The influence of radio frequency power on the characteristics of carbon-rich hydrogenated amorphous silicon carbide films

Juncao Bian, Zhe Li, Haiyan He, Xiwen Zhang, Jiang Lin, Qian Gao, Zhongdong Chen and Gaorong Han

1 State Key Laboratory of Silicon materials, Zhejiang University, Hangzhou 310027, PR China

E-mail: zhangxw@zju.edu.cn

Abstract. A series of carbon-rich hydrogenated amorphous silicon carbide (a-Si\textsubscript{1-x}C\textsubscript{x}:H) films were prepared at different radio frequency (RF) powers from silane-ethylene-hydrogen plasma. The effect of the RF power on the bonding configurations and microstructures has been investigated. The grown films were characterized by a collection of techniques including Scanning Electron Microscope, Fourier transform infrared(FTIR) spectroscopy, Raman scattering and photoluminescence spectroscopy. The deposition rate increases upon RF power due to the enhancement of chemical reactivity of plasma. The carbon to silicon ratio increases, for more C\textsubscript{2}H\textsubscript{4} molecules decompose with the enhancement of RF power and more carbon atoms are bonded into the films. Raman G peak position shifts to a higher wavenumber, which indicates that the size and concentration of sp\textsuperscript{2} carbon clusters increase as the RF power becomes stronger. Blue-green photoluminescence is detected at room temperature. The PL band can be attributed to the existence of the amorphous carbon clusters in films with high carbon concentrations.

1. Introduction
Hydrogenated amorphous silicon carbide (a-Si\textsubscript{1-x}C\textsubscript{x}:H) attracts much attention for use in solar cells, light emitting diodes, microelectronic dielectric layers, colour sensors and high temperature engineering materials etc [1-5]. The structural and optoelectronic properties of this material are known to be considerably sensitive to the nature of bonding of their constituent atoms. For instance, carbon can have two different probable bonding configurations characterized by the sp\textsuperscript{2} and sp\textsuperscript{3} hybridizations which exhibit very different physical properties. The relative proportions of the sp\textsuperscript{2} and sp\textsuperscript{3} components in these films are therefore believed to control the quality of the films and are expected to be

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To whom any correspondence should be addressed.

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influenced to a large extent by the deposition parameters such as the substrate temperature [6], radio frequency (RF) power [7, 8], gas flow rates [1, 9] and hydrogen dilution [10]. Even the nature of the source gases (CH$_4$ or C$_2$H$_4$) can affect the bonding properties [11]. Therefore, from the viewpoint of actual applications it is important to clarify the relationship between the deposition parameters and the film microstructures and demonstrate luminescence mechanism. In the work reported here, a-Si$_{1-x}$C$_x$:H thin films were fabricated by PECVD technique on Si (100) substrates at room temperature, and the influence of RF power on the characteristics of a-Si$_{1-x}$C$_x$:H thin films was investigated in details.

2. Experimental details

The a-Si$_{1-x}$C$_x$:H thin films were prepared in an RF-PECVD system equipped with a radio frequency source operated at a frequency of 13.56 MHz using SiH$_4$ (diluted to 10% in H$_2$) and C$_2$H$_4$ as gas sources. The deposition process was carried out at room temperature (RT) and the RF power was changed from 20 to 140 W increase by 30 W, named as P1~P6. The H$_2$-diluted 10% SiH$_4$ and C$_2$H$_4$ gas were fixed at 20 and 10 sccm respectively, and the chamber pressure was maintained at 50 Pa. P-type Si (100) wafers were used as substrates.

The chemical bonding within the films was determined by using Fourier transform infrared spectrometry (FTIR). RT micro Raman spectroscopy analyses were performed on a Labor Raman HR800 spectrometer at a laser power of 30 mW. The surface morphology and film thicknesses were studied by Hitachi S4800 field-emission scanning electron microscopy (FE-SEM). 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 FE-SEM image depicted in figure 1 clearly indicates the smooth interface between the a-Si$_{1-x}$C$_x$:H layer and the Si substrate, which is attributed to the enough density of reactants and a good dissociation of the gases [12]. Figure 2 shows the deposition rate as a function of RF power, which is calculated by dividing the film thickness by the deposition time. It is observed that the deposition rate increases as the RF power becomes higher and exhibits a quasi-linear relationship. The results are in good agreement with previously reported data obtained by Ciprian I et al [12]. This phenomenon can be explained as follows. The higher power enhances the plasma in the chamber, which subsequently yields higher energy electrons. The increased energy of the electrons enhances the dissociation of the main gases and, as a result, increases the deposition rate [13]. It is also found from figure 2 that when the RF power is more than 100W, the increase becomes slow. It most probably stems from the erosion effect of the plasmas and the limit of mass transport at high RF power.

Figure 3 shows the FTIR absorption spectra of all the samples. In order to compare the content of each bond among the films, FTIR spectra were normalized by the film thicknesses. They are characterized by 3 regions: a) 600-1200 cm$^{-1}$, b) 2000-2300 cm$^{-1}$ and c) 2800-3000 cm$^{-1}$. 
Figure 1. The cross-sectional SEM image of the film P2.

Figure 2. The variation of deposition rates as a function of RF power.

Figure 3. FTIR absorption spectrum of a-Si$_{1-x}$C$_x$:H films deposited at different RF powers.

Figure 4. 2000-2300 cm$^{-1}$ FTIR spectrum of a-Si$_{1-x}$C$_x$:H films deposited at different RF powers.

The mode at 790 cm$^{-1}$ is due to Si-CH$_3$ rocking/wagging or Si-C stretching modes [2, 5, 8-11]. 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 and thus indicates the formation of a-Si$_{1-x}$C$_x$:H film. A strong feature at 1040 cm$^{-1}$ is assigned both to the C-H wagging mode around 1000 cm$^{-1}$ [3-6, 8] and the Si-O stretching vibration at 1100 cm$^{-1}$ [4, 5]. The Si-O stretching mode is due to oxygen contamination during deposition process and sample preservation.

In the region between 2000-2300 cm$^{-1}$ displayed in figure 4, the band appearing at 2080 cm$^{-1}$ in the spectra corresponds to the shifted stretching mode of Si-H$_x$ vibrations [14]. This vibrational mode has a frequency of 2000 cm$^{-1}$ in pure a-Si:H while it shifts to higher frequencies in a-Si$_{1-x}$C$_x$:H films. This chemical shift is due to the bonding of C atoms with Si atoms bonded with H atoms.
The third absorption band around 2800-3000 cm\(^{-1}\), as shown in figure 5(a), is due to sp\(^3\) C-H\(_n\) stretching modes [8, 9]. 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\(^3\) C-H\(_n\) absorption band. The peak at 2956 cm\(^{-1}\) is attributed to sp\(^3\) C-H\(_3\) and sp\(^2\) C-H\(_2\). And the peak at 2875 cm\(^{-1}\) is attributed to sp\(^3\) C-H\(_2\) and C-H\(_3\). The relative intensity of C-H\(_n\) stretching modes (2000-2300 cm\(^{-1}\)) to that of Si-H\(_n\) stretching mode, displayed in figure 5(b), decreases with the increase of RF power. It indicates that the C/Si ratio of the films increases upon RF power. As the RF power increases, the energy of the electrons increases, which enhances the dissociation of the C\(_2\)H\(_4\), and hence more C atoms are cooperated into the films.

Figure 6 shows Raman spectra of various a-Si\(_{1-x}\)C\(_x\):H films deposited at different RF powers. No amorphous Si-C band at around 780 cm\(^{-1}\) are observed, which is due to their extremely low scattering cross-section and low absorption coefficient in the amorphous state [15]. Si-H\(_n\) Raman modes at 2000-2300 cm\(^{-1}\) [9] are also observed, which exhibit a redshift with increasing RF power. The
carbon-rich a-Si$_{1-x}$C$_x$:H basically has a structure similar to pure a-C:H, so the Raman spectrum can be analyzed relative to amorphous carbon [8, 12]. The broad band near 1400-1500 cm$^{-1}$ is attributed to the C-C intrinsic vibrations [15]. The vibrations of graphitic carbon have the characteristics of a high scattering cross-section and high absorption coefficient for the excitation frequency. Hence, the presence of even a small fraction of graphitic carbon can be detected. The G peak positions are obtained by fitting the region of 1500-1700 cm$^{-1}$ into Gaussian curves since the poor signal to noise ratio of Raman results. And the G peak positions are plotted in figure 6b, from which it is observed that the position of the G peak shifts to the higher wavenumber as the RF power increases. This shift implies that a fraction of sp$^2$ bonded carbon atoms are increased upon RF power. Based on the trend in the Raman spectra, it appears that high RF power promotes an increase in the size and number of sp$^2$ clusters in a-Si$_{1-x}$C$_x$:H.

Figure 7. PL spectrum of a-Si$_{1-x}$C$_x$:H films deposited at different RF powers.

Figure 7 presents the room temperature PL spectra of samples deposited at various RF power, from which no clear discipline is found. The PL mechanism of carbon-rich a-Si$_{1-x}$C$_x$:H films can be interpreted by Robertson’s model [16]. Photoexcited carriers are believed to be confined inside sp$^2$ clusters. The origin of the PL is the geminate recombination of electron-hole pairs within sp$^2$ bonded carbon clusters in a sp$^3$ bonded amorphous matrix. The π states of the sp$^2$ sites form the valence-band and conduction-band edges and lie closest to the band gap. Hence optical excitation creates electron hole pairs in the π and π* states. The narrow π-π* 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. The sp$^2$ clusters contain different structural units with double conjugated C=C bonds, which act as recombination centers.

4. Conclusion
The carbon-rich a-Si$_{1-x}$C$_x$:H films were deposited by PECVD technique with SiH$_4$ and C$_2$H$_4$ as reactant gases. The influence of RF power on the configurations and microstructures of carbon-rich
a-Si_{1-x}C_x:H films was explored. It is found that the RF power is an important parameter which affects the carbon content, the structure and the bonding configurations of the films. The carbon to silicon ratio increases due to more C_2H_4 molecules decomposed with the enhancement of RF power and more carbon atoms are bonded into the films. Raman G peak position shifts to a higher wavenumber, which indicates that the size and concentration of sp^2 carbon clusters increases as the RF power became stronger. Blue-green photoluminescence is detected at room temperature on the as-deposited samples with UV excitation. The PL band can be attributed to the existence of the amorphous carbon clusters in films with high carbon concentrations.

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