

Features of the 1640 cm^{-1} band in the Raman spectra of radiation-damaged and nano-sized diamonds

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Abstract. Raman spectra of irradiated with fast neutrons or MeV ion-implanted radiation-damaged natural and CVD diamonds and chemically purified detonation nanodiamonds are investigated. The influence of radiation damage level and effects of high-temperature annealing on the intensity and spectral shape of the 1640 cm^{-1} band is studied. It is shown that in radiation-damaged diamonds this band consists of at least six Gaussian peaks, the intensity of which varies one to one both with the level of radiation disordering and the temperature of the subsequent annealing. The “1640” band in radiation-damaged diamonds is completely annealed at temperatures above 1000°C , while in detonation nanodiamonds annealing up to 1200°C does not significantly affect its shape and intensity.

1. Introduction

Understanding and controlling radiation-induced defects is a key to optical and semiconductor applications in which diamond is subjected to irradiation during processing to tailor its properties. The band with a maximum near 1640 cm^{-1} dominates normally in the high-frequency part of the Raman spectra of radiation-modified diamonds and also of ultrafine detonation nanodiamonds (DND) [1]. This feature cannot be assigned to any pure form of sp^3 -carbon [2]. Various origins for the “1640” band are still proposed and discussed. Some researchers associate this band with the presence of sp^2 -hybridized carbon in different forms [3], mixed sp^2/sp^3 [4], with the $\langle 100 \rangle$ split-interstitial, which is obtained by replacing one carbon atom by two carbon atoms, displaced along the $[100]$ and $[-100]$ directions from the lattice site (dumbbell defect) [5], particularly stable isolated divacancy $[V-C=C-V]$ [6], and in DND also with different surface defects - small graphite flakes, sp^2 chain fragments, five or seven membered rings [7] or superposition of sp^2 -carbon band at 1590 cm^{-1} with a peak of hydroxyl group vibrations at 1640 cm^{-1} [8–9]. In this work we investigated the behavior of the “1640” Raman band during annealing runs with the aim to advance in understanding the nature of centers responsible for this band in radiation-modified and ultradispersed diamonds.



2. Samples and experimental

Three groups of samples were studied: (i) Polycrystalline CVD diamonds grown by microwave plasma-enhanced CVD system and irradiated with fast neutrons (neutron fluences in the range from 3×10^{18} to $2 \times 10^{20} \text{ cm}^{-2}$ [10] in a wet channel of an IVV-2M nuclear reactor in a fast neutron flux of $\sim 10^{14} \text{ cm}^{-2} \cdot \text{s}^{-1}$ (for energies $> 0.1 \text{ MeV}$) and fluencies of $\Phi = 3 \times 10^{18}$ and $2 \times 10^{19} \text{ cm}^{-2}$ at $325 \pm 10 \text{ K}$. The samples were annealed in an oven with graphite walls, in a vacuum of 10^{-5} Torr at temperatures from 200 to 1700°C (for 60 min at fixed temperature). (ii) Natural diamonds implanted with nickel (energy 335 MeV, fluence $5.0 \times 10^{14} \text{ cm}^{-2}$) and xenon ions (energy 130 MeV, fluence $6.5 \times 10^{14} \text{ cm}^{-2}$). During the of ion implantation, the temperature of the samples was no higher than 50°C . The Monte Carlo method (SRIM-2013 program package [11]) was used to calculate the distribution of Ni (Xe) atoms and the primary carbon vacancies (the measure of radiation damage in diamond) in ion implanted samples. For both MeV ion-implanted diamonds the oblique sections at small angles ($5 \div 10^\circ$) were mechanically cut over the entire depth of the damaged depth, which made it possible to perform confocal Raman measurements from sample areas with different fixed levels of radiation damage. (iii) DND with an average crystal size of 6 nm, obtained by a detonation method from a mixture of trinitrotoluene/hexogen and subjected to deep chemical purification from a disordered carbon sp^2 phase.

Raman spectra of diamonds following the ion implantation or neutron irradiation and high-temperature annealing were measured on LABRAM HR, NanofinderHE, Bruker Senterra Raman and Renishaw's in Via Reflex Raman spectrometers under excitation of diamond by laser radiation with wavelength $\lambda = 473, 488$ and 532 nm in backscatter mode.

3. Results and discussion

Raman spectroscopy may be considered as a method of choice to characterize the structure and phonon modes of the different carbon-based materials. Meanwhile the characteristic Raman spectra of radiation-modified and DND diamonds are very similar in spectral shape (figure 1(a)).

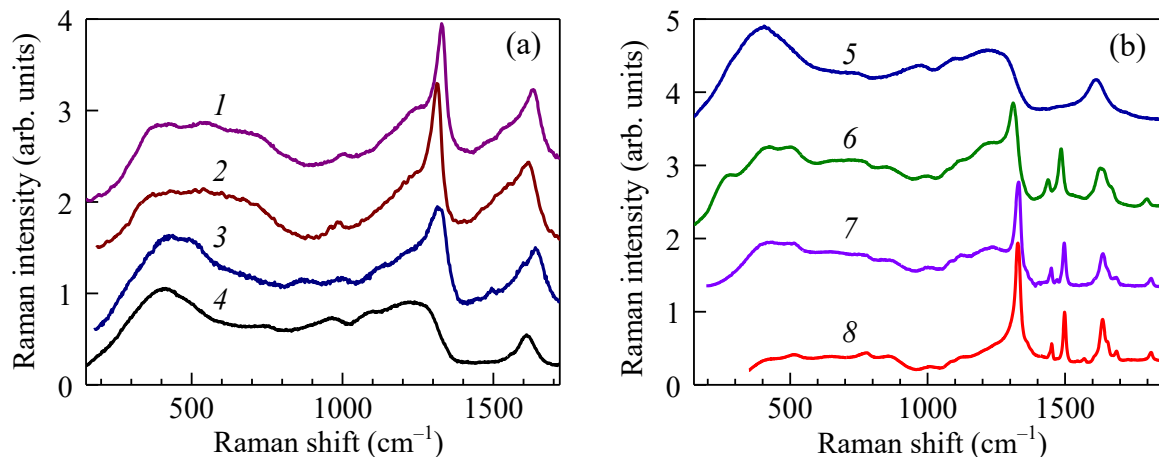


Figure 1. (a) Raman spectra of CVD diamond irradiated with neutrons with $\Phi = 2 \times 10^{20} \text{ cm}^{-2}$ (1), natural diamond implanted with 130 MeV Xe ions (concentration of vacancies $N_V = 10^{23} \text{ cm}^{-3}$) (2) and DND with an average crystallite size of 6 nm before (3) and after (4) annealing at 450°C . (b) Raman spectra of CVD diamond irradiated with neutrons with $\Phi = 2 \times 10^{19} \text{ cm}^{-2}$ before (5) and after annealing at 800°C (6), natural diamond implanted with 335 MeV Ni ions, $N_V = 10^{23} \text{ cm}^{-3}$ (7) and natural diamond implanted with 130 MeV Xe ions, $N_V = 4 \times 10^{21} \text{ cm}^{-3}$ (8). The Raman spectra were recorded at room temperature when diamond was excited by laser radiation at a wavelength of $\lambda = 488 \text{ nm}$ (spectra 1–6), 532 nm (spectrum 7) and 473 nm (spectrum 8). For clarity, the spectra are shifted vertically.

The Raman spectra of neutron-irradiated and ion-implanted diamonds are characterized by relatively narrow peaks with maxima near 1450, 1490–1500 and 1815 cm^{-1} (figure 1(b)) [12–14] the origins of which remain a matter of debate. Their positions shift to higher wavenumbers due to the elastic strain whereas the full-width at half maximum (FWHM) decreases for samples with lower radiation damage (figure 1(b)). The different tentative attributions have been formulated for the 1450 and 1490 cm^{-1} peaks, involving both vacancy [12, 15], intrinsic/nitrogen interstitial defects [16–17] or a vacancy or a divacancy surrounded by conjugated single and double carbon-carbon bonds (the R4/W6 center) [13, 18]. The recent calculations based on the B3LYP hybrid implementation of density functional theory [19] showed the absence of peaks in the region of 1490 cm^{-1} in the spectra of both divacancy V_2 and $V-C-C-V$ suggests that this line in the Raman spectra of irradiated diamonds is not attributable to both of these divacancy complexes [20]. According to the [21], the calculated Raman-active high-frequency oscillations of double interstitials (1461, 1495, 1813 and 1826 cm^{-1}) are agree well with the bands often observed in the Raman spectra of radiation-damaged diamonds (figure 1(b)).

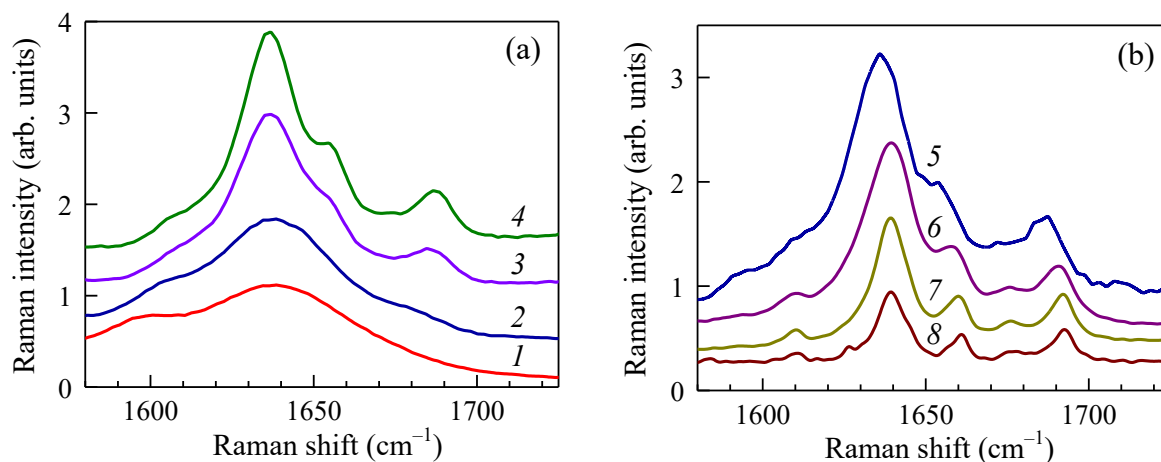


Figure 2. (a) Raman spectra of [Xe] implanted natural diamond, ion energy 130 MeV, fluence $6.5 \times 10^{14} \text{ cm}^{-2}$. Spectra corresponds to the positions where calculated by SRIM concentration of vacancies (cm^{-3}) are: 5.0×10^{22} (1), 2.0×10^{22} (2), 9.0×10^{21} (3) and 4.0×10^{21} (4). Spectra were recorded with excitation at $\lambda = 473 \text{ nm}$. (b) Raman spectra of [Ni] implanted natural diamond, ion energy 335 MeV, fluence $5 \times 10^{14} \text{ cm}^{-2}$. Spectra corresponds to the positions where calculated by SRIM concentration of vacancies (cm^{-3}) are: 2.6×10^{21} (5), 6.9×10^{20} (6), 3.0×10^{20} (7) and 2.5×10^{20} (8). Spectra were recorded with excitation at $\lambda = 532 \text{ nm}$.

Measuring Raman spectra of natural diamond implanted with nickel and xenon ions made it possible to establish that the “1640” band consists of several peaks, which shift to higher frequencies and become narrower with decreasing of the radiation damage level. The decomposition of the “1640” band showed that it consists of at least six Gaussian peaks, the maxima of which at low levels of radiation damage are located at 1610, 1626, 1639, 1660, 1667 and 1692 cm^{-1} and have FWHM of 6, 8, 10, 6, 9, and 7 cm^{-1} , respectively (figure 2).

Figure 3 demonstrates the Raman spectra variations of CVD and natural diamonds irradiated by fast reactor neutrons with isochronal annealing (for 1 hour). Annealing at 600–1000 $^{\circ}\text{C}$, like the decrease of the radiation-induced disorder during reduced ion implantation (figure 2), lower the intensity, FWHM (from 15–20 to 6–10 cm^{-1}) of the Raman peaks, as well as shifts (up to 15 cm^{-1}) them to higher frequencies. The set of peaks in figure 3 is the same as observed in the Raman spectra of Ni- and Xe-implanted diamonds (figure 2). This confirms the similarity of the radiation damages caused by implanted ions and irradiated neutrons, which are determined mainly by secondary collisions of knocked-out carbon atoms.

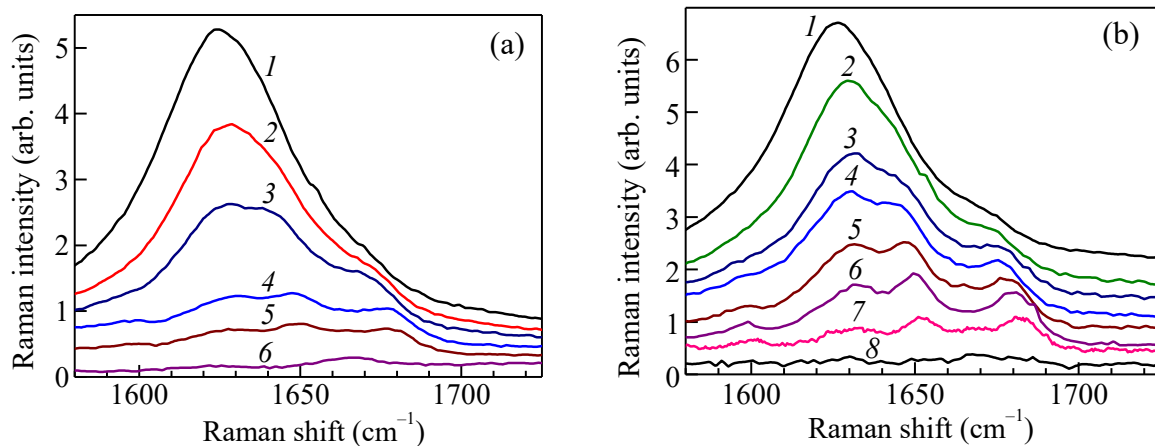


Figure 3. (a) The effect of vacuum annealing on the Raman spectra of CVD diamond irradiated with fast neutrons with a fluence of $2 \times 10^{19} \text{ cm}^{-2}$. The spectra were measured after annealing at temperatures (°C): (1) 625, (2) 700, (3) 800, (4) 900, (5) 940 and (6) 1005. Spectra were recorded with excitation at $\lambda = 488 \text{ nm}$. (b) The effect of vacuum annealing on the Raman spectra of natural diamond irradiated with fast neutrons with $\Phi = 1 \times 10^{20} \text{ cm}^{-2}$. The spectra were measured after annealing at temperatures (°C): (1) 625, (2) 675, (3) 750, (4) 775, (5) 812, (6) 877, (7) 950 and (8) 977. Spectra were recorded with excitation at $\lambda = 532 \text{ nm}$.

These peaks appear to refer to various radiation defects. The observed sharpness of the peaks indicates that they originate from well-defined local rather than extended defects. The relative intensities of the peaks forming the “1640” band vary both with the initial level of radiation damage and the temperature of the subsequent annealing. We noted, when the annealing temperature increases, the relative integral contribution of the 1639 cm^{-1} peak in the whole “1640” band steadily decreases from 80–85 % after annealing at 650–700 °C to 20–30% after annealing at 900–950 °C (figure 3). With a further increase of annealing temperature up to 1000–1040 °C, the band with a maximum at 1677 cm^{-1} dominates in Raman spectra of “1640” band (figure 3). The remaining four peaks have intermediate thermal stability. The temperature dependence of “1640” band in Raman spectra of CVD diamond irradiated with fast neutrons with a fluence of $3 \times 10^{18} \text{ cm}^{-2}$ (not shown here) has the same character, in the spectra of which the peak at 1633 cm^{-1} (shifted to 1639 cm^{-1}) is dominant prior to annealing.

The position of the “1640” band is higher than the graphitic mode at 1580 cm^{-1} (G-peak) [3]. The increase of the G-peak position to $1630\text{--}1640 \text{ cm}^{-1}$ for sp^2 dimers in ion-implanted diamond [12] with sp^3 content, is due to the change of sp^2 configuration from rings to olefinic groups, with their higher vibrational frequencies lying above the band limit of graphite [3]. Results from a series of implantation and annealing experiments [13] suggest that an irradiation-induced peak at $1630\text{--}1640 \text{ cm}^{-1}$ may be indicative of interstitials forming a dumbbell-type defect, which consists of an isolated double bonded carbon pair in a carbon site. Meanwhile, in line with a more recent *ab initio* density-functional-theory study [6] and the later investigations [22] rules out such an assignment as no Raman active modes are found in that spectral region.

Information obtained in present work on the spectral position, dependence on the level of radiation damage and temperature stability of the six peaks forming the “1640” band will be used in further works on modeling the structure of radiation defects in diamonds.

S. Praver et al. [23] suggested the common origin of the “1640” band in the detonation nanodiamond and radiation-damaged diamond and assigned this band to dumbbell defect which consists of a $\langle 100 \rangle$ split-interstitial.

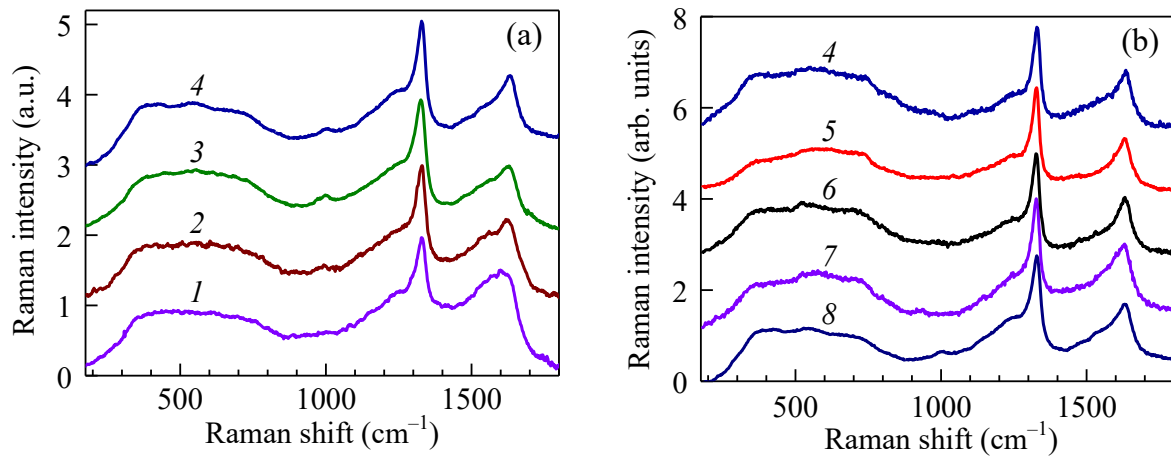


Figure 4. (a) Raman spectra of DND powder annealed in air at temperatures (°C): (1) 200, (2) 300, (3) 350 and (4) 450 for 0.5 hours. (b) Raman spectra of DND powder annealed in vacuum at temperatures (°C) 450 (4), 900 (5), 1000 (6), 1100 (7) and 1200 (8), followed by annealing in air at 450 °C. For clarity, the spectra are shifted vertically. Spectra were recorded at 25 °C with excitation at $\lambda = 488$ nm.

However, our experiments do not support this suggestion. While in fast neutron-irradiated and MeV-ion-implanted diamonds, with a decrease in the radiation damage level, the “1640” band splits into several components and almost completely disappears at temperatures above 1000 °C, in DND its behavior is significantly different. Vacuum heating at temperatures up to 1200 °C with subsequent annealing at 450 °C in air to remove the sp^2 -carbon layer forming on the DND surface during the heating does not lead to noticeable changes in the “1640” band relative to other components of the Raman spectrum (figure 4). The observed invariance of the “1640” band shape in DND after high-temperature heating in vacuum, at which graphitization of the crystallite surface occurs, allows us to assume that this band is most likely associated with bulk defects. This agrees well with weak dependence of this band on chemical treatment or in-air oxidation of DND [7, 24]. Apparently, this band is associated with thermostable defects in the volume of DND.

4. Conclusion

We have shown that, “1640” Raman band in radiation-damaged diamonds consists of at least six peaks, the intensity of which varies with the radiation damage level. Annealing of fast neutron irradiated diamonds at temperatures above 1000 °C was found to almost completely suppress the intensity of this band in Raman spectra. It is shown that annealing at temperatures up to 1200 °C has little effect on the “1640” band in the Raman spectra of DND, which indicates the bulk character of defects responsible for this band. It is concluded that “1640” band related defects in DND are of a different nature than the centers in radiation-damaged diamonds, which are responsible for the group of peaks in the spectral range near 1640 cm^{-1} .

5. Acknowledgments

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6. References

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