

Impedance studies of boron-doped CVD diamond electrodes

Matthew N. Latto, D. Jason Riley *, Paul W. May

School of Chemistry, University of Bristol, Cantock's Close, Bristol BS8 1TS, UK

Abstract

The mechanism of electron transfer across the boron-doped diamond electrode/electrolyte interface is investigated using impedance spectroscopy. At an oxygenated electrode surface, two time constants are observed in the impedance plots. The results are discussed in terms of surface-state-mediated electron transfer. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Boron doping; CVD; Electrode; Polycrystalline diamond

1. Introduction

The advent of cheap methods of preparing diamond using chemical vapour deposition (CVD) technology has resulted in a booming interest in the properties and uses of polycrystalline diamond films [1]. An area in which CVD diamond films are generating particular enthusiasm is electrochemistry [2]. It has been demonstrated that, as a result of very low catalytic activity for hydrogen and oxygen evolution, diamond electrodes in aqueous electrolytes possess a larger potential window than many alternative electrode materials [3]. It has, therefore, been suggested that diamond electrodes may prove useful in electrosynthesis [4,5] and electroanalytical reactions [6]. A second advantage of electrodes prepared from diamond is that they may be used in harsh environments, as they possess high mechanical strength and low chemical activity. Indeed, the benefit of diamond electrodes in sonoelectrochemical experiments has already been demonstrated [7].

Despite the growing interest in diamond electrochemistry, limited work on the mechanism of electron transfer across the electrode/electrolyte interface has been published. Most studies of diamond electrodes have focused on highly or moderately doped material for which direct electron transfer across a narrow space-charge region may occur. To gain a deeper understanding of the charge-transfer mechanism we have undertaken alternat-

ing-current (AC) impedance studies of moderately doped polycrystalline diamond electrodes grown by hot-filament CVD. This paper reports the results of our studies and a possible mechanism of electron transfer is discussed.

2. Experimental

A continuous diamond film was deposited on a 3 cm² silicon (100) wafer substrate by hot-filament CVD. The substrate was abraded manually with 1–3 μm diamond grit and then ultrasonically cleaned in 2-propan-ol. Two 0.25 mm diameter, 10-turn tantalum coils, in series, were used as filaments. The film was grown at a pressure of 20 torr with a total gas flow of 200 sccm. A hydrogen/methane/diborane gas mixture was used, with methane and diborane concentrations of 0.7% and 0.001% by volume, respectively. This boron concentration corresponds to a dopant density of the order of 10²⁰ cm⁻³. The deposition time was 9.7 h, giving a film thickness of approximately 4 μm. The film was cooled in a hydrogen atmosphere.

Prior to electrochemical studies the diamond electrodes were immersed in a chromic acid solution in order to obtain an oxygen-terminated surface. It was noted that this procedure resulted in a considerable reduction in the surface conductivity of the film. It has been postulated that the change in conductivity with surface termination results from a change in band bend-

* Corresponding author. Tel.: +44-117-928-7668;
Fax: +44-117-925-1295.

E-mail address: jason.riley@bristol.ac.uk (D.J. Riley)

ing, with a pinned surface level at $E_v = 1.7$ eV in oxygenated samples [8].

Electrochemical experiments were performed in two different nitrogen-purged solutions: $0.5 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ and $0.5 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4/0.01 \text{ mol dm}^{-3} \text{ Fe}(\text{SO}_4)/0.005 \text{ mol dm}^{-3} \text{ Fe}_2(\text{SO}_4)_3$. A three-electrode system was used — a diamond working electrode, a platinum gauze counter electrode and a silver/silver chloride reference electrode. All potentials are reported relative to the silver/silver chloride reference electrode. The diamond electrode was mounted in the cell such that 0.3 cm^2 of the diamond surface was exposed to electrolyte. Impedance measurements were performed with a Solartron 1286 potentiostat and a Solartron 1250 Frequency Response Analyser; the instruments were controlled using Z-plot software. The amplitude of the AC potential modulation was 5 mV in all the experiments.

3. Results and discussion

Fig. 1 shows Mott–Schottky plots, recorded at different frequencies, for an as-prepared diamond electrode immersed in an indifferent electrolyte. The plots are linear over a potential range of -0.2 V to 0.3 V and have a common intercept at 1.7 V. This points to a more positive flatband potential for an oxygen-terminated surface than that reported for hydrogen-terminated diamond, a result consistent with the change in polarisation of the surface bond. It is noted that, although Mott–Schottky theory suggests that a plot of $1/C^2$ against applied potential should be independent of the measuring frequency, such results are infrequently observed for semiconductor electrodes. Surface roughness, dielectric relaxation and impedance across the sample surface have all been advanced as possible explanations for frequency dispersion in Mott–Schottky plots [9].

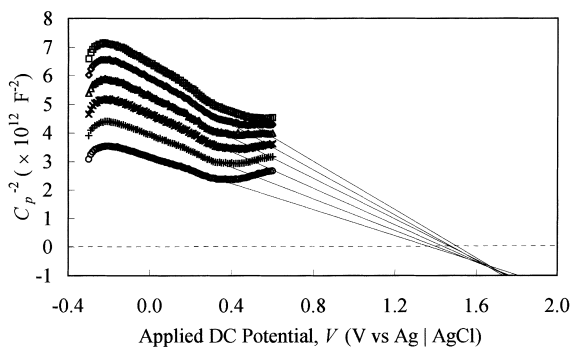


Fig. 1. Mott–Schottky plots recorded at frequencies of 315 Hz (\square), 280 Hz (\diamond), 245 Hz (\triangle), 210 Hz (\times), 175 Hz ($+$) and 140 Hz (\circ) in an aqueous solution of $0.5 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$. Straight-line fits are shown for the region from -0.2 V to 0.3 V.

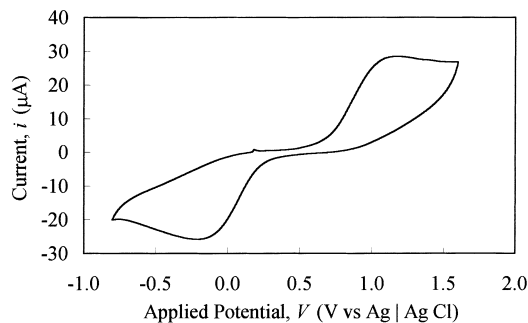


Fig. 2. A cyclic voltammogram for the diamond electrode in an aqueous solution of $0.5 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4/0.01 \text{ mol dm}^{-3} \text{ Fe}(\text{SO}_4)/0.005 \text{ mol dm}^{-3} \text{ Fe}_2(\text{SO}_4)_3$. The scan rate was 50 mV s^{-1} .

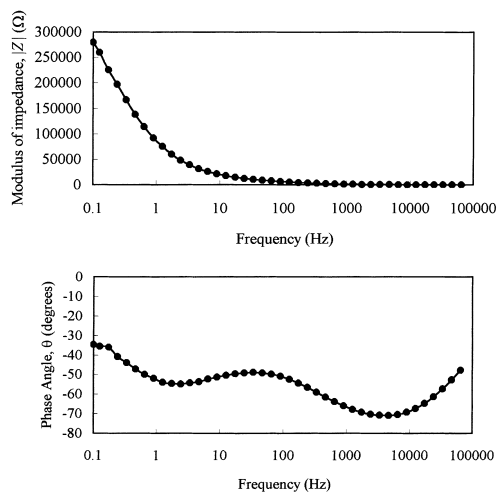


Fig. 3. Plots of the modulus (upper graph) and phase angle (lower graph) of the electrochemical impedance against frequency in an aqueous solution of $0.5 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4/0.01 \text{ mol dm}^{-3} \text{ Fe}(\text{SO}_4)/0.005 \text{ mol dm}^{-3} \text{ Fe}_2(\text{SO}_4)_3$.

A cyclic voltammogram of the electrode immersed in a solution containing $0.01 \text{ mol dm}^{-3} \text{ Fe}^{2+}/0.01 \text{ mol dm}^{-3} \text{ Fe}^{3+}$ is shown in Fig. 2. The kinetics appear to be irreversible for this classic outer-sphere electron-transfer system. To gain further information on the mechanism of charge transfer at the electrode/electrolyte interface, the impedance was recorded at a range of potentials. Fig. 3 displays plots of the electrochemical impedance at 0.4 V, near the open-circuit potential. At high over-potential the response shows an RC peak at high frequencies and a diffusional Warburg element at low frequencies; indeed, the data may be fitted using the classic Randles equivalent circuit. More interestingly, at the potential shown, two time constants are observed for the redox reaction, suggesting that the electron transfer does not occur via direct injection but in a two-step process. The results point to a surface-state-mediated electron-transfer process. Such a model has been proposed by van de Lagemaat for the electron-transfer process at single-crystal boron-doped diamond electrodes [10–12].

The results of capacitance–voltage and current–voltage studies of Metal-Insulator-Semiconductor (MIS) diodes formed on oxygenated diamond indicate that, at an oxygen-terminated diamond surface, the Fermi level is pinned at approximately 1.7 eV above the valence band [13,14]. The flatband potential of 1.7 V obtained in these studies for the electrode immersed in 0.5 mol dm⁻³ H₂SO₄ would suggest that the surface states lie at approximately -0.5 V on the silver/silver chloride potential scale. This corresponds closely to the region in which electron transfer to the redox couple is observed, and supports the surface-state-mediated electron-transfer model. Further evidence for a surface-state-mediated process is the fact that cyclic voltammetry studies of the ferri/ferrocyanide redox couple at a diamond surface, performed by ourselves and other groups [15], indicate that pretreatment of the electrode with oxidising acid solutions results in a more facile electron transfer. The importance of surface termination is further demonstrated in a recent paper by Yagi et al. [16], in which it is reported that treatment of a diamond electrode in an oxygen plasma results in a change in the rate of electron transfer.

4. Conclusions

The results obtained in this study indicate that the surface termination of boron-doped diamond electrodes is an important factor in the electrode kinetics. For oxygenated polycrystalline diamond electrodes, two time constants were observed in impedance studies of a simple redox reaction. The result suggests that the electron-transfer process is mediated by surface states, in agreement with a model proposed by van de Lagemaat

[10] in single-crystal studies. Modelling of the impedance data obtained in the experiments is in progress.

Acknowledgements

The support of the EPSRC is gratefully acknowledged, and P.W.M. would like to thank the Royal Society for their financial support.

References

- [1] B. Dischler, C. Wild (Eds.), *Low-Pressure Synthetic Diamond Manufacturing and Applications*, Springer Series in Materials Processing, Springer-Verlag, Berlin/Heidelberg, 1998.
- [2] G.M. Swain, in: *Advanced Materials '97: Topics in Diamond and c-BN Research: Proceedings of the 4th NIRIM International Symposium on Advanced Materials (ISAM '97)*, Tsukuba, Japan (1997) 59–64.
- [3] H.B. Martin, A. Argoitia, U. Landau, A.B. Anderson, J.C. Angus, *J. Electrochem. Soc.* 143 (1996) L133.
- [4] R. Tenne, K. Patel, K. Hashimoto, A. Fujishima, *J. Electroanal. Chem.* 347 (1993) 409.
- [5] N. Katsuki, S. Wakita, Y. Nishiki, T. Shimamune, Y. Akiba, M. Iida, *Jpn. J. Appl. Phys.* 36 (1997) L260.
- [6] J.S. Xu, M.C. Granger, Q.Y. Chen, J.W. Strojek, T.E. Lister, G.M. Swain, *Anal. Chem.* 69 (1997) 591A.
- [7] C.H. Goeting, J.S. Foord, F. Marken, R.G. Compton, *Diamond Relat. Mater.* 8 (1999) 824.
- [8] J. Shirafuji, T. Sugino, *Diamond Relat. Mater.* 5 (1996) 706.
- [9] W.P. Gomes, F. Cardon, *Progr. Surf. Sci.* 12 (1982) 155.
- [10] J. van de Lagemaat, D. Vanmaekelbergh, J.J. Kelly, *J. Electroanal. Chem.* 475 (1999) 139–151.
- [11] D. Vanmaekelbergh, *Electrochim. Acta* 42 (1997) 1121.
- [12] D. Vanmaekelbergh, *Electrochim. Acta* 42 (1997) 1135.
- [13] Y. Otsuka, S. Suzuki, S. Shikama, T. Maki, T. Kobayashi, *Jpn. J. Appl. Phys.* 34 (1995) L551.
- [14] S.M. Baker, G.R. Rossman, J.D. Baldeschwieler, *J. Appl. Phys.* 74 (1993) 4015.
- [15] G.M. Swain, *Adv. Mater.* 6 (1994) 388.
- [16] I. Yagi, H. Notsu, T. Kondo, D.A. Tryk, A. Fujishima, *J. Electroanal. Chem.* 473 (1999) 173.