Nano-Diamond Film Produced from CVD of Camphor

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Abstract

Nano-diamond films were deposited on glass (Corning), quartz (fused silica) and Si substrates by CVD of camphor ($C_{10}H_{16}O$) and hydrogen. The films were characterized by mechanical, optical and microstructural studies which indicated that camphor (with hydrogen) may be a suitable precursor material for the deposition of nano diamond films at low substrate temperature (573-713 K).

Introduction

Diamond is considered to be an ideal material in various applications in microelectronics, optical and cutting tool industry. Extensive research activities in diamond during the last decade have shown that preparation of large grain polycrystalline diamond film requires a high substrate temperature (>1000 K). Researchers were interested in producing tailored films at a lower deposition temperature, so that the field of application of the films may be increased manifold. In recent years, studies on diamond films with lower grain sizes and consequently having lower surface roughnesses were stimulated due to the search for new protective coatings on mechanical tools and optical instruments along with antireflection coatings for IR optics. Films rich in sp^3 carbon having grain size in the nanometer range (< 900 nm) may be called nano-diamond (or microcrystalline diamond) which may cater to the above need.

It is believed that methyl radical along with atomic hydrogen play the key role in diamond deposition. Several workers suggested that organic compounds which can easily generate methyl radical may also be suitable as the carbon sources for diamond deposition [1-4]. We have shown in the present work that camphor ($C_{10}H_{16}O$) may be a suitable precursor material for diamond deposition. The material is in abundance in several parts of the world, e.g. China, Japan and India.

Experimental

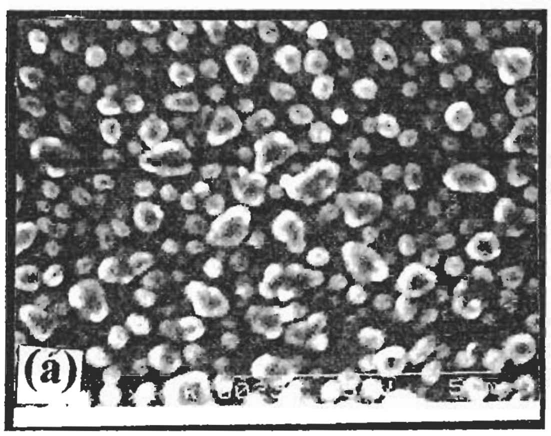
The precursor material, camphor, sublimes at room temperature. The material contains three carbon atoms attached to three methyl groups while the rest seven carbon atoms are associated with a ring structure. Heated stainless steel tube was used to allow the camphor vapour to enter the deposition chamber so that it does not get condensed before entering into the CVD chamber. The substrates (Si and quartz) were placed side by side on the substrate holder so that the films could be deposited simultaneously on the substrates under identical deposition condition. Substrate temperature during deposition was within 573-623 K for glass (Corning) and within 573-713 K for quartz (fused silica) and Si. Films were deposited by CVD of camphor and hydrogen at 1.5 kV with 75 mA current for a chamber pressure of ~0.3 mbar. Thicknesses of the films deposited on different substrates varied within 1-3.5μm.

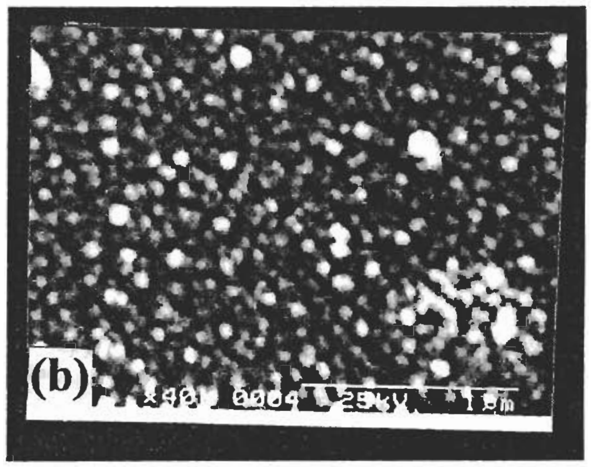
Results and Discussion

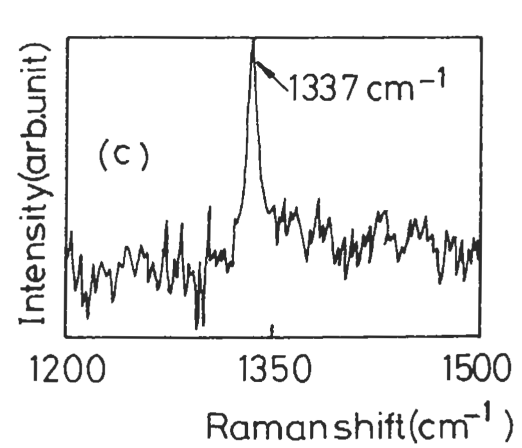
Scanning electron micrographs of two representative films deposited simultaneously on quartz (fused silica) and Si substrates (for deposition temperature of ~573K) are shown in figs. 1a and b respectively. It may be observed that the films consisted of large number of grains with average grain size (700 nm on quartz (fig. 1a) and (130 nm on Si (fig. 1b). No clustering effect was observed in these nano-diamond films as have been reported in our earlier publication [5]. In order to reveal the film quality, the XRD and Raman spectra were studied for several films. For lower thicknesses of the films (<3μm) no characteristic peak of diamond could be observed in the XRD. But thicker films (> 3μ m) showed (111) peak of diamond at ~43.2°. In addition, there were small peaks due to (220) and (311) planes at 75.5° and 94.7° respectively.

The Raman spectra (fig.1c) of the films deposited on Si showed signature of sp^3 C-C vibration with a prominent peak around 1337 cm^{-1}. The positive shift of the Raman peak from that of bulk diamond (at 1332 cm^{-1}) may be attributed to a high compressive stress (~ 13 GPa) [6]. A broad band could be noticed between 1533-1560 cm^{-1} in the Raman spectra due to the presence of sp^2 phases at the grain boundaries of the nanocrystalline films. The FWHM of the Raman peak (8.27 cm^{-1}) was wider than that of natural diamond (3.3 cm^{-1}). But, it was much lower than that reported by Gruen and co-workers [7] who obtained FWHM ~ 25 cm^{-1} for their nano diamond films deposited by magnetoactive microwave plasma CVD technique. The band gap (~4.8 eV) in the film was estimated from the plot of $(\alpha h\nu)^{1/2}$ versus hv. The surface roughnesses of our films, evaluated from the reflectance measurements, were ~ 17 nm. The details of the measurements were reported earlier [8]. The films were transparent in the IR region and FTIR spectra did not show prominent C-H absorption around 2900 cm^{-1}. Properties of the nano-diamond films presented above were correlated with the photoluminescence (PL) measurements which showed prominent PL peak (fig.1d) at room temperature due to carrier confinement within the sp^2 clusters (existing at the grain boundaries), embedded within a sp^3 matrix.

The indentation technique is used for the hardness measurement of thicker films since it requires a penetration depth (h) such that h<0.1d, d being the film thickness. This is necessary to eliminate the substrate effect [9]. The hardnesses (H_v) of our films (having low thicknesses) were determined by an indirect







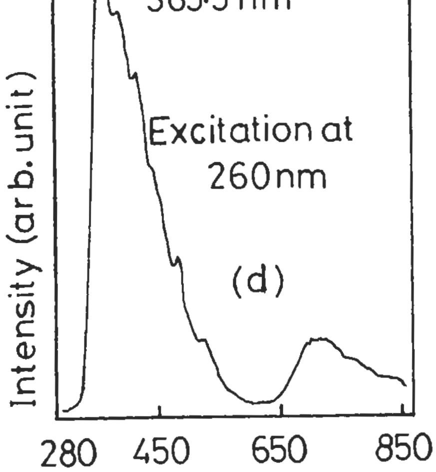


Fig.1 Scanning electron micrographs of repre-sentative films deposited simultaneously on quartz (a) and Si (b) substrates at ~573 K. Raman and PL spectra of the representative films are shown in (c) and (d) respectively.

method [10] by utilizing the optical absorption band tail measurements. We have studied the effect of mechanical stress on the optical absorption band tail in order to determine the strains ($\delta a/a$) in the films by theoretical curve fitting procedure. The stresses in the films were obtained from the relation $S=Y(\delta a/a)/(1-\nu)$ with Young's modulus Y=600 GPa and Poisson's ratio ν=0.11. Then the hardness (Hv) was obtained by using the following relation [11].

$$H_v=2.9[Y/(1-v)]\,(100.0/x)^{-p}\,(\delta a/a)^{1-p} \qquad (1)$$

where p is the strain hardening coefficient and x is the indentational strain. We have taken x=8% [12]. The average value of Hv, thus obtained, was ~ 45 GPa.

Conclusions

The nano-diamond films produced by CVD of camphor and hydrogen had high values of band gap (~4.8 eV on quartz substrate), hardness (~45 GPa) and IR transmittance. FTIR spectra of the films did not show prominent C-H absorption around 2900 cm^{-1}. Raman spectra showed sharp peaks around 1337 cm^{-1} indicating a high compressive stress (~13 GPa) in the films. Photoluminescence measurements (at room temperature) indicated strong carrier confinement within the sp^2 clusters existing at the grain boundaries of the nanocrystalline diamond films. These studies indicated that camphor (with hydrogen) may be a suitable precursor material for the deposition of nano-diamond film at low substrate temperature.

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