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MULTIBAND RESONANT RAMAN LIGHT SCATTERING IN DIAMOND WITH NITROGEN VACANCY CENTERS

We report results of polarized Raman scattering and photoluminescence studies of nitrogen-doped diamond. Experimental data demonstrates observation of an anomalous increase in the intensity of the inelastic light scattering by optical phonons and photoluminescence at room temperature by both zero-phonon lines: for the neutral nitrogen NV⁰ center at 575.468 nm and for the other negatively-charged nitrogen NV⁻ center 637.874 nm as well as for their vibronic phonon side bands correspondingly distributed in a wide spectral range. The data enables observation of the strong in-coming resonance for nitrogen NV⁰ and out-going resonance for nitrogen NV⁻ centers.

Keywords: multiband resonant Raman light scattering by optical phonons, zero-phonon lines, in-coming resonance for NV⁰ centers, out-going resonances for NV⁻ centers.

Inelastic or combinational process, also known as Raman scattering (RS), has, since its independent discovery in 1928 [1, 2], been an important instrument in physical sciences having capability to probe elementary excitations in condensed solid-state and soft materials in both bulk and nanoscale forms.

Quantum mechanically the scattering process is described by the transition of incident photons from ground state with excitation of a set of intermediate electronic states, which generate elementary excitations by transition to final state and radiate the corresponding energy-shifted scattering photons. Consequently,

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the intermediate electronic excitations play a key role as quantum pathways, determining non-resonant and resonant scattering behavior as well as interference in the incident and scattered channels. In contrast to the usually studied two-band resonant enhancement of the inelastic light scattering intensity in semiconductors (see, for example ref. [3]), the influence of the multiband intermediate states and the resultant resonant enhancement of light scattering were first theoretically predicted and experimentally detected for the case of Mandelstam – Brillouin scattering of light by zone-center acoustic phonons on the example of ZnSe crystals [4, 5]. The developed multiband resonant inelastic light scattering theory has been demonstrated to take into account the deformation-potential interaction for the electron-phonon coupling by the intra- and inter-band transitions with the discrete and continuous exciton states, involving the conduction band and different valence bands of the heavy and light holes as well as the split-off bands. The multiband resonance enhancement of the scattering intensity was also detected in the RS process from the optical phonons [4, 5]. The developed theoretical and experimental approaches of the multiband RS [4, 5] were used by Cantarero et al. [6] to revise their previously published theoretical and experimental results for a number of the most commonly used compound semiconductors of the II–VI and III–V groups. Since then, the decisive role of the multiband resonant RS was successively demonstrated for many other semiconductor materials and low-dimensional structures, including quantum dot systems. Here we report results of a systematic study of the multiband RS from the zone-center (Γ -point of the Brillouin diamond zone) optical phonons and photoluminescence (PL) by electronic excitations in an ensemble of nitrogen-vacancy (NV) centers in diamond. Nitrogen is one of the important doping impurities in both natural and synthetically-grown diamonds. With the nitrogen doping of a wide band-gap (5.5 eV) semiconductor diamond crystal, the lattice distortion appears when the nitrogen atoms enter into the lattice and, owing to their larger sizes, generate a vacancy site in the nearest-neighbor position, with a deep level at ~ 1.7 eV below the conduction band. The vacancy site is identified as the nitrogen substitutional defect, namely, neutral NV^0 and negatively-charged NV^- centers. During the past few years, the NV^- center in dia-

mond, owing to the unique physical properties of a single electron spin such as long-lived electron and nuclear spin coherence (even at room temperature), is considered as a small quantum processor (see, for example ref. [7]). Due to capability for individual optical initialization, readout and information storage and secure quantum-state teleportation and communication, the NV-center diamond is one of the most attractive solid-state systems for a rather stable single-photon emitter for quantum photonic technologies in order to develop future applications in quantum information systems, ultra-low-power nano-opto-electronics, and nano-scale sensing. They are also promising as nano-scale sensing fluorescent labels for developing biosensors integrated with biomedical materials. Creation and operation of the structures and devices, integrateable into a photonic quantum network and operable at the fundamental limit of coherent light-matter interactions, require, in parallel, development of novel techniques for characterization of NV centers in crystalline diamond. Therefore, development of the approaches to enhance the efficiency of optical emission is important problem for the NV-center diamond technology. Our studies using developed methods of the high spectral spectroscopy show that the observed resonant RS spectra are strictly correlated with the high resolution PL spectra detected simultaneously on the same diamond sample. The first sample studied was nearly electronic-grade single-crystal diamond (Element Six Corporation) with $[N_s]^0 < 5$ ppb and $[B] < 1$ ppb, laser cut into a (100)-oriented $3.0 \times 3.0 \times 0.5$ mm³ plate. The surface roughness of the additionally polished faces was less than 30 nm. Other nitrogen-rich samples were produced by defect engineering of the NV centers in diamond with electron irradiation at $\sim 10^{18}$ e/cm², 200 kV voltages (bulk samples), as well as irradiated by electrons irradiation at $\sim 10^{18}$ e/cm², 200 kV voltages, and H₂⁺ or N⁺ ion implantation with fluencies in range $(1-10) \times 10^{14}$ ions/cm². Measurements of the RS and PL spectra at room temperature were carried out at different excitation laser light wavelengths (632.8, 532.1 and 400.5 nm).

Broadband RS and photoluminescence spectra of the electronic-grade single-crystal diamond sample are shown in Figs. 1 (a) and 1 (b) in case of the crossed polarizations of the incident and scattered light, having higher intensity. The RS by the Brillouin zone-center optical

phonon (R) near 1332 cm^{-1} with the Lorentz profile linewidth Γ_L and the zero-phonon line (ZPL) from the NV^0 and NV^- centers are correspondingly marked on the spectra. The spectra in Figs. 1 (a) and 2 (a) were obtained at room temperature using the excitation laser line with the wavelength $\lambda_i = 632.817\text{ nm}$ ($\hbar\omega_i = 1.96\text{ eV}$) and laser power of 20 mW , here the spectral resolution $\Gamma_G = 0.9\text{ cm}^{-1}$ recorded with a neon spectral lamp. In this case the incident laser energy $\hbar\omega_i$ matches the energy required for the electronic transitions for the ZPL of the NV^- center with $\hbar\omega_{\text{NV}^-} = 1.945\text{ eV}$. At the same time the spectra in Figs. 1 (b) and 2 (b) were obtained using the excitation laser line with the wavelength of $\lambda_i = 532.070\text{ nm}$ ($\hbar\omega_i = 2.33\text{ eV}$), laser power of 12 mW and $\Gamma_G = 1.6\text{ cm}^{-1}$. In this case the out-going scattered light energy ($\hbar\omega_i - \hbar\omega_{\text{ph}}$) = 2.1583 eV matches well the energy required for the electronic transitions for the ZPL of the NV^0 center with $\hbar\omega_{\text{NV}^0} = 2.156\text{ eV}$. The obtained results demonstrate that the PL and RS processes in this case are close to the resonance and exhibit enhanced emission. Highly efficient increase of the RS and visible PL intensities by the both ZPLs are demonstrated: for the neutral NV^0 center at $\sim 575.47\text{ nm}$ and for the other negatively-charged NV^- center at $\sim 637.87\text{ nm}$ as well as for their phonon side bands distributed in a wide spectral range. We note that in the case of our non-resonant excitation at $\lambda_i = 400.5\text{ nm}$ ($\hbar\omega_i = 3.095\text{ eV}$) (not shown here) the intensity of the corresponding RS was more than ~ 3 times smaller than those presented in Figs. 2 (a) and 2 (b).

Observation of unexpected two-band resonant optical emission from the nitrogen-doped diamond with the both neutral and negatively-charged NV centers also shows appearance of a good additional experimental model for the verification of the multiband resonance enhancement of the intensity of the secondary radiation. The same type of the optical spectral responses, detected on the other electron-irradiated as well as nitrogen-ion-implanted diamond samples, indicate that the detected features of the enhanced RS and PL are the most common characteristic specificities of the NV centers in diamond crystals. In conclusion, the two-band resonance Raman scattering, reflecting the change in the electron states via an in-coming resonance for NV^0 center and out-going resonances for NV^- center, can be sharply distinguished at room temperature while

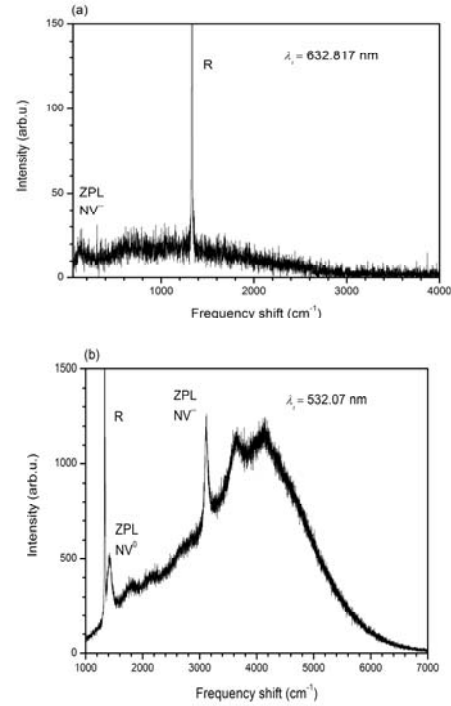


Fig. 1 (a) and (b). Broadband spectra of the (100)-oriented electronic-grade single-crystal diamond sample. The spectra were obtained with the excitation laser lines: a) $\lambda_i = 632.817\text{ nm}$ and b) $\lambda_i = 532.070\text{ nm}$

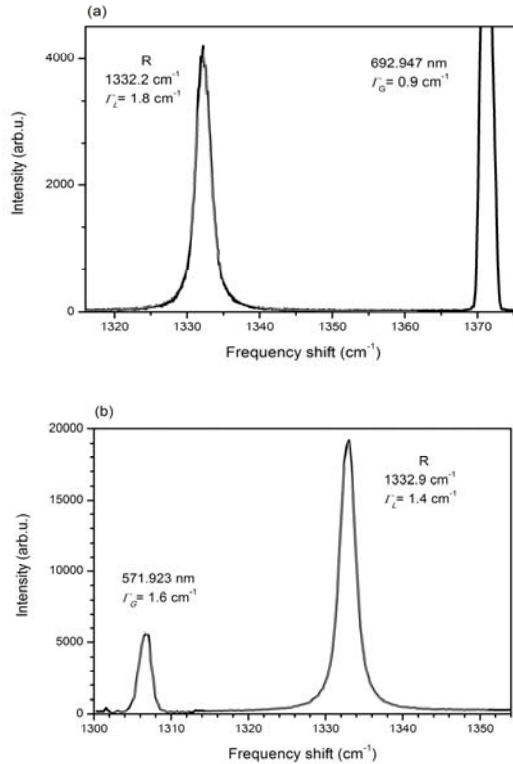


Fig. 2 (a) and (b). RS and PL spectra of the (100)-oriented electronic-grade single-crystal diamond sample, here with neon spectral lamp atomic lines, obtained under the same excitation laser lines: a) $\lambda_i = 632.817\text{ nm}$ and b) $\lambda_i = 532.070\text{ nm}$

in other materials the resonances are usually sufficiently broad and they cannot be easily distinguished.

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МНОГОЗОННОЕ РЕЗОНАНСНОЕ РАМАНОВСКОЕ РАССЕЯНИЕ СВЕТА В АЛМАЗЕ С АЗОТОЗАМЕЩЕННЫМИ ВАКАНСИОННЫМИ ЦЕНТРАМИ

Сообщается о результатах исследований поляризованного рамановского рассеяния света и фотолюминесценции в алмазе, легированном азотом. Экспериментальные данные демонстрируют наблюдение аномального увеличением интенсивности неупругого рассеяния света

оптическими фононами и фотолюминесценции при комнатной температуре при резонансном возбуждении с обеими бесфононными линиями азото-замещенными вакансионными (NV) центрами: нейтрального центра NV^0 при 575,468 нм и отрицательно заряженного центра NV^- при 637,874 нм, а также для их характерных электронно-колебательных комплексов, соответственно распределенных в широком спектральном диапазоне. Данные позволяют наблюдать сильный резонанс во входном канале для NV^0 центра и выходном канале для NV^- центра.

Ключевые слова: многозонное резонансное рамановское рассеяние света оптическими фононами, бесфононные линии, резонанс во входном канале для NV^0 центра и выходном канале для NV^- центра.

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