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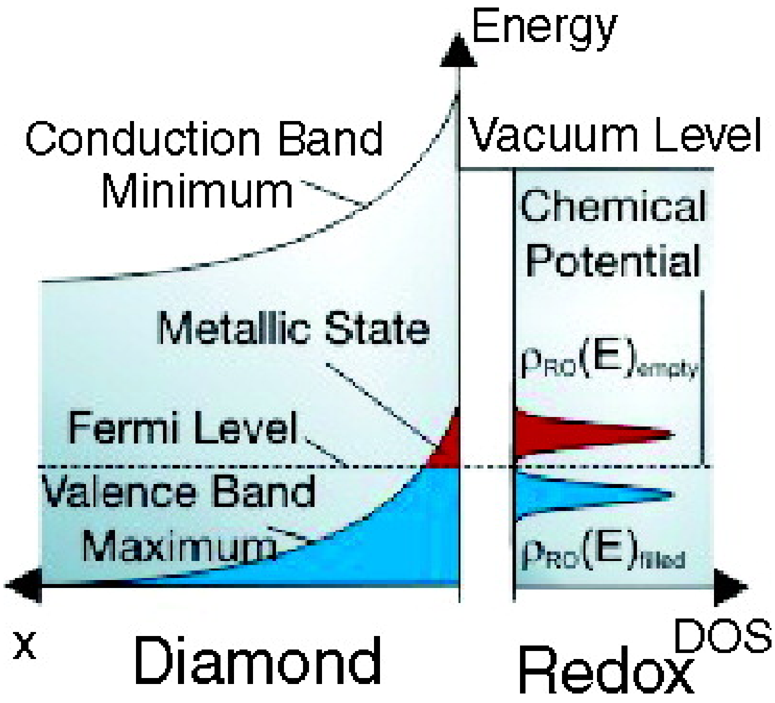

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Insulator−Metal Transition of Intrinsic Diamond

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Diamond is a well-known gemstone, but also famous among scientists for its combination of exceptional properties. Due to the indirect optical band gap of 5.47 eV, it belongs to the group of "narrow band gap insulators" and "wide band gap semiconductors". Thus, diamond can be a perfect insulator or a semiconductor by use of boron (p-type) or phosphorus (n-type) doping. Its superior electronic properties, including breakdown voltage, carrier mobilities, dielectric constant, and radiation hardness, have triggered many research activities on device applications.[1] Chemical vapor deposition (CVD) techniques using hot filament or plasma excitation have optimized the growth condition of synthetic diamond during recent years to a level which allows the controlled deposition of electronic grade quality with atomically flat surfaces.[2]

In addition, surface properties of diamond also attract increasing attention because the carbon dangling bonds at the surface can be terminated by oxygen, hydrogen, or other molecules. For oxygen termination, insulating properties are achieved with increased electron affinities, while hydrogen gives rise to a negative electron affinity due to the formation of carbon hydrogen dipoles.[3] In vacuum, H-terminated surfaces are insulating, too; however, if exposed to air, high surface conductivity can be detected.[4] Although it is certain that the conductivity is related to hydrogen, several controversial models have been proposed, ranging from (1) surface band bending due to valence-band electron transfer into an adsorbate layer ("transfer doping model"),[5] (2) shallow hydrogen-induced acceptors,[6] and (3) deep-level passivation by hydrogen.[7] While in-plane gate and ion-sensitive field effect transistors[8] have been manufactured already on H-terminated polycrystalline CVD diamond, utilizing this effect, the results are contradictory and do not favor one of the three models clearly.

Here, we report an insulator−metal transition of intrinsic (undoped) H-terminated single crystalline CVD diamond as predicted by the transfer doping model. According to this model, a switch from insulating to conductive state of diamond will occur if the chemical potential (μ) of an electrolyte is below the valence-band maximum (E_{VBM}) of H-terminated diamond (Figure 1A). In this case, valence-band electrons will tunnel into the adsorbate layer, giving rise to equilibration. This generates a p-type conductive layer on the diamond surface with metallic properties, as the Fermi level separates electronic states which are occupied by electrons (below E_F) from empty states above E_F (see Figure 1A). This model has been developed based on data from adsorbate films on diamond. Electrolytic properties of adsorbate films arising from atmospheric conditions are not really known; therefore, this model lacks supporting data. In this paper, we report for the first time the electrochemical redox reactions of H-terminated intrinsic (undoped) single crystalline CVD diamond, which is perfectly insulating in vacuum. We use redox couples with well-known chemical potentials to characterize transfer doping effects of H-terminated diamond in such liquids.

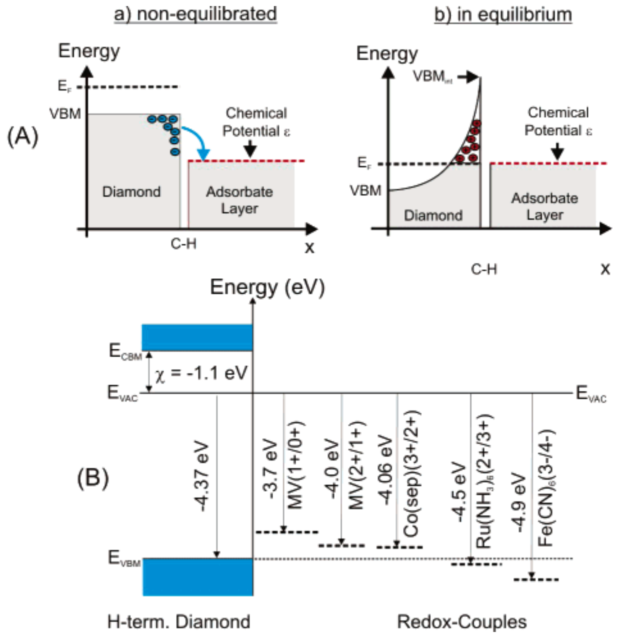

Figure 1. (A) Schematic description of the insulator−metal transition of H-terminated diamond from alignment of Fermi level (E_F) and chemical potential (*e*). (B) Energy diagram for H-terminated diamond surface−electrolyte interface with four redox couples.

We have applied cyclic voltammetry experiments using four different redox systems with different chemical potentials (Figure 1B). Energy levels are calculated by $\epsilon = eU - 4.44$ eV, where ϵ is the chemical potential with respect to the vacuum level (in eV), U is the electrode potential in volts versus SHE, e is the negative elementary charge, and 4.44 eV is the scaling parameter.[9] High-quality undoped single crystalline diamond with H-termination (in the following, termed CVD-D) have been grown homoepitaxially, using microwave plasma CVD, on synthetic (100) Ib diamond substrates (for details, see ref 2).

A summary and comparison of redox reactions with CVD-D is shown in Figure 2. Insulator−metal transition can be detected by reversible redox reactions of $\mathrm{Fe(CN)_6}^{3-/4-}$ (A) and $\mathrm{Ru(NH_3)_6}^{2+/3+}$ (B). The formal potentials of $\mathrm{Fe(CN)_6}^{3-/4-}$ and $\mathrm{Ru(NH_3)_6}^{2+/3+}$ are +0.224 and −0.219 V (vs SCE), respectively, as determined from cyclic voltammetric $E_{1/2}$ in 1 M KCl. The peak separations (ΔV_{pp}) are 296 mV for $\mathrm{Fe(CN)_6}^{3-/4-}$ and 365 mV for $\mathrm{Ru(NH_3)_6}^{2+/3+}$, compared to 64 and 65 mV as detected on metallic boron-doped polycrystalline diamond films.[10] The increased peak separation indicates rate-limited electron transfer at the interface. As the Fermi level is not very deep in the valence band (between 0 and 500 meV) and the surface conducting layer is only a few angstroms thick, we attribute the rate limitations to the small density of carriers in the surface conducting layer. After prolonged anodic oxidation (ap-

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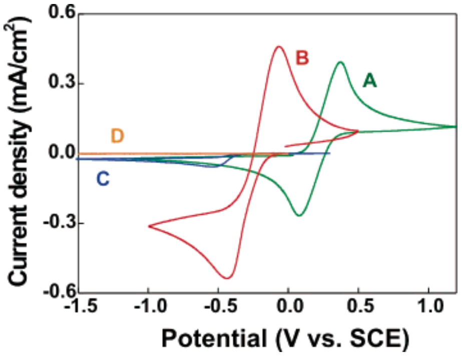

Figure 2. Cyclic voltammograms for (A) $Fe(CN)_6^{3-/4-}$, (B) $Ru(NH_3)_6^{2+/3+}$, (C) methyl viologen ($MV^{2+/1+}/MV^{1+/0}$), and (D) $Co(sep)^{2+/3+}$. Each analyte concentration = 10 mM in 0.1 M Na_2SO_4; sweep rate = 0.1 V/s.

plication of high positive voltages), the redox current becomes zero due to the removal of hydrogen and the surface conductivity is gone.

In contrast, methyl viologen ($MV^{2+/1+}/MV^{1+/0}$) (C) and Co(sep)$^{2+/3+}$ (D) exhibit no detectable redox reactions on CVD-D. Current densities are smaller than 5.5×10^{-5} A/cm^2, which is about 1 order of magnitude smaller than that for $Fe(CN)_6^{3+/4+}$ and $Ru(NH_3)_6^{3+/2+}$. Obviously, the immersion of CVD-D diamond into redox electrolytes containing methyl viologen or $Co(sep)^{2+/3+}$ does not result in a conductive surface layer, arising from the misalignment between the lower E_{VBM} of diamond with the higher electrochemical potentials of these two redox systems, as shown in Figure 1B.

Please note that H-terminated CVD-D films are perfect insulators if measured in vacuum with clean surfaces. This indicates that the Fermi level is not, any more, in the valence band of diamond. The same diamonds become metallic if immersed into redox-couple/electrolyte solutions, with electrochemical potential below the valence-band maximum ($Fe(CN)_6^{3-/4-}$ and $Ru(NH_3)_6^{2+/3+}$). At the surface of diamond, a highly conductive layer is generated with a two-dimensional electronic density-of-state (2D-DOS) if the diamond/electrolyte interface is perfect.[11] It is a spectacular shift which requires “defect-free” bulk properties and perfect hydrogen termination of the surface carbon dangling bonds to unpin the Fermi level. Both conditions seem to be fulfilled for these samples. It is certain that the insulator−metal transition is related to the presence of hydrogen at the surface as the electrochemical currents vanish after anodic surface oxidation.

Figure 3 shows background cyclic voltammograms of CVD-D in 0.1 M $HClO_4$ (A), 0.1 M Na_2SO_4 (B), and 0.1 M NaOH (C). The expected background reaction at negative potential is hydrogen evolution and at positive potential oxygen evolution. The onset of oxygen evolution reaction at positive potentials (U_{OX}) shifts from 0.7 V in pH 13 to about 1.6 V in pH 1 (see inset of Figure 3). The slope of about 60 mV/pH is in agreement with the Nernst prediction (59 mV/pH). Below U_{OX}, the current is basically zero. Application of potentials larger than U_{OX} gives rise to increasing oxidation of H-terminated surfaces. Hydrogen evolution cannot be detected in our experiments down to −3 V (vs SCE), which is the limit of our setup. We attribute this to a perfect H-terminated diamond surface, which is a dense alignment of about 4×10^{15} cm^{-2} ($C^- {-} H^+$) dipoles. This gives rise to Coulomb repulsion toward all positively charged ions in the electrolyte, preventing a significant H evolution.

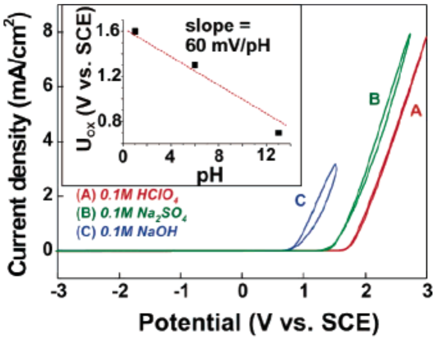

Figure 3. Cyclic voltammograms on H-terminated undoped diamond electrode in (A) 0.1 M $HClO_4$, (B) 0.1 M Na_2SO_4, and (C) 0.1 M NaOH. Potential sweep rate = 0.1 V/s.

It indicates that voltammetric responses of water discharge reactions with both H-terminated undoped and highly B-doped single crystalline (100) diamond is ruled by doping, and also by surface structure (sp^2/sp^3) and, especially, by H-termination properties, as hydrogen termination gives rise to strong repulsion toward protons or hydronium ions.

Finally, we want to address the oxidation phenomena as detected by cyclic voltammetry. As H-terminated diamond has a negative electron affinity of −1.1 to −1.3 eV, while oxidized diamond shows positive electron affinities, we expect a surface-vacuum energy level shift of diamond of more than $\Delta E = 1.3$ eV during oxidation, which will result in increasing misalignment of Fermi level and chemical potential. This is what we detected. Details will be given elsewhere.

In summary, H-terminated intrinsic single crystalline CVD diamond shows insulator−metal transitions if immersed into redox-couple/electrolyte solutions with electrochemical potentials below the valence-band maximum. We detect the same formal potentials as reported in the literature for H-terminated B-doped polycrystalline diamond. Applying oxidizing potentials larger than $+U_{OX}$ gives rise to surface oxidation, which terminates cyclic voltammetric measurements as the surface conductivity disappears. The observed redox reactions reveal details about electron-transfer mechanisms between redox/electrolyte and diamond and carry a similarity to the so-called transfer doping model of diamond.

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