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# **CCEPTED MANUSCRIPT**

## The spatial inhomogeneity and X-ray absorption spectroscopy of superconducting nanocrystalline boron doped diamond films

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### Abstract

The local electrical conductivity and impurity band evolution in superconducting nanocrystalline boron doped diamond (BNCD) film are investigated using conducting atomic force microscopy (C-AFM) and X-ray absorption spectroscopy (XAS). C-AFM has been employed to investigate the local conductivity of superconducting BNCD with  $T_c$  = 4.3 K and upper critical field H*<sup>c</sup>*2(0) = 5.2 T. A high local electrical heterogeneity of the BNCD film as evidenced from the C-AFM profile points to the uneven boron uptake during the process of doping. C-AFM also revealed that grain boundaries are the highly conducting regions, possibly, due to the presence of p-type trans-polyacetylene along with the C-C and C-H bonds in the grain boundaries. From the in-depth XPS profiling of the B 1s spectra we confirmed the macroscopic uniformity of the boron concentration across the depth of BNCD layers. X-ray absorption spectroscopy (XAS) measurements near B K-edge and C K-edge showed formation of in-gap states as a result of heavy boron doping. Near C K-edge, bandgap states at 282.8 eV and 284.1 eV are found which are responsible for superconductivity in the BNCD film. This work explores the non-uniform boron doping and its effect on the conduction band structure of a superconducting BNCD film.

#### 1. Introduction

Substitutional boron atoms form acceptor levels at 0.36 eV above the valence band maximum (VBM) [1]. Upon heavy boron doping, acceptor levels aggregate into a band. Superconductivity in boron doped diamond (BDD) sets in as substitutional boron atoms in the  $sp<sup>3</sup>$  bonded grains exceeds a critical concentration,  $n_c = 4.5 \times 10^{20} \text{cm}^{-3}$  [2, 3]. Although different mechanisms explaining superconductivity in BDD exist, [4, 5] it is widely accepted that BDD is a BCS-type superconductor [6]. Experimental evidence suggests that beyond n*c*, impurity band merges with the valence band driving BDD into a superconducting state at low temperature [7].

*T<sup>c</sup>* in superconducting BDD scales with boron concentration. Theoretical estimate of the maximum achievable  $T_c$  in BDD is 80 K [8]. This is however, limited by the solubility limit of boron in diamond and also by the formation of defective regions as a result of heavy boron doping. For the samples grown using

the high pressure high temperature (HPHT) technique, the grain size of the BDD samples are usually larger than 1  $\mu$ m [9, 4, 10]. The individual grains consist of  $sp<sup>3</sup>$  bonded atoms where substitutional boron atoms are randomly distributed. Also, isolated pockets of boron rich phase resembling  $B_{50}C$  or  $B_{4}C$ , with dimensions of up to 200 nm are found within the grains [4, 10]. These grains are separated by an amorphous [4] or crystalline[10] grain boundaries of thickness up to 10 nm. In the case of BDD films deposited using the chemical vapor deposition (CVD) technique, beyond a critical boron concentration, extended defects starts to form within the  $sp<sup>3</sup>$  bonded grains [11, 12]. Furthermore, formation of boron complex is a common characteristic widely studied in CVD grown BDD [13, 14]. Amorphous carbon layers of thickness ∼ 10 nm, with relatively high boron content [12, 15] are formed at the grain boundaries. While there has been a general consensus on how doping of boron in diamond modifies the sp<sup>3</sup>-bonded grains in both HPHT and CVD grown samples, similar consensus for the grain boundary components has not been reached so far. Probing of nanoscale conductivity in BDD also have shown contradictory re-

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