



Mechanism of hole doping into hydrogen terminated diamond by the adsorption of inorganic molecule

Yoshiteru Takagi^{a,b,*}, Kenji Shiraishi^a, Makoto Kasu^c, Hisashi Sato^d

^a Graduate School of Pure and Applied Sciences, University of Tsukuba, 1-1-1 Tennodai, Tsukuba 305-8571, Japan

^b CREST, Japan Science and Technology Agency, 5 Sanbancho, Chiyoda-ku, Tokyo 102-0075, Japan

^c Department of Electrical and Electronic Engineering, Saga University, Saga 840-8502, Japan

^d NTT Basic Research Laboratories, NTT Corporation, 3-1 Morinosato-Wakamiya, Atsugi, Kanagawa 243-0198, Japan

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ABSTRACT

We revealed a mechanism of hole doping into hydrogen (H) terminated diamond by the adsorption of inorganic molecules, based on first-principle calculation. Electron transfer from H-terminated diamond to adsorbate molecules was found in the case that the energy level of unoccupied molecular orbitals in an adsorbate molecule is below or around the valence band maximum of H-terminated diamond. The amount of doped hole carriers depends on the energy level of unoccupied molecular orbital of adsorbate molecules. The mechanism can explain the experimentally observed dependence of increasing hole sheet concentration at H-terminated diamond surface on the species of adsorbate molecule.

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1. Introduction

Diamond is regarded as an ideal semiconducting material for electronic devices. Diamond has wide electronic band gap, high mobility, and high thermal conductivity, and so on. Due to these properties, diamond-based electronic devices are expected to perform with high frequency under harsh conditions such as under high voltage and under high temperature. Carrier doping is indispensable to development and improvement of diamond-based electronic devices. However, it is hard to efficiently inject electrons and holes into the insulating diamond by impurity doping methods.

Exposure of hydrogen (H) terminated diamond to air generates hole carriers at the surface [1]. Various models have been proposed to explain the mechanism of hole doping into H-terminated diamond. The mechanism is explained in terms of oxidation by adsorbate molecules at the surface region [2–4], formation of hydrogen-related acceptor level [5], redox reaction in an adsorbed water layer [6–9], or the spontaneous polarization model [10]. However, the origin of the mechanism has been controversial. Additionally, it has been reported that hole carriers are doped into H-terminated diamond by the adsorption of C₆₀ [11] and F4-TCNQ [12].

Recently, two of us have experimentally reported [13–17] that exposure of H-terminated diamond to NO₂, O₃, NO, and SO₂ increased hole sheet concentration (p_s) at the surface region. The maximum critical value for p_s is up to the order of 10¹⁴/cm². On the other hands, N₂O, CO₂, and humid N₂ have little or no influence on p_s of

H-terminated diamond. The experiments show that p_s strongly depends on the species of adsorbate molecules. However, the mechanism of the dependence of p_s on the species of adsorbate molecule has not been cleared. Our purpose is to reveal the mechanism by first-principles calculations.

2. Calculation methods

In this work, we performed first-principle calculations based on the density-functional theory [18,19] to investigate the geometric and electronic structures of H-terminated diamond by the adsorption of inorganic molecules. To express the exchange-correlation energy among the interacting electrons, we used a functional form fitted to the Monte-Carlo results [20] for a homogeneous electron gas [21]. Ultrasoft pseudopotentials were used to describe the electron-ion interaction [22]. The valence wave functions were expanded in terms of the plane-wave basis set with a cut off energy of 36 Ryd. The conjugate-gradient minimization scheme was used for the electronic structure calculation and for geometry optimization [23]. The lattice parameters were fixed during the structural optimization. For the optimized geometry, the atoms were subjected to a force of less than 1.5×10^{-3} Eh/a.u. We considered a repeated slab model of H-terminated diamond (100) dimerized (2 × 1) surface comprising twelve carbon layers. Each slab model is separated from its repeated one by about 25 Å vacuum region. We used 2 × 2 periodicity in the lateral direction. There is one molecule in the unit cell. To avoid periodic image errors arising from the repeated slab model, we adopted the effective-screening medium method [24]. Integration over the two-dimensional Brillouin zone was carried out using 6 × 6 k-points for structure optimization and 30 × 30 k-points for density of states

* Corresponding author at: Graduate School of Pure and Applied Sciences, University of Tsukuba, 1-1-1 Tennodai, Tsukuba 305-8571, Japan. Tel.: +81 25 853 5600.

E-mail address: ytakagi@comas.frsc.tsukuba.ac.jp (Y. Takagi).

(DOS) and local density of states (LDOS). All calculations were done by using the TAPP code [25,26]. In this paper, p_s is evaluated by number of transferred electrons from H-terminated diamond to an adsorbate molecule per surface area in the unit cell. We should note that p_s which is evaluated by our method does not always correspond to the active hole carrier sheet concentration due to many-body interaction such as attractive Coulomb interaction between electrons and holes.

3. Results and discussion

First of all, let us summarize the experimental results to reveal the mechanism of the dependence of p_s on species of adsorbate molecules in H-terminated diamond. i) p_s strongly depends on the species of adsorbate molecules [13]. The adsorption of NO_2 , O_3 , NO , and SO_2 increases p_s , while the adsorption of N_2O and CO_2 has little or no influence on p_s . ii) An adsorbate water layer is unnecessary to increase p_s [15]. iii) Adsorbate molecules physically absorb on H-terminated diamond [16]. iv) Acceptors and hole channel are spatially separated [16].

Physisorption interaction among the adsorbate molecules and H-terminated diamond surface and no existence of an adsorbate water layer indicate that the adsorbate molecules remain their ground electronic states on the H-terminated diamond surface. Therefore, the dependence of p_s on the species of adsorbate molecules seems to relate to the electronic structure of isolated molecules. We compare electronic structures of isolated molecules with that of H-terminated diamond. Eigen energy of the highest occupied molecular orbital (HOMO), the lowest unoccupied molecular orbital (LUMO), and the single occupied molecular orbital (SOMO) of isolated inorganic molecule is shown in Fig. 1 with the valence band maximum (VBM) and the conduction band minimum (CBM) of H-terminated diamond with (100), (110), and (111) surface. These energy levels were calculated by us. Here, we plotted the energy levels measured from the vacuum level which is used as the reference state in each system. For H-terminated diamond, VBM and CBM lie around -3 eV below the vacuum level (E_v) and around 1.8 eV above E_v , respectively. The positive value of CBM means the electron affinity is negative for H-terminated diamond [27].

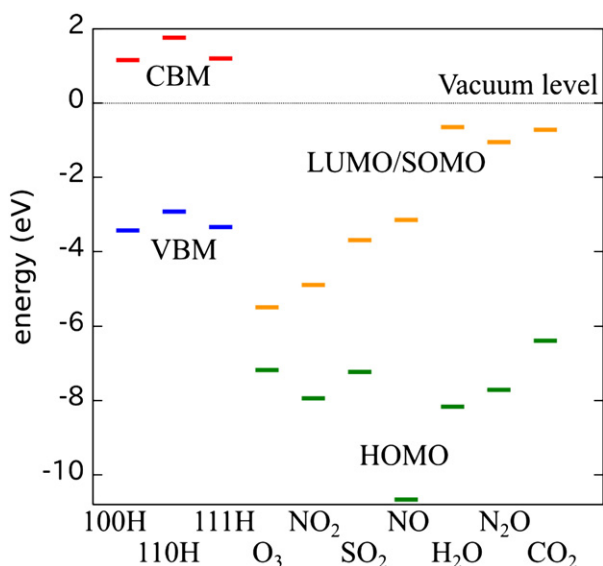


Fig. 1. Energy level of the valence band maximum (VBM) and the conduction band minimum (CBM) of H-terminated diamond with (100), (110), and (111) surfaces which are represented by blue and red bars, respectively, and of the highest occupied molecular orbital (HOMO), and the lowest unoccupied molecular orbital (LUMO) or the single occupied molecular orbital (SOMO) of inorganic molecules which are represented by green and yellow bars, respectively. The origin of energy is set at the vacuum level.

The molecules listed in Fig. 1 are classified into two groups. The first group is composed of NO_2 , O_3 , SO_2 , and NO , which have LUMO/SOMO level below or around VBM of H-terminated diamond. The second group is composed of H_2O , N_2O , and CO_2 , which have only HOMO level below VBM of H-terminated diamond. The classification consists with the experimental results: increasing of p_s at H-terminated diamond is induced by the adsorption of the molecules belong to the first group, while the molecules belong to the second group have little or no influence on p_s .

The consistency between the above classification and the experimental results suggests that increasing of p_s is induced by electron transfer from the H-terminated diamond surface to LUMO/SOMO of adsorbate molecules. The electron transfer induces the charge imbalance in adsorbate molecules and in H-terminated diamond and modifies the electronic structures of them. Schematic picture of band diagram of H-terminated diamond surface by the adsorption of molecules is shown in Fig. 2. Before the adsorption (Fig. 2(a)), the Fermi level lies on the center of band gap in H-terminated diamond. After the adsorption, electrons flow from valence band of H-terminated diamond to LUMO/SOMO of adsorbate molecules until equilibrium is reached (Fig. 2(b)). The amount of electron transfer, that is p_s , depends on the energy difference between the VBM of H-terminated diamond and the energy level of LUMO/SOMO. Of course, electron transfer does not occur between the H-terminated diamond and adsorbate molecules which has no unoccupied orbitals below or around VBM of H-terminated diamond, namely, p_s induced by the spontaneous dipole at the H-terminated diamond surface is very small. The electron transfer induces the upward band bending toward the surface of H-terminated diamond (Fig. 2(c)). There are three factors to determine the equilibrium states. One is the Coulomb repulsive interaction between electrons transferred from H-terminated diamond and native electrons in the adsorbate molecule. Second is an electric dipole induced by the electron transfer. Third is the permanent electric dipole in adsorbate molecules. We used first-principles calculations to investigate more realistic band diagram of H-terminated diamond by the adsorption of molecules.

Our calculation shows that the peak structure originated from the SOMO of NO_2 exists around VBM in spectrum of DOS of H-terminated diamond (100) surface by the adsorption of NO_2 (Fig. 3(a)). The Fermi level lies on the peak structure. From analysis based on LDOS (Fig. 3(b)) and the optimized structure (Fig. 3(c)), the peak structure is composed of mainly SOMO of NO_2 and slightly valence states of diamond. This means that hole carriers inject into H-terminated diamond surface by the adsorption of NO_2 which acts as an acceptor. States around C-H bonds do not contribute the peak structure. This indicates that NO_2 which is an acceptor is spatially separated from the hole doped region. The calculated p_s of this system is about $3.8 \times 10^{13}/\text{cm}^2$. Additionally, as illustrated in Fig. 2(b), the electron transfer from H-terminated diamond surface to NO_2 induces the conduction band bends upward at the surface. The amount of upward band bending is about 0.4 eV. Our calculated p_s , $3.8 \times 10^{13}/\text{cm}^2$, is slightly smaller than the experimental value, $9 \times 10^{13}/\text{cm}^2$ [16], because the energy level of SOMO of NO_2 is energetically close to VBM of H-terminated diamond and NO_2 cannot accept one valence electron in H-terminated diamond in the structural model used for the theoretical calculation. If the energy level of SOMO of NO_2 is clearly below the Fermi level, NO_2 can accept one electron, namely, p_s approaches to the experimental value. Accordingly, the experimental fact [16] can be quantitatively explained by the hole generation mechanism by the electron transfer from H-terminated diamond to adsorbate molecules.

In contrast to the above case, there are no any peak structures around VBM of H-terminated diamond by the adsorption of H_2O (Fig. 3(d)). The Fermi level lies on the center of band gap. From analysis based on the LDOS (Fig. 3(e)) and the optimized structure (Fig. 3(f)), the peak structures originated from HOMO and LUMO of

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