Large area heavily boron doped nano-crystalline diamond growth by MW-LA-PECVD

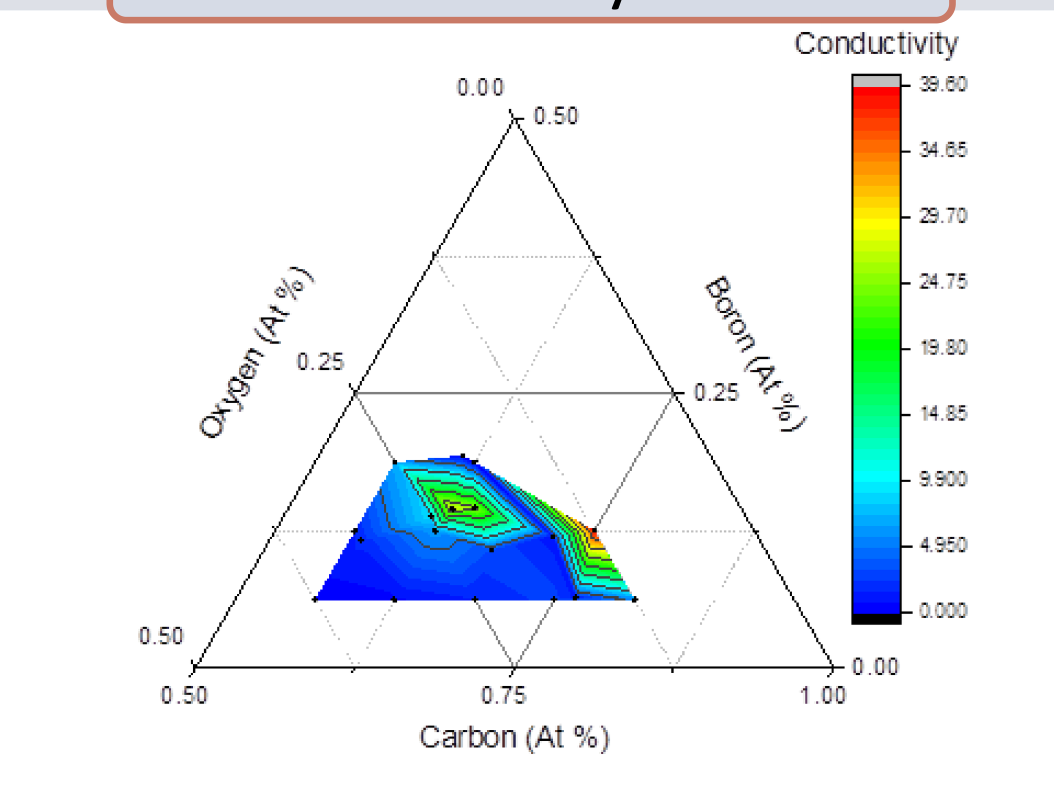
A. Taylor[1], P. Ashcheulov[1], P. Hubík[1], L. Klimša[1], J. Kopeček[1], Z. Remes[1], Z. Vlčková Živcová[3], M. Remzová[3], L. Kavan[3], A.M. Beltrán[4] and V. Mortet[1,2]

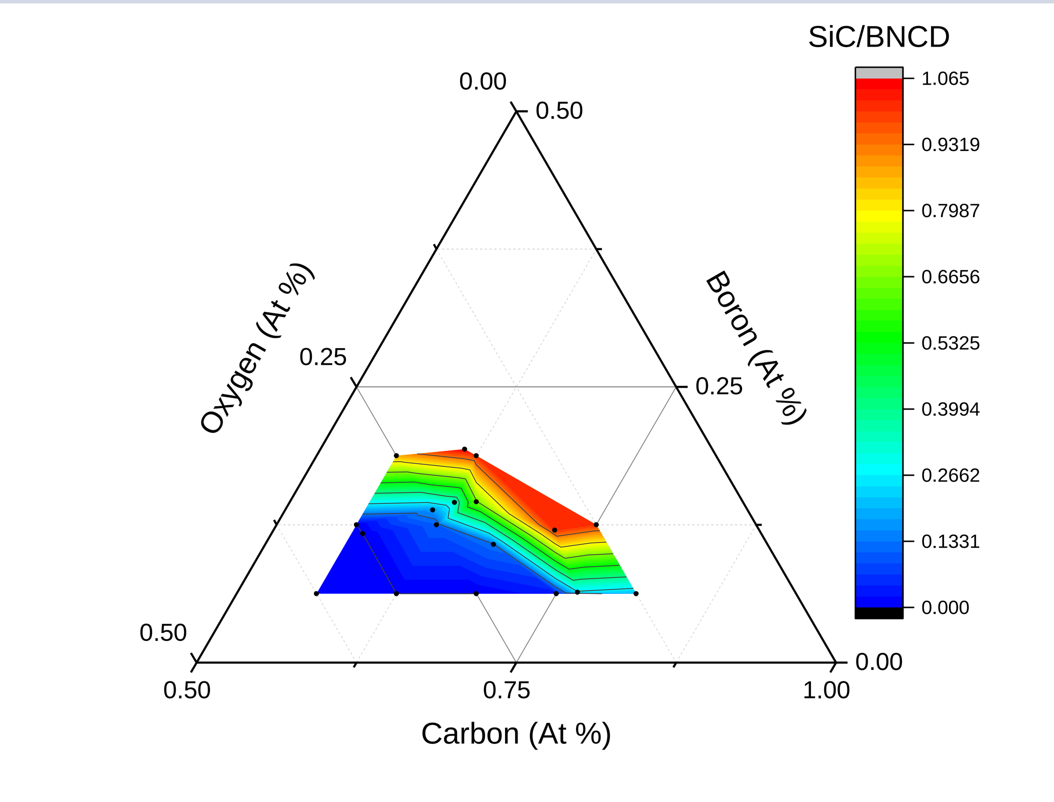
[1] Institute of Physics of the Czech Academy of Sciences, Prague, Czech Republic, [2] Czech Technical University, Faculty of Biomedical Engineering, Kladno, Czech Republic, [3]J. Heyrovský Institute of Physical Chemistry, AS CR, v.v.i., Prague 8, Czech Republic, [4] Escuela Técnica Superior de Ingeniería, Universidad de Sevilla, Sevilla, Spain

CONTACT : taylor@fzu.cz

Abstract: Diamond is a unique semiconductor with a wide bandgap which usually is easily doped with boron and is acknowledged as one of the best materials for electrochemical applications. Heavily boron doped, high quality single crystal synthetic diamond can reach electrical conductivity as high as 10^3 S.cm, whereas polycrystalline material usually reaches c.a. 10^2 S.cm. However, many potential applications are restricted by the deposition temperature and limited coating area of conventional MW PECVD systems. Deposition of boron doped nano-crystalline diamond (BNCD) layers using a microwave PECVD system with linear antenna delivery (MW-LA-PECVD), enabling large area coating, was first reported in 2014 [1]. However, layers showed lower electrical conductivity in comparison to BNCD layers deposited using conventional PECVD systems. In addition, deposition of BNCD by MW-LA-PECVD is complicated by the necessity for the addition of oxygen species, which are known to limit boron incorporation and the competitive growth of silicon carbide at low CO_2 concentrations [2, 3]. In this work, we further study the effect of deposition conditions on the synthesis of BNCD using the MW-LA-PECVD technique. In order to produce highly conductive BNCD with a low sp^2 fraction, we have investigated in greater detail the effect of deposition temperature, from 250 °C up to 750 °C, using temperature controlled substrate stages and the effect of precursor gas compositions.

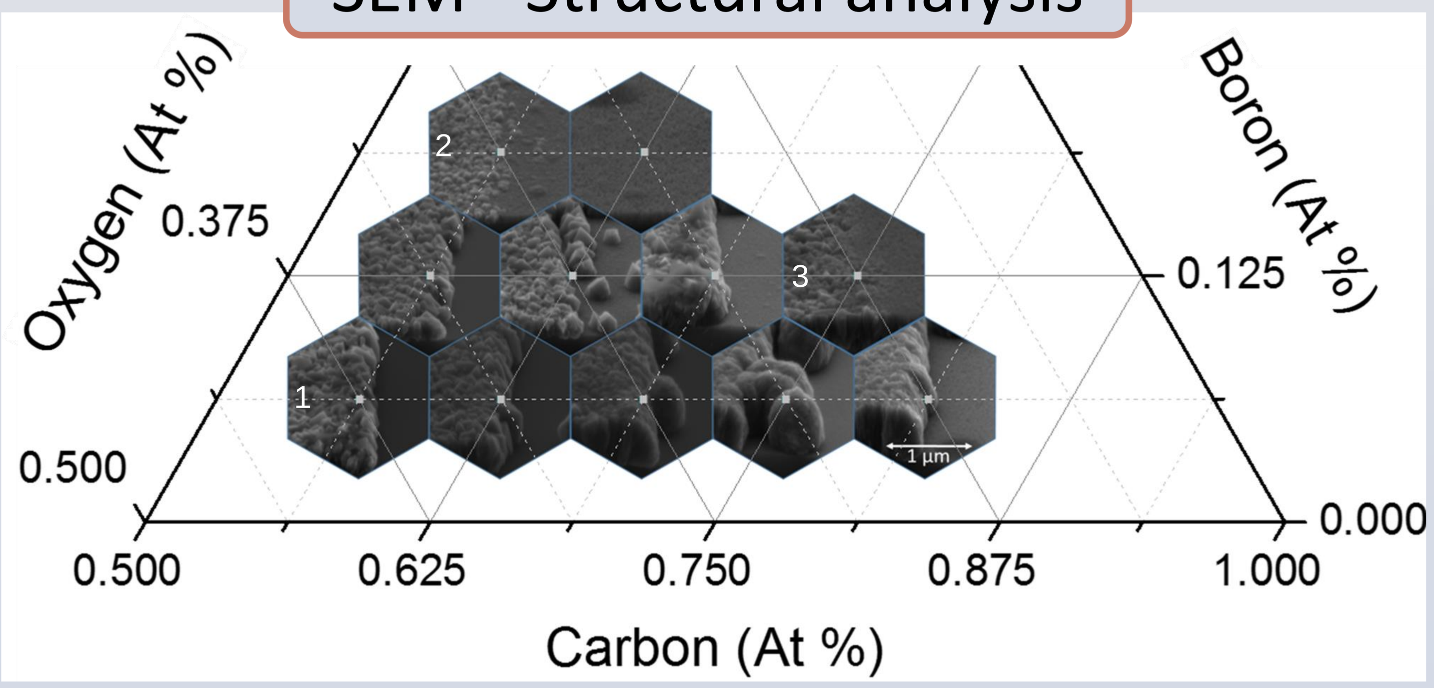
Gas chemistry effects





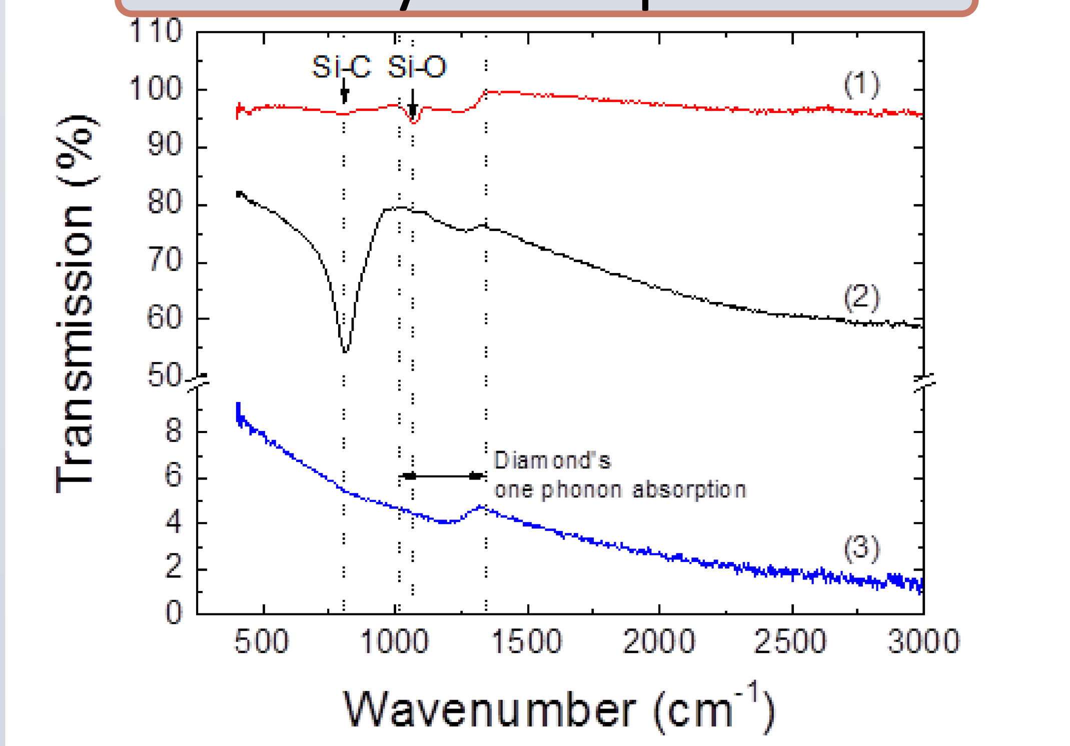
Ternary plots showing the effect of B/O/C atomic concentration on layer electrical conductivity and ratio of BNCD and SiC growth rates. Ideal conditions for highly conductive BNCD lay close to the point where SiC growth rates approach the values as for BNCD. BNCD growth rates ranged from 20 nm/h, at low C and high B concentrations, to 100 nm/h at high C and low B concentrations.

SEM - Structural analysis

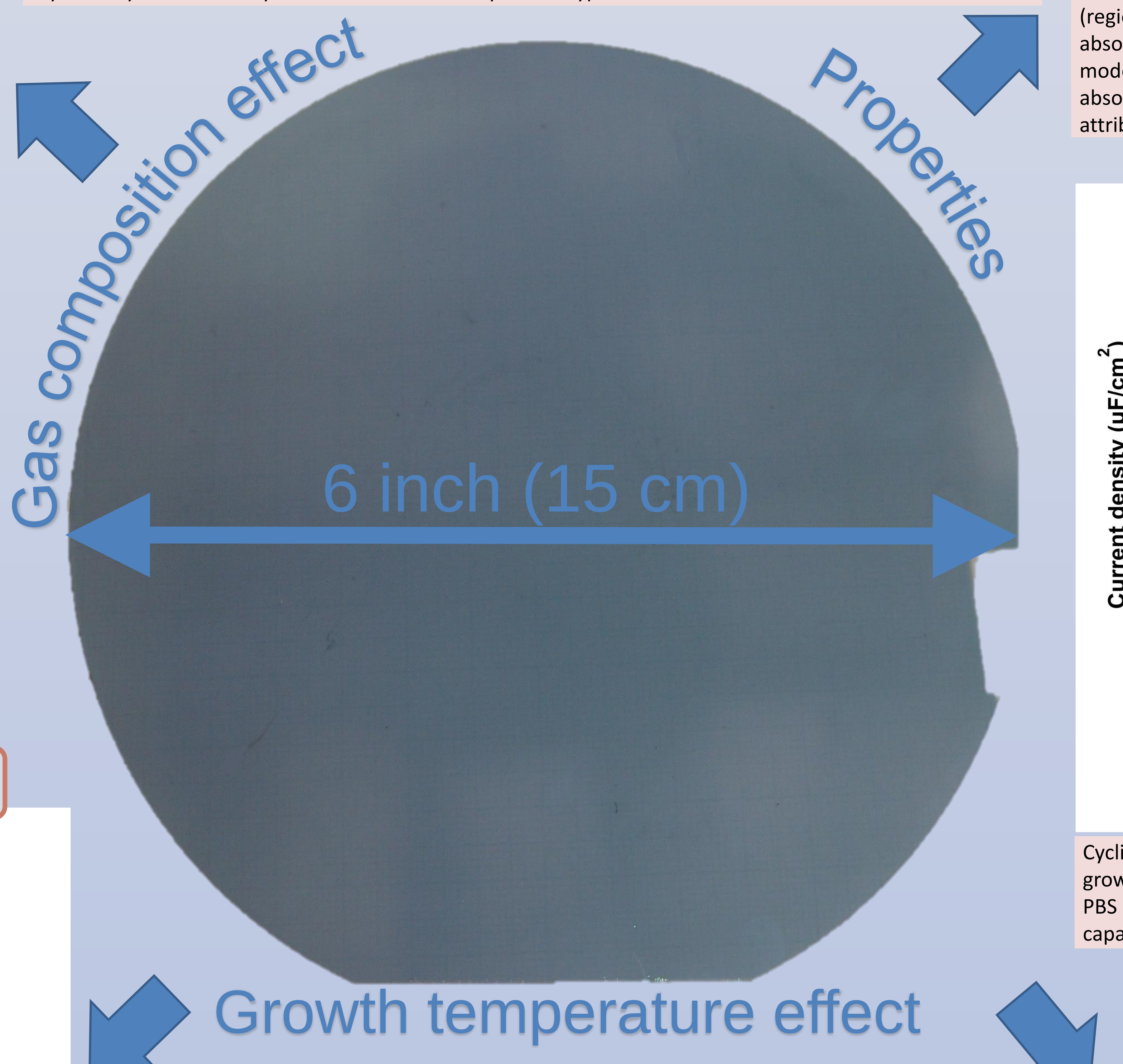


Ternary plot showing SEM cross-sectional images through seeded and unseeded regions of Si substrates showing change in crystalline structure of layers with variation in B/O/C atomic concentration. In particular it can be seen that, 1) as the O content is reduced SiC formation is higher 2) with increasing B content BNCD growth rate decreases and 3) as C content is increased BNCD growth rate increases with a change in crystallinity from nano-crystalline to ultra-nano-crystalline type structure.

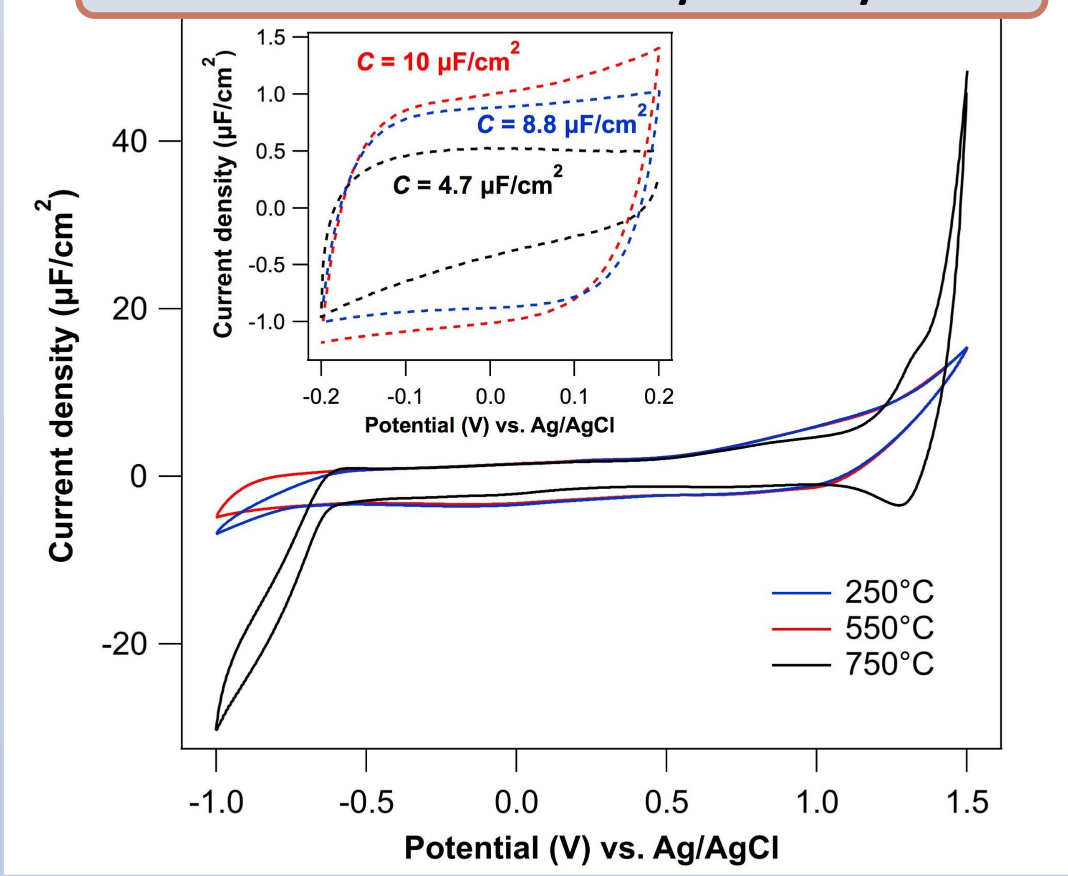
FTIR - Layer composition



Infrared transmission FTIR spectra of layers deposited in different growth regions (see labels in SEM images): (1) BNCD layers with low electrical conductivity, (2) BNCD layers with medium conductivity and incorporation of silicon impurity (region of deposition of SiC) and (3) BNCD with high electrical conductivity. The absorption peak at c.a. 810 cm-1 is attributed to Si-C bond vibration absorption mode, the absorption peak at c.a. 1060 cm-1 is attributed to Si-O bond vibration absorption mode and the absorption between c.a. 1000 and 1350 cm-1 is attributed to diamond one optical phonon absorption.

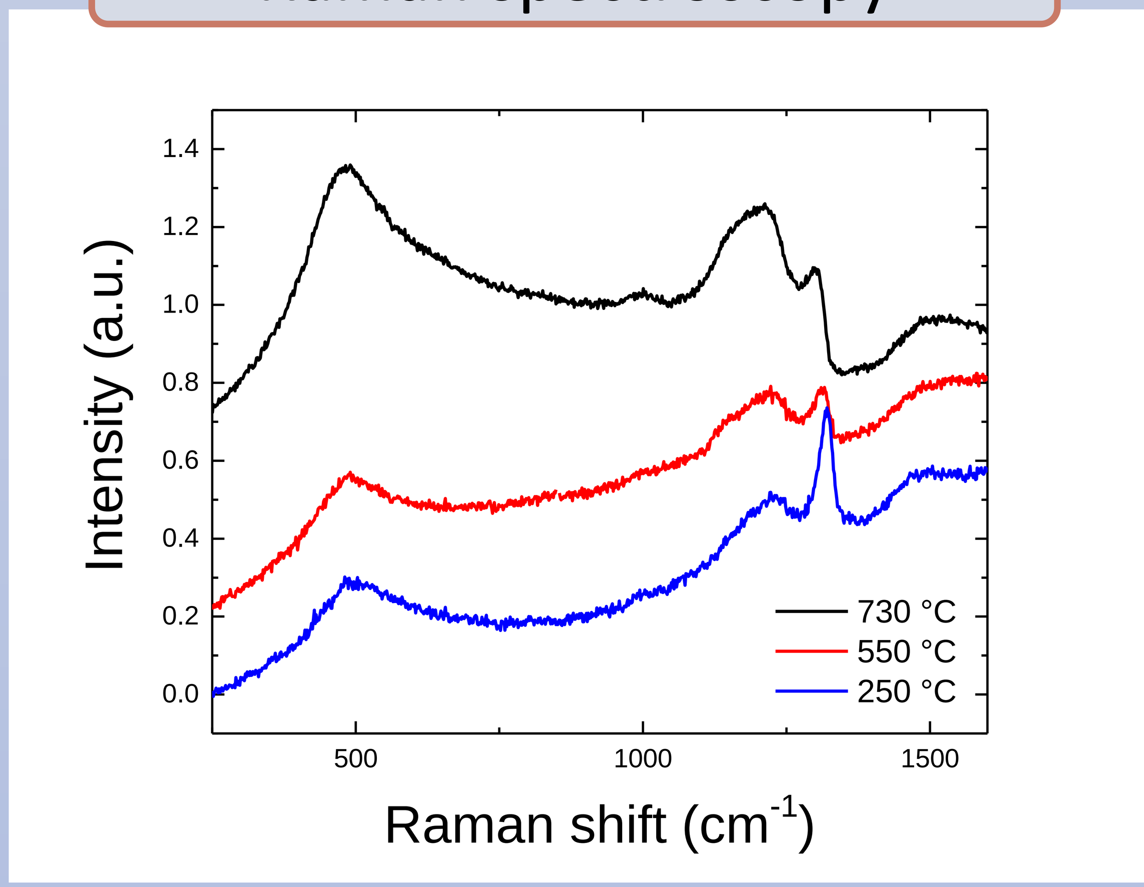


Electro-chemistry analysis



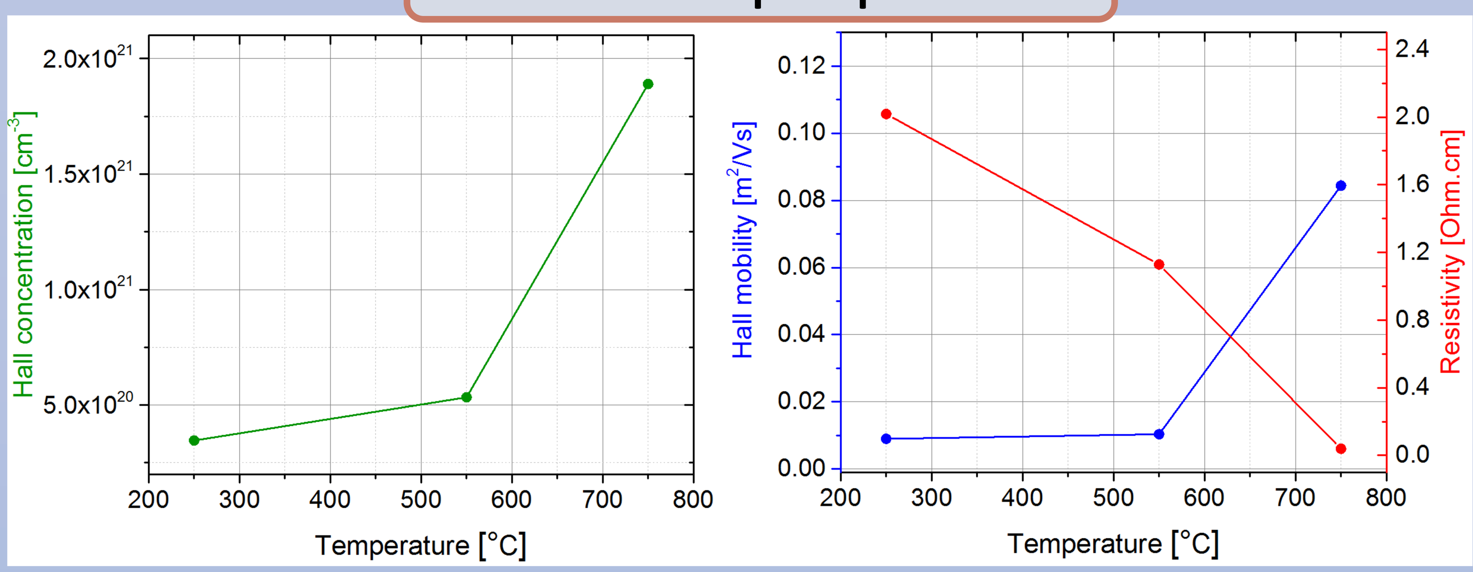
Cyclic voltammograms of thin (150 nm to 300 nm) H terminated BNCD layers grown at 250 °C, 550 °C and 750 °C showing a potential window of c.a. 1.5 V in PBS electrolyte solution vs Ag/AgCl ref. electrode (scan rate 100 mV/s) and capacitance values of 5 to 10 µF/cm².

Raman spectroscopy



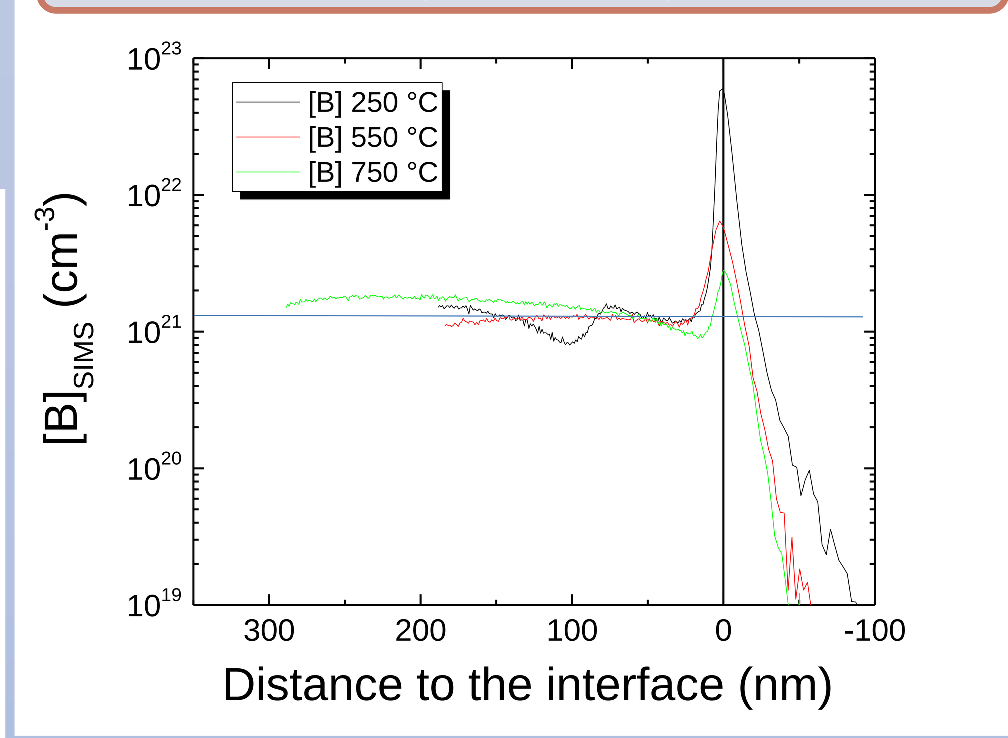
Raman spectra from conductive BNCD layers grown from low to relatively high temperatures. Boron related features can be observed at all temperatures. Specifically the diamond line (c.a. 1320 – 1300 cm^{-1}) is broadened and downshifted due to Fano and domain size effects. The band at c.a. 1200 cm^{-1} attributed to a maximum of phonon density of states appears and the broad feature at c.a. 500 cm^{-1} is visible, which is possibly related to a maximum in PDOS, boron dimers or boron-to-carbon vibration modes [4].

Electrical properties



Hall effect measurements showing a decrease in resistivity (2 Ω.cm to 0.04 Ω.cm) as the growth temperature is increased. Hall concentration levels are increased with growth temperature from 3.5×10^{20} cm^3 to 1.9×10^{21} cm^3 . Hall mobility levels are low, which is typical of nano-crystalline diamond layers.

SIMS - Layer composition



SIMS analysis of BNCD layers grown at 250 °C, 550 °C and 750 °C. Total ^{11}B levels in the bulk of all samples are remarkably similar, c.a. 1.7×10^{21} at/cm^3. The spike in levels at the layer/substrate interface is not fully understood and is currently under investigation.

Conclusions - 1

Optimal conditions have been determined for reproducible deposition of conductive thin BNCD layers over large areas with:

- High boron concentration (~ 2×10^{21} at/cm^3)
- High electrical conductivity (> 35 S.cm-1)
- Good electro-chemical characteristics
- Controlled SiC formation

Conclusions - 2

Study of evolution of electrically active boron incorporation with deposition temperature:

- B atoms uptake across the temperature range is constant
- Fraction of electrically active B atoms is reduced with a reduction in growth temperature, which might be explained by H passivation of B atoms in layers deposited at lower temperatures

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References:

[1] Diamond Relat. Mater. 47 (2014) 27; [2] Phys. Status Solidi A 212 (2015) 2418; [3] Diamond Relat. Mater. 69 (2016) 13; [4] Carbon 115 (2017) 279-284

KEYWORDS: conductive diamond, boron doping, large area deposition, MW-LA-PECVD