



A comprehensive study on hydrogenated diamond surfaces as obtained by using molecular hydrogen

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Abstract

Diamond surface hydrogenation is generally carried out with atomic hydrogen obtained by either microwave plasma or heated filaments. Both these techniques present some drawbacks, given by some instabilities and containment difficulties in the former case, and by some surface contamination by the elements of the filaments themselves, which must be very close to the substrate, in the latter. Surface hydrogenation can be easily obtained by molecular hydrogen, at substrate temperatures not much different from those used in the above methods, but only via thermal means and without the aforementioned drawbacks. In this paper we describe a systematic study carried out on hydrogenated surfaces obtained at different temperatures, from 700 to 900 °C, and on different diamond materials (natural and HPHT), by exposing different surfaces such as (100), (111) and (110) to molecular hydrogen. The results indicate that values of surface resistivity are comparable to those obtained using hot filaments, particularly at temperatures around 800 °C, and that the activation energy related to the establishment of surface conductivity is relatively low. Surface resistivity, XPS (X-ray Photoelectron Spectroscopy), AFM and μ -FTIR in reflection-transmission mode data indicate that the efficiency of surface hydrogenation with the consequent low values of surface resistivity is quite similar for the three surface orientations, but also that in the case of (100) orientation this efficiency is lower.

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1. Introduction

In the 1936, Barrer [1] showed that hydrogen chemisorbs readily on diamond at temperatures above 400 °C. The large heat of adsorption $\Delta H \approx 58$ kcal/mole (or 2.5 eV/atom) of this process indicates that hydrogen is strongly bonded. It was likely that the diamond surfaces were covered by at least one monolayer of chemisorbed hydrogen as a result of the hydrogen cleaning treatment in order to be able to carry out a low energy diffraction experiment to investigate surface reconstruction effects [2,3]. In fact, time-of-flight spectra obtained many years later [4] revealed the presence of ions such as CH, CH₂, CH₃ and CH₄ together with ions of larger masses (C₂H, C₂H₂, C₂H₃, etc.).

Similar results obtained by thermal molecular hydrogenations were observed on silicon [5], even if it is clear that silicon

is somewhat unable to crack a hydrogen molecule efficiently. This result confirms that hydrogen in diamond exhibits the same passivation role displayed very well in silicon. FTIR techniques are most commonly used in order to investigate hydrogen essentially in terms of C–H and C–H₂ vibrational spectra, since it has been proved that the amount of bonded H measured by FTIR is proportional to the total amount of hydrogen as measured by NMR [6]. By infrared reflection spectroscopy [7] it was shown that C–H stretching bands did not arise from hydrogen incorporated at the grain boundaries, but rather from hydrogen bonded to bulk diamond carbon atoms. This conclusion is in contrast with the presence of a broad Gaussian NMR component [8] which is attributed to high local hydrogen densities, very likely at grain boundaries. Another problem concerns the concentration profile of hydrogen on the surface. In fact [9], while in as-grown diamond hydrogen concentration is $2 \times 10^{19} \text{ cm}^{-3}$, in rf hydrogenated diamond at 500 °C a broad peak of about $2 \times 10^{21} \text{ cm}^{-3}$ appears with a FWHM of about 15 nm (very strangely, MW hydrogenation both at 600 and at 800 °C is not capable of increasing surface hydrogen by more

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