Solid State Communications 276 (2018) 33–36

Contents lists available at ScienceDirect

Solid State Communications

journal homepage: www.elsevier.com/locate/ssc

Communication

Raman scattering in boron doped nanocrystalline diamond films: Manifestation of Fano interference and phonon confinement effect

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ARTICLE INFO

Communicated by R. Merlin

Keywords:
Raman scattering
Diamond
Fano interference

ABSTRACT

Heavily boron doped nanocrystalline diamond films grown on glass substrates by the method of plasma-chemical deposition, were investigated using Raman spectroscopy. Analysis of the spectra showed both the phonon confinement effect in nanocrystalline grains and Fano interference effect due to the contribution of electron Raman scattering in heavily doped p-type diamond films. The increase of boron concentration led to decrease of the size of crystalline diamond grains. The films are semitransparent and have good conductivity, so that it can be used as transparent electrodes in giant-scale electronics and optoelectronics.

1. Introduction

Films of p-type diamond attract the interest of researchers due to many reasons. From some threshold concentration of boron, the diamond is low-temperature superconductor [1–3]. Since the diamond is a wide-gap semiconductor, it is promising for use in microelectronic devices operating at high temperatures. Recently, due to the progress of plasma enhanced chemical vapor deposition (PECVD) methods, heavily doped diamond films became a promising material as transparent electrodes for solar cells and other optoelectronic applications [4,5]. It is known that in heavily doped p-type semiconductors with diamond-type lattice the electronic transitions appear in Raman scattering. Due to the diamond valence band structure, the inelastic scattering of photons is possible due to transitions between the heavy-hole valley and the light-hole-valley – electronic Raman scattering. These quasi-continuous transitions interact (interfere) with discrete transitions by optical phonons, this effect is known as Fano interference [6]. Earlier it was observed for monocrystalline silicon [7,8], for monocrystalline diamond [9,10], and for polycrystalline diamond films [11–16]. This work is an attempt to investigate Fano interference in heavily boron doped semitransparent nanocrystalline diamond films deposited by PECVD.

2. Experimental details

The set of nanocrystalline diamond films was grown using PECVD on glass substrates from methane (CH_4) diluted by hydrogen: without doping gases and with the addition of trimethylborane ($B(CH_3)_3$). The ratio B/C was varied from 0 to 4000 particles per million (ppm). The parameters of the films are summarized in Table. The spectrometer T64000 (Horiba Jobin Yvon) with micro-Raman setup was used. The Ar^+ (514.5 nm), HeCd (325 nm) and solid-state (660 nm) lasers were used for excitation of Raman scattering. The spectral resolution was better than 2 cm^{-1}. The radiation power reaching the sample was ~1 mW, laser spot was about 10 μm, which is insufficient to cause significant local heating [17]. The back-scattering geometry was used; the polarization of scattered light was not analyzed.

3. Results and discussion

Fig. 1 shows experimental Raman spectra of a monocrystalline diamond, a glass substrate, and all studied samples 1–5 (see Table 1) measured with an excitation wavelength of 514.5 nm. For convenience, the vertical scale is on a logarithmic scale, and the signal from a mono-

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https://doi.org/10.1016/j.ssc.2018.04.004
Received 8 February 2018; Received in revised form 24 March 2018; Accepted 3 April 2018
Available online 6 April 2018

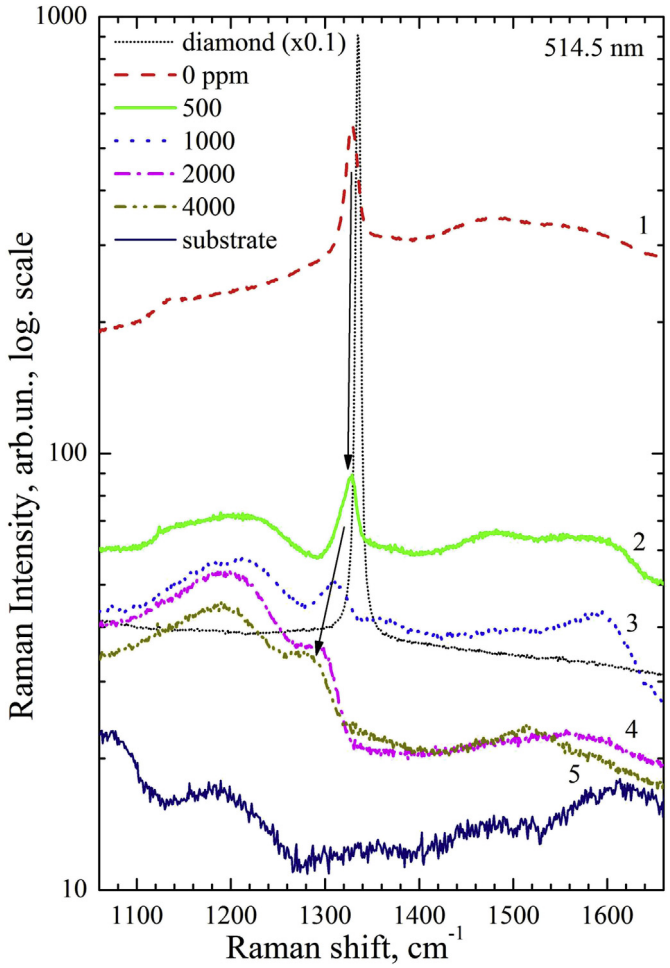

Fig. 1. Raman spectra of mono-crystalline diamond, glass substrate and diamond films 1–5 (see Table).

Table 1
Specification of samples.

Number	Boron ppm	Thickness nm	Conductivity $(Ohm{\cdot}cm)^{-1}$	Γ cm^{-1}	q abs. value	$\Delta\omega$ cm^{-1}
1	0	900	0.066	7	>50	5
2	500	350	25	10	2.5	6
3	1000	350	41	25	1.6	17
4	2000	300	63	27	1.5	22
5	4000	200	139	33	1.4	32

crystalline diamond is divided by one order of magnitude. In the undoped film (sample 1), a shift and broadening of the peak are observed, this is due to optical phonons confinement effects. Estimates of possible residual stress influence on Raman shift were carried out. The thermal expansion coefficients of diamond and JGS1 glass (used as substrate) are close, difference is about $0.5{\cdot}10^{-6}\,K^{-1}$. Even if one eliminates the effects of relaxation of mechanical stresses, the maximum residual strain (in plain) do not exceed $2.5{\cdot}10^{-4}$. According to anharmonicity coefficients for phonons in diamond, the strain induced shift is not exceeding $0.5\,cm^{-1}$. So, the shift is described in the framework of the phonon confinement model (PCM) [18–23]. It is well known that for mono-crystalline diamond longitudinal and transverse optical phonons are degenerated in the center of Brillouin zone and have frequency $1332.5\,cm^{-1}$ [22,23]. Confinement of optical phonons leads to decrease of frequency and to increase the width of the optical phonon peaks in Raman spectrum [18–23]. The frequency shift of optical phonon peak of the undoped diamond film compared to mono-crystalline diamond is $5\,cm^{-1}$. According to our PCM estimations, the average optic phonon correlation length should be ~6 nm. The optic phonon correlation length is defined by nano-crystalline grain size (for the case of ideal crystalline grain) or defect concentration inside the grains. It is known that defects can scatter and damping vibration modes. For doped films, the optical phonon peak is shifted (it is shown by arrows) and broadened. The analysis of this effect is described below. Beside this peak, a broad feature arises at $\sim1200\,cm^{-1}$ associated with the maximum density of vibrational states in a disordered diamond [14]. Note, that this peak shall not be confused the glass substrate signal due to stretching vibrations of Si—O bonds. The signal from the substrate is about an order of magnitude smaller, and it has a different shape. Boron incorporation disorders the crystalline structure of diamond. Both for undoped and doped films one can see broad features at $\sim1600\,cm^{-1}$ which is associated with G-mode in sp^2 hybridized carbon. Let us turn to the influence of doping and electronic Raman scattering.

As previously reported for silicon [7,8] and diamond [13,14] electronic Raman scattering manifest the stronger the longer the wavelength of the exciting light. Fig. 2 shows the spectra of sample 2 with red, green and ultraviolet (UV) excitations. It is known that the shape of the Raman peak in the case of Fano interference can be described using the Fano contour:

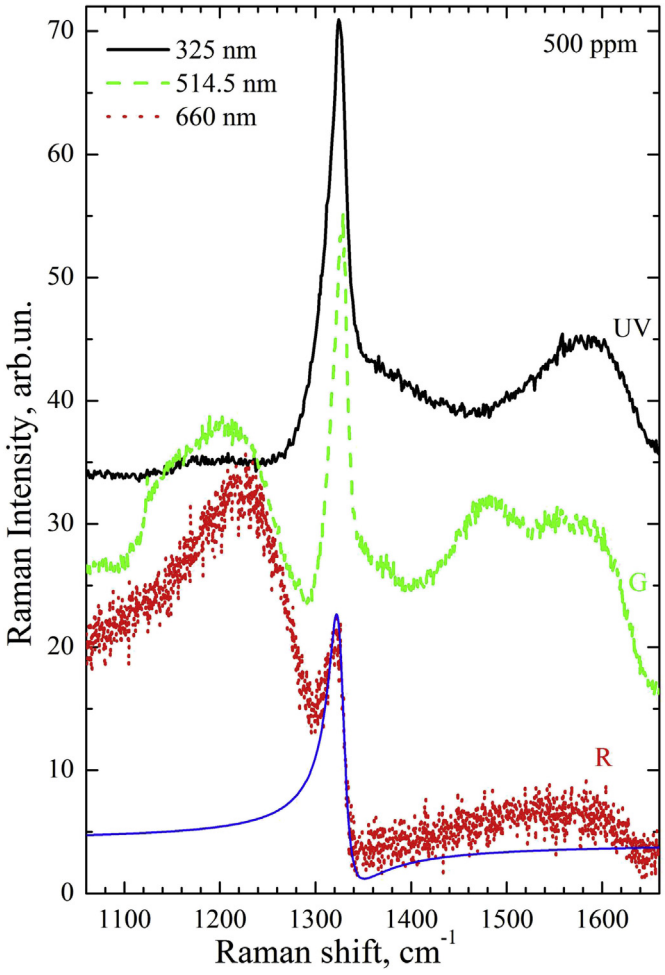

Fig. 2. Raman spectra of the doped diamond film (sample 2) with UV (325 nm), green (514.5 nm), and red (660 nm) excitations. Thin solid (blue) line is approximation of spectrum of sample 2 using Fano contour. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)