

Atomic Structure and Temperature-dependent Photoluminescence of Si-doped Epitaxial Diamond Layer on Nitrogen-rich HPHT Single Crystal Diamond

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Summary:

A single crystal diamond was epitaxially overgrown by MWCVD in the presence of Si wafer pieces. Such a simple approach enables direct growth of Si-doped diamond films (containing SiV color centers) on the nitrogen-rich substrate (containing NV color centers). The sample was studied by means of its atomic structure and its correlation with the temperature- (5–500 K) and excitation wavelength-dependent (405, 488, 532 and 633 nm) photoluminescence properties. Combining and understanding the behavior of different color centers in a single diamond sample opens up new possibilities for various applications.

Keywords: diamond, MWCVD, color centers, Raman spectroscopy, TEM

Background, Motivation and Objective

Diamond, as one of the wide-bandgap materials, is characterized by outstanding properties (such as biocompatibility, chemical and radiation inertness, etc.) that can be further improved by light-emitting color centers in the visible or infrared regions of the light spectrum. Diamonds with sharp, intense, and well-recognizable emission peaks are of significant interest for bio-imaging [1] and integrated quantum photonics [2] applications. Combining different color centers, e.g. NV and SiV, in one diamond sample is an interesting approach that opens up new possibilities in these research fields.

Description of the New Method or System

A high-temperature high-pressure (HPHT) type Ib (100) single crystal diamond (SCD) substrate (E6 Technologies Ltd., UK) with a high nitrogen content ([N]: < 200 ppm), was overgrown in a microwave plasma chemical vapor deposition (MWCVD) system in the presence of clean silicon wafer pieces. The main advantage of this method is that it enables the direct growth of silicon-doped epitaxial diamond films containing silicon-vacancy (SiV) centres [3].

Another advance related to the state of research in this field, is the complex analysis of the color centers (NV and SiV, both present in the prepared sample), including excitation wavelength- and temperature-dependent Raman and photoluminescence spectra measured by different

excitation wavelengths (405, 488, 532 and 633 nm) in a wide temperature range of 5–500 K. In addition, the Raman and PL spectra were correlated with HRTEM, SAED, and EDS data.

Results

The epitaxially grown diamond layer (approximately 2 μm thick) is characterized by crystals with a size of 2–4 μm (Fig. 1a). TEM image (Fig. 1b) showed preferential diamond growth normal to the (111) crystallographic planes, resulting in a polycrystalline surface texture characterized by high surface roughness and significant thickness variation (1.8–2.6 μm).

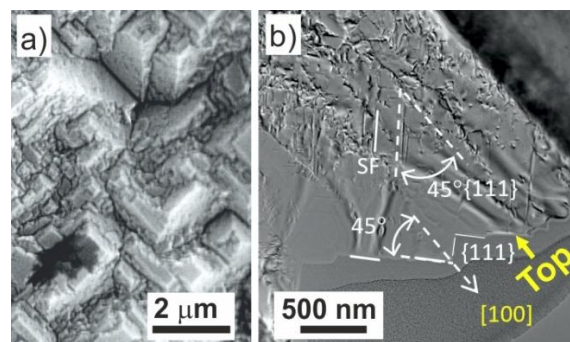


Fig. 1. a) Front-side SEM image and b) cross-section TEM of epitaxially overgrown SCD substrate.

The grown layer exhibits numerous stacking faults and dislocations, which induce local internal strain. Additional strain is also observed at the film–substrate interface. These structural defects are likely associated with Si doping. The

structure and elemental composition were further analyzed using selected-area electron diffraction (SAED) and energy dispersive spectroscopy (EDS) methods.

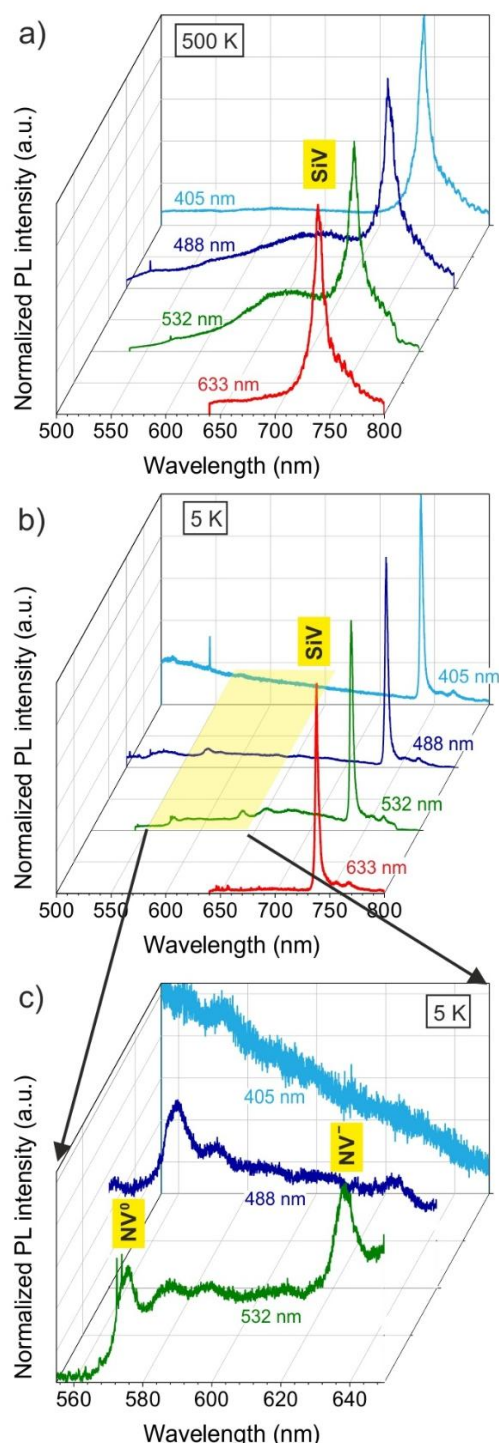


Fig. 2. PL spectra of epitaxially overgrown Ib (100) SCD substrate measured at 500 K (a) and at 5 K (b) with four excitation wavelengths of 405, 488, 532 and 633 nm. c) Detail on the PL spectra of NV centers measured with three excitation wavelengths at 5 K.

Raman spectroscopy showed only a sharp diamond peak at $\sim 1332 \text{ cm}^{-1}$ at room temperature.

However, within the temperature range 5–500 K, its position shifted from 1333.3 to 1330.5 cm^{-1} . This shift is caused by thermal expansion. Increasing temperature increases the average interatomic distance, causing the crystal lattice slightly to expand.

Photoluminescence spectra revealed three PL peaks corresponding to the NV^0 (575 nm), NV^- (638 nm) and SiV (738 nm) centers, whereas only a strong SiV peak was observed for the whole temperature range (5–500 K). The NV^0 and NV^- are visible only at $< 250 \text{ K}$ (see Fig. 2).

The NV peaks are more visible when excited by a green laser (Fig. 2c). This is related to several factors including also an increase in the absorption coefficient from approx. 0.15 to 0.3 cm^{-1} as the excitation wavelength decreases from 532 nm to 405 nm [4]. Thus, the epitaxially grown diamond layer absorbs more light from the 405 nm laser than from the 532 nm laser, and suppresses the information from the nitrogen-rich HPHT substrate. The zero-phonon line of the SiV was red-shifted by around 2 nm, while the positions of the NV^0 and NV^- peaks only deviated slightly. A significant decrease in the FWHM of the SiV peak was observed, from 14 cm^{-1} to 2 cm^{-1} , as the temperature decreased from 500 K to 5 K.

Acknowledgements

This work was supported by the Slovak Research and Development Agency (project nr. APVV-23-0361). M.V. acknowledges support from the project IM-2023-87 funded by the Slovak Academy of Sciences via the programme IMPULZ 2023.

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