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Raman bands in microwave plasma assisted chemical vapour deposited films

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Abstract

Raman spectroscopy is employed to characterize thin diamond films deposited by microwave plasma assisted chemical vapour deposition technique using a gas mixture of methane and hydrogen. The surface morphology of the films was analyzed by scanning electron microscopy. We have identified submicron crystals on (100) facets of diamond crystals which gave rise to bands in the Raman spectrum centred at ≈ 1170 and $\approx 1456 \text{ cm}^{-1}$.

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1. Introduction

Raman spectroscopy is a powerful method for identification of different carbon phases not only by detecting the characteristic frequencies related to stretching or angle deformation in the lattice but also thanks to its ability to determine the crystallographic arrangement. The technique allows to distinguish between various types of carbon such as diamond, nano-crystalline diamond, graphite, amorphous carbon, diamond-like carbon and hydrogenated carbon [1–4]. Furthermore, information about domain (crystal) size, stress and structural perfection can be obtained because these factors cause broadening and shifts of the Raman peaks. We employed Raman spectroscopy to analyze the diamond layer deposited by microwave plasma assisted chemical vapour deposition (MW CVD) on two different substrates.

2. Experiment

Diamond films were deposited by MW CVD on polished silicon substrates and tungsten wires in

a conventional bell jar (ASTeX-type) reactor. The deposition pressure, microwave power, substrate temperature and total flow rate were maintained 10^4 Pa, 1.2 kW, 800 °C and 300 sccm, respectively. A gas mixture of CH₄ and H₂ was used and the gas flow ratio of CH₄/H₂ was kept at 1.5 or 8% for deposition on silicon and at 5% for deposition on tungsten wires. Before deposition on silicon, the substrates were polished with a 1 μm diamond paste and then they were ultrasonically cleaned in alcohol. The films on silicon substrates and W wires were deposited for 9 and 2 h, respectively.

Raman spectra were recorded at room temperature by a Raman spectrometer DILOR-JOBIN YVON-SPEX, type LabRam confocal system using a He–Ne laser source of excitation (632.8 nm, 15 mW). Microscope objective $\times 100$ was used to focus the laser beam onto a spot of approximately 2–5 μm in diameter and to collect the scattered light which then passed through the spectrometer onto a CCD detector. Furthermore, a confocal hole with a diameter of 200 μm, a spectrograph entrance slit of 150 μm, and 1800 grooves/mm diffraction grating were employed. The spectra were evaluated by the software package LABSPEC. The spectrometer was calibrated to the 520.7 cm⁻¹ band of single crystalline Si and 1332 cm⁻¹ of natural diamond. Scanning electron microscope Philips

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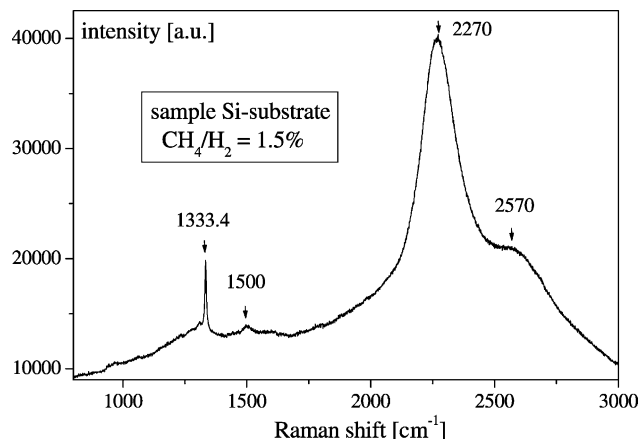


Fig. 1. Raman spectrum of a MW CVD diamond film on silicon.

505 operating in the secondary electron mode was used to study the microtopography of diamond layers.

3. Identification of Raman bands

Fig. 1 shows the Raman spectrum of a microcrystalline diamond film grown on silicon. The spectrum has two dominant features: a sharp line centred at $\approx 1333 \text{ cm}^{-1}$, known to be the characteristic line of diamond, and a broad band centred at about 2270 cm^{-1} . The broad band at $\approx 2270 \text{ cm}^{-1}$ is most likely a luminescence band of structural defects in diamond, which reveals a lower quality of the silicon/diamond buffer interface. We have repeatedly observed the presence of this band in layers with defects of diamond films. The band at $\approx 2270 \text{ cm}^{-1}$ has been observed also when analyzing diamond layers deposited in a hot filament (HF) CVD reactor [5]. A scanning electron microscopy (SEM) micrograph of the microcrystalline diamond film on silicon is shown in Fig. 2. The micrograph shows triangular facets typical for (111)-oriented

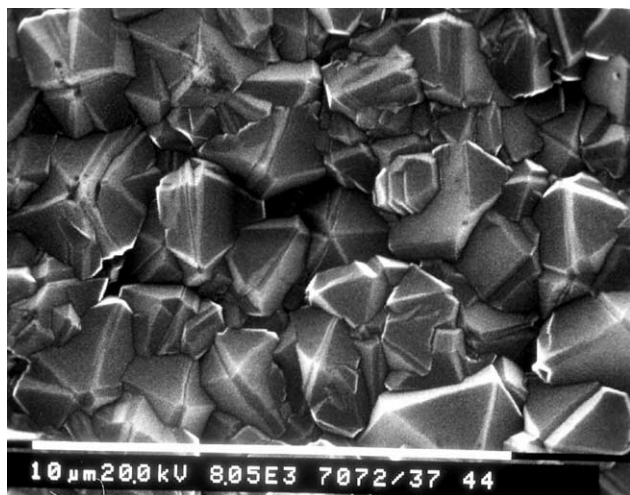


Fig. 2. Scanning electron micrograph of a MW CVD microcrystalline diamond film on silicon.

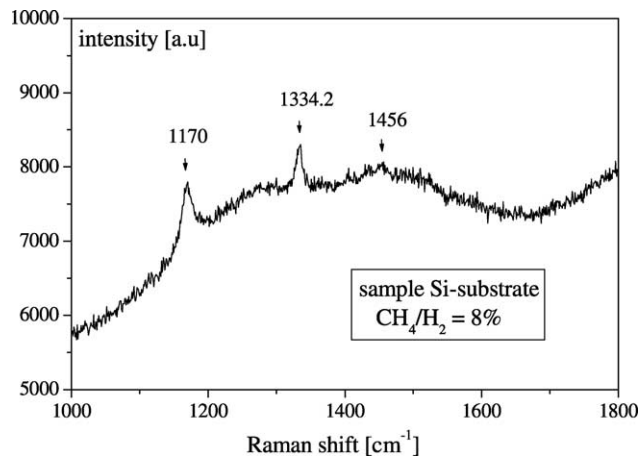


Fig. 3. Raman spectrum of a submicron nucleus of diamond on Si.

crystallographic planes of the grown diamond crystals. One can also see doubled edges and crystal twinning which developed already during the nucleation stage of film deposition.

In the Raman spectrum of another sample deposited in the same MW CVD reactor but at different conditions (methane concentration 8%, time of deposition 2 h) shown in Fig. 3 one can see bands centred at ≈ 1170 and $\approx 1456 \text{ cm}^{-1}$ which could be assigned to submicron diamond. The origin of these bands may be in submicron crystals which are clearly resolved in Fig. 4. In these micrographs one can also see square-shaped (100)-oriented facets and the growth of submicron crystals on previously developed faces of diamond crystals.

The Raman spectrum of the diamond layer on a W wire (the end of the wire with temperature about $600 \text{ }^\circ\text{C}$, placed approximately 3 cm from the plasma) deposited by MW CVD is shown in Fig. 5. The spectrum consists of two carbon bands: A higher one at 1318 cm^{-1} and a band centred at $\approx 1600 \text{ cm}^{-1}$. In the spectrum in Fig. 5 no band is found at $\approx 2270 \text{ cm}^{-1}$. The layers deposited on the W wire,

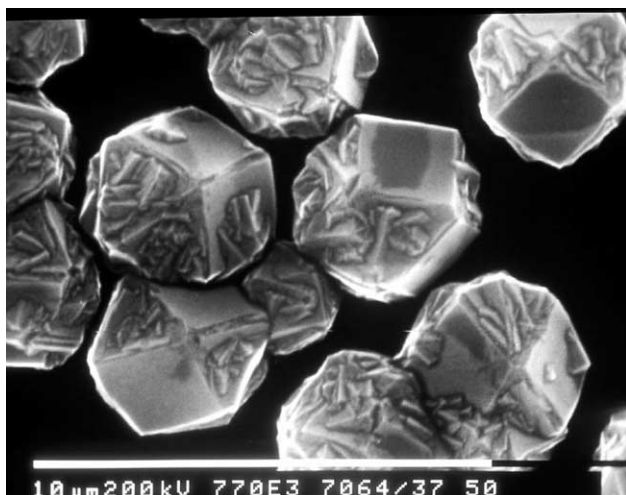


Fig. 4. SEM picture of the MW CVD submicron diamond nucleus shown in Fig. 3.

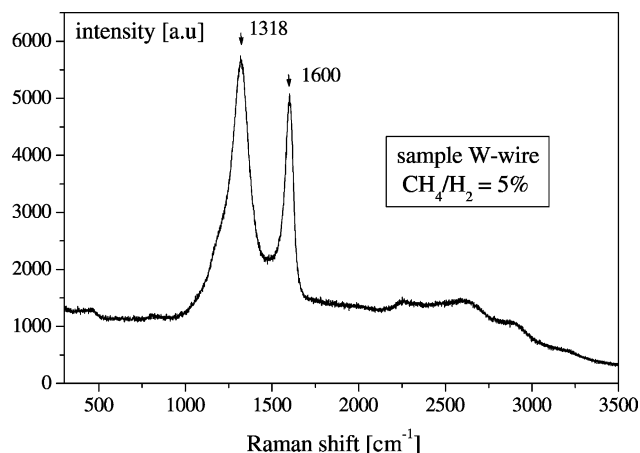


Fig. 5. Raman spectrum of a MW CVD film on W.

as deduced from Raman spectra, contain regions with well-developed diamond crystals as well as regions with predominance of non-diamond carbon phases. The spectral background in the Raman spectra of all samples is attributed to luminescence, which is generally related to the presence of impurities and defects and of mechanical stress induced in the sample [6].

4. Conclusion

The carbon phases and morphology of diamond films prepared by MW CVD were studied by Raman spectroscopy and scanning electron microscopy. In the diamond layers on Si substrates we detected diamond crystals with both (111) and (100)-orientations as well as a graphite component. The Raman spectra contain, besides the peak of diamond and/or graphite, also a broad luminescence band. We have observed a band at

$\approx 2270 \text{ cm}^{-1}$ in layers with pronounced diamond crystal twinning. The most interesting result is the detection of submicron diamond nuclei on (100)-oriented diamond faces and their identification by Raman bands centred at ≈ 1170 and $\approx 1456 \text{ cm}^{-1}$. We have not observed these bands in other studied layers.

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