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Electrochemical studies of moderately boron doped polycrystalline diamond in non-aqueous solvent

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Abstract

The electrochemistry of boron doped diamond is currently an active field of research. In the majority of studies of diamond electrodes it has been reported that the material acts as a semi-metallic electrode. This paper is concerned with studies of moderately doped diamond electrodes in non-aqueous solvent. The results of Mott–Schottky analysis and the cyclic voltammetry of both ferrocene and bis(pentamethylcyclopentadienyl)iron are reported. The influence of surface bond termination, either hydrogen or oxygen, is also considered. It is shown that a response characteristic of a semiconductor can be attained at diamond electrodes immersed in acetonitrile provided that the redox couple does not have a similar energy to the graphitic surface states. The results obtained are discussed in terms of the Gerischer–Marcus model of charge transfer at semiconductor electrodes. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Semiconductors; Diamond; Surface states; Mott-Schottky; Non-aqueous

1. Introduction

The advent of economic methods of preparing polycrystalline diamond via chemical vapour deposition (cvd) has resulted in considerable interest in developing commercial applications for this material [1–11]. Heat sinks [12–16], field emitters [17–24] and electronic devices [25–31] based on diamond are amongst some of the uses that have been proposed. Electrochemistry [32–82] is presently emerging as an area in which diamond offers distinct advantages over more traditional materials. Indeed devices in which diamond electrodes are an integral component are now being marketed [83,84].

The first paper on the electrochemistry of boron doped polycrystalline diamond was published by Pleskov et al. in 1987 [32]. The demonstration of the possibility of performing electrochemistry on polycrystalline diamond resulted in considerable interest in electrodes fabricated from this new material. Three advantages of diamond electrodes were identified. First, it was demonstrated that diamond electrodes have a large potential window in aqueous solution with low background currents [34–36,38–40,43,44,46,47,50,55,57–60]. Second, it was shown that electrodes formed from polycrystalline diamond possess physical properties similar to those of bulk diamond [85–90], including: hardness, low environmental impact, high hole mobility, high thermal conductivity and excellent resistance to radiation damage. Third, the surface is stable and there is little evidence of degradation of electrochemical activity with time [64,65,78,79]. These characteristics of diamond electrodes have been employed in a number of applications. It has been demonstrated that the wide potential window at diamond electrodes can be used in the generation of ammonia from aqueous nitrate solutions [35]. The mechanical strength of diamond electrodes has resulted in them being utilised in sonoelectrochemical experiments [75,80–82]. Whilst, the resistance to fouling has resulted in diamond being a material of choice for electroanalytical studies [52,53,61,62,66,67,69,72,76,77].

Most electrochemical studies of diamond have been performed on highly boron doped, p-type, material in aqueous solvents. It has been shown that for simple

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redox couples in aqueous solution the electrochemical response at a diamond electrode resembles that of a metal electrode [43,51,70,73]. Further, it has been illustrated that the rate of electron transfer reaction is dependent up on whether the surface is hydrogen or oxygen terminated [38,71]. It has been suggested that the valance band edge at hydrogen terminated diamond electrode lies at a greater energy than the aqueous H^+/H_2 couple, this would result in hydrogen terminated diamond always being in accumulation when in an aqueous electrolyte [74]. Thus any applied potential would be dropped across the Helmholtz layer and reversible electrochemical behaviour observed for simple redox couples. Indeed an accumulation of holes at a hydrogen terminated diamond surface exposed to the atmosphere has been used to explain the enhanced surface conductivity of the material [33,37,41,42,45,48,49,54,56,63,91]. At an oxygen terminated diamond surface reversible electron transfer occurs at potentials at which Mott–Schottky analysis suggests the surface is in depletion. Impedance studies [71,74] indicate that electron transfer at an oxygen terminated diamond surface occurs via surface states [38,71,74]. It has been postulated that sp^2 carbon surface impurities mediate the charge transfer.

In this paper we report electrochemical studies of moderately doped diamond electrodes in non-aqueous solvents. The use of acetonitrile as a solvent permits the hydrogen terminated diamond electrode to be studied at potentials at which holes do not accumulate at the electrode surface. In addition it allows redox couples to be employed that exhibit low overlap integrals with the graphitic surface states. It is demonstrated that in non-aqueous solvents diamond electrodes can show behaviour characteristic of a semiconducting material.

2. Experimental

Boron doped nanocrystalline diamond films were deposited on a 1.5 cm^2 undoped silicon (100) wafer by hot-filament cvd. Prior to the deposition process, the substrate was manually abraded with 1–3 μm diamond grit and then ultrasonically cleaned in propan-2-ol. The silicon was then placed in a hot-filament reactor containing a mixture of hydrogen, methane and diborane at a pressure of 20 Torr. Typical flow rates during deposition were 200 sccm of H_2, 1.4 sccm of CH_4 and 4×10^{-5} sccm of B_2H_6, corresponding to a boron to carbon ration of 50 ppm in the gas phase. Deposition of the polycrystalline diamond film was achieved by activating the gas phase with hot-filaments, two 0.25 mm diameter tantalum coils in series. The deposition time was 16 h, giving a film thickness of approximately 5 μm. The film was allowed to cool in the hydrogen atmosphere before removal from the chamber. A TiC ohmic contact was formed to permit electrochemical investigations of the as-prepared low doped samples. Before electrochemical studies the boron doped diamond films were characterised using Raman spectroscopy (Renishaw confocal imaging systems) and scanning electron microscopy (SEM) (JEOL JSM 5600LV).

It has been established that the surface of hot-filament cvd diamond is hydrogen terminated [92]. In order to ensure hydrogen termination was maintained samples were stored under vacuum. To generate oxygen terminated surfaces the diamond electrodes were immersed in a hot chromic acid solution [41,93]. It is noted that this procedure resulted in a considerable reduction in the surface conductivity of the film [94–96].

All electrochemical experiments were performed in a dry box in which the amount of water vapour was less than 6 ppm by volume. In the experiments anhydrous acetonitrile (99.9% pure) was used as solvent and 0.1 mol dm^{-3} tetrabutylammonium perchlorate (TBAP) as supporting electrolyte. Cyclic voltammetric studies were performed on solution containing 1×10^{-3} mol dm^{-3} of either ferrocene ($FeCp_2$) or bis(pentamethylcyclopentadienyl)iron ($FeCp_2^*$). A three electrode system was employed; a boron doped diamond working electrode, a platinum gauze counter electrode and a $FeCp_2^+/FeCp_2$ reference electrode. All potentials are reported relative to $FeCp_2^+/FeCp_2$ couple. The diamond electrode was mounted in the cell such that 0.4 cm^2 of the diamond surface was exposed to electrolyte. Impedance measurements were performed using a Solartron 1286 potentiostat and a Solartron 1250 frequency response analyser; the instruments were controlled using *Z*-plot software. In all ac experiments a modulation amplitude of 10 mV was applied. Cyclic voltammetry measurements were performed using a EG&G 273 Princeton Applied Research instrument that was controlled using Research Electrochemistry software.

3. Results and discussion

The quality of the polycrystalline boron doped diamond films was analysed using Raman spectroscopy and sem. The Raman spectrum, shown in Fig. 1, displays a sharp peak at 1332 cm^{-1} corresponding to sp^3 hybridised carbon. There is no evidence of sp^2 peaks between 1500 and 1700 cm^{-1} indicating that the film has a low graphitic content. This conclusion is supported by the sem image, shown in Fig. 2, in which amorphous regions associated with the presence of graphitic carbon are not observed. The film consists of crystals of dimension approximately 1–5 μm and appears continuous across the entire substrate.

To establish the position of the band edges of p-type diamond in acetonitrile Mott–Schottky analyses were

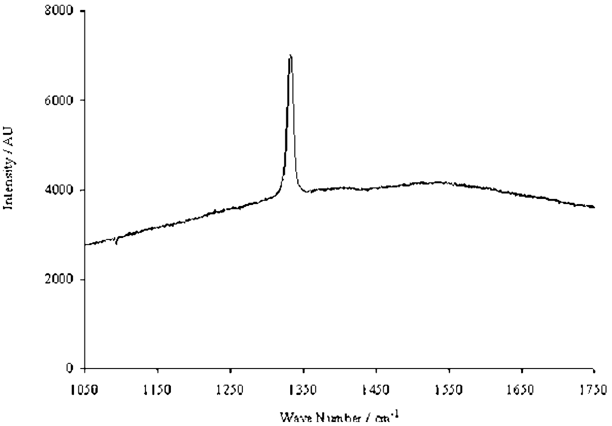

Fig. 1. Raman spectrum of boron doped diamond film grown by hot-filament cvd. Spectrum shows sharp crystalline diamond band at 1332 cm^{-1}.

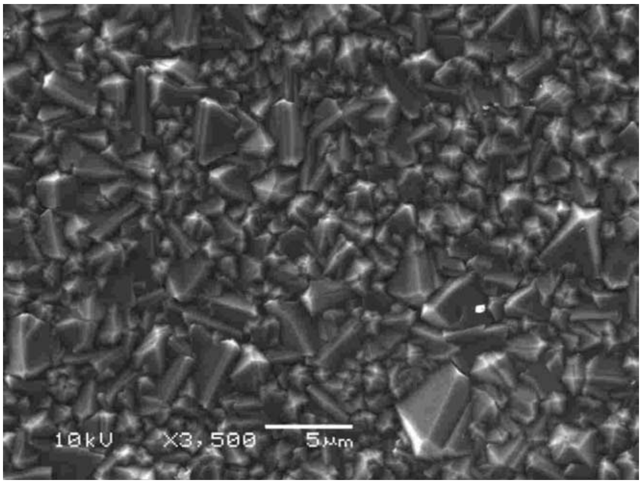

Fig. 2. Scanning electron micrograph of the morphology of a high quality boron doped diamond electrode.

undertaken. Plots of 1/(capacitance)^2 against applied potential, recorded at different frequencies, for both hydrogenated and oxygenated boron doped diamond electrodes immersed in acetonitrile containing 0.1 mol dm^{-3} TBAP are displayed in Fig. 3 and Fig. 4. Although Mott–Schottky theory suggests that the plots should be independent of the measuring frequency this behaviour is rarely observed for semiconductor electrodes. Surface roughness, dielectric relaxation and the influence of surface states have all been advanced as explanations of the frequency dispersion in Mott–Schottky plots [97]. Using the data recorded at a frequency of 10 kHz a free carrier concentration of 1.1×10^{18} cm^{-3} was determined for both the hydrogenated and oxygenated sample. This figure compares favourably with the experimental conditions employed during film preparation; a boron to carbon ratio of 50 ppm in the gas phase suggests a boron density of 5.7×10^{18} cm^{-3} in the crystal.

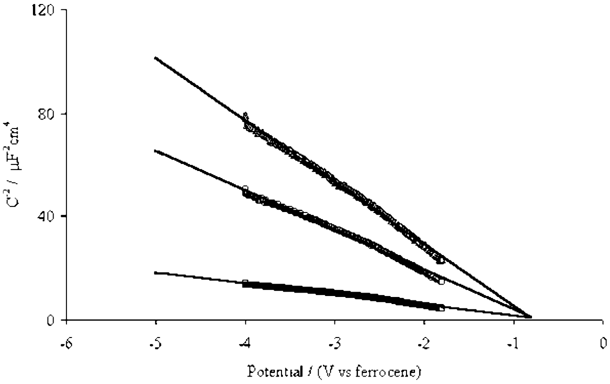

Fig. 3. Mott–Schottky plots for semiconducting hydrogen terminated boron doped diamond electrode Three frequencies of modulation were recorded; △ 10 KHz,○ 5 KHz and □ 1 KHz. Linear extrapolation of the experimental data has a common intercept approximately −0.8 V. Potential relative to the ferrocene standard redox couple.

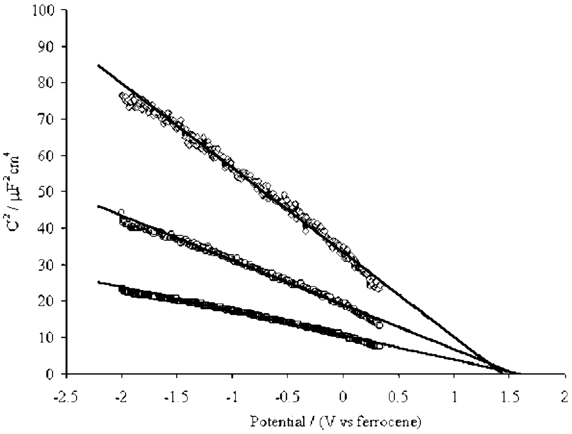

Fig. 4. Mott–Schottky plots for semiconducting oxygen terminated boron doped diamond electrode Three frequencies of modulation were recorded; ◇ 20 KHz, ○ 10 KHz and □ 5 KHz. Linear extrapolation of the experimental data has a common intercept approximately 1.5 V. Potential relative to the ferrocene standard redox couple.

At the hydrogenated surface the Mott–Schottky plots are linear between −1.8 and −4.0 V and possess a common intercept. The plots indicate that the valence band edge, relative to the ferrocene couple, lies at −0.8 V. Given that the band gap of diamond is 5.4 eV [98] this places the conduction band edge at −6.2 V on the same scale, or at +1.3 eV relative to an electron in a vacuum [99]. The fact that hydrogen terminated diamond has a negative electron affinity is one of the key reasons why this material is being considered in field emission devices [17–24].

The change in surface bond polarisation at the oxygen terminated surface relative to the hydrogenated surface results in a large shift in the band edges [71]. This is evident in the Mott–Schottky data for the oxygenated p-type diamond electrode. In the case of the oxygenated diamond surface a linear region is observed between 0.3 and −2.0 V; as for the hydrogen terminated surface frequency dispersion is evident but a common intercept is attained. Analysis of the data indicates that for an oxygen terminated p-type diamond electrode in acetonitrile the valence band edge lies at 1.5 V and the conduction band edge at −3.9 V [100], indicating a positive electron affinity.

In Fig. 5 the energy levels for the oxygen and hydrogen terminated surfaces of p-type diamond, as determined from the Mott–Schottky data, are shown. In addition the energy levels of some outer sphere redox couples are displayed [101,102]. To facilitate discussion the electron affinity of graphitic carbon is also plotted, this energy level is a guide to the energy of graphitic surface states at the diamond/electrolyte interface [99].

In Fig. 6 cyclic voltammograms for hydrogen and oxygen surface terminated diamond in both 1×10^{-3} mol dm^{-3} $FeCp_2$ and 1×10^{-3} mol dm^{-3} $FeCp_2^*$ are displayed. It is apparent that the redox behaviour of the electrodes is highly dependent on the surface termination.

At the hydrogen terminated surface, Fig. 6a, well defined oxidation and reduction peaks are observed for the $FeCp_2^+/FeCp_2$ redox couple. The cathodic peak is distorted and the peak separation is approximately 1.2 V; it should be noted that the material was highly resistive, no iR compensation was employed when recording the voltammograms, and the kinetics of the redox couple appears to be slow. In contrast Fig. 6b shows that the oxidation of $FeCp_2^*$ at the same surface is irreversible with negligible cathodic currents until voltages less than −2.5 V are achieved. This behaviour is explained in terms of the classical Marcus–Gerischer mechanism of electron transfer [103]. Reference to Fig. 5 indicates that the redox level of the $FeCp_2^+/FeCp_2$ couple lies within the valence band of the hydrogen terminated p-type diamond. Hence at the redox potential of the couple the Fermi level lies within a semiconductor band and reversible electrochemistry is observed. In comparison the redox level of the $FeCp_2^{*+}/FeCp_2^*$ couple lies within the band gap of the hydrogen terminated p-type diamond. Therefore, an anodic current flows only at potentials under which holes accumulate at the electrode surface whilst a small constant cathodic current flows due to the negligible overlap between the energy levels of the oxidised states and the valence band edge. At high negative overpotentials an increased cathodic current may be observed due to breakdown of the Schottky barrier. In summary the results indicate that the hydrogen terminated material is acting as a p-type semiconductor electrode when used in non-aqueous solvents.

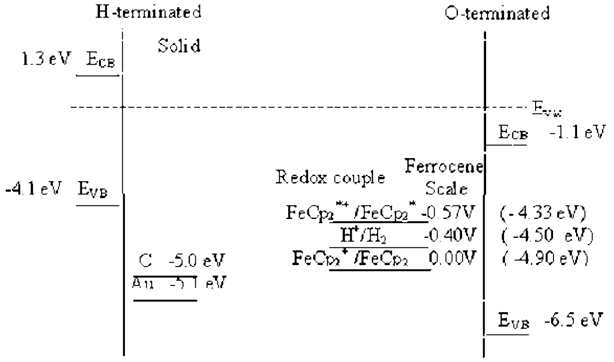

Fig. 5. Proposed energy diagram for the diamond-electrolyte interface for hydrogen and oxygen terminated samples.

The large shift in the band edges with change in surface termination of p-type diamond results in the cyclic voltammograms recorded at the oxygen terminated surface being markedly different to those of the hydrogen terminated surface. The cyclic voltammogram in Fig. 6c indicates that for the $FeCp_2^+/FeCp_2$ couple anodic and cathodic currents are observed at the oxygenated surface. The current magnitude is considerably less than that for the hydrogenated surface despite identical experimental parameters. In Fig. 6d the cyclic voltammogram for the $FeCp_2^{*+}/FeCp_2^*$ couple is displayed, it is apparent that this couple is inactive within the potential window of the solvent. The energy levels that are shown in Fig. 5 indicate that both redox couples investigated are situated between the band edges of the oxygen terminated surface. The observation that $FeCp_2^*$ is not oxidised indicates that in the potential range of interest the p-type oxygenated diamond surface is in depletion and not inversion. It is, therefore, difficult to justify the anodic peak observed in the $FeCp_2$ voltammogram simply in terms of direct charge transfer between the valence band of the material and the redox couple. In studies of oxygenated p-type diamond electrochemistry involving aqueous electrolytes evidence for surface state mediated charge transfer has been observed [38,71,74]. It has been suggested that the surface states involved in the charge transfer are graphitic in character. The results reported above support this proposal. Fig. 5 indicates that the $FeCp_2$ couple is close in energy to graphitic states whilst the $FeCp_2^*$ redox couple lies at greater energy than the surface states. This indicates that graphitic state mediated charge transfer will be facile for the $FeCp_2$ couple but difficult for the $FeCp_2^*$ couple, as observed.

4. Conclusions

Studies of moderately boron doped diamond in non-aqueous solvents have permitted the influence of surface termination on the electrochemical behaviour of this semiconductor to be investigated. It was shown that the surface termination is important in two respects. First, it determines the position of the band edges. These may shift by approximately 2.3 V on going from an oxygen terminated to a hydrogen terminated surface. Second,

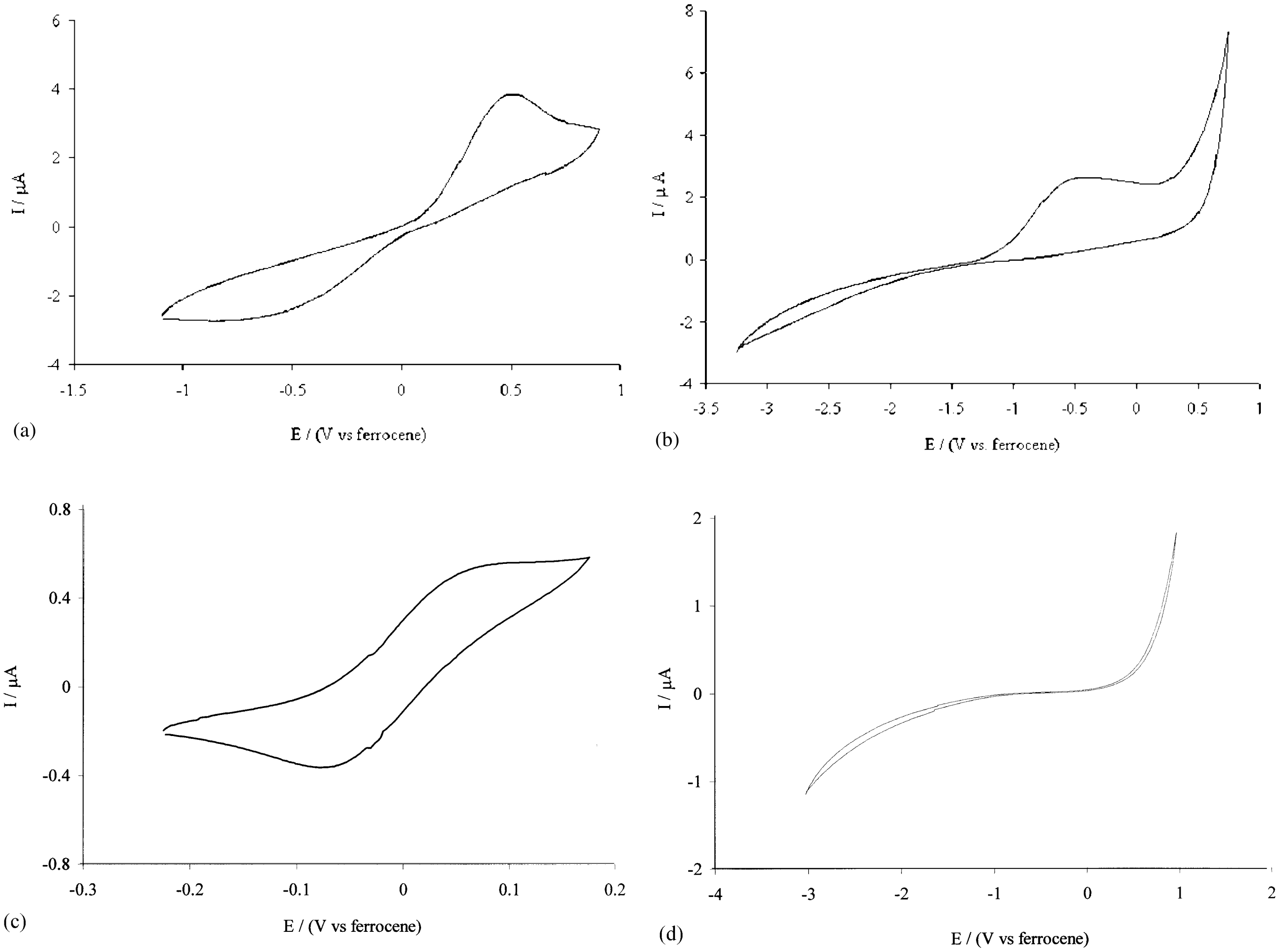

Fig. 6. Cyclic voltammetric i–E curves recorded at a scan rate of 0.1 V s^{-1}, of boron doped diamond electrodes. (a) A hydrogen terminated sample immersed in 1×10^{-3} mol dm^{-3} FeCp$_2$. (b) A hydrogen terminated sample immersed in 1×10^{-3} mol dm^{-3} FeCp$^*_2$. (c) An oxygen terminated sample immersed in 1×10^{-3} mol dm^{-3} FeCp$_2$. (d) An oxygen terminated sample immersed in 1×10^{-3} mol dm^{-3} FeCp$^*_2$. All potentials are related to the ferrocene standard redox couple.

graphitic surface states may mediate charge transfer. For the hydrogen terminated diamond surface the electrochemical studies in non-aqueous solvent showed characteristics of a non-degenerately doped p-type semiconducting material, to the authors' knowledge this is the first time such behaviour has been observed for a non-oxidised diamond electrode. For the oxygen terminated surface it was demonstrated that reversible cyclic voltammograms are only observed for redox couples of comparable energy to graphitic surface states.

Acknowledgements

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