Diamond & Related Materials xxx (2009) xxx–xxx

Contents lists available at ScienceDirect

Diamond & Related Materials

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

XPS and UPS investigation of the diamond surface oxidation by UV irradiation

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ARTICLE INFO

Available online xxxx

Keywords:
Hydrogenated nanocrystalline diamond
UV oxidation
UPS
XPS
Electron affinity

ABSTRACT

In this work we describe the effect of oxidation on undoped nanocrystalline H-terminated CVD diamond films. Surface oxidation was performed using UV photons in air and in pure dry oxygen atmosphere. The samples were then thermally treated to study the effect of the UV-induced oxidation on the electronic properties of diamond. Different annealing temperatures were applied to induce a controlled oxygen desorption. Both UV- and X-ray photoelectron spectroscopies were performed *in situ* in order to correlate the electron affinity changes to the oxygen atomic abundances detected on the diamond surfaces. Our results show that UV oxidation is less invasive if compared to other conventional processes like chemical or plasma oxidations. This enables a recovering of the surface electronic properties with the thermal desorption of oxygen from the diamond surfaces.

1. Introduction

Diamond, thanks to its outstanding electrochemical properties, is a very promising material for realizing electronic and biochemical devices [1–3]. In fact, the electrochemical surface properties of diamond may be changed by appropriate functionalizations. The hydrogen termination leads to conductive diamond surfaces while the oxidation renders them non-conductive [4]. Considering additional degree of complexity, the diamond terminated surfaces may be grafted with ammine groups which behave as active sites to bond specific biomolecules allowing surface bioengineering [5,6]. Concerning diamond oxidation, irradiation with UV-photons was recently proposed [7]. This oxidation technique is very promising allowing functionalization of selective regions of the diamond surface in order to realize sensors [8]. Although the use of UV irradiation is widely used, the chemical processes related to the ozone interaction with the H-terminated diamond surface remain still not completely clarified. It is well known that different surface terminations of the diamond surface lead to a strong modification of the electronic structure of diamond. In particular, a fully H-terminated surface shows a negative electron affinity (NEA) while an oxidized diamond surface exhibits a positive electron affinity (PEA) and insulating properties. Direct determination of NEA–PEA parameters is generally performed using Kelvin probes while, as in our case, indirect estimation of the diamond electron affinity is obtained via UV photoelectron spectroscopy (UPS). In HeI-UPS the secondary electron peak appears as a sharp feature whose position (the cut off) determines the minimum detectable kinetic energy (i.e. the maximum of binding energy referred to E_F) of electrons leaving the diamond surface into the vacuum. The HeII photons allow the estimation of the valence band maximum (VB_M) respect to E_F. Observe that here we use of E_F as a reference for the HeI, HeII spectra, i.e. a binding energy scale. Differently from the vacuum level (the reference for kinetic energies) which changes with the surface work function, E_F is fixed and this makes of all the calculation easier. Combining cut-off and VB_M, the electron affinity χ of the diamond sample can be calculated as:

$$\chi = \mathrm{hv} - E_g - W \quad (1)$$

where hv is the photon energy, E_g is the diamond band gap (5.5 eV), and W is the emission width [9] namely the difference between the VB_M and the cut-off positions. These positions are obtained with linear extrapolations of the HeI, HeII spectra as described in [10,11]. Applying the simple relation (Eq. (1)) in a previous work we showed that the diamond exposure to UV light in atmosphere is able to induce a surface oxidation and the correspondent changes of the electron affinity from NEA to PEA [12]. In this work we present a detailed study of the electron affinity modifications induced by thermal treatments applied to the oxidized diamond surface. It is known that high temperature annealing is able to induce oxygen desorption from the

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doi:10.1016/j.diamond.2009.02.003