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## *In situ* thermal treatment of UV-oxidized diamond hydrogenated surface

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### ABSTRACT

Surface properties of polycrystalline hydrogenated diamond produced by chemical vapour deposition upon oxidation under UV irradiation are studied. The diamond surfaces were cleaned in vacuum by thermal treatment. They were characterized estimating the electron affinity of the virgin surface by UV photoelectron spectroscopy and controlling the surface composition by X-ray photoelectron spectroscopy. The cleaned surfaces were then exposed to pure oxygen and UV radiation (deuterium lamp). Ozone induced surface oxidation was verified by XPS estimating the oxygen atomic concentration and the presence of specific chemical bonds. Surface oxidation was also verified analyzing the change in the diamond electron affinity. Oxygen was then removed *in situ* by a series of thermal treatments at increasing temperature. Already at  $\sim 300$  °C a remarkable reduction of the oxygen concentration occurs which persists increasing the annealing temperature. Contemporary, a progressive recovery of the initial electron affinity is also obtained. These effects are observed up to 970 °C, a temperature at which the electron affinity assumes a negative value. Specific chemical reactions are hypothesized to describe the oxidation process and to explain the electronic behaviour of the diamond surface.

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### 1. Introduction

Diamond has recently gained attention for an uncommon number of properties. Besides those derived from the bulk crystalline structure like the extremely high hardness and the optical transparency, there is also a list of properties which are derived from the characteristics of the diamond surface. These depend on the way the surface dangling bonds are accommodated or on the kind of surface terminations. Among these last, the hydrogen-terminated diamond surface shows the uncommon property to be conductive. This makes it a very special candidate for electrochemical applications [1]. Some experimental evidences were put forward to describe the role of hydrogen [2,3] on the origin of the surface conductivity. Different explanations were proposed to account for the surface conductivity of diamond. Deep level passivation by hydrogen or the presence of sub-surface hydrogen atoms acting as a shallow acceptor level were proposed as a cause of a rather large density of carriers [4–6]. On the other hand, these models could not explain the values of conductivity measured on hydrogenated diamond. Another mechanism was proposed by Maier et al. [7]. In their model not only the acceptor density but also the chemical interactions, which occur at the diamond surface, were considered.

Different chemical reactions were proposed in the literature to explain the charge transfer from the hydrogenated surface to the adsorbates. In the work of Shin et al. [8] different oxidizing molecules were used to induce surface conductivity. Cyclic voltammetry experiments demonstrate, that electron transfer can take place only when the acceptor levels are placed under the valence band maximum ( $VB_M$ ) of diamond [9]. The surface chemistry is then strongly involved in the process of surface conductivity. It directly influences the formation of a charge separation on the diamond surface. On the base of this model it is evident that changes of the diamond termination i.e. changes of its electron affinity (EA), strongly affect the diamond conductivity. This is why another interesting surface is the oxygen terminated diamond. The presence of oxygen determinates a completely different charge rearrangement on the surface. The different electronegativities of the C atoms and of that of the chemical elements terminating the surface (H, O) cause the formation of a specific dipole moment  $p$ . This last can be directed *in* or *out* of the diamond surface respectively. Consequently the change in electron affinity  $\chi$  can be expressed by the following equation [10]:

$$\Delta\chi = -epn/\epsilon_0 \quad (1)$$

where  $n$  is the dipole density on the diamond surface,  $e$  is the electron charge and  $\epsilon_0$  is the vacuum permittivity. This simple relation explains why the electron affinity turns from negative  $\sim -1.3$  eV to

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