Thin Solid Films 541 (2013) 62–67

Contents lists available at SciVerse ScienceDirect

Thin Solid Films

journal homepage: www.elsevier.com/locate/tsf

# Subtle Raman signals from nano-diamond and β-SiC thin films

Mohan Kumar Kuntumalla, Harish Ojha, Vadali Venkata Satya Siva Srikanth *

*School of Engineering Sciences and Technology (SEST), University of Hyderabad, Hyderabad 500046, India*

ARTICLE INFO

Available online 31 January 2013

*Keywords:*
Chemical vapor deposition
Diamond thin film
Beta-silicon carbide (β-SiC) thin film
Nanocrystalline
Raman scattering

ABSTRACT

Micro Raman scattering experiments are carried out in pursuit of subtle but discernable signals from nano-diamond and β-SiC thin films. The thin films are synthesized using microwave plasma assisted chemical vapor deposition technique. Raman scattering experiments in conjunction with scanning electron microscopy and x-ray diffraction were carried out to extract microstructure and phase information of the above mentioned thin films. Certain subtle Raman signals have been identified in this work. In the case of nanodiamond thin films, Raman bands at ~485 and ~1220 cm$^{-1}$ are identified. These bands have been assigned to the nanodiamond present in nanodiamond thin films. In the case of nano β-SiC thin films, optical phonons are identified using surface enhanced Raman scattering.

## 1. Introduction

Carbon allotropes such as graphite [1,2] or diamond [3,4] show unique Raman signals, thus allowing a fast and straightforward identification using micro Raman spectroscopy (μRS). The interpretation of Raman spectra of carbon nanostructures is, however, complex [5]. While numerous thorough studies have been conducted on all kinds of carbon forms, certain Raman signals obtained from nanodiamond were not implicit for a long time. For example, ~1140 cm$^{-1}$ Raman signal that was assigned to nanodiamond in diamond thin films for a very long time was confirmed as a consequence of trans-polyacetylene vibrations [6]. Similarly, ~1640 cm$^{-1}$ Raman signal that was assigned to nanodiamond phase in detonation nanodiamond was re-assigned to hydroxyl group bending vibrations [7]. The first-order Raman spectrum of a perfect bulk single crystal diamond displays one triply-degenerate Raman phonon band at 1332 cm$^{-1}$ with a full-width at half-maximum of only ~1–2 cm$^{-1}$ [6]. Nanodiamond thin films and powders show additional Raman signals that result from grain boundaries, structural defects, surface-related contributions, and impurities (e.g., amorphous and graphitic carbon) [8]. As a consequence, interpretation of Raman spectra corresponding to nanodiamond becomes quite complex and depends greatly on synthesis technique, structure, surface chemistry, and purity of the samples. Relation between the confinement-induced changes in the Raman spectrum of diamond and its size has also been studied [9]. Following the confinement model [10], nanodiamond crystallite sizes have been estimated. Modeling of the Raman signal corresponding to ~5.5 nm sized detonation diamond particles has also been done [11]. Red shift in the signal position and broadening in the signal width of 1332 cm$^{-1}$ band has been observed as the size of single nanodiamond particle decreased [12]; the shift and signal width broadening have been explained in terms of the phonon-confinement effects and are found to be in good agreement with the theoretical predictions [9,11]. Computational studies also showed that phonon wave vectors from small vibrational domains lead to a broad shoulder-like signal at ~1250 cm$^{-1}$, which was not so often observed in the Raman spectra corresponding to nanodiamond [13].

As for using μRS (using a visible Raman excitation wavelength) in characterizing nano β-SiC thin films, the noticeable β-SiC phonon modes should be the typical transverse optical (TO) and longitudinal optical (LO) phonon modes at 790 and 970 cm$^{-1}$ [14–16], respectively. Since β-SiC crystallites will be small in nano β-SiC thin films, TO and LO modes are expected to be broader. In the case of nano β-SiC thin films, there are certain issues that have to be understood/clarified such that more phonon related arguments can be used to characterize β-SiC phase using μRS. The prime issue: β-SiC is Raman active, but it is difficult to detect it using μRS if any carbon medium surrounds it. Since carbon is present in the gas phase reaction while depositing nano β-SiC thin films, it is bound to be present in one form or the other in the films which in turn will make the detection of β-SiC difficult using μRS. The reason being the lower (~40 times) Raman scattering efficiency of the Si—C bond than that of the C—C bond. Additionally, Si—C bond features in the Raman spectra obtained from thin films may not be discernable due to the strong interference of silicon's (substrate) second order broad phonon mode with the spectral region of TO and LO modes corresponding to β-SiC.

In this work, subtle but discernible Raman signals obtained from nanodiamond and nano β-SiC thin films will be discussed. The Raman signals to be discussed are an upshot of the routine Raman scattering experiments carried out on the above mentioned thin films. Scanning electron microscopy and x-ray diffraction are carried out (in conjunction with Raman scattering experiments) to extract microstructure and phase information of the above mentioned thin films.

---

* Corresponding author. Tel.: +91 40 2313 4453; fax: +91 40 23011087.
*E-mail address:* vvsssse@uohyd.ernet.in (V.V.S.S. Srikanth).

0040-6090/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.tsf.2013.01.051

**Table 1**
Experimental details of the as-deposited thin films considered in this work.

| Sample | % TMS | % $CH_4$ | Substrate temperature (°C) | Deposition time (h) | Bias voltage (V) | Microwave Power |
|---|---|---|---|---|---|---|
| NCD1 | – | <1% in $H_2$ | 700 | 6 | – | 700 W |
| NCD2 | – | 4% in $H_2$ | 850 | 3 | −160 | 700 W |
| NCD3 | – | 4% in $H_2$ | 850 | 3 | −200 | 700 W |
| NCS1 | <0.05% in $H_2$ | – | 700 | 6 | – | 700 W |
| NCS2 | <0.05% in $H_2$ | – | 700 | 10 | – | 700 W |

## 2. Experimental details

Nano-diamond and β-SiC thin films were deposited using microwave plasma enhanced chemical vapor deposition (MWCVD) technique on (100) silicon (Si) substrates. In this work, three nanodiamond and two nano β-SiC are considered. Table 1 shows the tabulated experimental details. Different methane ($CH_4$) and hydrogen ($H_2$) gas mixtures at a total gas pressure of 25 Torr were used during the deposition.

Zeiss ultra55 ultra high resolution field emission scanning electron microscope (FESEM) operated at an accelerating voltage of 5 kV was used to obtain secondary electron (SE) surface morphology images. To determine the crystallinity of the thin films considered in this study, Grazing incidence x-ray diffraction (GIXRD) measurements were performed in grazing-incidence geometry in the 2θ range of 30–160° with a step size of 0.03°. GIXRD patterns in this work have been measured using Bruker D8 Discover diffractometer which uses Cu Kα x-rays (λ = 1.54 Å), produced by impinging an 40 mA electron beam on a Cu target. The incidence angle was fixed at very low angle of 1.5° with respect to the sample surface and the detector was mounted on a separate rotating base, the rotating detector measures an angle 2θ.

Micro Raman scattering study was carried out using LabRam HR800 Raman spectrometer from Horiba Jobin Yvon. Raman spectra have been collected by using 514.5 nm green line of $Ar^+$ ion LASER as the excitation source. The LASER power was kept at 2.8 mW in all the measurements in order to avoid any thermal influences. The LASER beam was focused onto nanodiamond and nano β-SiC thin film surfaces by means of 50× (for LASER spot diameter ~1 μm) optical objective lens. The spectral resolution was 1 $cm^{-1}$. The scattered light was collected in the spectral range 50 to 2000 $cm^{-1}$ in a back scattering geometry perpendicular to (100) face of the Si substrate. Silver (Ag) nanoclusters are deposited on nano β-SiC thin film surfaces prior to carrying out the surface enhanced Raman scattering (SERS) experiments. Ag nanoclusters deposition was carried out using a magnetron cluster deposition system (NANODEP 60 from Oxford Applied Research, UK) following a previously reported procedure [17]. The power of the magnetron was maintained at ~70 W (with a voltage of 350 V and a plasma current of 200 mA). Base and working pressure have been maintained at $2.8 \times 10^{-6}$ and $8.5 \times 10^{-5}$ Torr, respectively with an Argon gas flow rate of 100 sccm. Ag cluster deposition was carried out for only 2 min in order to avoid formation of any thick coating of Ag which may be unfavorable for SERS activity.

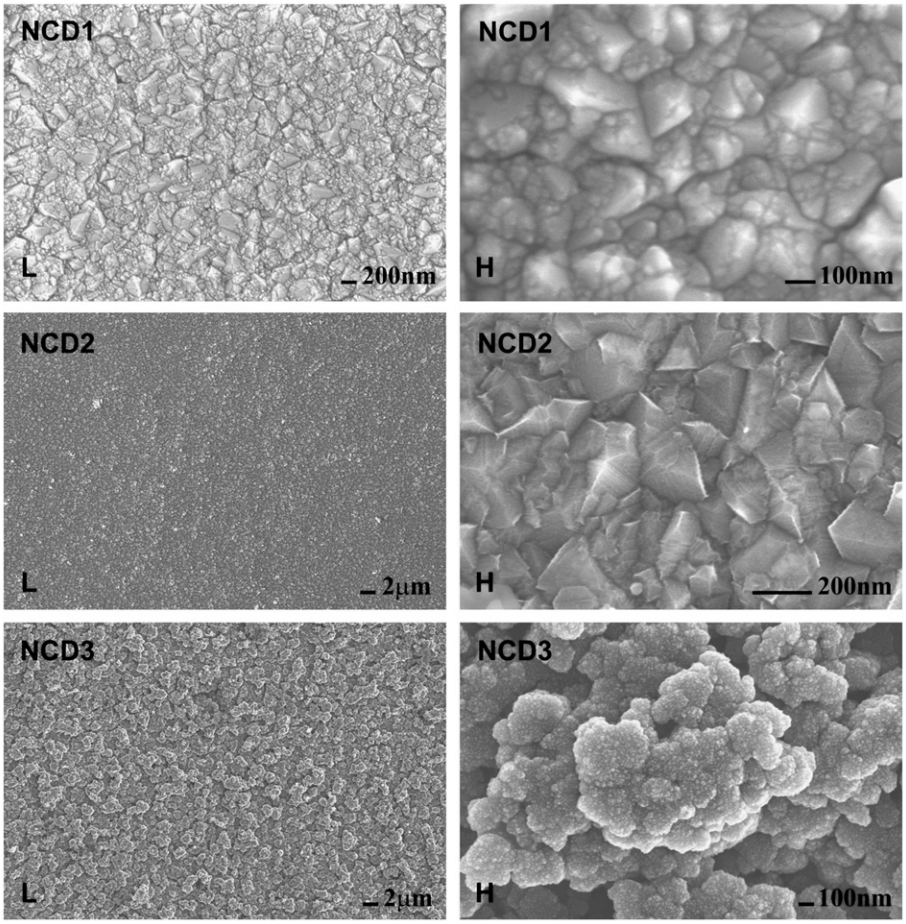

**Fig. 1.** Low (L) and high (H) magnification plane view secondary electron micrographs of nanodiamond thin films.