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Short communication

Direct amination of diamond surfaces by electroless treatment in liquid ammonia solution

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ABSTRACT

Diamond presents many interesting properties in terms of biocompatibility, chemical inertness and is attractive for applications notably in the biosensor field. The formation of amine functional groups at the diamond surface is of great interest for biomolecule's immobilization. In this work, we present for the first time, the "electroless" amination of diamond surfaces exposed to a liquid ammonia solution containing persulfate. Chemical surface modifications were followed by XPS analyses, while the distribution of amino-groups was studied by gold nanoparticles immobilization. This combined approach proved the growth of amino groups at the diamond surface during the electroless treatment.

1. Introduction

Diamond presents a number of exceptional properties, attractive for many applications. The surface termination is one of the most important parameter affecting its physicochemical properties. It is well reported that hydrogen-terminated surfaces are hydrophobic and have a high conductivity [1–3], whereas, oxygen-terminated ones are hydrophilic and have a low conductivity [4,5]. The surface of diamond may also be functionalized with nitrogen containing groups, which is particularly interesting for biotechnological applications.

Direct amination of diamond surfaces has been mostly performed through dry methods, as for example the chemical treatment of a chlorinated surface with ammonia gas [6,7], the UV irradiation in ammonia gas [8–10] or the use of radiofrequency plasmas of mixtures He + NH_3 [11–13]. Recently, works also evidenced the crucial role of oxygen in the one step UV–NH_3 gas process [14].

Beside, few works are devoted to treatments in liquid ammonia. In 2000, Compton et al. suggested the possibility to functionalize diamond with amine groups in the presence of solvated electron in NH_{3liq} [15]. Recently, our team reported the formation of amino functions at boron doped diamond (BDD) surfaces after anodic polarizations in NH_{3liq} [16,17]. Even if notable amounts of C-NH_2 have been produced by this electrochemical way [17], the method presents several drawbacks as the complexity to perform and the need of conductive surfaces. The aim of the present work was thus to study the formation in NH_{3liq} of amine-terminated BDD surfaces through a simpler method performed at Open Circuit Potential Conditions (O.C.P.) i.e. an electroless process.

BDD films have been exposed to a NH_{3liq} solution containing persulfate as oxidizer. XPS analyses was carried out after the OCP treatment to determine the concentration of amine groups, while their distribution was indirectly studied by gold nanoparticles immobilization.

2. Experimental

2.1. Materials

BDD films (1.5–2 μm) deposited on polycrystalline silicon substrates in a hot-filament-assisted chemical vapor deposition reactor supplied with diborane and methane in hydrogen are provided by Adamant (Neuchatel, Switzerland). The doping level checked by SIMS measurements is 10^{20} B · cm^{-3}.

The cell and equipment for condensing ammonia have already been described [20]. The chemical cell filed up with 150 cm^3 of NH_{3liq} was maintained at 223 K. The acidic medium was obtained by addition of 0.1 M NH_4Br (purest available quality from Aldrich).

2.2. Mott–Schottky measurements

Capacitance–voltage (*C–V*) measurements have been carried out in the NH_{3liq} acidic solution using a Fabelle–CNRS potentiostat, a lock-in amplifier (EG and G5208) and classical three-electrode device with a silver reference electrode (SRE) [19], BDD as working and a platinum wire as counter electrode.

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2.3. Electroless amination

Nitrogenation was performed at OCP conditions. BBD surfaces were immersed in a 0.1 M solution of ammonium persulfate in liquid ammonia for 48 h at 223 K. After treatment, surfaces were rinsed in purest NH_{3liq} and transferred towards an XPS analyzer using a procedure avoiding air contamination.

2.4. XPS analysis

XPS measurements were carried out in a VG 220i XL system, with a base pressure of 5×10^{-10} Torr and using the AlKα (1486.5 eV) X-ray monochromatized radiation with a pass energy of 20 or 8 eV (resolution 0.2 eV). Energy levels of XPS were calibrated with Au single crystal. The spectra were processed using the VG Eclipse Data System.

2.5. AuNPs deposition

Gold nanoparticles (AuNPs) were synthesized using the Turkevich–Frens [21–23] method. A 1 mL solution of sodium citrate (8.5×10^{-4} mol · L^{-1}) was added to a 19 mL solution of $HAuCl_4$ (2.5×10^{-4} mol · L^{-1}) at 80 °C under vigorous stirring for 45 min. Then, the solution was cooled down to room temperature and finally sonicated. This method yields reproducible monodispersed AuNPs with an average diameter of 15 nm [23,24]. AuNPs were subsequently deposited from the solution to the sample by dipping the diamond surfaces into the gold colloidal solution for 90 min. Under these conditions, the pH of the solution is around 5.5, so that the amine-terminated surfaces are protonated ($pKa_{NH3+/NH2} \approx 10$) in contact with the gold suspension [23,24]. To ensure that the AuNPs are firmly attached and to avoid multilayers, the surface is sonicated during 15 min after deposition.

3. Results and discussion

3.1. Energetic diagram of BDD in liquid ammonia

Capacitance–voltage measurements were performed to determine the energetic diagram of diamond in the liquid ammonia acidic solution. As evidenced in Fig. 1-a, the valence band (VB) edge position is set at ~0.9 versus SRE. Based on previous works [18,19], persulfate ion ($S_2O_8^{2-}$) was chosen as oxidizer in NH_{3liq} because of the good energetic overlap between its standard redox potential ($E°/_{NH3} = 1.6$. V/SRE) and the VB edge of diamond (Fig. 1-b), allowing hole injection and possibly, the formation of C – N bonds via hole collection (see ref [17]).

3.2. XPS analysis

To get qualitative and quantitative information about the nitrogen functionalities obtained after the amination process, XPS was performed on BDD interfaces before and after the treatment. The total nitrogen amount was obtained by dividing the relevant peak integrated areas of well defined C1s and N1s core level spectra by the appropriate bulk sensitivity factors following the method described in reference [25]. A nitrogen concentration of about 3% is measured on BDD surfaces after the 48 h dipping in ammonia solution with persulfate (Table 1). For control experiment, BDD have been exposed to an aqueous 1 M $(NH_4)_2S_2O_8$ solution. The [N] detected by XPS after the 48 h dipping remains below 0.5 at.% [18], evidencing the crucial role of NH_{3liq} in the formation of C–NH_2 groups.

To get information about the chemical functionalities present at the BDD surface before and after the amination treatment, the chemical shifts of the C1s and N1s core level were investigated.

The C1s XPS peak corresponding to BDD (Fig. 2-a) exhibits two main components at 284 eV (C_1) and at +0.8 eV (C_2), respectively attributed to the bulk diamond component and to polyhydride carbon species, CH_x [26]. Due to air exposure, samples exhibit additional components shifted towards higher energies, corresponding to oxidized carbon atoms. The peak at +2 eV with respect to the bulk (C_3) is attributed to singly oxidized carbons, in other words to hydroxyl or ether groups. The peaks noted C_4 and C_5, at +4 and +5 eV, are assigned to carbonyl and carboxylic species [26].

The C1s and N1s XPS spectra for samples after the amination process are reported in Fig. 2-b–c and the proportions of the different contributions (C_1 to C_5 and N_A to N_B) obtained by peak fitting are given in Table 1.

Compared to as-grown surface, the main evolution of the C1s peak is the increase of C_3 contribution (from 4–5 to 9%). As both the oxygen and the nitrogen concentrations increase, C_3 peak evolution is not patent and could be linked to the formation of either oxygen or nitrogen containing groups during the process. Most interestingly, the N1s XPS spectra of BDD treated in liquid ammonia in the presence of persulfate present two well defined contributions N_A and N_B at approximately 399 eV and 401 eV. Such N1s shape has already been observed in previous works using other nitrogenation methods [27]. According to literature data, N_A peak (~399 eV) can be ascribed to "C–NH_2" terminations [28–30]. The attribution of the N_B peak is less evident. The 2 eV shift is consistent with species associated with the protonation of the NH_2 [31] but can also have other explanations as nitrogen atoms linked to 2 carbon atoms, as double carbon–nitrogen bonds "C═N" or bridges "C – N – C"[11] or physisorbed species [32].

Here, the presence of the N_A peak attributed to "C–NH_2" terminations at the diamond surface is thus a really encouraging result for post-functionalization purposes.

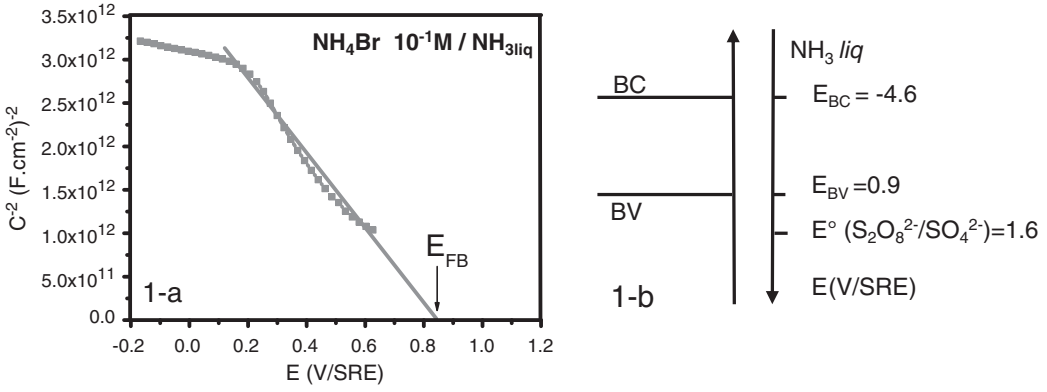

Fig. 1. a — Mott–Schottky representation $C^{-2}(V)$ of BDD recorded in NH_4Br 0.1 M in liquid ammonia at 223 K. The frequency was set at 1107 Hz. And b: Energetic diagram of BDD in NH_4Br 0.1 M in liquid ammonia at 223 K and position of the standard potential of the redox couple $S_2O_8^{2-}/SO_4^{2-}$.