Identification of β-SiC surrounded by relatable surrounding diamond medium using weak Raman surface phonons

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Abstract. It is difficult to detect β-SiC using micro-Raman scattering, if it is surrounded by carbon medium. Here, β-SiC is identified in the presence of a relatable surrounding diamond medium using subtle, but discernible Raman surface phonons. In this study, diamond/β-SiC nanocomposite thin film system is considered in which nanosized β-SiC crystallites are surrounded by a relatable nanodiamond medium that leads to the appearance of a weak Raman surface phonon band at about 855 cm^{-1}. Change in the nature of the surrounding material structure and its volume content when relatable, will affect the resultant Raman response of β-SiC phase as seen in the present case of diamond/β-SiC nanocomposite thin films.

Keywords. Carbon materials; nanocomposites; thin films; Raman; microstructure.

1. Introduction

In previous studies, micro-Raman scattering (μRS) was used to study diamond and nondiamond phases in diamond/β-SiC nanocomposite thin films in addition to X-ray diffraction (XRD), infrared (IR) spectroscopy and transmission electron microscopy; whilst only the latter three could be used to study β-SiC (Srikanth *et al* 2008). It is difficult to detect β-SiC using μRS if it is surrounded by carbon medium; reason being the lower ($\sim$40 times) RS efficiency of Si–C bond than that of C–C bond (Sasaki *et al* 1987; Hillel *et al* 1993). Also, if silicon (Si) is used as the substrate, Si–C bond Raman features are not discernible due to the strong interference of Si's 2nd order phonon mode with the typical transverse optical (TO) and longitudinal optical (LO) modes of β-SiC (Feldman *et al* 1968; Olego and Cardona 1981; Mukaida *et al* 1987). The upshot of this work is the detection of a weak Raman surface phonon (SP) band centred at 855 cm^{-1} that corresponds to β-SiC in diamond/β-SiC nanocomposite thin film deposited on Si.

2. Experimental

Diamond/β-SiC nanocomposite thin film which is the point of focus in this work was deposited on (100) Si using the previously reported experimental methodology and parameters (Srikanth *et al* 2008) except for the substrate temperature of 800 °C and tetramethylsilane concentration of 0·0384%. μRS with a spectral resolution of $\sim$1 cm^{-1} was carried out using LabRam HR800 Raman spectrometer equipped with 514·5 nm green laser. Scattered Raman signals are collected

in the spectral range 500–2000 cm^{-1}. Additionally, field emission scanning electron microscope, infrared (IR) spectrometer and glancing incidence X-ray diffraction are used to study the surface morphology, composition and crystallinity, respectively of thin film.

3. Results and discussion

Surface morphology of diamond/β-SiC nanocomposite thin film is shown in figure 1. Similar to the previous studies (Srikanth *et al* 2008), dark (β-SiC) and bright (diamond) regions can be clearly observed. A careful observation shows that both diamond and β-SiC nanocrystallites are well facetted and smaller than those observed in the previous studies. It can be observed from figure 1 that only 25–30% of the area on the micrograph is occupied by β-SiC (dark regions). It is evident from the broader X-ray diffraction lines (figure 2) that crystalline nanodiamond and β-SiC are present in thin film. Low intensity of β-SiC diffraction lines indicates low β-SiC content in comparison to diamond in thin film. This complements well with the electron micrograph observations. The broad IR band centred at 800 cm^{-1} (figure 3) is TO phonon of β-SiC (Spitzer *et al* 1959; Avigal *et al* 1974) that vindicates the presence of nanocrystalline β-SiC phase in thin film; this band is broader than the previous observations (Srikanth *et al* 2008) indicating a reduced β-SiC crystallite size.

Broad Raman bands (figure 4) centred at 1333 and 1575 cm^{-1} correspond to the presence of nanodiamond and graphite, respectively in the film (Wada and Solin 1981). However, the low intensity of 1575 cm^{-1} band (considering that RS efficiency for graphite is 6 times greater
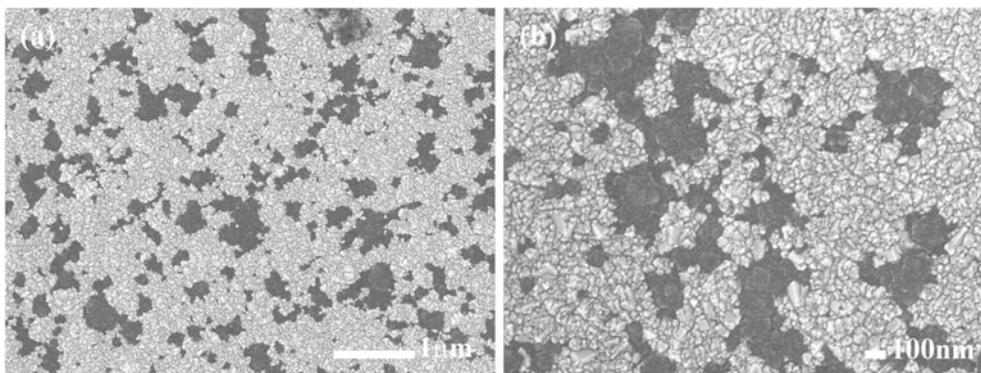
Figure 1. (**a**) Low and (**b**) high magnification secondary electron plane view micrographs of diamond/β-SiC nanocomposite film.
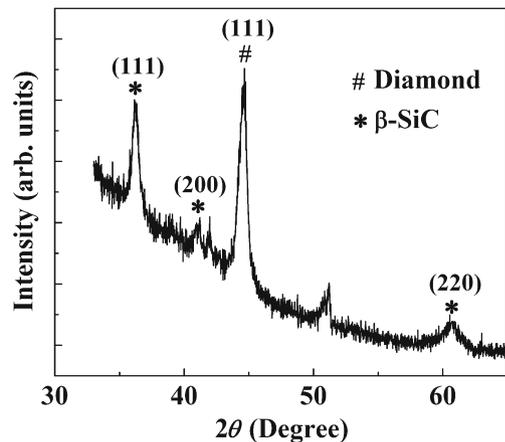

Figure 2. X-ray diffractogram obtained from diamond/β-SiC nanocomposite thin film.
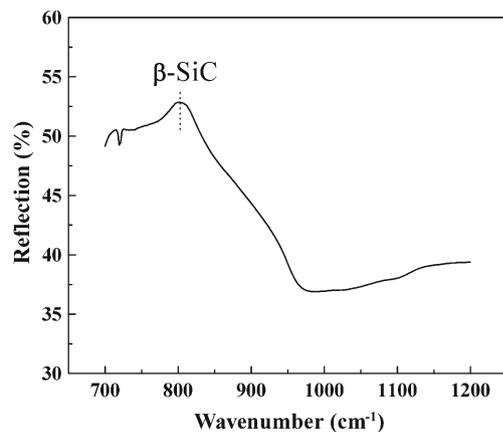

Figure 3. IR spectrum obtained from diamond/β-SiC nanocomposite thin film.
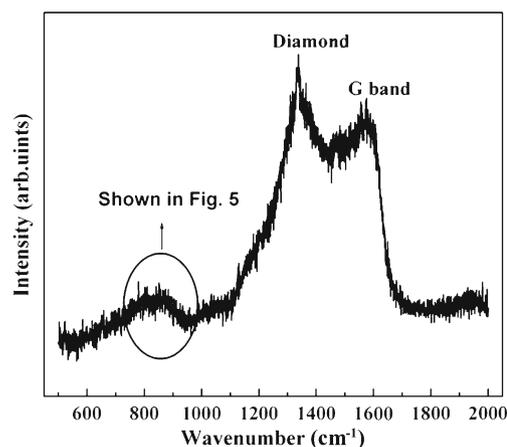

Figure 4. Raman spectrum obtained from diamond/β-SiC nanocomposite thin film in a back scattering geometry perpendicular to (100) Si.

(Wada and Solin 1981) than that of diamond for 514·5 nm laser wavelength) in comparison to diamond Raman band intensity implies very low graphite content in thin film. In figure 5 (encircled part in figure 4), a broad Raman band at 855 cm^{-1} can be clearly identified; but TO (at $\sim$790 cm^{-1}) and LO (at $\sim$970 cm^{-1}) bands corresponding to β-SiC are not discernible. As for bulk SiC, LO band is the only allowed one in back scattering on (001) plane (Feng *et al* 1988). Since the laser spot diameter is $\sim$2·5 μm, Raman scattering events average over several grains of both diamond and β-SiC. Therefore, the Raman measurements need not strictly exclude back scattering from directions other than (001) crystal plane as per Raman selection rules. As a result both TO and LO bands in general can be detected provided difficulties which are discussed in the introduction are overcome. However, this is not the case. Additionally, low β-SiC content in thin film makes its detection using μRS even more difficult.

The appearance of 855 cm^{-1} band is attributed to the dominance of SP mode in the shown Raman spectral region (figure 5) due to the reduced crystallite sizes of β-SiC. Based
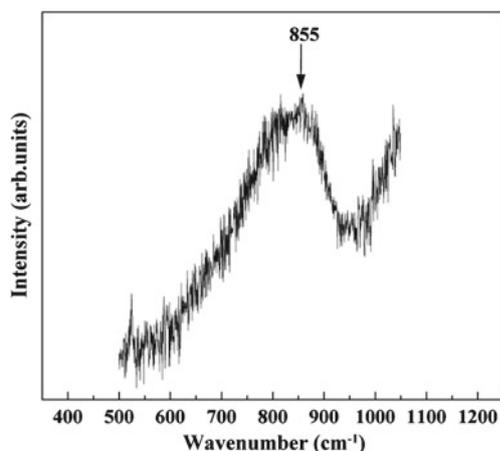
Figure 5. Encircled part in figure 4, Raman spectrum obtained from diamond/β-SiC nanocomposite thin film in spectral range 500–1100 cm^{-1}.

on 3-D quantum confinement (SiC 3-D grains with typical dimensions of only a few nm), it has been shown that LO mode (970 cm^{-1}) can slightly shift to a lower wavenumber (Zhang *et al* 1992, 1999). Therefore, the observed 855 cm^{-1} band which is far lower cannot be interpreted in terms of a strong size confinement effect. The size confinement effect on Raman phonons has another aspect attached to it; electron–phonon interaction and electronic structures may be considerably altered, resulting in Raman scattering modes like SP mode, which are otherwise forbidden in the case of bulk counterparts (Huang *et al* 1990; Yan *et al* 2003). SP modes are predominant only when the crystallite size $d < \lambda/\pi$, where λ is Raman excitation wavelength (Ruppin 1975; Hayashi 1984; Hayashi and Ruppin 1985). For 514·5 nm laser wavelength used in this study, if the crystallite sizes are just <160 nm, SP mode dominates Raman spectrum of that particular material. In the present case, β-SiC is (i) not the only phase present but surrounded by diamond, (ii) low in content when compared to diamond and (iii) with very low Raman scattering efficiency. Therefore, possibility of the appearance of TO and LO bands corresponding to β-SiC in diamond/β-SiC nanocomposite thin film is diminutive.

From figure 1, it is very clear that β-SiC crystallite sizes are almost one order or even less than the requirement for Raman SP mode to show up in β-SiC Raman spectral range. From the above observations and discussion, it appears that the presence of surrounding diamond phase in the nanocomposite thin film is the cause for the appearance of Raman SP mode corresponding to β-SiC. A simple calculation based on the effective medium theory (Genzel and Martin 1972; Hayashi 1984; Hayashi and Ruppin 1985) for the diamond/β-SiC system yields a surface optical mode (due to Fröhlich enhancement) close to 860 cm^{-1}. When ε_∞ is taken as 6·52 (a typical high frequency dielectric constant of SiC) (Patrick and Choyke 1970), ε_M is taken as 5·7 (a typical frequency-independent dielectric constant of diamond)

(Fontanella *et al* 1977), $\overline{\nu}^2_{TO}$ and $\overline{\nu}^2_{LO}$, the bulk TO and LO phonon mode frequencies are taken as 790 and 970 cm^{-1}, respectively and l is taken as 1 (orbital quantum number for Fröhlich mode), the surface phonon mode frequency is:

$$\overline{\nu}_{SP} = \sqrt{\frac{\frac{l+1}{l}\overline{\nu}^2_{TO} + \frac{\varepsilon_\infty}{\varepsilon_M}\overline{\nu}^2_{LO}}{\frac{l+1}{l} + \frac{\varepsilon_\infty}{\varepsilon_M}}} \approx 857 \, \text{cm}^{-1}.$$

However, 855 cm^{-1} band could not be detected in the case of other similar nanocomposite thin films studied previously. This shows that the change in the nature of the surrounding diamond and its volume content (which in other cases is quite different) will affect the resultant Raman response of β-SiC phase. The observed 855 cm^{-1} Raman band is therefore SP mode corresponding to nano β-SiC in diamond/β-SiC nanocomposite thin film.

4. Conclusions

β-SiC phase in diamond/β-SiC nanocomposite thin film was identified by using micro Raman spectroscopy. A broad Raman surface phonon band at about 855 cm^{-1} corresponding to nanosized β-SiC crystallites are detected.

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