JOURNAL OF MATERIALS SCIENCE **34** (1999) 1051 – 1054

Improvement in the optoelectronic properties of a-SiO:H films

DEBABRATA DAS*, S. M. IFTIQUAR, DEBAJYOTI DAS, A. K. BARUA
Energy Research Unit, Indian Association for the Cultivation of Science, Jadavpur, Calcutta-700 032, India

Hydrogenated amorphous silicon oxide (a-SiO:H) films prepared by rf plasma enhanced chemical vapour deposition (PECVD) method have recently proved their potential as a photovoltaic material for the fabrication of high efficiency multijunction amorphous silicon solar cells. If deposited under proper conditions, it may be a better wide band gap material than the normally used a-SiC : H. In this paper we report the improvements achieved over the previously reported results. The films have been characterized in detail in terms of their optoelectronic properties, structural characteristics, defect density and light induced degradation. © *1999 Kluwer Academic Publishers*

1. Introduction

It is now accepted that to achieve high efficiency a-Si solar cells it is necessary to fabricate multigap multijunction structures. The top cell should have a high quality wide band gap active material. Mostly a-SiC:H has been used for this purpose. Wide band gap a-Si:H films have also been produced but high efficiency multijunction cells have not yet been fabricated using this material. More recently a-SiO:H films have been used with reasonable success [1, 2].

Investigations on the structural properties of a-SiO:H films was done by Morimoto *et al.* [3]. They claimed that a-SiO:H is not inferior than a-SiC:H as wide optical gap material for application in a-Si solar cells. Suchaneck *et al.* [4] reported the presence of a clustered O-rich phase detected by IR absorption in a-SiO:H films having an oxygen content as low as 0.4 at % deposited by magnetic field enhanced PECVD. Sichanugrist *et al.* [5] deposited p-type and n-type amorphous silicon oxide films with a microcrystalline silicon phase by plasma CVD and found that it is easier to make these films microcrystallized than a-SiC:H films. Watanabe *et al.* [6] proposed a two-phase structure model for the a-SiO:H films, a silicon-rich phase and an oxygen-rich phase. They suggested that the oxygen rich phase is effective in increasing the optical gap of the films, while photogenerated carriers travel mostly through the silicon rich phase. Using p-type a-SiO:H as a window layer, Fujikake *et al.* [7] were able to increase the efficiency of multijunction a-Si solar cells.

However, a-SiO:H material is not yet fully understood and there is scope for further improvement. It may be noted that unlike a-SiC:H, a-SiO:H is most probably a two-phase material. Clusters of a-SiO:H in a matrix of a-Si:H is a possible structure. The bonding nature of oxygen with silicon is a key factor in improving the quality of a-SiO:H film.

In a previous paper [8] we have reported the properties of a-SiO:H films prepared by rf PECVD by varying various deposition parameters. By analysing the results so obtained we have tried to optimize further some of these parameters. In this paper we report the improvements in the quality of a-SiO:H films thus obtained. Films are characterized by dark and photoconductivity measurements, optical absorption measurements in the ultraviolet and visible regions, Fourier-transform infrared (FTIR) spectroscopy, constant photocurrent measurements (CPM), electron spin resonance (ESR) measurements and light induced degradation study of photoconductivity.

We have reached the conclusion that low concentration of CO_2, low chamber pressure and optimum hydrogen dilution are conducive to the production of high quality a-SiO:H films.

2. Experiment

The a-SiO:H films were deposited by radio frequency plasma enhanced chemical vapour deposition (RF-PECVD, 13.56 MHz). The anode was heated to maintain substrate temperature at 200 °C. A mixture of $SiH_4 + CO_2 + H_2$ was used as source gas. The gases were of high purity and supplied by Matheson, Inc., USA. The ratio of the CO_2 flow rate to SiH_4 flow rate ($= r_c$) was varied from 0.3 to 1.0 keeping the H_2 flow rate fixed at 85 sccm. The flow of gases was controlled by electronic mass flow controllers. The ratio of H_2 flow rate to SiH_4 flow rates ($= r_h$) was varied from 4.0 to 18.5 keeping the CO_2 flow rate fixed at 4.0 sccm. For all depositions, the SiH_4 flow rate was kept fixed at 10 sccm. The chamber pressure during deposition was varied between 0.16–0.35 Torr and a rf power density of 30 mW/cm^2 was used.

* *Present address*: Department of Physics, Ramakrishna Mission Residential College, Narendrapur-743508, India

The substrates used include Corning 7059 glass (for dark and photo conductivity and optical absorption/transmission measurements) and single crystal silicon wafers (for infra-red absorption measurements). The film thicknesses were above 5000 Å and were measured using a stylus type thickness measuring apparatus (Planar Products, UK). Electrical properties of the films were measured with a coplanar electrode (aluminium) structure. Dark conductivity, σ_d and photoconductivity, σ_{ph} (50 mW/cm^2, white light) measurements were carried out in a cryostat which was pumped down to a pressure of 10^{-6} Torr. The optical absorption measurements in the ultra violet, visible and near infrared regions were carried out with a Hitachi (model 330) double-beam spectrophotometer. Infrared (IR) vibrational spectroscopy was performed with a Perkin-Elmer (model 1750) Fourier transform infrared (FTIR) spectrophotometer. The hydrogen contents of the films were calculated from the Si-H stretching mode of the IR absorption spectra. The oxygen contents of the films were calculated from the absorption peak due to Si-O-Si stretching vibration at ~1030 cm^{-1} [9, 10].

The electron spin resonance (ESR) measurements were carried out with a JEOL JES-RE1X spectrometer in the X-band and at room temperature. The total spin density (N_s) was calculated with respect to a standard pitch material (Picein 80). The constant photocurrent measurements (CPM) were carried out to find the valence band tail width.

For the light induced degradation studies, films were exposed to white light at an intensity of 100 mW/cm^2, using a TCO coated glass as IR filter to reduce the heating effect and subsequent defect annealing of the films. The photoconductivity values were then monitored with 50 mW/cm^2 white light at regular time intervals upto 100 hr of light soaking.

3. Results and discussion

Fig. 1 shows the variation of photoconductivity (σ_{ph}) at 300K with r_c (= CO_2/SiH_4) at a chamber pressure, p = 0.16 Torr. It is seen that with increase in r_c, σ_{ph} decreases almost exponentially from 5×10^{-5} Scm^{-1} for $r_c = 0.3$ to 4.4×10^{-7} Scm^{-1} corresponding to $r_c = 1.0$. Fig. 2 shows the variation of optical gap (E_g, Tauc gap) of the films with r_c. E_g increases slowly with r_c in the range of $r_c = 0.3$–0.6, beyond which the increase is quite sharp for the increase of r_c upto 1.0.

Fig. 3 shows the variation of photoconductivity (σ_{ph}) with the variation of r_h (= H_2/SiH_4) for $r_c = 0.4$. With the increase in H_2 dilution, E_g increases (Fig. 4) and σ_{ph} decreases. The optical gap of the films (E_g) increases from 1.9 eV to 2.0 eV with the increase in r_h from 4 to 18.5 (Fig. 4).

Fig. 5 shows the variation of σ_{ph} with optical gap E_g for the set of films deposited at various r_c with $r_h = 8.5$. It is seen that σ_{ph} decreases exponentially from 5×10^{-5} Scm^{-1} to 4.4×10^{-7} Scm^{-1} for a change in E_g from 1.93 eV to 2.06 eV. In Fig. 5 we have compared the σ_{ph} values (plotted against E_g) obtained by us with those reported previously by others [1, 3] for

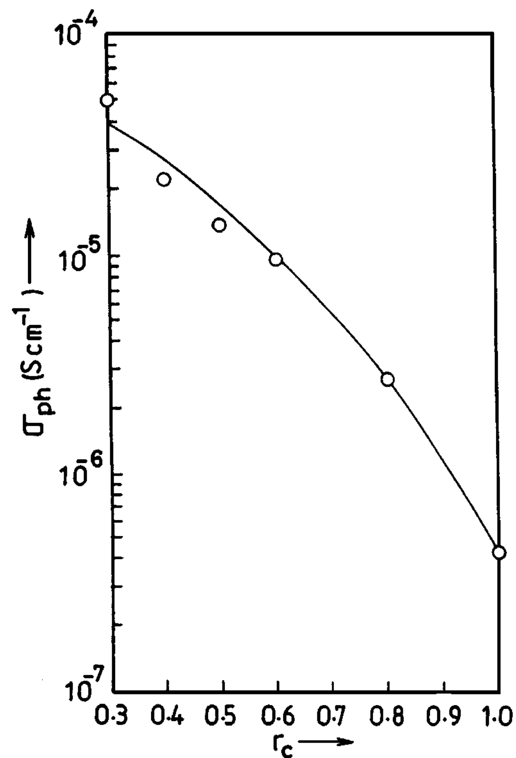

Figure 1 Variation of photoconductivity (σ_{ph}) with r_c at $r_h = 8.5$.

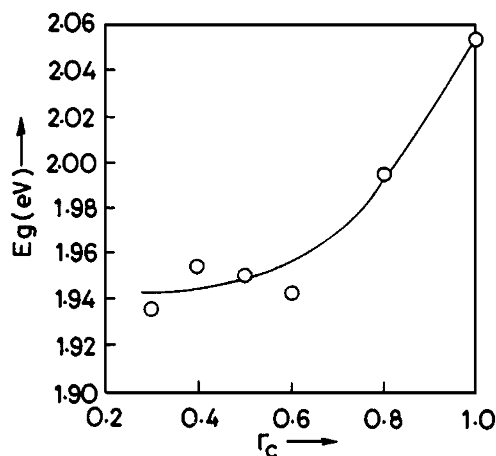

Figure 2 Variation of optical gap (E_g) with r_c at $r_h = 8.5$.

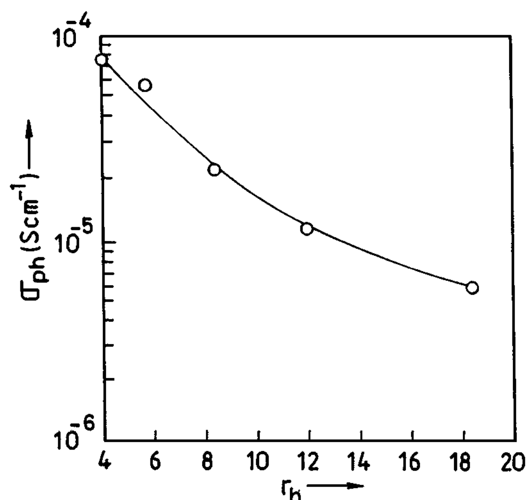

Figure 3 Variation of photoconductivity (σ_{ph}) with r_h at $r_c = 0.4$.

TABLE I Values of film deposition rate (R_D), bonded hydrogen content (C_H), bonded oxygen content (C_O), ESR spin density (N_S) and valence band tail width (E_o) for films prepared under different deposition conditions.

Sample number	Deposition pressure (p) (Torr)	CO_2/SiH_4 (r_c)	H_2/SiH_4 (r_h)	R_D (Å/min)	C_H (at %)	C_O (at %)	N_S (10^{16}/cc)	E_o (meV)
O-8	0.25	0.4	8.6	30.0	15.7	8.2	1.9	46.3
O-5	0.25	0.5	8.5	31.3	13.5	8.7	2.5	47.7
O-6	0.25	1.0	8.0	34.3	14.0	15.5	7.2	76.6
O-13	0.16	0.3	8.7	25.7	13.0	6.0	1.4	38.7
O-11	0.16	0.4	8.6	30.0	12.5	8.2	1.3	40.0
O-10	0.16	0.5	8.5	33.8	11.2	8.5	2.2	44.2
O-7	0.35	0.5	18.5	20.0	15.0	10.4	6.6	55.5

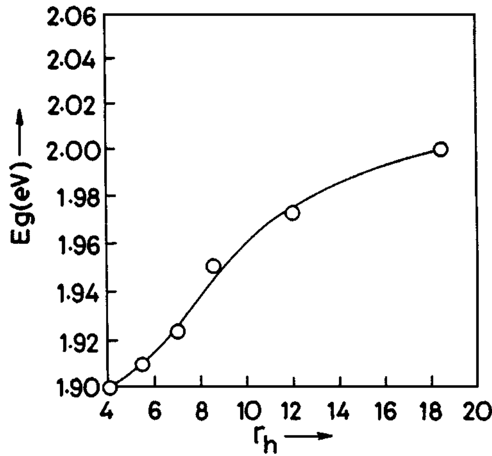

Figure 4 Variation of optical gap (E_g) with r_h at $r_c = 0.4$.

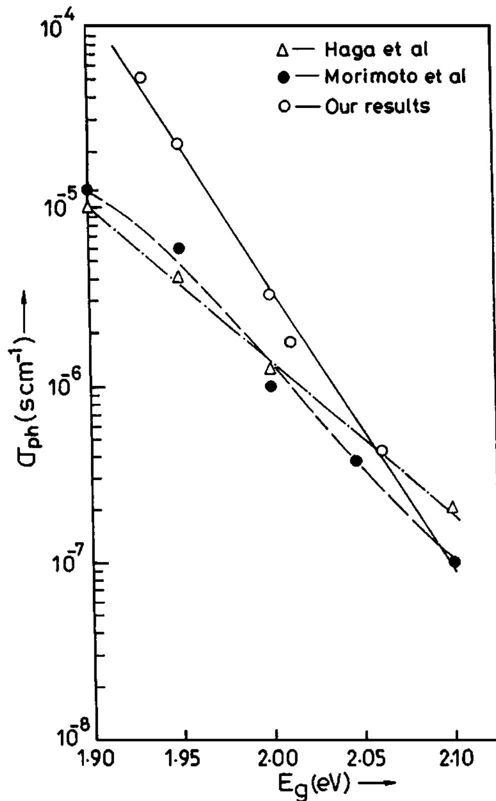

Figure 5 Variation of photoconductivity (σ_{ph}) with optical gap (E_g) for the set of films prepared at $r_h = 8.5$.

undoped a-SiO:H films. It is seen that we have been able to achieve a significantly higher value of σ_{ph} in the range of 1.9–2.0 eV which is used for the fabrication of the top cell of a multijunction a-Si solar cell.

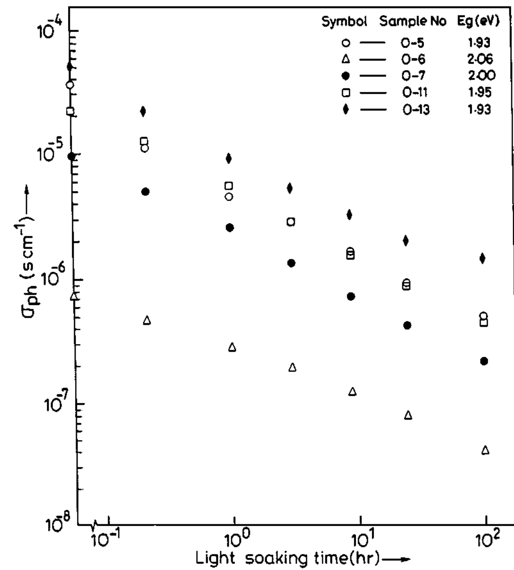

Figure 6 Variation of photoconductivity (σ_{ph}) with light soaking time for the films prepared under different deposition conditions having different optical gaps.

The film deposition rate (R_D), bonded hydrogen content (C_H) and bonded oxygen content (C_O) as obtained from infrared absorption spectra, ESR spin density (N_S) and valence band tail width (E_o) as obtained from CPM measurements for films prepared under different deposition conditions are summarized in Table I. It is seen that at any constant deposition pressure, with the increase in r_c, R_D increases, and C_O increases along with the increase in ESR spin density and valence band tail-width. The bonded hydrogen content, C_H of the films does not vary significantly with the change in deposition parameters like p, r_c, r_h. From the table it is seen that at a given r_c (say 0.4) and r_h (say, 8.6), there is a little variation in C_O and N_S with the change in p, whereas the E_o value is reduced significantly. With the increase in hydrogen dilution and the deposition pressure at a given r_c ($= 0.5$), both C_H and C_O are increased giving a higher optical gap of the film. At a given value of p ($= 0.25$ Torr), increase in C_O is accompanied by an increase in spin density, N_S, making the film more defective, it is still remaining well below 10^{17}/cc at an E_g value of 2.06 eV. The Urbach edge widths (E_o) of the a-SiO:H films as obtained from the constant photocurrent measurements are much less than those of optimized a-SiC:H films having comparable or even lower optical gaps. The values of E_o of the a-SiO:H films obtained are 40 meV, 55 meV and 76 meV for

optical gaps 1.93 eV, 2.0 eV and 2.06 eV respectively, whereas the best reported value of E_o is 66 meV for a-SiC:H films ($E_g = 1.95$ eV) [11].

Fig. 6 shows the variation of secondary photoconductivity, σ_{ph} with light soaking time for a set of films prepared under different deposition conditions (conditions are given in Table I). From the figure it is seen that the film prepared at low deposition pressure (0.16 Torr) degrades less (symbol ♦) than that prepared at higher (0.25 Torr) deposition pressure (symbol ○) although both of them have same optical gap (1.93 eV). This indicates that the film prepared at lower deposition pressure is less defective, which is also supported from the ESR spin density data (Table I). The 100 h light soaked values of σ_{ph} of a-SiO:H films are higher than those of a-SiC:H films having similar optical gaps prepared by conventional plasma-CVD.

4. Conclusion

Intrinsic hydrogenated amorphous silicon oxide films deposited by rf glow discharge decomposition of $SiH_4 + CO_2 + H_2$ gas mixture show optoelectronic properties superior to a-SiC:H films at similar optical gaps. The optimized film prepared from low CO_2 diluted plasma at a low chamber pressure shows a photoconductivity of 2.2×10^{-5} Scm^{-1} at an optical gap of 1.95 eV, which is significantly higher than that reported by other groups at similar optical gap. Thus, a-SiO:H film prepared under optimized conditions by rf glow discharge can be used as wide band gap active layer in the top cell of multijunction amorphous silicon solar cells.

Acknowledgements

This work was carried out under projects funded by Ministry of Non-Conventional Energy Sources and Department of Science and Technology, Government of India. S. M. Iftiquar wishes to acknowledge CSIR, Govt. of India, for providing research fellowship.

References

1. K. HAGA, A. MURAKAMI, K. YAMAMOTO, M. KUMANO and H. WATANABE, *Jpn. J. Appl. Phys.* **30** (1991) 3331.
2. Y. ICHIKAWA, S. FUJIKAKE, H. OHTA, T. SASAKI and H. SAKAI, Proc. 22-nd IEEE Photovoltaic Conf. (Las Vegas, 1991) p. 1296.
3. A. MORIMOTO, H. NORIYAMA and T. SHIMIZU, *Jpn. J. Appl. Phys.* **26** (1987) 22.
4. G. SUCHANECK, O. STEINKE, B. ALHALLANI and K. SCHADE, *J. Non-Cryst. Solids* **187** (1995) 86.
5. P. SICHANUGRIST, T. YOSHIDA, Y. ICHIKAWA and H. SAKAI *J.Non-Cryst.Solids*, **164–166** (1993) 1081.
6. H. WATANABE, K. HAGA and T. LOHNER, *J. Non-Cryst. Solids* **164–166** (1993) 1085.
7. S. FUJIKAKE, H. OHTA, P. SICHANUGRIST, M. OHSAWA, Y. ICHIKAWA and H. SAKAI, *Optoelectronics—Devices and Technologies* **9** (1994) 379.
8. DEBAJYOTI DAS, S. M. IFTIQUAR, and A. K. BARUA, *J. Non-Cryst. Solids* **210** (1997) 148.
9. G. LUCOVSKY, J. YANG, S. S. CHAO, J. E. TYLER and W. CZUBATYJ *Phys. Rev. B* **28** (1983) 3225.
10. L. HE, T. INOKUMA, Y. KURATA, and S. HASEGAWA, *J. Non-Cryst. Solids* **185** (1995) 249.
11. S. H. BAKER, W. E. SPEAR, and R. A. G. GIBSON, *Phil. Mag. B* **62** (1990) 213.

Received 3 June and accepted 21 August 1998