Heavily boron doped nano-crystalline diamond growth by MW-LA-PECVD

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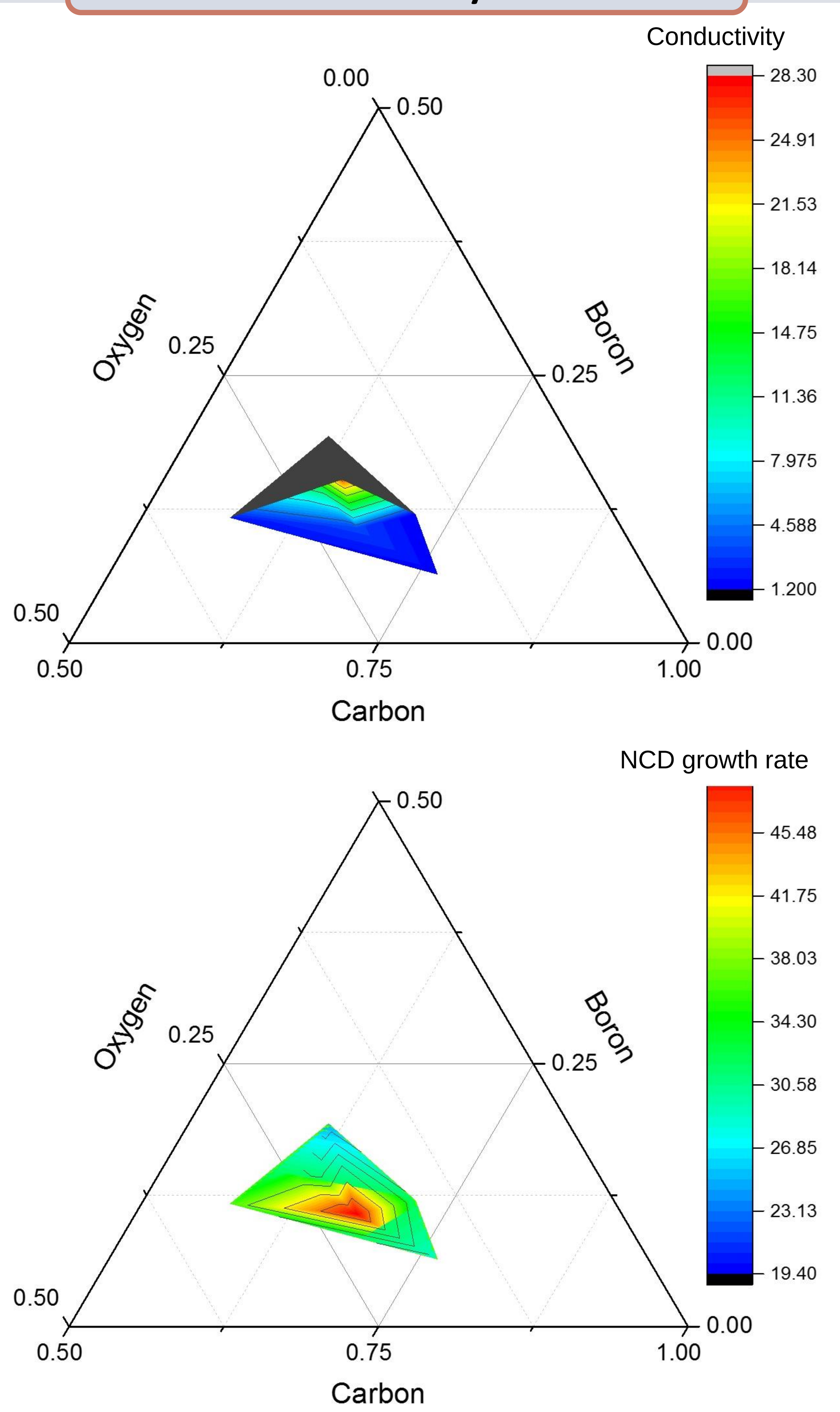
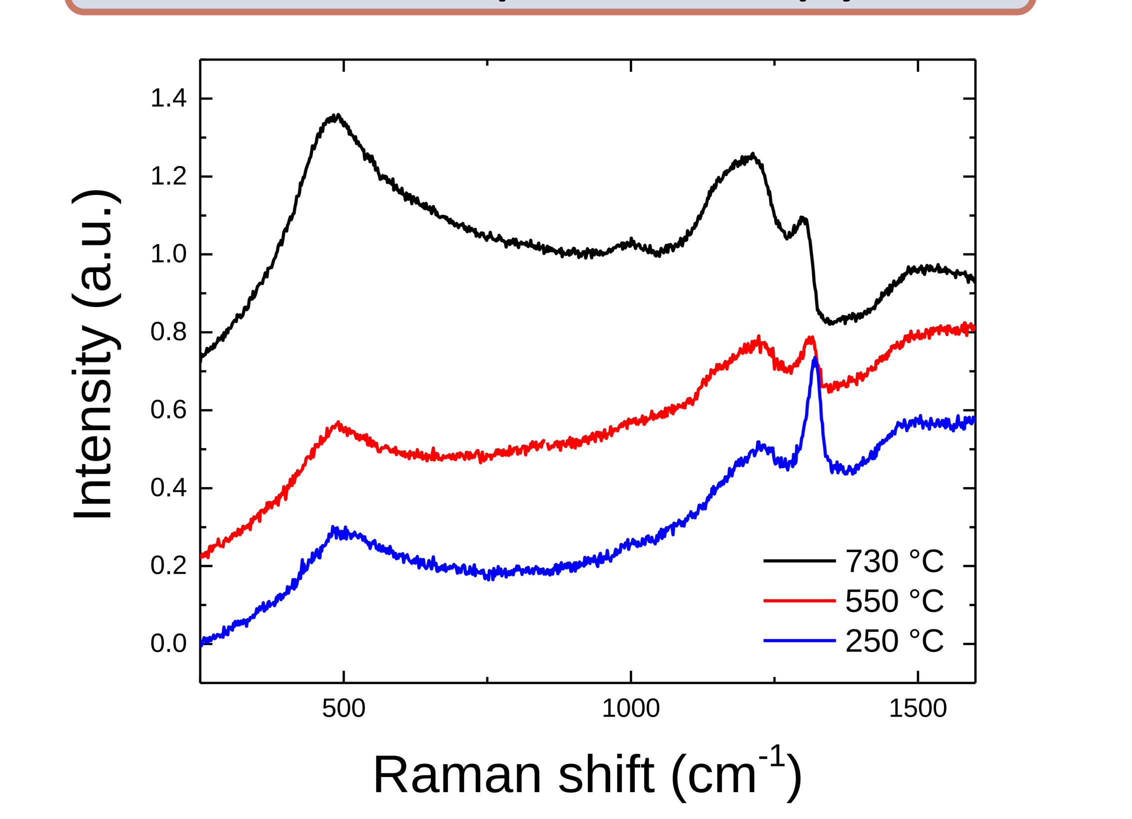
Abstract: Diamond is a unique semiconductor with a wide bandgap which is easily doped with boron and is acknowledged as one of the best materials for electrochemical applications. Heavily boron doped, high quality single crystal synthetic diamond can reach electrical conductivity of c.a. 10^3 S.cm, whereas polycrystalline material can reach 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 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 investigate the effect of deposition conditions on the synthesis of BNCD using the MW-LA-PECVD technique. In order to produce highly conductive BNCD, we have investigated the effect of CO_2 concentration, boron to oxygen ratio and boron to carbon ratio (to well above standard values). The effect of deposition temperature was also studied (from 250 °C up to 750 °C) using temperature controlled substrate stages.

Gas chemistry effects



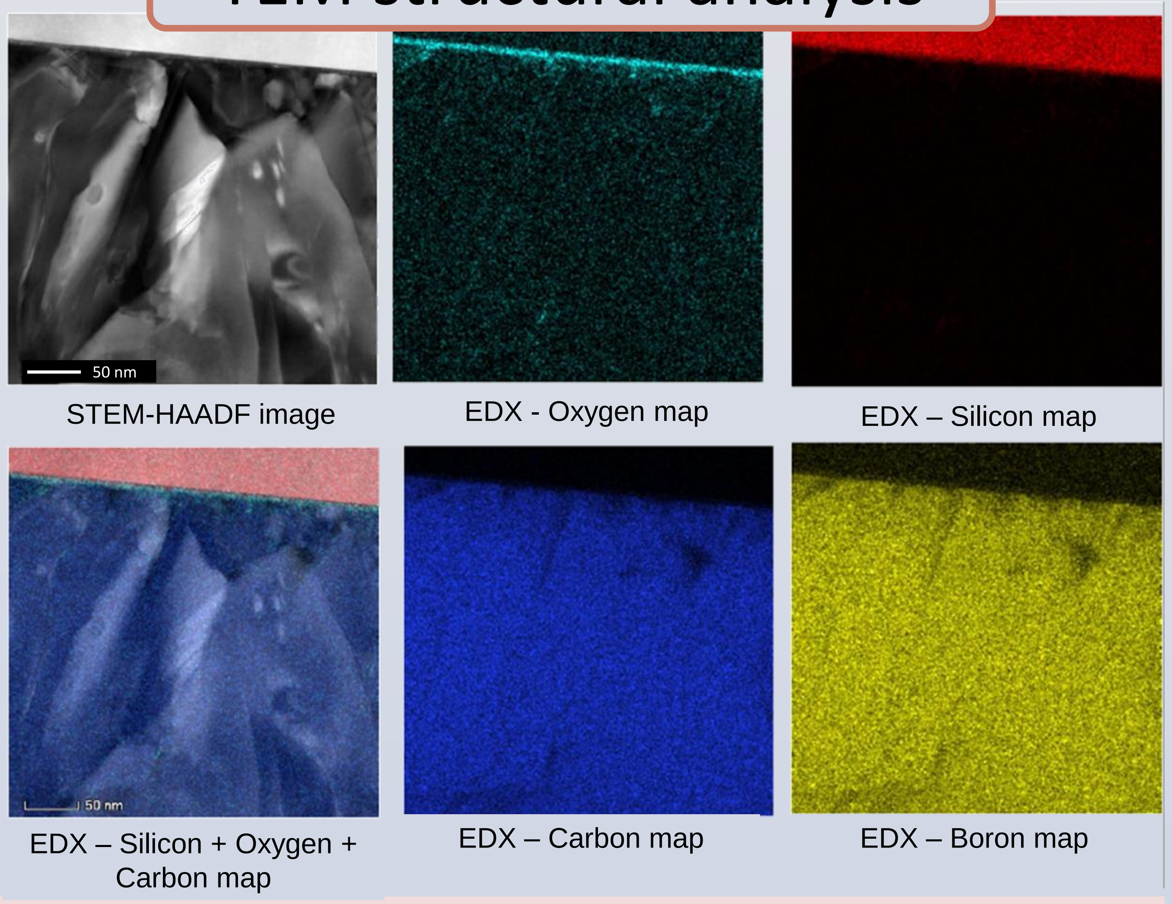
Ternary plots showing the effect of B/O/C on NCD growth and layer conductivity. Ideal conditions for highly conductive BNCD lay close to the point of SiC formation. Further data points are planned to be added to extend the parameter space. All axis show atomic ratio of B/O/C.

Raman spectroscopy

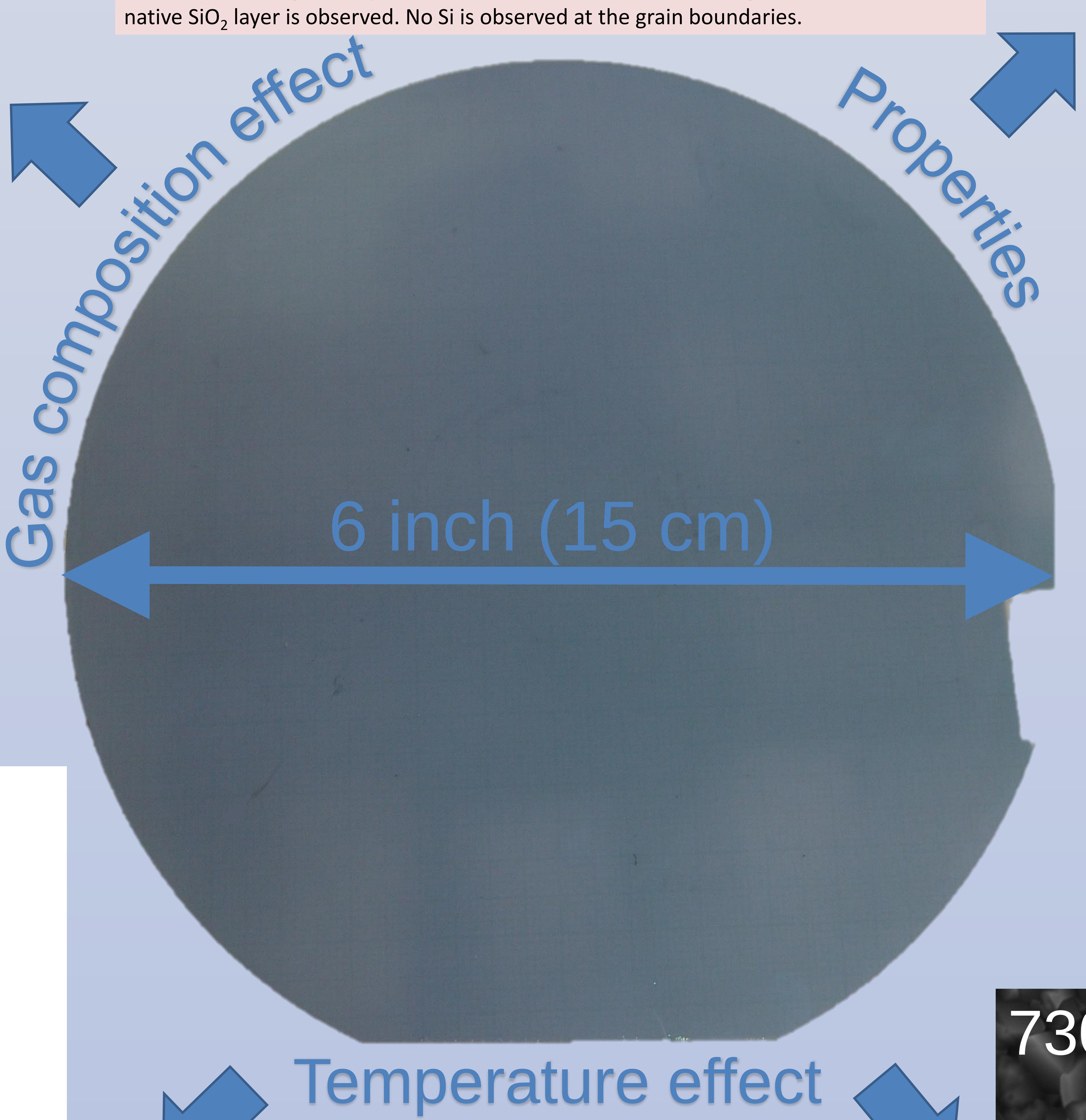


Raman spectra from conductive BNCD layers grown from low to relatively high temperatures. Boron related features can be observed at all temperatures. Specifically the diamond line (c.a. 1320 – 1300 cm^{-1}) is broadened and downshifted due to Fano and domain size effects. The band at c.a. 1200 cm^{-1} 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. ***For more discussion on boron related Raman features please see poster: 5.20***

TEM structural analysis

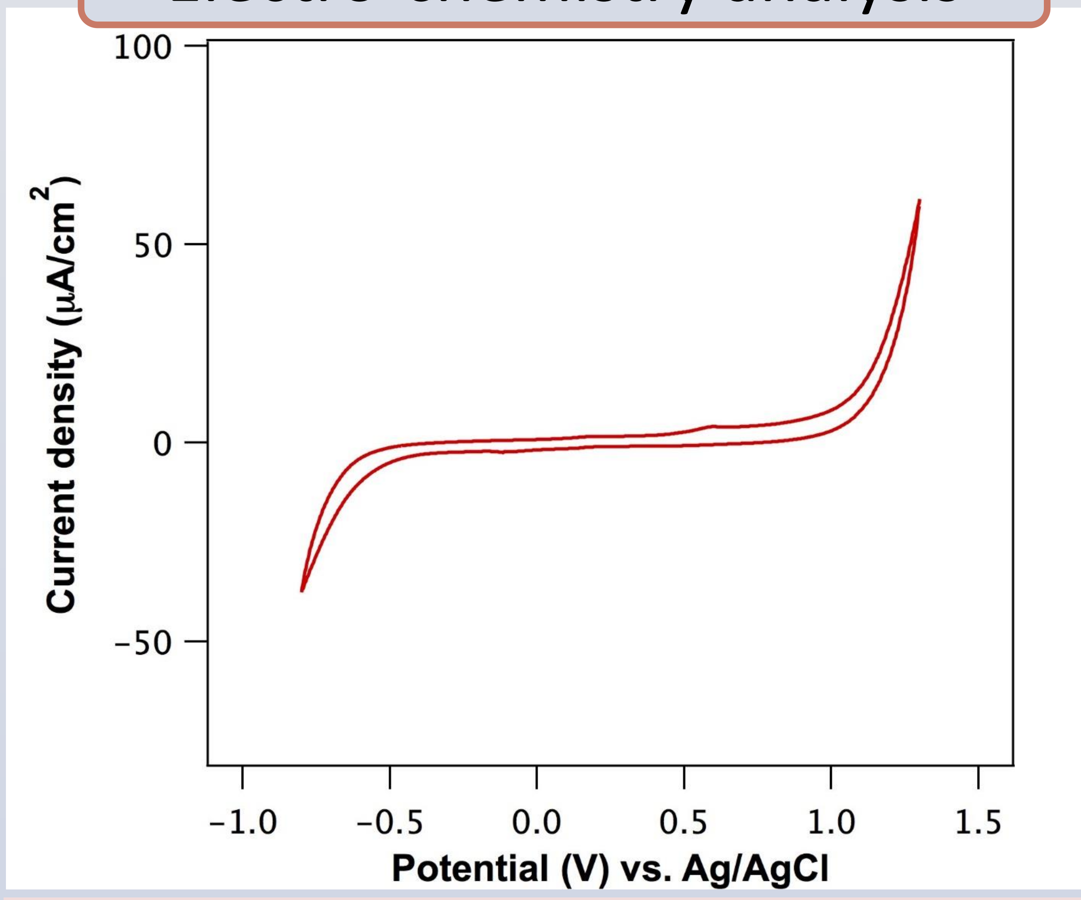


STEM-HAADF image and EDX maps of a cross section through a BNCD layer and Si substrate showing a sharp interface at the substrate and homogeneous B content. The native SiO_2 layer is observed. No Si is observed at the grain boundaries.



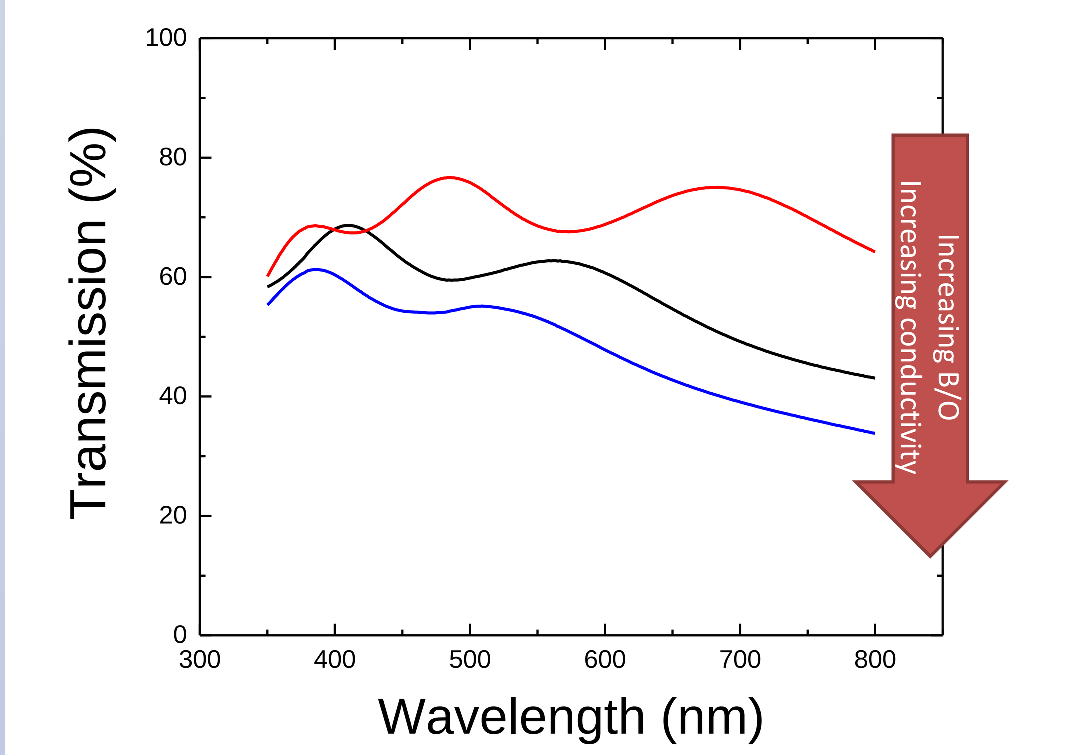
Above:
6 inch diameter quartz wafer coated with thin highly conductive BNCD layer ***(please ask the presenting author to see the real thing!)***. Currently 8 inch is also possible. As the deposition system is modular much larger sizes can be envisioned.

Electro-chemistry analysis



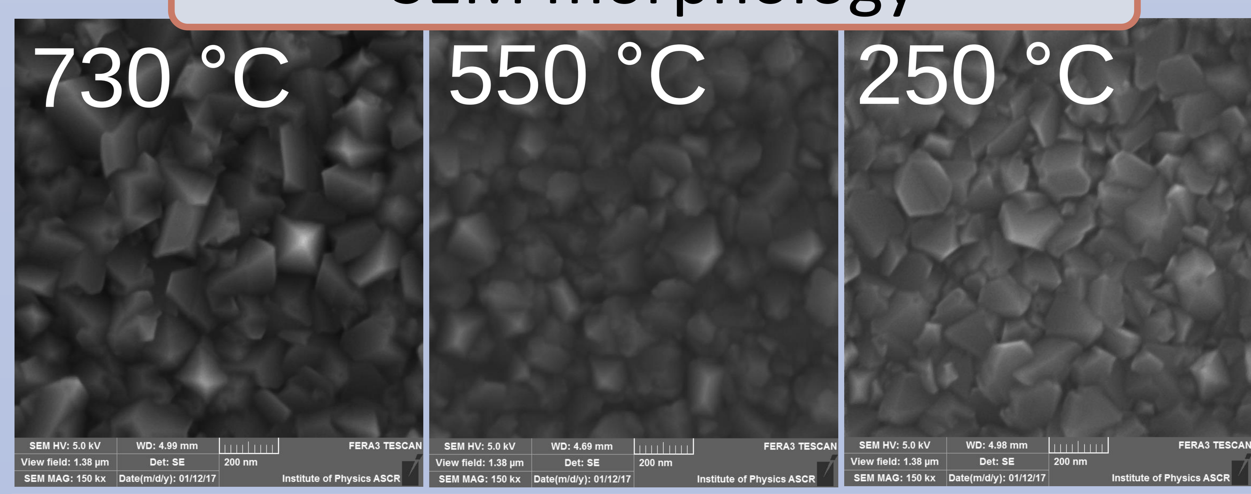
Cyclic voltammogram of a H terminated 300 nm thick BNCD layer showing a potential window of c.a. 1.5 V in PBS electrolyte solution vs Ag/AgCl ref. electrode and a capacitance value of is 13 μF/cm^2, which is comparable with BNCD layers with metallic conduction grown using "classical conditions" reported in [4] [5].

Optical transmission



Optical transmission of c.a. 350 nm BNCD layers with high electrical conductivity (2 to 21 S.cm) grown at various B/O ratios. Layer transmission can be seen to decrease from c.a. 75 % to 55 % @ 450 nm indicating higher incorporation of B, which is in agreement with conductivity values.

SEM morphology



SEM images showing BNCD layers with excellent crystallinity and no SiC formation at all growth temperatures.

Electrical properties

	730 °C	550 °C	250 °C
Conductivity ($S.cm^{-1}$)	25	1.10	0.8
Hall concentration (cm^{-3})	2×10^{21}	Not measured	Not measured
Hall mobility ($cm^2.V^{-1}.s^{-1}$)	0.08	Not measured	Not measured

Conclusions

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

- High boron concentration
- High electrical conductivity (> 25 S.cm-1)
- High optical transmission
- Good electro-chemical characteristics
- Well-defined crystalline structure
- Supressed formation of SiC

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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] Electrochimica Acta 179 (2015) 626–636. [5] Electrochimica Acta 87 (2013) 518–525

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