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Correlation study of microstructure and photoluminescence properties of a-C:H thin films deposited by plasma-enhanced chemical vapor deposition technique

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ABSTRACT

Hydrogenated amorphous carbon (a-C:H) thin films are deposited by plasma-enhanced chemical vapor deposition (PE-CVD) technique with different frequency (RF) powers at a low substrate temperature (fixed at 250 °C). In this work, the composition, the types of chemical banding, carbon hybridization structure and optical properties of the a-C:H thin films have been studied by FTIR, XPS, UV–Vis spectrum and PL spectrum testing techniques. The results show that the hydrogen content and carbon hybridization structure play an important role in the evolution of photoluminescence (PL) properties with increasing RF power. It is found that with the decrease of sp^3/sp^2 ratio, the peak energy for main PL emissions peaks (mode 2) showed a red shift. PL emission intensity of the a-C:H thin films is influenced by the hydrogen content and carbon sp^2 cluster. The enlargement of sp^2 rich clusters and the increase of the hydrogen content will lead to an enhancement of PL emission intensity, which is a consequence that the domain of sp^2 rich clusters creates more radiative recombination centers with the increase of RF power. Furthermore, different full width at half maximum (FWHM) of PL emissions peaks can be attributed to band-to-band recombination in various size sp^2 rich clusters.

1. Introduction

In recent years, a-C:H thin films as an optical material have gained a lot of attention due to their high hardness and transmittance, chemical inertness, excellent room temperature PL characteristic, tunable optical band gap [1–10]. The PL properties are meaningful for industrial application of a-C:H thin films in the solar cells, light emitting diodes, biomedical components, phototransistors and various photoelectric devices. At present, numerous reports demonstrated PL properties of the a-C:H thin films can be affected by microstructure [8,11]. However, the effect of microstructure such as the hydrogen content, sp^3 and sp^2 fractions of carbon and type of sp^2 rich clusters on the evolution of PL properties is still unclear. In amorphous carbon material, carbon can hybridize with varying percentages of sp^1 (acetylene-like), sp^2 (graphite-like), and sp^3 (diamond-like) bonding. The number of bonds with sp^1 hybridization is insignificant in typical a-C:H thin films [12], and the optical properties of amorphous carbon thin films are largely governed by the sp^2 phase, with the mechanical properties determined by the sp^3 phase. This composite structure of sp^2 and sp^3 in a-C:H thin films control the performance of the films. The sp^3 bonding in the a-C:H thin films is less stable than sp^2 bonding, especially in a-C:H thin film growth process. When the H/C ratio of reaction gas is very high, hydrogen atoms will preferentially etch sp^2 phase, and inhibit the formation and growth of sp^2 clusters on the films surface, which will form more smooth and dense a-C:H thin films [13–14]. In the a-C:H thin films, hydrogen helps to stabilize the diamond-like character of the films, while large hydrogen content leads to more polymeric character [7]. Based on the Robertson's cluster model [15], PL properties of the a-C:H thin films strongly depend on the graphite clusters, the ratio of sp^3 $C{-}C$ to sp^2 $C{=}C$ bond and hydrogen content. A large number of the previous research results have indicated that these structure and PL properties of the a-C:H thin films depend on the kinetic energy of the atoms which is controlled by deposition technique and deposition process parameters, such as deposition temperature, deposition pressure, bias voltage, frequency (RF) power and so on [7,13,16,17]. However, their mechanism is different. In general, substrate

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temperature mainly control particle energy and a series of chemical reactions on film surface while deposition pressure, bias voltage and RF power mainly influence the decomposition process of the precursor gas and particle characteristics. The reports about the influence of RF power on microstructure and PL properties are very few, and PL mechanism of the a-C:H thin films is still an open debate among researchers. Therefore, the study about the influence of RF power on structure and PL properties in a-C:H is very meaningful.

Various physical or chemical deposition methods have been employed to prepare a-C:H thin films in the references [3,5,7,18–21], one of the common and suitable deposition methods for preparation a-C:H thin films is PE-CVD technique. PE-CVD technique allows the growth at low substrate temperatures with high deposition rates and provides ion bombardment of the surface [5]. The a-C:H thin films deposited by PE-CVD technique allow to contain enough hydrogen to passivate/saturate dangling bond [4]. In this work, a-C:H thin films have been deposited by PE-CVD technique in various RF powers. This tunable PL properties in a-C:H thin films have been observed in this work. The influence of composition and microstructure on optical gap and PL properties of the a-C:H thin films has been investigated at different RF powers. The film thickness has been measured by cross-sectional images of SEM. Fourier transform infrared (FTIR) spectroscopy and X-ray photoelectron spectroscopy (XPS) have investigated the composition and microstructure of a-C:H thin films. The optical properties of a-C:H thin films were studied by UV–Vis spectrometer and fluorescence spectrophotometer. Under the preparation conditions of fixed reactive precursor gases, reactor pressure, methane flow rate, deposition temperature, the measurement results show that the PL properties of a-C:H thin films can be controlled by hydrogen content and carbon hybridization structure at different RF powers. It can be found that larger numbers and sizes of sp^2 carbon clusters, and lower non radiation recombination processes will result in stronger PL peak intensities as increasing RF power.

2. Experimental details

The a-C:H thin films were prepared at a low substrate temperature (fixed at 250 °C) by the plasma decomposition of pure CH_4 (purity 99.995%) in a radio frequency (RF = 13.56 MHz) PE-CVD system. In this work, about 1 mm thick microscope glass slides, 200 μm thick single-side polished n-type crystalline silicon (100) substrates and crystalline KBr substrates were used for the deposition of a-C:H thin films simultaneously. Before deposition of a-C:H thin films, the microscope glass slides and single-side polished n-type crystalline silicon (100) substrates were cleaned by ultrasonic cleaner successively dipped in acetone and alcohol, then single-side polished crystalline silicon substrates were dipped in a high dilute HF solution for 10 min to remove any silicon oxide on their surfaces. Finally the microscope glass slides and single-side polished crystalline silicon substrates were rinsed in de-ionized water and dried in nitrogen ambient. Prior to deposition, the PE-CVD chamber was evacuated to below 10^{-4} Pa. In this work, the deposition time, chamber pressure and methane flow were kept at around 60 min, 80 Pa and 15 sccm, respectively. Different values of RF power were selected for depositing a-C:H thin films, and the RF power were set to 120, 135, 150, 165 and 180 W, respectively.

The thickness of the films grown on crystalline silicon substrates were examined by cross-sectional images of scanning electron microscopy (SEM; JSM-7500F, JEOL Ltd., Tokyo, Japan). Optical transmission and absorption spectra of the a-C:H thin films prepared on microscope glass slide substrates were measured by a double beam UV–Vis spectrometer (UV-2550v, Shimadzu Corporation, Japan) over the spectral range of 300–800 nm. During this measurement, a blank glass was placed on the reference beam. Tauc optical band gap (E_g) of thin films has been fitted in the curve of ln α vs. $h\upsilon$ of a-C:H thin films. Steady state PL properties were measured at room temperature in reflection geometry on a spectro-fluorimeter (Hitachi Model F-4500) in which a high-pressure Xe lamp serves as an excitation light source. With 325 nm wavelength excitation, PL spectra were collected in the 350–800 nm (3.54–1.55 eV) region. The hydrogen content and chemical bonding properties of the thin films deposited on crystalline KBr substrates were observed using a Fourier transform infrared spectrophotometer (FTIR; NEXUS, ThermoNicolet Corporation, Madison, Wisconsin) in the range of 400–4000 cm^{-1} with a resolution 2 cm^{-1}. The oxygen content and carbon hybridization structure of the a-C:H thin films deposited on polished crystalline silicon substrates were characterized by X-ray photoelectron spectroscopy (XPS) (Escalab 250Xi PHI Quantera ll spectrometer). Before XPS measurement, the thin films surface was etched off 20 nm by Ar ion gun, in order to get rid of oxide layer. The spectra were collected with 0.1 eV step at 20 eV constant pass energy for the C1s and O1s narrow scan. Typical measurement areas of all the samples were constant about 0.5 × 0.5 mm.

3. Results

Transmission and absorption coefficient spectra are very helpful to explore the PL mechanisms of a-C:H thin films. Therefore, transmittance and absorption coefficient spectra have been measured at room temperature as a function of wavelength for a-C:H thin films with different thicknesses (as shown in Table 1) deposited at different RF powers as shown in Fig. 1. For all the samples deposited at RF power from 120 to 180 W, the optical transmittance of a-C:H thin film prepared at 135 W RF power is maximal, and the smallest transmittance appeared at 165 W RF power. Moreover, it can be easily found that a sharp absorption coefficient peak appear at around 325 nm, the peak intensity of the a-C:H thin films is increscent with increasing RF power from 135 to 180 W.

PL research of the a-C:H thin films deposited at different RF powers on silicon substrates has been performed at room temperature. PL emission spectra using 325 nm excitation are shown in Fig. 2. PL emission spectra include a broad PL feature peak and several sharp peaks, and this PL shape shows similarity with the literature [22]. The sharp peaks at around 400 nm (labeled as W1) and 653 nm (labeled as W2), appear not to vary significantly in intensity with RF power and they maybe are attributed to the first order Raman peak and double frequency scattering peak, respectively [8,20]. The other peaks are strictly dependent on RF power, which can be attributed to different radiative recombination [23]. To investigate further PL properties, PL spectra of a-C:H thin films deposited at different RF powers have been decomposed into two main peaks of mode 1 and mode 2 with the best Gaussian fit, as shown in Fig. 3(a–e). The peak positions and FWHM of mode 1 and mode 2 of PL emission spectra for the films deposited at different RF powers have been shown in Table 1. With increasing RF power from 120 W to 135 W, a blue shift from 566 to 541 nm in mode 2 PL peak position can be observed. And a series of red shifts of mode 2 PL peak position are observed from 541 to 588 nm with further increase of RF power from 135 W to 180 W. The FWHM of mode 2 continuously increases with increasing RF power from 120 to 165 W, and then decreases when the RF power is 180 W. In order to compare the PL emission intensity of mode 2, all mode 2 spectra of a-C:H thin films deposited at different RF powers have been normalized to the intensity

Table 1
The mode 1 peak position and FWHM (eV), mode 2 peak position and FWHM (eV) obtained after multi-peak distribution of PL spectra for the films prepared at different RF powers.

RF power (W)	Film thickness (nm)	Mode 1 peak position and FWHM (nm)	Mode 2 peak position and FWHM (nm)
120	227	–	566/189
135	503	440/60	541/194
150	520	436/70	571/214
165	500	437/57	584/233
180	195	–	588/218