Photoluminescent, wide-bandgap a-SiC:H alloy films deposited by Cat-CVD using acetylene

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Abstract

Hydrogenated amorphous silicon/carbon films (a-Si-C:H) are deposited from a silane and acetylene gas mixture by the catalytic chemical vapour deposition (Cat-CVD) technique. It is observed that under certain conditions of total gas pressure and filament temperature ($T_f$), the optical bandgap varies non-linearly with the acetylene to silane (CH\textsubscript{2}SiH\textsubscript{3}) ratio, having a maximum value of 3.6 eV for a C\textsubscript{2}H\textsubscript{2}/SiH\textsubscript{4} ratio $\geq$ 0.8. However, the deposition rate drastically reduces with an increase in acetylene fraction. FTIR spectra indicate that the total hydrogen content is lower compared to samples deposited by PECVD using similar gas mixtures, with hydrogen being preferentially attached to carbon rather than silicon atoms. The photoluminescence (PL) spectra of these films show PL in the visible spectral region at room temperature. The films with larger bandgap ( $> 2.5$ eV) exhibit PL at room temperature, with the emission having peak energy in the range 2.0–2.3 eV.

Keywords: Chemical vapour deposition (CVD); Acetylene; Fourier-transform infrared spectroscopy (FTIR); Opto-electronic devices

1. Introduction

Hydrogenated amorphous silicon/carbon (a-Si–C:H) alloy films are well suited for optoelectronic device applications, such as solar cells, LEDs, colour sensors \cite{1–5}, etc., mainly due to tailorability of the bandgap and high thermal conductivity. Earlier research has mostly concentrated on the use of plasma-enhanced chemical vapour deposition (PECVD) techniques using methane, acetylene or ethylene as carbon precursors and silane as the silicon source. Optimisation of the deposition conditions, the use of alternate carbon sources and hydrogen dilution have resulted in improved optoelectronic properties of the a-SiC:H films \cite{6–9}. The use of the starving conditions in the PECVD \cite{10} led to an increase in the bandgap of these films. In addition to a wide bandgap, these alloy films exhibited visible PL, which made them potentially useful for applications in light-emitting diodes (LEDs).

In this work, we present the deposition of a-Si–C:H films by the Cat-CVD technique using acetylene (C\textsubscript{2}H\textsubscript{2}) and silane (SiH\textsubscript{4}). Silicon-starving conditions were achieved by the combination of high filament temperature and a high C\textsubscript{2}H\textsubscript{2}/SiH\textsubscript{4} gas ratio. The influence of the gas flow ratio on the film properties was studied using FTIR, UV-Vis and photoluminescence (PL) spectroscopy.

2. Experimental details

The a-Si–C:H films were deposited by the Cat-CVD technique using Matheson grade C\textsubscript{2}H\textsubscript{2} and SiH\textsubscript{4} on crystalline silicon (c-Si) (100), fused quartz and Corning 7059 glass substrates. Changing the acetylene partial flow in the gas mixture from 0 to 0.83 varied the carbon content in the films, while the silane flow was kept constant at a low value. The deposition parameters were as follows:

- Gases used: SiH\textsubscript{4}, C\textsubscript{2}H\textsubscript{2}
- C\textsubscript{2}H\textsubscript{2} fraction: 0–0.83
The optical bandgap of the a-SiC:H films was deduced from transmittance and reflectance spectra of the films, deposited on fused quartz and Corning 7059 glass substrates, and were measured using a Shimadzu UV-Vis spectrophotometer in the range 250–900 nm. The infrared (IR) absorption spectra of the alloy films deposited on c-Si were recorded on a Nicolet Fourier-transform infrared (FTIR) spectrometer in the range 400–4000 cm⁻¹. The hydrogen concentration \( N \) was calculated from the relation \( N = A \times I_a \), where \( I_a \) is the integrated absorption coefficient and \( A \) is a constant. The values of \( A \) used here were \( 1.4 \times 10^{30} \) cm⁻² for the determination of hydrogen bonded to Si and \( 1.0 \times 10^{21} \) cm⁻² for that of the hydrogen bonded to carbon [11]. The film thickness was measured using a Dektak II surface profilometer from a step height in a masked area on the substrate. The PL spectra were recorded at room temperature using excitation at a wavelength of 350 nm.

3. Results and discussion

3.1. Optical bandgap

The optical bandgap of the films was determined from the Tauc plot by extrapolating the linear part of the absorption vs. photon energy \( (h\nu) \) curve. The absorption vs. energy plots of the a-SiC:H films deposited with increasing \( C_2H_2 \) fractions are shown in Fig. 1. Fig. 2 shows the variation of the bandgap as a function of the \( C_2H_2 \) fraction. The bandgap is observed to increase gradually from 2.0 to 2.65 eV, and then rapidly to 3.6 eV for the 0.8 \( C_2H_2 \) fraction. The initial slow increase in the bandgap for \( C_2H_2 \) fractions less than 0.6 may be due to the substitution of Si–Si bonds by Si–C, C–H and C–C strong bonds, while for \( C_2H_2 \) fractions greater than 0.6, the network becomes more carbon-rich, where the bandgap is controlled by the formation of C–C and C–H bonds.

3.2. Infrared absorption

Carbon incorporation and the formation of SiC in the films are indicated in the FTIR spectra of the films (Fig. 3). The major absorption bands observed are in the regions: 2800–3000; 2000–2100; 960–1100; and 740–800 cm⁻¹. The band corresponding to 2800–3000 cm⁻¹ is attributed to the stretching vibration of CH\(_n\) groups in sp\(^2\) (2880 cm⁻¹) and sp\(^3\) (2960 cm⁻¹) configurations, while that at 2000–2100 cm⁻¹ is attributed to the stretching vibration of SiH\(_n\) groups. The band at 960–1100 cm⁻¹ corresponds to CH\(_n\) wagging/bending modes, while the strong band at 780 cm⁻¹ corresponds to the SiC stretching mode. Small bands occur at 880 and 650 cm⁻¹ for the films deposited at \( C_2H_2 \) fractions less than 0.67. These correspond to SiH\(_2\) bending and SiH\(_n\) wagging modes, respectively. These bands are absent for the films deposited at higher \( C_2H_2 \) fractions. The shift of the 2100-cm⁻¹ Si–H stretching peak could be attributed to two things: (1) when nearest-neighbour silicon atoms are progressively
replaced by carbon, oxygen or nitrogen atoms; and (2) (SiH$_n$)$_n$ formation in microvoids. However, (SiH$_n$)$_n$ formation is generally reflected in a concurrent doublet at 840 and 890 cm$^{-1}$ in IR spectra, which is not evident in the samples deposited at high C$_2$H$_2$ fractions. Secondly, the total hydrogen content in our samples is also more than one order of magnitude lower than that in PECVD films. Considering these aspects, we may conclude that most part of the 2100-cm$^{-1}$ band is due to upward shift of the SiH stretch mode, due to the presence of carbon.

The SiC stretching band has a maximum intensity at a C$_2$H$_2$ fraction of 0.67. The integrated intensity of the SiC (stretch) and CH$_n$ (bend/wag) modes is plotted in Fig. 4. The band at 960 cm$^{-1}$, corresponding to the C–H wagging mode, increases with increasing C$_2$H$_2$ fraction and becomes comparable in intensity to the 780-cm$^{-1}$ band, which corresponds to the SiC stretch mode. The presence of a strong band at 960 cm$^{-1}$ (C–H wagging) indicates that there is an increase in hydrogen bonded to carbon at high C$_2$H$_2$ fractions. This strong band, which appears in the spectra of all films, corresponds to the bending and wagging vibrations of (CH$_2$)$_n$–Si and (CH$_3$)$_n$–Si species [12,13]. Such bonding is probably a result of the higher bonding preference of H for C. This is in contrast to the IR spectra of PECVD films, where this band is comparatively weak [14].

The concentration of hydrogen (H) bonded to carbon was evaluated from the integrated intensity corresponding to the band at 2800–3000 cm$^{-1}$ in the IR spectra, while the hydrogen bonded to silicon was obtained from the Si–H stretch band at 2100 cm$^{-1}$. The variation of H bonded to C and to Si as a function of the C$_2$H$_2$ fraction is shown in Fig. 5. The H bonded to carbon, which is larger than that bonded to silicon, is observed to increase with increasing C$_2$H$_2$ flow rate, while the H bonded to silicon decreases. It is observed that, for C$_2$H$_2$ fractions between 0.6 and 0.75, the H bonded to carbon increases slowly, while that bonded to silicon remains fairly constant.

It should be noted that the hydrogen incorporation into these films is more than one order of magnitude less than in PECVD a-SiC:H films [15]. It is also observed that in spite of the decrease in SiC bonding with an increase in the fraction beyond 0.67, the optical bandgap tends to increase, and reaches a maximum of 3.5 eV at a C$_2$H$_2$ fraction of 0.8. We believe that the increase in the bandgap is due to the increase in the sp$^3$-bonded CH$_n$ (observed at 960 cm$^{-1}$) component in the samples. This statement is supported by earlier observations [16,17]. The deposition rate decreases rapidly from 5.74 to 0.5 Å s$^{-1}$ until the C$_2$H$_2$ fraction reaches 0.6, and then gradually decreases to 0.3 Å s$^{-1}$ for high C$_2$H$_2$ fractions. This decrease in the deposition rate is due to the very low concentration of silane at high C$_2$H$_2$ fractions.

### 3.3. Photoluminescence

All the samples were observed to emit visible emission, under excitation of 350-nm photons, with the
carbon-rich films (deposited at \( C_2H_2 \) fraction > 0.6) showing stronger emission. The PL spectra were recorded at room temperature using an excitation wavelength of 350 nm. Fig. 6 shows the variation in room-temperature photoluminescence spectra of the a-SiC:H films with varying bandgaps. The emission colour changes from red to yellow with the increase in bandgap from 2.5 to 3.5 eV. In other words, the spectra shift towards higher energy with increasing optical bandgap. The PL spectra of the a-SiC:H film with a bandgap of 2.45 eV has a full width at half-maximum (FWHM) of 0.45 eV. This spectrum is broad compared to the PL spectra of a-SiH films, whose FWHM values are in the range 0.25–3.0 eV. The broadening of the PL spectra implies increased compositional fluctuations [18]. A closer look at the PL spectrum indicates two important aspects. The emission energy is always much lower than the \( E_g \), and two spectra have a shoulder in addition to the emission peak. For example, the PL spectra of the a-SiC:H film with a 3.5-eV bandgap have a shoulder at approximately 2.13 eV. This implies that the sample has very broad band tails and a high density of localised states. The double band structure for the high bandgap (carbon-rich) films implies the presence of a mixed phase in the amorphous network. The bands in the PL spectra of these films are probably due to the contributions from carbon-rich regions within the SiC network. The carbon-rich a-SiC:H films have earlier been observed to exhibit PL properties similar to those of hydrogenated amorphous carbon (a-C:H) [19,20]. The PL mechanism of a-C:H is still not very clear, due to the complexity of bonding in amorphous carbon and the ability of carbon to form \( sp^3 \) and \( sp^2 \) sites. Further studies are required to correlate the observed PL spectra to the film structure.

Thus, an increase in the bandgap of the films deposited at higher \( C_2H_2 \) fractions is observed, in spite of a decrease in the number of SiC bonds. Secondly, the presence of a prominent band at 960 cm\(^{-1}\) in the IR spectra, corresponding to C–H\(_n\) wag modes, is observed. The hydrogen atoms in this bond would enhance the \( sp^3 \) bonding nature of the carbon atom that may bond to Si to form SiC, or alternately to another carbon atom, resulting in enhanced diamond–like (\( sp^3 \) C–C bonding. The structure of the films obtained in this study is quite different from that observed by Nevin et al. [21], which contained \( sp^2 \) graphitic clusters. The PL spectra of the carbon-rich films have a double band structure. All these points suggest that the films consist of a mixed phase of \( sp^3 \)-bonded carbon atoms in a SiC matrix.

4. Conclusions

a-SiC:H films have been deposited by the Cat-CVD technique using silane and acetylene as the source gases. The dependence of the film properties on the acetylene fraction in the gas mixture has been studied. For acetylene fractions > 0.8, the bandgap reaches 3.5 eV. Hydrogen is preferentially attached to carbon as opposed to silicon atoms. The SiC content, as inferred from the 780-cm\(^{-1}\) IR absorption band, appears to reach a maximum at an acetylene fraction of 0.67. The formation of silicon–carbon bonds is favoured at this \( C_2H_2 \) fraction. For \( C_2H_2 \) fractions > 0.6, there is a decrease in the number of SiC bands, but an increase in H bonded to carbon widens the bandgap of the films. Thus, efficient incorporation of carbon into the silicon network is obtained. It is also possible to exceed the stoichiometric composition. The films seem to consist of a mixed phase of \( sp^3 \)-bonded carbon atoms in a SiC matrix. PL in the yellow spectral region is observed for films deposited at high \( C_2H_2 \) fractions. The tendency to exhibit visible PL makes the Cat-CVD a-SiC:H material potentially useful for applications in LEDs.

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References


