High growth rate of a-SiC:H films using ethane carbon source by HW-CVD method

MAHESH M KAMBLE¹, VAISHALI S WAMAN^{1,2}, SANJAY S GHOSH¹, AZAM MAYABADI¹, VASANT G SATHE³, T SHRIPATHI³, HABIB M PATHAN⁴ and SANDESH R JADKAR^{4,*}

¹School of Energy Studies, University of Pune, Pune 411 007, India

²Department of Physics, Modern College, Pune 411 005, India

³UGC-DAE-CSR, University Campus, Khandawa Road, Indore 452 017, India

⁴Department of Physics, University of Pune, Pune 411 007, India

MS received 16 July 2012; revised 6 December 2012

Abstract. Hydrogenated amorphous silicon carbide (a-SiC:H) thin films were prepared using pure silane (SiH₄) and ethane (C₂H₆), a novel carbon source, without hydrogen dilution using hot wire chemical vapour deposition (HW-CVD) method at low substrate temperature (200 °C) and at reasonably higher deposition rate (19.5 Å/s < r_d < 35.2 Å/s). Formation of a-SiC:H films has been confirmed from FTIR, Raman and XPS analysis. Influence of deposition pressure on compositional, structural, optical and electrical properties has been investigated. FTIR spectroscopy analysis revealed that there is decrease in C–H and Si–H bond densities while, Si–C bond density increases with increase in deposition pressure. Total hydrogen content drops from 22.6 to 14.4 at.% when deposition pressure is increased. Raman spectra show increase in structural disorder with increase in deposition pressure. It also confirms the formation of nearly stoichiometric a-SiC:H films. Bandgap calculated using both Tauc's formulation and absorption at 10⁴ cm^{−1} shows decreasing trend with increase in deposition pressure. Decrease in refractive index and increase in Urbach energy suggests increase in structural disorder and microvoid density in the films. Finally, it has been concluded that C₂H₆ can be used as an effective carbon source in HW-CVD method to prepare stoichiometric a-SiC:H films.

Keywords. a-SiC:H thin films; HW-CVD; FTIR spectroscopy; X-ray photoelectron spectroscopy (XPS); Raman spectroscopy.

1. Introduction

Silicon carbide (SiC) is especially attractive because of its outstanding properties such as large and tunable band gap, high mobility, high thermal conductivity (Bhatnagar and Baliga 1993), resistance to high temperature oxidation and to hard radiation (Dasgupta *et al* 2008a). This material utilized in a wide variety of applications such as solar cells (Han *et al* 1989), light emitting diodes (LEDs) (Kruangam *et al* 1985), microelectronics dielectric layers (Mearns 1969), thin film transistors (TFTs) (Choi *et al* 1996) and so on. The composition of Si and C in the films and hence physical properties of SiC is strongly dependent on Si and C source gases and the preparation technique employed.

Usually device quality SiC is prepared at high substrate temperatures above 1000 °C, which limits its application in thin film solar cells, where low cost substrates cannot withstand high temperatures (> 400 °C). The synthesis of SiC at lower temperatures has, therefore, been a research target for many years. Various processing techniques have been employed over the last two decades to synthesize SiC thin films to get the desired physical and electronic properties at

low substrate temperature. These include plasma enhanced chemical vapour deposition (PE-CVD) (Rajab *et al* 2006; Sha *et al* 2006), sputtering (Wang *et al* 2007; Jin *et al* 2008; Miyajima *et al* 2008), electron cyclotron resonance plasma-enhanced chemical vapour deposition (ECR-PE-CVD) (Ricciardi *et al* 2003), pulsed laser deposition (PLD) (El Khakani *et al* 1997; Soto *et al* 1998), ion implantation (Wang *et al* 2007) and also molecular beam epitaxy (MBE) (Ishihara *et al* 2006). For the synthesis of SiC films, various gases have been used. For Si precursors usually preferred source gases are silane (SiH₄), disilane (Si₂H₆) and tetrachlorosilane (SiCl₄) and for C precursors methane (CH₄), acetylene (C₂H₂), propane (C₃H₈), methylbenzene/toluene (C₇H₈), hexane (C₆H₁₄), methyl chloride (CH₃Cl) and carbon tetrachloride (CCl₄) gases are used for making these films (Mandracci 2001). Various organo-metallic precursors such as tetramethylsilane [(CH₃)₄Si, TMS] (Avigal *et al* 1974), methyltrichlorosilane [CH₃SiCl₃, MTS] (Takahashi *et al* 1992), and hexamethyldisilane [(CH₃)₆Si₂, MDS] (Jacob *et al* 2001) are also used as single-source system to reduce the substrate temperature. Among the various deposition techniques and Si and C source gases, PE-CVD with SiH₄ and CH₄ gas mixtures has been the most widely studied configuration for the synthesis of high-quality a-SiC:H

*Author for correspondence (sandesh@physics.unipune.ac.in)

films. However, this configuration is subject to some drawbacks such as low carbon incorporation efficiency and a low deposition rate (Ricciardi *et al* 2006).

Hot wire chemical vapour deposition (HW-CVD) method has received considerable attention in recent years owing to its capability to synthesize SiC films at low substrate temperature (Kaneko *et al* 2006; Klein *et al* 2006; Tabata *et al* 2009) at higher deposition rates. Recently, the method has been successfully employed for the synthesis of silicon carbide window layers in thin film silicon solar cells achieving maximum conversion efficiency of 9.6% (Chen *et al* 2012). This method has showed a lot of potential to replace the PE-CVD method for the processing of all Si-based thin films. The two major advantages of employing HW-CVD method for the synthesis of Si-based alloy thin films are (i) the absence of the deleterious electrons and ions and surface charges which avoid powder formation and (ii) high dissociation rate of source gases which leads to higher deposition rate. Various carbon source gases like methane (CH_4) (Badaruddin *et al* 2011), monomethylsilane (SiH_3CH_3 , MMS) (Dasgupta *et al* 2008b; Chen *et al* 2011) and acetylene (C_2H_2) (Wu *et al* 2011; Swain and Dusane 2006) etc have been used in HW-CVD for the synthesis of a-SiC:H thin films. These gases have shown strong influence on the physical properties and morphology of the a-SiC:H films. So far, the HW-CVD method has not been studied for the synthesis of a-SiC:H films using ethane (C_2H_6) as carbon source gas and no reports exist in the literature. It is with this motivation that we initiated detailed study of synthesis and characterization of a-SiC:H films using SiH_4 and C_2H_6 gas mixture by HW-CVD method. In this paper, we present detailed investigation of influence of deposition pressure on compositional, structural, optical and electrical properties of a-SiC:H films deposited by HW-CVD from SiH_4 and C_2H_6 gas mixture.

2. Experimental

2.1 Film preparation

In order to meet requirement of the different analysis techniques, a-SiC:H thin films were deposited simultaneously on corning #7059 glass and c-Si wafers in a HW-CVD system, details of which have been described elsewhere (Jadkar *et al* 2000). Films were prepared using a mixture of pure silane (SiH_4) (Matheson Semiconductor Grade) and ethane (C_2H_6) as the reactive gas sources. The pressure during deposition was controlled using manual throttle valve and was varied between 5 and 55 mTorr. The temperature of the tungsten (W) filament was maintained at $2000 \pm 25^\circ\text{C}$. Other deposition parameters are listed in table 1.

The glass substrates were initially cleaned with distilled water and then in hot chromage solution ($70\text{--}80^\circ\text{C}$) for about 15 min. Before the nitrogen flush, the substrates were again cleaned with double distilled water. Whereas, the c-Si wafers were given an HF etch to remove native oxide layer.

Table 1. Deposition parameters employed for synthesis of a-SiC:H films from ethane using HW-CVD method.

Deposition parameter	Value
Deposition pressure (P_{Dep})	5–55 mTorr
Filament temperature (T_{Fil})	2000°C
Substrate temperature (T_{Sub})	200°C
SiH_4 flow rate (F_{SiH_4})	5 Sccm
C_2H_6 flow rate ($F_{\text{C}_2\text{H}_6}$)	0.5 Sccm
Filament to substrate distance ($d_{\text{f-s}}$)	2 cm
Deposition time (t)	10 min

The above cleaning method could give good adhesion of the films to substrates. The substrates were loaded to the substrate holder and then the deposition chamber evacuated to a base pressure of $< 10^{-7}$ Torr. Prior to each deposition, substrate holder and deposition chamber were baked for 2 h at 150°C to remove any water vapour absorbed on the substrate and to reduce the oxygen contamination in the film. Then, the substrate temperature was brought to the desired value by appropriately setting thermocouple and temperature controller. Deposition was carried out for desired amount of time and films were allowed to cool to room temperature in vacuum. Then films were taken out for characterization.

2.2 Film characterization

Dark conductivity (σ_{dark}) and photoconductivity (σ_{photo}) were measured using samples of dimension 3×1 cm deposited on glass substrate with coplanar Al electrodes 0.5 mm apart deposited by vacuum evaporation. The measurements were carried out at room temperature and atmospheric pressure. A constant d.c. voltage was applied to the electrodes and the current passing through the film was measured by a source meter (Keithley, 2400). FTIR spectra were recorded in transmission mode by using FTIR spectrophotometer (JASCO, 6100-type A) in the range of $400\text{--}4000\text{ cm}^{-1}$. The optical bandgap of the a-SiC:H films was deduced from transmittance and reflectance spectra of the films deposited on corning #7059 glass substrates and were measured using a JASCO, V-670 UV-visible spectrophotometer in the range of $250\text{--}1100\text{ nm}$. Raman spectra were recorded with Raman spectroscopy (Jobin Yvon Horibra LABRAM-HR) in the range of $200\text{--}1800\text{ cm}^{-1}$. The spectrometer had backscattering geometry for detection of Raman spectrum with a resolution of 1 cm^{-1} . The excitation source was 632.8 nm line of He-Ne laser. The power of the Raman laser was kept at $< 5\text{ mW}$ to avoid laser induced crystallization on the films. XPS studies were carried out using VSW ESCA machine, having vacuum $> 10^{-9}$ Torr, with $\text{AlK}\alpha$ (1486.6 eV) radiation with a resolution of 1 eV . XPS signal was obtained after several scans in the acquisition process. The spectra were recorded for all the elements as well as for the specific elements (Si, C, O, etc). The charge correction was done by applying silver paste between film surface and metallic sample holder. Low angle X-ray diffraction spectra were obtained by X-ray

Figure 1. Variation of deposition rate as a function of deposition pressure for a-SiC:H films deposited by HW-CVD method.

diffractometer (Bruker D8 Advance, Germany) using CuK α line ($\lambda = 1.54 \text{ \AA}$) at a grazing angle of 1° . Thickness of films was determined by profilometer (KLA Tencor, P-16+) and was further confirmed by UV-visible spectroscopy using the method proposed by Swanepoel (1983).

3. Results and discussion

Low angle XRD pattern for the films deposited in the present study show a broad hump $\sim 2\theta = 27^\circ$ implying that all films are amorphous and no traces of crystalline components were seen. The film characteristics such as deposition rate (r_d), hydrogen bonding configuration, Si-H, Si-C and C-H bond densities and hydrogen content (as revealed by FTIR spectroscopy), optical bandgap, thickness, refractive index and Urbach energy (as revealed by UV-visible spectroscopy), structural disorder (as revealed by Raman scattering) and elemental composition (as revealed by X-ray photoelectron spectroscopy) are presented as a function of deposition pressure.

3.1 Variation of deposition rate

Films are deposited for a desired period and the deposition rate is calculated from thickness measurement. The variation of deposition rate (r_d) as a function of deposition pressure (P_{dep}) is shown in figure 1. As seen from the figure, the deposition rate increases from 19.5 to 35.2 Å/s, when deposition pressure increases from 5 to 55 mTorr. The impingement rate of gas molecules on filament is given by (Kasap and Capper 2006),

$$\frac{P_{\text{dep}}}{\sqrt{2\pi mk_B T}}, \quad (1)$$

where m is the molecular mass, k_B the Boltzmann's constant and T the gas temperature. With increase in deposition

pressure the impingement rate of SiH $_4$ as well as C $_2$ H $_6$ on the hot filament increases. This increases the number of film-forming radicals. As a result, the deposition rate increases with increase in deposition pressure. It is interesting to note that the deposition rate obtained in the present study for SiC films is reasonably high suggesting that C $_2$ H $_6$ is easy to crack both by heated filament and by collision with other ambient gas molecules.

3.2 Fourier transform infra-red (FTIR) spectroscopy analysis

The strongest evidence of formation of SiC films using C $_2$ H $_6$ as carbon source gas in HW-CVD method comes from the Fourier transform infra-red (FTIR) spectroscopy analysis. FTIR transmission spectra (normalized for thickness) of SiC films were deposited by HW-CVD method at different deposition pressures and are shown in figure 2. For clarity, spectra have been broken horizontally into two parts. Following major absorption bands have been identified from the FTIR spectra for the films deposited at different deposition pressures: Si-C stretching mode at $\sim 670 \text{ cm}^{-1}$, Si-H wagging or rocking mode at $\sim 649 \text{ cm}^{-1}$, C-H $_n$ wagging/bending mode at $\sim 1045 \text{ cm}^{-1}$, Si-H $_n$ stretching mode at $\sim 2100 \text{ cm}^{-1}$ and C-H $_n$ stretching mode at $\sim 2800\text{--}3000 \text{ cm}^{-1}$ band (McKenzie 1985; Bulloot and Schmit 1987; Lee *et al* 1991a; Demichelis *et al* 1992). The band at $\sim 2800\text{--}3000 \text{ cm}^{-1}$ is attributed to C-H $_n$ groups in sp^2 ($\sim 2880 \text{ cm}^{-1}$) and sp^3 ($\sim 2960 \text{ cm}^{-1}$) configurations (Kim and Lee 1997). In addition to these, other features observed in the FTIR spectra are the appearance of an absorption band $\sim 1050 \text{ cm}^{-1}$ associated with the asymmetric Si-O-Si stretching mode (Montero *et al* 1994) and a peak centred at $\sim 2250 \text{ cm}^{-1}$ assigned to the H-SiO $_3$ vibration (Lucovsky *et al* 1983). As seen from the FTIR spectra, the absorption, $\sim 670 \text{ cm}^{-1}$, increases with increasing deposition pressure indicating the enhancement of Si-C bond density. Increasing the deposition pressure, the C-H $_n$ absorption band located in the range of $\sim 2800\text{--}3000 \text{ cm}^{-1}$ becomes weak and bond density of C-H bond decreases. The simultaneous appearance of absorption of $\sim 981 \text{ cm}^{-1}$ and $\sim 2960 \text{ cm}^{-1}$ in the FTIR spectra suggest that the Si-C-H $_3$ group has a substantial fraction in a-SiC:H alloys.

The absorption coefficient, α , can be obtained through the Beer-Lambert law

$$T = T_0 e^{-\alpha(\omega)d},$$

where d is the film thickness, T and T_0 are the transmittance of the film-substrate and substrate, respectively and $\alpha(\omega)$ the absorption coefficient at frequency, ω . The number of Si-C ($N_{\text{Si-C}}$), Si-H ($N_{\text{Si-H}}$) and C-H ($N_{\text{C-H}}$) bonds can be estimated from the following (Shanks *et al* 1980; Ray *et al* 1987; Basa and Smith 1990),

$$N = A_\omega \int \frac{\alpha(\omega)}{\omega} d\omega = A_\omega I_\omega, \quad (2)$$

Figure 2. FTIR spectra of a-SiC:H films normalized to thickness deposited by HW-CVD using C_2H_6 carbon source at different deposition pressures.

where the oscillator strength, A_ω , has a value of $2.13 \times 10^{19} \text{ cm}^{-2}$ (Basa and Smith 1990), $1.4 \times 10^{20} \text{ cm}^{-2}$ (Shanks et al 1980) and 1.35×10^{21} (Basa and Smith 1990) cm^{-2} for Si-C, Si-H and C-H, respectively. The merged Si-H, C-H and Si-C bands are de-convoluted to separate out the different bonding configurations present in the films. The variation of Si-C, Si-H and C-H bond densities and the total hydrogen content (C_H) obtained using (2) are displayed in figure 3. As seen from the figure, the bond densities of C-H and Si-H decreases, while Si-C bond density increases with increase in deposition pressure. These results suggest that at higher deposition pressure, unbounded carbon atoms attach with silicon and at lower deposition pressure, it is attached to hydrogen. The decrease in total hydrogen content with increase in deposition pressure further support this. The total hydrogen content decreases from 22.6 to 14.4 at% when deposition pressure increases from 5 to 55 mTorr.

3.3 X-ray photoelectron spectroscopy (XPS) analysis

The formation of SiC films using C_2H_6 as carbon source gas in HW-CVD method was further confirmed from the

Figure 3. Variation of Si-C, Si-H and C-H bond densities and total hydrogen content as a function of deposition pressure for a-SiC:H films deposited by HW-CVD method.

X-ray photoelectron spectroscopy (XPS) measurements. Figure 4(a) shows typical XPS wide scan of HW-CVD grown a-SiC:H film at a deposition pressure of 55 mTorr. The scan

Figure 4. Typical XPS spectra for a-SiC:H film deposited at 55 mTorr by HW-CVD method: (a) wide scan, (b) de-convoluted XPS spectra of Si(2p) in the range of 94–106 eV, (c) de-convoluted XPS spectra of C(1s) in the range of 274–292 eV and (d) de-convoluted XPS spectra of O(1s) in the range of 526–538 eV.

Table 2. Energy peak positions obtained in analysis of XPS results of amorphous silicon carbide films prepared by HW-CVD using C_2H_6 as carbon source gas.

Bond configuration	Energy peak position (Binding energy) (eV)
Si-Si/Si:H	99.2
Si-C	100.5
Si-O _x	103.2
C-Si	283.2
C-C/C-H	284.6
C-O-H	286.4
O-Si	531.2
O-C-H	531.9
O=C	532.8
O-O	533.8

shows the silicon (Si 2p and Si 2s), carbon (C 1s) and oxygen (O 1s) peaks. The oxygen peak was due to adsorbed oxygen and surface oxidation of the film (Wu *et al* 2011). This is consistent with FTIR spectroscopy analysis discussed in previous section (see figure 2). The oxygen found to be incorporated in SiC films which are prepared at even lower base pressure than the pressure employed for the XPS measurements (Wu *et al* 2011). Figures 4(b–d) shows typical narrow scan de-convoluted XPS spectra of the Si(2p), C(1s) and oxygen O(1s) electron state, respectively for the SiC film deposited at 55 mTorr. The spectrum has been decomposed into several peaks based on the assumption that each peak consists of Gaussian/Lorentzian sum function. The Si (2p) peak (94–106 eV) was de-convoluted into the Si-Si, Si-C and Si-O peaks (El Khakani *et al* 1993). The C (1s) peak (274–292 eV) was de-convoluted into the C-Si, C-C, C-OH and C=O peaks (Soloman *et al* 1988a). The O (1s) peak (526–538 eV) was de-convoluted into O-Si, O-CH, O=C and O-O peaks. All films show essentially the same peak components, but with different relative intensities and compositions. The energy positions (Lee 1980; Smith and Black 1984; Soloman *et al* 1988a; Hick *et al* 1990; Lee and Fieselmann 1991b; Gat *et al* 1992; El Khakani *et al* 1993; Choi *et al* 1995; Katiyar *et al* 1995) of these peaks are listed in table 2. The Si (2p) peak could be fitted with three peaks due to Si-C at 100.5 eV, Si-Si/Si:H at 99.2 eV and Si-O_x at 103.2 eV, respectively. The peak at 283.2 eV is due to the carbon atoms in C-Si bonds and the peak at 284.6 and 286.4 eV corresponds to carbon atoms having graphitic and diamond bonding. As Si-Si/Si:H and C-C/C-H peak energy positions are very close to each other, more detailed de-convolutions are not possible at the present stage of the precision in the measurement of XPS spectra. However, it is interesting to note that we have successfully grown the a-SiC:H films using HW-CVD method from C_2H_6 as carbon source gas at reasonably high deposition rates. This is important from the technology point of view.

Figure 5. Raman spectra of a-SiC:H films deposited by HW-CVD at various deposition pressures.

3.4 Raman spectroscopy analysis

Raman spectroscopy is a powerful technique for the characterization of SiC structures in particular, since it allows the identification of various polytypes (Nakashima and Tahara 1989; Pelletier 1999; Nakashima *et al* 2000). The Raman efficiency of SiC is sufficiently high because of the strong covalent bonds in the material. In addition, Raman spectral parameters such as peak position, intensity and linewidth provide useful information on the crystal quality (Choyke *et al* 1997). Figure 5 shows Raman spectra in the range of 200–1800 cm^{-1} of the a-SiC:H films deposited at 5, 25, 35 and 55 mTorr by HW-CVD method using C_2H_6 as carbon source gas. The spectra clearly show a small band centred at $\sim 300 \text{ cm}^{-1}$ corresponding to Si-Si LO (longitudinal optic) mode and its intensity decreases with increase in deposition pressure. Also, Raman spectra show a broad peak centred at $\sim 490 \text{ cm}^{-1}$. This may be assigned to either SiC acoustic phonons particularly reported for smaller SiC crystallites (Nakashima and Harima 1997) or to the transverse optic (TO) phonon mode of a-Si:H (Tanaka *et al* 1999). As mentioned earlier, there are no c-Si phases in the SiC films

Figure 6. Variation in optical bandgap estimated using Tauc's formulation and absorption at 10^4 cm^{-1} as a function of deposition pressure.

over the entire range of deposition pressure studied. Therefore, broad peak centred at $\sim 490 \text{ cm}^{-1}$ in the Raman spectra may be assigned to a-Si:H and its intensity declines with increase in deposition pressure indicating decrease in Si-Si bond concentration. In addition to these, the Raman spectra show a broad shoulder centred at $\sim 642 \text{ cm}^{-1}$. Chen *et al* (2011) also observed similar broad shoulder for $\mu\text{c-SiC:H}$ films deposited by HW-CVD method. However, the origin of this broad shoulder is not still clear. Also, the Raman spectra show a broad shoulder for SiC LO (longitudinal optic) phonon peak and centred at $\sim 974 \text{ cm}^{-1}$ (Feldman *et al* 1968; Karch *et al* 1994), for all deposition pressures. The intensity of both these broad shoulders shows increasing trend with increase in deposition pressure and shift towards lower wave numbers 617 and 945 cm^{-1} , respectively. The increase in intensity implies increase in Si-C bond concentration in a-SiC:H films with increase in deposition pressure. This is consistent with FTIR spectroscopy analysis (see figure 3). The shifting towards lower wavenumber suggests that the structure order deteriorates drastically due to increase in carbon content in the film with increase in deposition pressure. Another interesting point observed in our C_2H_6 carbon source prepared a-SiC:H films is the complete absence of Raman band in the region 1300–1600 cm^{-1} associated with C-C bonds (Wada *et al* 1980) indicating negligible C-C bond concentration in a-SiC:H films over the entire range of deposition pressures studied. This result is indicative of formation of nearly stoichiometric a-SiC:H thin films by HW-CVD method using C_2H_6 carbon source gas.

3.5 UV-visible spectroscopy analysis

Near the absorption edge, absorption coefficient (α) and optical bandgaps (E_g) can be described as follows

$$(h\nu - E_g) \propto (\alpha h\nu)^{1/\gamma}, \quad (3)$$

where $h\nu$ is the photon energy and γ a constant. In the one-electron approximation, $\gamma = 1/2, 3/2$ and 2 for allowed

Figure 7. Variation of static refractive index and Urbach energy of a-SiC:H films deposited by HW-CVD using C_2H_6 as carbon source gas at different deposition pressure.

direct transitions, forbidden direct transitions and indirect transition, respectively (Nakajima *et al* 1996). It is well known that a-SiC:H is the direct gap semiconductor, so $\gamma = 2$ can be used to determine the optical bandgaps of a-SiC:H thin films. However, it is agreed that the determination of bandgap is not accurate using Tauc's formulation (Rajagopalan *et al* 2003) because of the extent of the valence and conduction-band tails in the gap. Furthermore, it is difficult to define a linear dependence of $(\alpha E)^{1/2}$ as a function of $E (= h\nu)$ in the fundamental absorption region, so we used the optical gap E_{04} defined as the energy at which the absorption coefficient is 10^4 cm^{-1} . Figure 6 shows estimated values of optical bandgap using both the Tauc's formulation (E_{Tauc}) and the absorption at 10^4 cm^{-1} (E_{04}) as a function of deposition pressure (P_{dep}). It is seen that both these values follow similar trend with increase in deposition pressure and consistent with the values reported by Solomon *et al* (1988a, b). Also, the optical bandgap values derived using E_{04} method is always higher than the E_{Tauc} values calculated from the Tauc's plot. The three main factors that affect the optical bandgap of hydrogenated SiC films are C to Si ratio, the amount of hydrogen and crystalline fraction (Rajagopalan *et al* 2003). The dependence of optical bandgap on crystalline fraction in the present study is ruled out as all films are amorphous. Our FTIR results and XPS analysis show increase in Si-C bonding and hence carbon content in the film with increase in deposition pressure. As a result, the optical bandgap should increase with increase in deposition pressure. However, in the present study, both E_{04} and E_{Tauc} exhibit decreasing trend with increase in deposition pressure. Thus, only a small amount carbon content cannot account for the bandgap in HW-CVD grown a-SiC:H films. We attribute decrease in bandgap to the decrease in total hydrogen content in the film with increase in deposition pressure.

Variation of static refractive index (n_0) and Urbach energy (E_U) of a-SiC:H films deposited by HW-CVD method using C_2H_6 as carbon source gas is displayed in figure 7. The refractive index values are deduced from the successive

Figure 8. Effect of deposition pressure on dark conductivity and photoconductivity of a-SiC:H films deposited by HW-CVD using C_2H_6 as carbon source gas.

maxima of the interference fringes observed in the UV-visible spectra in the wavelength range from 250 to 1100 nm. Decrease in refractive index with increase in deposition pressure originates from the enhancement of microvoid density (Mui *et al* 1987) and structural disorder in the films with increase in deposition pressure (Swain 2006). This inference is further strengthened by the observed variation in Urbach energy with deposition pressure. The Urbach energy was extracted from exponential tail region in which the absorption coefficient (α) follows the exponential decay with photon energy ($h\nu$) as

$$\alpha = \alpha_0 \exp\left(\frac{h\nu}{E_U}\right), \quad (4)$$

where α_0 is a constant and E_U the Urbach energy that characterizes the exponential slope of the energy dependence. The Urbach energy increases from 142 to 166 meV when deposition pressure increased from 5 to 55 mTorr. The increase in Urbach energy suggests the increase in structural disorder resulting from alloying of silicon with carbon (Conde *et al* 1999).

3.6 Dark conductivity and photoconductivity measurements

Figure 8 shows both dark conductivity (σ_{dark}) and photoconductivity (σ_{photo}) as functions of deposition pressure. As seen from the figure, σ_{dark} was found in the range of $\sim 10^{-7}$ – 10^{-10} S/cm, whereas the σ_{photo} was observed to be almost constant ($\sim 10^{-7}$ S/cm) over the entire range of deposition pressures investigated. As a result, photosensitivity, taken as the ratio of photoconductivity to dark conductivity ($\sigma_{\text{photo}}/\sigma_{\text{dark}}$) decreases from 10^3 to 0.5, when deposition pressure increases from 5 to 55 mTorr. The declination in the photosensitivity may attribute to increase in microvoid density due to increase in structural disorder with increase in deposition pressure. These will act as trapping centres and hampers the photosensitivity. This inference is further strengthened

from refractive index and Urbach energy measurements (see figure 7).

4. Conclusions

Using ethane (C_2H_6) as a carbon source, a-SiC:H thin films were prepared using HW-CVD method without hydrogen dilution at low substrate temperature (200 °C) and at reasonably high deposition rates ($19.5 \text{ Å/s} < r_d < 35.2 \text{ Å/s}$). Formation of a-SiC:H films has been confirmed from FTIR, Raman and XPS analyses. Influence of deposition pressure on structural, optical and electrical properties has been investigated in detail. The deposition pressure was varied between 5 and 55 mTorr. FTIR spectroscopy analysis shows that the bond densities of C–H and Si–H decreases, whereas Si–C bond density increases with increase in deposition pressure. The total hydrogen content drops off from 22.6 to 14.4 at%, when deposition pressure is increased. The absence of band at $\sim 1300\text{--}1600 \text{ cm}^{-1}$ in the Raman spectra implies negligible C–C bond concentration and formation of nearly stoichiometric a-SiC:H films. The optical bandgaps, both E_{Tauc} and E_{04} show decreasing trend with increase in deposition pressure. Decrease in refractive index and increase in Urbach energy with deposition pressure suggests increase in structural disorder and microvoid density in the films. Finally, it has been concluded that C_2H_6 can be used as an effective carbon source in HW-CVD method to prepare stoichiometric a-SiC:H films.

5. Acknowledgements

This work was financially supported by the Department of Science and Technology and Ministry of New and Renewable Energy, Government of India. One of the author (VSW) is thankful to the Bank of Maharashtra, University of Pune branch, for financial support and (MMK) is thankful to the University Grants Commission, New Delhi, for the UGC-BSR research fellowship.

References

- Avigal Y, Schieber M and Levin R 1974 *J. Cryst. Growth* **188** 24
- Badaruddin M R, Muhamad M R and Rahman S A 2011 *Thin Solid Films* **519** 5082
- Basa D K and Smith F W 1990 *Mater. Res. Soc. Symp. Proc.* **162** 439
- Bhatnagar M and Baliga B J 1993 *IEEE Trans. Electron Devices* **40** 645
- Bullot J and Schmit M P 1987 *Phys. Status Solidi B* **143** 245
- Chen T, Huang Y, Dasgupta A, Luysberg M, Houben L, Yang D, Carius R and Finger F 2012 *Sol. Energy Mater. Sol. C* **98** 370
- Chen T, Köhler F, Heidt A, Huang Y, Finger F and Carius R 2011 *Thin Solid Films* **519** 4511
- Choi K, Uchida Y and Matsomuta M 1996 *Jpn. J. Appl. Phys.* **35** 1648
- Choi W K, Loo F L, Ling C H, Loh F C and Tan K L 1995 *J. Appl. Phys.* **78** 7289
- Choyke W J, Matsunami H and Pensl G 1997 *Silicon carbide—A review of fundamental questions and applications to current device technology, 1st edn.* (Akademie Verlag, Berlin: Wiley-VCH)
- Conde J P, Chu V, da Silva M F, Kling A, Dai Z, Soares J C, Arekat S, Fedorov A, Berberan-Santos M N, Giorgis F and Pirri C F 1999 *J. Appl. Phys.* **85** 3327
- Dasgupta A, Huang Y, Houben L, Klein S, Finger F, Carius R and Luysberg M 2008a *Thin Solid Films* **516** 622
- Dasgupta A, Klein S, Houben L, Carius R, Finger F and Luysberg M 2008b *Thin Solid Films* **516** 618
- Demichelis F, Pirri C F, Tresso E and Trapinski T 1992 *J. Appl. Phys.* **72** 5641
- El Khakani M A, Chaker M, Jean J, Boily S and Pepin H 1993 *J. Appl. Phys.* **74** 2834
- El Khakani M A, Chaker M, O'Hern M E and Oliver W C 1997 *J. Appl. Phys.* **82** 4310
- Feldman D W, Parker J H, Choyke W J and Patrik L 1968 *Phys. Rev.* **173** 787
- Gat E., El Khakani M A, Chaker M, Jean J, Boily S, Pepin H, Kieffer J C, Durand J, Cross B and Rousseaux F 1992 *J. Mater. Res.* **7** 2478
- Han M K, Mastsumoto Y, Hirata G, Okamoto H and Hamakawa Y 1989 *J. Non-Cryst. Solids* **115** 195
- Hick S E, Fitzgerald A G, Baker S H and Dines T J 1990 *Philos. Mag. B* **62** 193
- Ishihara H, Murano M, Watahiki T, Yamada A, Konagai M and Nakamura Y 2006 *Thin Solid Films* **508** 99
- Jacob C, Pirouz P and Nishino S 2001 *Mater. Sci. Forum* **127** 338
- Jadkar S R, Sali J V, Takwale M G, Musale D V and Kshirsagar S T 2000 *Sol. Energy Mater. Sol. C* **64** 333
- Jin C G, Wu X M and Zhuge L J 2008, *Res. Lett. Phys. Chem.* p. 5
- Kaneko T, Hosokawa Y, Suga T and Miyakawa N 2006 *Microelectron. Eng.* **83** 41
- Karch K, Pavone P, Windl W, Shutt O and Strauch D 1994 *Phys. Rev. B* **50** 17054
- Kasap S and Capper P 2006 *Springer handbook of electronic and photonic materials* (USA: Springer Publication) p. 663
- Katiyar M, Yang Y H and Abelson J R 1995 *J. Appl. Phys.* **78** 1659
- Kim M T and Lee J 1997 *Thin Solid Films* **303** 173
- Klein S, Carius R, Finger F and Houben L 2006 *Thin Solid Films* **501** 169
- Kruangam D, Endo T, Wei G P, Nonomura S, Okamoto H and Hamakawa Y 1985 *J. Non-Cryst. Solids* **77–78** 429
- Lee W Y 1980 *J. Appl. Phys.* **51** 3365
- Lee Y M and Fieselmann B F 1991b *Appl. Phys. Lett.* **59** 1720
- Lee R C, Aita C R and Tran N C 1991a *J. Vac. Sci. Technol. A* **9** 1351
- Lucovsky G, Yang J, Chao S S, Tyler J E and Czubyti W 1983 *Phys. Rev. B* **28** 3225
- Mandracci P 2001 Ph.D. Thesis, Trento University, Italy
- McKenzie D R 1985 *J. Phys. D* **18** 1935
- Mearns A M 1969 *Thin Solid Films* **3** 201
- Miyajima S, Sawamura M, Yamada A and Konagai M 2008 *Jpn. J. Appl. Phys.* **47** 3368
- Montero I, Galan L and Najmi O 1994 *Phys. Rev. B* **50** 4881
- Mui K, Basa D K and Smith F W 1987 *Phys. Rev. B* **35** 8089
- Nakajima A, Sugita Y, Kawamura K, Tomita H and Yokoyama N 1996 *J. Appl. Phys.* **80** 4006
- Nakashima S and Harima H 1997 *Phys. Status Solidi A* **162** 39
- Nakashima S, Harima H, Tomita T and Suemoto T 2000 *Phys. Rev. B* **62** 16605

- Nakashima S and Tahara K 1989 *Phys. Rev. B* **40** 6339
- Pelletier M J 1999 *Analytical applications of Raman spectroscopy* (UK: Blackwell Science).
- Rajab S M, Oliveira I C, Massi M, Maciel H S, Dos S G, Filho S and Mansano R D 2006 *Thin Solid Films* **515** 170
- Rajagopalan T, Wang X, Lahlouh B, Ramkumar C, Dutta P and Gangopadhyay S 2003 *J. Appl. Phys.* **94** 5252
- Ray S, Das D and Barua A K 1987 *Sol. Energy Mater.* **15** 43
- Ricciardi C, Fanchini G and Mandracci P 2003 *Diamond Relat. Mater.* **12** 1236
- Ricciardi C, Primiceli A, Germani G, Rusconi A and Giorgis F 2006 *J. Non-Cryst. Solids* **352** 1380
- Sha Z D, Wu X M and Zhuge L J 2006 *Phys. Lett. A* **355** 228
- Shanks H, Faug C J, Ley L, Cardona M, Demand F J and Kalbitzer S 1980 *Phys. Status Solidi B* **100** 43
- Smith K L and Black K M 1984 *J. Vac. Sci. Technol. A* **2** 744
- Soloman I, Schmidt M P, Celemand C and Driss Khodja M 1988a *Phys. Rev. B* **38** 13263
- Solomon I, Schmidt M P and Tran-Quic H 1988b *Phys. Rev. B* **38** 9895
- Soto G, Samano E C, Machorro R and Cota L 1998 *J. Vac. Sci. Technol. A* **16** 1311
- Swain B P 2006 *Surf. Coat. Technol.* **201** 1132
- Swain B P and Dusane R O 2006 *Mater. Chem. Phys.* **99** 240
- Swanepoel R 1983 *J. Phys. E: Sci. Instrum.* **16** 1214
- Tabata A, Komura Y, Narita T and Kondo A 2009 *Thin Solid Films* **517** 3516
- Takahashi K, Nishino S, Saraie J and Harada K 1992 *SPP amorphous and crystalline silicon carbide IV* (eds) C Y Yang, et al. (Berlin, Heidelberg: Springer-Verlag) **Vol. 71**, p. 78
- Tanaka T, Maruyama E, Shimida T and Okamoto H 1999 *Amorphous silicon* (Chichester: John Wiley & Sons Ltd.) p. 78
- Wada N, Gaczi P J and Solin S A 1980 *J. Non-Cryst. Solids* **35/36** 543
- Wang M, Diao X G, Huang A P, Chu P K and Wu Z 2007 *Surf. Coat. Technol.* **201** 6777
- Wang Q, Fu S Y, Qu S L and Liu W J 2007 *Solid State Commun.* **144** 277
- Wu T, Shen H, Cheng B, Pan Y, Liu B and Shen J 2011 *Appl. Surf. Sci.* **258** 999