

Electrochemical Characterization on Semiconductors p-Type CVD Diamond Electrodes

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Received February 8, 1999

Semiconductor boron-doped CVD diamond films were prepared on Si substrates by the hot filament technique. The surface morphology analysis by SEM presented continuous and well faceted films. The samples were grown with different boron concentrations by controlling the B/C ratio in the feeding gas. Raman results showed a drastic change of diamond films for different doping levels. The characteristic line at 1332 cm^{-1} decreases and shifts to lower energy as a function of the film resistivity. It was also observed a broad peak around 1220 cm^{-1} caused by the incorporation of boron in the diamond lattice. Photocurrent-voltage behaviour of undoped and boron-doped diamond electrodes was investigated in dark and UV visible irradiation. The voltammograms showed that doped electrodes illuminated with a xenon lamp exhibited currents significantly higher because of the increased conductivity. For undoped electrodes it was observed a small photocurrent for anodic and cathodic polarization in the order of μA for the potential range of $+1.0\text{ V}$ and -1.0 V (Ag/AgCl), for 1.0 M KCl . Mott-Schottky plots studied the interfacial processes at diamond-electrolyte junction. The flatband potential U_{fb} was found between 0.6 and 0.8 V (Ag/AgCl) which varies with the presence of sp^2 -type carbon as an impurity. From the curve slope the acceptor concentrations were found in the range of 10^{18} and 10^{21} cm^{-3} . These values agree with the estimated concentration obtained by Raman measurements.

I Introduction

The evolution of research on semiconductor diamond has shown promising results with doping process during CVD growth. Due to its easy production and high stability, there is a great interest in studying the development of boron doped diamond leading to the application of these films as electrode for, photoelectrochemical (PEC) cells, sensors, etc [1-3].

The standard methods used for CVD boron-doped diamond were initially thermal diffusion [4,5] and ion implantation [6,7]. These processes were made "ex situ", after the film growth. The main advantage is the no-contamination of the growth reactor. Martin et al. [4] have obtained highly doped films, using "in situ" process from a solid source of boron inside of the reactor. Better results that evidenced more homogeneous films were observed. CVD-grown polycrystalline diamond films, depending on growth conditions, can have

a wide spectrum of electrophysical properties. Their properties depend on the concentrations of defects in diamond grains, on the volume fraction of the nondiamond intergrain boundary phase, and on its nature.

Okano et al [8] have proposed the boron doping during the CVD growth process using the hot filament reactor introducing B_2O_3 dissolved in methanol-acetone mixture, that works as a carbon source for diamond growth. Their results showed films with linear relation between the doping levels and boron concentration.

Pleskov et al. [9] have studied, for the first time, the electrochemical and PEC behaviour of diamond electrodes. Tenne and Swain [10,11] have made cyclic voltammograms in the presence of redox couples. Sakharova et al. [12] have studied the mechanism of charge-transfer at the diamond/electrolyte interface. They have evaluated the flatband potential and the acceptor concentration. Patel et al. [13] have also studied the PEC behaviour of boron-doped diamond films.

They concluded that their behaviour corresponds to a typical p-type semiconductor and these CVD diamond electrodes may be suitable for application as inert electrode.

The importance of PEC investigations for characterization of boron-doped diamond electrodes is the main purpose of this work. We have carried out PEC investigations from photoeffects measurements and Mott-Schottky plots. The morphology and film quality were analyzed by SEM and Raman spectroscopy. We have also evaluated the intrinsic stress from Raman spectra to show the effect of boron incorporation in the diamond lattice.

II Experimental

The films were deposited on silicon substrate after seeding pre-treatment [14] in the usual hot filament-assisted CVD reactor. The films were grown at 800 °C during 6 hours. Boron source was obtained from a H_2 line forced to pass through a bubbler containing B_2O_3 dissolved in methanol. This system permits the control of boron concentration using a flow controller for the gas inlet. The CH_4 flow is kept at 0.5 sccm for all experiments and the H_2 and $B_2O_3/CH_3OH/H_2$ flows are controlled in order to obtain the desired B/C ratios. The dissolution of 5000, 10000, 15000 and 20000 ppm of B_2O_3 in methanol was necessary to cover the whole range of B/C ratios studied. Raman spectra were recorded using a Renishaw Microscope System 2000. PEC investigations were made using an electrochemical cell irradiated by a xenon lamp. The reference electrode and counter-electrode were $Ag/AgCl$ and platinum, respectively. The voltammograms were obtained in the potential range of +1.0 V and -1.0 V using a solution of 1.0 M KCl . The capacitance of the interface was measured using a potentiostat EGG/PAR 362 connected with a Lock-in EGG/PAR 124 and a x-y recorder.

III Results and Discussion

a) SEM and Raman

The surface analysis made by scanning electron micrograph for boron-doped diamond films showed a small variation on surface morphology by comparison with undoped diamond. The films are faceted with symmetrical and smooth faces with uniform texture that show a surface morphology with predominant (111) orientation. For all doping levels studied the films evidenced small grains of around 2-3 μm .

Raman spectroscopy is commonly used in characterizing the structure and quality of synthesized diamond films. A drastic change of Raman spectra of diamond films with different doping levels was observed. Fig. 1 shows the Raman spectra for samples obtained with B/C ratios in the range 0 to 20000 ppm in methanol. The characteristic diamond line at 1332 cm^{-1} decreases and downshifts to lower energy as the doping level of the film increases. For samples D e E ($B/C = 15000$ and 20000 ppm, respectively), this peak almost disappears and the broad peak at 1200 cm^{-1} becomes more evident due to the incorporation of boron in the diamond lattice.

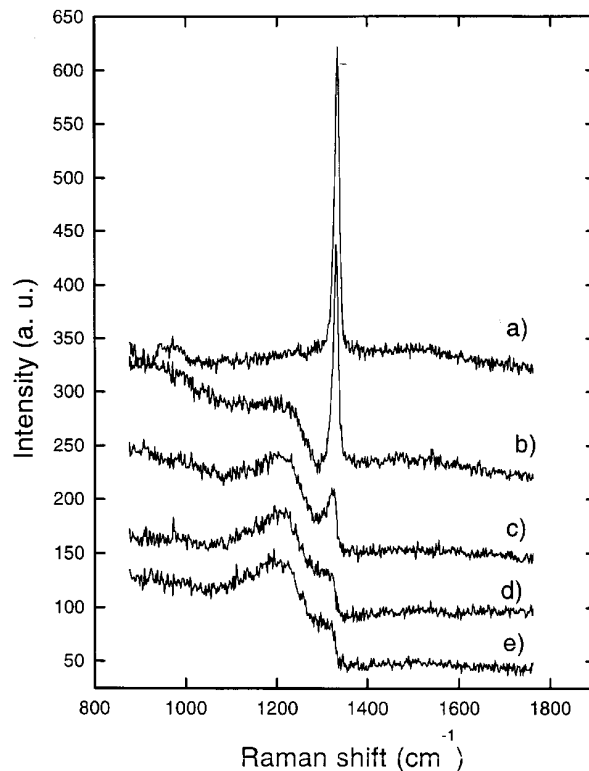


Figure 1. Raman spectra for undoped and boron-doped diamond films. a) $B/C=0$ ppm, b) $B/C=5000$ ppm, c) $B/C=10000$ ppm, d) $B/C=15000$ ppm, e) $B/C=20000$ ppm.

b) PEC investigations

1. Photocurrent-voltage behaviour

Photoelectrochemical analysis are of fundamental importance in order to explore the attractive electronic properties of diamond electrode. PEC investigations on p-type diamond would enhance the understanding of photoeffects in the diamond-electrolyte system and diamond itself.

For a preliminary analysis of these processes, the current-voltage (I-V) behaviour of undoped and doped

diamond electrodes was investigated in dark and under UV-visible irradiation. A typical voltammogram of a doped electrode ($B/C = 20000$ ppm in methanol) is shown in Fig. 2. It was observed that the anodic current presents an increase of 100% under irradiation. The same measurements were made for undoped electrode. Small photocurrents under anodic as well as cathodic polarization were also observed. The results showed anodic current 20 times smaller than for highly doped film. The generation of photocurrent and its dependence on potential indicate the semiconducting nature of the electrode and the formation of a Schottky-type barrier.

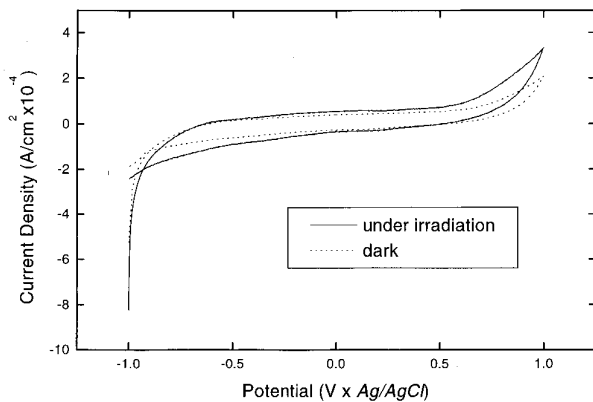


Figure 2. I-V curves at boron-doped diamond electrode in the dark (dot line) and under irradiation (straight line), electrolyte 1.0 M *KCl*.

2. Mott-Schottky plots

The measurements of differential capacitance in the space charge region or depletion layer for semiconductor/electrolyte interface can extend the understanding of the interfacial process. This measurement permits to find the flatband potential and the energy bands of diamond with respect to the redox potential. Besides, the dependence of differential capacitance C with potential V of a depletion layer also allows the evaluation of the acceptor concentration, with the equation [15,16]:

$$N_A = \frac{2}{e\epsilon_0\epsilon} [d(C^{-2})/dV]^{-1} \quad (1)$$

Here e is the electron charge; ϵ_0 and ϵ are the permittivity of vacuum and semiconductor, respectively.

The differential capacitance study was also made for samples with different doping levels, in the range of $B/C = 0$ and 20000 ppm in methanol. According to such analysis, the Mott-Schottky plots were more linear in the anodic region of the potential x *Ag/AgCl* and 1.0 M *KCl* for all electrodes studied, in the frequency of 1 kHz. The acceptor concentration N_A and the flatband potential U_{fb} were determined from the slope and the

intercept of the linear region of the M-S plot. The flat-band potential U_{fb} were found between 0.6 and 0.8 V x *Ag/AgCl*, that agree with the values showed in other works [9,17,18]. The acceptor concentrations were also evaluated for all samples studied. For a doping level with B/C ratio in the 5000 - 20000 ppm range the acceptor densities were found in the range $1,9 \times 10^{19}$ - $1,5 \times 10^{21}$ cm^{-3} . These are highly doped films and the acceptor densities are in close agreement with the B/C ratio and with the estimation from Raman spectra [19]. These measurements show that the Mott-Schottky plot method is valid for highly doped films. Fig. 3 shows the dependence of capacity on the electrode potential, for the boron-doped electrode for $B/C = 20000$ ppm, that correspond an acceptor concentration of 1.5×10^{21} cm^{-3} . The flatband potential determined from the intercept on x-axis was 0.75 V x *Ag/AgCl*.

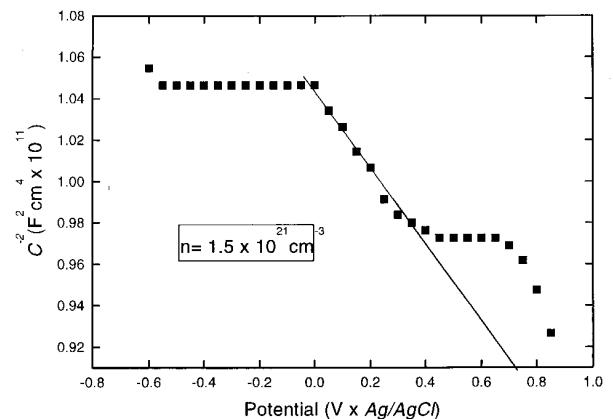


Figure 3. Mott-Schottky plots of boron-doped diamond electrode, where C is the capacitance and V is the electrode potential, at 1kHz and electrolyte 1.0 M *KCl*.

IV Conclusion

We have made a series of experiments using boron-doped diamond films by controlling different doping levels. SEM analyses have shown uniform and symmetrical films and smooth faces with predominant (111) orientation. Raman study evidenced high doped films showing a decrease of characteristic diamond line at 1332 cm^{-1} and a line shift to lower energy as a function of the doping level. For samples *D e E* ($B/C = 15000$ ppm and 20000 ppm, respectively), this peak almost disappears and the broad peak at 1200 cm^{-1} becomes more evident due to the boron incorporation in the diamond lattice.

PEC investigations have shown a typical photocurrent - voltage behaviour for p-type semiconductor. It

was observed that the anodic current presents an increase of 100% under irradiation. The same measurements were made for the undoped electrode. Small photocurrents under anodic as well as cathodic polarization were also observed, but by comparison with the doped film, this electrode presented an anodic current 20 times smaller. The generation of photocurrent and its dependence on potential indicate the semiconducting nature of the electrode and the formation of a Schottky-type barrier. The differential capacitance study has permitted to evaluate the flatband potential and the acceptor concentrations. The values obtained for U_{fb} were found between 0.6 and 0.8 V *x* Ag/AgCl and agree with the range showed in the literature. Acceptor densities were found in the range of 10^{19} to 10^{21} cm⁻³, that evidences high doped films and are in good agreement with Raman results.

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