Highly conducting doped microcrystalline silicon ($\mu\text{c-Si:H}$) at very low substrate temperature by Cat-CVD

R.O. Dusane^{b,*}, Frank Diehl^a, U. Weber^a, B. Schröder^a

^a*Fachbereich Physik, Universität Kaiserslautern, D67653, Kaiserslautern, Germany*

^b*Department of Metallurgical Engineering and Materials Science, Indian Institute of Technology, Powai, Bombay, Mumbai-400076, India*

Abstract

In this paper we report the synthesis of highly conducting doped hydrogenated micro-crystalline silicon films, prepared by Cat-CVD deposition using silane and trimethyl boron (TMB) with hydrogen dilution at substrate temperatures as low as 110°C, having a conductivity of approximately $1\ \Omega^{-1}\text{ cm}^{-1}$. All the films are microcrystalline and show the characteristic X-ray signature pertaining to the same. The optical transmission data also reveal a high transmission over the spectral range of 450–600 nm. The variation in film characteristics with gas pressure was also studied, and reveals that the pressure is a very important parameter in determining the microcrystallinity of the films. The hydrogen dilution was varied over the range 30–70 sccm. However, no significant effect on the room-temperature conductivity was observed over this range.

Keywords: Microcrystalline; Amorphous materials; Deposition process; Chemical vapor deposition

1. Introduction

The demand for an efficient window layer for a-Si:H-based thin-film solar cells in terms of (a) optical transmission, (b) conductivity and (c) defect density is ever increasing since the inception of the single and tandem solar cells [1]. The evolution of this layer has witnessed material candidates such as p-a-Si:H, p-a-Si:C:H, p- $\mu\text{c-Si:H}$, and recently, p- $\mu\text{c-Si:C:H}$ [2,3]. Studies carried out so far reveal that p- $\mu\text{c-Si:H}$ can act as a good window layer, provided the various issues involved in optimizing the material with respect to its properties and the p-i interface defects are addressed [4]. Moreover, the capabilities of the recently introduced thermo-catalytic chemical vapor deposition (TCCVD) method for obtaining good-quality p- $\mu\text{c-Si:H}$ have not yet been fully established [5–7]. Many of the efforts at fabricating TCCVD-based a-Si:H solar cells involved deposition of the intrinsic layer by TCCVD, while the

doped layers were deposited by either sputtering or the conventional glow-discharge method [8,9]. However, to make the TCCVD method a viable alternative to the glow discharge technique, it is necessary to prove that the doped layers, and consequently the complete solar cell, can be fabricated entirely by TCCVD with acceptable conversion efficiency.

There have been some attempts to this effect by a few groups [10,11]. However, there is a lot of room for improvement in these devices. It is with this aim that we initiated a detailed study of preparing p- $\mu\text{c-Si:H}$ material and optimizing the process conditions so as to yield p- $\mu\text{c-Si:H}$ layers with all the desired properties. Secondly, there is a need for good p-type dopants to make the window layers for a-Si:H-based solar cells. As diborane has low dissociation energy, the adsorbed diborane poses the possibility of dopant contamination across the p-i interface. Hence, we have tried to deposit the $\mu\text{c-Si:H:B}$ films using trimethyl boron (TMB) as the dopant source gas.

Fig. 1. Variation of conductivity with total gas pressure for TCCVD p-type $\mu\text{c-Si:H:B}$ films.

2. Experimental

The TCCVD system used during this study is a newly developed multi-chamber stainless steel system with independent reactors for the three layers to avoid any cross contamination. All the UHV chambers are pumped with Balzers turbomolecular pumps (Model TPH270) to a base pressure of 5×10^{-8} torr prior to each deposition. Inside each of the reactors is a closed box assembly, which offers the possibility of the desired gas-phase chemistry during deposition. This box contains a vertically mounted substrate holder with a thermocouple, the filament holder, the gas distribution shower and a mechanical shutter. A capacitance manometer (Balzers CMR 274) reads the silane pressure inside this box during deposition. The filament used in the present study is a 0.5-mm-diameter tantalum wire that is mounted vertically in the form of a 'W'-shaped loop in front of the substrate holder at a distance of 3.5 cm from the substrate. The total length of the filament is approximately 25 cm. All depositions were carried out with a gas mixture of silane, TMB and hydrogen, and the gas flow was monitored by mass flow controllers (Tylan model FC260). Samples were prepared on Corning 7059 glass and c-Si substrates to enable various characterization techniques. The film thickness was determined with a thickness profiler (Dektak II) and all the films had a thickness in the range 0.5–1.0 μm . The hydrogen bonding configuration was studied from the IR spectra obtained from a Nicolet FTIR spectrometer. The process conditions maintained during the depositions were as follows:

T_{sub} : 90–300°C

Pressure: 50–700 mtorr

$F(\text{TMB})/F(\text{SiH}_4)$ flow: 2 sccm

T_{fil} : 1850°C

H_2 : 30–70 sccm

3. Results and discussion

Fig. 1 shows the variation of room temperature conductivity as a function of total gas pressure for p-

Fig. 2. Variation of deposition rate of the p-type $\mu\text{c-Si:H}$ films as a function of pressure.

type $\mu\text{c-Si:H}$ films prepared with TMB. Fig. 2 shows the rate of deposition of these films as a function of pressure. In Fig. 3, we show the variation of room temperature conductivity (σ_{RT}) as a function of substrate temperature, T_s , for the p-type films prepared with the TMB dopant source. Results of effective doping in microcrystalline-Si, have also been reported by Brugera et al. [12]. In Fig. 4, the deposition rate of the films as a function of T_s is depicted. Fig. 5 shows the typical FTIR spectrum of a $\mu\text{c-Si:H:B}$ film, which exhibits the sharp peak at 2100 cm^{-1} indicative of SiH_2 modes on the microcrystalline grain surfaces in the films. As an indication of the microcrystallinity of the films, Fig. 6 shows X-ray diffraction data of a typical high-conductivity film. From Fig. 1, it is evident there is a particular pressure, for a given geometry and the other process conditions, which yields a very high room-temperature conductivity value. Corresponding to this, Fig. 2 shows that there is a small but significant decrease in the deposition rate of films in the region of the optimum pressure, which, from a growth kinetics point of view, could lead to a high microcrystalline volume fraction

Fig. 3. Variation of room-temperature conductivity of the $\mu\text{c-Si:H:B}$ films as a function of substrate temperature.

Fig. 4. Variation of deposition rate of the p-type $\mu\text{c-Si:H}$ films as a function of T_s .

and good microstructure, and therefore a lower defect density in the films. This can subsequently yield a higher conductivity, as observed in the present data. The low deposition could be due to more effective atomic hydrogen-mediated etching of the amorphous phase in the growing film. [13]. From this point of view, the data in Figs. 3 and 4 can be explained in a consistent fashion. As seen in Fig. 3, the conductivity is significantly high at approximately 100°C, and falls by over two orders of magnitude as the substrate temperature, T_s , increases to 300°C. On the other hand, the deposition rate variation also shows a minimum in the region of this temperature. Thus, we get a confirmation of the trends observed in Figs. 3 and 4, based on the efficient hydrogen-etching of the amorphous phase at low deposition rates. Incidentally, Voz et al. report a similar result, where they find a decrease in the crystalline fraction with increasing substrate temperature from Raman measurements [5]. The fact that in both of the above variations a correlation between the conductivity and the deposition rate evolves, indicates that the microcrystalline volume fraction is indeed determined by the hydrogen-etching mechanism during deposition. However, what is important in the present work is that we have been able to deposit $\mu\text{c-Si:H:B}$ films using TMB as the dopant source at quite low substrate temperatures. In Fig. 5, it is evident that the hydrogen bonding has changed significantly due to the formation of microcrystallites in the film. The hydrogen is predominantly bonded as SiH_2 on the crystallite surfaces, as evidenced by the IR transmission peak at 2100 cm^{-1} instead of the Si-H-related peak at 2000 cm^{-1} .

Finally as confirming evidence that our films are microcrystalline with a high volume fraction of crystallinity, Fig. 6 shows a typical X-ray diffraction pattern. It is clear that the Si microcrystals are (111)-oriented with a high volume fraction of crystallinity, which is evident from the small full width at half-maximum (FWHM) of the diffraction peaks. One issue that remains to be explicitly proven is that doping has

Fig. 5. A typical infrared spectrum of the $\mu\text{c-Si:H}$ film deposited with process parameters similar to those for the doped films.

actually occurred. For this, chemical analysis of the samples is required. However, we can give indirect support to our contention that doping has indeed taken place. The conductivity of microcrystalline samples prepared without TMB, which show a similar X-ray diffraction, is approximately $10^{-6} \Omega^{-1} \text{cm}^{-1}$. Thus, the high conductivity value, of the order of $1 \Omega^{-1} \text{cm}^{-1}$, observed in the samples prepared with TMB can only be due to effective doping in the material.

4. Conclusion

The Cat-CVD process was successfully employed to deposit highly conducting p-type $\mu\text{c-Si:H:B}$ films at substantially low temperatures of approximately 110°C. The formation of such highly conducting microcrystalline films seems to result from efficient hydrogen-mediated etching of the amorphous phase during growth of the films. These films could thus be used as window layers in a-Si:H-based p-i-n solar cells.

Fig. 6. Typical X-ray diffraction data for our $\mu\text{c-Si:H}$ films.

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