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Raman scattering in boron-doped single-crystal diamond used to fabricate Schottky diode detectors

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ABSTRACT

Thanks to its exceptional physical and electronic properties, diamond is an attractive material for electronic devices working at high temperature and in harsh chemical environment. Its use as a semiconducting material for electronics is related to the possibility of doping it in order to control its conductivity. Semiconducting p-type diamond films can be grown when boron is introduced into the film. In this work, boron-doped (B-doped) homoepitaxial diamond films are grown by Microwave Plasma Enhanced Chemical Vapor Deposition. Raman and electrical characterizations are carried out on the films as a function of boron doping level. As the boron content increases, we observe systematic modifications in the Raman spectra of single-crystal diamonds. A significant change in the lineshape of the first-order Raman peak, as well as a wide and structured signal at lower wavenumbers, appears simultaneously in samples grown with higher boron content. A single crystal diamond Schottky diode based on a metal/intrinsic/p-type diamond junction is analysed.

1.Introduction

Diamond is an ideal material for the fabrication of compact solid-state ionizing radiation detectors [1]. Visible-blindness, chemical inertness, large heat conductance, high charge mobility and low dark current are the properties that make diamond particularly interesting for the realization of photodetectors [2,3]. In addition, due to its low atomic number, diamond is a tissue equivalent material, and thus it can be used to realize dosimeters for radiotherapy [4,5]. Natural diamond, mainly because of lack of standardisation, high cost and inclusion of impurities, is not a feasible proposal as an engineering material. Homoepitaxial growth by Chemical Vapour Deposition (CVD) has enabled the synthesis of high-quality single crystal diamond on low-cost high-pressure high-temperature (HPHT) diamond substrates. Semiconducting p-type diamond films can be grown when boron is introduced into the film. Heavy boron incorporation induces metallic conduction in diamond. Boron-doped (B-doped) diamond has attracted considerable attention for its application in the fabrication process of novel diamond based multilayered Schottky diode detectors for X-ray and ultraviolet radiation [1], alpha particles, thermal and fast neutrons [6] and radiation therapy dosimetry [7]. In this paper, a series of B-doped homoepitaxial diamond films have been analyzed by Raman spectroscopy. The measurements have been performed at room temperature on films with different boron contents. The conductivity of the samples has been also measured to evaluate the activation energy as a function of boron content. A new class of detectors with a layered structure based on CVD diamond has been investigated.

2. Experimental

The B-doped homoepitaxial diamond films used in this study have been grown at the University of Rome

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"Tor Vergata" by Microwave Plasma Enhanced Chemical Vapor Deposition (MWPECVD) on commercial low cost synthetic type Ib (100) HPHT single crystal diamond substrates, $4\times4\times0.5$ mm^3 in volume. The samples are coded as A,–D in order of increasing boron content in the grown layers. The four films have been grown at different concentrations of a 100 ppm diborane–hydrogen gas mix added to a methane–hydrogen source gas. The grown samples have been electrically characterized by means of electrical resistance vs. temperature measurements. The measurements have been performed by placing in turn the B-doped diamond samples into a temperature controlled furnace and the resistance vs. temperature data have been recorded during spontaneous cooling to room temperature, after a maximum temperature of about 500 °C has been reached. A Keithley 2000 multimeter has been used for a 2-wire resistance measurement and a Keithley 2001 multimeter has been connected to a type-S platinum/rhodium thermocouple for temperature measurement.

The Raman scattering measurements have been carried out at room temperature with an Instrument S.A. Ramanor U1000 double monochromator, equipped with a microscope Olympus BX40 for micro-Raman sampling and with an electrically cooled Hamamatsu R943-02 photomultiplier for photon-counting detection or with a CCD detector. The 514.5 nm (2.41 eV) line of an Ar^+ ion laser (Coherent Innova 70) has been used to excite Raman scattering. Using a X100 objective, the laser beam has been focused to a diameter of approximately 1 μm. A depth resolution of approximately 4 μm has been obtained with a confocal aperture of 200 μm. The resolution of the double monochromator is approximately 0.15 cm^{-1}. After normalisation, all the spectra collected are analysed using a commercially available spectroscopic analysis software package. Lorentzian bands, superimposed to a constant background, are used to fit the spectra. The wavenumber position, width (FWHM) and intensity of the bands are chosen by a least-square best-fit method.

A single crystal diamond Schottky diode detector based on a metal/intrinsic/p-type diamond junction has been produced. The multilayered structure is obtained by a well-established two-step Chemical Vapor Deposition process. A heavily boron doped CVD diamond film, with a boron concentration of approximately 0.5×10^{20} cm^{-3}, is deposited, at first, on a low cost commercial synthetic single crystal HPHT diamond substrate. A nominally intrinsic diamond film, which acts as a sensing layer of the device, is then homoepitaxially deposited on the doped one. This second step is performed in a completely separate CVD reactor in order to avoid unintentional boron contamination of the intrinsic layer. A circular aluminum (Al) electrode, about 3 mm in diameter, is thermally evaporated on the diamond surface, forming a rectifying Schottky junction with the intrinsic diamond. An annealed silver (Ag) paint is utilized in order to provide an ohmic contact to the boron doped layer. A sketch of the multilayered device structure and of the electrical connections is shown in Fig. 1. The highly conductive boron doped diamond film acts as backing contact. The sensing volume of the detector is the depletion region that from the Schottky metal–diamond interface extends into the intrinsic diamond layer [1]. Such a sandwich geometry has been adopted to avoid any contribution to the response of the high quality, detector grade intrinsic CVD sensing layer coming from the HPHT diamond substrate, with no need to mechanically remove it.

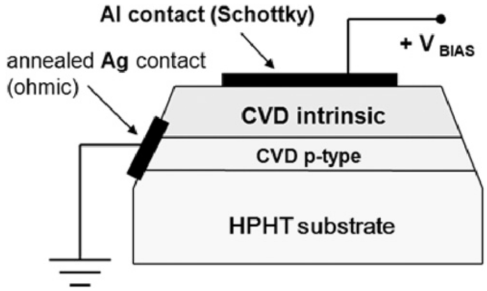

Fig. 1. Scheme of the typical device configuration of synthetic single crystal diamond detectors fabricated at the University of Rome "Tor Vergata".

3. Results and discussion

3.1. Electrical characterization of B-doped diamond films

Boron doping makes the diamond films p-type semiconductors [8]. At low boron concentration ($\sim10^{18}$ cm^{-3}) an electrical conductivity on the order of $10^{-2}\,\Omega^{-1}$ cm^{-1} has been measured at room temperature in homoepitaxial diamond films [9,10]. The acceptor level lies rather deep into the band-gap with an activation energy of about 0.37 eV from the valence band [8–10]. When the boron concentration exceeds the value of 3×10^{20} cm^{-3}, an impurity band is formed and a metallic-like conductivity is observed [11,12]. The change in conductivity of diamond film from p-type semiconductor to metallic diamond is highlighted by the decrease towards zero of the boron activation energy [9,10].

In order to evaluate the activation energy, the conductivity of the samples has been measured between room temperature and 700 K(Fig. 2). Activation energies, reported in Table 1, have been obtained from the best fit of the Arrhenius plot of the measured data in the temperature range 500–700 K. From the activation energy values, the acceptor densities N_a have been roughly estimated by the model developed by Pearson and Bardeen [13] for silicon:

$E_a = E_0 - \alpha N_a^{1/3}$ where E_0 is the ionization energy of an isolated dopant and α is a material dependent constant, whose value for diamond is about 6.7×10^{-8} eV cm. From this model, for activation energies ranging between 0.23 and 0.04 eV, boron concentrations from $\sim10^{18}$ to $\sim10^{20}$ cm^{-3} are evaluated. Such values are approximate, due to the low accuracy in the activation energy measurements and the simplified model used for their determination. The decrease of the values of the activation energy with increasing boron content highlights the gradual change of conductivity of the samples from p-type semiconductor to metallic diamond.

3.2. Raman characterization of B-doped diamond films

Raman spectroscopy is a nondestructive and powerful technique to investigate the structure and the properties