Influence of negatively charged physisorbates on hydrogen-terminated diamond surface

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It is known that hydrogen terminated surface of as grown intrinsic diamond has p-type useful high conductivity that closely related to surface physisorbates. The sheet resistance and the sheet carrier density, the carrier mobility of usual single crystalline hydrogen-terminated diamond (100) surface is about 10k [ohm/sq] and 10^{13}[/cm^2], 150[cm^2/Vs], respectively. Especially, through the use of very simple fabricate process (do nothing other than replacing hydrogen atom for surface atom of undoped diamond) and ability to separate nano-scale conductive and insulating region used by insulating layer of oxygen-terminated surface of diamond, it is going to be important quality for nanostructured device of diamond. In fact, some microstructured devices with this surface conductivity (SC) have already been made and its utility has been sufficiently proven [1,2]. So it is very important to have a sufficient understanding of a formation mechanism of surface conductive layer.

Some models have been proposed to explain the origin of the SC. Above all models, transfer doping model that Maier et al. proposed [3] attracts a lot of attention. In this model, electrons near the valance band maximum of diamond are transferred to an electrochemical potential (H_3O^+/H_2) of adsorbed water layer. According to the model, the surface conductivity increases as pH decreases.

But we have so far observed that the sheet carrier density of SC doesn't depend on the concentration of hydronium ions (pH) when the surface is terminated by hydrogen [4], but the concentration of negatively charged halogen ions in the solutions, from the characterization of electrolyte-solution gated diamond FETs (SGFETs)[5]. This pH insensitivity contradicts to the transfer doping model which is based on electrochemical potential.

Sheet carrier density of the SC is constantly 10^{13}[/cm^2] order in air. As shown in figure 1, hydrogen-terminated diamond surface has surface dipoles by the electronegativity

difference between C (2.1 Pauling units) and H (2.5 Pauling units) at (100) surface and the density of surface positive charge by hydrogen atoms is $6x10^{13}$ [/cm^2]. So it is numerically reasonable that negative charged physisorbates induce hole accumulation at hydrogen-terminated surface by band-bending like inversion layer of MOSFET and produce the SC on hydrogen-terminated diamond surface.

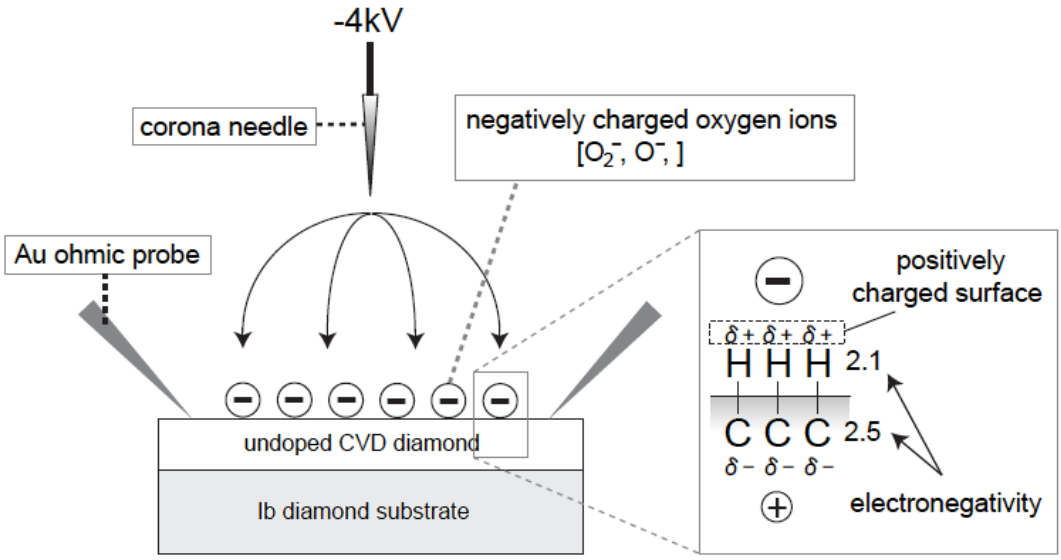

Figure 1. Schematic illustratioin of a point electrode corona charging method and the surface dipole of hydrogen-terminated diamond. The surface conductivity is measured by Au ohmic probe.

In this work, as described in figure 1, we have introduced large amount oxygen negative ion (O_2^-: to be found in air) by corona charging method on hydrogen-terminated surface that SC was removed by heat treatment in vacuum, and measured the transition of the electrical conductivity.

Figure 2 shows the result of attempt to, with negatively charged oxygen ion, bring the SC to hydrogen-terminated diamond (100) surface that the SC was removed by the heat treatment at 550K. The initial SC ($4.2x10^{-6}$[S]) was removed by heat treatment in high vacuum. After that we induced pure O_2 in chamber till 76 torr at t=-10 [min]. At this time, SC was just a little made a recovery, but keep low conductivity. And between t=0 and 20 min, negative oxygen ions were produced in chamber by corona charging method. At t=20 min, SC was made a recovery up to $3.5x10E^{-6}$[S] and kept the SC after exposed to air at 50 min. Additionally, we confirmed that In the negatively charged ions atmosphere, the density of surface two-dimensional hole gas was increased twice as large as that in initial air.

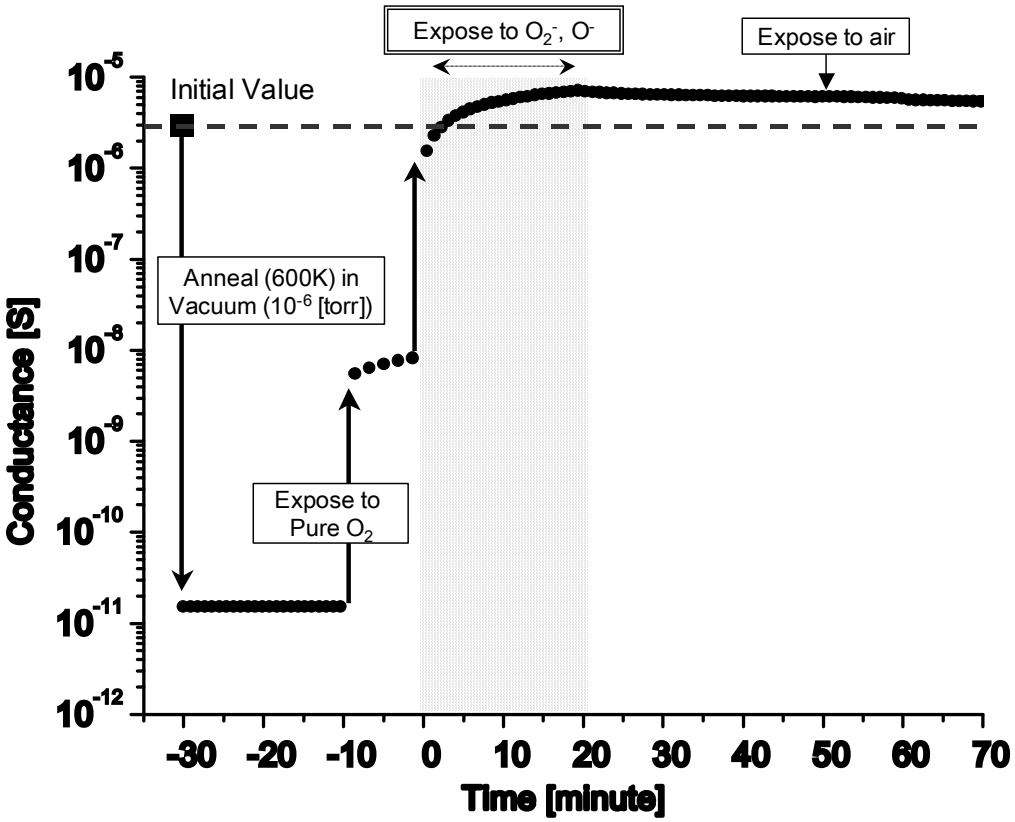

Figure 3. Transition of the conductance of hydrogen-terminated diamond surface when it exposed to negatively charged oxygen atmosphere. Negatively charged oxygen was generated by corona discharge in 76 torr pure oxygen atmosphere.

These results with negatively charged ions indicate that it is possibility that negative charged molecules in air are closely linked to the origin of the SC. We are going to show other evidence that support this negatively charged physisorbates model in our presentation.

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