

CVD-Diamond ^{13}C : A New SRS-Active Crystal

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Abstract—Stimulated Raman scattering has been discovered in a monoisotopic ^{13}C diamond single crystal grown by chemical vapor deposition. The first results of the experimental study of impulsive $\chi^{(3)}$ -nonlinear lasing under femtosecond IR pumping are presented.

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1. Numerous studies of the isotopic effect in diamond have been aimed at revealing its influence on the fundamental physical properties of diamond and at finding new fields of application of modified diamonds (see, for example, [1–4] and review [5]). Particular attention was paid to the change in the natural isotopic composition of *nat*C diamond (98.93% for ^{12}C and 1.07% for ^{13}C) by enriching it with isotope ^{12}C to 99.93%. Measurements showed that the thermal conductivity of these modified ^{12}C diamonds increased by almost half (31.7 W/cmK [6] and 33.2 W/cmK [7]) in comparison with the thermal conductivity of *nat*C diamond. This fact motivated, in particular, our recent experiments on the growth of ^{12}C diamond single crystals by chemical vapor deposition (CVD) and on generation of stimulated Raman scattering (SRS) in these crystals [6]. It is beyond question that the combination of high thermal conductivity with the SRS effect in ^{12}C diamond crystals should give a new impetus to the improvement and search for new applications of diamond SRS lasers (laser converters). This study is a continuation of our previous investigations of the iso-

topic effect in diamond [6]. Here, we report the discovery of the SRS effect in another modification of single-crystal diamond (enriched in the ^{13}C isotope to 99.96%) and present the first results of studying this effect.

2. A ^{13}C diamond single crystal was grown by the CVD method (deposition in microwave plasma (2.45 GHz) in a methane–hydrogen ($^{13}\text{CH}_4/\text{H}_2$) mixture on an ARDIS-100 system) [8]. Homoepitaxial growth was performed using methane enriched in ^{13}C isotope to 99.96% ($^{13}\text{CH}_4$) onto an oriented (100) substrate prepared from a commercial high pressure/high temperature (HPHT) diamond crystal of the Ib type. The following CVD parameters were used: $^{13}\text{CH}_4$ flow rate 50 mL min⁻¹, H₂ flow rate 450 mL min⁻¹, chamber pressure 130 Torr, microwave power ~3350 W, substrate temperature ~950°C, and growth rate 31 μm h⁻¹. At various stages of growth, the single-crystal layer of ^{13}C diamond was analyzed by spontaneous Raman scattering using a LabRam HR840 spectrometer. In these measurements, excitation at a wavelength of 0.473 μm was performed by a cw semiconductor laser beam focused into a spot of about 1 μm in diameter on the surface of the growing ^{13}C diamond layer. With an increase in the thickness of the ^{13}C diamond layer, the intensity of its Raman line at 1281 cm⁻¹ increased with respect to the Raman line of the *nat*C diamond substrate at 1332.3 cm⁻¹ (see Fig. 1). The diamond sample for the SRS experiment was a “sandwich” 4.6 × 4.6 mm² in size with a single-crystal ^{13}C diamond layer of thickness ~95 μm on an HPHT *nat*C diamond substrate 570 μm thick. Its large faces were

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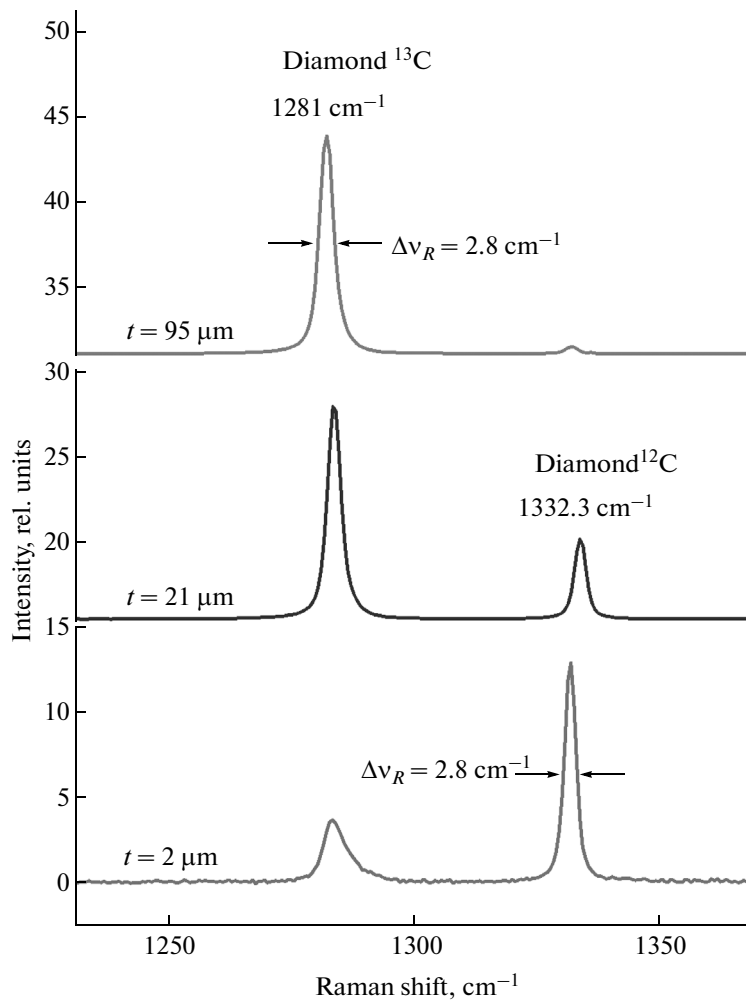


Fig. 1. SRS spectra of samples of two-layer synthetic $^{13}\text{C}/^{nat}\text{C}$ diamond with epitaxially grown (in several stages) layers of isotopically enriched ^{13}C diamond (only three layers with their thicknesses t are shown) on a 0.57-mm-thick HPHT ^{nat}C diamond substrate. Raman spectra of diamond samples were recorded in the confocal scheme upon excitation by a semiconductor laser with a wavelength of 473 nm from the side of the ^{13}C diamond layer. The amplitudes of Raman peaks with maximum intensity in each spectrum are normalized; the spectra are shifted along the vertical axis for convenience.

oriented in the $\{100\}$ crystallographic planes, the other faces were $\{110\}$ planes, and the long side had the $\langle 110 \rangle$ direction. Some physical properties of ^{13}C and ^{nat}C diamonds are compared in the Table 1.

3. The mode of $\chi^{(3)}$ nonlinear impulsive lasing of ^{13}C diamond was implemented using a laser spectroscopic system with a femtosecond single-wave Yb pumping ($\lambda_p \sim 1.0645 \mu\text{m}$, pulse width $\tau_p \sim 500$ fs at a frequency of 80 MHz) and the method for detecting impulsive Stokes SRS signals, which were described in detail in [12]. The scheme of cavity-free laser excitation, which was traditionally used by us in the experiments on SRS spectroscopy of crystals (see, e.g., [13]), made it possible to excite a two-layer $^{13}\text{C}/^{nat}\text{C}$ diamond sample by a collinear pump beam

($\varnothing \sim 100 \mu\text{m}$, intensity $10^{11} \text{ W cm}^{-2}$) without optical damage of its surface. The IR Stokes spectrum of impulsive SRS was recorded using a diffraction monochromator (300 lines/mm) with a linear InGaAs-CMOS detector (G9204-512D, Hamamatsu). One of the recorded spectra is shown in Fig. 2, which convincingly exhibits the difference in the energies of SRS-promoting phonon modes F_{2g} for monoisotopic diamond ^{13}C (99.96%) ($\omega_{\text{SRS}} \sim 1281 \text{ cm}^{-1}$) and ^{nat}C diamond with a natural content of carbon isotopes ^{12}C (98.93%) and ^{13}C (1.07%) ($\omega_{\text{SRS}} \sim 1332.3 \text{ cm}^{-1}$).

4. The synthesis conditions were found, and monoisotopic single-crystal ^{13}C diamond layers up to 95 μm thick were grown by CVD. Their SRS in the

Some physical properties of diamonds isotopically enriched in carbon ^{13}C and diamonds of natural isotopic composition (^{nat}C) (data at room temperature)

Property	^{13}C	^{nat}C
^{13}C isotope content, %	~99.96	1.07
Space group	$O_h^7 - Fm\bar{3}d$ (No. 227)	
Unit-cell parameter, a_0 , Å [9]	3.56658 [9]	3.56712 [9]
Atomic density, 10^{23} cm^{-3} [10]	1.7632*	1.7625
Elastic moduli, $10^{13} \text{ din cm}^{-2}$ [5]	$c_{11} = 10.833(5)**$, $c_{12} = 1.248(14)$, $c_{44} = 5.776(7)$	$c_{11} = 10.804(5)$, $c_{12} = 1.270(10)$, $c_{44} = 5.766(5)$
Thermal conductivity κ , $\text{W cm}^{-1} \text{ K}^{-1}$	22 [1]***	22 [11]
Energy of promoting phonon mode ω_{SRS} , cm^{-1}	~1281	~1332.3
Phonon relaxation time T_2 , ps****	~3.8	~3.8

* As was stated in [10], this is the highest atomic density among known solids.

** According to the data of [13], $c_{11} = 10.833(5) \times 10^{13} \text{ din cm}^{-2}$.

*** Data for an HPHT sample with a ^{13}C content of about 99%.

**** $T_2 = \frac{1}{\pi \Delta \nu_R}$, where $\Delta \nu_R$ is the SRS linewidth both for ^{13}C diamond and ^{nat}C diamond (see Fig. 1).

mode of impulsive Stokes generation was excited for the first time using femtosecond laser 1- μm Yb pumping. Thus, diamond ^{13}C became the third SRS-active

diamond material (to form a triad of SRS diamonds: ^{nat}C , ^{12}C , and ^{13}C) with a unique scientific and application potential.

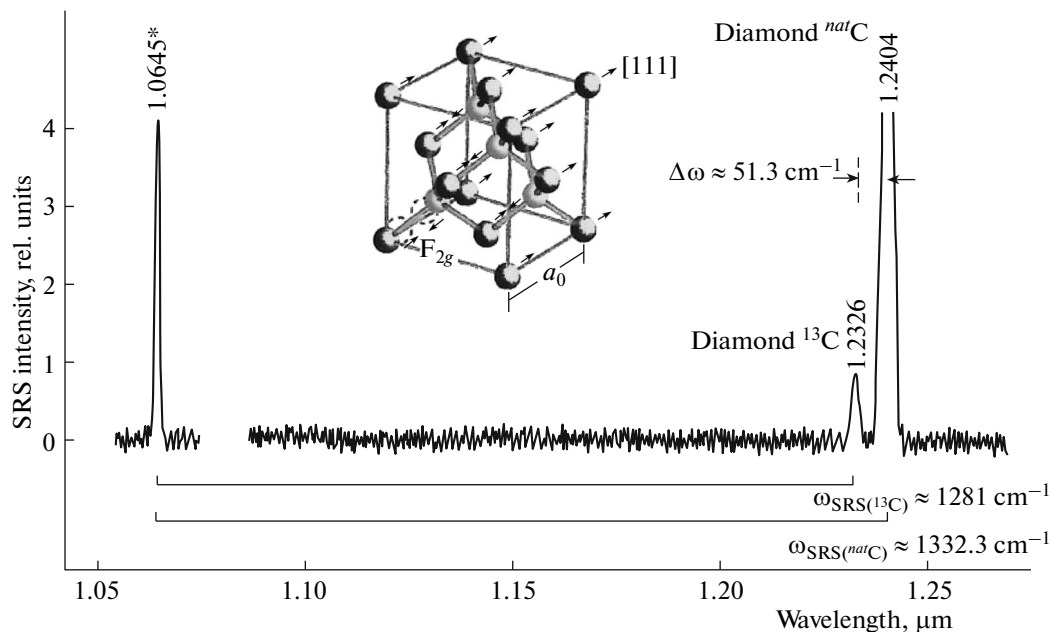


Fig. 2. Impulsive SRS spectra of ^{13}C and ^{nat}C diamonds (the pump line is indicated by an asterisk). Horizontal parentheses show the energies of SRS promoting phonon modes: $\omega_{\text{SRS}(^{13}\text{C})} \approx 1281 \text{ cm}^{-1}$ for the monoisotopic ^{13}C diamond and $\omega_{\text{SRS}(^{nat}\text{C})} \approx 1332.3 \text{ cm}^{-1}$ for the diamond with natural content of ^{12}C and ^{13}C carbon isotopes. The inset shows tetrahedral bonds of carbon atoms in diamond and clarifies the nature of its triply degenerated F_{2g} optical vibrations, which are strictly oriented (along the [111] crystallographic axis) vibrations of carbon one against another of two of its interpenetrating structural lattices (arbitrarily shown by different color hues and empty circles) (see, for example, [5]).

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