Polycrystalline boron-doped diamond (BDD) films, mainly deposited on p-silicon substrates, exhibit a large set of characteristics, such as high electrical conductivity, low coefficient of thermal expansion, wide potential window, weak adsorption of polar molecules, and high corrosion resistance, that make BDD an attractive material for many applications including electrode material, electronic and optical devices. However, diamond thin films, usually grown by chemical vapor deposition (CVD), have a nonuniform grain size, randomly oriented crystals, non-diamond carbon impurities, and surface roughness (2-30 μm) that limits its usefulness in many applications.

To overcome some of these limitations diamond films must be polished to reduce the surface roughness. However, because of the hardness of diamond, polishing is a difficult task and consequently many polishing techniques have been studied.1 Mechanical polishing of diamond films has been used for a long time and is commonly used in polishing single-crystal diamonds, polishing times can be long (several days), and the force applied to the sample to effect polishing can cause subsurface microcracking.2 Thermochemical polishing of diamond has been reported by many authors using hot transition metals and rare earths to dissolve atomic carbon.3-5 This technique produces smooth surfaces, but the contamination of the diamond film by inclusion of metallic contaminant is possible.6 Laser polishing has been proposed as a suitable method for the treatment of curved and localized surface.7-9 However, the laser can generate shock waves and cracks that affect the adhesion between the diamond and substrate. Many other polishing techniques have been suggested including chemical-assisted mechanical,10 reactive ion,11,12 ion-beam,13,14 and abrasive liquids.15

Electropolishing is a well-known method for smoothing, brightening, and improving surface finish of metals that enhances mechanical and corrosion resistance properties. Although thus far many studies have been carried out on fundamental aspects and application of electropolishing of metals,6-20 to our knowledge no reports have appeared concerning the electrochemical polishing of BDD.

In this paper we report preliminary results on the electrochemical polishing of a BDD electrode in organic media. The characterization of the electropolished diamond has been performed by scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), and electrochemical measurements.

**Experimental**

BDD films were synthesized by the hot-filament CVD technique (HF-CVD) on single-crystal p-type Si(100) wafers (1-3 mΩ cm, Siltronix). The temperature range of the filament was 2440-2560°C and that of the substrate was monitored at 830°C. The reactive gas used was methane in an excess of dihydrogen (1% CH₄ in H₂). The doping gas was trimethylboron with concentration of 1-3 ppm.21 The gas mixture was supplied to the reaction chamber with a flow rate of 5 L/min giving a growth rate of 0.24 μm/h for the diamond layer. The doping level of boron in the diamond layer expressed as B/C ratio was about 3500 ppm. The obtained diamond film thickness was about 1 μm with a resistivity of 10-30 mΩ cm.

Then the BDD electrodes were electropolished at constant anodic current density (1 A cm⁻²) in 3 M acetic acid in 1 M H₂SO₄ using a platinum wire as counter electrode. The solution was continually stirred during the treatment and the temperature was maintained at the constant value of T = 40°C. The exposed apparent area of the BDD electrodes was 1 cm². At different polarization times, the BDD was characterized by SEM, XPS, and electrochemical measurements.

The SEM analysis was performed using a JEOL JMS-6300-F scanning electron microscope. The surface bonds were analyzed by XPS using a Kratos Axis-ultra spectrometer with a monochromatic Al Kα X-ray source, operated at 15 kV and pass energy of 20 eV. Carbon 1s spectra were deconvoluted using the CasaXPS computer program.

Electrochemical measurements were recorded in 0.5 M H₂SO₄ with a scan rate of 100 mV s⁻¹ in a conventional three-electrode cell using a computer-controlled EG&G potentiostat, model M 273. BDD was used as the working electrode, Hg/Hg₂SO₄-K₂SO₄ (sat) as reference, and Pt as counter electrode. The value of the double-layer capacitance, which is related to microscopic area and consequently to the roughness of the surface, as also estimated by cyclic voltammetry using the relation

\[ i_{\text{lim}} = 2C_{\text{dl}}v \]  

where \( i_{\text{lim}} \) is the total anodic and cathodic current density (A cm⁻²), \( C_{\text{dl}} \) is the double-layer capacitance (F cm⁻²), and \( v \) is the scan rate (V s⁻¹).

**Results**

Figure 1 shows SEM micrographs of the surface morphology of BDD before and after electropolishing in 1 M H₂SO₄ or in 3 M acetic acid in 1 M H₂SO₄. The untreated electrode (Fig. 1a) consists of a polycrystalline diamond film of randomly oriented crystallites with well-developed triangular [111] facets. There is a range of crystallite size reflecting special differences in growth rate, and the surface is rough. After 256 h of polarization at 1 A cm⁻² in 1 M H₂SO₄ (Fig. 1b) the diamond surface, due to its corrosion resistance in acidic media, exhibits no sign of any etching or morphological smoothing. On the contrary, after 4 h of electropolishing in acetic...
acid media, which is a commonly used electrolyte for electropolishing, the surface was etched and the average crystallite size was seen to strongly decrease. After 17 h of treatment the morphology of the diamond film had completely changed. The polycrystalline morphology was no longer visible and the crystal edges were smoother as the typical results of the polishing process and material removal.

X-ray photoelectron spectra of the diamond films were obtained before and after electropolishing in acetic acid media to determine the elemental composition of the surface and the results are shown in Fig. 2. The survey spectrum of the untreated BDD reveals that, in addition to the large peak from the C 1s core level located at 285 eV, only a very small peak due to O 1s core level at 532.5 eV is present, meaning that the surface is without detectable impurities. After 4 h of electropolishing, the intensity of the O 1s peak increased due to oxidation of the diamond surface. Some S 2p (169 eV) and Si 2p (102 eV) can also be observed, most likely exchanged from the electrolyte (H2SO4) and silicon substrate during polarization. The O 1s/C 1s atomic concentration ratios, calculated from XPS analysis, during the polarization increased ten times from 0.02 to 0.21, meaning that the electrochemical treatment causes significant oxidation of the surface making it more hydrophilic. The surface chemical bonds were investigated by the deconvolution of C 1s spectra during electropolishing (Fig. 3). For the untreated electrode (Fig. 3a) besides the main peak, which is due to C-C, we observe the existence of a broad peak at about +0.5 eV that can be assigned to a specific surface state involving only carbon and hydrogen. Significant changes occurred on the surface during the polishing. After 4 h of polarization the peak at +0.5 V was not present and there appeared two peaks with shifts between 1.0 and 1.9 eV with respect to the bulk peak, which can be attributed to hydroxyl and ether groups. No significant changes in the surface chemical bonds were observed after 17 h of treatment.

Figure 4 shows cyclic voltammetry recorded in 0.5 M H2SO4 at BDD before and after electropolishing in acetic acid media. In the region between potential limits, the voltammogram for the untreated electrodes was rather featureless, which is typical for diamond, reflecting the ideally polarizable nature of the thin-solid electrolyte interface. After electropolishing in acetic acid media (curve b) the current density and the total voltammetric charge significantly decreased. During the electropolishing treatment, the

Figure 1. SEM microphotographs of a BDD electrode (a) before treatment; after electropolishing (b) for 256 h in 1 M H2SO4; (c) for 4 h in 3 M acetic acid in 1 M H2SO4; (d) for 17 h in 3 M acetic acid in 1 M H2SO4. Applied current: \( i = 1 \text{ A cm}^{-2}, T = 40^\circ\text{C} \).

Figure 2. XPS spectra of BDD (a) before and (b) after 4 h of electropolishing in 3 M acetic acid in 1 M H2SO4 at \( i = 1 \text{ A cm}^{-2}, T = 40^\circ\text{C} \).

Figure 3. Deconvoluted XPS C 1s spectra of BDD (a) before and (b) after 4 h of electropolishing in 3 M acetic acid in 1 M H2SO4 at \( i = 1 \text{ A cm}^{-2}, T = 40^\circ\text{C} \).

Figure 4. Cyclic voltammetry recorded in 0.5 M H2SO4 with a scan rate of 100 mV s\(^{-1}\) on a BDD (a) before and (b) after 4 h of electropolishing in 3 M acetic acid in 1 M H2SO4 at \( i = 1 \text{ A cm}^{-2}, T = 40^\circ\text{C} \).
double-layer capacitance, also decreased to a very low value comparable with that of the single-crystal diamond (0.85-0.92 μF cm⁻²) (Fig. 5). The decrease of the charge and the capacitance results first from oxidative removal by gasification of non-diamond carbon impurities (sp² sites) and from etching of the surface, confirmed reduction of the surface roughness already observed by SEM analysis.

Conclusions

In this paper a BDD film deposited by CVD has been electropolished in acetic acid media and the surface has been characterized by SEM, XRD, and electrochemical measurements. In 1 M H₂SO₄ no polishing of the surface was observed even after 256 h of treatment. On the contrary, in electrolyte containing 3 M acetic acid in 1 M H₂SO₄ the morphology was changed in a few hours. Crystal edges became smoother as the typical results of polishing process and material removal. Capacitance measurements confirmed a decrease in surface roughness. Preliminary data are promising and suggest that electropolishing in acetic acid media may be a useful technique to reduce the surface roughness of BDD.

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