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Opto-electrical properties of amorphous carbon thin film deposited from natural precursor camphor

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Abstract

A simple thermal chemical vapor deposition technique is employed for the pyrolysis of a natural precursor ''camphor'' and deposition of carbon films on alumina substrate at higher temperatures (600–900 °C). X-ray diffraction measurement reveals the amorphous structure of these films. The carbon films properties are found to significantly vary with the deposition temperatures. At higher deposition temperature, films have shown predominately sp^2-bonded carbon and therefore, higher conductivity and lower optical band gap (Tauc gap). These amorphous carbon (a-C) films are also characterized with Raman and X-ray photoelectron spectroscopy. In addition, electrical and optical properties are measured. The thermoelectric measurement shows these as-grown a-C films are p-type in nature.

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1. Introduction

Although synthesizing artificial diamond is a technological challenge, the so obtained material is not much cheaper than the natural one. Therefore, it is quite understandable why there was euphoria among scientific community on the first discovery of diamond like carbon (DLC) [1]. Aisenberg and Chabot had coined this particular metastable form of carbon as diamond like carbon (DLC) due to its properties similar to diamond [1]. Thereafter, different names have been used for similar films of DLC while the same name has been used to describe entirely different films, e.g. i-C (ion assisted carbon films), H-carbon (hydrogenated carbon films) [2], a-C (amorphous carbon) [3,4], a-C:H (hydrogenated amorphous carbon in both hard and soft form) [5], ta-C (tetrahedral amorphous carbon), ta-C:H (tetrahedral hydrogenated amorphous carbon) films [6], etc. This inconsistent nomenclature is primarily due to the broad spectrum of properties and variety of methods used for preparing the carbon films [7]. Diamond and graphite have completely 100% sp^3 and sp^2 network in their lattice, respectively. Inter-mediating percentage of sp^3 and sp^2 has been found in the examples given above. The important properties of any such carbon films are mapped by the methods used for deposition, sp^3/sp^2 ratio, % of hydrogen, disorderliness in the films, etc. With the superior properties of carbon films (having high sp^3 percentage) such as micro-hardness like sapphire, low frictional coefficient, inertness to any aggressive chemical and also ability to coat geometrically complex bodies; these carbon films can be used in the applications like antisticking overcoats for computer disks [8], anticorrosive coating for surgical instruments [9], solar cells [10,11], electron field emission [12,13] and electrodes in electrochemical reactions [14], etc. It is worthwhile to mention that the nature and properties of carbon films play an important role in various applications.

In the present study, a simple thermal chemical vapor deposition (CVD) technique is adopted for the preparation of carbon films from a natural precursor ''camphor ($C_{10}H_{16}O$)'' unlike plasma CVD (PECVD, MPCVD, PLD, etc.) that are commonly used for the deposition of various types of carbon

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films [7]. It is worth noting that for deposition on complex geometrical structures and large sized substrate, thermal CVD is an ideal choice. In the preparation of carbon films, a high percentage of sp^3 bonded carbon atoms is preferred in crystal lattice. Use of camphor as a precursor for depositing carbon film could be more favorable than any other precursors because a single camphor molecule contains nine sp^3-bonded carbon. At the same time, one oxygen atom inside the camphor molecule could help in oxidizing some non-diamond like carbons during deposition. This is a novel precursor that we have used to deposit amorphous carbon (a-C) films in the present study unlike methane or acetylene or graphite target normally used for same [15]. Additionally, lower H/C ratio in case of camphoric gas has another advantage in producing lower hydrogen contents in the film compared to methane gas. We have previously synthesized various carbonaceous materials, e.g. fullerene [16], spongy carbon beads [17], carbon nanotube [18], carbon nanofibers [19,20] using camphor as precursor. Besides precursor there are many other deposition parameters that decide sp^3/sp^2 carbon ratio in the carbon films. As the correct terminology used to designate the different types of carbon films of different sp^3/sp^2 ratio is still being ambiguous, we designate ‘‘amorphous carbon (a-C)’’ to the films obtained by pyrolysis of camphor as these films are found to be amorphous structure by X-ray diffraction study.

2. Experimental

2.1. Films deposition

The deposition unit consisted of a quartz tube (1.5 m long and 0.025 m in diameter), an electric furnace and an argon gas cylinder. The quartz tube was kept inside a horizontal tubular furnace. In the center of quartz tube, an alumina substrate (over which camphor is to be pyrolysed and deposited) was placed. Prior to deposition of carbon films on alumina substrate, the whole deposition chamber was purged with argon for at least 15 min. Then the temperature of electric furnace was elevated from room temperature to desired deposition temperature under argon atmosphere. Once the substrate reached the desired temperature, camphor (2 g) was vaporized at ~300 °C and the vaporized gas was allowed to pass inside the quartz tube having a set temperature of 650, 700, 750 and 900 °C. The evaporation of 2 g of camphor and deposition normally take around 6–12 min. However, the substrate was kept at that high temperature for 1 h and then furnace was cooled down to room temperature in same argon medium.

2.2. Characterization

Raman spectra of deposited carbon films were taken using an Ar-laser of wavelength 514.5 nm at 20 mW power. A 100× objective lens was used to observe micro-Raman spectra with an illumination spot size of 1 μm and acquisition time of 90 s in a Ramanor T64000 (Jobin Yvon) instrument. X-ray photoelectron spectroscopic (XPS) study was done with a VAMAS Surface Chemical Analysis, VG Scientific, EscaLab 220-IXL apparatus using an aluminum K-alpha source at 1486.6 eV. The high-resolution spectra of carbon (C 1s peak), was recorded in the fixed analyzer transmission (FAT) mode. The experimental data were then fitted to peak fitting program (CASA-XPS) for distinguishing different carbon peaks. X-ray diffraction (XRD) was carried out with Philips PW1729 X-ray generator using Cu Kα ($\lambda = 1.54$ Å). The optical gap was measured by home fabricated spectrophotometer in the range of 400–1200 nm using a tungsten–halogen lamp. The absorbance spectrum was collected using a germanium detector. To measure the electrical resistance, two platinum wires were bound to both ends (kept 1 cm apart) of the alumina plate on which carbon film deposited. Resistance of a-C films versus temperature was measured in argon atmosphere.

3. Results and discussion

3.1. Raman spectroscopic studies

Raman spectroscopy is a prime technique for the analysis of bonding types, domain size, internal stress, etc. in carbon film [21]. The Raman peak shapes, positions, shifts, half-width and intensity give all the detailed information about the chemistry and structure of carbon films. Inelastic, incoherent stokes Raman scattering of light from the lattice of diamond was first observed by Ramaswamy [22] and investigated in detail by Solin and Ramdas [23]. The 1st order zone center sharp Raman peak of diamond and graphite lies at 1332.5 ± 0.5 and 1580 ± 0.5 cm^{-1}, respectively. All other types of carbon show broad peaks between 1100 and 1600 cm^{-1} [24,25]. Fig. 1 shows the Raman spectra of a-C films obtained at different deposition temperatures. The amorphous nature of as-grown carbon films was confirmed from the X-ray diffraction (XRD) study. The Raman spectra are deconvoluted by the Gaussian peak-fitting method. Two broad bands observed at ~1340 and 1580 cm^{-1} were named D-band (disorder/defect band) and G-band (graphitic band or E_{2g2} mode), respectively. These two bands are commonly observed in a-C films [3,26]. These bands are also observed in glassy carbon. Interestingly, in most cases the intensity of the D-band is higher than the G-band in glassy carbon [24,25,27]. Raman spectra of camphor pyrolysed films are found very similar to a-C films containing 60% sp^2-bonded carbon [3,28]. Another prominent broad peak that observed in the range of 1540–1560 cm^{-1} can be attributed to sp^2-bonded carbon normally observed in the grain boundaries of diamond films at 1520 cm^{-1} [29]. The D-band intensity is found to increase markedly with the deposition temperature indicating increase of disorderliness in the film. The disorderliness in the a-C films originated from micro-crystalline disordered graphite due to intermingling of σ-(sp^3-like) domains in the clusters of π-(sp^2-like) graphite. Tuinstra and Koenig had explained it to be due to decrease in the size of microcrystalline graphitic domains and based on X-ray analysis proposed for graphite [30]. However, Tarmor et al. ruled out this fact for a-C from optical measurements [31]. Another explanation could be a transformation of a-C types of films to nano-crystalline glassy carbon [32]. In the present study, we observed increase in the