Thermal annealing effects on structural properties of Si-doped/undoped a-CH thin films

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Abstract

Plasma enhanced chemical vapor deposition (PECVD) synthesized hydrogenated amorphous carbon (a-CH) and Si doped a-CH (a-CH:Si) thin films shows thermal annealing temperature dependence within the temperature range 400-600°C for their micro-structural as well as photoluminescence (PL) properties that are studied using the Raman spectra measurements. In case of a-CH thin films, the PL is increases with increase of thermal annealing temperature up to 400°C and then remains almost constant within the experimental error, whereas in case of a-CH:Si thin films the PL remains same up to 400°C and then decreases above 400°C of annealing temperatures. Within this thermal stability, these thin films could be used in the fabrication of optoelectronics devices.

Introduction

Hydrogenated amorphous carbon (a-C:H) materials have attracted much attention because of their intriguing physical properties and various potential applications [1-4]. Unlike crystalline forms of carbon (graphite and diamond), a-C:H films are composed of \(sp^2\) (graphite) and \(sp^3\) (diamond) hybridized carbon bonds with different ratios along with hydrogen bonds. The fraction of the \(sp^2\) and \(sp^3\) contents (or the \(sp^2/sp^3\) content ratio) strongly influences the properties of a-C:H films [5,6]. These \(sp^2\) and \(sp^3\) contents and their ratio can be tuned by adjusting the various growth parameters during deposition and/or post-deposition processes. The presence of hydrogen content in the film structure also depends on the precursor gases used and the technique(s) employed during the synthesis processes. Dangling bonds are created where hydrogen atoms terminate a chain structure. In the post annealing process after gaining the thermal energy these bonds re-order to form a considerably different micro-structure with a peculiar physical property. Carbon atoms in themselves forms bonds with different co-ordinates and hybridizations and in the presence of hydrogen can form carbon hydrogen terminations that

![Raman spectra of a-CH thin films at different thermal annealing (200-600°C)](image-url)
are depending on the degree of energy gain or loss in the atoms or structures. Dangling bond however is usually present as C-H terminus in a-CH structures and on the application of heat lead to atomic energy gain and hence atomic rearrangement in the a-CH film structure matrix that changes both micro-structural and physicochemical properties. These sp³, sp², and/or hydrogen in the film structure could be changed of by the process of low/high energy irradiation (Ar⁺ and/or else) and even thermal irradiation too. In the present work, we studied the effects of post-thermal annealing on a-CH and a-CH:Si thin films using Raman and PL spectra.

**Experimental Details**

The films were deposited on argon-cleaned (100) silicon wafer using a Diavac RF 13.56 MHz, Plasma enhanced chemical vapor deposition (PECVD) system at 400 V bias voltage. The a-CH films were deposited with argon-acetylene gases and a-CH:Si films are deposited in with the addition of tetramethylsilane (TMS) vapour. Before deposition, the substrates were cleaned using Ar⁺ ions in the RF sputtering system for 5 min. The a-CH diamond like carbon (DLC) thin films were deposited using a gas mixture of Ar and C₂H₂ (1:2), whereas silicon doped DLC films (a-C:H:Si) were deposited using tetramethylsilane vapour [Si(CH₃)₄, TMS] introduced into the chamber during deposition as a silicon precursor with a vapour flow rate of 10sccm (standard cubic centimeters per minute). The thicknesses of the films were 100 ± 10 nm and were controlled by the deposition time. Thermal treatment of the as-deposited films was carried out in an alumina tube furnace under flowing nitrogen (50 sccm), for 2 hrs and left to cool in-situ. The room temperature PL (25°C) effects were carried out using ISA-Labram equipped with BX 40 coupled confocally to a liquid nitrogen cooled CCD spectrograph at 2.41 eV having Ar⁺ laser excitation energy. A micro-Raman monochromator was used in order to simultaneously acquire well-resolved Raman peaks and obtain information on possible sample annealing during the measurements at the highest excitation powers. In order to compare the PL intensity of different films, we have calibrated the

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**Fig. 2:** (a) The effect of annealing temperature (200-600 °C) on the PL intensity/slope, (b) PL intensity, FWHM, and peak versus annealing temperature of a-C: H thin films.
spectrum on the 520 cm$^{-1}$ Raman peak of the Si bare substrate and normalized the measured values considering the different absorption coefficients in the films. The measurements were performed at excitation power of 3.5 mW at the sample surface, on a spot diameter of 200 µm, allowing a scan of the film homogeneity with a relatively good spatial resolution.

Results and Discussion

The over layer Raman spectra of a-CH films at different thermal annealing temperatures ranging from 200-600°C are shown in figure 1. The intensities of different peaks mainly the D-peak and G-peak and their overtones are shifted with change of their peak intensity. The spectra also show a change in the Raman slope with the change of thermal annealing temperatures. The slope seems to increase as the temperature decreases from 600°C to 200°C. This suggested that the a-C:H films are becoming more graphitic in nature with less disorder and tends to have less photoluminescence effect. However, we have used different parameters for this study that obtained from the Raman spectra. The different parameters that are obtained from Raman spectra are the PL and their intensity, full width at half maximum (FWHM) and the highest peak energy which are changes with annealing temperature due to the associated atomic rearrangements, silicon addition or the presence or absence of hydrogen in the films structure. Figure 2 presents the PL emission spectra of undoped DLC films (a-C:H) and in figure 3 presents the PL emission spectra of Si-doped DLC films (a-CH:Si) annealed within the temperature range 200-600°C. In both cases, overall PL spectra show a broad-band and structure-less. Both the spectra indicate that the room temperature PL is in the visible range. It seems that the PL intensity in the a-C:H films increase with annealing temperature from 200°C to 400°C, and

![Graph](image)

**Fig. 3:** (a) The effect of annealing temperature (200-600°C) on the PL intensity/slope, (b) PL intensity, FWHM, and peak versus annealing temperature of a-C:H:Si (Si-DLC) thin films.
then peaks and steady from -400°C to 600°C (figure 2a-b). The full width at half maximum (FWHM) of the PL band is about 0.55 ± 0.02 eV at 200-300°C annealing temperature, and then falls a little at around 400-600°C to about 0.5-0.45 eV. The PL intensity for the a-C:H:Si films annealed at 200-600°C (Figure 3) shows that the PL intensity increased from 0.85 eV (200°C) to ~1.0 eV (400°C), and then falls to ~0.5 eV at 600°C. The FWHM equally increased from 200°C to peak at 400°C, and then falls again as you anneal to 600°C, figure 3b. In general, features of PL in several amorphous semiconductors such as a-Si:H, a-C:H, and a-C:H:Si are attributed to tail-to-tail states recombination of localized electron-hole pairs (EHPs). The PL is generally the PL is higher for silicon doped compared to undoped films. The variation of PL observed here [7, 8] is similar to that found by Rusli et al. [9] in a-C:H film. It is proposed that this PL arises from the radiative recombination of the electron-hole pairs confined to the π states of the sp2 bonded clusters in an sp3 bonded amorphous matrix. The microstructure of our a-C:H:Si films resemble that of a-C:H because Si percentage is <20% and also room temperature PL is observed. Therefore, the PL mechanism of these films can be interpreted using the framework of a-C:H, which is attributed to the radiative recombination of photoexcited EHPs in sp3 bonded clusters. The π–π* gap in sp3 sites are much narrower than the σ–σ* gap, and the latter acts as a barrier that strongly localizes the π–π band edge states. Therefore, the EHPs are closely correlated by Coulomb interaction and display a short lifetime. Correspondingly, the PL has a strong polarization memory, is not quenched by the electric field and can be observed at room temperature [9]. In order to investigate the structural variation of the films, we have analyzed the evolution of the G and D peaks of the Raman signal superimposed on the PL peak, recorded at the same time by collecting photons coming from the same microscopic region of the film. The PL effect can be interpreted with this cluster size too. The broadening of PL as we observed in our films may be attributed to the disorder broadening arising from the broadband tails [10, 11]. The PL of a-C:H and Si:DLC films are dependent on C-H(s) and Si-H(s) bonding concentrations; and that the PL peak position shifted in lower energy level with increasing these bonding concentrations. The PL peak energies are also correlated to evolution of hydrogen due to annealing, and the C-H(s) and Si-H(s)-bonding ratio, as it increases with lowering the peak positions.

**Conclusion**

In this study we observed the variation in the Raman shifts and hence the PL effects in terms of PL intensity of a-C:H and a-CH:Si thin films. The PL intensity, FWHM, and the peak height all varied with variation of annealing temperature. We also observed the evolution of hydrogen and the effects of silicon in exhibiting thermal stability in a-C:H films. In case of a-CH thin films, the PL is increases with increase of thermal annealing temperature up to 400°C and then remains almost constant within the experimental error, whereas in case of a-CH:Si thin films the PL remains same up to 400°C and then decreases below 400°C of annealing temperatures. Within that thermal stability, using these thin films optoelectronics devices like photoluminescence cell could be fabricated in future.

**References**