

## Reduction of microstructures in amorphous silicon by Ar dilution : Influence on stability of solar cells

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**Abstract:** The hydrogenated amorphous silicon thin films have been developed by Ar dilution in rf plasma enhanced chemical vapour deposition. The change in film microstructure is associated with the metastable Ar bombardment to the growth surface. The microstructural heterogeneity in the intrinsic amorphous silicon film is liable to cause the light induced degradation of electron transport in films as well as in p-i-n solar cells.

**Keywords :** Microstructure, Light induced degradation, Solar cell

**PACS Nos. :** 81.15.Gh, 81.40.-z, 73.40.Lq

### 1. Introduction

It is believed that the amorphous silicon based p-i-n single junction solar cell degrades considerably under prolonged light illumination owing to the degradation of electronic properties of the intrinsic (i) amorphous silicon material. In that context several models have been proposed for the light induced instability in a-Si:H [1,2]. Model proposed by Stutzmann *et al* [2] explains that the dangling bond density in the material increases due to breaking of the weak Si-Si bonds into two dangling bonds by taking energy from non radiative recombination of photo excited carriers. The hydrogen bonded in vicinity of the weak bond plays a crucial role in stabilizing this process. The increase of hydrogen content in the film is associated with the increase of microstructure parameter R which is defined by  $R = \frac{I_{2080}}{I_{2000} + I_{2080}}$ , where  $I_{2000}$  and  $I_{2080}$  are the areas under the deconvoluted IR absorption spectra at wave numbers  $2000\text{cm}^{-1}$  and  $2080\text{cm}^{-1}$  corresponding to the stretching modes of SiH and SiH<sub>2</sub> respectively [3]. The increase of R consequently enhances the light - degradation of the material.

In this study we have developed intrinsic amorphous silicon material using Ar as a diluent gas in rf glow discharge decomposition of silane (SiH<sub>4</sub>).

The microstructures in the film as estimated from IR and Small Angle X-ray Scattering study, varies with Ar dilution. The light-degradation of electronic quality of a-Si:H films and performance of solar cells seem to have some correlation with the microstructure in the material.

## 2. Experimental

The a-Si:H films and single junction solar cells were prepared in a capacitively coupled rf (13.56 MHz) glow discharge chamber with background pressure of  $\sim 10^{-9}$  Torr. The other deposition parameters for a-Si:H films and the i-layer of *p-i-n* solar cells are the rf power density,  $35\text{mW/cm}^2$ ; pressure, 0.5Torr and substrate temperature,  $250^\circ\text{C}$ . The Ar dilution was varied from 0% (undiluted) to 99%. The films on Corning 7059 glass substrates were used for studying degradation of photoconductivity under white light illumination (intensity of  $100\text{mW/cm}^2$ ). The single junction *p-i-n* solar cell was fabricated with i-layer deposited by Ar dilution on TCO coated glass substrates. The solar cell efficiency and the fill factor was obtained from *I-V* curve under a class 'A' solar simulator (WACOM) with AM1.5G insolation. High purity Al foil was used as a substrate for studying SAXS. The samples on crystalline Si(111) wafer were used for IR study.

## 3. Results

The total bonded hydrogen content ( $C_H$ ) in a-Si:H material was calculated from the integrated intensities for Si-H wagging mode centered at  $630\text{cm}^{-1}$ .

**Table 1.** Variation of bonded hydrogen content ( $C_H$ ) and microstructures as estimated from IR (R) and SAXS (Q) study.

Argon diln(%)	$C_H$ (at%)	R	Q ( $10^{22}\text{cu/cm}^3$ )
0	7.0	0.13	6.0
85	19.6	0.10	2.2
90	18.7	0.095	1.2
95	22.0	0.07	3.8
99	35.7	0.17	11

in IR spectra. The value of  $C_H$ , microstructure parameter R and the integrated SAXS intensity Q at different Ar dilutions are listed in Table-1. The value of Q is obtained from the relation [4],

$$Q = \int q I_N(q) dq$$

where  $q$  is the scattering vector ( $q = \frac{(2\pi)(2\theta)}{\lambda}$ ,  $\lambda$  is the wavelength of incident X-ray) and  $I_N(q)$  is the X-ray scattering intensity due to the nanostructural features of size range between 1 – 30nm for a particular  $q$ . Thus the total integrated SAXS intensity  $Q$  reflects the electron density variation on nano scale. The hydrogen content increases significantly with the addition of Ar in the plasma (from 7at% for undiluted to ~ 20at% for the Ar diluted a-Si:H) (Table-1). The amount of microstructures as predicted from SAXS ( $Q$ ) and  $IR(R)$  exhibit a gradual decrease with Ar dilution up to 90 – 95%. Thus an appreciable improvement in structural heterogeneity (in terms of microstructures) of a-Si:H films can be achieved by varying Ar to SiH<sub>4</sub> ratio. However, further increase of Ar dilution is associated with the increase in  $C_H$ ,  $R$  [5] and  $Q$ .

Degradation of photoconductivity ( $\sigma_{ph}$ ) of a-Si:H films is found to be very much dependent on microstructures in the material. The degradation of  $\sigma_{ph}$  and hence the device parameters of single junction  $p-i-n$  solar cell fabricated using the material as an  $i$ -layer increases with the increase of  $Q$ . In figure 1 we have shown changes in the values of photoconductivity ( $\sigma_{ph}$ ), efficiency ( $\eta$ ) and fill factor (FF) on 1000hrs light soaking by the ratio of the light soaked values (with 's' within the parenthesis) of these parameters to their initial values (with 'i' within the parenthesis) with respect to microstructure parameter  $Q$ . Stability of these parameters for material and solar cell decreases as  $Q$  of the undoped layer increases.

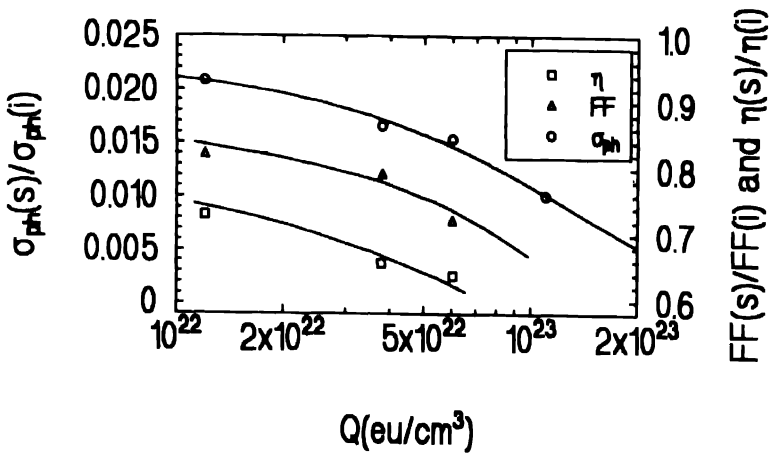


Figure 1. The stability parameters of material ( $\sigma_{ph}(s)/\sigma_{ph}(i)$ ) and solar cell ( $\eta(s)/\eta(i)$  and  $FF(s)/FF(i)$ ) as a function of  $Q$ .

#### 4. Discussion

In the plasma Ar is fractionally raised to the excited state  $Ar^*$  ( $^3P_{0,2}$ ) and ionised state  $Ar^+$  by collision with electrons. Reaction rates of  $Ar^*$  and  $Ar^+$  with  $SiH_4$  are  $2.6 \times 10^{-10} \text{ cm}^3/\text{sec}$  and  $1.18 \times 10^{-11} \text{ cm}^3/\text{sec}$  respectively. Equilibrium densities of  $Ar^*$  and  $Ar^+$  in the plasma depend upon  $SiH_4$  to Ar flow ratio. The density of  $Ar^*$  rises gradually with increase in Ar dilution up to 90% and beyond that it rises sharply [6]. On the other hand, density of  $Ar^+$  remains almost constant over the entire range of Ar dilution. Bombardment of the growing film by  $Ar^*$  and  $Ar^+$  also varies in the same manner with Ar dilution. It was argued that bombardment of  $Ar^*$  on the film surface is much softer than that of  $Ar^+$ .  $Ar^*$  impinges the film surface with thermal velocities and gives its excess energy to the growth zone while deexcitation. This energy is absorbed by the lattice and is used in the formation of more compact network. On the other hand, bombardment by  $Ar^+$  being assisted by the coulombic attraction of the anode is a violent process and creates more defects. The  $Ar^*$  bombardment to the growth surface reduces the number of weak Si-Si bonds and consequently the electron density fluctuations (heterogeneity) in the material which decreases the value of  $Q$ . Moreover the increase of bonded hydrogen for Ar diluted films indicate that an appreciable amount of broken weak Si-Si bonds are passivated by hydrogen. The excess energy released by  $Ar^*$  may also lead the weak Si-Si bonds to reconstruct into stronger Si-Si bonds. Both the processes result in an ultimate decrease of microstructures ( $Q$  and  $R$ ) in the film. At high Ar dilution ( $> 90\%$ ) the enormous rise in  $Ar^*$  bombardment on to the growth surface helps some regions to grow denser (more ordered network with strong Si-Si bonds) which are devoid of hydrogen. However, the boundary of these dense regions consists a lot of hydrogen and structural defects. As a consequence the heterogeneity in the film and hence the value of  $Q$  at high Ar dilution increases.

The detrimental effect of these nanostructural features in a-Si:H material is evident from fig.1. As the value of  $Q$  increases the light induced degradation of photoconductivity of a-Si:H material increases. The surfaces of nanostructures contain lot of clustered monohydride or dihydride which eventually weaken the nearby Si-Si bonds. This increase of weak bonds causes an enhanced instability of photoconductivity of the film in conformity with the Stutzmann's bond breaking model [2]. Thus there appears an apparent relation between light induced instability in a-Si:H film and the amount of microstructural features in the film. The enhanced degradation of intrinsic a-Si:H layer under light illumination effectively reduces the short circuit current density and the fill factor of single junction  $p - i - n$  solar cell. Thus the stabilised solar cell effi-

ciency can be significantly improved by reducing the heterogeneity in intrinsic (active) layer.

## 5. Conclusions

(1) The microstructures in a-Si:H films as determined from Infra Red study and small angle X-ray scattering techniques, can be reduced significantly by using Ar as a diluent in plasma enhanced chemical vapour deposition.

(2) The variation of microstructure with Ar dilution can be explained on the basis of variation in  $Ar^+$  bombardment on to the growth surface.

(3) The reduction of film microstructure leads to less light induced degradation in the material properties as well as the solar cell device performance.

## Acknowledgements

The authors are grateful to Dr. Don Williamson, Colorado School of Mines, USA for measuring SAXS of our samples and Prof. A. K. Barua, Energy Research Unit, IACS for constant encouragement in completing this work. One of the author(UKD) acknowledges the financial support from CSIR, India.

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