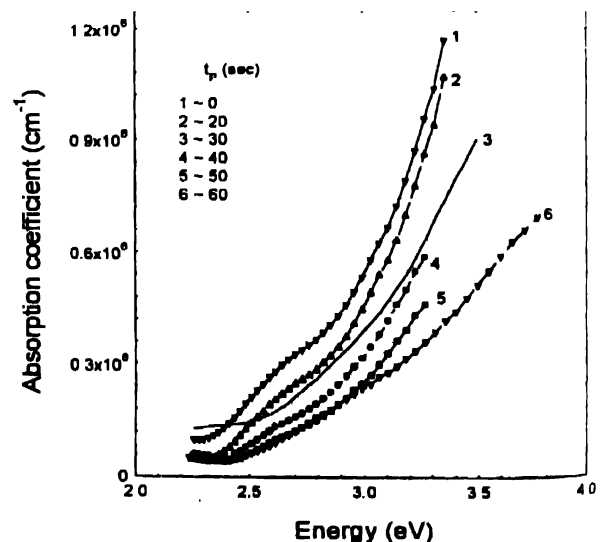


Figure 3. Optical absorption coefficient spectra of Si:H films prepared at different plasma exposure times ( $t_p$ ) in the LBL growth

The improvement in microcrystalline network has been clearly demonstrated by Raman spectra presented in Figure 4. It was observed that at  $t_p = 0$  s, there was a significant component of amorphous tissue as evidenced from the presence of extended imp at  $\sim 470 \text{ cm}^{-1}$  which is assigned to TO mode vibration of amorphous silicon. But at  $t_p = 60$  s, amorphous component was very low, rather crystalline component at  $\sim 520 \text{ cm}^{-1}$  increased in intensity along with corresponding reduction of FWHM and

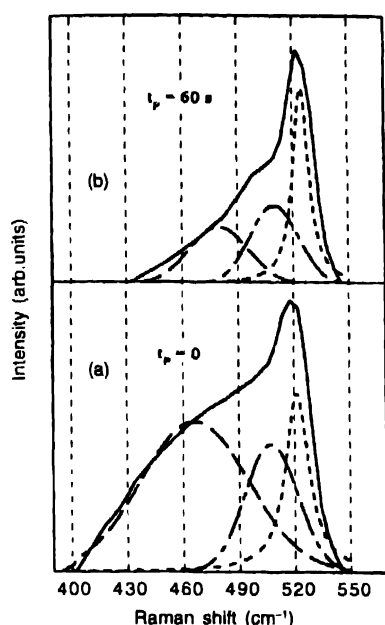


Figure 4. Raman scattering spectra of the  $\mu$ c-Si:H films prepared at (a) continuous mode of deposition ( $t_p = 0$ ) and (b)  $t_p = 60$  s and  $t_p = 60$  s in LBL growth technique

indicated increased microcrystallinity of the material. To get a numerical estimation of volume fraction of crystallinity, we deconvoluted each spectrum into three satellite spectra. The integrated intensity of the components were assigned to I(a) for amorphous, I(c) for crystalline and I(b) for intermediate one with peak at  $\sim 500 - 510 \text{ cm}^{-1}$ . This intermediate component is ascribed to crystalline phase of such mixed phase materials but the origin is still controversial. Mavi *et al* [9] and He *et al* [10] associated this component in the Raman spectra to the thermodynamically stable micrograins of size in the range  $\leq 30 \text{ \AA}$ . According to another school of thought, a possible explanation for its occurrence is the presence of a local wurtzite structure which can be caused by twin boundaries or stacking faults [11]. We calculate the net crystalline volume fraction from the empirical relation

$$X_C = [I(c) + I(b)] / [I(a) + I(b) + I(c)]. \quad (1)$$

The crystalline volume fraction increased from 44% to 72% with the increase of  $t_p$  from 0 s to 60 s.

Crystallinity of the film was identified by Transmission electron microscope (TEM) studies. Figure 5(a) demonstrates TEM features of the film prepared at  $t_p = 0$  s. A low density and almost homogeneous distribution of very small micrograins, with

70-200  $\text{\AA}$  in diameter, was found to be embedded in the amorphous network. The corresponding electron-diffraction pattern has been shown in Figure 5(b), in which crystallographic

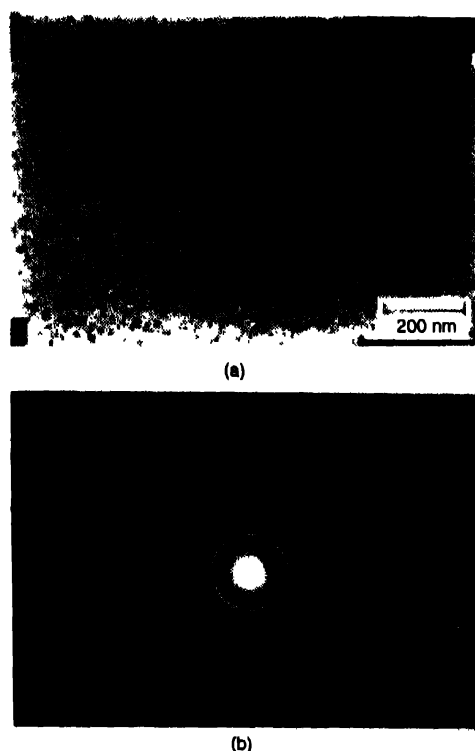


Figure 5. (a) TEM micrograph and (b) Electron diffraction pattern of  $\mu$ c-Si:H film prepared in continuous mode of deposition ( $t_p = 0$ )

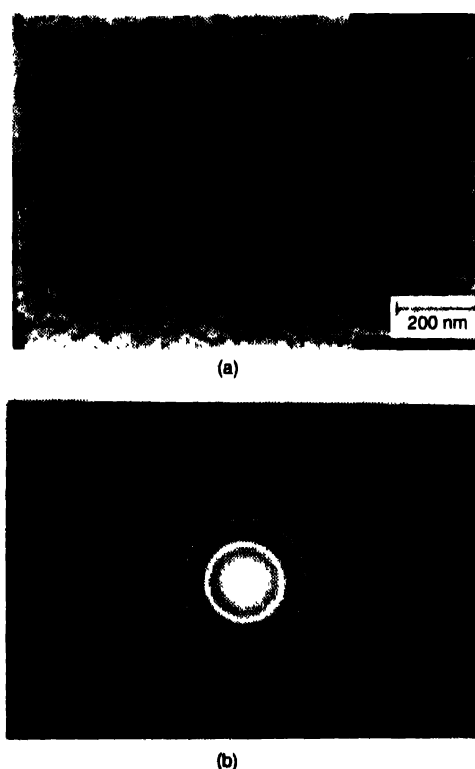


Figure 6. (a) TEM micrograph and (b) Electron diffraction pattern of  $\mu$ c-Si:H film prepared by the LBL growth technique at  $t_p = 60$  s and  $t_p = 60$  s.

rings associated to (111), (220) and (311) planes of c-Si has been depicted. The grain size as well as its number density increased in the film prepared at  $t_p = 60$  s. A uniform and dense distribution of crystallites with a diameter ranging from 150 – 400 Å was revealed as shown in Figure 6(a). Crystallographic rings in the electron diffraction pattern (Figure 6(b)) identified (400), (311) and (422) planes of c-Si in addition to the planes mentioned above. Due to the enhanced dose of plasma exposure, an improved microcrystallization in the network has been clearly observed from the TEM studies.

Structural investigation of the highest conducting film has been performed by X-ray diffraction (XRD) studies also. X-ray diffraction spectrum for the film prepared at  $t_p = 60$  s, has been presented in Figure 7. Presence of (111) and (220) planes of c-Si was observed. The observed planes exactly corroborated the transmission electron diffraction (TED) results, though other planes those obtained in TED pattern were not visible because of lower sensitivity of XRD at very low thickness of the film used in the study. The intensity of the observed peaks was very low due to similar reason and the grain size could not be estimated from the associated FWHM.

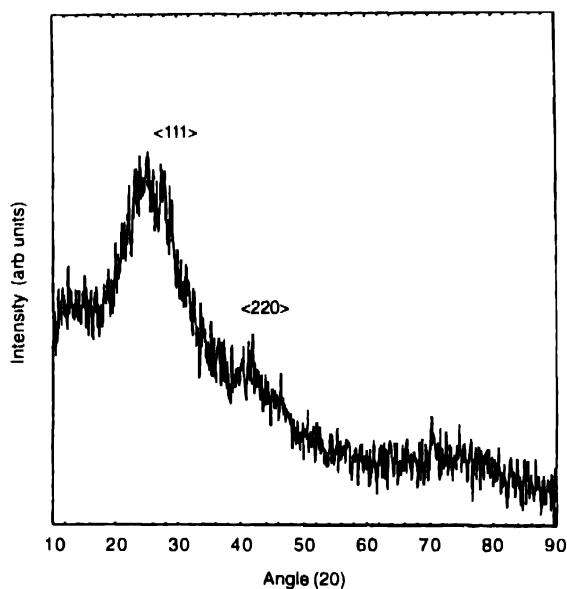


Figure 7. X-ray diffraction pattern of  $\mu\text{c-Si:H}$  film prepared at  $t_p = 60$ s at a low thickness of 650 Å

The Layer-by-Layer growth process was utilized to prepare doped  $\mu\text{c-Si:H}$  films. With a stacking layer growth condition of  $t_D = 60$  s and  $t_p = 30$  s, a set of doped  $n$ -type  $\mu\text{c-Si:H}$  films were prepared by varying  $\text{PH}_3/\text{SiH}_4$  ratio in the plasma down to a minimum magnitude of 0.10%, as determined by the instrumental limitation. The film thickness was maintained at  $< 1000$  Å. Figure 8 shows the variation of dark conductivity and its activation energy as a function of  $\text{PH}_3/\text{SiH}_4$  ratio. The most conducting ( $\sigma_D = 26.2 \text{ S.cm}^{-1}$ ) doped  $\mu\text{c-Si:H}$  film was grown from the lowest dopant concentration. Higher doping ratio, however, introduced additional defects in the network leading to an almost

linear reduction in  $\sigma_D$  with the increase in  $\text{PH}_3/\text{SiH}_4$  ratio. The associated minimum in activation energy ( $\Delta E = 16.4 \text{ meV}$ ) was in conformity with regular trend.

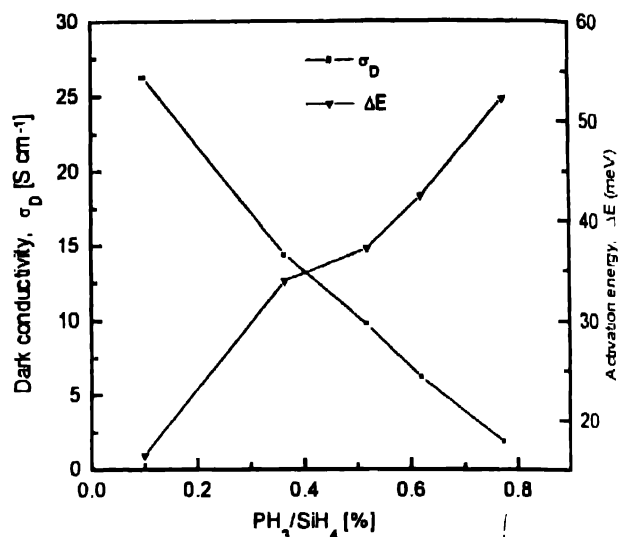


Figure 8. Doped  $\mu\text{c-Si:H}$  films, prepared by LBL growth exhibiting higher conductivity and lower activation energy at lighter dopant dilution in the plasma

The optical absorption coefficient spectra were obtained for the films having different dopant concentrations. To get a comprehensive view regarding the change of optical density data, the absorption coefficient ( $\alpha$ ) was compared at a relatively high energy of 2.9 eV, at the interference free region. Figure 9 shows the variation of  $\alpha$  (at 2.9 eV) and optical gap ( $E_g$ ) as determined from Tauc's plot for the films with increasing dopant concentration. The films with lower dopant concentration exhibited lower optical absorption and higher optical gap. Higher dopant concentration giving rise to higher optical absorption and lower optical gap indicated increased defects in the material

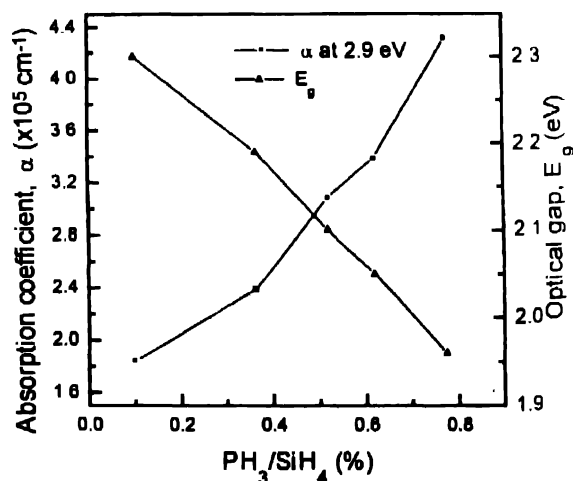


Figure 9. Changes of optical absorption coefficient ( $\alpha$ ) at 2.90 eV and optical gap ( $E_g$ ) of the P-doped  $\mu\text{c-Si:H}$  films with dopant dilution  $\text{PH}_3/\text{SiH}_4$ .

The bonded hydrogen content ( $C_H$ ) in the films was estimated from the infrared absorption spectrum in the wagging

mode vibration of Si-H bonds. Figure 10 shows the variation of H-content with the  $\text{PH}_3/\text{SiH}_4$  ratio. The films prepared at lower  $\text{PH}_3/\text{SiH}_4$  ratio possess lower amount of bonded hydrogen (11.8 at %) in the network. However, the absolute magnitude of the bonded hydrogen content appears to be significantly high even in the highly conducting doped microcrystalline film. Increase of bonded hydrogen content with the increase of  $\text{PH}_3/\text{SiH}_4$  ratio indicates the deviation of the network from microcrystallinity. Large amount of dopants may introduce additional defects at the grain boundary and inhibits the crystallization process.

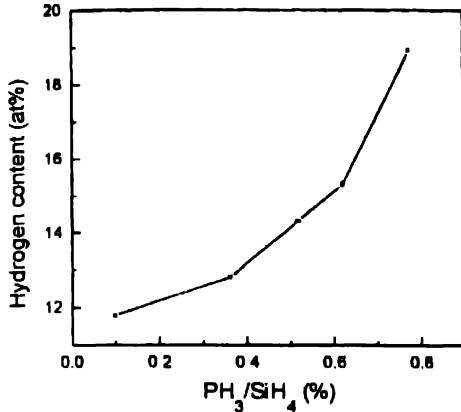


Figure 10. Variation of hydrogen content ( $C_H$ ) of the  $n$ -type  $\mu c$ -Si:H films as a function of dopant dilution in the plasma

The LBL growth technique conclusively helps to expedite the crystallization process and it provides good microcrystallinity at a very low thickness, which could be lowered further by extending the period of plasma exposure. The growing surface of the film at the growth zone [12, 13] is supposed to remain at a quasi-equilibrium state when it is highly reactive to atomic hydrogen compared to the bulk of the material. The equilibrium and kinetics at the growing solid surface and plasma boundary could be smoothly controlled with the assistance of a chemical mediator such as atomic hydrogen, because of the strong chemical reactivity as well as diffusivity of monoatomic hydrogen in Si network [14, 15]. The chemical reactivity of atomic H in the plasma may influence in modulating the structure through its reaction with and redistribution of weak and broken Si bonds. The stable structure is formed when there is sufficient hydrogen mobility to complete the reaction of elimination of excess hydrogen and reduction of disorder structure [16]. The effect of extended period of hydrogen plasma exposure can be explained by considering subsurface zone reaction by atomic hydrogen. The penetration depth of atomic hydrogen during H-plasma treatment is determined by its diffusion length ( $L_D$ ) into the network and is related to the diffusion coefficient  $D$  as [17]

$$L_D = (4Dt)^{1/2} \quad (2)$$

At a specific parametric condition, the diffusion coefficient ( $D$ ) is fixed but  $L_D$  increases with the increase of plasma exposure time  $t = t_p$ . When the stacking layer thickness is of the order of diffusion length i.e. at  $L \sim L_D$ , the one way atomic H reaction

should be complete and structural modulation and/or removal of disorder state should reach its saturation level, resulting in the highest degree of ordering of the material. So keeping stacking layer thickness fixed, when  $t_p$  was increased, a large number of nuclei were formed, and on repetition of deposition and plasma exposure a high-density microcrystalline film was produced. Increase of microcrystallinity with plasma exposure time was evident from sharp rise of  $\sigma_D$  and associated reduction of  $\Delta E$ . The reduction of disordered material resulted in lowering of optical absorption in the UV-VIS region. Enhancement of degree of crystallinity due to increase of  $t_p$  is also confirmed by Raman scattering spectra and TEM study.

The films prepared with this technique exhibited very high doping efficiency. The highly conducting  $n$ -type  $\mu c$ -Si:H has been achieved at a  $\text{PH}_3/\text{SiH}_4 \sim 0.10\%$ . Higher doping ratio in the gas mixture introduced additional defects in the material as evident from the increase of optical absorption and bonded hydrogen content, correlated with the deterioration of electrical properties.

#### 4. Conclusions

Layer-by-Layer growth and H-plasma exposure on the growing surface contributed a significant enhancement in the optoelectronic and structural properties of undoped and doped  $\mu c$ -Si:H films prepared by RF glow discharge. The atomic H of the plasma reacts from the surface into the bulk through the growth zone. This LBL growth process allows the growth zone to remain exposed to the H-plasma for an extended period of time, expedites the crystallization process compared to the continuous mode of deposition and initiates microcrystallization of the network at a considerably low film thickness. Increase of dark conductivity and reduction of optical absorption due to extended period of hydrogen plasma annealing was noted. An associated improvement in the network structure towards crystallinity was observed by Raman, TEM and XRD studies. The highest conducting undoped film ( $\sigma_D \sim 6 \times 10^{-3} \text{ S.cm}^{-1}$  and  $\Delta E \sim 136 \text{ meV}$ ) was obtained at a stacked layer thickness of 650 Å. LBL growth and H-plasma exposure on the growing surface enhanced the doping efficiency in the Si-network. P-doped  $\mu c$ -Si:H films exhibited a  $\sigma_D = 26.2 \text{ S.cm}^{-1}$  along with low  $\Delta E = 16.4 \text{ meV}$ , when prepared at a very low dopant dilution of  $\text{PH}_3/\text{SiH}_4 = 0.10\%$  to the plasma. Large number of dopants introduced additional defects at the grain boundary and inhibited the crystallization process. The Layer-by-Layer growth and H-plasma exposure basically appears to be a process of network modulation by plasma highly diluted in hydrogen, extended in the time-space.

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