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Organic modification of surface electronic properties: A first-principles study of uracil on Si(001)

K. Seino,* W. G. Schmidt, and F. Bechstedt

Institut für Festkörpertheorie und Theoretische Optik, Friedrich-Schiller-Universität Jena, Max-Wein-Platz 1, 07743 Jena, Germany

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The electronic properties of the uracil-covered Si(001) surface have been studied by density-functional calculations. Dative-bonded configurations are characterized by a high density of surface states in the energy region of the fundamental gap, whereas the surface is perfectly passivated when covalent bonds form between the molecule and the substrate. A remarkable influence of the adsorption configuration on the ionization energy is predicted. The results show that semiconductor surface electronic properties can be tuned within a very wide range by organic functionalization even with only one molecular species.

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In recent years, much knowledge about the atomic structure of semiconductor surfaces covered with small organic molecules has been accumulated.[1–5] The interesting electronic properties of such systems, however, we are only beginning to understand (see, e.g., Refs. 6–9). In the case of metal-covered semiconductor surfaces many electronic properties, for example the ionization energy, depend mainly on the coverage.[10–12] Molecular adsorption, however, can be expected to lead to an additional dependence on the character of the interface chemical bonding.[13]

The adsorption of uracil on Si(001), investigated experimentally by scanning tunneling microscopy (STM) and high-resolution electron energy-loss spectroscopy (HREELS),[14] leads to what can be considered a prototypical interface between a polyfunctional molecule and a semiconductor surface. The (001) surface of silicon is the starting point for the fabrication of most microelectronic devices. Uracil ($C_4H_4N_2O_2$) is a small molecule featuring one $C{=}C$ double bond, two $N{-}H$ and two carbonyl groups, and may thus bond to the surface in various ways. In addition, its tautomerism and electrostatic effects have been found to be important for the interface formation.[14,15] Recently, the modification of the Si(001) surface optical properties upon uracil adsorption has been investigated computationally.[16]

Here we show by means of first-principles calculations that different uracil adsorption configurations corresponding to different preparation conditions lead to drastically different surface electronic properties. The electronic-structure calculations are performed using the Vienna *ab initio* simulation package (VASP) implementation[17] of the gradient-corrected[18] density functional theory (DFT-GGA). The electron-ion interaction is described by non-normconserving ultrasoft pseudopotentials,[19,20] allowing for the accurate quantum-mechanical treatment of first-row elements with a relatively small basis set of plane waves. We expand the electronic wave functions into plane waves up to an energy cutoff of 25 Ry, which has been demonstrated to be sufficient in our previous studies on pyrrole adsorption on Si(001) (Ref. 13) and DNA base molecules.[21]

The Si(001) surface is modeled with a periodically repeated slab. The supercell consists of 8 atomic Si layers plus adsorbed molecules and a vacuum region equivalent in thickness to 12 atomic layers. The topmost five layers of the slab as well as the adsorbed molecules are allowed to relax. The Si bottom layer is hydrogen saturated. All calculations are performed using the calculated Si equilibrium lattice constant of 5.456 Å. The Brillouin zone integrations are performed using sets corresponding to 64 $\mathbf{k}$ points in the full (1×1) surface Brillouin zone.

From our previous total-energy calculations[15] in conjunction with experimental work[14] it was concluded that uracil adsorption on Si(001) is governed by the carbonyl groups and is likely to result in the dimer bridging configurations shown in Fig. 1. Starting from a dative-bonded configuration, where uracil is attached to the electron-poor "down" Si dimer atom via one carbonyl group, a relative low energy barrier of about 0.3 eV needs to be overcome for hydrogen dissociation, molecular rotation around the surface normal and tilting towards the neighboring Si dimer.[15] This leads to the configurations where uracil is partially dative, i.e., with one covalent and one dative bond (D-1 in Fig. 1), or completely covalently (C-1) bonded to the Si surface, bridging two Si dimer rows. The latter structure requires in addition a dienol to keto-enol transition of the gas-phase uracil or during the tilting process, because the direct pathway from D-1 to C-1 via diffusion of hydrogen is hindered by a relative

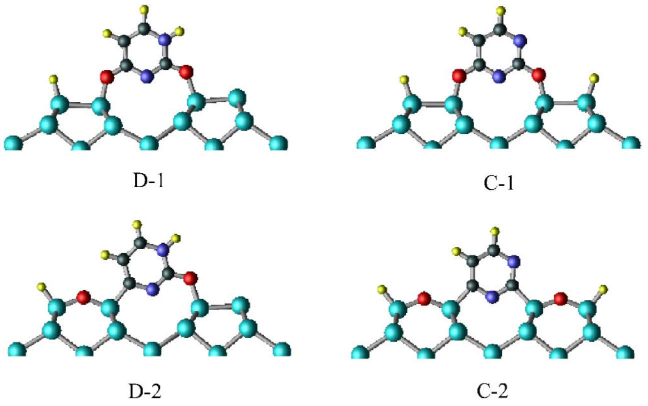
D-1 C-1
D-2 C-2

FIG. 1. (Color online) Uracil/Si(001) adsorption configurations. Gray, purple, blue, red, and yellow symbols indicate C, N, Si, O, and H atoms, respectively.

high energy barrier of more than one eV. A similar barrier larger than one eV needs to be overcome for oxygen insertion into Si dimers, leading to the very favorable interface configurations D-2 and C-2.[15] The formation of these structures therefore requires annealing at elevated temperatures. The calculated adsorption energies of the models D-1, C-1, D-2, and C-2 amount to 2.77, 3.66, 3.78, and 5.27 eV, respectively. The dative bond in the structures D-1 and D-2 occurs between the electron-rich uracil carbonyl group and the electron-poor atom of the clean Si dimer. It is about 0.1 Å longer than the corresponding covalent Si—O bond.[15]

The surface band structures calculated for the structural models discussed above can be clear-cut classified. Models C-1 and C-2, where exclusively covalent bonds occur, lead to a perfect surface passivation, as shown for the latter case in Fig. 2. The Si-dimer related D_{up} and D_{down} bands characteristic for the clean Si(001) surface[22] disappear, due to the formation of Si—O and Si—C σ bonds, which lie energetically below the bulk Si valence band edge. The corresponding antibonding σ^* combinations occur above the Si conduction band edge. No molecular electronic states exist in the energy region of the Si fundamental gap. The highest occupied and lowest unoccupied molecule states V_M and C_M, respectively, occur below and above the bulk valence and conduction band edges (see Fig. 2).

The situation is very different for the partially dative bonded models D-1 and D-2. We find two prominent surface states S_1 and S_2 in the energy region of the Si bulk band gap (see Fig. 2). At least within DFT-GGA, which usually suffers from an underestimation of excitation energies,[23] these two states give rise to a semimetallic band structure and pin the Fermi level. The orbital character of S_1, shown in Fig. 2, is very similar to the surface state localized at the "up" dimer atom of the clean Si(001) surface.[22] The dispersion of S_1 perpendicular to the dimer row direction is very small, whereas a large dispersion is calculated for the direction parallel to the dimer rows. The S_2 state is uracil derived. It is mainly formed by nonbonding carbon and nitrogen p orbitals. Again, due to the interaction between neighboring molecules, a strong dispersion for the direction parallel to the dimer rows is predicted. The oxidation of the first Si layer (D-1 → D-2) decreases the energy separation between S_1 and S_2.

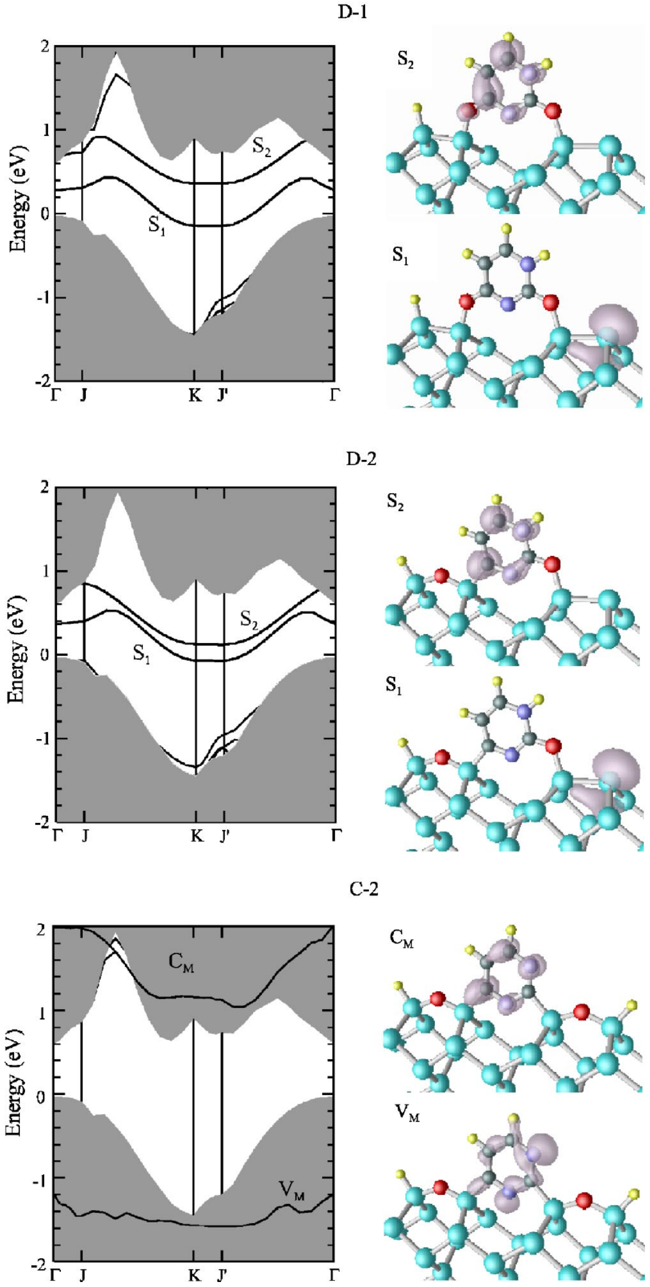

FIG. 2. (Color online) Surface band structures for the interface models D-1, D-2, and C-2 in Fig. 1. Gray regions indicate the projected Si bulk bands. In the right panel, the orbital character of specific states is indicated by isosurfaces for 0.05 Å^{-3}.

The electronic structure calculated for D-1 and D-2 indicates one-dimensional metallic character (conductivity along the dimer row direction). It thus suggests the adsorption and self-organization of organic molecules as a viable alternative to the fabrication of dangling-bond (DB) wires by manipulating single atoms.[24–26] The hydrogen-induced dangling-bond formation on the SiC(001)-3 × 2 surface[27] is a recent example of the successful creation of metallic nanowires by adsorption and self-assembly. In order to study the feasibility of uracil for DB wire formation on Si(001) we performed additional calculations. From STM it is known that the uracil molecules form lines parallel to the Si dimer rows.[14] There are, however, two possible orientations: the molecules may either arrange in a (4 × 1) translational symmetry, or every second molecule can be rotated by 180°, forming a (4 × 2) surface. The total energies calculated here show that the latter case is energetically slightly preferred, by tenths of an eV. The alternating arrangement of the uracil molecules (and, consequently, hydrogen atoms) leads to a spatial separation of the Si dimer dangling bonds, resulting in a much reduced energy dispersion of the S_1' surface state. This can be seen in Fig. 3. Here the band structure of the (4 × 2) D-1 model is shown in comparison with the S_1 and S_2 surface bands of the (4 × 1) D-1 structure calculated along the high symmetry lines of the (4 × 2) Brillouin zone. The rotation of every second uracil molecule also reduces the molecular interaction and, consequently, dispersion of the S_2' band. The arrangement of dative-bonded uracil molecules in (4 × 2) symmetry leads to the opening of a small energy gap between the

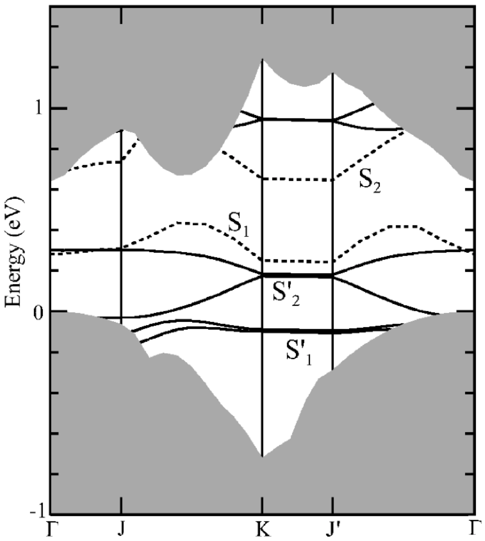

FIG. 3. Surface bands of the (4×2) D-1 model in comparison with the results for (4×1) symmetry (dashed lines). Gray regions indicate the projected Si bulk band structure.

S_1' and S_2' surface states and thus suppresses the formation of a one-dimensional conducting structure.

The ionization energy (or photoelectric threshold) of a surface is given by the energy difference between the vacuum level and the valence-band maximum. It can be calculated by combining bulk and surface calculations.[11,28–30] For sufficiently large slabs the variation of the ionization energy upon adsorption can be obtained by comparing the respective values of the electrostatic potentials in the central layers of the slab. To this end we consider the microscopic electrostatic potential calculated within DFT-GGA

$$V_C(\mathbf{r}) = V_{ps}^{\mathrm{local}}(\mathbf{r}) + V_H(\mathbf{r}). \tag{1}$$

Here $V_{ps}^{\mathrm{local}}(\mathbf{r})$ is the local part of the pseudopotential and $V_H(\mathbf{r})$ is the Hartree potential. The averaged and smoothed electrostatic potential in [001] direction is given by

$$\overline{V_C}(z) = \frac{1}{L}\int_{z-L/2}^{z+L/2} dz' \frac{1}{A}\int_A dxdy V_C(x,y,z'), \tag{2}$$

where A is the area of the surface unit cell and L the distance between the substrate layers. In Fig. 4 the difference $\overline{\Delta V_C}(z)$ between the uracil/Si interface configurations and the clean relaxed Si(001)(4×2) surface is shown. By comparing the value of the potential inside the slab it can be seen that the D-1 and D-2 bonding configurations of uracil on Si(001) lead to a drastic reduction of the ionization energy by more than two eV. After the formation of covalent bonds, i.e., for the structures C-1 and C-2, the ionization energy approaches the value of the clean surface.

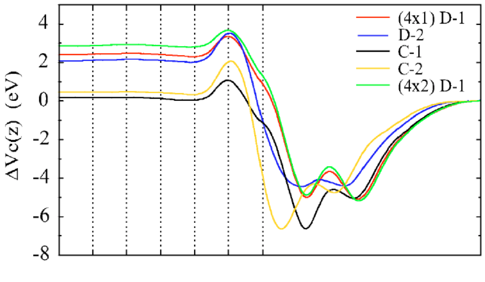

FIG. 4. (Color online) Difference of the averaged and smoothed electrostatic potentials of uracil:Si adsorption configurations and the clean Si(001) surface plotted along the surface normal in the interface region. Dashed lines mark the position of the Si layers.

TABLE I. Dipole lengths d_z and $d_\parallel$ (in Å), dipole charges $Q^\pm$ and $Q_\parallel^\pm$ (in e), dipole moment p_z (in Debye), and changes of the ionization energy ΔI due to uracil adsorption (in eV).

	d_z	$d_\parallel$	$\lvert Q^\pm\rvert$	$\lvert Q_\parallel^\pm\rvert$	$p_z=\lvert Q^\pm\rvert\times d_z$	ΔI
D-1	−0.6	−2.4	4.8	1.3	−14.6	−2.4
D-2	−0.7	−2.2	5.8	1.9	−20.4	−2.1
C-1	−0.4	−1.4	4.8	1.3	−8.5	−0.2
C-2	−0.5	−1.5	7.6	2.5	−17.9	−0.5

Clean Si(001) surfaces experience a reduction of the ionization energy by about 0.35 eV upon exposure to atomic hydrogen. This is explained by the hydrogen-induced conversion of tilted into untilted dimers, neutralizing the electric double layer formed by filled and empty Si dimer atom dangling bonds.[10] The effect found here is much stronger and not correlated to the tilting of the Si surface dimers. In order to explore the uracil induced changes of the electronic structure in more detail we compute the charge difference

$$\Delta\rho(\mathbf{r}) = \rho_{\mathrm{U/Si}}(\mathbf{r}) - \rho_{\mathrm{Si}}(\mathbf{r}) - \rho_{\mathrm{U}}(\mathbf{r}), \tag{3}$$

where $\rho_{\mathrm{U/Si}}$ is the (negative) electron density calculated for the slab describing the uracil adsorbed Si(001) surface, ρ_{Si} is that for the clean relaxed Si(001) surface, and ρ_{U} is that for a gas-phase uracil molecule in the (possibly dissociated) configuration assumed for the respective bonding geometry. The positive and negative charge differences allow us to calculate the average adsorption induced dipole charge $Q^\pm$ and the dipole length projected onto the surface normal d_z,[12]

$$Q^\pm = \int_{\Delta\rho(\mathbf{r})\gtrless 0} d\mathbf{r}\Delta\rho(\mathbf{r}), \tag{4}$$

$$d_z = \frac{1}{Q^+}\int_{\Delta\rho(\mathbf{r})>0} d\mathbf{r}\Delta\rho(\mathbf{r})z - \frac{1}{Q^-}\int_{\Delta\rho(\mathbf{r})<0} d\mathbf{r}\Delta\rho(\mathbf{r})z. \tag{5}$$

In order to determine the charge transferred parallel to the surface normal $Q_\parallel^\pm$ and its separation $d_\parallel$, we start from the charge difference averaged over the surface unit cell

$$\overline{\Delta\rho}(z) = \frac{1}{A}\int_A dxdy\Delta\rho(\mathbf{r}) \tag{6}$$

and proceed in analogy to Eqs. (4) and (5).

The calculated values for these quantities are compiled in Table I. Obviously, the overall uracil induced charge transfer is rather large, with $Q^\pm$ values of 5–8 electrons. This is simply due to the substantial rebonding processes taking place upon molecule adsorption. In particular for the models C-2 and D-2 already about 50% of the charge transfer is due to

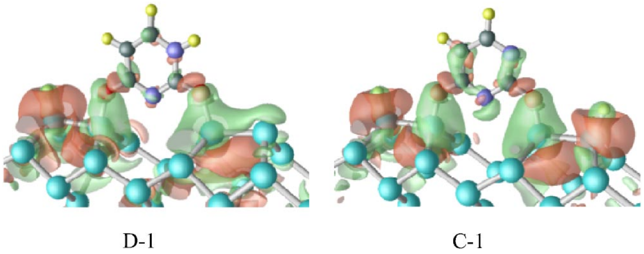

FIG. 5. (Color online) Calculated electron density differences $\Delta\rho(\mathbf{r})$ for the D-1 and C-1 model. Green and orange isosurfaces for ± 0.03 Å^{-3} indicate electron accumulation and depletion regions.

the breaking of Si dimers. Only between 1–3 electrons are transferred parallel to the surface normal, with a charge separation between 1.4–2.4 Å (see Table I). These values are of similar magnitude than the ones calculated for the Cs/GaAs interface.[12] The electrons forming the bonds between uracil and the substrate originate from the substrate rather than from the molecule. There is even some accumulation of additional charge at the adsorbed molecule, as can be seen in Fig. 5. This is plausible, giving the high electronegativity of carbon (2.55), nitrogen (3.04), and oxygen (3.44) compared to the one of silicon (1.9). However, the net electron transfer from the substrate towards the molecule seemingly contradicts the calculated decrease of the ionization energy by up to 2.4 eV. Rather, an increase of the ionization energy would be expected, such as for example found usually upon chlorine adsorption on semiconductor surfaces.[10] The apparent contradiction is due to the dipole moments of the uracil molecules themselves, that form the outermost layer of the adsorbate system. The uracil dipole moment is mainly carbonyl group related, and therefore depends strongly on the specific tautomer. For gas-phase molecules it is up to 7.5 Debye.[31] The molecular dipole points away from the carbonyl groups, thus along the surface normal in the adsorption configurations studied here. Obviously, the ionization energy of organically modified semiconductors depends in a complex way on the nature of the chemical bonds between the organic molecule and the substrate, the closely related molecule-induced charge transfer across the interface as well as the molecular dipole itself.

In summary, from first-principles calculations we find that the electronic properties of the uracil/Si(001) interface depend strongly on the details of the chemical bonding and adsorption symmetry. Dative-bonded interfaces are characterized by a high density of states in the energy region of the fundamental gap and a very strong reduction of the ionization energy. The formation of covalent bonds at the interface accompanied by a transfer of protons from the molecule to the semiconductor surface leads to an electronically passivated surface with an ionization energy close to the value of the clean surface. The results obtained for different adsorption configurations of the same molecular species on Si suggest the tailoring of surface electronic properties by means of choosing suitable preparation conditions such as temperature or by chemically protecting or activating specific molecular functional groups, thus controlling the molecular bonding and orientation with respect to the substrate.

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*Electronic address: seino@ifto.physik.uni-jena.de

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