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Photoluminescence of amorphous carbon films fabricated by layer-by-layer hydrogen plasma chemical annealing method*

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A method in which nanometre-thick film deposition was alternated with hydrogen plasma annealing (layer-by-layer method) was applied to fabricate hydrogenated amorphous carbon films in a conventional plasma-enhanced chemical vapour deposition system. It was found that the hydrogen plasma treatment could decrease the hydrogen concentration in the films and change the sp^2/sp^3 ratio to some extent by chemical etching. Blue photoluminescence was observed at room temperature, as a result of the reduction of sp^2 clusters in the films.

Keywords: hydrogen plasma annealing, amorphous carbon, photoluminescence
PACC: 6855, 6140, 7855

1. Introduction

Hydrogenated amorphous carbon (a-C:H) and carbon-rich amorphous silicon carbide (a-SiC:H) films have attracted much attention both for their interesting physical properties and for their applications in various opto-electronic devices.[1−3] Usually, a-C:H films are prepared by using methane (CH_4) gas in a plasma chemical vapour deposition (CVD) system. A strong visible, room-temperature photoluminescence (PL) has been observed from these materials and the PL spectra show a single broad peak with a half peak width about 0.5eV. So far, many papers have been published on the fabrication and PL behaviour in a-C:H films,[4−10] but most of the observed PL bands are located in the red to green spectral range. Not much work has been performed on blue light emission from a-C:H films though this is very important for realizing full colour flat screen display devices. Very recently, it was reported that blue emission (∼2.95eV) can be obtained from polymer-like a-C:H films by using UV photons as the excitation source, though the blue light intensity is still weak compared with that of the main PL peak.[11]

It is well known that the carbon configurations, sp^2/sp^3 ratio and hydrogen content play important roles in controlling the physical properties of a-C:H films, and these parameters can be varied over a wide range depending on the fabrication process and conditions.[3−5,12] In this paper, we describe the preparation of a series of a-C:H films by using a novel deposition method which alternates the deposition of a nanometre-thick film layer with subsequent exposure of the growing surface to hydrogen plasma treatment. This method, known as the layer-by-layer or chemical annealing technique, has been used to prepare device-quality hydrogenated amorphous Si (a-Si:H) and SiGe (a-SiGe:H) films.[13−15] The microstructures and PL properties of a-C:H films were investigated and compared with the sample which did not undergo hydrogen plasma annealing. It was found that the sp^2/sp^3 ratio could be varied by using hydrogen plasma treatment, and consequently blue PL was observed at room temperature.

2. Experimental procedure

Hydrogenated amorphous carbon films in the present study were fabricated in a modified capacitance-coupled plasma CVD system. Figure 1

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shows a schematic diagram of the CVD set-up. The substrates were placed on an earthed electrode instead of a powered electrode. Besides the radio-frequency (rf) power used to decompose the reaction gases, an independent dc bias (+20V) was applied between the two parallel-plate electrodes, which were 2.5cm apart in order to assist the carbon film growth.

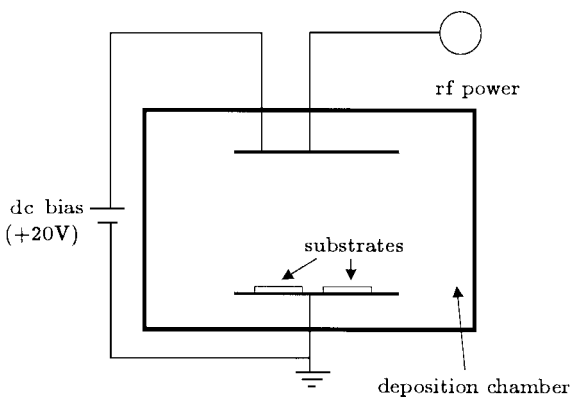


Fig.1. Schematic diagram of the CVD set-up for a-C:H deposition.

During the deposition, the substrate temperature and rf power were kept at 100°C and 50W, respectively. Three kinds of deposition conditions were used to prepare the a-C:H films. For the sample marked as S271, only 10sccm methane (CH_4) gas was introduced into the reaction chamber. For sample S274, a mixture of CH_4 and hydrogen (H_2) gases was used. For sample S275, a thin a-C:H layer of 5nm thickness was first deposited by using a CH_4 and H_2 gas mixture, followed by subsequent exposure of the growing surface to hydrogen plasma for 20s. The above procedure was then repeated sixteen times. The details of the deposition conditions are listed in Table 1. Silicon (100) wafers were used as substrates for the PL, Fourier transform infrared (FT-IR) spectroscopy and x-ray photoelectron spectroscopy (XPS) measurements, while quartz glass plates were used for optical absorption experiments, and the optical bandgap of the a-C:H films was deduced from the Tauc plot.

Table 1. Deposition conditions in the present study.

Sample No.	Layer description	Gas flow rate/sccm CH_4	Gas flow rate/sccm H_2	Pressure /Pa	Optical bandgap/eV
S271	a-C:H	10	/	6.3	2.7
S274	a-C:H	10	10	18.3	3.0
S275	a-C:H	10	10	16.3	3.5
	H_2 plasma treatment	/	10	10.5	

3. Results and discussion

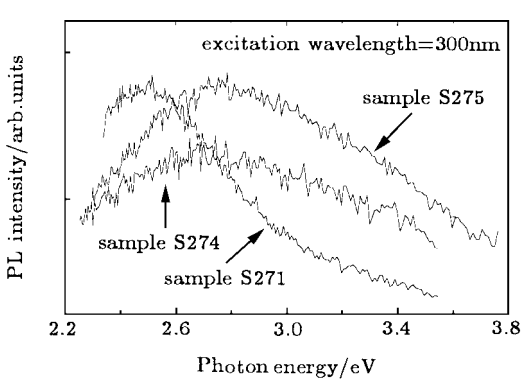


Fig.2. Room-temperature PL spectra for a-C:H films deposited under different conditions.

Photoluminescence measurements were carried out at room temperature by using a xenon lamp as the excitation source in a spectrofluorometer system (FluoroMax-2, ISA Inc.). Figure 2 shows the PL spectra excited by UV light of 300nm wavelength (~4.1eV) for the a-C:H samples deposited under the various conditions. A PL band centred at about 2.5eV was observed for sample S271. When hydrogen dilution was used, as in the case of sample S274, the PL peak shifted to 2.7eV. A blue PL was obtained for sample S275 by using layer-by-layer deposition. The PL peak is about 2.8eV and the full width at half maximum (FWHM) about 0.8eV. It is worth pointing out that the thickness of the measured samples are quite thin, especially for S274 and S275 (less than 100nm), which results in the weak PL signals in the measured spectra. However, the shift of the PL peak is still very clear, as shown in Fig.2. It can be seen that the PL bandwidth of sample S275 is broader than that of sample S271, and the signal at the high photon energy side is enhanced. We have also investigated the influences

of the hydrogen plasma treatment condition on the PL behaviour. It was found that the PL characteristics change obviously with the treatment conditions, and a new luminescent centre can be introduced. The details will be summarized elsewhere.

Generally, a-C:H contains sp^3 and sp^2 carbon-related sites with a hydrogen content ranging from 5% to 50%. The sp^3 C–C and C–H sites give rise to σ valence and σ^* conduction bands with a wide bandgap of about 6eV. The sp^2 clusters are embedded in the sp^3 bonded matrix, which results in a narrow bandgap and the formation of spatially localized states. The optical bandgap of a-C:H is thus controlled by the π and π^* states of sp^2 clusters, and the PL of a-C:H films is considered to be the result of recombination of photo-excited electron–hole pairs within sp^2 clusters. More recently, the exciton-like radiative recombination has been proposed to explain the PL in a-C:H films.[11] It has been reported that the PL peak energy varies significantly with the bandgap, which is determined by the size of the sp^2 clusters.[7,8]

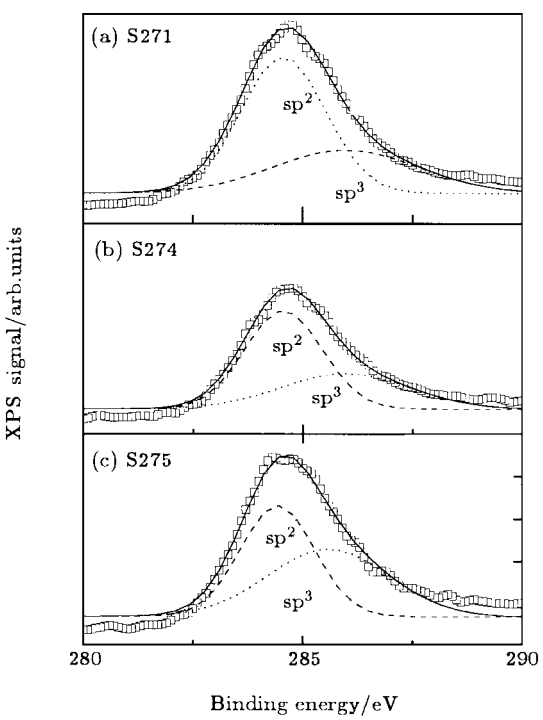


Fig.3. XPS spectra for different a-C:H films: □, experimental data; —, Gauss fit result; - - -, Gauss fit sp^2 peak; ···, Gauss fit sp^3 peak.

Layer-by-layer or chemical annealing was previously used to obtain a rigid and stable amorphous Si and SiGe network.[13–15] By alternately repeating the deposition of a thin amorphous semiconductor layer and subsequent exposure of the surface to hydrogen plasma, it was reported that the opto-electronic properties of amorphous films could be markedly improved. The hydrogen plasma scavenges weak bonds and increases the hydrogen coverage on the growing film surface, resulting in the formation of a well-relaxed amorphous film network. The blueshift of the PL peak in our case can be ascribed to the reduction of sp^2 content due to the hydrogen plasma treatment. It has been reported that the bandgap and PL peak position can be changed by changing the sp^2 fraction in a-C:H films.[8] The sp^2 and sp^3 contents of the a-C:H films are roughly estimated by integrating the area of the separated sp^2 and sp^3 components in the C1s photoemission spectra, as shown in Fig.3.[16] The sp^2/sp^3 ratio is about 1.9 and 1.7 for samples S271 and S274, respectively. By using hydrogen plasma annealing, this value is decreased to 1.0 for sample S275, which suggests that sp^2-related clusters can be significantly reduced by the annealing since the weak carbon sites on the growing surface are chemically etched away and the growth of sp^2 clusters is suppressed. As a result, the optical bandgap of a-C:H films deposited by chemical annealing was as high as 3.5eV, and the growth rate became much slower for sample S275 compared with sample S271.

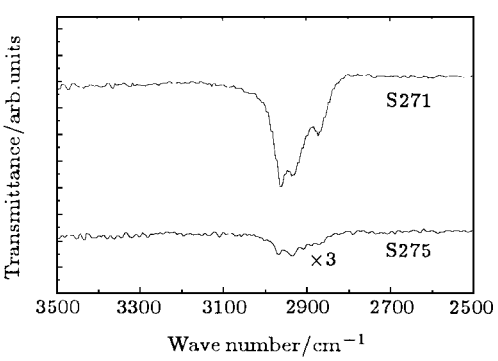


Fig.4. FT-IR spectra for a-C:H films deposited under different conditions.

Park *et al.*[17] have reported on the deposition of hydrogen-free diamond-like carbon films using the layer-by-layer technique with CF_4 plasma treatment. The hydrogen content was found to be less than 1% after 120 s of CF_4 plasma exposure. However, by using hydrogen plasma in the layer-by-layer technique, the absorption bands of sp^3 C–H vibration modes are still observed in the FT-IR spectra, as shown in Fig.4, although the intensity is significantly reduced compared with that of sample S271. This is reasonable because some hydrogen atoms absorbed on the growing surface can diffuse into the growth zone of a-C:H films, and

this will passivate the dangling bonds by forming C–H bonds. Similar behaviour was also observed in the case of a-Si:H and a-SiGe:H films by using a similar deposition technique.[13,14]

4. Summary

In summary, amorphous carbon films have been prepared using a layer-by-layer technique in a plasma-enhanced CVD system. It was found that the sp^2/sp^3 ratio can be decreased by hydrogen plasma treatment, resulting in a wide optical bandgap and the reduction of hydrogen content in the films. As a consequence, blue photoluminescence with an emission peak centred at 450nm was achieved at room temperature.

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