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## Secondary Electron Emission from Boron Doped Diamond Films Grown by MPCVD

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**Abstract:** Behavior of negative electron affinity (NEA) from B-doped diamond films is investigated. Largest secondary electron emission (SEE) yields were found to be 18.3 and 10.9 at 1 keV primary beam energy for samples doped with 10 mg/L and 2 mg/L  $B_2H_6/CH_4$  flow rate ratios, respectively. Note that these samples were left in air for weeks before loaded into SEE system, and subject to no treatment prior to SEE measurements. The higher SEE yields indicate that the NEA effect is well retained though the samples were exposed in air for weeks. Meanwhile, oxidation treatment of the sample doped with 10 mg/L  $B_2H_6/CH_4$  flow rate ratio in a boiled acid destroys NEA as evidenced from the lower SEE yields, whereas heating up in vacuum brings NEA back substantially, resulting in a largest yield of 10.2 at 1 keV.

**Key words:** B-doped diamond films; negative electron affinity; secondary electron emission yield; oxidation treatment

## MPCVD 生长 B 掺杂金刚石膜的二次电子发射研究

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**摘 要:** 研究了 B 掺杂金刚石膜的负电子亲和势(NEA)的行为。对于  $B_2H_6/CH_4$  为 10 mg/L 和 2 mg/L 的样品, 一次电子能量为 1 keV 时最大二次电子发射系数(SEE)分别达到 18.3 和 10.9。值得注意的是, 这两个样品在测试前已在大气中搁置了几个星期, 并且测量前未经过任何处理。如此高的 SEE 表明, 样品在大气中暴露后 NEA 效应仍得到了保留。另外, 10 mg/L  $B_2H_6/CH_4$  掺杂样品在酸溶液中处理后 NEA 消失, SEE 较低, 而在真空中加热后 NEA 明显恢复, SEE 在 1 keV 时达到 10.2。

**关 键 词:** B 掺杂金刚石膜; 负电子亲和势; 二次电子发射系数; 氧化处理

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## 1 Introduction

Synthetic diamond films possess a number of outstanding properties [1-5]. One of them is well known negative electron affinity (NEA) [6-7] when some diamond surfaces are terminated with hydrogen atoms or other electropositive elements, resulting in negative charge transfer from the ad-atom to the carbon atom on the surface [7-8]. The NEA effect means that the vacuum energy level lies below the conduction band minimum, so that electrons in the conduction band will be able to escape into the vacuum with no potential barrier. Therefore, the application of diamond films with NEA in electron multipliers, electron field emitters and particle/photon detectors, has received much attention. However, there are some obstacles concerning the applications of NEA. One is how to retain or regain NEA after a device is made from the diamond film. To regain NEA, e. g. re-hydrogenation by high temperature dissociation of H<sub>2</sub> molecules into active H atoms or H<sub>2</sub> plasma treatment, can be used. For many applications, however, it is not practical to do so. In this work, we studied NEA behavior from B-doped diamond films prepared by microwave plasma chemical vapor deposition (MPCVD), aiming at developing simple processes to retain or regain NEA effect of the diamond films.

## 2 Preparation and Characterization of B-Doped Diamond Films

N (100) Si wafers were used as substrates for growing diamond films. Boron-doped diamond films (2~3 μm thick in thickness) were grown in a lambda MPCVD reactor (Diamo-Tek 700) that has been described in reference [8]. Briefly, the growth parameters are as follows: absorbed microwave power 2 kW, total pressure 14.6 kPa, substrate temperature 900 °C, and gas flow rate ratio of 1% CH<sub>4</sub>/H<sub>2</sub> and 2~10 mg/L B<sub>2</sub>H<sub>6</sub>/CH<sub>4</sub>, and total gas flow rate 200

mL/min. Following the growth process, the B-doped diamond film was subject to H plasma treatment for 10 minutes as to enhance NEA effect.

Scanning Electron Microscopy (SEM), X-Ray Diffraction (XRD) and raman were used to examine the properties of the B-doped diamond film. Fig. 1 shows a typical SEM image of the film, indicating a [111] orientation. This film texture is confirmed by the XRD spectrum as shown in Fig. 2, where the (111) peak dominates. The raman spectrum as shown in Fig. 3, exhibits one single diamond peak at 1 332.8 cm<sup>-1</sup>, which is slightly shifted towards higher wave number as compared to 1 332.6 cm<sup>-1</sup> of the non-doped film [9]. The absence of SP<sub>2</sub> carbon trace indicates a reasonable high quality diamond film, though the (111) peak width at half maximum of ~5.5 cm<sup>-1</sup> is much larger than that of the non-doped film [9]. In addition, the B-doped diamond film exhibits a lower resistivity as examined by the avometer.

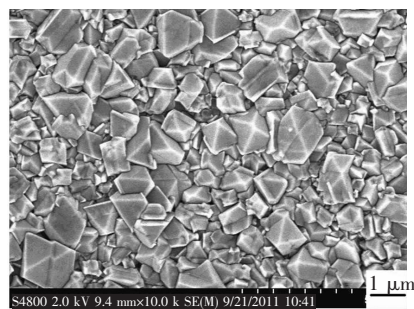


Fig. 1 SEM image of the B-doped diamond film, showing dominated (111) faces.

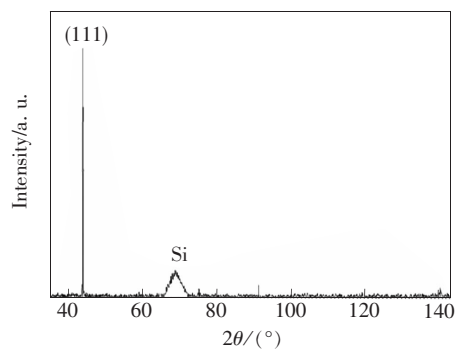


Fig. 2 XRD spectrum of the diamond film with the most intensive (111) peak

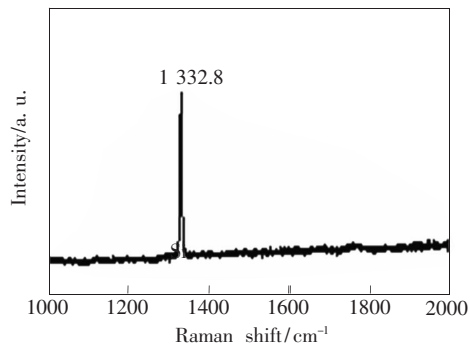


Fig. 3 Raman spectrum of the diamond film showing a single diamond feature at  $1\,332.8\text{ cm}^{-1}$

### 3 Results and Discussions

SEE yield  $\delta$  is defined as the ratio of secondary electron current  $I_2$ , including the elastically scattered, to the primary electron beam current  $I_1$  (a few  $\mu\text{A}$ ), i. e.  $\delta = I_2/I_1$ , and measured against primary electron beam energy up to 1 keV.

#### 3.1 Yields from B doped samples with no treatments

Fig. 4 shows SEE yield  $\delta$  as a function of primary electron energy  $E_p$  for samples doped with  $\text{B}_2\text{H}_6/\text{CH}_4$  flow rate ratio: (a) 10 mg/L, and (b) 2 mg/L. The largest yield ( $\delta_{\text{max}}$ ) reaches 18.3 and 10.9 at 1 keV for (a) and (b), respectively. Yater et al reported a maximum of 20 at 1 keV from B-doped diamond only after rehydrogenation<sup>[10]</sup>. It should be noted that our samples that were exposed in air for weeks before loaded into a SEE measurement system, had no

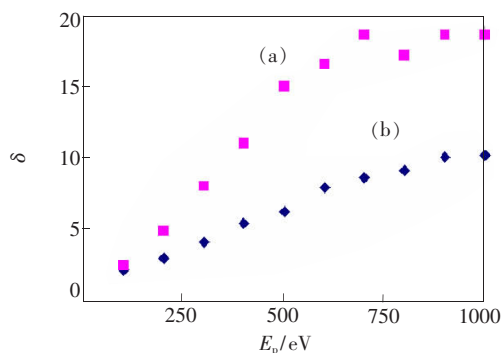


Fig. 4 SEE yield *vs.*  $E_p$  with the samples prepared by  $\text{B}_2\text{H}_6/\text{CH}_4$  flow rate ratio: (a) 10 mg/L, and (b) 2 mg/L.

treatment at all. This is desirable since in many applications of SEE, in-situ treatment like rehydrogenation, is impractical. Meanwhile, the higher SEE yield ( $\delta_{\text{max}} = 18.3$ ) as compared to the reported value of 20<sup>[10]</sup> indicates that H-atom terminated NEA from the B-doped diamond film is essentially retained even after exposed in air for weeks.

#### 3.2 Yields from B doped samples after heating

To further study the NEA behavior, SEE yields were measured from a sample prepared with 10 mg/L  $\text{B}_2\text{H}_6/\text{CH}_4$  flow rate ratio following a successive heating. Fig. 5 plots  $\delta$  against the primary electron beam energy for the treatment: (a) before heating (RT), (b) after heating to 300 °C for 30 minutes, and (c) after heating to 400 °C for 30 minutes. Obviously, as compared to these before the heating, there was little change in yields after 300 °C heating, while 400 °C heating resulted in slight decrease in yields. Reports<sup>[10-11]</sup> have shown that heating or flash-heating would increase SEE yields due to removing additional species adsorbed during the transport of the sample through the air. However, our heating experiments did not show any increase in yields, implying little or less effect of the additional species on SEE. We do not know if it had something to do with the post H plasma treatment in the diamond reactor, which could

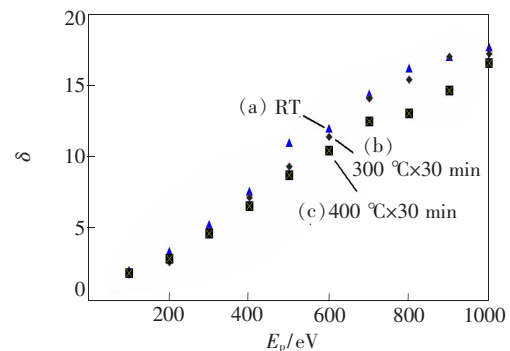


Fig. 5 SEE yields against the primary electron beam energy for the treatment: (a) before heating (RT), (b) after heating to 300 °C for 30 minutes, and (c) after heating to 400 °C for 30 minutes. sample was prepared by 10 mg/L  $\text{B}_2\text{H}_6/\text{CH}_4$  flow rate ratio.

have enhanced NEA. In this regard, more work is needed to confirm our suggestion.

### 3.3 Effect of B doping level

As seen in Fig 4, the sample (a) prepared with 10 mg/L  $B_2H_6/CH_4$  flow rate ratio shows a much better SEE performance as compared to the sample (b) prepared with 2 mg/L  $B_2H_6/CH_4$  flow rate ratio. This indicates that a high B doping level is necessary to give rise to an intensive NEA effect. This is because the formation of NEA results from the downward band bending of a P-type semiconductor surface due to its carrier depletion following adsorption of some atoms like H or Cs. Therefore, the higher B doping level would result in a more intensive NEA due to a larger amount of electron charge transfer from ad-atoms to the surface and thus a sharper downward band bending with a narrower width of the depletion region. On the other hand, to achieve a higher SEE yield as shown in Fig 4(a), it is essential for most secondary electrons excited in the bulk to transport to the surface without being scattered or trapped. Unfortunately, the higher B concentration in the film is likely to result in a high probability of electron-impurity scattering, i. e. a short escape depth. As such, the role of B dopants in the SEE process is complex, and needs a better understand as to optimize B concentration for the high SEE yield [10].

### 3.4 Effect of oxidation and heating in vacuum

To get insight into NEA behavior, the sample doped with 10 mg/L  $B_2H_6/CH_4$  flow rate ratio was oxidation treated in an acid solution of  $HNO_3 : H_2SO_4$ . The surface resistivity went up immediately, indicating the removal of NEA. Then the sample was loaded into the SEE system. SEE yields were measured before and after heated to 400 °C in vacuum ( $1 \times 10^{-5}$  Pa) for 30 minutes, as shown in Fig. 6. The lower yield ( $\delta_{max} = 2.2$ ) before heating confirms the loss of NEA as a result of the oxidation process. On the contrarily, following the heating-up, the

yields are much high with a largest value of 10.2, and increase steadily with an increase in  $E_p$ , showing clearly the recovery of NEA. The NEA recovery is believed to be attributed to the diffusion of H atoms onto the diamond surface from the bulk [12]. Obviously, such a process—just by heating-up in vacuum, is much feasible in comparison with other techniques, such as in-situ dissociation of  $H_2$  under high temperature or H plasma treatment.

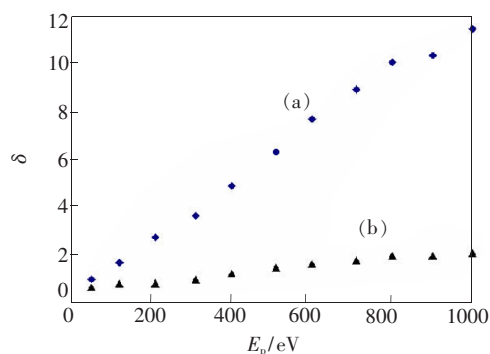


Fig. 6 SEE yields *vs.*  $E_p$ . The sample was grown with 10 mg/L  $B_2H_6/CH_4$  flow rate ratio and treated in acid, followed by: (a) heating to 400 °C in vacuum for 30 min, and (b) no treatment.

## 4 Conclusions

We have investigated NEA behavior from B-doped diamond films grown by MPCVD, followed by H plasma treatment. SEE yields were found to be up to 18.3 and 10.9 at 1 keV primary beam energy for samples doped with 10 mg/L and 2 mg/L  $B_2H_6/CH_4$  flow rate ratios, respectively. It is interesting to note that the NEA effect was well retained, though the samples were left in air for weeks before loaded into SEE system, and subject to no treatment prior to SEE measurements. This is important for the application of NEA diamond films to the devices. We also demonstrated the removal and recovery of NEA from the B-doped diamond film by the process of oxidation treatment and heating up in vacuum, which is much feasible as compared to in-situ re-hydrogenation process or H plasma treatment.

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