

## Theory of reflectance anisotropy of clean and hydrogenated (001) diamond surfaces

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Density-functional theory is used to study the linear optical response of the (001) surface of diamond. The equilibrium atomic configurations of the atomic structures are determined from fully converged self-consistent total energy calculations within the local density approximation. The electron-ion interaction is treated by using norm-conserving *ab initio* fully separable pseudopotentials in the Kleinman-Bylander form. To account for the excitation aspect quasiparticle shifts are added to the single-particle energies. The influence of hydrogen adsorption is studied using a  $(2 \times 2)$  translational symmetry. Optical transitions which involve surface states cause significant resonances in the reflectivity in the visible and near ultraviolet ranges which exhibit a strong polarization anisotropy. Adsorption of hydrogen strongly modifies the atomic structure and optical reflectance of the (001) diamond surface. [S0163-1829(97)06531-4]

At present there is significant interest in the study of diamond surfaces due to recent technological progress in the growth of diamond films.<sup>1-6</sup> It is of importance to study the processes which influence the atomic geometry of the surface, its chemical activity, the role of the impurities (especially hydrogen), etc.<sup>7</sup> Theoretically equilibrium atomic structures of low-index diamond surfaces have been studied by utilizing the semiempirical tight-binding method,<sup>3,8</sup> cluster method of modified intermediate neglect of differential overlap,<sup>4</sup> as well as local density approximation (LDA) methods.<sup>5,7</sup> Adsorption of hydrogen strongly modifies the atomic structure and electronic properties of diamond surfaces. The hydrogenated diamond (111) surface is known to exhibit negative electron affinity (NEA).<sup>9</sup> NEA on the hydrogenated (001)( $2 \times 1$ ) surface also has been reported as findings of experimental<sup>10</sup> and theoretical<sup>5</sup> investigations. The understanding of the physical and chemical aspects of the diamond surfaces (clean surface as well as those covered with hydrogen or oxygen) is necessary for further successful work in this field. In such highly reactive atmospheres and at high ambient pressures optical spectroscopy has the obvious advantage of *in situ* investigations of the processes on the surface.<sup>11</sup>

In this work the linear optical response of (001) diamond surface has been studied based on the density-functional theory<sup>12</sup> (DFT) in LDA and random phase approximation. The equilibrium atomic configurations of the atomic surface structures are determined from the fully converged self-consistent total-energy calculations.<sup>13</sup> The electron-ion interaction is treated by using norm-conserving *ab initio*, fully separable pseudopotentials in the Kleinman-Bylander form.<sup>14</sup> The C potentials are softened by careful choosing of the core radii.<sup>15</sup> The electronic wave functions are expanded in terms of plane waves. The energy cutoff of the plane-wave expansion is chosen to be 42 Ry. This is sufficient for converged total-energy, lattice-constant, and electronic structure calculations. The total-energy optimizations give rise to theoretical cubic lattice constants of  $a = 6.681$  a.u. for bulk diamond.

This value is used, although it slightly underestimates the experimental one<sup>16</sup> and, hence, enlarge somewhat the DFT-LDA transition energies.

In calculating the optical functions of diamond we also include the influence of many-body quasiparticle (QP) effects. We performed such calculations already for bulk diamond.<sup>17</sup> The QP corrections to the DFT-LDA eigenvalues are computed within the *GW* approximation for the exchange correlation self-energy<sup>18</sup> according to a simplified scheme (see Ref. 19 and references therein). The corresponding shift values have been used to calculate linear optical properties for bulk diamond in Ref. 20. The problems accompanying the inclusion of wave-vector- and band-index-dependent quasiparticle shifts beyond the scissors-operator approximation have been discussed in detail in this paper. The wave functions are identified with those obtained from the DFT-LDA. Consequently, the optical transition matrix elements are fixed at the corresponding values. The effects due to the energy dependence of the self-energy operator on the spectral distributions of the excited electrons and holes are neglected. The DFT-LDA energies in the spectra are replaced by such energies shifted by the wave-vector- and band-index-dependent many-body corrections  $\Delta_n(\mathbf{k})$ . These corrections also vary remarkably for bulk C. In the upper valence bands  $\Delta_n(\mathbf{k})$  varies from 0.0 eV ( $\Gamma_{15}$ ) to about 1.4 eV ( $X_1, L_1$ ). The shifts of the lower conduction bands with about 1.4 eV are rather independent. The variations are only of the order of 0.1 eV. However, for the higher conduction bands ( $X_5, L_1$ ) there is an increase to about 2.0 eV (or more) at the zone boundaries.

Considering the bulk optical absorption over a wide energy range including its  $E_1$  and  $E_2$  peaks we observe an overestimation of the quasiparticle shifts of the transition energies. It seems to be related in part due to a linearization of the self-energy operator and an overestimation of the downward shift of the valence band maximum. The overestimation is computed using the following rescaling procedure. Using the positions of the zero in the real part of the

macroscopic dielectric function in order to define an averaged scissors operator  $\Delta$ , one derives from the alignment of the function including the wave-vector- and band-index-dependent QP corrections the value of  $\Delta=2.65$  eV. However, in comparison with experimental spectra, the averaged scissors operator being necessary only amounts to  $\Delta=0.40$  eV.<sup>17</sup> Therefore, the calculated QP shifts  $\Delta_n(\mathbf{k})$  are rescaled by  $A \cdot \Delta_n(\mathbf{k})$  with scaling factors  $A=0.2$ . This rescaling reduces the effect of the wave-vector- and band-index-dependent quasiparticle shifts calculated for bulk C (Refs. 20 and 19) and brings the theoretical optical functions in reasonable agreement with experimental data with respect to energetical positions.<sup>17</sup> The values of  $\Delta_n(\mathbf{k})$  calculated for bulk are used further to extract QP corrections for surface states. The  $\mathbf{k}$  points of three-dimensional Brillouin zone (BZ) are projected into  $\mathbf{k}_{\parallel}$  of the two-dimensional surface BZ and assume  $\Delta_n(\mathbf{k}_{\parallel}) = \Delta_n(\mathbf{k})$ .

The equilibrium atomic configurations of the diamond (001) surfaces are determined by means of the total-energy minimization method. To simulate the surface the repeated-slab method is used. A symmetric slab of twelve atomic layers is considered. The supercell is completed by a vacuum region equivalent in thickness. The energy minimization is based on a Car-Parrinello molecular-dynamic scheme for the self-consistent treatment of the single-particle orbitals and the atomic motion.<sup>21</sup> For calculation of the total energy, the electron density, and the atomic structure of the slab we use four special points in the irreducible part of the  $(2 \times 2)$  surface BZ.

Symmetric dimers are found as the structural unit of the clean reconstructed C(001) surface. Atomic geometry and surface electron band structure of the (001)( $2 \times 1$ ) surface obtained in this work do not differ substantially from these reported previously in Ref. 7. Adsorption of hydrogen is studied using a (001)( $2 \times 2$ ): $n$ H surface unit cell, where index  $n = 1, 2, 3$  denotes the number of the dangling bonds of surface atoms saturated by hydrogen. The cases of  $n = 1, 2, 3$  simulate initial stages of the hydrogen adsorption. Atomic structure of the (001)( $2 \times 2$ ): $n$ H ( $n = 1, 3$ ) surfaces relax to a dimerized geometry. In this case the unit cell includes two types of dimers: symmetric dimers—with two dangling bonds ( $n = 1$ ) or with two hydrogen atoms saturating the dangling bonds ( $n = 3$ ), and asymmetric dimers where one dangling bond is saturated by a hydrogen atom. The atomic structure of the (001)( $2 \times 2$ ):2H surface unit cell relaxes either to a structure with two symmetric dimers (hydrogen atoms located on the same dimer) or to a surface with two asymmetric dimers (hydrogen atoms located on two neighboring dimers). In the last case the atomic geometry of the asymmetric dimers differs not substantially from those obtained for the (001)( $2 \times 2$ ):3H unit cell.

In Fig. 1 we represent band structure of (001)( $2 \times 2$ ): $n$ H surfaces with  $n = 0$  [Fig. 1(a)],  $n = 1$  [Fig. 1(b)], and  $n = 3$  [Fig. 1(c)]. The band structure of the clean ( $2 \times 1$ )(001) diamond surface is characterized by well pronounced bands of bonding ( $D^+$ ) and antibonding ( $D^-$ ) surface states. It agrees quite well with that reported previously.<sup>5,7</sup> Saturation of one dangling bond of the surface atoms with hydrogen leads to the appearance of an additional surface band ( $D_H$ ) within the fundamental gap. It is half-filled, pins the Fermi level, and makes the surface metallic [see Fig. 1(b)]. The

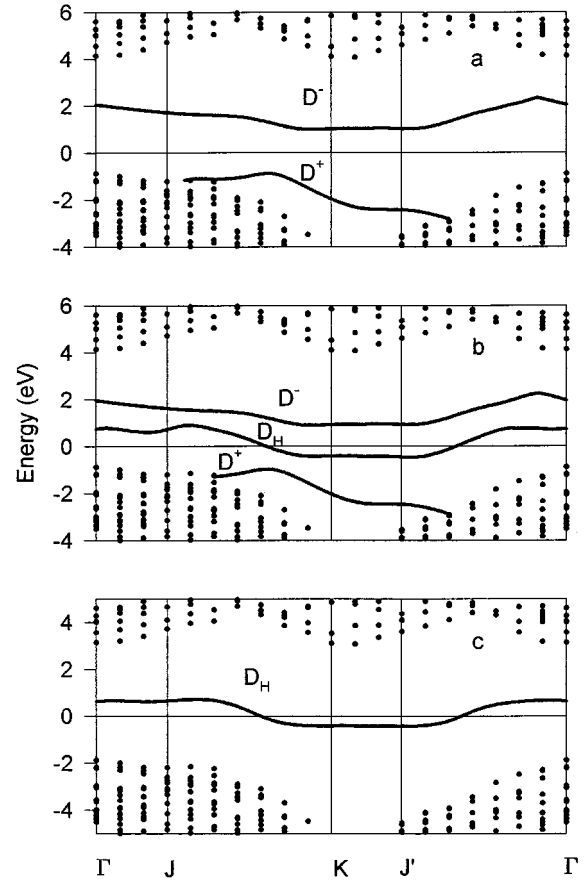


FIG. 1. Electronic band structures of (001) diamond surfaces along high-symmetry lines in the square BZ of the  $(2 \times 2)$  translational symmetry: *a*— $(2 \times 1)$  clean surface; *b*— $(2 \times 2)$ :1H surface with one hydrogen atom saturating one surface dangling bond; *c*— $(2 \times 2)$ :3H surface with three hydrogen atoms in the unit cell. Bonding ( $D^+$ ), antibonding ( $D^-$ ), and unpaired dangling bond ( $D_H$ ) related surface states are shown by solid lines. The dotted regions indicate the projected bulk band structure.

surface band structure which corresponds to the (001)( $2 \times 2$ ):3H surface only exhibits the half-filled dangling bond band  $D_H$  in the gap [Fig. 1(c)].

The reflectance anisotropy spectra (RAS) of the diamond surface is calculated according to the scheme described in Refs. 22 and 23. Anisotropy of the surface reflectance of the normally incident light polarized along the two directions  $x$  and  $y$  is given by<sup>11</sup>

$$\frac{\Delta R}{R} = \frac{8\pi\omega d}{c} \frac{\alpha_{xx}^{hs}(\omega) - \alpha_{yy}^{hs}(\omega)}{\text{Im} \frac{\epsilon_b(\omega) - 1}{\epsilon_b(\omega) - 1}}, \quad (1)$$

where  $\epsilon_b(\omega)$  is the bulk dielectric function and  $\alpha_{\beta\beta}^{hs}(\omega)$  is the polarizability of the half slab in  $\beta$  direction. We choose  $x \parallel (110)$  and  $y \parallel (1\bar{1}0)$ .  $d$  is the thickness of the slab and  $c$  the speed of light. In order to account for the finite number of  $\mathbf{k}$  points in our calculations we use an energy broadening of 0.1 eV taken into the  $\mathbf{k}$ -point sampling of the irreducible part of the BZ.

In Fig. 2 we present the calculated RAS spectrum  $\Delta R/R$ , which can be directly compared to the measured data. Con-

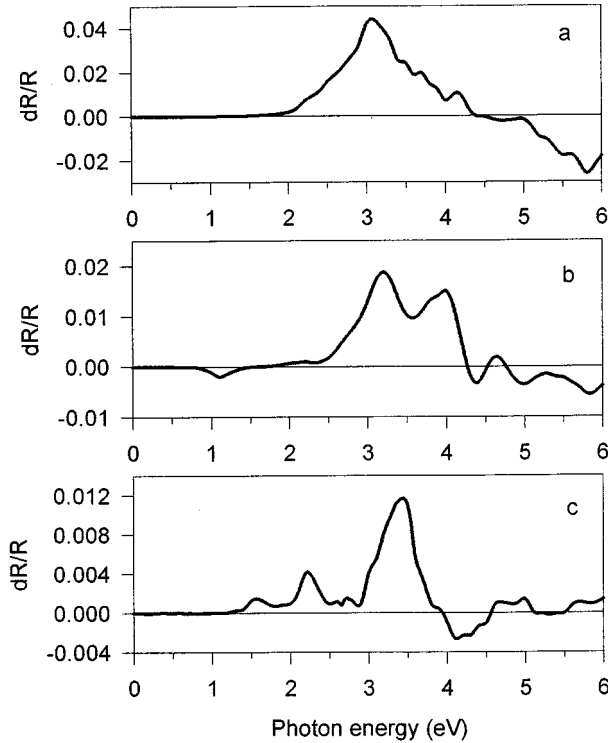


FIG. 2. Reflectance anisotropy spectra of the (001) diamond surface: *a*—clean  $(2 \times 1)$  surface; *b*— $(2 \times 2):1\text{H}$  surface with one hydrogen atom on a surface dangling bond; *c*— $(2 \times 2):3\text{H}$  surface with three hydrogen atoms and one unsaturated dangling bond in the unit cell.

Considering the optical properties of the clean  $(001)(2 \times 1)$  surface of diamond with symmetric dimers one should note that the bonding/antibonding surface states in the gap show an even/odd symmetry with respect to the  $[110]$  mirror plane. Therefore the optical transitions between the surface states inside the fundamental gap should be allowed only for  $x$ -polarized light (with the electric field vector parallel to the dimer bond direction). The calculated RA spectrum, presented in Fig. 2, illustrates this conclusion. The main RAS peak of the clean  $(001)(2 \times 1)$  surface [Fig. 2(a)] is rather broadened, and completely polarized along the dimer direction (110). The peak appears for photon energies in the region between 2.0 and 4.3 eV. No optical response is found in the region  $\hbar\omega < 4.0$  eV for  $\mathbf{e} \parallel \mathbf{y}$  geometry, where  $\mathbf{e}$  denotes the light polarization vector. The broad negative RAS signal between 4.5 and 7 eV is related to mixed (surface to bulk and bulk to surface) transitions and negative light polarized, which is opposite to the surface-to-surface transitions. The optical response in the bulk region is practically isotropic when compared with the very strong anisotropy of the surface states absorption in the region near 3.1 eV.

It is instructive to compare the RAS spectrum obtained in this work with the data published in the literature.<sup>11,8,24</sup> For the  $(001)(2 \times 1)$  diamond surface the empirical tight-binding method<sup>11</sup> (ETBM) places a sharp RAS peak in the region 2.3 to 3.4 eV with the maximum located at 2.75 eV. Our results show that main RAS peak is shifted towards higher energies, and remarkably broader than that described by ETBM.<sup>11</sup> The electronic surface band structure resulting from the ETBM

shows quite good agreement with our present *ab initio* calculations near the  $\Gamma$  point. However there are remarkable deviations in the region of  $K$  and  $J'$  points of the  $(2 \times 1)$  BZ. According to our results, optical transitions between  $D^+$  and  $D^-$  surface states [see Fig. 1(a)], which are located in the region between  $J'$  and  $K$  points in  $(2 \times 1)$  BZ, are responsible for the maximum at 3.10 eV in the calculated  $\Delta R/R$  spectrum [see Fig. 2(a)]. Our data presented in Fig. 2(a) agree well with the results obtained in Ref. 24, where a similar calculation method has been used. The smooth RAS response obtained by ETBM was a consequence of the rather weak dispersion of the surface bands,<sup>11,8</sup> which may be explained by a less realistic description of many particle effects within ETBM.

The appearance of metallic surface band ( $D_H$ ) in the gap on the  $(001)(2 \times 2):1\text{H}$  surface causes additional optical transitions, and remarkable changes of the  $\Delta R/R$  spectrum [Fig. 2(b)]. Transitions between  $D_H$  and  $D^-$  states [see Fig. 1(b)] are responsible for a tiny negative peak around 1 eV. The phase of this optical structure is opposite to the main spectrum because these transitions are allowed only for  $y$  polarization, i.e., perpendicular to the dimer orientation. Optical features between 3.7 and 4.6 eV arise due to the  $D_H$  - conduction-band transitions. Electronic transitions of the types valence band to  $D_H$  and valence band to  $D^-$ , are responsible for weak structure in the region 1.7–2.8 eV [see Fig. 2(b)].

The RAS spectrum of the  $(001)(2 \times 2):3\text{H}$  surface is characterized by the well pronounced peak located at 3.45 eV [see Fig. 2(c)]. Optical transitions from  $D_H$  to conduction band, located in the region between  $J'$  and  $K$  points in  $(2 \times 2)$  BZ, are responsible for this feature. The nature of this part of the RAS spectrum is the same as that of the optical features of  $(001)(2 \times 2):1\text{H}$  surface in the region between 3.7 and 4.6 eV [see Fig. 2(b)], but it is shifted to the lower energies due to the change in the Fermi energy of the system. Less intense peaks in the spectral region 1.5–2.8 eV are due to the electron transitions from valence bands to  $D_H$  states around the  $\Gamma$  point in BZ [see Fig. 1(c)].

A direct comparison of calculated and measured spectra is now in progress.<sup>25</sup> We have to mention, that the RAS of plasma-treated  $(001)$  diamond surface exhibits similar features as the spectrum for the  $(001)(2 \times 2):3\text{H}$  diamond face. In particular, this holds for the appearance of the main peak around photon energies of 3.4 eV. However after exposure to the air this peak vanishes.

In conclusion, we have determined the equilibrium atomic configurations of clean as well as hydrogen covered  $(001)$  diamond surfaces from fully converged self-consistent total-energy calculations within DFT-LDA method. Electronic band structure and optical functions have been calculated by taking into account QP corrections related to the electron self-energies. Optical transitions which involve surface states cause significant resonances in the reflectivity in the visible and near ultraviolet ranges which exhibit a strong polarization anisotropy. The most intense optical features in RAS spectra of  $(001)$  diamond surfaces are caused by the electronic transitions located far away from the center of two-dimensional BZ. The same optical response could be only

qualitatively predicted by empirical theories and requires a more precise description of the dispersion of surface bands. In the absence of partial hydrogenation the RAS spectrum exhibits features which are experimentally observed for fresh plasma-treated (001) diamond surface.

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