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Gold nanoparticles immobilization: Evidence of amination of diamond surfaces in liquid ammonia

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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 diamond surface is of great interest for the incorporation of biomolecules. In the present work, we present an efficient direct amination method using anodic treatment in liquid ammonia on oxygen terminated diamond surface. Chemical surface modifications were followed by XPS analyses, while the distribution of amino-groups was indirectly studied by gold nanoparticles immobilization. The resulting surfaces were examined using FEG-SEM imaging. This combined approach has been powerful evidencing both the presence of notable amounts of amino groups after the electrochemical treatment in NH_{3liq} and their homogeneous distribution at the diamond surface.

1. Introduction

The detection of biomolecules requires materials with specific properties as biocompatibility, stability and sensitivity [1]. Semi-conductive diamond is highly biocompatible, chemically inert and presents a very large electrochemical window, making it an attractive substrate for biosensing [2–9]. As described in the literature, amine terminal groups would be of great interest for the immobilization of biomolecules [10,11].

The surface termination is one of the most important parameters affecting the properties of diamond [12–14]. Several accurate methods relating to the modification of as-grown H-terminated boron-doped diamond (BDD) are described in the literature. Even if as-deposited hydrogen terminations are rather stable, they can be converted to nitrogen terminations, either by dry or wet techniques. For example, interesting preconditioning of the diamond surface can be reached on H-BDD with the diazonium spontaneous reaction [15,16].

Several amination methods of diamond films are thus proposed in the literature. Two main strategies have been developed. On one hand, the covalent bonding of amine terminated alkyl chains has been investigated using for example silanes [17–23] or diazonium salts [14,24–29]. These methods can be seen as indirect ones because they provide an organic spacer between the surface and the functional group.

On the other hand, more direct methods, where the nitrogen-containing group is directly bonded to diamond have been developed, as for example the chemical treatment of a chlorinated surface with ammonia gas [30,31], the UV irradiation in ammonia gas [32] or the use of radiofrequency plasmas of mixtures $He+NH_3$ [33–35]. In 2009, our team reported the formation of nitrogen containing groups at diamond surface after an anodic polarization in liquid ammonia [36]. As small N concentrations were detected after this process, the increase of the direct amination efficiency in NH_{3liq} was still a challenge.

Recently, works evidenced that the presence of oxygen either in the gas phase or bonded to the diamond surface was essential to obtain surface amination in one step UV $-NH_3$ gas process [37]. Based on these results, we propose to study in the present work the direct amination of diamond surface by anodic treatments in liquid ammonia on both as-grown H-terminated and previously oxidized surfaces. The formation of surface nitrogen-containing groups was followed by XPS measurements. As a homogeneous surface distribution of amino groups is required for functionalization purposes, the repartition of these functional groups has been investigated by using an indirect probe: the deposition of gold nanoparticles. The resulting samples were examined by scanning electron microscopy and XPS analysis.

2. Experimental

2.1. Preparation of the diamond surfaces

The polycrystalline boron-doped diamond (BDD) films, deposited on silicon substrates in a hot filament-assisted chemical vapor deposition process, were provided by Adamant (Neuchatel, Switzerland).

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The morphology of these surfaces was studied by AFM and XPS. Grains are around 1 μm large. The surface roughness is about hundreds of nanometers. The number of boron atoms in the diamond layer was determined to be 1×10^{20} B cm^{-3} by SIMS measurements. Because of the deposition process, the surface is mainly hydrogenated and samples will be termed H-BDD.

Samples were oxidized by immersion into an oxidizing solution: MnO_4^- 0.1 M in H_2SO_4 0.5 M [38]. Potassium permanganate ($KMnO_4$) was purchased from Aldrich and used without further purification. Sulfuric acid (H_2SO_4) was provided by Prolabo (Normapur quality). Oxidized surfaces will be named O-BDD.

Amination of H-BDD and O-BDD surfaces was obtained by an electrochemical anodization in liquid ammonia. A galvanostatic treatment with a current density $J_a = 10$ mA cm^{-2} was applied during 500 s. Ammonia condensation, from gaseous ammonia ("electronic grade" from Air Liquide) was provided by a glass column assembly and required a low operating temperature under atmospheric pressure. An electrochemical cell filed up with 150 cm^3 of liquid ammonia was maintained at 213 K in a cryostat. The acidic medium was obtained by addition of 0.1 M NH_4Br (purest available quality from Aldrich). All potentials were measured vs. a silver reference electrode [39]. After the treatment, electrodes were rinsed in the purest liquid ammonia and then in milliQ water (18 MΩ cm). The samples were finally handled under a water drop protection before being dried under a nitrogen gas stream and being transferred towards an XPS analyzer using a procedure avoiding any air contamination. Aminated surfaces will be termed N-BDD.

2.2. Preparation and deposition of the gold nanoparticles

Gold nanoparticles (AuNPs) were synthesized using the Turkevich-Frens [40,41] method under conditions yielding 15 nm nanoparticles stabilized by a citrate layer in aqueous solution. A 1 mL solution of citrates (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. The stirring was maintained for 45 min at 80 °C (color gradually changing from slight yellow to gray, purple, and finally dark red). Then, the solution was cooled down to room temperature and finally sonicated. This well-documented method yields reproducible monodispersed AuNPs with average diameter of 15 nm (standard deviation less than 1 nm) [42,43]. The aggregation of AuNPs is prevented by the negatively charged citrate layer surrounding the particles. However, citrates do not form a covalent bond with gold and can be easily replaced by other molecules or chemical groups anchored on surfaces.

AuNPs were subsequently deposited from the solution to the sample by dipping the diamond surfaces (both H- and O-BDD) into the gold colloidal solution for 90 min. Under these conditions, the pH of the solution is around 5.5, so that the amino-terminated surfaces (pKa ≈ 10) are protonated (acid form: NH_3^+) in contact with the gold suspension [42,43]. The quality (size, shape, and dispersion) of the nanoparticles solution is characterized by UV–visible absorption (see Fig. 1). When the surface plasmon resonance (SPR) is monitored, which is dependent on these properties [44], a systematic control of the particle size and dispersion is possible. For 15 nm particles, for instance, the SPR has a sharp maximum around 520 nm. Importantly, to ensure that the AuNPs are firmly attached and to avoid multilayers, the surface is sonicated during 15 min after deposition.

2.3. Instrumentation

XPS measurements were performed on a VG220i 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 eV or 8 eV (resolution 0.2 eV). The incidence angle of the X-ray probe was 90°. Energy levels of XPS were calibrated with Au single crystal. The spectra were processed using the VG Eclipse Data system.

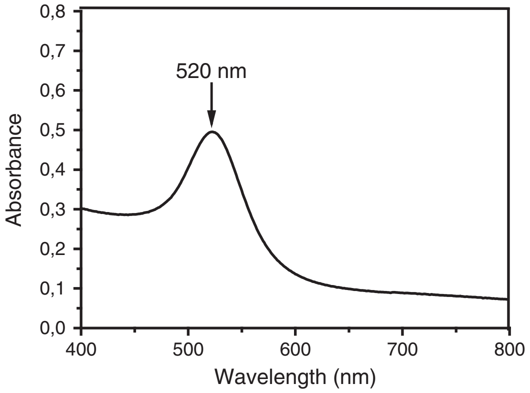

Fig. 1. UV spectroscopy of gold nanoparticle solution.

SEM micrographs were acquired with a Jeol JSM 7001-F at 5 kV accelerating voltage.

3. Results and discussion

3.1. Amination treatment in liquid ammonia

In a preliminary work [36], we showed that it was possible to create carbon–nitrogen bonds on diamond films by anodic treatments in liquid ammonia. Small but encouraging amounts of nitrogen were detected by XPS measurements (about 3 XPS % atomic) after anodization in NH_{3liq} of as grown H-BDD samples [36]. Besides, recent work [37], suggests that amination treatments of diamond surfaces are more efficient in the presence of oxygen. So, in order to optimize the direct amination of diamond film in liquid ammonia, electrochemical treatments have been studied on both previously oxidized BDD samples (O-BDD) and as-grown H-BDD for comparison. The resulting surfaces will be now respectively named: N + O-BDD and N + H-BDD.

Therefore, some as-grown samples were first oxidized using a process already described in a previous work [38]. H-BDD electrodes were immersed into a solution containing 0.1 M of MnO_4^- (as potassium) in 0.5 M H_2SO_4, for 2 days. The resulting O-BDD surfaces were then exposed to the anodic treatment in liquid ammonia.

To get qualitative and quantitative information about the resulting Nitrogen functionalities after amination treatment, XPS analyses were performed on BDD interfaces before and after the different steps: oxidation and amination.

Various current densities ranging from 1 μA cm^{-2} to 100 mA cm^{-2} and durations (1 to 30 min) have been tested. When $J_a < 1$ mA cm^{-2}, whatever the duration (up to 30 min) XPS analysis does not reveal the formation of nitrogen containing groups. At the opposite when J_a becomes too high (100 mA cm^{-2}), the result is the same, the XPS signal of N is absent. Finally the best results are obtained for an intermediate current density of 10 mA cm^{-2} and duration of 500 s. Similar observations have been made concerning the effect of current density on the formation of C–O groups after anodic processes in aqueous media [45], best coverage of BDD surfaces with oxygenated groups were obtained for electrodes oxidized with intermediate current densities.

Both chronopotentiograms corresponding to the electrochemical surface activation with $J_a = 10$ mA cm^{-2} on H- and O-BDD in liquid ammonia are presented in Fig. 2.On both graphs, the voltage strongly increases from the open circuit potential values (respectively ~0.9 V/SER and ~1.2 V/SER for H-BDD and O-BDD) up to a similar value ~2.5 V/SER for the two kinds of samples. The potential reached during the first seconds of treatment remains quite stable during the whole process. The evolution of BDD surfaces submitted to these processes will be described in the following parts of the manuscript.

Figs. 3 and 4 show the surveys obtained respectively for as-grown and oxidized diamond surfaces before and after the amination process.