



# High pressure Raman spectroscopic studies on ultrananocrystalline diamond thin films: Anharmonicity and thermal properties of the grain boundary



K.K. Mishra<sup>a</sup>, Revati Rani<sup>a</sup>, N. Kumar<sup>a,\*</sup>, T.R. Ravindran<sup>a,\*</sup>, K.J. Sankaran<sup>b,c</sup>, I-Nan Lin<sup>d</sup>

<sup>a</sup> Materials Science Group, Indira Gandhi Centre for Atomic Research, #HBNI, Kalpakkam 603102, India

<sup>b</sup> Institute for Materials Research (IMO), Hasselt University, 3590 Diepenbeek, Belgium

<sup>c</sup> IMOMEC, IMEC vzw, 3590 Diepenbeek, Belgium

<sup>d</sup> Department of Physics, Tamkang University, Tamsui, Taiwan

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## ABSTRACT

Ultrananocrystalline diamond (UNCD) thin film has been attracted widely to scientific community due to its attractive thermal and mechanical properties. Herein, we report the high-pressure behavior of grain boundary (GB) originated phonon modes and their correlation with thermal properties in UNCD film grown by microwave plasma enhanced chemical vapor deposition method. Spherical ultrananocrystalline grains with size 3–4 nm in these films were investigated by high-resolution transmission electron microscopy (HRTEM). Raman spectroscopic studies of UNCD with a pressure transmitting medium (up to 16 GPa) and uniaxial pressure (up to 28 GPa) revealed the presence of grain boundary phonons which are found to harden upon compression. GB phonons contribution to the specific heat of UNCD at room temperature is estimated to be 4.7314 J/mol-K, which is ~80% of the reported theoretical molar specific heat  $C_v$  value (5.568 J/mol-K). Using our experimentally obtained mode Grüneisen parameters, GB contribution to the thermal expansion coefficient of UNCD is estimated to be  $0.5 \times 10^{-6} \text{ K}^{-1}$ . Grain boundaries of UNCD are found to be highly stable and Raman spectra showed reversible behavior upon release of pressure. Phonon spectra as a function of temperature down to 90 K were used to obtain the anharmonicity of GB phonon modes. The first order temperature coefficient of trans-polyacetylene modes ( $\nu_1$ ,  $\nu_2$  and  $\nu_3$ ) and  $E_{2g}$  in-plane (G-band) modes of GB are obtained as  $-0.38 \times 10^{-2}$ ,  $1.69 \times 10^{-2}$ ,  $-1.55 \times 10^{-2}$  and  $-1.41 \times 10^{-2} \text{ cm}^{-1} \text{ K}^{-1}$ , respectively.

## 1. Introduction

Thin films of diamond with grain sizes of the order of a few nm are known as ultrananocrystalline diamond (UNCD) thin films. They possess greatly modified and superior properties in comparison with the bulk single crystal counterpart [1–3]. These films are of current interest because of their potential applications in nanoscale systems due to their improved field emission [4,5], better optoelectronic behavior [6], reduction in band gap [7], enhancement in toughness [8] and robust tribological properties such as ultra-low friction coefficient and exceptionally high wear resistance [9,10]. UNCD grains are surrounded by a thin and narrow disorder crystal regions (thickness ~ a few Å) known as grain boundaries (GBs) [11]. Core atoms of grain are made by  $sp^3$  bonded ordered carbon atoms whereas grain boundary contains transpolyacetylene (t-PA) segments, short ranged  $sp^2$ , and  $sp^1$  hybridized disordered carbon atoms [12]. t-PA forms during plasma enhanced-chemical vapor deposition growth processes, and it consists of  $sp^2$  hybridized carbon atoms in which H atoms are bonded to each

carbon atom [12,13]. Several theoretical and experimental investigations on UNCD suggest that its physical properties such as electrical conductivity [14], thermal transport [11,15] behaviors are controlled by grain boundaries. It is widely accepted that the central feature to the thermal transport properties of UNCD is based on the intrinsic properties of the grain boundaries [11,15]. Specific heat computed using temperature dependent phonon vibrations [11] suggest a predominant contribution from GB phonon vibrations with molar specific heat  $C_v$  value 5.568 J/mol-K at ambient (300 K). However, the contribution of GB phonons on  $C_v$  is yet to be examined experimentally. The phonons behavior of GB in UNCD and their anharmonicity is required to understand its various physical and transport properties. Phonon anharmonicity involves an intrinsic phonon-phonon interaction and a quasi-harmonic contribution which solely depends on the volume change. Change in mode frequency upon temperature variation has an effect of these dual contributions while with pressure, the only effect of volume change on mode frequency can be expected [16,17]. Therefore, by investigating the Raman spectra of UNCD with temperature and pressure

\* Corresponding authors.

E-mail addresses: [niranjan@igcar.gov.in](mailto:niranjan@igcar.gov.in) (N. Kumar), [trr@igcar.gov.in](mailto:trr@igcar.gov.in) (T.R. Ravindran).

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separately, it is possible to gain insight about these anharmonic contributions to phonon vibrations and thermal properties. Besides its thermal behavior, the mechanical stability of UNCD is important from an applications point of view and there are no reports of mechanical stability of UNCD in the literature. Diamond anvil cell (DAC) based high pressure studies offer a convenient way to investigate phase stability of carbon based materials such as graphite [18], graphene [19,20] and carbon nanotubes [21]. Mode Grüneisen parameter  $\gamma_i$  is a dimensionless microscopic quantity that is proportional to the rate of change of mode frequency with pressure and directly proportional to the bulk modulus of the material, provides valuable information about the effect of pressure on the corresponding chemical bonds and their stability.  $\gamma_i$  values are required to estimate the thermal transport properties of the material. However, no report of measurement of  $\gamma_i$  values of UNCD is available in the literature so far. In addition, the pressure dependent behavior of Raman modes on UNCD can also be used as a calibration curve for improving the performance of UNCD based nanoelectronic devices used in extreme pressure environment.

At room temperature, Raman spectra of UNCD [10,12] exhibit intense bands as in other carbonic materials such as graphite, graphene, and carbon nanotubes. Therefore, it is possible to study its spectral features to shed light on transport and mechanical stability by analyzing its Raman spectroscopic results [19,20]. The Raman spectra of UNCD film exhibit several Raman bands. A characteristic D<sup>\*</sup>-band located at  $1332\text{ cm}^{-1}$  is associated with a  $T_{2g}$ -phonon related to  $sp^3$  hybridized carbon atom (in grain) vibrations; this band often broadens and weakens in intensity due to its nanocrystalline size related to phonon confinement effect [22]. The spectrum is dominated by two other bands called the D- and G-bands [23,24]. The D-band corresponds to  $A_{1g}$  mode symmetry associated with a zone boundary phonon and is manifested in the Raman spectrum due to crystalline defects and breakdown of lattice symmetry of graphitic phase [23,24]. In contrast, the G-band arises from a doubly degenerate in-plane vibration of Raman active zone center  $E_{2g}$  phonon mode activated by a first-order Raman scattering process involving intra-layer stretching of in-plane carbon atoms [23]. In addition, three other bands  $\nu_1$ ,  $\nu_2$ , and  $\nu_3$  appear at around  $1150$ ,  $1215$ , and  $1480\text{ cm}^{-1}$ , respectively, and are assigned as t-PA Raman bands [12,13,25]. Thus, these five Raman bands (D, G,  $\nu_1$ ,  $\nu_2$  and  $\nu_3$ ) are associated with GB phase of UNCD. Sustainability of UNCD films at high pressure and temperature is one of the important criteria for device applications. Michaelson et al. studied the effect of annealing temperature on Raman spectral behavior of UNCD film and showed a complete stability of t-PA phase up to as high as  $1273\text{ K}$  [26].

Here, we report our pressure and temperature dependent Raman spectroscopic studies of UNCD grown by plasma enhanced chemical vapor deposition method. Pressure dependent in-situ measurements were carried out up to  $16\text{ GPa}$  using a diamond anvil cell in a quasi-hydrostatic condition to study the behavior of phonons associated with GB. The microstructure of the UNCD grains was examined using a transmission electron microscopy (TEM). The spectral frequencies and line-widths were quantitatively analyzed to study their phonon behavior. Grüneisen parameters for these GB phonons are calculated; modes sensitive to the pressure are identified and pressure effect on several modes under compression is discussed. GB phonons contribution to the specific heat of UNCD at room temperature is estimated and compared with the reported theoretical value. Temperature dependent Raman spectra down to  $90\text{ K}$  were investigated to estimate the anharmonicity of GB phonon modes. We believe that this is the first report of vibrational spectra of UNCD under external stimuli such as pressure and temperature and also its specific heat evaluation from spectroscopic results.

## 2. Experimental

The UNCD films were deposited on mirror polished silicon (100) substrate using microwave plasma enhanced chemical vapor deposition

(MPECVD) system (2.45 GHz 6" IPLAS-CYRANNUS). Prior to deposition, the substrates were ultrasonicated in a methanol solution containing a mixture of nano-diamond ( $\sim 5\text{ nm}$ ) and titanium ( $\sim 325\text{ nm}$ ) powders for 45 min to facilitate the generation of nucleation sites at the surface. The UNCD film was deposited using  $\text{CH}_4$  (1%)/Ar plasma as feed stock gas with a microwave power delivery of  $1200\text{ W}$  and pressure  $120\text{ Torr}$  while maintaining a substrate temperature of  $723\text{ K}$ . The microstructure of the UNCD films was examined using high-resolution transmission electron microscopy (HRTEM; Joel 2100). Raman spectra of the sample were measured using a  $514.5\text{ nm}$  laser excitation from an Ar-ion laser. The spectra were collected using a *micro*-Raman spectrometer (Renishaw, UK, model Invia) equipped with a charge coupled device (CCD) detector. A  $20\times$  long working distance objective was used to align the laser beam into a spot size about  $1\text{ }\mu\text{m}$  on the sample. In situ temperature-dependent Raman spectra were recorded from  $90$  to  $613\text{ K}$  using a Linkam (THMS 600) stage ensuring a temperature stability of  $\pm 0.1\text{ K}$ . Laser power and data acquisition time were optimized to improve the signal-to-noise ratio of recorded Raman spectra. High pressure in-situ Raman experiments were carried out using a compact, symmetric diamond anvil cell. UNCD films grown on Si substrate were gently peeled off from the substrate using a steel sharpener. A few specks of UNCD film were loaded into a  $200\text{-}\mu\text{m}$  hole of a stainless steel gasket (preindented to a  $70\text{-}\mu\text{m}$  thickness) in the DAC. 4:1 methanol-ethanol mixture as a pressure transmitting medium and Ruby as pressure marker were loaded along with the sample. For pressure calibration, Ruby R1 fluorescence technique was used. Raman spectra were also recorded in the decompression cycle.

## 3. Results and discussion

### 3.1. Microstructure

Fig. 1a shows the bright field TEM micrograph of the UNCD film with the inset showing the selective area electron diffraction (SAED) pattern. The SAED contains sharp diffraction rings corresponding to (111), (220) and (311) lattices of diamond structure, confirming that the film content is diamond. The continuous diffraction rings imply that the diamond grains are very small and are randomly oriented. It should be mentioned that some grains are of dark contrast, which are oriented along some zone-axis and diffract electrons strongly, whereas some grains are of light contrast, which are oriented away from the zone-axis and diffract electrons weakly. There appears diffused ring in the center of SAED, indicating the existence of amorphous carbon ( $\alpha\text{-C}$ ), which is presumably contributed from the t-PA located in the grain boundaries.

In typical HRTEM, the structure image is shown in Fig. 1b. In the Fourier transform diffractogram corresponding to the entire structure image ( $\text{FT}_0$  in Fig. 1b), the diffraction spots were arranged in the form of a ring, which reveals the presence of diamond materials, and a large diffuse ring of full-moon geometry appears in the middle, which is related to the existence of  $\alpha\text{-C}$  phases. Region 1 confirms the presence of diamond materials and region 2 corresponds to the  $\alpha\text{-C}$  phases, which are highlighted as  $\text{ft}_1$  and  $\text{ft}_2$  images inset Fig. 1b, respectively.

### 3.2. Temperature dependent Raman spectroscopy

The room temperature Raman spectrum recorded from the UNCD grown on Si substrate is shown in Fig. 2. Four prominent Raman bands are observed at  $1138$ ,  $1365$ ,  $1468$ , and  $1559\text{ cm}^{-1}$ . Using peakfit, the spectrum can be analyzed into six bands in the frequency range  $900\text{--}1850\text{ cm}^{-1}$  (Fig. 2). Since the instrumental broadening of the Raman spectrometer is found to be negligible, a simple Lorentzian line-shape is used to analyze the spectra.

The characteristic peaks of UNCD are located at  $1138$ ,  $1195$ , and  $1468\text{ cm}^{-1}$  and are assigned as non-degenerate  $A_g$  mode [27]. These bands arise from resonance Raman scattering processes involving  $\pi$  state of  $sp^2$  bonded carbon atoms, associated with t-PA segments in the

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