Fabrication and electrochemical properties of diamond layers grown on tungsten wire by HF CVD method

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Un-doped polycrystalline diamond thin films have been grown on tungsten substrates by hot filament chemical vapor deposition (HF CVD) using a hydrogen and methanol vapor mixture. Diamond films have been analyzed by Raman spectroscopy and scanning electron microscopy (SEM). Cyclic voltammetric behavior of diamond films of different quality and morphology has been studied in acetonitrile with (n-Bu)$_4$NClO$_4$ and in 0.1 M KCl aqueous solutions. Preliminary cyclic voltammetry (CV) measurements showed that our electrodes have a wide potential range over which negligible background response current is observed. The potential windows depend on the type of solvent. In the case of water solution the decomposition of water occurs electrochemically and evolves O$_2$ during positive (anodic) polarization and H$_2$ evolution during negative (cathodic) polarization. The electrochemical properties of diamond electrodes have been evaluated by performing cyclic voltammetry measurements in [Fe(CN)$_6$]$^{3-/4-}$ with 0.1 M KCl. The electrode demonstrates reversible kinetics during electrochemical analysis.

Keywords: CVD diamond, diamond, cyclic voltammetry, Raman spectroscopy, scanning electron microscopy (SEM).

1. Introduction

Diamond has unusual chemical and physical properties such as the highest hardness and lowest compressibility compared to any known material, high thermal conductivity, high electrical resistivity, high corrosion resistance, wide bandgap, high breakdown strength, high Young's modulus, and high electron and hole mobility. Therefore, several potential applications may be anticipated in electronics, thermal management, optics, protective mechanical coatings, electrochemical, electroanalytical, bio-electro-

-analytical, electrochemical detection of toxic metal ions, electrochemical sensors, and passivating and corrosion-resistant coatings [1−3]. However, progress in diamond technology is hindered to a large extent by many factors. The growth temperature in most of the techniques reported in the literature is higher than 800 °C, the necessity of scratching the substrates to enhance the nucleation density, surface non-uniformity, presence of stress in the films, unsuccessful attempts of large area heteroepitaxial growth, and lack of adhesion of diamond to various substrates – these are some of the problems associated with the chemical vapor deposition (CVD) diamond technology. Inherent high electrical conductivity of CVD diamond thin films, as opposed to high electrical resistivity, due to the trapped hydrogen in the diamond film, could defeat the purpose of using it as a dielectric material in electronic device applications. Atomic hydrogen, along with a carbon source gas, is a highly desirable way to grow diamond over graphite in CVD techniques. Atomic hydrogen etches non-diamond carbon, *e.g.*, graphite at a substantially higher rate than diamond. Therefore, the growth of diamond is feasible by CVD techniques. It was discovered on practically every undoped diamond sample that the electrical resistivity is lower than that of the natural undoped diamond.

The electrical resistivity of as-deposited CVD diamond films has been reported to be in the range of 10^2–10^6 Ω cm [4]. This low resistivity of diamond films could be due to hydrogen passivation of defect sites. According to Landstrass and Ravi [5], the resistivity of the as-grown diamond films is increased by several orders of magnitude upon annealing in an inert ambient. This effect is explained to be due to the removal of hydrogen from the films or the shift in hydrogen position in the films. The mechanism for the removal of hydrogen is corroborated by an observed decrease in resistivity upon hydrogen plasma treatment. Similar effects are observed for a single crystal diamond [6]. Celii *et al*. [7] correlated the measured electrical resistivity of the microwave plasma deposited diamond films with the amount of hydrogen present in the films. Albin and Watkins [8] have reported that the electrical properties of diamond films could be controlled by hydrogen plasma treatment. Exposure of oxyacetylene diamond films grown on a silicon substrate to hydrogen plasma has resulted in a decrease in electrical resistivity by several orders of magnitude [9].

As-grown diamond layers can be used in electrochemistry, which is presently an emerging area in which diamond electrode offers distinct advantages over more traditional electrode materials. Cyclic voltammetry (CV) is the most common electro-analytical technique used for studying electroactive species and often is the first experiment performed in an electrochemical evaluation of an electrode surface. The redox reactions usually provide information about the concentration, reaction mechanism, kinetics, chemical status and other behavior of the species in solution. The working electrode plays a critical role in the electrochemical experiments. An ideal working electrode used in cyclic voltammetry should possess two very important features, *i.e.*, it should have a large potential window and very low background current. In this work, we show the applicability of diamond layers as a working electrode for CV technique.

2. Experiment

The diamond films were synthesized by HF CVD method from methanol/hydrogen gas mixture at the pressure of 50 mbar. The tungsten filament operated at 2100 °C was placed 6 mm above substrate. As a substrate a tungsten wire 0.2 mm in diameter was used. The substrate surface before diamond growth process was prepared according to standard procedure, *i.e.*, the surface of the substrate was polished mechanically and then cleaned in acetone, methanol and distilled 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 back scattering geometry using Renishaw inVia Raman spectrometer. The 488 nm argon laser line was used for excitation.

Cyclic voltammetric characteristics were recorded by CS-1087 computer controlled potentiostat (Cypress System Inc., Lawrence, KS) in a three-electrode configuration. A platinum electrode served as the counter and Ag/AgCl (3 M KCl) was used as a reference electrode.

3. Results and discussion

The quality of the polycrystalline diamond layer deposited on tungsten wire was analysed using SEM and Raman spectroscopy. The diamond morphology is shown in Fig. 1. As one can see, the tungsten wire is completely covered by diamond layer. The layer is relatively smooth, diamond microcrystals show clear crystal features and are not bigger than 1 μm (Fig. 1**c**).
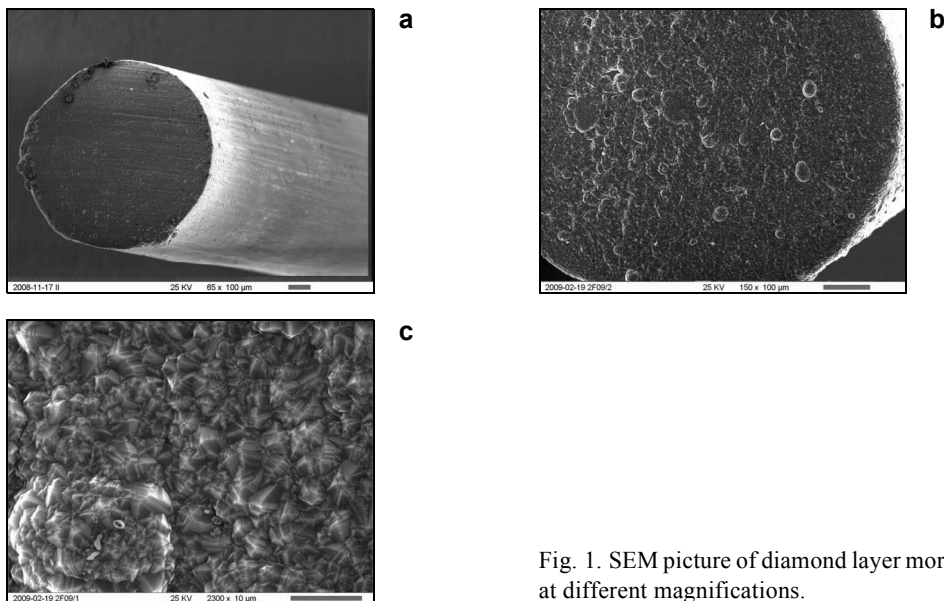

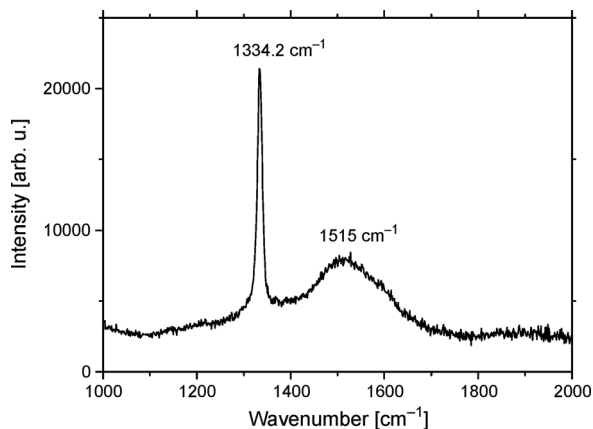Fig. 1. SEM picture of diamond layer morphology at different magnifications.

Fig. 2. Raman spectrum of the diamond layer shown in Fig. 1.

Figure 2 shows the Raman spectrum of the diamond layer from Fig. 1. The Raman spectrum is typical of CVD diamond and displays sharp Raman line with the maximum at 1334.2 cm^{-1}. The position of this line is shifted by about 2 cm^{-1} in comparison to the Raman line of natural diamond which has a characteristic line peaked at 1332.5 cm^{-1} [10].

The Raman line shift is probably caused by the difference in the thermal expansion coefficients of diamond and tungsten, which introduces the compressive stress in diamond layer. This can also cause the broadening of the diamond Raman spectrum.

Except the characteristic diamond line the spectrum from Fig. 2 shows also a broad band at the maximum at 1515 cm^{-1} which is characteristic of sp^2-hybridized amorphous carbon phase [11].

The volume fraction of this amorphous carbon admixture is about 0.04 and was estimated using a procedure described by Ballutaud *et al.* [12]. Such amount of
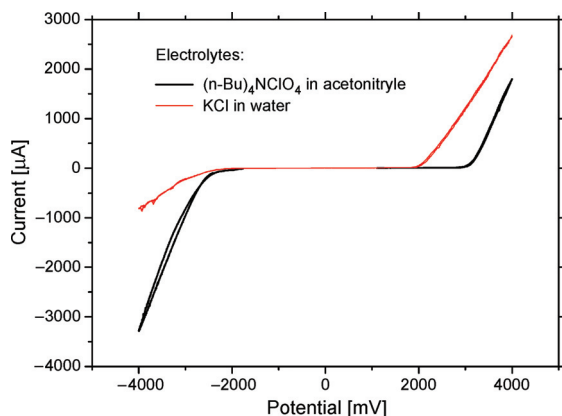

Fig. 3. CV curves recorded by diamond electrode used in 0.1 M KCl in aqueous and 0.1 M (n-Bu)$_4$NClO$_4$ in acetonirtyle solutions at a scan rate of 0.1 mV/s.

amorphous carbon phase corresponds to the hydrogen concentration in the diamond layer of the order of 10^{21} H atom/cm^{-3}, which is probably responsible for the relatively good electrical conductivity [9].

The cyclic voltammograms (CV) recorded by diamond electrode in 0.1 M KCl aqueous and acetonitryle solutions with addition of 0.1 M $(n\text{-Bu})_4\text{NClO}_4$ are shown in Fig. 3. The potential window in a non-aqueous medium is wider than aqueous one.

Insignificant decomposition of water has occurred over a wide potential range of (−1900–1800 mV). In both types of solutions the background currents are very low.

The CV curves recorded by diamond undoped electrode at different scan rates in 0.1 M KCl solutions containing 0.01 M $[\text{Fe(CN)}_6]^{3-/4-}$ redox couple are shown in Fig. 4. The symmetrical anodic and cathodic peaks are associated with the oxidation
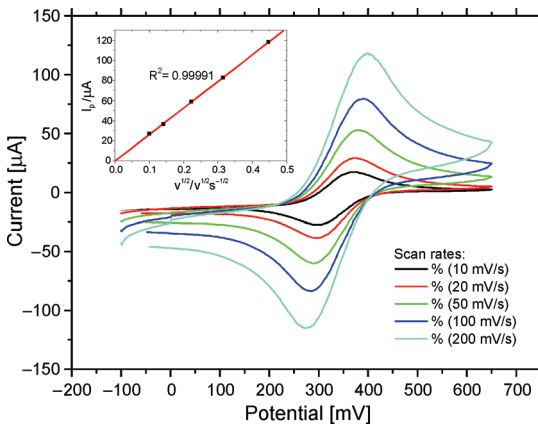

Fig. 4. CV voltammograms recorded by diamond electrode in 0.1 M KCl + 0.01 M $[\text{Fe(CN)}_6]^{3-/4-}$ at the scan rates of 10, 20, 50, 100, 200 mV/s. (The inset: peak current *vs.* the square root of the scan rate.)
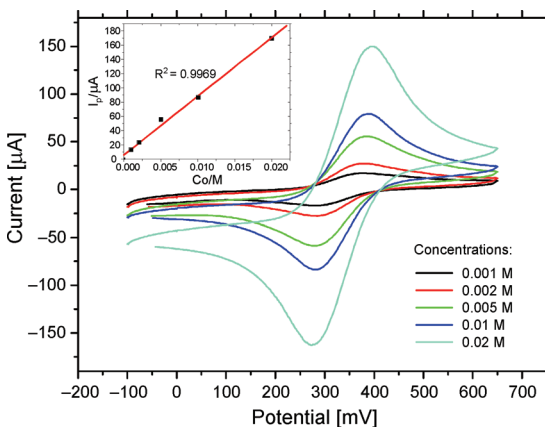

Fig. 5. CV voltammograms recorded by diamond electrode at the scan rate of 100 mV/s in 0.1 M KCl containing $[\text{Fe(CN)}_6]^{4-/3-}$ of different concentrations (Co = 0.001, 0.002, 0.005, 0.01, 0.02 M). (The inset: peak current vs. $[\text{Fe(CN)}_6]^{3-/4-}$ concentrations in 0.1 M KCl.)

and reduction of the ferricyanide−ferrocyanide couple at the diamond solutions interface. The ratios of anodic/cathodic peak curvents approache 1, indicating that both ferricyanide and ferrocyanide are stable in solution and present the reversibility of the electrode process. A linear relationship of anodic peak current I_p versus square root of scan rate $\nu^{1/2}$ is observed (inset in Fig. 4), which indicates that, according to Randles−Sevcik theory, the electrode works correctly and the process on electrode surface has diffusion-controlled character [13].

In order to check the sensitivity of the electrode to the different concentration of both ferricyanide and ferrocyanide, suitable (adequate) measurements were performed and the results are shown in Fig. 5.

The oxidation and reduction potentials are constant and independent of $[Fe(CN)_6]^{3-/4-}$-concentrations [14]. The peak current increases with an increase in $[Fe(CN)_6]^{3-/4-}$- concentration (inset in Fig. 5).

4. Conclusions

It was found that the diamond electrode on the tungsten substrate exhibits exellent performance in CV and shows wide potential window, which is almost twice as wide compared to platinum electrode [15]. Well-defined voltammograms were obtained, which exhibited high sensitivity and demonstrated significant advantage over classical platinum electrode. The use of diamond electrode is simple because no chemical modification is required. Besides cleaning of the electrodes is not necessary due to the long-therm stability of the electrode response. Additionally, the background current is very low.

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