The effect of relatively low hydrogen dilution on the properties of carbon-rich hydrogenated amorphous silicon carbide films

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Abstract. Carbon-rich hydrogenated amorphous silicon carbide (a-Si_{1-x}C_x:H) films were deposited by plasma enhanced chemical vapor deposition (PECVD) using silane, ethylene and hydrogen as gas sources. The effect of relatively low hydrogen dilution on the properties of as-deposited samples was investigated. A variety of techniques including Scanning Electron Microscope (SEM), Fourier transform infrared spectroscopy (FTIR), Raman scattering (RS), UV-VIS spectrophotometer and photoluminescence (PL) spectroscopy were used to characterize the grown films. The deposition rate decreases with hydrogen dilution. The silicon to carbon ratio increases slightly with the addition of hydrogen. The phenomenon can be attributed to the dissipation of power density caused by hydrogen dilution. Raman G peak position shifting to a lower wave number indicates that hydrogen dilution reduces the size and concentration of sp^2 carbon clusters, which is caused by the etching effect by atomic hydrogen. The optical band gap, which is controlled by the sp^2 carbon clusters and Si/C ratio, changes unmonotonously. The as-deposited samples exhibited a blue-green room-temperature (RT) PL well visible to the naked eye with UV excitation. The PL band can be attributed to the radiative recombination of electron-hole pairs within small sp^2 clusters containing C=C and C-H units in a sp^3 amorphous matrix.

1. Introduction
The hydrogenated amorphous silicon carbide (a-Si_{1-x}C_x:H) films have been extensively studied in recent years due to its optoelectronic and electronic applications in solar cells, light emitting diodes, microelectronic dielectric layers, color sensors and high-temperature engineering materials etc [1-5]. The structural, optical and electrical properties of this material can be controlled by the carbon, silicon and hydrogen composition of the films. However, the chemical bonding configurations and film microstructures of a-Si_{1-x}C_x:H materials are very complicated due to the incorporation of carbon and hydrogen since carbon atom can be in a form of sp^2 or sp^3 configuration when it is bonded to Si and H [5]. It is well accepted that the film structures and in turn the physical properties of a-Si_{1-x}C_x:H materials are strongly influenced by the preparation techniques and conditions [5]. a-Si_{1-x}C_x:H films with low carbon content have been studied for many years and are presently used in many fields. However, a-Si_{1-x}C_x:H films with high carbon content emitting visible photoluminescence (PL) at room...
temperature has led to studies of this material for application as the active layer in large-area electroluminescent devices [1, 6]. a-Si$_{1-x}$C$_x$:H films were usually prepared by the plasma enhanced chemical vapor deposition (PECVD) [1, 2, 4, 5], hot wire CVD [3], electron-cyclotron resonance CVD [6] or r.f. sputtering techniques [7] etc. It was reported that the use of reactive plasmas is an effective way to obtain very high deposition rates for a-Si$_{1-x}$C$_x$:H films [1]. And the films prepared by plasma deposition from hydrogen diluted source gases had superior photoelectric properties due to fewer defects, a much less clustered hydrogen phase and more ordered network [4]. Moreover, uniform films with good electronic properties could be easily deposited over a large area by PECVD, so a-Si$_{1-x}$C$_x$:H is quite suitable to be used in flat-screen display devices. Considering its compatibility with semiconductor integrated circuit technology, a-Si$_{1-x}$C$_x$:H is also a good candidate for application in Si-based electroluminescent or optoelectronic devices [8].

The effect of high hydrogen dilution on the structural and optical properties of a-Si$_{1-x}$C$_x$:H has been investigated [9]. However, the influence of relatively low hydrogen dilution on this material has not been systematically studied. In this investigation, we have explored the role and effect of hydrogen dilution on the optical and structural properties of carbon-rich a-Si$_{1-x}$C$_x$:H thin films grown by PECVD technique. A variety of techniques, including FTIR spectroscopy, Raman scattering, SEM and PL spectroscopy were used to characterize the grown films.

2. Experimental details

The a-Si$_{1-x}$C$_x$:H thin films were prepared in an r.f.-PECVD system using SiH$_4$ (diluted to 10% in H$_2$), C$_2$H$_4$ and H$_2$ as gas sources. The reactor was capacitively coupled, consisting of two parallel electrodes, powered electrode and grounded electrode, within a stainless steel chamber (grounded), operated at a radio frequency of 13.56 MHz. During deposition the C$_2$H$_4$ and H$_2$-diluted 10% SiH$_4$ gas were fixed at 10 and 20 sccm respectively. The total flow rates of H$_2$ (with 18 sccm in H$_2$-diluted 10% SiH$_4$) were controlled at 18, 20, 43 and 88 sccm, and the samples were marked as H1–H4 respectively. The total gas flow rate of all precursors was in the range of 30-100 sccm. P-type silicon (100) wafers and glass slides (7101) were used as the substrates. The chamber pressure and plasma power were maintained at 80 Pa and 50 W, respectively. The growth temperature was fixed at room temperature.

The film thicknesses were obtained by cross-sectional SEM (Hitachi S4800) images of the samples. The FTIR measurements were carried out in transmission mode by using a Nicolet 380 FTIR Spectrometer in the mid-IR region with a resolution of 4 cm$^{-1}$. RT micro Raman spectroscopy analyses were performed on a Labor Raman HR800 spectrometer. A laser line 514.5 nm was used as the excitation source. The RT PL spectra were obtained with a FLS920 (Edinburgh Instruments Ltd.) fluorescence spectrometer using a 325 nm UV xenon lamp as the excitation source.

3. Results and discussion

The cross-sectional SEM of film H2 is shown in figure 1. The surface of the film and the interface between the Si substrate and the a-Si$_{1-x}$C$_x$:H layer is smooth. The film is homogeneous, and no crystallites are observed in figure 1.

The thicknesses of all films were obtained from SEM images, and the film deposition rate is calculated by dividing the film thickness by the deposition time. Figure 2 shows the deposition rate as a function of hydrogen flow rate. The deposition rate of the a-Si$_{1-x}$C$_x$:H film decreases as the hydrogen flow rate increases because of the decreasing partial pressure of silane and ethylene and an etching effect of hydrogen plasma [10]. With the increase in hydrogen flow rate, the deposition rate decreases from 26.1 nm/min at the hydrogen flow rate of 18 sccm to the minimum value of 13.8 nm/min at 88 sccm.
Figure 1. The cross-sectional SEM image of film H2

Figure 2. The variation of deposition rate as a function of total H2 flow rate

Figure 3(a) shows the FTIR transmission spectra of the a-Si1-xCx:H films as a function of hydrogen flow rate. In order to compare the content of each bond between the films, FTIR spectra were normalized by the film thicknesses. The spectra are characterized by 3 regions:

a) 500-1200 cm⁻¹
b) 2000-2300 cm⁻¹
c) 2800-3000 cm⁻¹

The spectra between 500-1200 cm⁻¹ cannot be fitted into several Gaussian peaks precisely because of too many IR-characteristic peaks in this region. We had to pick peaks directly from the absorption spectra of this region (figure 3(b)), and plotted them in figure 3(c) as a function of hydrogen flow rate. Although the peak positions cannot indicate corresponding IR vibration modes accurately, we can obtain some bonding information from their shifts. The peak at 790 cm⁻¹ is due to Si-CH₃ rocking/wagging or Si-C stretching mode [1, 2, 5, 8, 11, 12]. The peak associated with a Si-C stretching mode should be at 670 cm⁻¹, which is covered by the strong 790 cm⁻¹ peak. The absorption band at 845 and 890 cm⁻¹ is attributed to (SiH₂)ₓ bending [9]. The relative intensity of (SiH₂)ₓ bending modes to that of Si-C stretching mode decreases with the increase of hydrogen flow rate, shown in figure 3(b). This result indicates that the SiH₂ radicals of the films decrease upon hydrogen dilution. A strong feature at 1040 cm⁻¹ is assigned both to the C-H wagging mode around 1000 cm⁻¹ [1, 3-5, 9, 11, 13] and the Si-O stretching vibration at 1100 cm⁻¹ [2, 11]. The Si-O stretching mode is due to oxygen contamination during deposition process and sample preservation. The absorption band at around 1250 cm⁻¹ is attributed to the bending mode of Si-CH₃ bonds [1, 4, 5, 8, 11]. From figure 3(c), it was found that the 790 cm⁻¹ and 840 cm⁻¹ peak position tend to shift to a lower wavenumber upon hydrogen dilution. The 1040 cm⁻¹ peak has the same trend except for sample H2 whose blue-shift may be caused by a stronger Si-O peak. As will be discussed later, the downward shift of these peaks is caused by the decreasing carbon content.

Figure 3(a) also shows the band of Si-Hₓ stretching between 2000-2300 cm⁻¹ [1, 2, 4, 5, 8]. Si-H and Si-H₂ stretching mode are supposed to be located at 2000 and 2090 cm⁻¹ respectively. The two peaks in our experiment shift to a higher wavenumber than those of a-Si:H. This is caused by the increase in electronegativity due to C substitution when C is bonded to Si, which shortens the Si-H distance and increases the vibrational frequency of Si-H bonds. The broad Si-Hₐ absorption peak was fitted with two Gaussians and a linear background. From this curve fitting, it was found that the positions of these two peaks tended to shift to a lower wavenumber (figure 3(d)), which means less carbon content upon hydrogen dilution. Meanwhile we plotted the ratio of integrated intensities of the Si-H and Si-H₂ stretching mode as a function of hydrogen flow rate. The decrease of Si-Hₓ/Si-H ratio indicates that SiHₓ radicals in the films decreases upon hydrogen dilution. The result is consistent with the discussion of figure 3(b).
The absorption band around 2800-3000 cm\(^{-1}\) [1, 2, 5, 8, 14] is attributed to sp\(^3\) C-H\(_n\) stretching modes. The sp\(^2\) C-H\(_n\) absorption band is around 2975-3085 cm\(^{-1}\), which is so weak that it is covered by the broad sp\(^2\) C-H\(_n\) absorption band. Within the 2800-3000 cm\(^{-1}\) region, notably the peak at 2956 cm\(^{-1}\) (attributed to sp\(^3\) C-H\(_3\) and sp\(^2\) C-H\(_n\)) becomes weaker compared with 2875 cm\(^{-1}\) peak (sp\(^3\) C-H\(_2\) and C-H\(_3\)). It indicates the reduction of sp\(^2\) C-H\(_n\) upon H\(_2\) dilution, and this is supported by the following Raman spectra analysis. Sp\(^1\) C-H\(_n\) absorption band at 3300 cm\(^{-1}\) is not observed [8, 14]. The relative intensity of C-H\(_n\) band (2000-2300 cm\(^{-1}\)) to that of Si-H\(_n\) band (2000-2300 cm\(^{-1}\)) decreases with the increase of H\(_2\) flow rate (shown in figure 3(d)). This indicates that the Si/C ratio of the films increases upon H\(_2\) dilution. With increasing H\(_2\) flow rate, less C atoms are cooperated into the films. And the decrease of carbon content leads to all the FTIR peaks shifting to lower wavenumbers.

In this experiment, the flow rates of SiH\(_4\) and C\(_2\)H\(_4\) is 40% of total flow rate to 12% for sample H1 to H4. Hence, the power density distributed to SiH\(_4\) and C\(_2\)H\(_4\) decreases notably from 40% of the total input power to 12% with the increase of H\(_2\) flow rate. It has been reported that r.f. power density is an important parameter which affects the carbon content of the films [15]. SiH\(_4\) and C\(_2\)H\(_4\) contribute to the formation of a-Si\(_{1-x}\)C\(_x\):H films. As the addition of H\(_2\) leads to less power density distributing to SiH\(_4\) and C\(_2\)H\(_4\), the Si/C ratio increases with increasing H\(_2\) flow rate. In the case of high H\(_2\) dilution, the Si/C ratio dose not change with the addition of H\(_2\). It can be explained that the power density distributed to the C and Si related precursors is not affected evidently, since their content is very low compared with H\(_2\). For example, in the report of Park et al. [9], the tetramethylsilane (TMS) is no more than 3% of the total flow rate. So the change of power density with H\(_2\) dilution is less than 3% of the total input power. Thus the Si/C ratio kept almost constant.

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**Figure 3.** (a) FTIR spectra of a-Si\(_{1-x}\)C\(_x\):H films deposited at different H\(_2\) flow rates, (b) FTIR absorption spectra between 600-1200 cm\(^{-1}\), (c) FTIR peak positions at 800, 840, and 1040 cm\(^{-1}\), (d) FTIR peak positions of Si-H and Si-H\(_2\) stretching mode, and the ratio of integrated intensities of Si-H/Si-H\(_2\) peak and C-H/Si-H peak.
Figure 4. (a) Raman spectra a-Si$_{1-x}$C$_x$:H films deposited at different H$_2$ flow rates, (b) The variation of G peak position and optical band gap as a function of H$_2$ flow rate.

Figure 4(a) shows Raman spectra of the as-deposited a-Si$_{1-x}$C$_x$:H films as a function of hydrogen flow rate under visible excitation (514.5 nm). In accordance with FTIR, Si-H n Raman modes at 2000-2300 cm$^{-1}$ [4] are also observed, which exhibit a redshift with increasing hydrogen flow rate. No amorphous Si-Si Raman mode at 480 cm$^{-1}$ was detected, indicating no amorphous silicon clusters exist in our samples. The Si-C band, which is expected to be at around 780 cm$^{-1}$, is not observed since the Raman efficiency of the Si-C band is much smaller than that of C-C and Si-Si bands [1, 4].

The carbon-rich a-Si$_{1-x}$C$_x$:H basically has a structure similar to that of pure a-C:H, so the Raman spectra can be analyzed relatively to that of amorphous carbon [9, 16]. The typical Raman spectra of a-C:H consists of two broad bands: G band (G for graphite) at about 1580 cm$^{-1}$ and D band (D for disordered) at approximately 1350 cm$^{-1}$. The G band is the stretching vibration of any pair of sp$^2$ sites, whether in C=C chains or in aromatic rings, while the D band is breathing mode of those sp$^2$ sites only in rings, not chains [14]. G band is observed at about 1590 cm$^{-1}$ in our experiment. The result indicates that the samples contain amorphous carbon clusters consisting of sp$^2$ C=C chains. The sp$^2$ sites are organized in very small clusters because D band is absent in all samples [14]. Since the signal to noise ratio of Raman results is poor, the G peak positions are obtained by fitting the region of 1500-1700 cm$^{-1}$ into Gaussian curves then plotted in figure 4(b). In a typical Raman spectra for amorphous carbon, the position of the G band shifts significantly if the sp$^2$/sp$^3$ carbon ratio of the film varies [9]. As is seen from figure 4(b), the position of the G peak shifts to the lower wave number region as the flow rate of hydrogen increases. This shift implies that hydrogen dilution promotes a reduction in the size and number of sp$^2$ carbon clusters in a-Si$_{1-x}$C$_x$:H [9]. The peak around 1400 cm$^{-1}$ is attributed to carbon network attached with Si [12]. The peak at 1450 cm$^{-1}$ assigned by Ferrari and Robertson [17] arises from vibrations of trans-polyacetylene like structural units.

The optical band gap derived from optical transmission spectra for a-Si$_{1-x}$C$_x$:H films deposited at different hydrogen flow rates are shown in figure 4(b). The optical band gap first slightly increases, then decreases as the hydrogen flow rate increases. The result is different from the report of high hydrogen dilution [9]. The optical band gap behavior as a function of hydrogen dilution is rather complex because it is controlled by two factors: the sp$^2$ carbon clusters and the Si/C ratio. As revealed by Raman spectra, carbon-rich a-Si$_{1-x}$C$_x$:H films contain sp$^2$ carbon clusters embedded in sp$^3$-bonded matrix, and hydrogen dilution promotes a reduction in the size and number of sp$^2$ clusters in a-Si$_{1-x}$C$_x$:H. The σ-bonds of sp$^2$ sites have a wider band gap than that of the sp$^2$ carbon cluster sites. Therefore, the optical band gap is partly determined by the size and distribution of sp$^2$ carbon clusters. A reduction in relative concentration of sp$^2$ carbon results in increase in optical band gap [9]. However, in this experiment, Si/C ratio increases upon hydrogen dilution. More silicon content leads to lower optical band gap. The two factors contributing to the optical band gap simultaneously causes the non-monotonous change shown in figure 4(b).
The room temperature PL spectra from samples deposited at various hydrogen flow rates are shown in figure 5. The as-deposited samples exhibited a blue-green room-temperature PL well visible to the naked eye. Using the framework of a-C:H, the PL mechanism of carbon-rich a-Si$_{1-x}$C$_x$:H films can be interpreted by Robertson’s “cluster” model[1, 9]. Photoexcited carriers are believed to be confined inside sp$^2$ clusters in the films. The origin of the PL is the geminate recombination of electron hole pairs within sp$^3$ bonded carbon clusters in a sp$^3$ bonded amorphous matrix. The $\pi$ states of the sp$^2$ sites form the valence- and conduction-band edges and lie closest to the band gap, so optical excitation creates electron hole pairs in the $\pi$ and $\pi^*$ states. The narrow $\pi$-$\pi^*$ gap of sp$^2$ sites surrounded by the wider gap of sp$^3$ sites creates large band-edge fluctuations which tend to strongly localize tail states. PL occurs by the radiative recombination of photo-excited electrons and holes in localized tail states within sp$^2$ clusters after loosing their excess energy through the thermalization processes [18, 19]. The sp$^2$ clusters contain different structural units with double conjugated C=C bonds, which act as recombination centers [10].

Figure 5. Room temperature photoluminescence spectra of a-Si$_{1-x}$C$_x$:H films at different H$_2$ flow rates.

4. Conclusion
The properties of carbon-rich a-Si$_{1-x}$C$_x$:H films prepared by PECVD was investigated. The samples were deposited using silane, ethylene and hydrogen as gas sources at a relatively low hydrogen dilution. The flow rates of silane and ethylene and other deposition parameters were kept constant, meanwhile the concentration of hydrogen was controlled between 60%-88%. A variety of techniques including SEM, FTIR, RS, UV-VIS spectrophotometer and PL were used to characterize the grown films. The deposition rate decreases with hydrogen dilution due to the decreasing partial pressure of silane and ethylene and an etching effect of hydrogen plasma. The Si/C ratio slightly increases with the addition of hydrogen, which is different from that of high hydrogen dilution. The phenomenon can be attributed to the dissipation of power density caused by hydrogen dilution. And less power density leads to higher Si/C ratio. The shift of the Raman G peak position to a lower wave number indicates that hydrogen dilution reduces the size and concentration of sp$^2$ carbon clusters, caused by the etching of sp$^2$ clusters by atomic hydrogen. The optical band gap, which is controlled by the sp$^2$ carbon clusters and the Si/C ratio, changes unmonotonously. The as-deposited samples exhibited a blue-green room-temperature PL well visible to the naked eye with UV excitation. The PL band can be attributed to the radiative recombination of electron-hole pairs within small sp$^2$ clusters containing C=C and C-H units in a sp$^3$ bonded amorphous matrix.
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