



# Interaction of water molecules with bare and deuterated polycrystalline diamond surface studied by high resolution electron energy loss and X-ray photoelectron spectroscopies

R. Akhvlediani, Sh. Michaelson, A. Hoffman\*

Schulich Faculty of Chemistry, Technion, Haifa 32000, Israel

## ARTICLE INFO

### Article history:

Received 4 July 2010

Accepted 3 September 2010

Available online 21 September 2010

### Keywords:

Water adsorption

Dissociative adsorption

Molecular adsorption

Diamond chemical vapor deposition

Grain boundaries

Chemisorption

Surface vibrations

## ABSTRACT

In this work we study the interaction of water molecules with deuterated and bare polycrystalline diamond surfaces upon exposure to water vapor by X-ray photoelectron spectroscopy (XPS) and high resolution electron energy loss spectroscopy (HR-EELS). To distinguish the molecular origin of hydrogen bonds (i.e. C–H, O–H, C–O–H, etc.) formed on the diamond surface upon interaction with the water molecules, deuterated and hydrogenated gases were used in our experiments. Diamond films were deposited from a deuterated gas mixture to induce C(di)–D surface terminations. Water adsorption on bare diamond surface gives rise to the appearance of well defined and pronounced C–H and C–OH vibrational HR-EELS peaks and an intense O (1s) XPS peak. These chemically adsorbed water fragments survive 300 °C anneal temperature under ultra-high vacuum conditions. Annealing at 600 °C of the water exposed bare diamond surface results in disappearance of the C–OH vibrational modes alongside with a pronounced reduction of the C–H vibrational modes, whilst only upon annealing to ~800 °C the O (1s) XPS peak decreased substantially in intensity. We associate these effects with dissociative adsorption of the water molecules on the bare diamond surfaces.

Water exposure onto a deuterated surface, on the other hand, does not result in the appearance of the C–OH vibrational peaks but only to an increase of the C–H vibrational HR-EELS mode along side with the appearance of a weaker XPS O (1) peak, as compared to the same experiment, performed on the bare surface. 300 °C anneal significantly diminishes surface oxygen concentration, as monitored by XPS. We associate these results with H<sub>2</sub>O decomposition reactions and also with molecular adsorption on deuterated diamond surfaces. Annealing of the water exposed deuterated diamond surface, results in a pronounced decrease and disappearance of the O (1s) XPS peak at a temperature of ~800 °C.

© 2010 Elsevier B.V. All rights reserved.

## 1. Introduction

Interaction of the water molecules with solid surfaces is an interesting problem in fundamental physical chemistry and is also important for practical applications [1,2]. For example, the so-called wet oxidation of silicon is widely used in semiconductor industry [3]. Since each kind of interaction starts from the surface and proceeds towards the bulk of material, deeper understanding the mechanism of the chemical reactions involved requires well defined surface conditions. In the case of chemically reactive materials (e.g. silicon or metals) interaction with water molecules occurs in sub-surface region due to the presence of unavoidable oxide layer. Diamond is known as the hardest and chemically inert material [4] and therefore water (or oxygen) related reactions may be studied directly on top of its well defined surface.

Water molecules may play an important role in the mechanism of diamond nucleation and growth. For example, water affects drastically the quality of the high temperature high pressure (HPHT) formed diamond, where the use of a water-rich fluid phase is essential for formation of impurities free diamond crystals [5,6]. Recent development of hydrothermal synthesis and the reduction of carbide (HSRC) for the synthesis of well defined large scale diamond crystals utilize reaction of water with SiC [7]. The properties of the deposited crystallites, their surface and bulk composition do also depend on the SiC/H<sub>2</sub>O ratio [7]. In the field of nano-diamond formation by the detonation method [8] water is utilized during the explosion itself and also for post-synthesis treatment (the so-called dry (CO<sub>2</sub>) and wet (H<sub>2</sub>O) cooling). Nanodiamonds can be produced by blasting an explosive in water or by spraying water in the chamber space [9]. Blasting in water vapor at optimal conditions increases the diamond yield and essentially changes the hydrophilic/hydrophobic balance of active surface centers [10]. Water is produced in chemical vapor deposition (CVD) reactors upon addition of O<sub>2</sub> (or oxygen containing species) and the following hydrogen oxidation [11–13]. It was found that at low temperatures (<800 °C), the addition of oxygen not only

\* Corresponding author.

E-mail address: [choffman@tx.technion.ac.il](mailto:choffman@tx.technion.ac.il) (A. Hoffman).

enhances the growth rate but also extends the region of diamond formation [14]. In addition, water is present at impurity level in all CVD reactors due to leakages. In nearly all aforementioned cases diamond growth occurs by means of surface reactions on top of a pre-existing nucleus or seeds. Therefore, a deeper understanding of the water induced surface reactions, water adsorption and related phenomena are vital to control diamond quality and possible surface functionalization mechanisms.

Interaction of water with diamond surfaces is of great importance in different fields of diamond science and technology. For example, this interaction is critical in the diamond based electrode area, since most electrochemistry is performed in aqueous solution [15]. Recently it has been reported that immersion of nano-diamond particles into aqueous solutions result in changes in pH and oxygen concentrations [16]. It has been suggested that multi layer adsorption of water onto diamond is promoted by the initial adsorption stages of water onto the diamond surface through the initial formation of a surface dipole, which enhances the ability of water to adsorb onto an otherwise hydrophobic surfaces [16].

The electronic properties of diamond surfaces are also strongly affected and determined by surface impurities, in particular, by water molecules [17,18]. Thus, the well known p-type surface conductivity of diamond surfaces is determined by proper hydrogen surface termination followed by exposure of the surfaces to H<sub>2</sub>O molecules [19,20]. Recently, it has been shown that adsorption of H<sub>2</sub>O molecules on bare diamond surfaces may also produce NEA conditions [21].

Despite its importance, the chemistry of diamond surface interaction with H<sub>2</sub>O molecules is not well established hitherto. There are a few experimental works, studying H<sub>2</sub>O adsorption on diamond surfaces [21–27] alongside with few theoretical investigations using density-functional theory (DFT) methods [28,29] and combined DFT and *ab initio* molecular-orbital calculations [30–32]. X-ray absorption near edge structure (XANES) spectroscopy revealed no water adsorption on poly-crystalline boron doped diamond films [25], however, significant interaction occurs with low energy ion produced defects. Two kinds of water molecules adsorption states were found by Fourier transform infra-red (FTIR) spectroscopy, applied to study single crystal type IIa (001) diamond surface [22] and ultra-dispersed diamond (UDD) powder obtained by detonation methods [24]. Different mechanisms of dissociative water molecules adsorption were suggested to occur on single crystal (001) diamond surfaces [22], while *molecular* adsorption was proposed on different sites of UDD [24]. High resolution electron energy loss spectroscopy (HR-EELS) was also applied to study the interaction of diamond surfaces with water molecules [21,27]. The research that was done partially in our lab [27] and was conducted on bare and hydrogenated polycrystalline diamond surfaces, revealed that water molecules dissociate on both kinds of surfaces, while the degree of adsorption of water fragments is larger in the case of more reactive bare diamond surface (estimated quantitatively by X-ray photoelectron spectroscopy, XPS). However, the nature of the bonds and their thermal stability were not established. Recent work performed by Gao et al. [21] on boron doped single crystal (100) bare diamond sample revealed dissociative adsorption of water molecules alongside with appearance of NEA, detected by ultra-violet photoelectron spectroscopy (UPS).

To the best of our knowledge there are no systematic studies of thermal stability of the water molecules and their fragments following dissociative adsorption on diamond surfaces. This study is of high importance, since moderate thermal annealing of water exposed diamond films at >300 °C results in considerable decrease of surface conductivity, which has been associated to the thermal induced desorption of water molecules (or their fragments) [19,33]. In addition, there are no spectroscopic evidence about the nature of the chemical bonding on the surface upon annealing.

In the present work we study the chemical state of hydrogenated and bare polycrystalline diamond films surfaces in situ exposed to

water vapor and systematically monitor the thermal stability of the developed bonds by XPS and HREELS. This investigation was carried out by monitoring the O (1s)-XPS peak line shape, binding energy position and integral intensity for quantitative elemental analysis of the near-surface region and bonding configuration of oxygen. HREELS measurements were used to establish the surface atoms bonding configuration and fragmentation of the adsorbed water molecule with particular emphasis to hydrogen (deuterium) bonding. In this study we are investigating non-reversible adsorption process: i.e. we expose the diamond surfaces to water molecules at normal equilibrium vapor pressure at RT (water vapor pressure of ~20 Torr), while spectroscopic measurements are carried out at UHV conditions.

## 2. Experimental

Diamond samples were grown by hot filament chemical vapor deposition (HF CVD) for 1 h from CD<sub>4</sub>/D<sub>2</sub> (1/99) or CH<sub>4</sub>/H<sub>2</sub> (1/99) gas mixture [34]. These films have a poly-crystalline character with ~300 nm grain size at the film's surface and thickness of ~700 nm in the case of common CH<sub>4</sub>/H<sub>2</sub> growing gas mixture and ~150 nm grain size and ~300 nm thickness in the case of CD<sub>4</sub>/D<sub>2</sub> gas mixture (detailed study of the kinetic isotopic impact on diamond film growth was recently reported by us) [35]. Scanning electronic microscopy, Raman, X-ray photoelectron and HR-EEL spectroscopies were applied to characterize the morphology, bonding configuration and chemical composition of the film's surfaces [34,35]. In the present research, samples were immediately transferred to ultra high vacuum (UHV) chamber following the deposition and the total ambient exposure time was <5 min. Water vapor exposure was carried out in situ in the preparation chambers adjunct to our main analysis UHV chamber. Either deuterated or bare diamond films were exposed at room temperature for 10 min to water vapor introduced at the pressure of ~20 Torr.

HR-EELS and XPS experiments were carried out in a UHV system equipped with a surface analytical techniques consisting of a double monochromator and a single analyzer housed in a UHV system with base pressure of ~8 × 10<sup>-10</sup> Torr. The HR-EELS spectra were recorded at room temperature up to loss energies of 600 meV. The primary electron energy was 5 eV and the spectra were recorded in the specular geometry with an incident angle of 55° from the normal surface. The full width half maximum (FWHM) of elastically scattered beam was 5–6 meV in the case of fresh diamond samples, while in the case of contaminated surface FWHM was 9–10 meV. The XPS measurements were carried out using AlK $\alpha$  radiation and a hemispherical electron analyzer operated at pass energy of 97 eV. All spectroscopic measurements were carried out at RT and under UHV conditions.

## 3. Results and discussion

We begin the discussion with the analysis of the main HR-EELS features relevant for the present study for hydrogenated, deuterated and bare polycrystalline diamond surfaces. Then we analyze water adsorption onto the bare diamond surface by HR-EEL spectroscopy, following by water adsorption onto deuterated diamond surfaces. XPS was applied for quantitative chemical analysis of the water molecules and their fragments adsorbed onto the bare and D-covered diamond surfaces.

### 3.1. Analysis of the basic HR-EELS features of hydrogenated, deuterated and bare diamond polycrystalline surfaces

In Fig. 1 are shown HR-EEL spectra of as-deposited HF-CVD diamond film from hydrogenated and deuterated gas mixtures and after annealing in vacuum at 800 °C and 1000 °C. Annealing at 800 °C ensures desorption of any ambient contaminants, which may be

Download English Version:

<https://daneshyari.com/en/article/5423864>

Download Persian Version:

<https://daneshyari.com/article/5423864>

[Daneshyari.com](https://daneshyari.com)