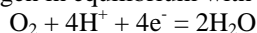


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The effect of pH on the surface conductivity of diamond was first discussed experimentally by Gi *et al.*<sup>1</sup> and an electrochemical explanation was proposed by Maier *et al.*<sup>2</sup> and later elaborated by Foord *et al.*<sup>3</sup> It is proposed that the surface conductivity arises from the transfer of electrons from the diamond to an electrochemical couple in an adsorbed water film. The chemical potential of electrons in the film is determined by an electrochemical equilibrium, most likely involving dissolved oxygen in equilibrium with the air.



The pH of the film may be fixed by acidic or basic gases in the air. For example, CO<sub>2</sub> would fix the pH at slightly acidic values. If the film is made more acidic, *i.e.*, increased concentration and increased chemical potential of H<sup>+</sup>, the equilibrium chemical potential of the electrons,  $\mu_e$ , in the film is reduced correspondingly; if the film is made more basic, the chemical potential of electrons in the film is increased. If the chemical potential of electrons,  $\mu_e$ , in the film is less than the Fermi level,  $E_F$ , of the diamond, electrons can transfer from the diamond into the film, leaving a positive space charge layer in the diamond. This space charge layer populated with holes gives rise to the observed surface conductivity. If  $\mu_e$  is greater than  $E_F$ , then electrons can transfer from the film to the diamond and the surface conductivity is quenched.

The chemical potential of the electrons in the adsorbed film can be estimated using the Nernst equation, and the electrochemical scale linked to the vacuum scale through the equation:  $eE = 4.44 + \epsilon$ , where  $E$  is the electrode potential vs. SHE,  $\epsilon$  is the electron energy and  $e = -1$  is the charge on an electron.

To investigate the mechanism of p-type surface conductivity of diamond, several types of experiments were performed on hydrogen terminated diamond. First, the surface conductivity was measured in air and with the diamond in contact with HCl and NH<sub>3</sub> vapors that were in equilibrium with solutions of controlled pH ranging from 1 to 13. The conductivity increased sharply when exposed to the acid gases and decreased when exposed to the basic gases. Figure 1 illustrates this effect. The baseline current in both instances was for diamond in contact with room air.

Oxidation or fluorination of the diamond surface introduces a surface dipole that lowers the electron energies in the diamond, *i.e.*, increases the electron affinity and lowers the work function. If this lowering is sufficient, the surface conductivity effect will disappear at all pH. The above experiments were repeated with diamonds with fluorinated and oxygenated diamond surfaces, and the pH effect disappeared as expected.

Other conductivity experiments were performed in the presence of octane, which strongly wets hydrogen terminated diamond. The surface conductivity decreased upon exposure to an organic liquid. Results for a (110) diamond surface are shown in Figure 2. Upon addition of octane, the current immediately drops. As the octane evaporates from the diamond surface, the equilibrium between the diamond sample and the air is slowly re-established and the current returns to its baseline value.

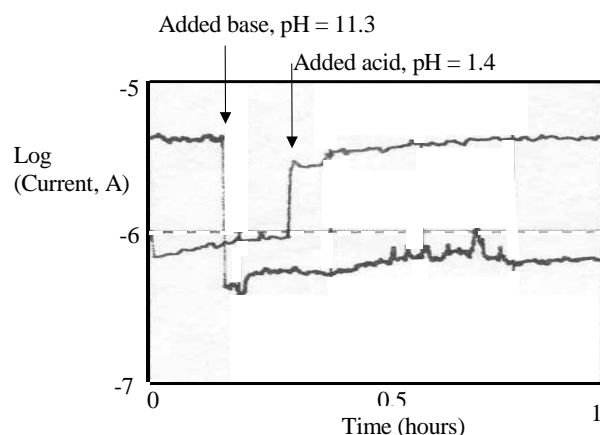


Figure 1. Changes in surface conductivity of diamond when exposed to gases in equilibrium with solutions of HCl and NH<sub>3</sub> of the indicated pH.

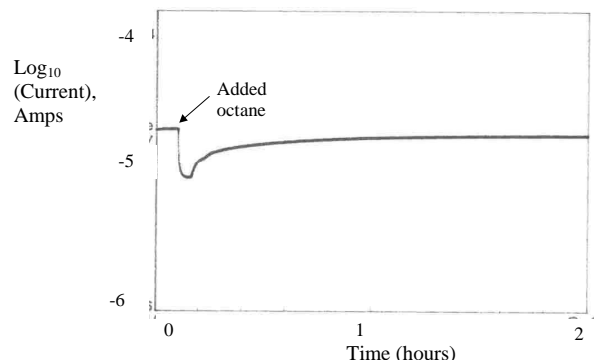


Figure 2. Change in the surface conductivity of a (100) diamond surface upon exposure to normal octane.

The effect of moderate heating (25°C- 250°C) in air on the surface conductivity was studied. An increase in the resistivity was observed at the higher temperatures as demonstrated in Figure 3. The observed activation energy was close to the enthalpy of evaporation of water, which provides further, but somewhat indirect, evidence that adsorbed water is responsible for this effect.

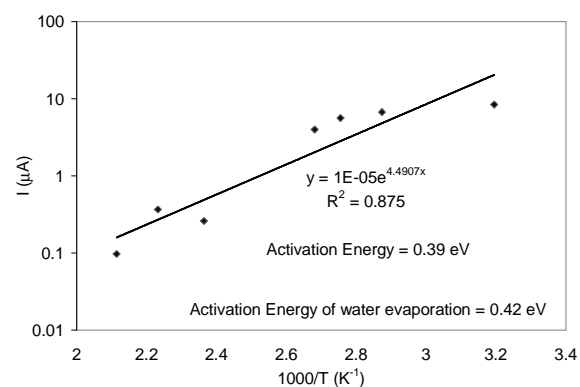


Figure 3. Effect of temperature on surface conductivity

Although the results are consistent with the proposed electrochemical mechanism for the surface conductivity, the nature of the adsorbed film and how it is formed on hydrophobic surfaces is not clear.

<sup>1</sup> R. I. S. Gi, T. Ishikawa, S. Tanaka, T. Kimura, Y. Akiba, M. Iida, *Jap. J. Appl. Phys.* **36** (1997) 2057.

<sup>2</sup> F. Maier, M. Riedel, B. Mantel, J. Ristein, L. Ley, *Phys. Rev. B* **85** (2000) 3472.

<sup>3</sup> J. S. Foord, C. H. Lau, M. Hiramatsu, R. B. Jackman, C. E. Nebel, P. Bergonzo, *Diam. and Relat. Mater.* **11**, (2002) 856.

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