Journal of Non-Crystalline Solids 103 (1988) 143–148
North-Holland, Amsterdam

INFLUENCE OF DIFFERENT DEPOSITION PARAMETERS ON THE PROPERTIES OF HYDROGENATED AMORPHOUS SILICON FILMS PREPARED BY MAGNETRON SPUTTERING

Debajyoti DAS, Ratnabali BANERJEE, A.K. BATABYAL and A.K. BARUA

Energy Research Unit, Indian Association for the Cultivation of Science, Calcutta-700 032, India

Received 10 August 1987
Revised manuscript received 10 November 1987

Hydrogenated amorphous silicon films have been reactively sputtered with different flow rates of hydrogen in an $Ar-H_2$ gas mixture. The films have been characterized by optoelectronic and structural properties. The susceptibility to light induced changes has been studied. The effects of variation of the rf power density and the total pressure on the film properties have also been examined. Each of the deposition parameters have been found to exercise considerable control on the film characteristics. Parametric optimisation has yielded encouraging results in terms of film quality.

1. Introduction

It has been possible to prepare low defect density films of a-Si : H by the rf magnetron sputtering method [1,2]. So it has started receiving attention as an alternative to film deposition by the glow discharge decomposition of silane. A detailed study of the effect of deposition temperature (T_s) on magnetron sputtered a-Si : H films has been carried out in this laboratory [3]. With an arbitrarily chosen (17%) flow rate of hydrogen in an $Ar + H_2$ gas mixture, fairly encouraging results have been obtained in terms of the dark conductivity, σ_D, photoconductivity, σ_{Ph}, spectral response and neutral dangling bond density for $T_s = 180\,^\circ C$. In this work, further optimisation in terms of hydrogen flow rate, power density and pressure has been carried out for films deposited at 180 °C. Light induced effects in selected films have been studied since presence of photo induced changes is considered as an index of quality for the material [4]. Different light soaking temperatures have been used to understand the process better.

It has been shown that fabrication of a-Si : H solar cells by glow discharge decomposition of silane should preferably be carried out at low temperatures, to prevent the degradation of the transparent, conducting base layer by the hydrogen plasma [5–7]. RF magnetron sputtering has also been tried as an alternative method for the fabrication of a-Si : H solar cells [8]. Therefore, it has been thought worthwhile to do some optimisation work on a-Si : H films deposited at 60 °C also. In this case, mainly the effect of different hydrogen concentration has been studied.

2. Experiment

Films have been fabricated in a rf magnetron sputtering system (CVC Inc., USA). Details have been described elsewhere [9]. The electrodes are in a parallel plate configuration and the gas mixture ($Ar + H_2$) has been introduced directly into the plasma region in the form of a shower through the upper electrode which serves as the substrate holder. In such a system the composition of the gas mixture can be closely approximated from the ratio of the flow rates of the gases. The parameter that has mainly been varied is R_H, which is the flow rate of hydrogen (sccm) expressed as a percentage of the total flow rate of Ar and H_2. R_H has been varied between 0 to 80%. The other deposition parameters which have been varied in-

0022-3093/88/$03.50

clude the rf power density (0.5–2.2 W/cm^2, target dia 20.9 cm) and the total pressure (0.8–7.8 mTorr). The substrate temperature, T_s, has been maintained at 180 °C. R_H variations for T_s = 60 °C have also been carried out over a limited region.

Films have been characterized by dark conductivity and its temperature dependence, photoconductivity (tungsten halogen lamp, 50 mW/cm^2), optical band gap, IR spectrum and ESR spin density. Light induced changes on selected samples have been studied after illumination of films with white light from a tungsten halogen lamp (intensity = 100 mW/cm^2) for one hour. Light soaking has been carried out at different temperatures, T_I, and recovery effect tested by subsequent annealing at 150 °C. Exposure has also been done at 150 °C itself to observe resultant changes.

3. Results and discussion

3.1. Effect of hydrogen concentration

The effect of increasing R_H on the properties of magnetron sputtered a-Si : H films deposited at 180 °C have been tabulated (table 1). The power density has been maintained at 1.2 W/cm^2 and the pressure at 2mTorr. The room temperature dark conductivity, σ_D, progressively decreases (fig. 1) and the optical band gap increases with R_H, (table 1). This is consistent with the role of hydrogen as a compensator of dangling bonds. With increasing R_H, more and more hydrogen is incorporated into the silicon network of the film. This is also found from IR studies by calculating the amount of bonded hydrogen of some samples from the wagging mode absorption (table 1). An extreme value of R_H = 80% has also been tried which shows a virtual saturation in σ_D beyond R_H = 30%.

The effect of variation in R_H for films deposited at 60 °C has also been studied. The results have been given in table 2. Here, the special feature is the higher activation energy at low temperatures compared to films deposited at 180 °C. For R_H = 5%, the two activation energies are nearly equal. However the photoconductive gain (σ_{Ph}/σ_D) decreases. The density of dangling bonds has been calculated from ESR spectra. For R_H = 5% it is higher ($5.9 \times 10^{17}\,cm^{-3}$) than that, for example, of a film deposited with R_H = 17% ($1.2 \times 10^{17}\,cm^{-3}$).

Table 1
Properties of magnetron sputtered a-Si : H films deposited at 180 °C

R_H (%)	σ_D ($\Omega^{-1}\,cm^{-1}$)	σ_{Ph} ($\Omega^{-1}\,cm^{-1}$)	Gain	Activation energy (eV)	Optical band gap (eV)	H_{wag} (at%)
unhydrogenated	2.6×10^{-5}	–	–	0.18 (below 100 °C) 0.30 (above 100 °C)	1.53	
5	2.9×10^{-8}	6.9×10^{-5}	2.4×10^{3}	0.25 (below 25 °C) 0.76 (above 25 °C)	1.71	8.6
10	4.8×10^{-9}	3.2×10^{-5}	6.7×10^{3}	0.23 (below 40 °C) 0.78 (above 40 °C)	1.78	12.2
13	2.0×10^{-9}	3.0×10^{-5}	1.5×10^{4}	0.20 (below 40 °C) 0.86 (above 40 °C)	1.80	13.2
15	1.7×10^{-9}	2.5×10^{-5}	1.5×10^{4}	0.18 (below 40 °C) 0.92 (above 40 °C)	1.94	19.3
17	2.7×10^{-9}	3.4×10^{-5}	1.3×10^{4}	0.17 (below 40 °C) 0.84 (above 40 °C)	1.91	19.1
20	5.6×10^{-10}	1.5×10^{-5}	2.7×10^{4}	0.24 (below 45 °C) 0.91 (above 45 °C)	1.88	19.0
30	1.1×10^{-10}	3.1×10^{-6}	2.8×10^{4}	0.19 (below 45 °C) 0.92 (above 45 °C)	1.92	19.3
80	1.1×10^{-10}	1.6×10^{-6}	1.4×10^{4}	0.58 (below 65 °C) 0.92 (above 65 °C)	2.07	25.5

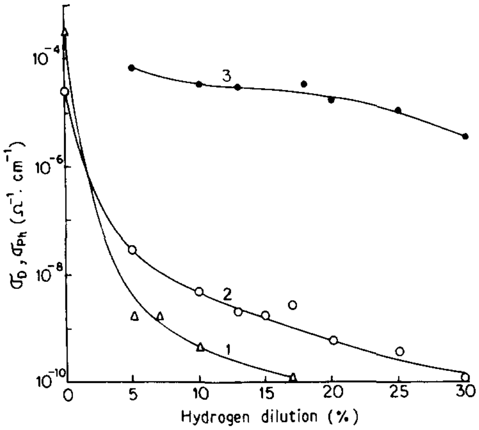

Fig. 1. Variations of dark conductivity (σ_D) and photoconductivity (σ_{Ph}) with hydrogen dilution (R_H) for magnetron sputtered a-Si:H films prepared at different temperature (T_s). Curve-1 (Δ): σ_D for $T_s = 60\,°C$; curve-2 (O): σ_D for $T_s = 180\,°C$; curve-3 (●): σ_{Ph} for $T_s = 180\,°C$.

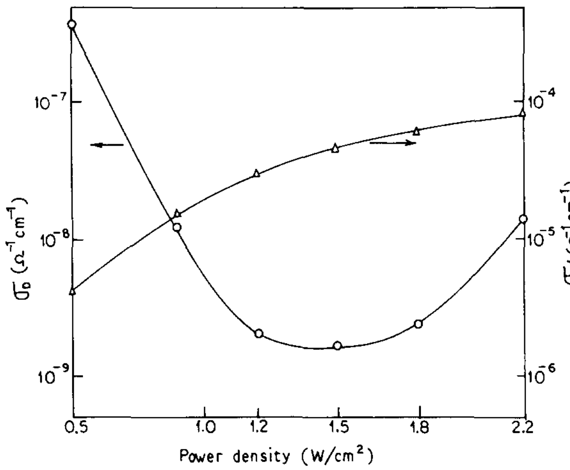

Fig. 2. Variations of dark conductivity (σ_D) and photoconductivity (σ_{Ph}) with power density for magnetron sputtered a-Si:H films prepared at 180 °C.

So inspite of the presence of two largely differing values of activation energy, films with $R_H > 5\%$ show superiority in other properties. An extreme case of $R_H = 80\%$ has also been studied. Although a very low value of σ_D and a large photoconductive gain has been obtained, the σ_{Ph} value itself is quite low (table 2).

In general, films deposited at 180 °C show a higher value of σ_{Ph} compared to films deposited at 60 °C. It is related to the nature of Si–H bonding. With increasing deposition temperature, it has been found from IR absorption spectra that the hydrogen bonding equilibrium shifts towards the monohydride configuration. This could result in the reduction in defect gap states [10].

3.2. Effect of power and pressure

The effect of variation in rf power density, P, on the room temperature σ_D and σ_{Ph} for magnetron sputtered a-Si:H films deposited at 180 °C ($R_H = 13\%$, pressure = 2 mTorr) is shown in fig. 2. σ_D decreases upto $P = 1.5$ W/cm^2 after which it increases again. Combining with σ_{Ph} data, the gain is highest (2.7×10^4) for $P = 1.5$ W/cm^2. The initial decrease in σ_D with an increase in rf power could be attributed to the higher kinetic

Table 2
Properties of magnetron sputtered a-Si:H films deposited at 60 °C

R_H (%)	σ_D (Ω^{-1} cm^{-1})	σ_{Ph} (Ω^{-1} cm^{-1})	Gain	Activation energy (eV)	Optical band gap (eV)
unhydrogenated	3.2×10^{-4}	–	–	0.17	1.56
5	1.7×10^{-9}	9.1×10^{-6}	5.2×10^{3}	0.72 (below 30 °C) 0.87 (above 30 °C)	1.72
7	1.7×10^{-9}	1.8×10^{-5}	1.1×10^{4}	0.41 (below 40 °C) 0.89 (above 40 °C)	1.78
10	4.3×10^{-10}	2.0×10^{-6}	4.6×10^{3}	0.40 (below 35 °C) 0.85 (above 35 °C)	1.85
17	1.2×10^{-10}	1.3×10^{-6}	1.0×10^{4}	0.35 (below 40 °C) 0.89 (above 40 °C)	1.98
80	5.0×10^{-13}	2.7×10^{-8}	5.3×10^{4}	–	2.22

Table 3
Effect of power (P) and pressure (P) on the properties of a-Si:H films deposited at 180 °C (R_H = 13%)

P (W/cm^2)	P (mTorr)	σ_D (Ω^{-1} cm^{-1})	σ_{Ph} (Ω^{-1} cm^{-1})	Activation energy (eV)	Optical band gap (eV)
0.5	2	3.8×10^{-7}	4.3×10^{-6}	0.46($T\leqslant 50$ °C) 0.64($T > 50$ °C)	2.15
1.2	2	2.0×10^{-9}	3.0×10^{-5}	0.20($T\leqslant 40$ °C) 0.86($T > 40$ °C)	1.80
1.5	2	1.7×10^{-9}	4.5×10^{-5}	0.22($T\leqslant 40$ °C) 0.90($T > 40$ °C)	1.82
1.8	2	2.5×10^{-9}	6.1×10^{-5}	0.40($T\leqslant 35$ °C) 0.85($T > 35$ °C)	1.84
2.2	2	1.4×10^{-8}	8.3×10^{-5}	0.40($T\leqslant 35$ °C) 0.75($T > 35$ °C)	-
1.2	0.8	1.0×10^{-8}	1.9×10^{-5}	0.23($T\leqslant 70$ °C) 0.82($T > 70$ °C)	2.00
1.2	7.8	1.7×10^{-8}	1.5×10^{-5}	0.79	1.91
1.5	7.8	7.1×10^{-10}	9.7×10^{-6}	0.87	

energy of silicon atoms arriving at the substrate which could help in the migration of atoms along the substrate surface and consequently in the formation of a better amorphous network. However, after a certain point, further increase in the power density is likely to produce damage, specially by Ar^+ bombardment. So, σ_D shows a gradual increase after a minimum. Our results agree in part with those obtained by Webb and Das [11], where a progressive increase in the room temperature σ_D has been obtained with increasing power density in the range 1.3–6.4 W/cm^2. However, their lower limit of P corresponds to the value at which σ_D starts increasing in the present study. So the decrease of σ_D with P in the region of still lower powers has not been observed by them.

The effect of variation of the system pressure, p, has also been studied and the results are given in table 3. Photoconductive gain-wise, the best result has been obtained at $p = 2$ mTorr. However, for $p = 7.8$ mTorr the conduction throughout the range of measurement is characterized by a single activation energy. Now at high pressure, the velocity of the ions bombarding the substrate, decreases and this leads to extended state conduction with single slope in the log σ_D versus $10^3/T$ plot. This leads us to speculate that bombardment by Ar^+ ions may cause the formation of two phases during the growth of the film. The more defective second phase may be randomly distributed on each monolayer of the matrix and connected in a random fashion through different layers so that a parallel conduction path is formed in between the electrodes. The conductivity of this phase (comparitively defective one) may dominate at low temperatures.

For $T_s = 60$ °C, it has been observed that the low temperature slope has higher values than for films deposited with $T_s = 180$ °C. At low temperatures, since the deposition rate of silicon is higher, it could be that Ar^+ ions are not as effectively implanted in the films as in case of higher T_s. From ESCA survey scans too it has been confirmed that the Ar content in the film increases with increasing T_s. So for lower T_s, this may lead to a less defective second phase, although the matrix improves with increasing T_s. For deposition at high pressures, the detrimental effect of Ar^+ bombardment could be minimized leading to a more homogeneous growth. So, when a film is deposited with the optimum power density of 1.5 W/cm^2 at a system pressure of 7.8 mTorr, better results are obtained in terms of σ_D, σ_{Ph} and activation energy (table 3).

3.3. Light induced changes

The influence of extended illumination on the electrical properties of selected films has been investigated. Defects have been generated by il-

Table 4
Light induced changes in a-Si : H films

T_s (°C)	R_H (%)	σ_D (Ω^{-1} cm^{-1})	σ_{Ph} (Ω^{-1} cm^{-1})	T_I (°C)	$(\sigma_D)_A/(\sigma_D)_B$	$(\sigma_{Ph})_A/(\sigma_{Ph})_B$	ΔE_A (eV)	ΔE_B (eV)	$(\sigma_D)_R$ (Ω^{-1} cm^{-1})	$(\sigma_{Ph})_R$ (Ω^{-1} cm^{-1})
180	5	2.9×10^{-8}	6.9×10^{-5}	30	3.7	3.9	0.76	0.81	3.2×10^{-8}	6.5×10^{-5}
	15	1.7×10^{-9}	2.5×10^{-5}	30	26.2	8.1	0.92	1.17	2.2×10^{-9}	2.1×10^{-5}
				−90	2.7	2.0	0.92	0.97		
				150	0.8	2.0	0.92	0.81		
	80	1.1×10^{-10}	1.6×10^{-6}	30	13.0	3.4	0.92	0.98	9.9×10^{-11}	1.6×10^{-6}
60	7	1.7×10^{-9}	1.8×10^{-5}	30	22.8	30.7	0.89	0.99	1.9×10^{-9}	1.6×10^{-5}
				−90	2.0	7.5	0.89	0.94		
				150	0.7	3.0	0.89	0.79		

lumination with white light from a tungsten halogen lamp (intensity = 100 mW/cm^2) for one hour and the recovery effect tested by subsequent annealing at 150 °C. The samples have been found to nearly regain their original dark conductivity as well as photoconductivity (table 4). Light soaking at different temperatures, T_I, has been carried out (including $T_I = 150$ °C) for samples deposited with $T_s = 180$°C and $R_H = 15$%. This is because, for these, the change in σ_D and σ_{Ph} for $T_I = 30$ °C is more prominent compared to other values of R_H (table 4). Samples deposited at 60 °C with $R_H =$ 7% have also been tested on account of their initially good σ_D and σ_{Ph} values, matching those obtained for $T_s = 180$ °C, $R_H = 15$%. A and B refer to states before and after exposure, respectively. ΔE is the activation energy for conduction. σ_D and σ_{Ph} refer to room temperature values. $(\sigma_D)_R$ and $(\sigma_{Ph})_R$ indicates the recovery values after annealing.

The results support the model given by Kumeda et al. [12] who have proposed the formation of an unstable state A′, just after the breaking of a Si–Si bond by illumination. There is a barrier between A′ and the metastable state B. The height of this barrier has a distribution, varying from site to site. At $T_I = -90$ °C, as seen from table 4, the net Staebler–Wronski effect is smaller, as carriers do not have sufficient energy to cross the higher barrier sites.

For $T_I = 150$ °C, the trend changes. σ_D increases and ΔE decreases, although σ_{Ph} decreases as usual. The decrease in σ_{Ph} indicates photocreation of dangling bonds. However, here some Si–H bonds could also break. That is, illumination at 150 °C could in a way expedite hydrogen evolution, leading to the observed effects. IR studies too show a marginal decrease (by 1 at%) in the concentration of bonded hydrogen after light soaking at 150 °C, supporting the above view.

4. Conclusions

In this paper, results from characterization experiments on rf magnetron sputtered a-Si : H films have been reported. Optimization of hydrogen flow rate, power density and pressure have yielded films characterized by high photoconductivity as well as large photoconductive gain.

Light induced changes on selected films have been studied. Light soaking at 150 °C has resulted in unusual changes in film properties which may be attributed to the breaking of Si–H bonds.

This work has been done under a project funded by the Department of Non-Conventional Energy Sources, Govt. of India.

References

[1] P.K. Bhat, A.J. Rhodes, T.M. Searle, I.G. Austin and J. Allison, Phil. Mag. B 47 (1983) L 99.
[2] S. Gangopadhyay, S. Iselborn, H. Rübel, B. Schröder and J. Geiger, Phil. Mag. B 51 (1985) L 33.
[3] R. Banerjee, D. Das, A.K. Batabyal and A.K. Barua, submitted.
[4] D. Adler, presentation at Materials Issues in Applications of Amorphous Silicon Technology (San Francisco, April 15-17, 1985).

[5] K. Tsuge, M. Kondo, K. Nishimura, N. Fukada, Y. Tawada and Y. Hamakawa, Technical Digest Int. PVSEC-1 (Kobe, Japan) (1984) p. 179.
[6] Y. Tawada, J. Takada, N. Fukada, M. Yamaguchi, H. Yamagishi, K. Nishimura, M. Kondo, Y. Hosokawa, K. Tsuge, T. Nakayama and I. Hatano, Appl. Phys. Lett. 48 (1986) 584.
[7] R. Banerjee, S. Ray, N. Basu, A.K. Batabyal and A.K. Barua, J. Appl. Phys. 62 (1987) 912.
[8] W. Müller, H. Rübel, B. Schröder and J. Geiger, Solar Energy Mat. 13 (1986) 385.
[9] A.K. Batabyal, P. Chaudhuri, S. Ray and A.K. Barua, Thin Solid Films 112 (1984) 51.
[10] M.C. Ozturk and M.G. Thompson, Appl. Phys. Lett. 44 (1984) 916.
[11] J.B. Webb and S.R. Das, J. Appl. Phys. 54 (1983) 3282.
[12] M. Kumeda, H. Yokomichi, A. Morimoto and T. Shimizu, Japan. J. Appl. Phys. 25 (1986) L654.