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Spectroscopic investigation of homoepitaxial CVD diamond for detection applications

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Abstract

Three-layer structures consisting of intrinsic/B-doped homoepitaxial CVD diamond grown onto commercial HPHT Ib substrates have been studied by means of Raman spectroscopy and photoluminescence (PL). The intrinsic layers have been deposited, at fixed methane to hydrogen ratio (1%), by systematically changing the substrate temperature (620–820 °C). Raman measurements point out the excellent crystalline quality and phase purity of the samples. Moreover, flat PL spectra in a wide energy range (1.7 eV–2.7 eV) indicate also their great purity. As the free-exciton recombination can be used to further probe the quality of synthetic diamond, measurements of free-exciton emission at room temperature have been also performed. The excitation was produced by a 5 ns pulsed tunable laser irradiation. The results have been compared with the detection characteristics of simple alpha-particle detector prototypes based on the analyzed samples. A clear correlation between excitonic emission and detector sensitivity is demonstrated. On the basis of these results, low methane concentrations (approx. 1% CH_4/H_2) in the deposition gas mixture and intermediate substrate temperatures (approx. 720 °C–770 °C) have been identified as the best working conditions of our growth reactor.

Keywords: Chemical Vapor Deposition; Synthetic diamond; Excitons; Detectors

1. Introduction

Great effort is currently devoted all over the world to the optimization of the deposition process of high-quality homoepitaxial CVD diamond. In fact, encouraging results have been obtained on UV and particle detectors [1–8] based on homoepitaxial CVD diamond samples. However, such results [3,5,9,10] suggest that a further optimization of the material quality is necessary, in order to obtain diamond-based detectors really competing with Si-based standard devices. In this regard, characterization techniques such as Raman spectroscopy and photoluminescence, already successfully used to optimize the crystalline quality and detection properties of polycrystalline diamond films [11–13], may provide precious hints also for the optimization of the deposition process of detector-grade homoepitaxial diamond.

Luminescence in the UV range (5.27 eV) due to the excitonic recombination near the band edge (edge emission) has been recognized as a very sensitive tool for the study of the crystalline perfection of homoepitaxial CVD diamond. In fact, in early studies edge emission was observed only at low temperatures in natural and single-particle synthetic diamond [14,15]. Only after the great improvement of the deposition technique of high-quality homoepitaxial diamond, in 1998 Watanabe et al. [16] succeeded in observing strong excitonic recombination radiation at room temperature in CL spectra from homoepitaxial CVD diamond films. In a recent work [17], the study of the room-temperature edge emission of homoepitaxial CVD diamond samples deposited at increasing methane to hydrogen ratio (from 1% to 7%) has

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Table 1
Growth parameters of the samples studied in this work

Sample	Substrate temperature (°C)	Thickness (μm)	Growth rate (μm/h)
A	620	18	0.8
B	670	22	1
C	720	17	1
D	720	18	1
E	770	18	1
F	820	29	1.7

shown that the increase of the methane concentration in the growth mixture lowers the excitonic lifetime. The decay of the excitonic lifetime at increasing methane concentration suggests that the quality of homoepitaxial CVD diamond samples, even if high, may be at a non optimal level when methane concentration is increased in the deposition gas mixture. Thus, we believe that a further investigation of the crystalline perfection by systematically changing the deposition conditions is necessary. To this aim, in this work we report on the edge emission of homoepitaxial CVD diamond samples grown at different substrate temperatures (620–820 °C) and low methane to hydrogen ratio (1% CH_4/H_2), comparing these results with the alpha-particle detection properties of devices realized utilizing the same samples. On the basis of this comparison, a clear correlation between excitonic emission and detection properties has been found. Moreover, the best working conditions of our deposition reactor have been also deduced.

2. Experimental

The samples studied in this work consist in three-layer structures where the upper intrinsic layer has been deposited by CVD using a 1% CH_4/H_2 gas mixture. The substrate temperature has been systematically changed from 620 °C to 820 °C (step 50 °C). The intrinsic layer is separated from the commercial type-Ib diamond substrate (Sumitomo) by a B-doped homoepitaxial layer, 15 μm thick, previously deposited in a different growth reactor. Details of the deposition are indicated in Table 1. It is worth noting that the substrate temperatures indicated are measured by means of an optical pyrometer which has not been calibrated for measurements of absolute temperatures. However, a difference not greater than 50 °C between the measured temperature and the real temperature is expected. Notwithstanding this, the relative differences between the substrate temperatures of the samples are correctly considered.

Alpha-particle detectors have been realized by depositing Al contacts onto the intrinsic layer, whereas the B-doped layer has been used as the backing contact [18]. This configuration has been designed to avoid any contribution to the response of the device coming from the Ib substrate, whose mechanic removal is hard to obtain without damaging the homoepitaxial layer deposited on it.

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. The 514.5 nm (2.41 eV) and 457.9 nm (2.71 eV) lines of an Ar^+ ion laser (Coherent Innova 70) have been used to excite Raman scattering. Using a X100 objective, the laser beam was focused to a diameter of approx. 1 μm. A depth resolution of approx. 4 μm was obtained with a confocal aperture of 200 μm. To minimize the slit-induced line broadening of the diamond Raman peak, a very narrow slit aperture (50 μm) was used. The resolution of the double monochromator is approximately 0.15 cm^{-1}. Micro-photoluminescence (PL) measurements were carried out at room temperature by using the same experimental set-up used for micro-Raman spectroscopy.

Time-resolved photoluminescence has been carried out at room temperature by exciting the sample with 5 ns laser pulses at 215 nm wavelength produced by an optical parametric oscillator tunable laser (Opolette by Opotek). The photoluminescence signal is then focused at the entrance slit of a 25 cm focal length spectrograph with a 1200 lines/mm grating and detected by an intensified CCD with 2 ns time resolution. The lifetimes of the excitons in the samples have been calculated by means of standard fitting procedures applied to the time decay of the emission at 235 nm.

The detection properties were tested by using an ^{241}Am α particle source. The detectors were connected through an Ortec 142A charge preamplifier to a 2 μs shaping amplifier and then to a multichannel analyzer. In order to perform absolute measurement of the charge collection efficiency, the electronic chain was calibrated by using a 100% collection efficiency Si detector and the measured charge was related to the energy measured by diamond assuming 13.1 eV as the average energy for creating an electron-hole pair.

3. Results

In Fig. 1, typical Raman and photoluminescence spectra detected at room temperature on the homoepitaxial diamond

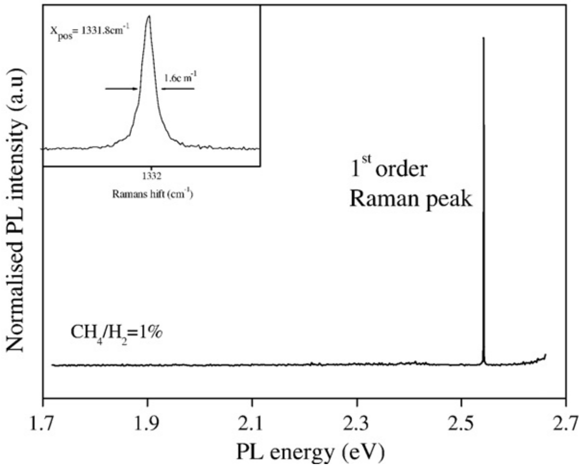

Fig. 1. Typical room-temperature photoluminescence spectrum detected on the homoepitaxial diamond samples studied in this work. Exciting wavelength λ=457.9 nm. In the inset, a typical Raman spectrum detected on the samples is shown. Exciting wavelength λ=514.5 nm.