

## EFFECT OF BORON CONCENTRATION ON NANO-CRYSTALLINE DIAMOND DEPOSITED ON NIOBIUM SUBSTRATES

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Different Boron concentrations have been used to study the effect and quality of boron doped diamond film formed on the Niobium substrate. Deposition of nanocrystalline diamonds films on Niobium substrate have been carried out by HF-CVD technique using mixture of methane and hydrogen gases. The surface roughness of the substrates and the resultant morphology of nanocrystalline diamond have been studied using Atomic force microscope (AFM). Raman spectroscopy was used to investigate the diamond film quality while the surface conductivity of boron doped diamond film has been characterized using current image tunneling spectroscopy (CITS). The results of the measurements show that the grains sizes were decreasing as increasing the levels of boron concentration, as well as the surface has homogenous distribution of conductivity as the boron concentrations increasing. Moreover, Raman measurements show a shift to lower energy of characteristic diamond line at  $1330\text{ cm}^{-1}$  as a function of the doping level.

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### 1. Introduction

Boron doped nanodiamond(BDD) are well known structures and attracted by many researchers for their application in bio-sensing, electronics, water purification electrodes, unipolar devices, ultraviolet light generators and electrochemical applications [1-4]. BDD are a unique material because of its outstanding mechanical, thermal, optical, electronic and electrochemical properties [5, 6]. The BDD film can be prepared using different techniques as mentioned in the literatures such as; the microwave plasma enhanced-chemical vapor deposition (MW PE-CVD) [7] and Hot filament chemical vapor deposition (HF-CVD) [8] as this method involves activation of a mixture of hydrogen and hydrocarbon gases.

The motivation of using BDD in application refers to the conductivity of diamond thin films, where the conductivity can be adjusted typically by carrying out suitable doping procedures. The conductivity of diamond thin films can be fabricated by substitution doping atoms such as B, Al, N, P, S, Si, Ni, Fe, Sb, Cr, etc. As mentioned in the literature, boron is one of the most used and successful because of its ability to be substituted for carbon atoms in the diamond lattice [9]. BDD thin films are synthesized by substituting some of the hybridized carbon atoms in the diamond lattice with boron atoms during diamond thin film synthesis (In situ) or after diamond thin film synthesis (Ex situ). In situ doping involves addition of certain amount of boron containing gas species to the diamond forming gas mixtures during the diamond thin film

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synthesis. However, Ex situ doping involves boron doping into the already synthesized diamond thin films mainly through ion implantation [10,11].

The BDD electrode's electrical properties depend on several structural factors such as dopant concentration, conductivity distribution, and structural defects in the diamond film and non-diamond carbon impurity content like amorphous graphite. However, the understanding of enhancing the electrical properties is still not clear and under investigation. In the present work, the effect of the boron concentration on the morphology and quality of nanodiamond film deposited on Niobium substrate has been investigated and discussed. AFM, CITS and Raman spectroscopy have been used to identify and characterize the deposited diamond film.

## 2. Material and methods

The boron doped nanodiamond films were produced by a hot filament chemical vapor deposition (HFCVD) process. The substrate used for the deposition of BDD film was Niobium substrates and cleaned ultrasonically in acetone to remove any impurities such as dust and debris. Then, the substrates were pretreated by sand blasting in order to roughen the surface and therefore to enhance the adhesion strength between diamond and substrate, and meanwhile, the specific surface area was increased to expectably improve the electrochemical performance. The sand blasting was followed by twice ultrasonic cleaning in ethanol. Afterwards the substrates were seeded by ultrasonic seeding in a diamond powder suspension. The CVD-diamond coating took place in a CVD Hot Filament Coating machine CC800/8 DIA with 1% methane  $\text{CH}_4$  and a small amount of trimethyl borate  $\text{B}(\text{OCH}_3)_3$  to enhance the electrical conductivity of diamond by boron-doping. In this study two different surfaces of BDD, doped with gas-phase  $\text{B}(\text{OCH}_3)_3$  concentration of 0.5 and 1.5 ppm.

The AFM has been used to characterize the surface topography, roughness, and the grain size of the boron doped nanodiamond films. An extensive STM was employed to characterize the surface of the prepared BDD film as well as the surface conductivity by performing current image tunneling spectroscopy (CITS) measurements [12-16]. WSxM software was used to both acquire and analyze the AFM and STM images [17]. Raman spectra have been used to study the quality of BDD layers deposited on niobium substrate.

## 3. Results and discussion

Atomic force microscopy (AFM) and root mean square method (RMS) were used to study and analyze the effect of increasing the boron concentration on the surface topography, surface roughness, and the grain size of the prepared film. Fig. 1 shows the 2D topography images for the sample prepared with 0.5 ppm  $\text{B}(\text{OCH}_3)_3$  as shown in Fig.1a and the sample prepared with 1.5 ppm  $\text{B}(\text{OCH}_3)_3$  represented in Fig1b. Morphology of cauliflower was shown in all 2D topography images of the prepared boron doped nanodiamond film. The figure also shows the profile of the AFM image taken along the line and is clearly seen in the inset in both images. Moreover, The diamond layer surface shows well (111)-faceted crystals and the visible roughness of few micrometers can be claimed as a result of surface roughening pretreatment of the Niobium substrate surfaces. However, the decreasing in the grain size with different levels of boron concentration, the average grain size decreases from 3  $\mu\text{m}$  for 0.5 % boron to 2.5  $\mu\text{m}$  for 1.5% boron, were attributed to the effect of boron. This variation of grain sizes decrease enhanced the nucleation formation during the first step of growth as previously reported in the literatures [18-21]. The quality of BDD layers deposited on niobium substrate correlated with the quality of the coating process, as it has been noticed, there were no cracks or holes appearing as well as the peeling phenomenon does not occur during coating process. The preparation quality of BDD layers deposited on niobium substrate is very important for application in the electrochemical wastewater treatment, which means the electrode area can totally be used for electrochemical oxidation and this consequently increased the prepared electrodes efficiency.

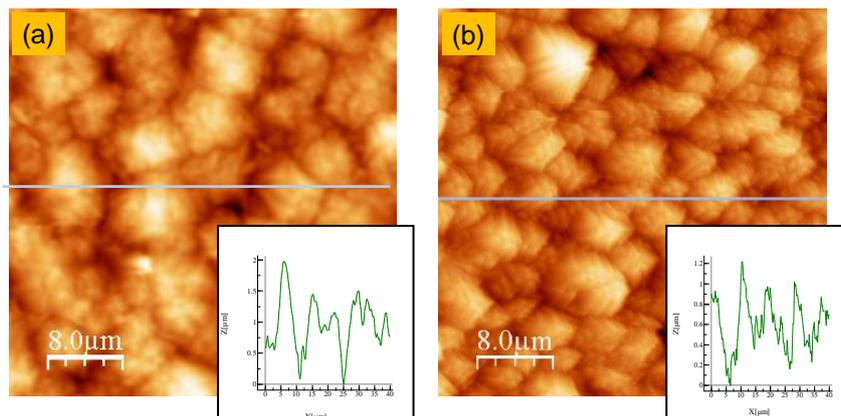


Fig 1. AFM image analysis of BDD in Niobium substrate (a) 2D topography image under 0.5% boron concentration (b) 2D topography image under 1.5% boron concentration. The inset in both figures is the surface roughness along the blue line in the 2D topography image

Further investigation and analysis have been done with STM/CITS technique to understand the effect of increasing the boron concentration in the surface conductivity of the prepared BDD film. The current image, while applying a bias voltage of  $-400$  mV to the sample, is recorded as shown in CITS image in Fig. 2. It is clearly seen, in particular the bright spots of Fig. 2a, the local conductivity of the 0.5 % boron concentration sample is not homogeneous and variations in the conductance were identified by the presence of high conductivity islands and intermediate conductive regions surrounding these islands. However, a homogenous distribution and increasing in conductivity in the BDD surface are clearly seen in the 1.5% boron doped diamond sample as shown in the CITS image in Fig. 2b. These observations in the conductivity behavior indicate the effect of boron concentration on the sample conductivity as the boron concentration increase then the conductivity and homogenization of diamond film will increase.

Even though, the diamond films were doped with boron and were electrically conducting, it still requires good electron transport path, such as the grain boundaries, to supply sufficient amount of electrons to enhance field emission properties of the materials. Therefore, by increasing the boron concentration in the prepared diamond film, the size of diamond grains was reducing. Cheng et al [22] has observed that a decreasing in the grain size will increase in the proportion of grain boundaries which is highly defective are expected to be a good conduction path for the electrons.

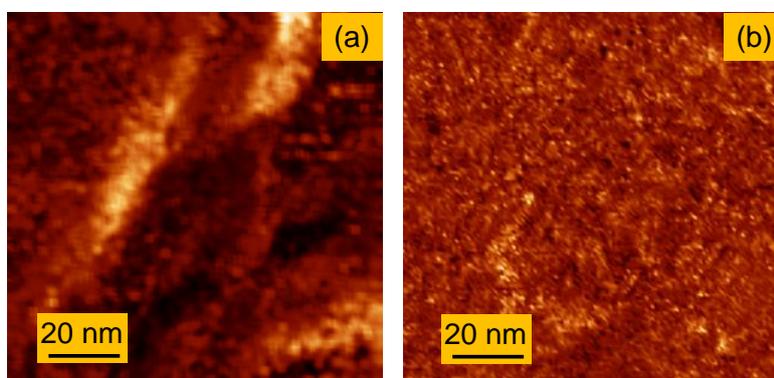


Fig 2: CITS current image taken at a bias voltage of  $-400$  mV of BDD film (a) 0.5% boron concentration (b) 1.5% boron concentration

Fig. 3 shows Raman spectra that have been used to test the quality of BDD layers deposited on niobium substrate with different boron concentrations. A sharp peak is clearly seen at  $1330\text{ cm}^{-1}$  which is usually associated with diamond  $\text{sp}^3$  bonding. The negative shift in the Raman peak from the reported value which equal to  $1332\text{ cm}^{-1}$  can be referred to the low thickness of the deposited diamondfilm ( $\sim 8\mu\text{m}$ ) [23]. Moreover, the broad peak shown in Raman spectrum with maximum at  $1500\text{ cm}^{-1}$  is assigned to C–H chains and is a typical feature of the Raman spectrum of nano-crystalline diamond [24]. The absence of other amorphous carbon or  $\text{sp}^2$  graphite peaks that usually appear in the range between  $1450\text{ cm}^{-1}$  and  $1600\text{ cm}^{-1}$  is evidence that BDD layers can be considered as phase-pure (high quality) diamond material.

Raman spectra also indicate that the boron could not be detected and was not detected in the Raman spectra due to its low content. Nevertheless, the characteristic diamond peak at  $1330\text{ cm}^{-1}$  decreases to a lower energy, as the doping level increases due to the relaxation of the  $\Delta k = 0$  selection rule caused by the small coherence length of diamond crystallites [25].

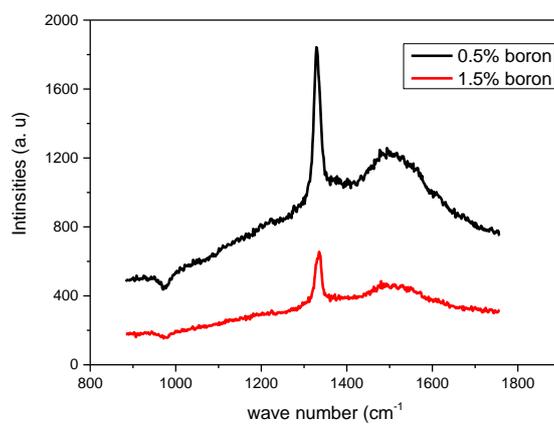


Fig 3. Raman spectrum of the boron doped diamond film with different boron concentration

#### 4. Conclusions

The effect of boron doping on the surface roughness, the grain size, surface conductivity and the quality of the nanodiamond films was examined using AFM technique, CTIS and Raman spectroscopy. As a conclusion, the surface morphology and grains sizes measured by AFM technique indicate that the grains size were decreasing as changing the levels of boron concentration due to the effect of boron, which enhanced the nucleation formation during the growth. In addition, the CITS images of the prepared boron doped nanodiamond film showed that the electrical conductivity of the diamond film is increasing as the boron concentration increasing. Moreover, Raman study of BDD films showed a shift to lower energy of characteristic diamond line at  $1330\text{ cm}^{-1}$  as a function of the doping level.

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