



# About orientation dependence of physico-chemical properties of HPHT diamond surfaces thermally treated in H<sub>2</sub> and D<sub>2</sub> environments

Ch. Manfredotti\*, P. Bonino, M. De La Pierre, E. Vittone, C. Manfredotti

Experimental Physics Department and NIS-Nanostructures Interfaces and Surfaces-Excellence Centre, University of Torino, Turin, Italy

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## ABSTRACT

Recently [1] we reported on some preliminary results on different physico-chemical properties of diamond (100), (110) and (111) surfaces hydrogenated by using molecular hydrogen only. The main conclusions were that thermal hydrogenation was as efficient as plasma one and that the creation of the conducting surface channel was activated by a larger energy on the (100) surface with respect to the other two. The reason, at least in the case of the comparison between (100) and (111) surfaces, could be either attributed to the presence of a carbon – oxygen double bond before hydrogenation in the former case [2] or to a better coverage by carbon – hydrogen bonds in the latter one. In the present work, further results on surface conductivity after hydrogenation steps carried out at different temperatures are described and discussed, in order to discriminate between purely thermal and kinetic effects. Moreover, other results are reported on diamond powders (0.25 micrometer mean size) in order to draw some qualitative and quantitative conclusions about hydrogen presence and behavior at the diamond surfaces. In order to better clarify the results, a large part of chemical measurements were performed after deuteration steps carried out using the same conditions as thermal hydrogenation.

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## 1. Introduction

Diamond surface hydrogenation appears to be very attractive for applications in different fields, since the availability of a true transparent electrical contact on diamond is of real interest in sensors, biology, electronics, etc. [3–5]. Even if a model able to describe the creation of a surface p-channel has been existing for almost eight years, a real understanding of the physico-chemical processes leading to this situation (hydrogenation, air exposure, etc.) is still far to be reached. A possible way to simplify the situation is the adoption of a pure thermal approach, in order to avoid impurities, defects created by plasma, etc. and the use of high quality single crystal samples like HPHT ones. Thermal hydrogenation actually is a diamond surface catalysis due to the lower dissociation energy of hydrogen molecule with respect to C–H bond. Different crystallographic surfaces, even reconstructed, display different kinds of bonds and, as a consequence, should have different activation energies for the creation of the surface p-channel. This is really what has been proved very preliminarily in a previous paper [1] and what will be definitively proved in this one. Bond types present at the surface are also quite important in order to describe the occurring reactions; however, it is very difficult to obtain such data by spectroscopic methods, since the p-channel layer is only 0.5 nm FWHM thick and particular spectro-

scopies such as attenuated total reflection (ATR) and similar ones are not easy to apply. Our results are a confirmation that (100) surface is much harder to be thermally hydrogenated with respect to (111) and (110) and that, most probably, only CH<sub>2</sub> and CH<sub>3</sub> species are present at the surface. In effect, the hydrogenation of (100) surface is impossible to observe and, moreover, values of resistivity obtained in this case after air exposure are much larger than in the case of the other two crystallographic orientations. In effect, what may be called “activation energy” for the creation of a p-channel is almost a factor of 5 higher in the case of a (100) surface.

## 2. Experimental

HPHT single crystal diamonds (IIa, dimensions 1.5 × 1.5 × 0.5 mm<sup>3</sup>), (100), (111) and (110) oriented, were supplied by Sumitomo Electric Co. Ltd. Before each hydrogenation process, in order to better remove surface contaminants and to leave a clean oxygen-terminated surface, samples were oxidized using a sulphochromic acid solution at 120 °C for 4 h, rinsed in deionized water, then in acetone and in 2-propanol, and dried in argon flow. Synthetic monocrystalline diamond powders were supplied by Advanced Abrasives Corp. (mean particle size 250 nm, size range 0.0–0.5 μm, specific surface area SSA<sub>BET</sub> = 19 m<sup>2</sup>/g). Before hydrogenation processes, powders were treated in sulphonic mixture 9:1 (H<sub>2</sub>SO<sub>4</sub>:HNO<sub>3</sub>) for 1 h at 80 °C, then washed in deionized water until neutrality, cleaned with acetone and 2-propanol and finally dried in vacuum first and then in ambient air.

\* Corresponding author. Experimental Physics Department, University of Torino, Via P. Giuria 1, 10125 Turin, Italy. Tel.: +39 011 6707879; fax: +39 011 6691104.  
E-mail address: [chiara.manfredotti@to.infn.it](mailto:chiara.manfredotti@to.infn.it) (C. Manfredotti).