

Investigation of diamond coatings on titanium substrates for electrochemical applications

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Abstract

Diamond coated titanium electrodes show outstanding properties in alkaline electrolytes as they are corrosion resistant by forming stable TiO_2 layers. This quality is of decisive importance for this kind of application. Boron doped diamond layers were deposited on Ti sheets by the hot-filament method, using Triethylboron ($\text{B}(\text{C}_2\text{H}_5)_3$) as a boron source to produce electrodes for electrochemical applications. Ratios of $\text{B}(\text{C}_2\text{H}_5)_3:\text{CH}_4$ were varied between 0 and 10 000 ppm and silicon was used as a reference material. Diamond growth on metallic titanium is preceded by the formation of an intermediate TiC layer, which ensures a good electrical connection between the Ti substrate and the diamond but leads to poor adhesion of the layers. Additionally, boron influences the interlayer formation due to the formation of borides or carbo-borides. Correlations between diamond layer adhesion and boron addition during diamond deposition can be shown. To examine the electrochemical properties of diamond layers with various morphologies, cyclic voltammetry measurements were carried out in different solutions (0.1 N H_2SO_4 , 6 N NaOH). Thereby large potential windows up to 4.7 V could be observed. It could be shown that boron has a positive influence on diamond deposition on Ti substrates in terms of better adhesion corresponding with a very large potential window in acid as well as basic solutions.

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1. Introduction

As already shown in previous works [1–3] the doping of diamond with boron can be done easily and has been thoroughly investigated. It could be shown that boron incorporation mainly occurs in the (111) growth sectors [4–6] which appear lighter in SEM pictures than the (100) facets. Furthermore the Raman peak at 1332 cm^{-1} vanishes at (111) facets whereas it still occurs at (100) facets, which contain less boron.

In recent years, diamond has become a more and more interesting topic in the field of electrochemistry, which has led to thorough investigations in this area [7–9]. Boron-doped diamond (p-type conductor) shows high electrical conductivity, high chemical inertness and good electrochemical properties such as a high overpotential for oxygen and hydrogen evolution, and, there-

fore it is a promising electrode for industrial wastewater treatment. The potential window of such electrodes is larger than that of conventional electrodes and can reach 2.4–3.4 V. DiaChem[®] electrodes showed an overvoltage of 2.8 V towards oxygen evolution and –1.3 V towards hydrogen evolution in acid solutions [10].

As these electrodes are used under very harsh and rough conditions, which also put high demands on the substrate, titanium turns out to be an interesting material, which has the ability to passivate in alkaline solutions by forming TiO_2 . The different thermal expansion coefficients of the two materials used (diamond: $0.84 \times 10^{-6}\text{ C}^{-1}$, Ti: $8.50 \times 10^{-6}\text{ C}^{-1}$, TiC: $7.42 \times 10^{-6}\text{ C}^{-1}$), however, cause high shearing stress at the interface and this leads to a poor adhesion of the diamond layers on the substrate.

The main aim of this work was to find out in how far the different deposition parameters have an influence on nucleation, growth and quality of the deposited diamond layers and their adhesion on the substrate.

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Table 1
Experimental conditions for diamond deposition

T_{Fil} : filament temperature (°C)	2300–2500
T_{Sub} : substrate temperature (°C)	700–880
Filament to substrate distance (mm)	20
Methane concentration CH_4/H_2 (%)	1–3
B/C ratio (ppm)	0–10 000
Total gas flow rate (sccm)	500
Deposition pressure (mbar)	20
Deposition time (h)	3 and 15

2. Experimental details

Diamond deposition experiments were carried out in a *hot-filament CVD reactor* [11,12]. A tantalum wire (0.8 mm wire diameter) was used as a filament and the filament temperature was measured with a two-colour pyrometer (IRCON Mirage OR15). Prior to diamond deposition the filament was carburised for 2 h under deposition conditions, which are summarized in Table 1.

The *reaction gases* used were hydrogen (H_2) and methane (CH_4). Triethylboron ($\text{B}(\text{C}_2\text{H}_5)_3$, vapour pressure at -10°C : 9.74 mbar) was used for boron addition, whereby a supporting H_2 flow was saturated with $\text{B}(\text{C}_2\text{H}_5)_3$ and added to the reaction gas mixture (pressure in the evaporator: 1466 mbar; condenser temperature: -10°C). The amount of boron was calculated.

The *substrates* were placed on a molybdenum substrate holder 20 mm below the filament. Diamond films were deposited on titanium and silicon substrates of 12×25 mm size. The silicon substrates functioned as reference samples and were always coated together with a Ti substrate. The substrate surface temperature was measured with a Ni–(Cr–Ni) thermocouple positioned 0.1 mm below the surface of the substrate holder. Prior to diamond deposition the substrates were scratched for diamond nucleation enhancement using a $0.25\ \mu\text{m}$ diamond suspension.

The *diamond growth rates* were calculated from the weight differences of the substrates before and after deposition. Concerning the Ti substrates difficulties occurred because of the formation of an intermediate TiC layer, which is responsible for the poor adhesion and splitting off of the diamond layers. Therefore Si substrates were used as reference samples to specify growth rates.

Diamond layer morphologies were determined by scanning electron microscopy (SEM) and Raman Spectroscopy was used to measure the film quality and phase purity.

Cyclo voltammetric measurements were carried out to determine the electrochemical properties of the boron doped diamond layers. A three electrode set-up was used, whereby the diamond sample was used as a

working electrode. Ohmic back contacts were made by rubbing an abrasive paper on part of the backside of the Ti substrates. For the working electrode a special cell was constructed to make sure that only a defined area ($0.25\ \text{cm}^2$) of the diamond layer was in contact with the electrolyte. For contacting the diamond layer a stainless steel bar was fixed at the backside of the sample. A platinum electrode served as a counter electrode and a SMSE was used as a reference electrode. $0.1\ \text{N}\ \text{H}_2\text{SO}_4$ and $6\ \text{N}\ \text{NaOH}$ were used as electrolytes. The potential window was determined by the difference of the electrode potentials at hydrogen and oxygen evolution conditions, at a current density of $5\ \text{mA}\ \text{cm}^{-2}$. This current density was chosen because this point still lies within the exponential part of the current–voltage characteristic. A higher value would be influenced by the ohmic drop.

3. Results and discussion

Different amounts of Triethylboron ($\text{B}(\text{C}_2\text{H}_5)_3$) were added to the reaction gas to study the influence of boron on the diamond nucleation and growth on Ti substrates. For all deposition parameters experiments were carried out with and without the addition of boron and two deposition times (3 and 15 h).

3.1. Diamond nucleation and growth

In general diamond nucleation on titanium is delayed because of the previous TiC layer formation. The diffusion of the carbon atoms into the substrate (carbide formation) is a competitive reaction to the diamond nucleation. Only after the saturation of the surface and after the carbide layer has a certain thickness, the carbon atoms form clusters and diamond can nucleate [13,14].

By variation of the boron concentration the influence of boron on the nucleation could be determined. With increasing boron addition more nucleation crystals can be found in comparison to experiments without boron. It is interesting that a maximum of nucleation crystals can be found at a boron addition of 6000 ppm B/C. This maximum increases with higher temperature (Fig. 1).

After diamond nucleation the individual crystals grow to form clusters and finally diamond layers [15]. Once again diamond layer formation is favoured through boron addition.

As already mentioned problems occur with regard to growth rates. As the weight difference consists of the weight increase of the diamond as well as of the formed TiC-layer, whose thickness was impossible to calculate, as this layer is very porous, it was only possible to clarify the absolute weight increase of the samples. Furthermore, it was quite inaccurate as many layers on Ti substrates showed poor adhesion and sometimes split

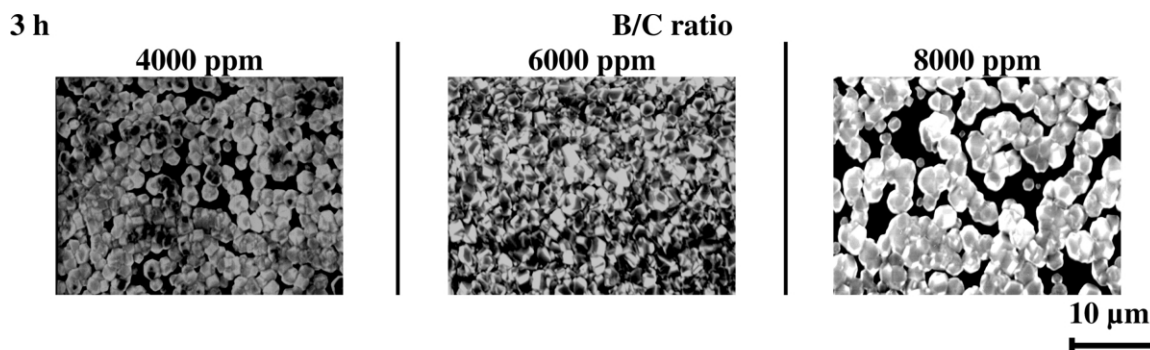


Fig. 1. Diamond nucleation crystals after 3 h deposition varying the boron concentration ($T_{\text{Fil}}=2400\text{ }^{\circ}\text{C}$, $T_{\text{Sub}}=800\text{ }^{\circ}\text{C}$, $\text{CH}_4/\text{H}_2=1\%$, $\text{H}_2=500\text{ sccm}$, 20 mbar, 20 mm, 3 h).

off the substrate. Statements are only possible through the reference samples on Si substrates.

After diamond deposition a slight weight decrease with increasing boron addition can be observed, only at very high temperatures ($T_{\text{Fil}}=2500\text{ }^{\circ}\text{C}$) a weight increase was observed. In general with increasing temperature the weight of the samples increases.

As boron prefers the incorporation into (111) facets to (100) facets, the (111) morphology is preferred with increasing boron addition [1,16]. So diamond growth in (111) orientation is favoured.

In diamond layers without boron addition or only low boron concentrations (111) and (100) facets appear together. With increasing boron concentration more (111) facets can be found. This different incorporation of boron and the different layer orientations can be seen well in SEM pictures (Fig. 2). (111) facets appear darker than (100) ones in SEM. From 6000 ppm B/C onwards the preferred boron incorporation into (111) growth regions seems to have reached saturation and boron is incorporated homogeneously.

To gain information about the influence of methane on the layer growth the methane concentration was varied at a constant boron concentration. The concentration of 6000 ppm B/C was chosen as good results could be reached at this specific concentration in regard to morphology and layer adhesion. Concerning the growth rate a maximum could be observed at 2% CH_4/H_2 on Ti substrates as well as on the Si substrates (Fig. 3). Once again there is poor adhesion of the diamond layers on the Ti substrates. These samples are marked in the figure. The calculated growth rates are shown in Fig. 4. The samples of 15 h depositions also show this maximum at 2% CH_4/H_2 (1.54 $\mu\text{m}/\text{h}$) whereas concerning the diamond nucleation (3 h) this maximum is not so significant.

By variation of the methane concentration an impairment of the diamond quality could be observed (Fig. 5), which can also be seen in the Raman spectra (Fig. 6). The diamond phase purity declines as the share of

amorphous and graphitic parts increases with increasing methane concentration. At a methane concentration of 2.5% the diamond deposition reaches a limit. Above this concentration no diamond deposition could be done anymore. Each time the filament was coated with a carbon layer after deposition and its activity was disparaged [15]. The ability of the dissociation of the hydrogen is reduced and leads to a lesser etching effect.

By variation of the methane concentration the morphology of the deposited diamond layers varies from (111) facets via (100) facets to Ballas [17].

At high methane concentrations spicular depositions are observed, which could not be identified (Fig. 5). Similar structures were ascribed to graphite formation in [18]. In the Raman measurements carried out graphitic features can be observed (Fig. 6). Through thermodynamic calculations Bohr [19] assumes that the formation of B_4C is probable.

3.2. TiC-formation and diamond layer adhesion

Titanium is an active carbide forming element and, therefore has great influence on diamond deposition [13,20]. Prior to diamond deposition a TiC interlayer is formed, which leads to poor adhesion of the layers caused by the different dilatation coefficient. The TiC-layer is of rough and porous nature and tends to split off easily.

The formation of this interlayer is certainly influenced by boron addition. It could be shown that an increasing boron concentration leads to a better adhesion of the layers on the substrates. Therefore, it can be assumed that boron influences this interlayer probably by inhibiting the TiC formation. However, formation of TiB could not be verified. Through calculations—considering the thickness of the diamond layer and the absolute weight increase—the decrease of the TiC interlayer could be determined. With the help of SEM pictures the grain size of the diamond could be estimated.

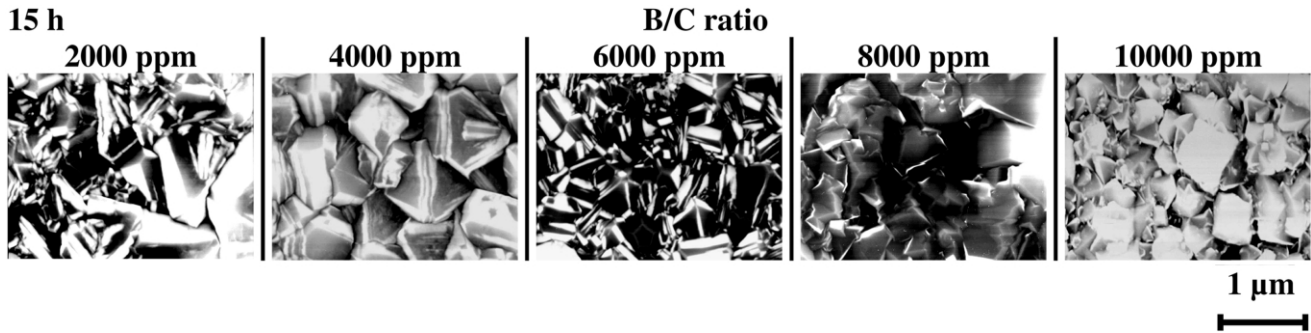


Fig. 2. Diamond layers after 15 h deposition varying the boron concentration between 2000 and 10 000 ppm B/C ($T_{\text{Fil}} = 2400^\circ\text{C}$, $T_{\text{Sub}} = 800^\circ\text{C}$, $\text{CH}_4/\text{H}_2 = 1\%$, $\text{H}_2 = 500$ sccm, 20 mbar, 20 mm, 15 h).

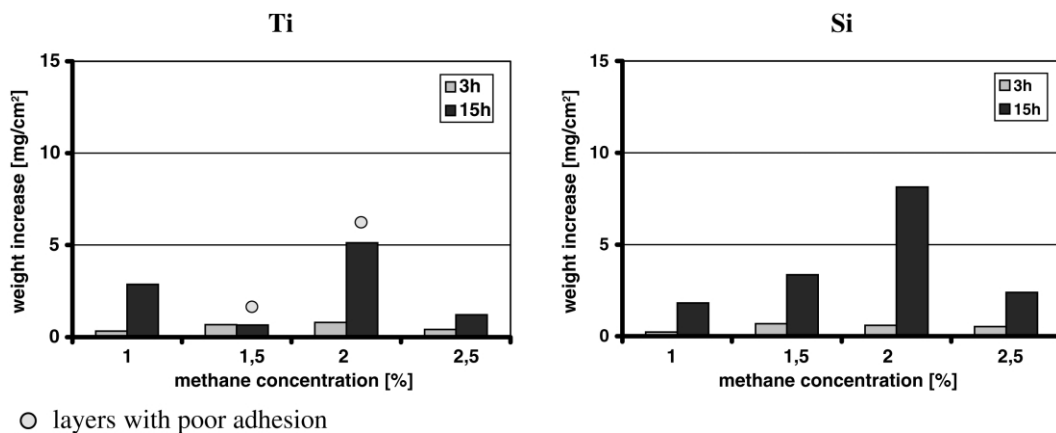


Fig. 3. Weight increase of boron doped diamond layers on different substrates varying the methane concentration at a constant boron concentration (6000 ppm B/C) ($T_{\text{Fil}} = 2400^\circ\text{C}$, $T_{\text{Sub}} = 800^\circ\text{C}$, B/C = 6000 ppm, $\text{H}_2 = 500$ sccm, 20 mbar, 20 mm, 15 h).

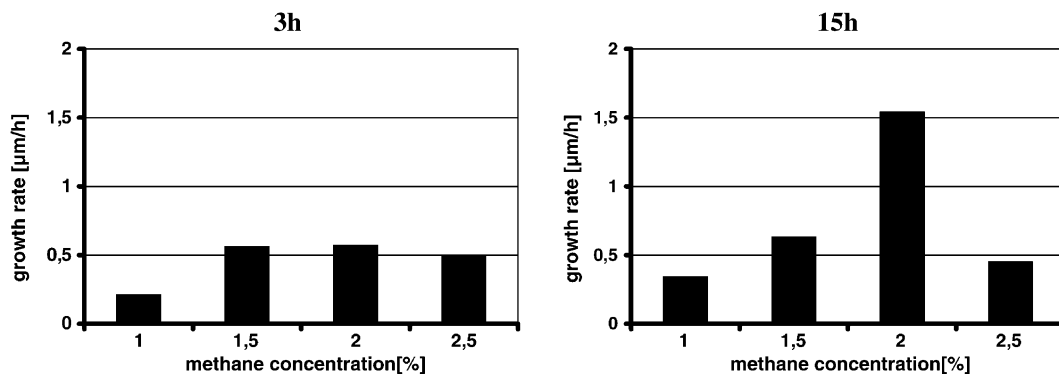


Fig. 4. Growth rates of deposited layers on Si substrates varying the methane concentration ($T_{\text{Fil}} = 2400^\circ\text{C}$, $T_{\text{Sub}} = 800^\circ\text{C}$, B/C = 6000 ppm, $\text{H}_2 = 500$ sccm, 20 mbar, 20 mm, 15 h).

As mentioned before TiC has a different dilatation coefficient than diamond and titanium. Under certain deposition conditions a deformation of the Ti substrate could be observed (Fig. 7). It is quite interesting that this deformation is particularly striking at 2000 and 4000 ppm B/C. The reason for this phenomenon is certainly the formed interlayer, which expands by heat-

ing and afterwards contracts by cooling down. With increasing substrate temperature this deformation increases. Through the addition of boron an improvement concerning this deformation can be reached. With higher boron concentrations the deformation vanishes.

It could be shown that boron has an influence on diamond deposition on titanium substrates. It seems to

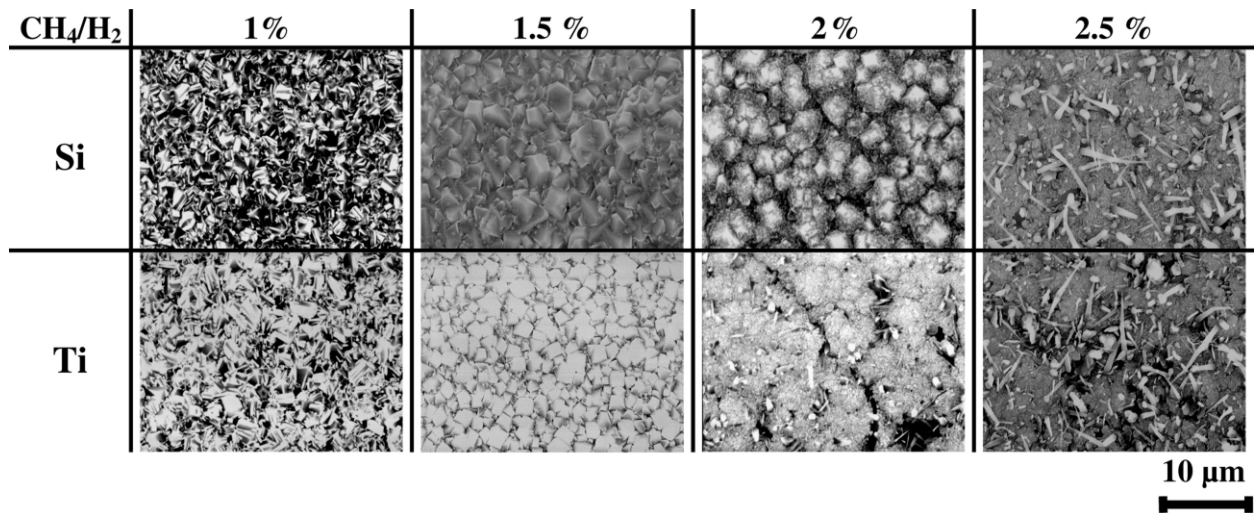


Fig. 5. Deposition results for 15 h experiments varying the methane concentration at a constant boron concentration of 6000 ppm B/C ($T_{\text{Fil}} = 2400^\circ\text{C}$, $T_{\text{Sub}} = 800^\circ\text{C}$, B/C = 6000 ppm, $\text{H}_2 = 500$ sccm, 20 mbar, 20 mm, 15 h).

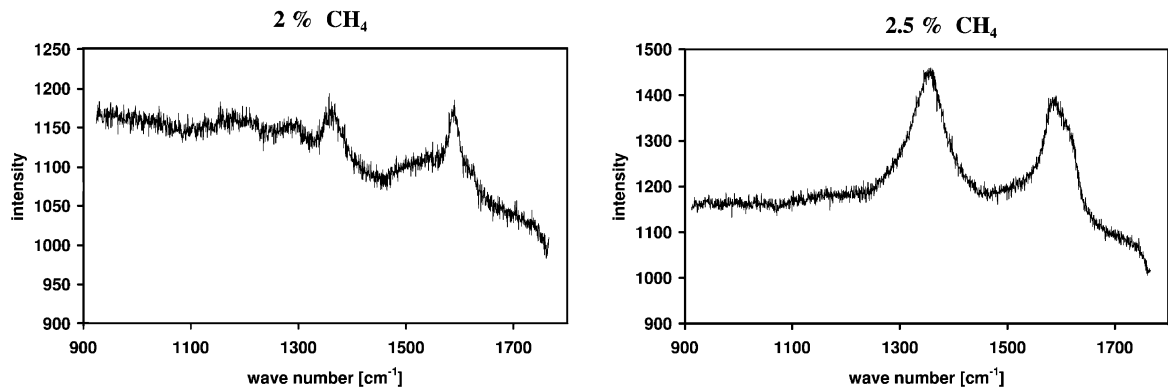


Fig. 6. Raman spectra of diamond layers with varied methane concentration at a constant boron concentration of 6000 ppm B/C ($T_{\text{Fil}} = 2400^\circ\text{C}$, $T_{\text{Sub}} = 800^\circ\text{C}$, B/C = 6000 ppm, $\text{H}_2 = 500$ sccm, 20 mbar, 20 mm, 15 h).

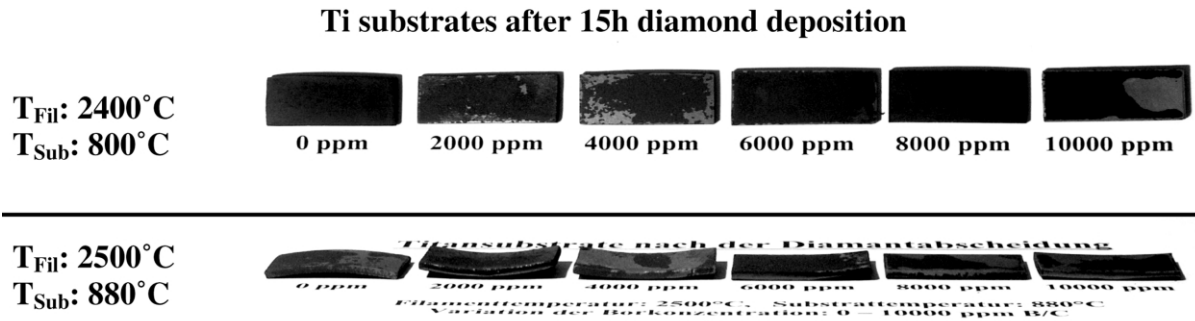


Fig. 7. Deformation of the Ti substrates after diamond deposition with various boron concentrations ($\text{CH}_4/\text{H}_2 = 1\%$, $\text{H}_2 = 500$ sccm, 20 mbar, 20 mm).

improve the adhesion as well as the deposition of diamond on titanium.

3.3. Electrochemical measurements

For the electrochemical measurements layers with a thickness between 3 and 5 μm were used. These

diamond coatings showed no pinholes in SEM investigations, furthermore the electrochemical measurements showed no interactions with the Ti-substrate. To gain information about the electrical conductivity of the electrodes some preliminary measurements were carried out. The lateral specific electrical conductivity of the Ti

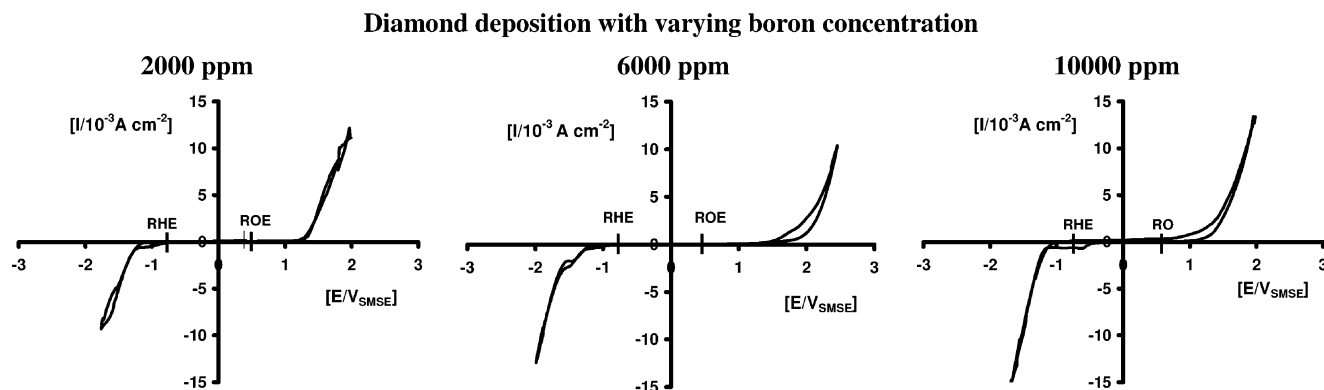


Fig. 8. Cyclic voltammograms of different boron doped diamond layers on Ti substrates in 0.1 N H_2SO_4 ($T_{\text{Fil}}=2400\text{ }^\circ\text{C}$, $T_{\text{Sub}}=800\text{ }^\circ\text{C}$, $\text{CH}_4/\text{H}_2=1\%$, $\text{H}_2=500\text{ sccm}$, 20 mbar, 20 mm, 15 h) vs. SMSE.

electrodes coated with boron doped diamond was between 900 and $25\,000\text{ }\Omega^{-1}\text{ cm}^{-1}$.

The potential windows of the boron doped diamond layers were determined in acid and basic solutions through cyclo-voltammetric measurements.

It could be shown that Ti passivates in acid as well as in basic solutions and, therefore it is a good and resistant electrode material. The formed interlayer TiC is also an important reason for the successful fabrication of these diamond electrodes as it ensures a good electric connection between the diamond and the substrate.

3.3.1. Measurements with diamond layers of different morphology

Diamond layers with different boron concentrations were measured in 0.1 N H_2SO_4 . Typical cyclic voltammograms can be seen in Fig. 8. As no other substances are in the solution, which could be electrochemically converted between these potentials, the observed current corresponds to the evolution of hydrogen or oxygen or the formation and consumption of hydrogen or oxygen surface layers. If the hydrogen or oxygen potential is reached the cathodic, respectively, anodic current increases. It could be shown that various boron concentrations have an influence on the width of the potential window.

By varying the methane concentration at a constant boron concentration (6000 ppm B/C) diamond layers with different morphologies were deposited. Therefore the influence of different morphologies ((111) and (100) faceted layers) on the size of the potential window could be determined.

As boron is preferably incorporated into (111) facets, these layers show good electric conductivity. Through increasing methane concentration the formation of facets gets worse as there is a lesser amount of hydrogen in the gas phase, which etches the graphitic depositions. Therefore the formation of (100) facets and Ballas is

favoured. The size of the potential window gets smaller with increasing methane concentration (Fig. 9).

3.3.2. Measurements in various electrolytes

Boron doped diamond layers were measured in different solutions. On the one hand, measurements were carried out in acid solutions, 0.1 N H_2SO_4 , on the other hand in basic ones, 6 N NaOH.

In basic solutions the potential window is shifted to the negative because of the pH-dependence of the RHE (reversible hydrogen electrode).

The potential windows of the different boron doped diamond layers on Ti substrates show an increase in size with increasing boron concentration and reach a maximum at a concentration of 6000 ppm B/C (at 5 mA/cm^2 : $\Delta E=4.2\text{ V}$) (Fig. 10). Above 6000 ppm B/C the size of the potential window gets smaller. At 6000 ppm B/C there can also be found the largest potential window in basic solutions. In general larger potential windows are found in basic solutions than in acid ones.

The changing of the potential windows in regard to various boron concentrations in different solutions can be seen in Fig. 11.

4. Conclusion

Titanium electrode material is of high interest because of its passivation and corrosion resistance. Due to these properties the electrochemical properties of the diamond layers are not influenced in case of defects or pores in the diamond coatings.

The results from this research show clearly, that diamond growth and layer adhesion on titanium electrodes is influenced by the boron concentration during deposition. This effect can be observed without special methods for surface treatments, which makes it interesting for industrial electrode applications.

Diamond deposition on titanium substrates by the hot-filament method was studied for various boron additions

diamond deposition with varying methane concentration

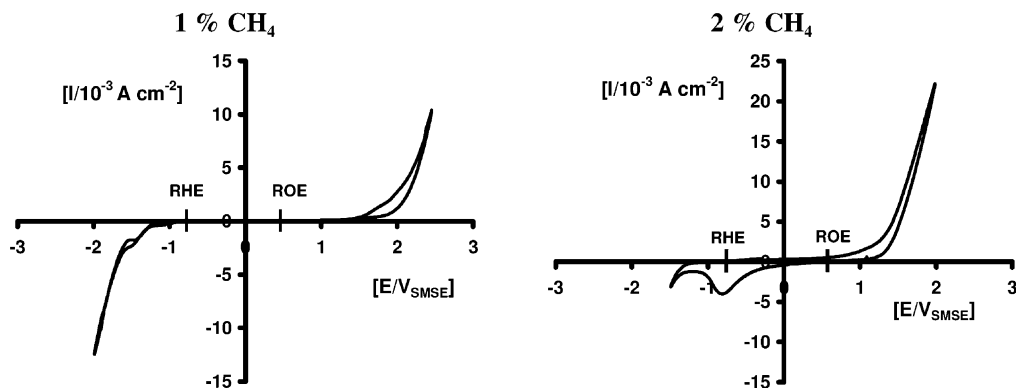


Fig. 9. Cyclic voltammograms of boron doped diamond layers in 0.1 N H_2SO_4 (B/C 6000 ppm) varying the methane concentration ($T_{\text{Fil}} = 2400$ °C, $T_{\text{Sub}} = 800$ °C, $\text{H}_2 = 500$ sccm, B/C = 6000 ppm, 20 mbar, 20 mm, 15 h) vs. SMSE.

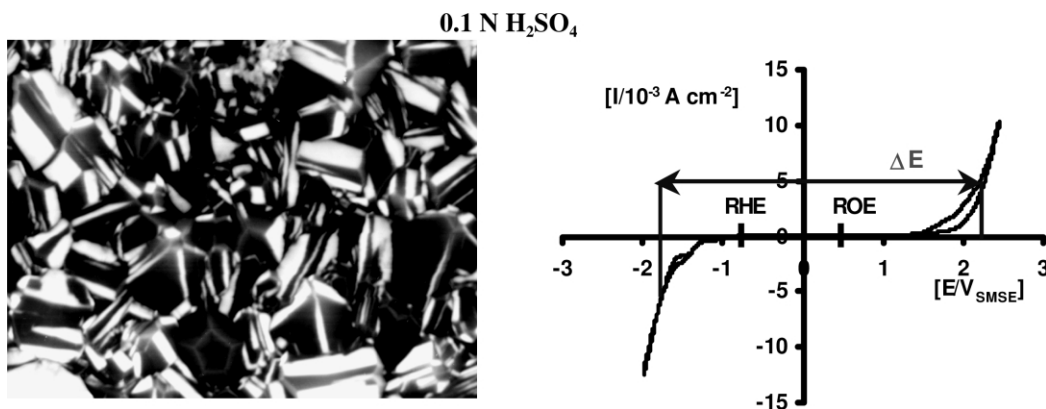


Fig. 10. Diamond layer with the largest measured potential window (4.1 V) at a boron concentration of 6000 ppm B/C ($T_{\text{Fil}} = 2400$ °C, $T_{\text{Sub}} = 800$ °C, $\text{CH}_4/\text{H}_2 = 1\%$, $\text{H}_2 = 500$ sccm, 20 mbar, 20 mm, 15 h) vs. SMSE.

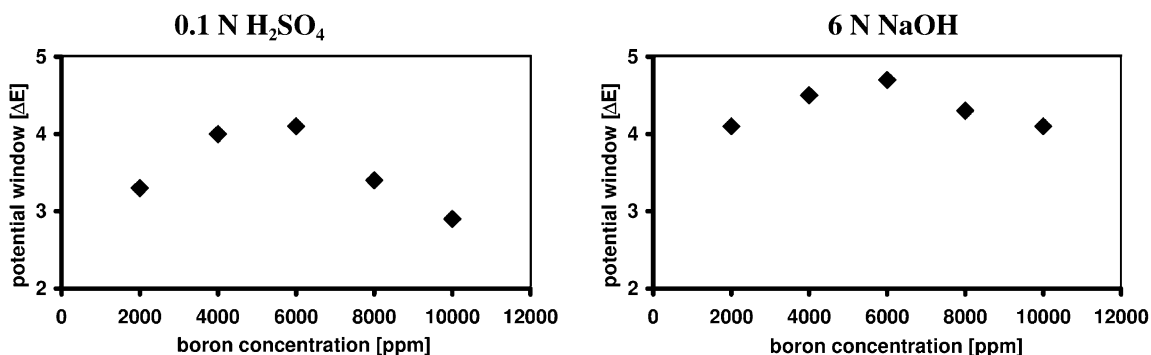


Fig. 11. Comparison of potential windows of different boron doped diamond layers in various solutions ($T_{\text{Fil}} = 2400$ °C, $T_{\text{Sub}} = 800$ °C, $\text{CH}_4/\text{H}_2 = 1\%$, $\text{H}_2 = 500$ sccm, 20 mbar, 20 mm, 15 h) vs. SMSE.

between 0 and 10 000 ppm B/C. As the Ti substrate shows an interaction with the carbon of the gas phase the diamond deposition is influenced negatively. Diamond nucleation is delayed and the adhesion of the formed layers is poor, which is partly due to the occurring deformation of the substrates but also to the

different thermal expansion coefficients of the different materials.

The addition of $\text{B}(\text{C}_2\text{H}_5)_3$ to the gas phase has an positive influence on the diamond deposition process. It could be shown that through boron addition the diamond nucleation and growth as well as the adhesion of the

diamond layers on the substrates were improved. A maximum in adhesion as well as in the potential window was observed at 6000 ppm B/C.

At a boron concentration of 6000 ppm B/C the methane concentration was varied to gain information about different morphologies. It could be shown that the diamond phase quality deteriorates with increasing methane concentration. At high methane concentration (> 2%) spicular depositions, which could be identified as graphitic depositions by the Raman measurements, were observed. Diamond deposition is no longer possible above this concentration.

Boron doped diamond layers show good electrochemical properties. Large potential windows could be reached in acid as well as in basic solutions. The best results could be achieved at doping concentrations of 6000 ppm B/C. Potential windows of 4.1 V in acid and 4.7 V in basic solutions could be found. Due to the pH dependency of the RHE the potential window is shifted to negative values in basic solutions.

By variation of the morphology of the diamond layers caused by different methane concentrations—via (100) facets to Ballas—the electrochemical properties get worse and potential windows of only 3.0 V in acid and 3.6 V in basic solutions are found.

Acknowledgments

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