Electrochemical Properties and Chemical Oxygen Demand Depending on the Thickness of Boron-Doped Diamond

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Abstract: In this study, boron-doped diamond (BDD) film was deposited by hot-filament chemical vapor deposition (HFCVD) using acetone as the carbon source and trimethyl borate (TMB) as the boron source with the aim of lowering the manufacturing cost of BDD electrodes. The BDD film was deposited for 12 and 60 h to observe changes in the morphological behavior of the film as well as subsequent changes in the electrochemical properties. The morphology of the BDD film was not affected by the deposition time, but the thickness increased with increasing deposition time. As the deposition time increased, the deposition rate of the BDD film did not increase or decrease; rather, it remained constant at 100 nm/h. As the thickness of the BDD film increased, an increase in the potential window was observed. On the other hand, no distinct change was observed in the electrochemical activation and catalytic activity depending on the thickness, and there were not many differences. Chemical oxygen demand (COD) was measured to determine the practical applicability of the deposited BDD film. Unlike the potential window, the COD removal rate was almost the same and was not affected by the increase in the thickness of the BDD film. Both films under the two deposition conditions showed a high removal rate of 90% on average. This study confirms that BDD electrodes are much more useful for water treatment than the existing electrodes.

Keywords: HFCVD; boron-doped diamond; BDD; COD; wastewater; wastewater treatment

1. Introduction

Due to industrial development, large quantities of various organic compounds and recurrent wastewater are being discharged into bodies of water, negatively impacting the environment. In many parts of the world where industries are concentrated, environmental pollution has become a serious problem. Various methods have been developed for wastewater treatment, including biodegradation, chemical decomposition, electrochemical oxidation, and other physicochemical methods [1–3]. Among them, electrochemical wastewater treatment methods are widely used due to their cost and efficiency advantages. Compared to physical and biological treatment methods, electrochemical methods are environmentally friendly because of the low treatment cost and the fact that there is no residue after treatment. Moreover, high wastewater treatment is possible without the addition of toxic oxidants [4–6]. Electrochemical wastewater treatment is superior to other methods because it is possible to effectively oxidize and decompose contaminants using insoluble electrodes that produce...
hydroxyl radicals, which are more powerful than oxidants used in ordinary oxidation processes [7,8]. Therefore, many studies on electrochemical wastewater treatment electrodes have been conducted.

Boron-doped diamond (BDD) electrode is currently in the spotlight and attracting attention. Because it has a higher potential window value than the IrO$_2$ electrode, which is currently the most widely used electrode for water treatment, it produces more hydroxyl radicals and a stronger oxidizing agent on the surface [4,5,8,9]. Due to the excellent properties of BDD films, many studies are being conducted on BDD electrodes in the field of insoluble electrodes compared to IrO$_2$ electrode, which is currently widely used in industries. However, as is well known, although the manufacturing method of BDD is relatively simple, its deposition and manufacturing cost are expensive. Therefore, considering the cost aspect, its efficiency is not good for widespread industrial use. As a result, the production and use of BDD electrode for water treatment is not very common.

The purpose of this study was to manufacture a BDD electrode, evaluate and analyze whether it can be used for water treatment, and further develop an electrode with better performance than the existing electrodes, such as IrO$_2$. Furthermore, changes were made to the deposition method in order to solve the cost problem, which is a fundamental reason for BDD films not being widely used despite having better performance and efficiency than the currently used IrO$_2$. Conditions such as the optimum filament temperature and the distance between the filament and the susceptor, which are considered to be the most important factors in diamond deposition, were determined based on the results of previous experiments [10,11]. In a previous experiment [10] on filament temperature, an appropriate applied power was derived for depositing a diamond film through hot-filament chemical vapor deposition (HFCVD). The temperature of the filament with respect to the applied power was first calculated through ANSYS computer simulation, and the actual experiment was conducted based on the calculation result. The filament temperature in the actual experiment was measured using a two-color pyrometer. It was confirmed that there was little difference between the calculated filament temperature and the actual filament temperature measured using the two-color pyrometer. To study the temperature with respect to work distance [11], the applied power was determined based on the filament temperature study, and the temperature change of the susceptor with respect to the working distance was calculated using ANSYS computer simulation and then verified through an actual experiment. Here, the temperature of the susceptor was measured using an infrared thermometer.

In addition, instead of methane gas and trimethyl borate (TMB) gas, which are generally used for diamond deposition, acetone solution was taken as the carbon source and TMB solution was used for boron doping. The use of acetone solution and TMB solution can reduce the material cost by at least 10 times compared to when gas is used. Acetone and TMB solutions were introduced into the chamber using a bubbling system using hydrogen gas as the carrier gas. The deposition of the BDD film was performed for 12 and 60 h, with all other conditions except for the time variable kept identical, and the morphological deposition behavior of the BDD film with respect to the deposition time was examined. Furthermore, the possibility and performance of the deposited BDD film as a water treatment electrode were evaluated. The chemical oxygen demand (COD) decomposition capacity of wastewater and the electrochemical properties were compared and evaluated with respect to deposition conditions.

2. Experimental Details

HFCVD was used for BDD deposition. Figure 1 shows a schematic diagram of the diamond deposition equipment (PNU, CW2014, Busan, Korea) and bubbling system for acetone and TMB. Tungsten filament should be used to reduce cost during diamond deposition, but tantalum filament was used instead of tungsten filament in this experiment. With tungsten filament, even when the same power is applied to the filament, the temperature of the filament is lower than that of the tantalum filament. It is also difficult to load tungsten filament into the HFCVD chamber because it is difficult to deform the material properties. In addition, when the temperature of the filament is increased by applying power during deposition and carbonization, it breaks at the end of the experiment, meaning
it can only be used once. On the other hand, tantalum filament does not break immediately after the experiment and therefore can be reused several times in succession. In consideration of all the advantages and disadvantages and cost aspects, a tantalum filament was used instead of the relatively inexpensive tungsten filament. Twelve rows of tantalum filaments with length of 32 cm and diameter of 0.7 mm were loaded into the HFCVD chamber with a spacing between the filaments of 20 mm.

![Figure 1. Schematic diagram of hot-filament chemical vapor deposition (HFCVD) and bubbling system.](image)

If deposition is performed without rotating the susceptor, the temperature underneath the filament and between the two filaments is different. This causes nonuniform substrate surface temperature, resulting in nonuniform BDD film deposition. Therefore, the susceptor was rotated at 1 rpm for uniform deposition of the BDD film. Acetone was used as the carbon source required for diamond deposition, and hydrogen was used as the reaction gas. To impart electrochemical properties, diamond was doped with boron using TMB. Acetone solution and TMB solution were supplied into the chamber through a bubbling system using hydrogen gas as the carrier gas. When acetone solution and TMB solution are in liquid (not gaseous) phase, the vapor pressure is different depending on the temperature. Therefore, it is very important to control the temperature of the two solutions in order to supply a certain amount into the chamber. A thermostat was used to bring the two solutions to 0 °C and supply them into the chamber. Water freezes when it reaches 0 °C, so the temperature was adjusted to 0 °C using an antifreeze solution. The bubbler of acetone solution and TMB solution was immersed in an antifreeze solution, which was maintained at 0 °C using a thermostat and supplied into the chamber while maintaining 0 °C.

The BDD film was deposited on two substrates at the same time. To accurately measure the thickness of the BDD film, a square silicon wafer with thickness of 0.5 mm and width of 900 mm² was used. A niobium substrate with thickness of 1 mm and width of 900 mm² was used for all measurements except the thickness, such as morphologies, crystallinity, and electrochemical properties of the BDD film.

Prior to diamond deposition through HFCVD, a pretreatment process of the substrate surface is required. The pretreatment process refers to seeding of diamond particles with improved roughness on the surface using diamond particles. If the seeding is not performed on the surface of the substrate using diamond particles, the deposition of diamond does not proceed [12–14]. The pretreatment consisted of the following processes. First, the silicon and niobium substrates were cleaned using ethanol, and ultrasonic cleaning was performed for 10 min by immersing them in ethanol to remove fine foreign substances on the substrate surface. A mixed solution of 500 nm particle size diamond powder and glycerin in a weight ratio of 1:1 was evenly applied to the washed substrate and then rubbed for 3 min. Then, the surface was washed with ethanol again to remove the residue and glycerin on the substrate surface. Such a pretreatment process not only gives the seeding effect of diamond particles to the substrate surface but also increases the roughness of the substrate surface due to the rubbing effect during seeding, thereby facilitating diamond deposition.

In previous studies, computer simulations and practical experiments have been conducted to determine the appropriate applied power, working distance, pressure, amount of acetone, hydrogen,
etc. [10,11]. For applied power, if the power is higher than 16 kW, a lot of amorphous carbon is deposited due to the high temperature, which causes a low deposition rate. On the other hand, if the power is less than 16 kW, diamonds do not become a complete film, resulting in a very low deposition rate [10]. A previous study that looked at diamond deposition behavior with respect to the distance between the filament and the susceptor found that when the working distance is longer than 10 mm, the diamond does not become a complete film due to low temperature. On the other hand, when the working distance is shorter than 10 mm, amorphous carbon is formed due to the temperature being higher than the proper temperature, thereby causing a decrease in the deposition rate [11]. Based on the results of these previous experiments, the BDD film deposition conditions were determined in this study (Table 1). Unlike previous studies, in this study, diamond was doped with boron. When carbon is substituted with boron in the diamond lattice, it exhibits electrochemical properties that pure diamond does not have [4,5,8]. A previous study that calculated the amount of boron doped in diamond film using the Antoine equation [15] found that 11,400 ppm of boron was doped. This means that about 1% of boron is doped in diamond. However, this doping amount is too small for quantitative analysis, and it is difficult to measure because it is a light element. Thus, Raman spectroscopy was used to approximate the amount of boron doping [7,8,15].

Table 1. Deposition conditions used in the experiment.

| Deposition Conditions                        | Value  |
|---------------------------------------------|--------|
| Filament input power (kW)                  | 16     |
| Number of filaments used                    | 12     |
| Length of each row of filament (mm)        | 320    |
| Pressure during deposition (Pa)             | 4000   |
| Distance between filament and susceptor (mm)| 10     |
| Distance between filaments (mm)            | 20     |
| Amount of acetone (sccm)                   | 90     |
| Amount of trimethyl borate (TMB) (sccm)    | 6      |
| Amount of hydrogen (sccm)                  | 400    |
| Deposition time (h)                         | 12 and 60 |

Using a BDD film deposited on a niobium substrate, the morphological behavior of the surface with respect to the deposition time was analyzed using FE-SEM (Hitachi, S-4800, Tokyo, Japan). BDD film deposited on a niobium substrate cannot be easily cut, and the deposited BDD film may be damaged during cutting. Therefore, the thickness of the BDD film was observed by FE-SEM using a silicon wafer, which allowed accurate cross-sectional verification without damaging the deposited BDD film during cutting. Diamond characterization peaks were identified through XRD measurements. The XRD measurements (Bruker, D8-Advance, Karlsruhe, Germany) were made in the coupled scanning diffraction (CSD) mode. The 2 theta scan range was 30 to 80°, and an acceleration voltage of 40 kV and a current of 40 mA were used. Raman spectroscopy (Horiba, Jobin Yvon, Longjumeau, France) analysis was used to confirm whether boron was doped as well as study the quality of the diamond. Raman analysis was performed using an argon laser at an excitation wavelength of 514.5 nm.

Cyclic voltammetry (CV) curves were measured using a potentiostat (WonATech Co., ZIVE SP2, Seoul, Korea) to determine the possibility of using BDD as an electrode by evaluating the electrochemical properties of the surface of BDD films. To measure the potential window of oxygen and hydrogen reactions, 0.5 M Na₂SO₄ solution was used as an electrolyte. To measure the electrochemical activation and catalytic ability of BDD films, 0.5 M Na₂SO₄ solution and 50 mM K₃[Fe(CN)₆]/K₄[Fe(CN)₆] solution were mixed. Measurements were made at a scan rate of 20 mV/s using a Pt counter electrode and an Ag/AgCl reference electrode.

COD was measured to determine the practical applicability of the deposited BDD film. For COD analysis, nonbiodegradable organic contaminants in wastewater samples were collected from farm
A in Yangsan, Korea, and refrigerated at 4 °C to prevent spoilage. COD was analyzed according to the standard method for water pollution measurement in US Environmental Protection Agency (EPA) method 410.3.

3. Results and Discussion

The morphology and thickness of the BDD film with respect to the deposition time are shown in Figure 2. It was determined that the morphology of the BDD film did not change significantly with respect to the deposition time. On the other hand, as the deposition time increased, the BDD film deposited for 12 h showed a thickness of 1.1 ± 0.2 µm, and the BDD film deposited for 60 h showed a thickness of 5.6 ± 0.5 µm. As the deposition time increased by 5 times, the thickness also increased by about 5 times, demonstrating that there was a constant deposition rate of 100 nm/h, which did not increase or decrease over time.

![Figure 2. Surface morphology and cross-sectional FE-SEM images of boron-doped diamond (BDD) films deposited for (a) 12 h and (b) 60 h.](image)

XRD pattern analysis was performed to confirm the success of diamond deposition through the diamond characterization peak. The results of 12 h BDD film deposition (Figure 3a) showed the (111) peak near 44° and the (220) peak with very low intensity values around 75°. Likewise, for the 60 h BDD film deposition (Figure 3b), the (111) and (220) peaks were observed around 44° and 75°, respectively. Compared to the 12 h result, both peaks showed relatively high intensity values. In addition to the diamond characterization peak, a niobium carbide peak was also observed in both results. This indicated that the surface of the substrate used for diamond deposition was carbonized. In XRD diffraction analysis, the depth of the measurement range of the characterization peak is greater than the diamond deposition thickness [16–18]. The reason the (111) and (220) diamond characterization peaks were relatively high in the BDD film deposited for 60 h was because the thickness was relatively higher than the BDD film deposited for 12 h; it was not due to any other reason or difference in the quality of the diamond.
Through the XRD pattern analysis, it was not possible to determine whether the diamond was doped by substitution of boron. Therefore, Raman spectra analysis was carried out, and the results are shown in Figure 4. The boron doping amount in this study was 11,400 ppm, calculated based on the flow rate and vapor pressure of acetone and TMB solution according to the temperature in the experiment. In the Raman analysis, unlike the XRD pattern analysis or morphology analysis through FE-SEM, significant changes due to boron doping were observed. The peak in the 1332 cm\(^{-1}\) region, the diamond characterization peak, disappeared and new peaks were observed. However, regardless of the change in thickness of the BDD film, there was no difference in the Raman results with respect to the deposition time.

For these spectral changes in Raman analysis, Ushizawa [19] and Mortet [20] found that the characteristic peak of diamond observed at 1332 cm\(^{-1}\) changes when boron is doped in diamonds above 400 ppm. It was observed that as the boron doping amount increases, the diamond characterization peak gradually decreases and disappears at 1332 cm\(^{-1}\), which shifts to a lower frequency and becomes broader. In this study, the same phenomenon as the references was observed. As 11,400 ppm of boron was doped, the diamond characterization peak gradually decreased, shifted to a lower frequency, and broadened. This refers to the broad peak found at 1210 cm\(^{-1}\) in Figure 4a,b. The change in the diamond characterization peak due to boron doping is due to impurities and defects due to relaxation of the selection rule of the wave vector due to disturbance [21–24]. Additionally, when boron is doped into the diamond film, a broad peak is observed at 490 cm\(^{-1}\) due to interference between continuous
electron excitation and the central optical phonon in the discontinuous region, as Ushizawa and Mortet noted [21–24]. A broad peak at 490 cm$^{-1}$ was also observed in this study. Therefore, the results of Raman spectra analysis indicated that boron was successfully doped into the diamond film.

In order to analyze and evaluate the electrochemical properties of the deposited BDD film with respect to deposition time, the CV curve was measured using a potentiostat. The potential window, catalytic activity, and electrochemical activation were measured. Figure 5a shows the potential window. The potential window is the range of potential that can neglect the disturbances caused by the reaction of the electrode, solvent, and supporting electrolyte. The value of the potential window is the distance between both ends of the inflection point, that is, the length from the inflection point where the current density starts to increase to the inflection point where the current density starts to decrease [23,25,26]. With the potential window, the particle density and thickness of the electrode are affected. As shown in Figure 5a, the thickness of the BDD film increased as the deposition time increased, and thus the potential window slightly increased. The possibility of using the deposited BDD film as an electrode should be measured by the potential window as well as catalytic activity and electrochemical activation.

The catalytic activity and electrochemical activation measurement results are shown in Figure 5b. The prominent peaks at ~0.35 and ~0.18 V confirm that the catalytic activity and electrochemical activation do not have much effect on the deposition time, which is only affected by the exposed electrode surface [23,25,26]. The catalytic activity and electrochemical activation of BDD films were almost the same with respect to deposition time because the properties of the exposed surfaces were the same with the same amount of boron doping.

COD results are shown in Figure 6a. The initial COD concentration of nonbiodegradable organic contaminants in wastewater was 6500 ppm. To evaluate the organic removal efficiency of the BDD anodes, changes in COD concentration with electrolysis duration of equal volume (900 mL) samples were analyzed using a standard method under a constant voltage of 5 V. For the BDD anode samples, the COD concentrations decreased to 712 and 508 ppm after electrolysis for more than 2 h, with COD removal rates of 89% and 92%, respectively. On the other hand, the IrO$_2$ electrode showed a low removal rate of 47.35% with a COD concentration of 3422 ppm after electrolysis for more than 2 h. As shown in Figure 6b, each BDD sample exhibited the highest degradation rate in the initial 1 h, and the reaction was finished after 2 h. However, in the IrO$_2$ electrode, nonbiodegradable organic contaminant degradation occurred in the initial 90 min, but there was no further degradation after 90 min. This shows that the BDD electrode, which is capable of generating stronger oxidizing agents (OH$^-$, O$_3$) than the IrO$_2$ electrode, can remove more nonbiodegradable organic contaminants.
4. Conclusions

The morphology of the BDD film was not affected by deposition time, whereas the thickness increased with increasing deposition time. The deposition rate of the BDD film did not increase or decrease with deposition time; rather, it remained constant at 100 nm/h. In addition, after boron doping, the diamond film had electrochemical properties that the pure diamond film did not have. As the thickness increased, there was an increase in the potential window. It was confirmed that there was no change in electrochemical activation and catalytic activity. The COD removal rates were almost the same with electrochemical activation and catalytic activity without being affected by the thickness of the BDD film; a high removal rate of 90% on average was observed. This experiment confirms that BDD electrodes would be much more useful for water treatment than the existing electrodes as low-cost production is possible through the reduction of manufacturing cost.

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References
1. Sun, J.R.; Lu, H.Y.; Lin, H.B.; Huang, W.M.; Li, H.D.; Lu, J.; Cui, T. Boron doped diamond electrodes based on porous Ti substrates. Mater. Lett. 2012, 83, 112–114. [CrossRef]
2. Fang, Y.L.; Yin, W.Z.; Jiang, Y.B.; Ge, H.J.; Li, P.; Wu, J.H. Depth treatment of coal-chemical engineering wastewater by a cost-effective sequential heterogeneous Fenton and biodegradation process. Environ. Sci. Pollut. Res. 2018, 25, 13118–13126. [CrossRef]
3. Garcia-Becerra, F.Y.; Ortiz, I. Biodegradation of Emerging Organic Micropollutants in Nonconventional Biological Wastewater Treatment: A Critical Review. Environ. Eng. Sci. 2018, 35, 1012–1036. [CrossRef]
4. Schmalz, V.; Dittmar, T.; Haaken, D.; Worch, E. Electrochemical disinfection of biologically treated wastewater from small treatment systems by using boron-doped diamond (BDD) electrodes—Contribution for direct reuse of domestic wastewater. Water Res. 2009, 43, 5260–5266. [CrossRef]
5. Du, L.L.; Sun, J.R.; Cui, H.; Li, H.D.; Cu, T.; Lin, H.B. Synthesis and Temperature-dependent Electrochemical Properties of Boron-doped Diamond Electrodes on Titanium. *Chem. Res. Chin. U* 2012, 28, 507–510. [CrossRef]

6. Beck, F.; Kaiser, W.; Krohn, H. Boron doped diamond (BDD)-layers on titanium substrates as electrodes in applied electrochemistry. *Electrochim. Acta* 2000, 45, 4691–4695. [CrossRef]

7. Wilson, N.R.; Clewes, S.L.; Newton, M.E.; Unwin, P.R.; Macpherson, J.V. Impact of grain-dependent boron uptake on the electrochemical and electrical properties of polycrystalline boron doped diamond electrodes. *J. Phys. Chem. B* 2006, 110, 5639–5646. [CrossRef]

8. Arevalo, E.; Calmano, W. Studies on electrochemical treatment of wastewater contaminated with organotin compounds. *J. Hazard. Mater.* 2007, 146, 540–545. [CrossRef]

9. Stolte, S.; Abdulkarim, S.; Arning, J.; Blomeyer-Nienstedt, A.K.; Bottin-Weber, U.; Matzke, M.; Ranke, J.; Jastorff, B.; Thoming, J. Primary biodegradation of ionic liquid cations, identification of degradation products of 1-methyl-3-octylimidazolium chloride and electrochemical wastewater treatment of poorly biodegradable compounds. *Green Chem.* 2008, 10, 214–224. [CrossRef]

10. Song, C.W.; Lee, Y.H.; Heo, S.Y.; Hwang, N.M.; Choi, S.; Kim, K.H. Computer Simulation of Temperature Parameter for Diamond Formation by Using Hot-Filament Chemical Vapor Deposition. *Coatings* 2018, 8, 15. [CrossRef]

11. Song, C.W.; Lee, Y.H.; Choi, S.; Hwang, N.M.; Kim, K.H. Temperature Simulation and Diamond Deposition Behavior with Distance Between Filament and Susceptor During Hot-Filament Chemical Vapor Deposition. *Nanosci. Nanotech. Let.* 2018, 10, 761–766. [CrossRef]

12. Zhang, T.; Zou, Y. The Effect of Deposition Parameters on the Growth Rate of Microcrystalline Diamond Powders Synthesized by HFCVD Method. *Coatings* 2017, 7, 95. [CrossRef]

13. Amaral, M.; Silva, D.J.; Fernandes, A.J.S.; Costa, F.M.; Oliveira, F.J.; Silva, R.F. Surface activation pre-treatments for NCD films grown by HFCVD. *Vacuum* 2009, 83, 1228–1232. [CrossRef]

14. Yang, T.M.; Wei, Q.P.; Qi, Y.; Yu, Z.M. The diffusion behavior of carbon in sputtered tungsten film and sintered tungsten block and its effect on diamond nucleation and growth. *Diam. Relat. Mater.* 2015, 52, 49–58. [CrossRef]

15. Yaws, C.L. *The Yaws Handbook of Vapor Pressure: Antoine Coefficients*; Gulf Professional Publishing: Waltham, MA, USA, 2015.

16. Yang, Y.; Yan, M.F.; Zhang, Y.X.; Li, D.Y.; Zhu, Y.D.; Wang, Y.X. Catalytic growth of diamond-like carbon on Fe3C-containing carburized layer through a single-step plasma-assisted carburizing process. *Carbon* 2017, 122, 1–8. [CrossRef]

17. Patsalas, P.; Logothetidis, S. Crystallization effects and diamond formation in amorphous carbon films under low energy ion beam irradiation. *Nucl. Instrum. Methods B* 2001, 178, 247–251. [CrossRef]

18. Polini, R.; D’Antonio, P.; Traversa, E. Diamond nucleation from the gas phase onto cold-worked Co-cemented tungsten carbide. *Diam. Relat. Mater.* 2003, 12, 340–345. [CrossRef]

19. Usui, K.; Watanabe, K.; Ando, T.; Sakaguchi, I.; Nishitani-Gamo, M.; Sato, Y.; Kanda, H. Boron concentration dependence of Raman spectra on {100} and {111} facets of B-doped CVD diamond. *Diam. Relat. Mater.* 1998, 7, 1719–1722. [CrossRef]

20. Mortet, V.; Taylor, A.; Zivcova, Z.V.; Machon, D.; Frank, O.; Hubik, P.; Tremouilles, D.; Kavan, L. Analysis of heavily boron-doped diamond Raman spectrum. *Diam. Relat. Mater.* 2018, 88, 163–166. [CrossRef]

21. Long, H.Y.; Luo, H.; Luo, J.Q.; Xie, Y.N.; Deng, Z.J.; Zhang, X.W.; Wang, Y.J.; Wei, Q.P.; Yu, Z.M. The concentration gradient of boron along the growth direction in boron doped chemical vapor deposited diamond. *Mater. Lett.* 2015, 157, 34–37. [CrossRef]

22. Mortet, V.; Zivcova, Z.V.; Taylor, A.; Frank, O.; Hubik, P.; Tremouilles, D.; Kavan, L. Insight into boron-doped diamond Raman spectra characteristic features. *Carbon* 2017, 115, 279–284. [CrossRef]

23. Liu, Z.L.; Li, H.J.; Li, M.J.; Li, C.P.; Qian, L.R.; Su, L.; Yang, B.H. Preparation of polycrystalline BDD/Ta electrodes for electrochemical oxidation of organic matter. *Electrochim. Acta* 2018, 290, 109–117. [CrossRef]

24. Song, C.W.; Jin, R.; Hwang, N.M.; Kim, K.H. Deposition Behavior of Boron-Doped Diamond with Varying Amount of Acetone by Hot Filament Chemical Vapor Deposition. *Electron. Mater. Lett.* 2019, 15, 630–638. [CrossRef]
25. Son, M.J.; Zhang, T.F.; Jo, Y.J.; Kim, K.H. Enhanced electrochemical properties of the DLC films with an arc interlayer, nitrogen doping and annealing. *Surf. Coat. Technol.* 2017, 329, 77–85. [CrossRef]

26. Jo, Y.J.; Zhang, T.F.; Son, M.J.; Kim, K.H. Synthesis and electrochemical properties of Ti-doped DLC films by a hybrid PVD/PECVD process. *Appl. Surf. Sci.* 2018, 433, 1184–1191. [CrossRef]

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