

Adsorption of hydrogen on the (001) surface of diamond

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The electron-energy structure, total, and local densities of states of the clean (001)-(1×1), π -bonded symmetric dimer (001)-(2×1), monohydride (001)-(2×1):H, and dihydride (001)-(1×1):2H surface structures of diamond are investigated utilizing the self-consistent tight-binding method. The total-energy minimization method has been used to determine the equilibrium geometry of the (001) diamond surface. Clean (001)-(1×1) and π -bonded symmetric-dimer (001)-(2×1) surfaces are characterized by sharp dangling bonds near the middle of the gap. Adsorption of H completely removes surface states from the gap in the dihydride phase. In the dihydride phase, hydrogen-induced bonding surface states occur near the top of the valence band and at the bottom of the conduction band, resulting in an enhancement of the surface conductivity due to the adsorption of hydrogen. In the monohydride (001)-(2×1):H symmetric-dimer phase the bonding surface states occur in the range around the top of the valence band and near the middle of the gap. The results obtained are discussed and compared with experimental data available in the literature.

I. INTRODUCTION

Recently, there has been significant interest in the study of the diamond surface due to its structural similarity to silicon, and recent technological results in the growth of diamond films by chemical vapor deposition (CVD) techniques.^{1,2} Hydrogen plays an integral role on the diamond surface. Despite intensive study, important questions remain concerning the details of the reconstruction and the effect of hydrogen adsorption on the surface structure.³⁻⁵ The diamond cleavage surface exhibits a bulklike structure believed to be hydrogen terminated.^{4,6} Ultraviolet photoelectron spectroscopy (UPS) does not reveal any filled states near the valence band on the (1×1):2H surface, although relatively high surface-state density in the 1.5-eV range above the top of the valence band has been reported.¹

The reconstruction of the (001):H diamond surface has been studied by quantum-chemistry methods,^{5,7} and the empirical tight-binding method (ETBM) has been used to investigate the unrelaxed (001) surface by the use of the slab model.⁸

Thermodynamical characteristics of the (001) surface have been calculated by molecular mechanics,⁹ and the empirical potentials for hydrocarbons have been determined.¹⁰ The total-energy minimization method in ETBM has been used¹¹ to determine the equilibrium geometry of a symmetric (2×1) dimer phase on a (001) diamond surface.

The influence of hydrogen treatment on the electrical conductivity of single crystals and CVD films of diamond has been studied.^{12,13} It has been found that such a treatment caused a marked reduction (up to several orders of magnitude) in the resistivity of the samples, which probably points to the surface nature of the conductivity of diamond after the adsorption of hydrogen.¹⁴

In this paper, the self-consistent ETBM has been used to investigate the hydrogen adsorption on the (001) sur-

face of diamond by the use of the slab model of the surface. A total-energy minimization method in the tight-binding theory^{11,15} has been used to study the relaxation on (001)-(1×1) and (001)-(2×1) surfaces.

II. METHOD

The surface electronic band structure has been calculated using the supercell (slab) method.¹⁶⁻¹⁸ The electron-energy structure of the 30-layer slab is obtained by solving the two-dimensional (2D) Schrödinger equation

$$\hat{H}\psi(n, \mathbf{k}_{\parallel}) = E_n \psi(n, \mathbf{k}_{\parallel}), \quad (1)$$

with the Hamiltonian¹⁹

$$\hat{H} = \sum_{\lambda, i} |\lambda, i\rangle \epsilon_{\lambda i} \langle \lambda, i| + \sum_{\lambda, \lambda', i, i'} |\lambda, i\rangle t_{\lambda', \lambda}(\mathbf{R}_i - \mathbf{R}_{i'}) \langle \lambda', i'|. \quad (2)$$

Basis functions are labeled by $\lambda(l, m)$, where l and m denote the appropriate angular-momentum quantum numbers.¹⁹ To achieve a better description of the conduction band of the bulk diamond, the sp^3s^* states have been used as a basis.²⁰ Interatomic interactions between the first and second neighbors of the carbon atoms have been considered by calculating the matrix elements of the Hamiltonian matrix. The tight-binding parameters of C-C interactions have been chosen to reproduce the bulk band structure of diamond, and are listed in Table I. The values of the orbital energies in diamond have been taken²⁰ as $E_s = -19.19$ eV, $E_p = -11.79$ eV, and $E_{s^*} = -4.26$ eV.

In Table II, the values of some important energies of symmetry points in bulk diamond as calculated in this work, as well as those available in the literature, are presented for comparison. It can be seen that our model reproduces quite well the valence and lower conduction

TABLE I. Tight-binding matrix elements of the interactions (in eV) between C-C orbitals.

Parameters	First neighbors	Second neighbors
($ss\sigma$)	-1.58	-0.41
($ss^*\sigma$)	0.0	0.0
($sp\sigma$)	1.71	0.32
($s^*p\sigma$)	1.55	0.29
($pp\sigma$)	2.60	0.59
($pp\pi$)	-0.55	-0.05

bands of the bulk diamond.

In this work, the matrix elements of C-H interactions have been determined from molecular-energy levels of CH₄ using molecular-orbital theory (as has been done for the Si-H interaction¹⁸). Details are given in the Appendix. In this investigation, the H-H repulsive interaction has been taken into account. A comparison of the total density of states calculated in this work with experimental results of photoelectron spectroscopy on the C(001):H surface of diamond (see below) show that matrix elements of the C-H interaction determined in such a manner are realistic. Numerical tight-binding parameters of C-H interactions used in the calculations are listed in Table III.

The total [$D(\omega)$] density of states has been calculated by integration over the 2D surface Brillouin zone (BZ) using the special \mathbf{k} -points method:²¹

$$D(\omega) = \frac{1}{\Omega} \sum_n \int_{\mathbf{k}_{\parallel}} \delta[E_n(\mathbf{k}_{\parallel}) - \hbar\omega] d^2\mathbf{k}_{\parallel}. \quad (3)$$

The equilibrium atomic structure of diamond covered with hydrogen on a (001) surface has been determined by the total-energy-minimization method.^{11,15} The total energy per unit cell of the system is determined¹⁵ by

$$E_{\text{tot}} = E_{\text{atom}} - E_{\text{coh}}, \quad (4)$$

$$-E_{\text{coh}} = E_{\text{cov}} + E_{\text{overlap}} + E_{\text{transfer}}, \quad (5)$$

$$E_{\text{cov}} = \frac{1}{N} \sum_{n,\mathbf{k}}^{\text{occ}} E_n(\mathbf{k}) - \sum_{\lambda i} \epsilon_{\lambda i}. \quad (6)$$

One-electron energies are given by

TABLE II. A comparison between the values (in eV) of some important energies of symmetry points in diamond as calculated in this work and those available in the literature.

Energy gap	This work	Data of Ref. 24
Γ_{15c}	6.05	6.00
$\Gamma_{2'c}$	14.8	15.3
$\Gamma_{25'v}$	0.00	0.00
Γ_{1v}	-21.4	-21.03
Δ_{1c}	5.45	5.48
X_{1c}	5.82	5.91
X_{1v}	-12.87	-12.43
X_{4v}	-6.65	-6.27
L_{3c}	8.86	9.23
L_{3v}	-2.95	-2.82
L_{1v}	-12.96	-12.8

TABLE III. The orbital energy and matrix elements of tight-binding interactions (in eV) between C-H orbitals, determined from molecular-orbital energies of CH₄.

Parameters	Energy (eV)
E_H	-11.59
($ss\sigma$) _{H-C}	-5.27
($ss^*\sigma$) _{H-C}	0.0
($sp\sigma$) _{H-C}	-2.32
($ss\sigma$) _{H-H}	0.88

$$\epsilon_{\lambda i} = \omega_{\lambda i} - U_i(Z_i - Q_i) - \sum_{i' \neq i} (Z_{i'} - Q_{i'}) V(\mathbf{R}_i - \mathbf{R}_{i'}) + f_{\lambda i}, \quad (7)$$

where Z_i is the atomic number, Q_i is the total valence electron occupancy, $\omega_{\lambda i}$ represents the orbital energies of the free neutral atoms on the site i , and V is the electrostatic potential, which is assumed to be strictly Coulombic.

The overlap $f_{\lambda i}$ is determined in the framework of extended Hückel theory,²² where

$$E_{\text{overlap}} = \sum_{\lambda, i}^{\text{occ}} Q_{\lambda, i} f_{\lambda, i}, \quad (8)$$

$$E_{\text{transfer}} = \sum_{\lambda, i}^{\text{occ}} (Q_{\lambda, i} - Z_{\lambda, i}) \omega_{\lambda, i} + \frac{1}{2} Z^{*2} (U_a + U_c - 2U_M). \quad (9)$$

The Madelung energy U_M and the electrostatic potential V have been determined as already described.¹⁵

To investigate the relaxation process on the surface of diamond, we have calculated the forces acting on the atoms in the unit cell. The Hellmann-Feynman force acting on the atom l of the unit cell is given as²³

$$\begin{aligned} -\mathbf{F}_l &= \frac{\partial E_{\text{tot}}}{\partial \mathbf{R}_l} \\ &= \sum_{\lambda, i}^{\text{occ}} Q_{\lambda, i} \frac{\partial f_{\lambda, i}}{\partial \mathbf{R}_l} + \sum_{\lambda, i}^{\text{occ}} \sum_{n, \lambda', j}^{\text{occ}} C_{\lambda, i}^{*n} C_{\lambda', j}^n \frac{\partial t_{\lambda, i, \lambda', j}}{\partial \mathbf{R}_l} \\ &\quad + \frac{1}{2} \sum_{i, j}^{\text{occ}} (Q_i - Z_i)(Q_j - Z_j) \frac{\partial V(\mathbf{R}_j, \mathbf{R}_i)}{\partial \mathbf{R}_l}. \end{aligned} \quad (10)$$

The force vector acting on each particular atom on the surface indicates the direction of the atomic movement by the relaxation.

First we solve Eq. (1) using Eqs. (4)–(9) self-consistently with respect to occupancies $Q_{\lambda, i}$. Then cohesive energy in Eq. (5) is calculated as a function of the coordinates of the atoms to be relaxed. The corresponding equilibrium geometry is found by calculation of the Hellmann-Feynman forces, and subsequent minimization of E_{tot} . Finally the surface electronic band structure and densities of states are obtained for the surface phases considered.

III. RESULTS AND DISCUSSION

In Fig. 1, the electron-energy structures of the $(1 \times 1):2\text{H}$ and $(2 \times 1):\text{H}$ phases are presented. Total and local densities of surface states and the influence of hydrogen adsorption on the surface states are shown in Figs. 2–4. Our model reproduces the bulk band structure of diamond quite well, as demonstrated in Table II. The total density of states agrees well with that obtained for the bulk diamond.²⁴

The equilibrium geometry of the surface atoms has been determined by minimization of the total energy of the system. We found that in the dihydride phase, the C-H bond length is somewhat shorter (1.06 Å) than that of the $(2 \times 1):\text{H}$ dimer phases (1.10 Å), in agreement with published results.^{9,25} The C-H bond angle is found to be 20.5° and 41.3° in the $(2 \times 1):\text{H}$ symmetric dimer and $(1 \times 1):2\text{H}$ phases, respectively. These values are in reasonable agreement with those found earlier by cluster calculations.^{5,7}

Let us now compare our obtained results with experimental data available in the literature. In UPS experiments,¹ no filled surface states have been observed on the $(1 \times 1):2\text{H}$ surface, in contrast to the $(2 \times 1):\text{H}$ surface, where an intense signal has been observed in the 1.5-eV

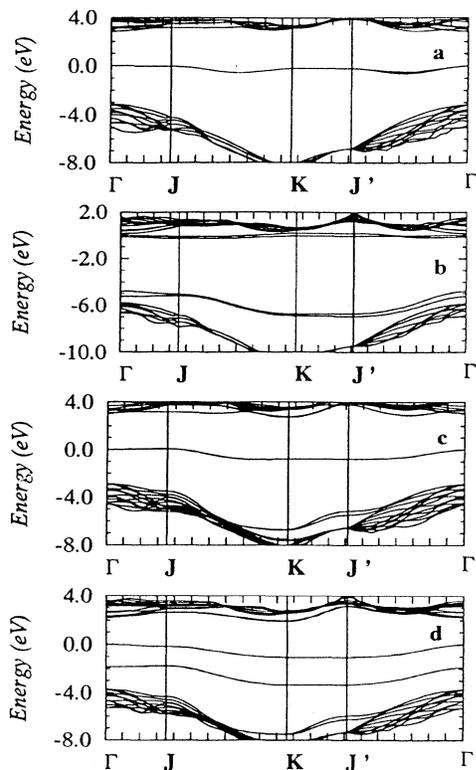


FIG. 1. The electronic band structure of the (001) surface of diamond. (a) The cleaved (1×1) surface. (b) The relaxed $(1 \times 1):2\text{H}$ dihydride phase. (c) The symmetric π -bond dimer (2×1) surface. (d) The monohydride symmetric-dimer $(2 \times 1):\text{H}$ phase. The zero of the energy scale indicates the highest filled state position at the center of the BZ.

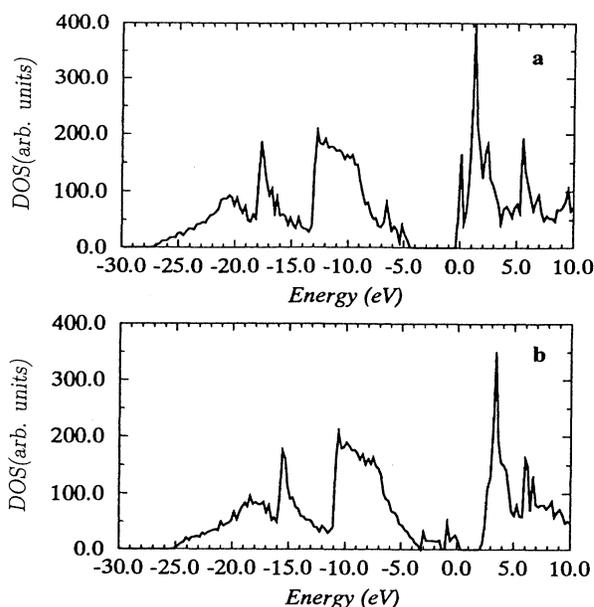


FIG. 2. The total density of states (TDOS) of the (001) surface of diamond. (a) The dihydride $(1 \times 1):2\text{H}$ phase. (b) The monohydride $(2 \times 1):\text{H}$ symmetric-dimer phase. The zero of the energy scale indicates the highest filled state position at the center of the BZ.

range of energies above the valence-band maximum. Comparison of calculated densities of states (see Fig. 2) shows that our results are in reasonable agreement with the experimental data mentioned: there are no filled states in the gap in the dihydride phase; however, in the $(2 \times 1):\text{H}$ symmetric-dimer phase, the filled surface states occupy the lower half of the gap. Thus one can suggest that our tight-binding parameters for the C-H interaction (see Table III) are quite realistic.

Further, one of the very important problems in applications is the nature of the electrical conductivity of diamond and the influence on it by the adsorption of hydrogen. The experimental results show that the treatment of hydrogen by both single crystals and microcrystalline CVD films of diamond results in a marked reduction (up to several orders of magnitude) in the resistivity of the samples.^{12,13} These results point to the probable surface nature of the electrical conductivity of diamond covered with hydrogen.¹⁴

As follows from the results presented, the effect of hydrogen adsorption on the surface band structure of diamond is quite different from that obtained earlier on silicon.¹⁸ In the $(2 \times 1):\text{H}$ symmetric-dimer phase, the H-induced bonding states are placed in the forbidden gap. In the dihydride $(1 \times 1):2\text{H}$ phase, the surface states are pushed away from the gap. But in contrast to Si:H, one part of the H-induced bonding states is placed in the valence band, while another part is in resonance with C electrons in the conduction band.

The resonance of hydrogen-bonding states with the electronic states in the conduction band implies a metallic surface electrical conductivity in C(001)- $(1 \times 1):2\text{H}$.

This means that diamond covered with hydrogen in the dihydride phase must reveal a drastic enhancement of the electrical conductivity due to the adsorption of hydrogen. One can conclude that the effect of the marked reduction of the resistivity of diamond after the treatment by a hydrogen ambient, which has been observed experimentally,^{12,13} is caused by the resonance of H-induced surface-bonding states with the lowest electronic states of the conduction band. The results of the calculations of the local density of states of the dihydride $(1 \times 1):2\text{H}$ phase of diamond (see Fig. 3) show that the electrons from the surface carbon atoms are responsible for the lowest electronic states of the conduction band. This means that the effect of drastic enhancement of the electrical conductivity of diamond after the adsorption of hydrogen is of a surface nature.

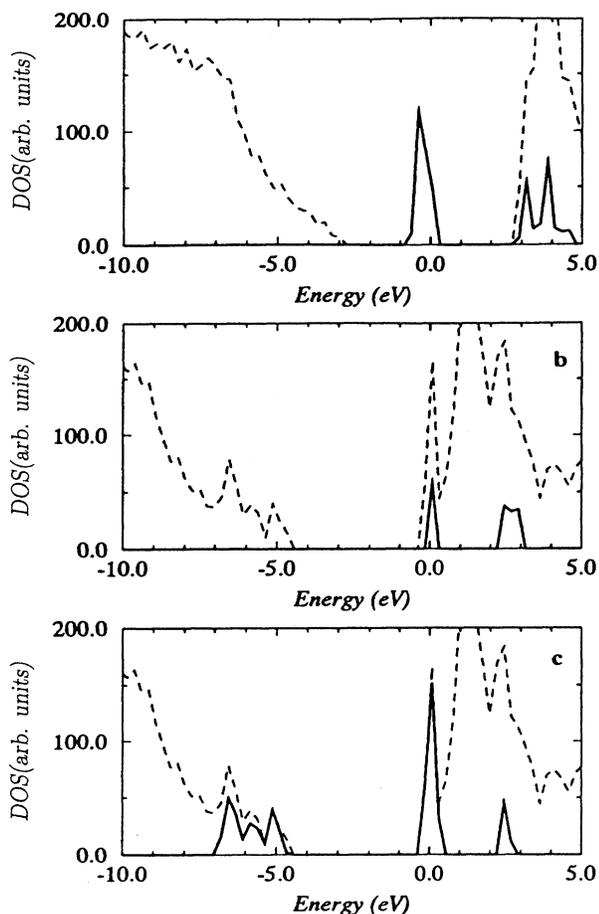


FIG. 3. The local densities of states (LDOS) (solid line) of hydrogen and surface C atoms of the $(001)-(1 \times 1)$ surface of diamond. The total density of states is represented by the dashed line. (a) The LDOS of the surface C atoms of the unrelaxed $(001)-(1 \times 1)$ surface (without hydrogen). (b) The LDOS of hydrogen atoms of the relaxed $(001)-(1 \times 1):2\text{H}$ surface. (c) The LDOS of surface C atoms of the relaxed $(001)-(1 \times 1):2\text{H}$ surface. The zero of the energy scale indicates the highest filled state position at the center of the BZ.

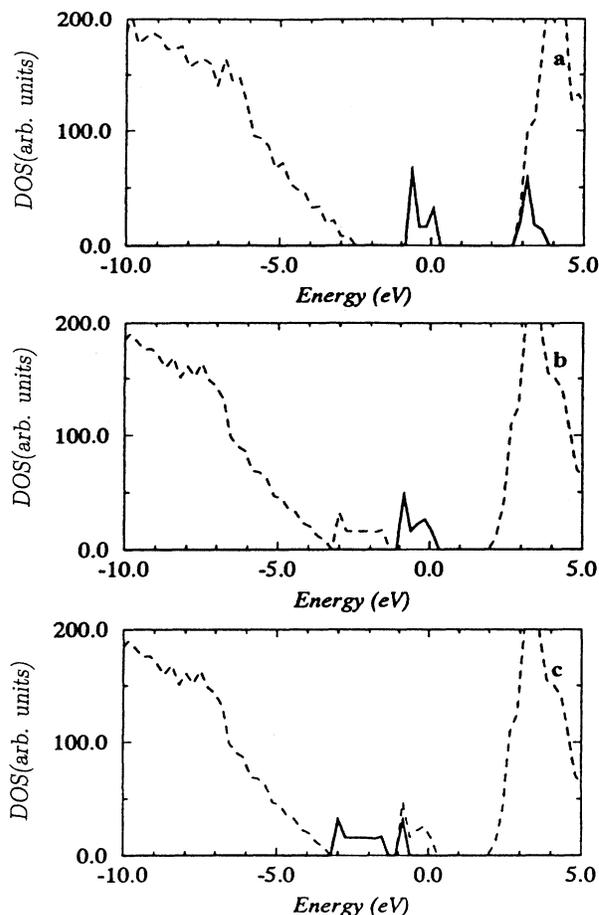


FIG. 4. The local densities of states (solid line) of hydrogen and surface C atoms of the reconstructed $(001)-(2 \times 1)$ symmetric-dimer surface phase of diamond. The total density of states is represented by the dashed line. (a) The LDOS of the surface C atoms of the π -bonded symmetric-dimer $(001)-(2 \times 1)$ surface phase (without hydrogen). (b) The LDOS of hydrogen atoms of the $(001)-(2 \times 1):\text{H}$ surface. (c) The LDOS of surface C atoms of the $(001)-(2 \times 1):\text{H}$ surface. The zero of the energy scale indicates the highest filled state position at the center of the BZ.

IV. SUMMARY

In this paper, the electron-energy structure, total, and local densities of states of the clean $(001)-(1 \times 1)$, π -bonded symmetric dimer $(001)-(2 \times 1)$, monohydride $(001)-(2 \times 1):\text{H}$, and dihydride $(001)-(1 \times 1):2\text{H}$ phases are investigated using a self-consistent empirical tight-binding method. The total-energy-minimization method has been used to determine the equilibrium geometry of the (001) diamond surface covered with the monolayer of hydrogen. Clean $(001)-(1 \times 1)$ and π -bonded symmetric-dimer $(001)-(2 \times 1)$ surfaces are characterized by the sharp dangling-bonds band near the middle of the gap. In the monohydride $(001)-(1 \times 1):\text{H}$ symmetric-dimer phase, the bonding surface states are placed in the lower half of the gap. In the dihydride phase, there are no filled

states in the gap; however, bonding H-induced states are in resonance with the electronic states in the valence and conduction bands of the carbon atoms. The existence of surface H-induced bonding states in the conduction band of diamond covered with hydrogen causes the marked enhancement of electrical conductivity, which has been observed experimentally.

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APPENDIX

The matrix elements of C-H interactions are determined from molecular-energy levels of CH₄ by the following procedure. Singlet and triplet molecular orbitals are calculated by a projection of the wave functions constructed from atomic orbitals on the A_1^\pm and F_2^\pm representations of the T_d point group, respectively. As a re-

sult, the Hamiltonian matrix of the CH₄ molecule is separated into four blocks, namely, for bonding and antibonding singlet and triplet states. The secular equation is then analytically solved and the following expressions for eigenenergies are obtained:

$$E_{A_1^\pm} = \frac{1}{2}(E_s + E_s^H + 3d) \pm \left\{ \frac{1}{4}(E_s - E_s^H - 3d)^2 + 4(ss\sigma)^2 \right\}^{1/2},$$

$$E_{F_2^\pm} = \frac{1}{2}(E_p + E_s^H - d) \pm \left\{ \frac{1}{4}(E_p - E_s^H + d)^2 + \frac{4}{3}(sp\sigma)^2 \right\}^{1/2},$$

where $d = (ss\sigma)_{\text{H-H}}$ denotes the matrix element of H-H interaction.

Valence energy levels of CH₄ are known from x-ray-photoemission experiments,²⁶ and energies of antibonding energy levels have been taken from theoretical calculations.²⁷

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