Applied Surface Science 433 (2018) 408–418

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Full Length Article

Oxygen termination of homoepitaxial diamond surface by ozone and chemical methods: An experimental and theoretical perspective

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ARTICLE INFO

Article history:
Received 25 July 2017
Received in revised form 3 October 2017
Accepted 9 October 2017
Available online 14 October 2017

Keywords:
Diamond
Surface O termination
XPS
HRTEM analysis
DFT calculations

ABSTRACT

Phenomena related with the diamond surface of both power electronic and biosensor devices govern their global behaviour. In particular H- or O-terminations lead to wide variations in their characteristics. To study the origins of such aspects in greater depth, different methods to achieve oxygen terminated diamond were investigated following a multi-technique approach. DFT calculations were then performed to understand the different configurations between the C and O atoms. Three methods for O-terminating the diamond surface were performed: two physical methods with ozone at different pressures, and an acid chemical treatment. X-ray photoelectron spectroscopy, spectroscopic ellipsometry, HRTEM, and EELS were used to characterize the oxygenated surface. Periodic-DFT calculations were undertaken to understand the effect of the different ways in which the oxygen atoms are bonded to carbon atoms on the diamond surface. XPS results showed the presence of hydroxyl or ether groups, composed of simple C—O bonds, and the acid treatment resulted in the highest amount of O on the diamond surface. In turn, ellipsometry showed that the different treatments led to the surface having different optical properties, such as a greater refraction index and extinction coefficient in the case of the sample subjected to acid treatment. TEM analysis showed that applying temperature treatment improved the distribution of the oxygen atoms at the interface and that this generates a thinner amount of oxygen at each position and higher interfacial coverage. Finally, DFT calculations showed both an increase in the number of preferential electron transport pathways when π bonds and ether groups appear in the system, and also the presence of states in the middle of the band gap when there are π bonds, C=C or C=O.

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1. Introduction

Intensive research is being performed into high power diamond devices after recent publications reported their outstanding electrical and thermal properties [1,2]. Volpe et al. reported a high breakdown field (higher than 7.7 MV/cm) [1]. However, other important aspects, such as high hole and electron mobility ($\mu_p = 2000\ cm^2\ V^{-1}\ s^{-1}$, $\mu_n = 1000\ cm^2\ V^{-1}\ s^{-1}$) [3–5], and high thermal conductivity ($\sim 22\ W\ cm^{-1}\ K^{-1}$) [6] should encourage diamond use in devices fabricated in the future. Among the different expected developments are a higher technological control of their characteristics and stability versus temperature and time in service. Compared with other diamond power devices, Schottky barrier diodes (SBD) are the most promising in terms of the highest breakdown voltage reported (8–12 kV) [1,7]. The main technological issue with SBDs is their design and controlling the metal-semiconductor barrier. Such interfaces require precise control of the band alignment. Previous results show that the choice of the diamond termination before metallization is a critical step in obtaining good characteristics [8,9]. Oxygen is used during met-

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https://doi.org/10.1016/j.apsusc.2017.10.065
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allization to increase the barrier height and contact with a metal, preferably one with a high O-affinity such as Zr, which makes it possible to stabilize the oxide monoatomic layer up to relatively high temperatures (450 °C in the case of Zr). This shows the importance of building well-defined nanometric interfaces to improve electrical rectifiers, and the specific surface termination should be designed in correspondence with the desired characteristics of the device. In particular, hydrogen termination results in a negative electron affinity (NEA), which suggests that the conduction band lies above the vacuum level [10,11]. The diamond surface becomes conductive [12], which is a unique behaviour among semiconducting materials. Moreover, theoretical calculations have shown that adsorbed organic molecules (1,3-butadiene, acetylene and ethylene) on the diamond surface and their coverage favoured the NEA conditions in a similar way to that of the surface hydrogen termination [13]. In contrast, oxygen termination produces a positive electron affinity (PEA), which leads to downward band bending. This behaviour is attributed to the dipoles generated at the diamond surface, where the electronegativity of the species at the surface modifies the spatial distribution of the charges related with bonding [14]. However, this surface behaviour is very sensitive to the termination state. Indeed, an oxygen termination can be in a variety of states: ether (C—O-C) (with a PEA of 2.7 eV), hydroxyl (C—OH) with a lower PEA value, ketone (C═O), or a combination of all three [15,16]. The stability of those surface configurations is still not clear. Indeed, some calculations seem to indicate that the hydroxyl state is the most stable [17], whereas others indicate that the ketone state is the most stable configuration for high surface coverage [18]. The effect of dopants in the presence of different degrees of coverage of the surface by oxygen groups has even been studied [19,20].

Obviously, this surface state depends directly on the experimental conditions of the diamond surface treatment. UV/ozone treatment is usually used to convert the H-terminated surface of the diamond after MPCVD growth into an O-terminated one [21,22] when manufacturing efficient diamond electronic devices. Higher Schottky barrier heights are obtained with this treatment [23]. However, other methods, such as RF oxygen plasma, anodic polarization in an alkaline electrolyte, or simple acid solutions, are alternatives for converting an H-termination in an O-termination [24].

The most widely used experimental technique to study diamond surfaces is x-ray photoelectron spectroscopy (XPS) [24], which reveals the binding energy states inside a 20 nm thick layer at the surface, and Kelvin force microscopy (KFM), where the surface potential is deduced [25]. In XPS, the expected peaks on the diamond surface are sp^3 (about 284.5–285 eV), polyhydride carbon species (285 eV), hydroxyl and ether groups (about 286.5 eV) [26,27]. The peak at about 283.5 eV is usually assigned to π-bonded C atoms [28]. Some authors assign the contribution at about 280–281 eV to the emission from surface atoms missing a nearest neighbour [29] or caused by the non-monochromatic source [30]. On the other hand, oxidation processes induce several kinds of carbon oxygen bonds. As reported previously, –C—OH or –C—O—C– bonds appear at a BE of 286.5 eV. At about 288 eV, —O—C—O— or carbonyl groups are assigned; and —(O═C)—O— carboxyl groups are found at about 289 eV [29].

The present study analyses the state of the diamond surface after different vacuum-ultraviolet (VUV) ozone treatments and a chemical acid attack to convert a hydrogen termination into an oxygen one. A multi-technique approach involving XPS, spectroscopic ellipsometry, and High Resolution Transmission Electron Microscopy – Electron Energy Loss Spectroscopy (HRTEM-EELS) made it possible to determine the chemical surface bonding, identify optical changes on the surface, and show the uniformity of the oxygen content on the diamond surface after those treatments.

Table 1
Oxygenation treatment applied to the samples.

Samples	Treatments
GD11-2C	UV/ozone treatment. P = 500 mbar.
GD13-1A	UV/ozone treatment. Atmospheric Pressure.
GD13-1B	Acid chemical treatment using HNO_3 and H_2SO (1:3), at 200 °C for 2 h.

Finally, periodic-DFT calculations were performed to understand the effect of the different ways in which the oxygen atoms are bonded to carbon atoms on the diamond surface.

2. Materials and methods

2.1. Samples and treatments

All the samples were single crystal, undoped, and previously hydrogenated in a MPCVD reactor. The GD11-2C sample was exposed to an ozone treatment produced by deep UV light. The substrate was inserted into a secondary vacuum chamber before the injection of pure oxygen gas at a constant pressure of 500 mbar. Then, the UV lamp was turned on and ozone was produced for 2 h. The GD13-1A sample was subjected to a different ozone treatment. The treatment was performed using FHR© equipment, model UVOH150. The system injected pure oxygen (flow 0.8 slm) under atmospheric pressure for 20 min at 80 °C. Both systems used a low pressure Hg-vapor lamp. The last sample, GD13-1B, was immersed in a boiling acid solution at 200 °C for 2 h. The acid mixture was nitric acid and sulphuric acid (1:3) in order to obtain sulfonitric mixed acid, which is an effective oxidant solution. A summary of the treatments is shown in Table 1.

2.2. Characterization

X-ray photoelectron spectroscopy was used to analyse the chemical bonding states on the surface. The XPS spectra were recorded using a Kratos Axis UltraDLD spectrometer, with monochromated Al Kα radiation (1486.6 eV) and 20 eV pass energy. The binding energy scale was given with an accuracy of 0.1 eV. Electrostatic charging effects could be stabilized with the help of the specific device developed by Kratos.

To analyse the effect of the ozone treatments and the chemical acid attack on the surface termination, first, experiments were performed to measure the ellipsometric angles (Ψ, Δ). In spectroscopic ellipsometry, (Ψ, Δ) spectra are measured by changing the wavelength of light in the UV/visible/NIR region or infrared region. In principle, ellipsometry measures the two values (Ψ, Δ) that represent the amplitude ratio, Ψ, and phase difference, Δ, between p- and s-polarized light waves. Thus, reflection ellipsometry makes it possible to determine the ratio ρ of the complex Fresnel reflection coefficients for the p and s polarizations:

$$\rho = \frac{R_p}{R_s} \equiv tan\Psi e^{i\Delta} \quad (1)$$

where ρ is a complex function of the optical constants of the incident and transmitted media, and (Δ,Ψ) are the ellipsometric angles.

The identification of the oxide layer and the evaluation of its thickness were carried out by a combination of HRTEM and EELS techniques. HRTEM and EELS measurements were performed using either the beam of a JEOL 2010F STEM microscope, or that of a FEI-TITAN THEMIS, on electron-transparent specimens, fabricated by a lift-off technique in a focused ion beam (FIB) FEI Quanta 200-3D dual beam microscope.

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