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Redox-couple interactions with undoped single crystalline CVD diamond

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Abstract

Intrinsic CVD diamond is well known as insulator, however if the surface is hydrogen terminated, a surface conduction can be detected if exposed to air and covered by an adsorbate layer. In this paper we show that hydrogen terminated intrinsic single crystalline CVD diamond undergoes an insulator metal transition if immersed into redox electrolyte solutions with chemical potentials below the valence-band maximum. We have applied cyclic voltammetry experiments using different redox couples to characterize this phenomenon. The experiments reveal a large chemical window (>4.6 V) of undoped diamond. We detect the same formal potentials as reported in the literature for H-terminated boron doped polycrystalline diamond. The peaks show comparable symmetries but are shifted towards higher and lower potentials, and are significantly broadened. We attribute this to the rate limited electron transfer at the interface. The results are discussed based on the transfer doping model.

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1. Introduction

Diamond is a well-known gemstone, but also famous among scientists for its combination of exceptional properties [1]. Due to the indirect optical band gap of 5.47 eV it belongs to the group of "narrow-bandgap insulators" and "wide-bandgap semiconductors". The bulk structure of diamond is a tetrahedral lattice of carbon atoms, which is a metastable phase, grown at high temperatures and high pressures or by chemical vapor deposition (CVD) techniques using hot filament or plasma excitation of CH_4 and H_2 mixtures. The growth of CVD diamond has been optimized during recent years to a level which allows the controlled deposition of electronic grade quality with atomically flat surfaces [2–5]. Diamond can be a perfect insulator or a semiconductor by use of boron (p-type) [6] or phosphorus (n-type) [7] doping. Many different types of devices that use the excellent bulk electronic properties of diamond are currently in research and development [8]. In addition, surface properties of diamond attracts increasing attention as the carbon dangling-bonds at the surface can be terminated by a variety of elements, the most important ones are oxygen and hydrogen. For oxygen termination insulating properties are achieved with increased electron affinities while hydrogen gives rise to negative electron affinity due to the formation of carbon–hydrogen dipoles [9,10]. In vacuum such surfaces are insulating too, however, if hydrogen terminated diamond films are exposed to air, surface conductivity can be detected [11–13]. It is certain that the conductivity is related to hydrogen [9–14] however, 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") [12,15,16], 2) shallow hydrogen induced acceptors [17–19], 3) deep-level passivation by hydrogen [20]. Although in-plane gate [21,22] and ion-sensitive field effect transistors [23,24] have been manufactured already on hydrogen terminated polycrystalline CVD diamond, utilizing this effect, the results are contradictory and do not favor one of the three models clearly.

Here we report about the insulator–metal transition of hydrogen terminated intrinsic single crystalline CVD diamond if immersed into a redox-electrolyte solution with a chemical potential below the valence-band maximum of diamond. A metallic property of diamond is generated by tunneling of valence-band electrons into the redox-electrolyte solution until Fermi-level, E_F, and chemical-potential, μ, are aligned, as shown schematically in Fig. 1. At the surface of diamond a highly conductive layer is generated which would have a two-dimensional electronic density-of-state (2D-DOS), if the

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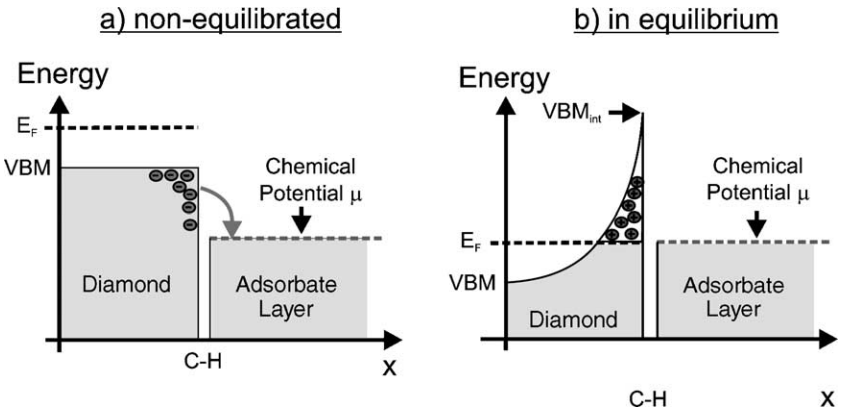

Fig. 1. Schematic insulator metal transition of H-terminated diamond (alignment of Fermi level E_F and chemical potential μ) before (a) and after (b) establishing equilibrium conditions.

interface would be perfect [25]. Such Fermi-level shifts require defect-free sub-surface diamond layers with perfect H-termination of the surface. To characterize the insulator–metal transition of diamond we have applied cyclic voltammetry experiments [26] using different redox systems with different chemical potentials. The observed oxidizing and reduction currents clearly reveal electron transfer mechanisms between redox-electrolytes and diamond if the chemical potential of the redox couples is below the valence-band maximum of diamond and carry a similarity to the so-called surface conductivity of diamond [9–13] seen when hydrogen-terminated diamond films are exposed to air or covered with C_{60} [27].

2. Experimental

Highly boron doped polycrystalline diamond is a well-characterized electrode in electrochemistry. The electronic properties of polycrystalline diamond are governed by doping with boron or nitrogen with densities in the range (10^{19}–10^{20}) cm^{-3}, sp^2-bonded carbon at grain-boundaries and defects at the surface, which is sometimes oxidized or H-terminated [28–30]. For our experiments we selected high quality undoped, single crystalline diamond with H-termination. These films have been grown homoepitaxially, using microwave plasma chemical vapor deposition (CVD), on synthetic (100) Ib diamond substrates. A detailed discussion of their quality has been given in Refs. [2–5]. We use mainly the free-exciton emission intensities at 5.27 and 5.12 eV, measured at room temperature to classify the quality. In addition, the surface morphology is atomically flat [2–5]. Growth parameters of the microwave-plasma CVD deposition are: substrate temperature 800 °C, microwave power 750 W, total gas pressure 25 Torr, total gas flow 400 sccm with 0.025% CH_4 in H_2. Temperature ramping, gas flow, and plasma switching are shown as function of time schematically in Fig. 2. To achieve H-termination after growth, the CH_4 is switch off and the diamond is exposed to a pure hydrogen plasma for 5 min with otherwise identical parameters. The surface-electronic properties of our H-terminated diamond films were characterized applying several experiments which will be discussed in detail elsewhere. Most important results are: 1) Hall-effect experiments show room temperature hole mobilities of up to 340 cm^2/V [31]. 2) Wetting angle experiments results in typical angles of >94° [32]. 3) Total photoelectron emission experiments results in negative electron affinities of −1.1 eV [33].

For the electrochemical experiments we evaporated 200 nm thick Au films on the H-terminated surface with rotational symmetry as shown in Fig. 3. The electrochemical active area

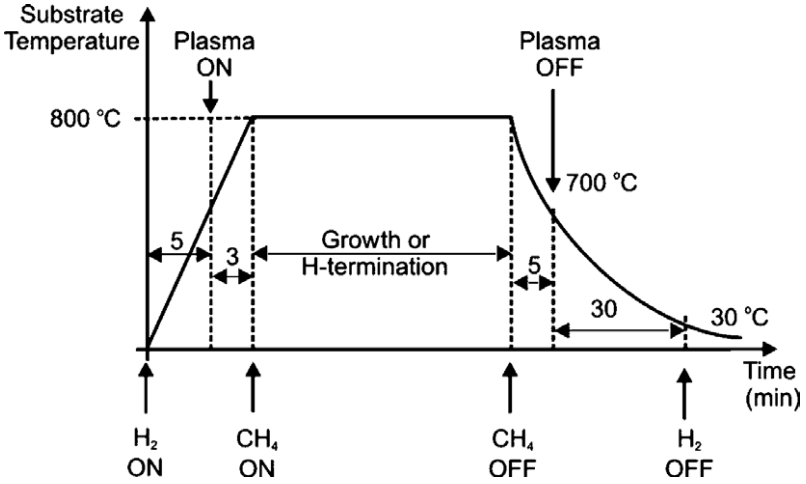

Fig. 2. Temperature and gas flow variations, plasma switching cycles for growth or H-termination of CVD diamond.