

# Cyclic voltammetry and impedance studies of undoped diamond films

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The undoped, polycrystalline diamond films were deposited on tungsten wire substrates by hot filament chemical vapor deposition (HF CVD), using a precursor gas mixture of methanol with excess of hydrogen. The morphology and quality of the as-deposited films were monitored by scanning electron microscopy (SEM) and Raman spectroscopy. The surface morphology analyzed by SEM resembles a continuous and well faceted diamond film. Raman results showed essential differences in qualities of diamond films grown at different hydrocarbon concentrations. The electrochemical properties of diamond electrodes were examined with cyclic voltammetry (CV) and the electrochemical impedance spectroscopy (EIS). The CV experiments revealed a large chemical window ( $> \sim 4.3$  V) of undoped diamond. Analysis of the ferrocyanide-ferricyanide couple at a diamond electrode suggests some extent of electrochemical quasi-reversibility, but the rates of charge transfer across the diamond substrate interface vary with diamond quality.

Keywords: *CVD diamond, Raman spectroscopy, cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS)*

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## 1. Introduction

A conducting diamond thin film is a new electrode material that has received great attention recently because of its numerous technologically important characteristics such as an inert surface with low adsorption properties, remarkable corrosion stability even in strong acidic media, and an extremely wide potential window in aqueous and non-aqueous electrolytes. Thanks to these properties diamond electrodes meet the requirements for a wide range of electrochemical applications. Undoped diamond is a perfect insulator but its surface properties attract increasing attention as carbon dangling-bonds at the surface can be terminated by a variety of elements, especially by oxygen and hydrogen. In the case of oxygen termination, insulating properties are achieved with increased

electron affinities while hydrogen gives rise to a negative electron affinity due to the formation of carbon-hydrogen dipoles [1]. In vacuum such surfaces are insulating too, however, if hydrogen terminated diamond films are exposed to air, the surface conductivity can be detected [2]. It is certain that the conductivity is related to hydrogen [3] however, a detailed understanding of this phenomenon is still lacking.

In this study, we describe the fabrication of modified electrodes, made by growing undoped diamond films on tungsten substrates. All films have sufficient conductivity to allow the passage of current, therefore enabling us to correlate the electrochemical behavior of the electrodes with diamond film quality checked by SEM and Raman spectroscopy. Thermodynamic and kinetic properties of the well-characterized redox couple  $[\text{Fe}(\text{CN})_6]^{4-}/^{3-}$  were studied with cyclic voltammetry and electrochemical impedance spectroscopy.

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## 2. Experimental

The diamond films, which are polycrystalline in nature, were deposited on tungsten substrate by hot filament chemical vapor deposition (HF CVD) technique. The tungsten filament operating at the temperature of 2300 K was placed 8 mm above the substrate. The mixture of methanol vapor and hydrogen ( $\sim 0.5 \div 5.0$  % of  $\text{CH}_3\text{OH}$  in  $\text{H}_2$ ) was used as a working gas. The parameters of growth process were as follows: total pressure in reaction chamber – 50 mbar, substrate temperature – 1000 K and working gas flow rate – 100 sccm. In order to enhance the diamond nucleation density, the substrate was scratched with diamond paste before the deposition process was started. After mechanical polishing with diamond paste the substrate was washed in ultrasonic bath with methanol and deionized water.

The diamond film morphology has been studied by Scanning Electron Microscope (SEM) Jeol JSM-820 operating at a voltage of 25 kV. The Raman spectra were recorded at room temperature in backscattering geometry using Renishaw in Via Raman spectrometer. The 488 nm argon laser line was used for excitation.

Cyclic voltammetric measurements were made with CS-1087 computer-controlled potentiostat (Cypress Systems Inc., Lawrence, KS) in a three electrode configuration. A platinum rod served as the counter electrode and Ag/AgCl (0.1 M KCl) was used as the reference electrode. The electrolyte was deoxygenated with  $\text{N}_2$  for at least 15 min prior to the measurements.

The electrochemical impedance spectra in the frequency range  $10 \text{ mHz} < f < 1 \text{ MHz}$  with 50 mV ac-amplitude were measured using Hioki type 3522-50/3532-50 LCR HiTESTER equipment. The working electrodes were cleaned in an ultrasonic bath and activated by electrochemical cycling between oxygen and hydrogen evolution before starting the experiments.

## 3. Results and discussion

Fig. 1 shows a SEM picture of a polycrystalline diamond film deposited on tungsten substrate in

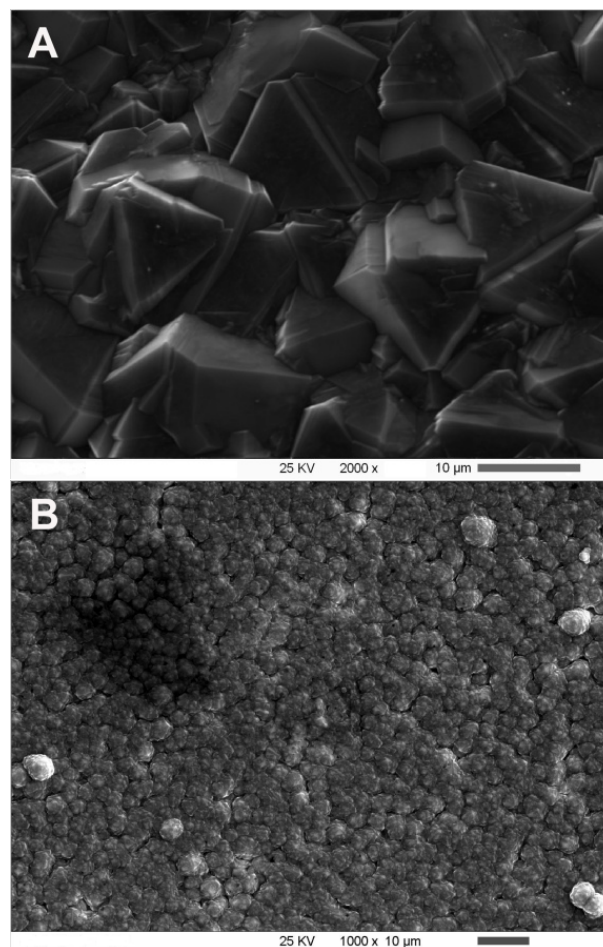


Fig. 1. SEM picture of a diamond layer deposited at different concentrations of methanol in hydrogen: A)  $\sim 0.5$  % – A electrode, B) 5% – B electrode.

the form of tungsten wire, 1 mm in diameter. The morphological grain sizes, as observed by SEM, are in range of  $0.5 \div 10 \mu\text{m}$ . The grains are heavily twinned. Clearly, the grain size decreases and the intergrain regions containing nanodiamond crystals increase with increasing hydrocarbon concentration in the CVD reaction chamber. M. Mermoux *et al.* [4] showed that non-diamond carbon impurities in polycrystalline diamond films often occur locally in the grains boundaries and determine the diamond film quality. The trends observed by SEM are reflected in corresponding Raman spectra (see Fig. 2). Fig. 2 shows the Raman spectra of diamond films grown for 5 h on tungsten substrate using 0.5 % (A) and 5 %

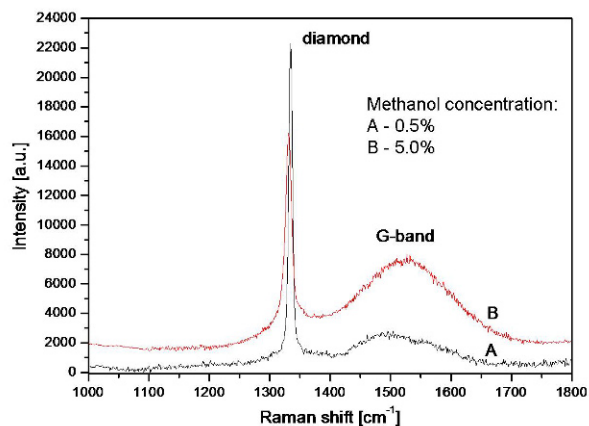


Fig. 2. Raman spectra of the diamond layers shown in Fig. 1.

(B) of methanol in hydrogen, respectively. Each diamond film reveals the presence of diamond structure, as evidenced by the  $1332.5\text{ cm}^{-1}$  peak, which is characteristic of the  $t_{2g}$  vibrational mode of diamond lattice. The diamond film (Fig. 1A) deposited at 0.5 % of methanol in hydrogen is composed of relatively large (about  $10\text{ }\mu\text{m}$ ), well defined diamond microcrystals. The corresponding Raman spectrum (Fig. 2, spectrum A) shows a sharp first order diamond Raman line at  $1333\text{ cm}^{-1}$ . The broad Raman band with the maximum between  $1500\text{ cm}^{-1}$  and  $1600\text{ cm}^{-1}$ , usually observed for CVD diamond layers [5], in this case is very weak what indicates small amounts of amorphous carbon admixture.

The diamond film deposited at 5 % of methanol in hydrogen shows much more complex morphology (Fig. 1B) which is composed of much smaller diamond microcrystals (smaller than  $1\text{ }\mu\text{m}$ ) and contains high concentration of grain boundaries. Its Raman spectrum, Fig. 2, except the first order diamond line at  $1332.4\text{ cm}^{-1}$  shows also well pronounced broadband at  $1556\text{ cm}^{-1}$  (G-line) ascribed to amorphous carbon phase. Using the procedure described elsewhere [5] we estimated the  $sp^2/sp^3$  bond ratio from the Raman spectra. For the A electrode this ratio is 1.8 % and for the B electrode the  $sp^2/sp^3$  ratio is of one order of magnitude higher reaching the value of 16.8 %. It means that quality of the electrodes is significantly different.

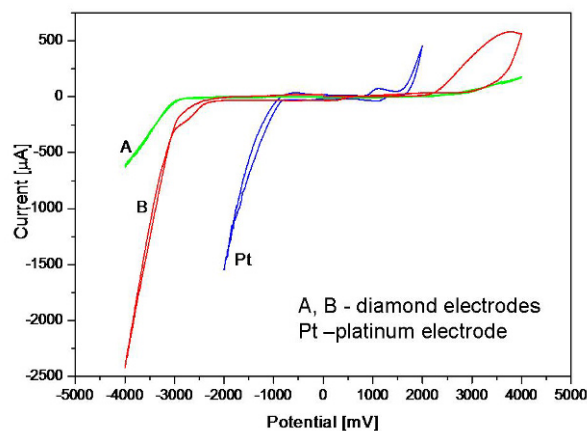


Fig. 3. Background voltammetric i-E curves recorded in 0.1 M KCl at a scan rate of 0.1 V/s for different electrodes.

Cyclic voltammetry is a commonly used electrochemical technique in which the potential applied to the working electrode is changed linearly in time, from an initial value to a switching value, and back to the initial value, with the resulting current being measured. The background voltammetric i-E curves for different diamond electrodes, including platinum electrode, in 0.1 M KCl at a scan rate of 0.1 V/s are shown in Fig. 3. The voltammograms recorded for diamond electrode in KCl solution containing  $0.01\text{ M }[\text{Fe}(\text{CN})_6]^{4-/3-}$  at different scan rates are shown in Fig. 4.

The CV voltammograms (Fig. 4) have well defined symmetrical shapes. The peak currents, both anodic  $I_{pa}$  and cathodic  $I_{pc}$ , increase with the scan rate and are proportional to square root of scan rate;  $\Delta E_p$  is larger than 59 mV and the ratio of peak currents  $I_{pa}/I_{pc}$  is kept around 1. EIS generally provides the data on electrode capacitance and charge transfer kinetics. Fig. 5 shows Nyquist plots obtained in 0.1 M KCl acid at polycrystalline diamond electrodes.

The impedance behavior of the diamond electrodes (Fig. 5) can be well expressed, over a wide frequency region, with the electrical equivalent circuit shown in Fig. 6, which includes a constant phase elements (CPE). The slightly flattened semicircle at high frequency (Fig. 5)

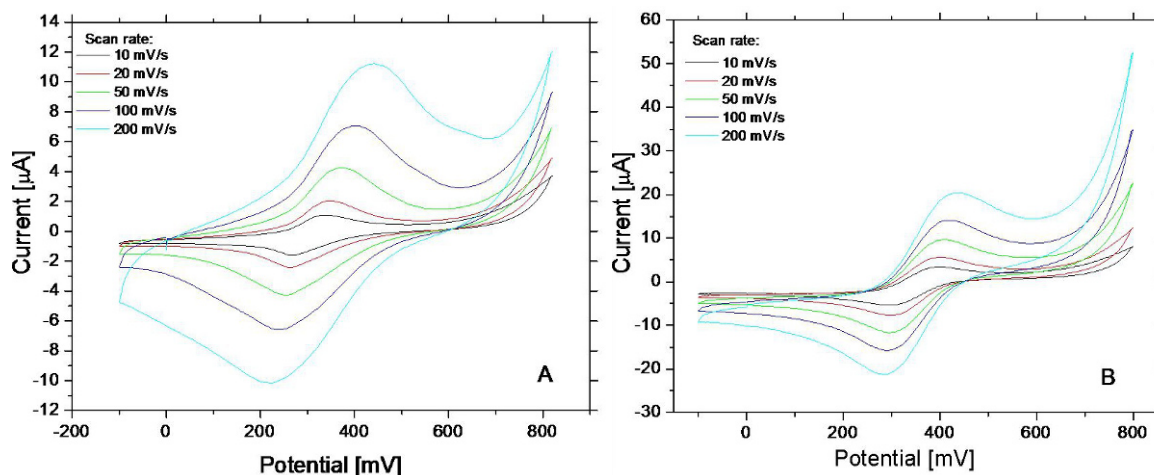


Fig. 4. Voltammograms recorded for the investigated A and B electrodes in 0.01 M  $[\text{Fe}(\text{CN})_6]^{4- / 3-}$  + 0.1 M KCl at different scan rates.

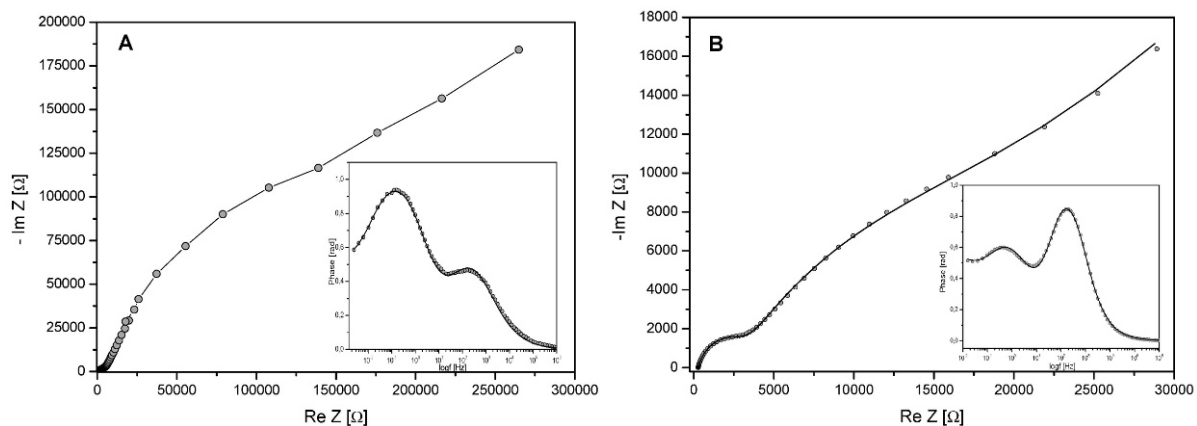


Fig. 5. Nyquist plots of diamond electrode A and B in 0.1 M KCl acid (The insets are the Bode plots); scatter – experimental, solid line – theoretical model.

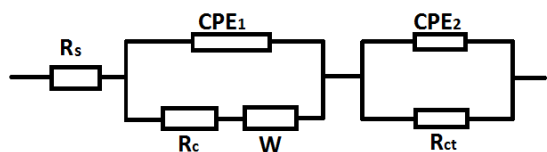


Fig. 6. Equivalent electrical circuit (theoretical model).

associated with the contact impedance resulted from the electrical connection between diamond particles as well as that between the diamond and the backing tungsten wire. The Bode plots (insets

in Fig. 5) show two humps in phase shift vs. log frequency data indicating two time constants at the diamond electrode/solution interface.

Due to this fact the equivalent circuit shown in Fig. 6 should be composed of two RC (R-CPE) type sub-circuits.

The first sub-circuit describes the diamond/solution interface, the second one diamond/tungsten substrate interface and  $R_s$  is bulk solution resistance.

The contact interface between the electrode and the electrolyte solution can be described as a capacitive constant phase element ( $\text{CPE}_1$ ),  $R_c$  is the charge transfer resistance in parallel with  $\text{CPE}_1$  and

Table 1. Fitting parameters of the equivalent circuit elements in Fig. 6.

electrode	$R_s$ [ $\Omega$ ]	$R_c$ [ $\Omega$ ]	$R_{ct}$ [ $\Omega$ ]	$CPE_1[F^\alpha \Omega^{\alpha-1}]$	$\alpha_1$	$CPE_2[F^\alpha \Omega^{\alpha-1}]$	$\alpha_2$
A	272	$3.4 \cdot 10^5$	$3.90 \cdot 10^3$	$2.6 \cdot 10^{-5}$	0.72	$6.2 \cdot 10^{-6}$	0.62
B	291	$2.7 \cdot 10^3$	$1.44 \cdot 10^4$	$2.6 \cdot 10^{-6}$	0.86	$8.9 \cdot 10^{-5}$	0.67

W is a Warburg diffusion element. The obtained fitting parameters using the electrical circuit from Fig. 6 are collected in Table 1.

The solution resistance, evaluated from Nyquist plots (Fig. 5), was found to be 272  $\Omega$  and 291  $\Omega$  and was independent of the tested electrode. The Warburg element W, which is responsible for mass transfer resistance, becomes unimportant in relation to  $R_c$  at high frequencies.

The origin of the CPE circuit element for the diamond is still not understood. In general, one of the possible origins of a CPE is the presence of a particular type of surface morphology, e.g., a fractal-type surface structure [6]. The physical interpretation of the CPE at diamond electrodes is still under debate, but it may be considered as a result of a relaxation process on the crystal surface and/or in the space charge region [7]. The lower frequency region can be expressed as the double-layer capacitance,  $C_{dl}$  ( $CPE_2$ ) generated from the charge transfer inside the inner pores in parallel with a charge transfer resistance,  $R_{ct}$ . The constant phase element  $CPE_2$  describes the effect of inhomogeneous porous structure of the diamond layer. It is clearly seen that electrochemical properties of diamond electrodes depend on diamond quality.

## 4. Conclusions

We have reported the growth of undoped diamond layers over the tungsten substrate by HF CVD process using hydrogen with methanol as a carbon source. SEM images and Raman spectra showed that it is possible to synthesize the diamond layers of different qualities by changing the methanol concentration.

Background cyclic voltammograms of the diamond electrodes showed that they are stable in supporting electrolyte over a wide potential range and show very low background current.

The impedance spectra were measured and the equivalent circuit of the diamond electrode/solution interface was proposed. It was shown that the electrochemical properties of a polycrystalline diamond electrode depend on diamond quality.

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