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Control of the properties of wide bandgap a-SiC : H films prepared by RF PECVD method by varying methane flow rate

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Abstract

The influence of increase in flow rate of CH_4 in a source gas mixture of $SiH_4 + CH_4 + H_2$ for the preparation of high-quality wide band gap a-SiC : H film by the RF PECVD method has been studied. We have been able to increase the optical gap of the film by increasing CH_4 flow rate under appropriate deposition conditions. These films are structurally better which also shows good opto-electronic properties. This has been achieved mainly by using CH_n (where $n = 3$, 2 or 1) precursors in the plasma as the etchant for weak bonds on the growing surface of a-SiC : H films. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: RF PECVD; a-SiC : H films; Photoconductivity

1. Introduction

Wide band gap photosensitive a-SiC : H film has many device applications specially in a-Si solar cells [1]. In multijunction a-Si solar cells this material is being used as the active layer of the top cell [2]. The p-type a-SiC : H film is used as the window layer of the cell [3].

Considerable work has been done on the preparation and characterization of a-SiC : H films deposited by the RF PECVD method [1–7]. The a-SiC : H film is generally prepared by the radio frequency (RF) glow discharge decomposition of

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a mixture of silane with a suitable carbon source gas. It is well known that incorporation of carbon in a-Si : H network increases the void structure which deteriorates significantly the opto-electronic and other properties of the material [8,9]. Matsuda et. al. [9] first improved significantly the properties by strongly diluting the source gas mixture of $SiH_4 + CH_4$ with hydrogen. The basic physics of this improvement is that there is significant coverage of the film growth surface with atomic hydrogen so that SiH_3 and CH_3 radicals react with H atom to produce SiH_4 and CH_4, respectively, so that the diffusion length of the precursors are increased and the deposited film is more ordered [9]. By using the method it is possible to have photosensitive a-SiC : H film with optical gap $\leqslant 1.9$ eV.

There is scope for improvement of the quality of the material specially at higher optical gap. We have considered the possibility of using CH_n ($n = 1, 2$ or 3) precursors (specially CH_3) for achieving this. The basic concept is that CH_n precursors (basically CH_3) will remove weak H bonds in the growing a-SiC : H films leading to lowering of hydrogen content and increasing the concentration of Si–C bonds in the film.

In this paper we have reported the results of our investigations on control/improvement in the properties of a-SiC : H films by varying the ratio of flow rates of CH_4 and SiH_4 in source gas mixture.

2. Experimental details

2.1. Preparation of a-SiC : H films

The a-SiC : H films were prepared by the usual RF (13.56 MHz) PECVD method from a source gas mixture of $SiH_4 + CH_4 + H_2$. The gases used were of high purity (Matheson, USA). The deposition chamber has UHV capability with turbomolecular pump (base vacuum $\sim 10^{-9}$ Torr).

Within the deposition chamber one of the two electrodes, which are parallel to each other, acted as the substrate holder. The substrates were kept at 200°C. The other deposition parameters, viz. RF power density, gas flow rates, hydrogen dilution were varied to obtain different sets of a-SiC : H films. The emphasis of these variations was to see the role of increasing the relative concentrations of CH_4 in the source gas mixture so that the influence of CH_n radicals in the plasma on the film properties can be ascertained. The films were deposited on Corning 7059 glass and crystalline silicon (c-Si) substrates for opto-electronic and structural studies, respectively.

The SiH_4 flow rate was varied from 2.5 to 5.0 sccm and that of CH_4 from 2.5 to 4.0 sccm. RF power density was varied from 20 to 30 mW cm^{-2}.

2.2. Characterization of the films

Thickness of the film has been determined by stylus-type instrument (Planar Product, UK). The optical absorption in the ultraviolet and visible range has been measured with UV–VIS–NIR spectrophotometer (Hitachi 330) by taking reflection and transmission spectra of the films deposited on glass. The samples were used for the measurement of opto-electronic properties which were done in a cryostat under vacuum ($\sim 10^{-6}$ Torr). Constant photocurrent method (CPM) of measurement has been carried out for the determination of Urbach energy (E_0), density of states in the midgap region (N_d), product of mobility (μ) lifetime (τ) and quantum efficiency (η). The product $\eta\mu\tau$ has been calculated at 660 nm wavelength.

The bonding structural study of the films has been done by infrared (IR) vibrational spectroscopy (Perkin-Elmer 1700 FTIR spectrophotometer). The bonded hydrogen content $[H_{\text{conc}}]$ can be estimated from 1990 cm^{-1} IR absorption peak from the relation [10]:

$$[H_{\text{conc}}] = A(H)I(2000\ \text{cm}^{-1}) \tag{1}$$

where $A(H) = 0.77$ at%/(eV cm^{-1}) and $I(2000\ \text{cm}^{-1})$ is integrated absorption (in unit of eV cm^{-1}) within 1850–2250 cm^{-1} region.

The microstructural defect introduced by carbon incorporation in a-Si : H film is indicated by the shift of Si-H_n related peak from 1990 to 2090 cm^{-1}. This microstructure parameter may be defined as

$$R_H = I_{2090}/[I_{2090} + I_{1990}], \tag{2}$$

where I indicates the intensity of the IR absorption at the position mentioned in subscript.

The peak at 990 cm^{-1} is due to wagging vibration of H in CH_n and is an indication of the direct effect of carbon incorporation on the microstructure of the film. Infrared absorption peak assignments have been done following Demichelis et al. [11].

3. Experimental results and discussions

In Table 1 the deposition conditions, optical gap (E_g) and deposition rate (R_d) of some typical samples have been shown. Φ indicates the flow rate of the gas and

Table 1
Deposition conditions of samples with different optical gap have been given. An enhanced optical gap has been obtained by raising $Y(CH_4)$. Substrate temperature = 200°C and deposition pressure = 0.7 Torr

Set no. of samples	$Y(CH_4)$	$\Phi(CH_4)$sccm	$\Phi(SiH_4)$sccm	$\Phi(H_2)$ sccm	Power (mW cm^{-2})	E_g (eV)	R_d (Å min^{-1})
I	0.33	2.0	4.0	100	20	1.86	33.6
	0.38	2.5	4.0	100	20	1.87	37.7
	0.43	3.0	4.0	100	20	1.88	46.2
II	0.38	3.0	5.0	100	30	1.90	81.0
	0.43	3.0	4.0	100	30	1.91	62.7
	0.50	4.0	4.0	100	30	1.92	57.5
	0.50	3.0	3.0	100	30	1.93	49.5
	0.55	3.0	2.5	100	30	1.95	49.4
	0.60	3.0	2.0	100	30	1.97	49.0

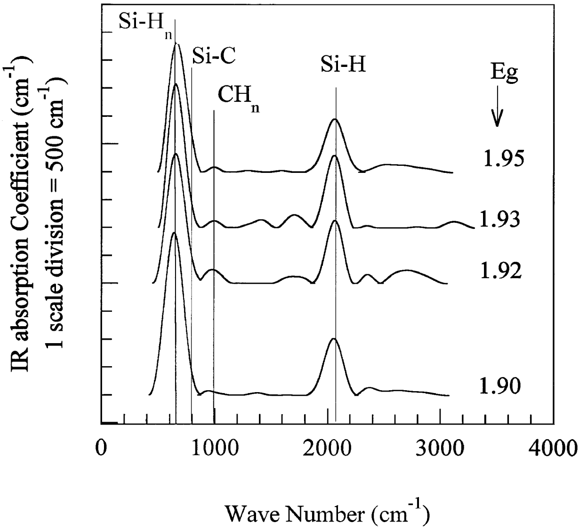

Fig. 1. FTIR absorption spectra of a-SiC : H films having different optical gap, prepared with varying Y(CH_4).

Y(CH_4) is the ratio $\Phi(CH_4)/\Phi(SiH_4 + CH_4)$. In our studies Y($CH_4$) has been varied keeping $\Phi(H_2)$ fixed at 100 sccm.

It may be seen from the Table 1 that at the lower RF power density of 20 mW cm^{-2} there is virtually no increase of E_g with the increase of Y(CH_4). This may be due to the fact that at this power density there is no significant increase in CH_n precursor concentration with the increase of Y(CH_4). However, at an RF power density of 30 mW cm^{-2} there is systematic increase of E_g from 1.90 to 1.97 eV with the increase of Y(CH_4) from 0.38 to 0.60. This is probably due to the fact that CH_4 needs relatively high power density for breaking into CH_n precursors.

The IR spectra of the films having optical gap in the range 1.90–1.95 eV have been given in Fig. 1. It is seen from the figure that Si–C bond formation (790 cm^{-1}) is more at higher Y(CH_4). The interesting result is that with the increase in optical gap from 1.90 to 1.95 eV, the peak intensity at 2090 cm^{-1} as well as that CH_n wagging mode (990 cm^{-1}) decrease. That is the a-SiC : H film quality improves structurally when the band gap is increased by increasing CH_4 flow rate keeping H_2 flow rate at a reasonably high level. Concentration of CH_n precursors increases with increase in CH_4 concentration in the plasma. In Fig. 2, the dark conductivity and photoconductivity of the samples have been shown. It indicates that although photoconductivity lowers with widening optical gap but photosensitivity of the materials remain around 10^5 for all the samples.

It can be seen from Table 2 that with the increase in Y(CH_4) the optical gap increases but the bonded hydrogen content [H_{conc}] is reduced. Thus the widening of the optical gap of a-SiC : H films is due to an increase in the concentration of Si–C bond and not due to an increase in hydrogen incorporation.

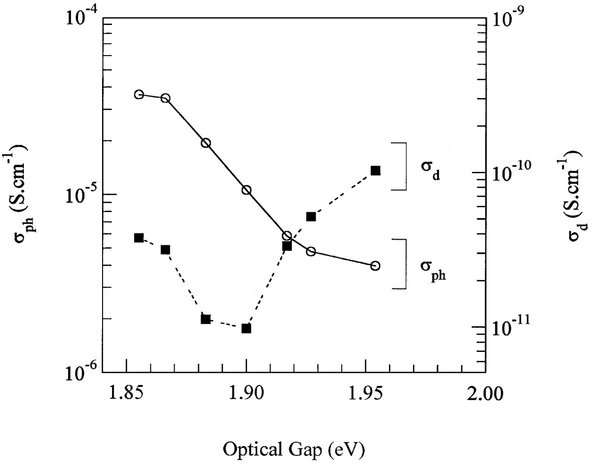

Fig. 2. Photoconductivity (σ_{ph}) and dark conductivity (σ_d) have been plotted with optical gap.

Table 2
Variation in hydrogen content in Si-H$_n$ mode, i.e. [H_{conc}] and carbon and silicon related microstructure, denoted as I_{990} and R_H, respectively, has been given in this table

E_g (eV)	$\Phi(H_2)$(sccm)	$Y(CH_4)$	[H_{conc}](at%)	I_{990}(cm^{-1})	R_H	I_{790}(cm^{-1})
1.90	100	0.38	8.7	258.2	0.57	108.6
1.92	100	0.50	7.5	230.1	0.58	542.9
1.93	100	0.50	9.1	100.7	0.58	677.8
1.95	100	0.55	6.4	86.3	0.57	716.7
1.97	100	0.60	5.3	72.1	0.56	833.4

Table 3
$\eta\mu\tau$, Urbach energy E_0 (under 100 V cm^{-1} drift field), mid gap defect density N_d of different a-SiC : H samples

Eg (eV)	$\eta\mu\tau$(× 10^{-7}) (V cm s^2)	E_0 (meV)	N_d (× 10^{16}) (cm^{-3})	I_{790} (cm^{-1})	I_{990} (cm^{-1})
1.86	3.63	48.9	8.23	508.3	23.8
1.88	2.10	54.1	4.27	477.8	58.8
1.89	6.40	50.3	2.10	274.1	97.5
1.90	1.50	57.5	5.43	108.6	258.2
1.92	1.36	56.2	8.93	542.9	230.1
1.93	1.66	66.7	9.03	477.8	100.7
1.95	1.90	68.5	–	716.7	86.3

In Table 3, the $\eta\mu\tau$ product, Urbach energy E_0, and midgap defect density N_d of different a-SiC : H samples have been recorded. It may be seen that for set II (RF power density 30 mW cm^{-2}) the $\eta\mu\tau$ product does not increase significantly with

Table 4
Degradation of photoconductivity under white light soaking (100 mW cm^{-2}), where σ_{ph0} is initial and σ_{phss} is steady-state photoconductivity (after 1000 h of light soaking)

Optical gap (eV)	σ_{ph0} (S cm^{-1})	σ_{phss} (S cm^{-1})	$\sigma_{\text{ph0}}/\sigma_{\text{phss}}$
1.88	1.95×10^{-5}	4.88×10^{-7}	40.0
1.90	1.06×10^{-5}	3.69×10^{-7}	28.7
1.92	5.88×10^{-6}	1.14×10^{-7}	51.6
1.93	4.84×10^{-6}	3.69×10^{-7}	13.1
1.95	4.00×10^{-6}	3.92×10^{-7}	10.2

increase in optical gap. In fact, there is some evidence of its decrease. The CH_n related peak intensity is significantly reduced for set II samples with increase in E_g, which is opposite to that observed for set I. Thus carbon incorporation is mostly in the form of Si : C bond leading to a structurally better material.

The photoconductivity σ_{pho} before light soaking, shown in Table 4, shows that it virtually remains constant with increase in optical gap. There is general trend of reduced light soaking effect with increase in optical gap (increase in Si–C bond formation). This may be due to lower hydrogen content of the film and increase in the concentration of more stable Si–C bond.

4. Conclusions

The results reported in this paper indicate the following:

1. It is possible to use CH_n radicals in the plasma to etch out weak H atoms from the growing surface of a-SiC : H films. The vacancy created on the growth surface may be filled by CH_3 or SiH_3 radicals.
2. The process described in 1 leads to an increase in the Si–C bond and lowering of bonded hydrogen content of the a-SiC : H films.
3. Thus if the optical gap of a-SiC : H films is increased by increasing CH_4 flow rate (keeping appropriate hydrogen dilution) it is possible to have wide band gap a-SiC : H film with better opto-electronic and structural characteristics.

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References

[1] F. Demichelis, F. Giorgis, C.F. Pirri, E. Tresso, Phil. Mag. B 71 (1995) 1015.
[2] Y. Kumano, H. Nishiwaki, S. Tsuda, T. Fukatsu, K. Enomoto, Y. Nakashima, H. Tarui, Proc. 16th IEEE PVSC, IEEE, New York 1982, p. 1338.

[3] J. Bullot, M.P. Schmidt, Phys. Stat Sol. B 143 (1987) 345.
[4] P. Chaudhuri, S. Ray, A.K. Batabyal, A.K. Barua, Sol. Ener. Mater. Sol. Cells 36 (1995) 45.
[5] Y. Liu, F. Giorgis, C.F. Pirri, Phil. Mag. B 75 (1997) 485.
[6] R. Robertson, D. Hills, H. Chatham, A. Gallagher, Appl. Phys. Lett. 43 (1983) 544.
[7] H. Sugai, H. Toyoda, J. Vac. Sci. Technol. A 10 (1992) 1193.
[8] T. Fuji, M. Yoshimoto, T. Fuyuki, H. Matsunami, Jpn. J. Appl. Phys. 36 (1997) 289.
[9] A. Matsuda, Y. Yamaoka, S. Wolf, M. Koyama, Y. Imanishi, H. Kataoka, H. Matsuura, K. Tanaka, J. Appl. Phys. 60 (1986) 4025.
[10] G. Lucovsky, J. Yang, S.S. Chao, J.E. Tyler, W. Czubatyj, Phys. Rev. B 28 (1983) 3225.
[11] F. Demichelis, F. Giorgis, C.F. Pirri, E. Tresso, Phil. Mag. B 71 (1995) 1015.