

SURFACE CONDUCTIVITY OF UNDOPED, HYDROGEN-TERMINATED DIAMOND

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ABSTRACT:

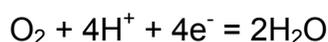
A unique feature of hydrogen-terminated diamond is its surface conductivity.¹ Although its origin is not fully understood, the proposed electrochemical transfer-doping model² is gaining acceptance. A p-type accumulation layer forms in the diamond when the Fermi level of the diamond is higher than the chemical potential, μ_e , of electrons in an adsorbed water layer on the diamond surface. The chemical potential of electrons in the water film is most likely fixed by the oxygen redox couple.

The conductivity increases upon exposure to acidic vapors and decreases when exposed to basic vapors, which lower and raise μ_e respectively. Addition of hydrogen peroxide, an intermediate in the electrochemical reduction of oxygen, increases the effect. Increasing the surface work function by fluorinating or oxidizing the diamond eliminates the surface conductivity. Measurements of conductivity in air and in vacuum were made as a function of temperature and are consistent with the electrochemical transfer-doping model.³ This effect may not be unique to diamond, but may also be responsible for observed conductivity in semiconducting carbon nanotubes.

The results, in general, support the electrochemical transfer-doping model; however, some uncertainty remains in the nature of the electrochemical couple. Full understanding of the effect may enable a new class of sensors.

INTRODUCTION

Hydrogen-terminated diamond with its p-type surface conductivity is a promising material for sensor applications; however, a fundamental understanding of the mechanism is still lacking. In this paper we address experimental results that support the electrochemical transfer-doping model proposed by Maier et al.² It is believed that an electrochemical redox reaction in the adsorbed water film acts as an acceptor for electrons from the diamond. This electron transfer leaves behind holes in the diamond, which form a positive space charge layer. The chemical potential of electrons in the film is determined by an electrochemical redox couple; most likely involving dissolved oxygen in equilibrium with air.^{4 5}



However some uncertainty remains about the existence of a water layer on a hydrophobic surface. In this work we monitored the contact angle and zeta potential of oxidized and hydrogen-terminated diamond as the pH of the aqueous phase was changed. The results provide a mechanism for the formation of a water film on a hydrogenated diamond surface.

CONTACT ANGLE MEASUREMENTS

Sample Preparation and Experimental Procedure:

The contact angles were measured with a KRÜSS K100 Processor Tensiometer on (111) diamond macles. Oxidized diamond surfaces were obtained by boiling in a 1:1 mixture of HNO₃ and H₂SO₄ for 5 minutes and then washing in a stream of ultra pure distilled water. Hydrogen termination of the macles was performed in a microwave reactor for a period of 2 hours at a chamber pressure of 35 torr and H₂ flow of 196 sccm. The microwave power was 800 W. The samples were cooled under hydrogen to room temperature.

Contact angles of the diamond surface in solutions of different pH were determined by the Wilhelmy plate technique. The method involves dipping the solid in the liquid while measuring the force on the sample due to wetting. The value of contact angle depends on the measured force, wetted length of the sample, and the surface tension of the liquid. The surface tension of aqueous solutions is measured using a roughened platinum plate, which is optimally wetted so that the contact angle is virtually 0°. By measuring the force acting on the plate when immersed in the liquid, the surface tension of the liquid can be calculated. Before each run, the plate was cleaned by heating it to red heat in a Bunsen burner. The diamond samples were cleaned ultrasonically in Milli-Q water for 10 minutes and dried under flowing N₂ between runs. The samples were then attached to the arm of the electrobalance and immersed in the solution at a constant rate of 3 mm/min.

Results and Discussion:

Figure 1 shows the contact angle of on oxidized diamond macle versus pH of the aqueous phase. (A macle is a twinned single crystal of diamond presenting {111} facets.) The contact angle exhibits a maximum near pH ~ 3 (isoelectric point) and decreases for other values of pH. The relatively low contact angle ($\theta_{\text{Adv}} = 55$, pH = 6) indicates that the surface is

hydrophilic. It is known that oxygenated surfaces contain a variety of functional groups such as epoxide, C-O-C; carbonyl, C=O; carboxylic, COOH; and hydroxyl, OH. At high pH, these functional groups can ionize to produce a net negative charge, which lowers the contact angle. At low pH, hydronium ions may adsorb to the oxygen functional groups, which will also lower the contact angle.

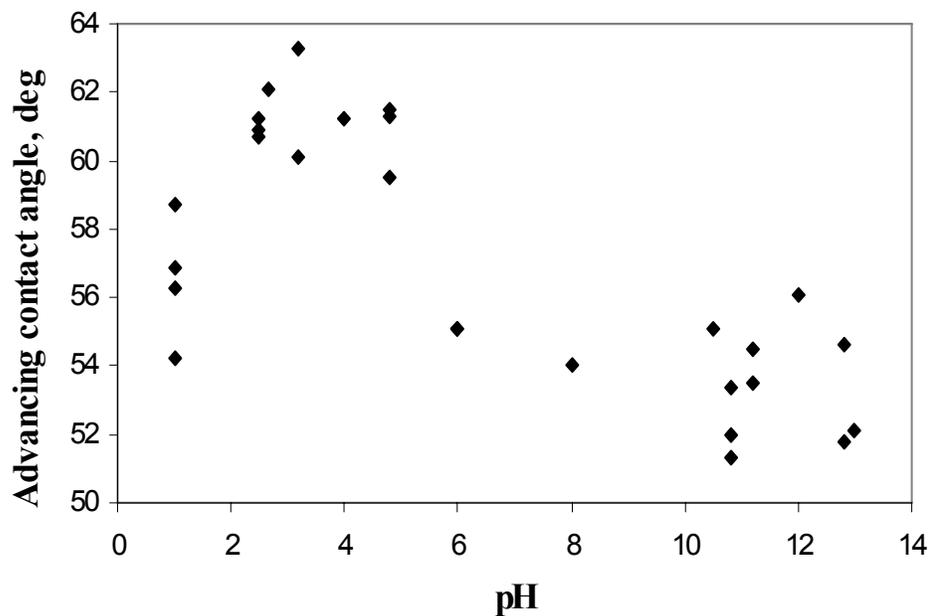


Figure 1. Contact angle of an oxidized (111) surface of a diamond made as a function of pH of the aqueous phase.

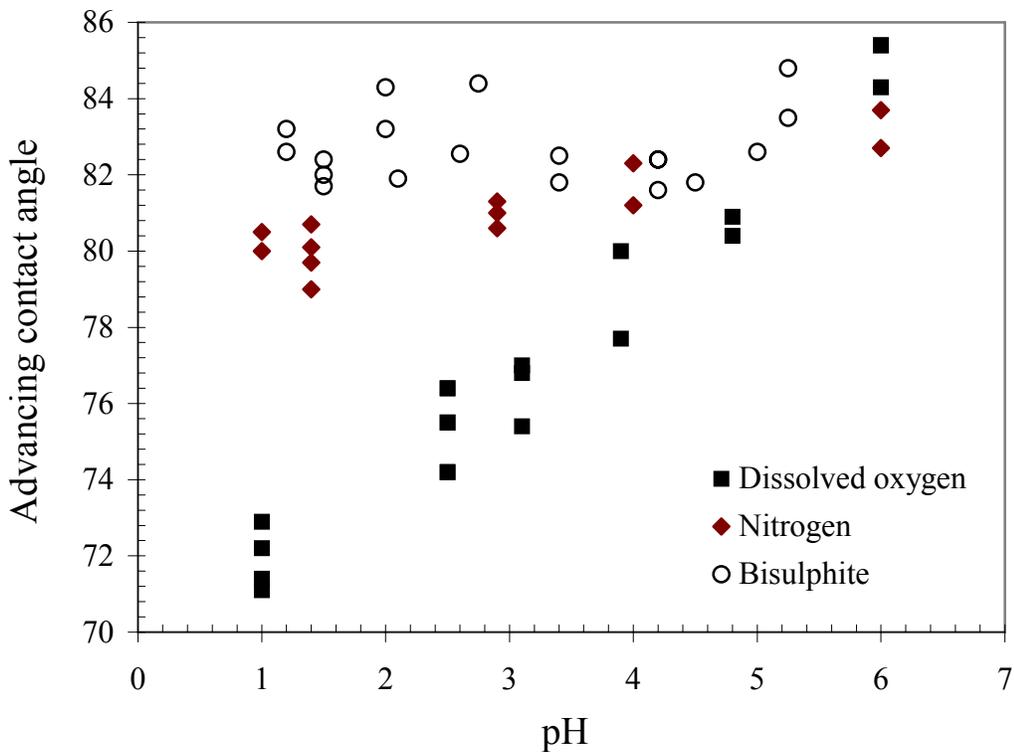


Figure 2. Contact angle on a (111) surface of a hydrogen-terminated diamond made as a function of pH of the aqueous phase.

Figure 2 shows the effect of pH on the advancing contact angle of a hydrogen-terminated diamond made. The higher contact angles indicate that the surface is more hydrophobic than the oxidized diamond surface (Figure 1). This hydrophobicity is due to the chemically bound surface hydrogen. A completely hydrogenated diamond should remain unionized down to pH = 1. We attribute, the lowering of the contact angle with decrease in pH below 6 to the uncompensated anions in the aqueous phase arising from the electrochemical transfer doping. These excess solvated anions are bound to the diamond surface by electrostatic attraction to the positive space charge layer in the diamond. Thus the solvated anions provide a mechanism for binding the water film to the hydrogen-terminated, hydrophobic diamond surface. Reduction of the concentration of electrochemical acceptors, *i.e.*, the dissolved oxygen, should decrease the electron transfer from the diamond and reduce the effect of pH on contact angle. Reduction of dissolved oxygen was accomplished by blowing nitrogen through the solution and adding sodium bisulfite. The effect of pH on contact angle essentially disappeared at all pH after the addition of excess sodium bisulfite as expected.

ZETA POTENTIAL MEASUREMENTS

Sample Preparation and Experimental Procedure:

Zeta potential measurements were performed using a ZETAMASTER-S. Experiments were done using 1 μm nominal size diamond powder (SJK-5, Kay Industrial Diamond Corp.). The as-purchased powder is oxygen terminated and hydrophilic. Hydrogenation of the diamond powder was done under H_2 in a microwave reactor at 35 torr for a period of 8 hrs.

Aqueous solutions of different pH were prepared from reagent grade HCl and NH_4OH and filtered through a 0.1 μm filter. The diamond powder was then dispersed in the solutions and sonicated for 15 minutes before each experiment. The dispersions were dilute and did not show significant coagulation.

Results and Discussion:

When a particle is immersed in an aqueous solution, its surface may acquire charge due to (i) ionization of surface groups, (ii) preferential adsorption of ions, or (iii) through other reactions at the interface. This surface charge gives rise to an electrical double layer in the liquid. The electrical potential in the double layer is distributed from the surface to the bulk liquid. The zeta potential (ζ) is the potential at the position of the shear plane that separates the hydrodynamically mobile liquid from the stagnant layer near the solid surface. The magnitude of the zeta potential depends on the net amount and sign of the charge inside the shear plane.

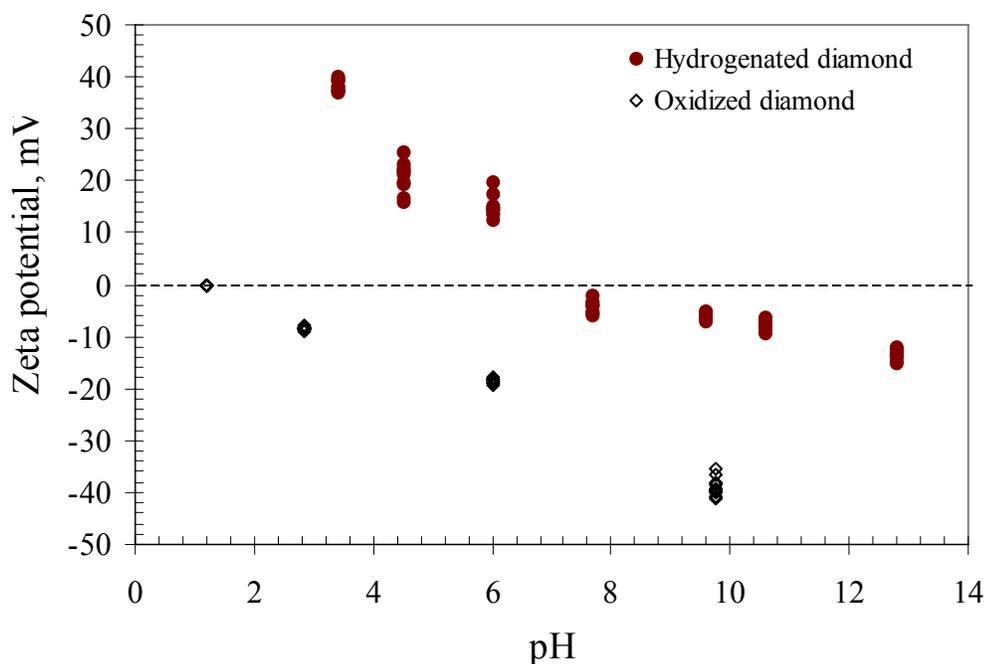


Figure 3. Zeta potential as function of pH for oxidized and hydrogen-terminated diamond powder. The isoelectric point occurs at $\text{pH} \cong 1.2$ for oxidized diamond and $\text{pH} \cong 8$ for hydrogenated diamond.

Figure 3 shows the zeta potential for both oxidized and hydrogenated diamond powder as a function of pH. From the figure it is evident that the zeta potential is a strong function of pH and becomes more negative as the pH increases. For oxidized diamond powder, this is likely due to the functional groups on the surface, which ionize at high pH to produce a net

negative charge. The isoelectric point, which corresponds to the point of zero zeta potential, occurs at pH = 1.2. These results are in general agreement with the contact angle measurements shown in Figure 1.

Hydrogenation reduces the oxygen containing groups on the surface thereby shifting the isoelectric point from 1.2 to ~8. The positive zeta potential measured at low pH is consistent with a positive space charge layer in diamond arising from electrochemical transfer doping, which increases with decrease in pH. The negative zeta potentials observed at high pH are attributed to ionization of residual oxygen group from incomplete hydrogenation.

These results are very similar with those obtained by Yamanaka *et al.*,⁶ who measured the isoelectric pH point to be 1 and 8.8 for oxygen and hydrogen terminated diamond respectively.

HIGH TEMPERATURE MEASUREMENTS:

Figure 4 shows the transient change in the conductivity when a step change in temperature is imposed on a polycrystalline diamond sample. Conductance was measured between two evaporated gold contacts on sample in high vacuum (10^{-7} torr). The conductance increases with temperature, which is different from that observed in air (shown in the inset). In air, the conductivity first increases upon increasing the temperature, which is interpreted as due to the thermal excitation of electrons to form holes. The subsequent slow decrease arises from desorption of water and the re-equilibrium of electrochemical acceptor between the ambient and the water layer.

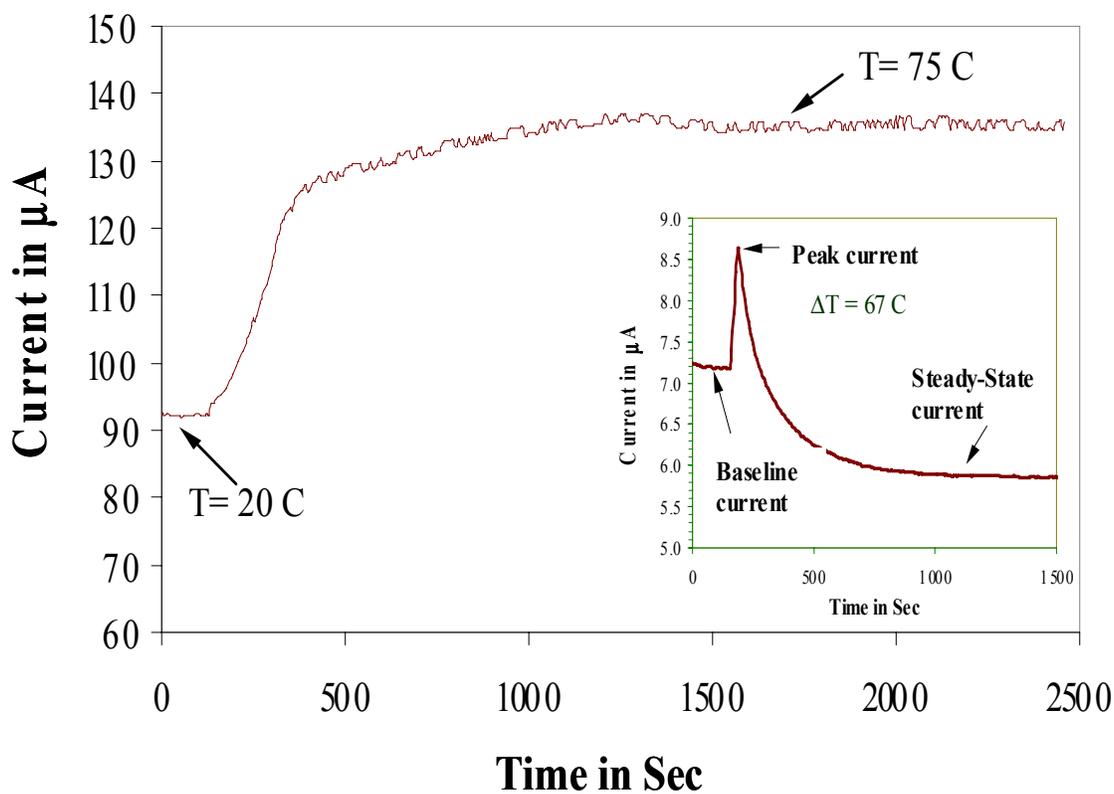


Figure 4. Transient change in conductivity when a step change in temperature is imposed in

vacuum. Inset shows the same experiment performed in air.

However in vacuum, the conductivity of the sample is preserved due the adsorbed anions, which are bound to the surface. Re-equilibrium with the atmosphere is impossible. Increase in temperature causes further excitation of electrons from the diamond to the redox couple in the water layer. However, some uncertainties remain about the nature of redox couples in high vacuum. We believe that trace metal impurities such as iron can act as an electrochemical acceptor.

Figure 5 shows conduction as function of inverse temperature for samples, which were previously exposed to air and to NH_3 vapors. The lower conductivity of NH_3 -exposed sample is due to the lower charge carrier concentration. The activation energies were approximately 0.05 eV.

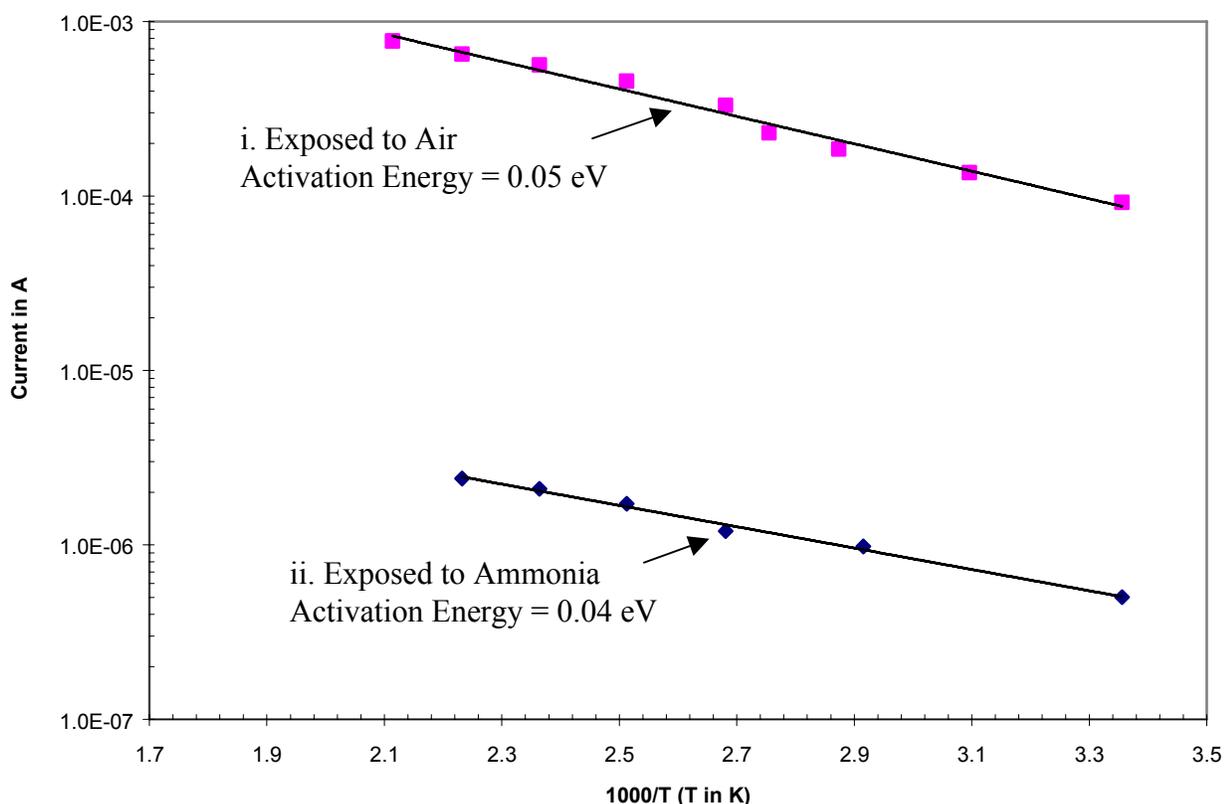
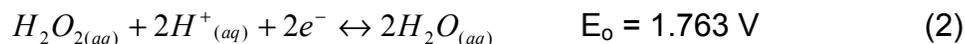


Figure 5. Surface conductivity change as a function of temperature upon annealing in vacuum for polycrystalline diamond previously exposed to i. air, ii. ammonia.

EFFECT OF HYDROGEN PEROXIDE

It is believed that the overall four-electron reduction of O_2 to water proceeds via

hydrogen peroxide as an intermediate, as shown below



Albu and Anderson have calculated potential-dependent activation energies for the uncatalysed four-electron reaction in the 0-2 V range and have predicted that reaction 2 involving the reduction of H_2O_2 to H_2O has the highest activation energy of 1.12 eV, which is ~0.5 eV higher than that needed for reduction of O_2 (reaction 1).⁷ However, the kinetics of these reactions would be greatly affected by the presence of any metal impurities such as transition metals, which could act as a catalyst giving a transition state with lower activation energy.

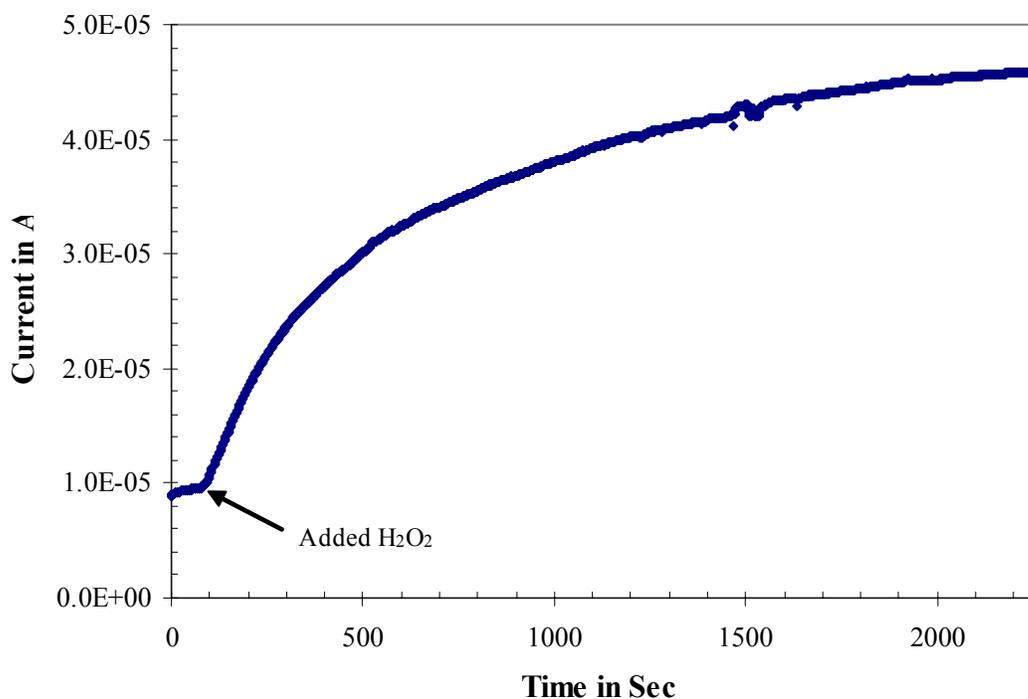


Figure 6. Conductivity change when a (111) diamond surface was exposed to H_2O_2 vapors.

Figure 6 shows the effect of 30 wt% aqueous solution of H_2O_2 on the conductivity of (111) diamond surface. The observed change is consistent with a mechanism in which hydrogen peroxide plays a role.

SUMMARY

The wetting behavior of diamond surfaces is a strong function of the surface termination. Contact angle measurements show that oxygen-terminated diamond surfaces are hydrophilic, whereas hydrogenation leads to higher contact angles. The decrease of the

contact angle at low pH on hydrogenated diamond is attributed to electrochemical transfer doping at the surface. This process leaves excess anions in the water layer and a positive space charge layer in the diamond.² The resulting electrostatic interaction provides a mechanism for binding of a water film to a hydrophobic surface. The conductivity increases upon annealing in vacuum with activation energy of 0.05 eV, which is attributed to the thermal excitation of electrons to form more holes. Hydrogen peroxide has a marked effect on the conductivity consistent with the electrochemical transfer-doping model.

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