Available online at www.sciencedirect.com
SCIENCE DIRECT®
Electrochemistry Communications 7 (2005) 937–940
electrochemistry communications
www.elsevier.com/locate/elecom

Photochemical oxidation of hydrogenated boron-doped diamond surfaces

Rabah Boukherroub [a,b,*], Xavier Wallart [b], Sabine Szunerits [c], Bernadette Marcus [c], Pierre Bouvier [c], Michel Mermoux [c]

[a] *Institut de Recherche Interdisciplinaire (IRI), France*
[b] *Institut d'Electronique, de Microélectronique et de Nanotechnologie (IEMN), CNRS-8520 Cité Scientifique, Avenue Poincaré- BP. 60069, 59652 Villeneuve d'Ascq, France*
[c] *Laboratoire d'Electrochimie et de Physicochimie des Matériaux et des Interfaces (LEPMI), CNRS-INPG-UJF, 1130 rue de la piscine, BP 75, 38402 St. Martin d'Hères Cedex, France*

Received 12 May 2005; accepted 31 May 2005

Abstract

We describe the photochemical oxidation of polycrystalline boron-doped diamond films by UV irradiation in air at room temperature. The reaction generates surface hydroxyl groups that have been coupled with perfluorodecyl trichlorosilane to yield an organic layer covalently attached to the diamond surface. The resulting surfaces were characterized using X-ray photoelectron spectroscopy, contact angle and cyclic voltammetry.

Keywords: Boron-doped polycrystalline diamond; Photochemical oxidation; Electrochemical properties; Surface chemical reactivity

1. Introduction

Diamond films are of particular interest due to their excellent mechanical properties and good biocompatibility. Boron-doped diamond (BDD) layers display good electrical conductivity and thus they are widely investigated as electrodes for various electrochemical processes [1]. Indeed, a BDD electrode exhibits low background current density and a large potential window in aqueous electrolytes [2]. Because the deposition of diamond films was undertaken in reductive medium (hydrogen plasma), it is believed that the as-deposited diamond surface is hydrogen-terminated. However, a small fraction of oxygen is always found in freshly deposited diamond films after exposure to ambient atmosphere. The presence of oxygen on the diamond surface has a significant influence on the chemical reactivity [3,4], electrical conductivity [5,6], field emission [7,8] and Schottky barrier heights [9]. Various conditions for diamond oxidation were reported in the literature including thermal [10,11], plasma [12,13], electrochemical techniques [14,15], singlet oxygen [16] and ozone treatment [17,18]. Thermal oxidation of hydrogen-terminated diamond under various conditions showed a surface composition dominated by ether (C–O–C) and carbonyl (C=O) groups. Electrochemical anodization or plasma treatment of diamond surface generates surface termination composed of ether, carbonyl, and hydroxyl (OH) groups. The presence of the surface hydroxyl species was demonstrated by further coupling of the oxidized surface with alkyltrichlorosilanes [15] and biotinylated esters [16]. There is only one report using photochemical conditions for surface oxidation [19]. It consists on the

---

[*] Corresponding author. Tel.: +33 3 20 19 79 87; fax: +33 3 20 19 78 84.
E-mail address: rabah.boukherroub@iemn.univ-lille1.fr (R. Boukherroub).

1388-2481/$ - see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.elecom.2005.05.010

irradiation of hydrogen-terminated polycrystalline diamond with vacuum ultraviolet light (VUV) at $\lambda = 172$ nm for 3 h in the presence of O_2 and H_2O. The generated surface hydroxyl groups were coupled with *p*-aminophenyltrimethoxysilane to yield an organic layer terminated with amino groups.

Here, we report our preliminary results on the photochemical irradiation of hydrogen-terminated boron-doped diamond using a low pressure mercury arc lamp and further coupling of the hydroxyl surface groups with a perfluorotrichlorosilane.

2. Experimental

Polycrystalline diamond layers were synthesized on a silicon high purity p-type wafer by microwave plasma enhanced chemical vapour deposition in a conventional reactor [20]. The growth conditions used were as follows: substrate temperature 700–900 °C; total gas flow of a mixture of 0.7% methane in hydrogen 100 sccm; total pressure in the reactor 20 Torr (30 mbar); microwave power 700 W. The dopant source was boron oxide set in a Pt crucible placed on the substrate holder near the silicon substrate. Before commencing the diamond growth, the silicon substrates were ultrasonically damaged with diamond powder in ethanol in order to improve the nucleation density [21]. After deposition, the methane flow was stopped and the films were kept under hydrogen plasma for an additional 30 min. After 24 h of deposition, the film thickness averaged 8 mm. Dopant concentration in the diamond layers, as estimated from Raman spectroscopy measurements [22] was in the range 10^{19}–10^{20} B cm^{-3}. The film resistivity was $\leqslant 0.1\ \Omega$ cm as measured with a four-point probe.

Electron microscopy was carried out with a LEO 982 field-emission scanning electron microscope (SEM) with an image resolution of 2.1 nm at 1 kV and 1.5 nm at 15 kV at the analytical working distance.

For X-ray photoelectron spectroscopy (XPS) measurements, we use a monochromatic Al Kα X-ray source and an analyzer pass energy of 12 eV. Under these conditions, the overall resolution as measured from the full width at half-maximum (fwhm) of the Ag 3d5/2 line is 0.55 eV. The binding energy scale is calibrated using the Au 4f7/2 line at 84.0 eV. The acceptance angle of the analyzer has been set to 14°, and the angle between the incident X-rays and the analyzer is 90°. The detection angle of the photoelectrons is 25°, as referenced to the sample surface.

The electrochemical properties of the diamond surfaces were evaluated using $[Fe(CN)_6]^{3-/4-}$ as the redox couple in solution. The diamond film working electrode ($A \approx 0.28\ cm^2$) was sealed against the bottom of a single compartment electrochemical cell by means of a rubber O-ring. The electrical contact was made to a copper plate, through the bottom of the silicon substance where the diamond was deposited. A platinum electrode and a Ag/AgCl reference electrode were used.

3. Results and discussion

Fig. 1 displays a SEM image of a typical as-grown diamond film. The polycrystalline diamond film consists of randomly oriented crystallites of few microns size and with predominantly cubic (1 0 0) and triangular (1 1 1) faces.

X-ray photoelectron spectroscopy was used to analyze the chemical composition of the diamond surfaces before and after chemical modifications and the nature of the chemical bonding associated with transformations occurred on the surface. Fig. 2(a) displays an XPS survey of the as-deposited boron-doped diamond surface showing signals due to C 1s at 284 eV. A small signal due to O 1s at 531 eV was present in the spectrum. However, it is difficult to assign precisely the origin of the peak whether it is due to surface contamination or to interstitial incorporation within the C–C backbonds. After UV irradiation in air for 2 h using a low pressure mercury arc lamp, an increase of the signal of O 1s was observed, consistent with surface oxidation. High-resolution XPS spectrum displays two signals due to C 1s from the bulk and from the surface C–O features at 284 and 287 eV, respectively. The latter peak results most likely from a contribution of carbonyl groups on the surface. Based on the diamond structure, it is expected that the sp^3 C–H bonds on the (1 1 1) facets will be terminated with hydroxyl groups, while the CH_2 bonds on the (1 0 0) facets will be transformed to

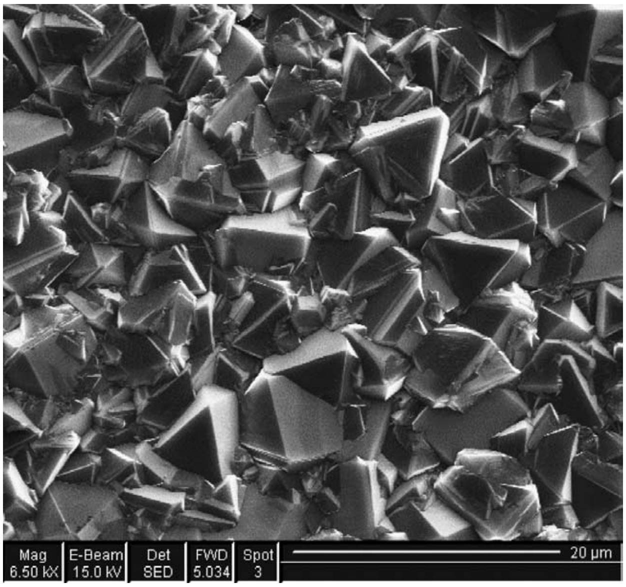

Fig. 1. Scanning electron microscopy image of as-prepared boron-doped diamond surface.