Quasiparticle Effects on Tunneling Currents: A Study of C_2H_4 Adsorbed on the Si(001)-(2 × 1) Surface

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We present a first-principles calculation of the quasiparticle electronic structure of ethylene adsorbed on the dimer reconstructed Si(001)-(2 × 1) surface. Within the *GW* approximation, the self-energy corrections for the adsorbate states are found to be about 1.5 eV larger than those for the states derived from bulk silicon. The calculated quasiparticle band structure is in excellent agreement with photoemission spectra. Finally, the effects of the quasiparticle corrections on the scanning tunneling microscope images of the adsorbed molecules are shown to be important as the lowering of the C_2H_4 energy levels within *GW* strongly reduces their tunneling probability.

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Adsorption of molecules on silicon surfaces is a very active research field. This interest is motivated by their technological importance in microelectronic device manufacturing and also by the fundamental interest in the interaction of molecules with the dangling bond states of semiconductor surfaces. One typical example is the adsorption of the ethylene (C_2H_4) molecule on the Si(001)-(2 × 1) surface which is particularly important for diamond film growth, and formation of silicon carbide on crystalline silicon. On more general grounds, the study of the relative position in energy of substrate and adsorbate electronic states is of great importance in a number of technologically relevant fields such as surface growth and catalysis.

As far as the structure of the C_2H_4/Si(001)-(2 × 1) surface is concerned, there is strong experimental evidence [1,2] that the ethylene chemisorbs nondissociatively on the surface, through the interaction of its π bond with the π bond of the surface Si dimers. The cleavage of the π bonds permits the formation of two new Si-C σ bonds [1]. This picture was confirmed by some recent density functional theory (DFT) calculations [3] which also established that the σ bond of the Si dimer is hardly perturbed.

In contrast with the large amount of literature about the structural properties, investigations of the electronic structure of this system are rare. In a very recent angle-resolved photoemission study [4], seven ethylene-derived states have been identified. Two of these states, $1b_{3u}$ and $1b_{2g}$, were found to delocalize along the Si-dimer rows while they are localized in the direction perpendicular to the rows. In connection with this study, a DFT calculation of the electronic structure has also been carried out for a fully covered surface [5] showing a qualitative agreement with experiment: the 1D-dispersion features of the $1b_{3u}$ and $1b_{2g}$ states are well reproduced, but *the calculated absolute energies of the adsorbate states are systematically shifted up with respect to the substrate states.*

By performing a careful analysis of the scanning tunneling microscope (STM) images obtained for various coverages of the C_2H_4/Si(001)-(2 × 1) surface [6], it was found that the ethylene molecules appear slightly darker than the bare Si dimers when tunneling out of the surface (i.e., the STM tip moves lower in order to maintain the same tunneling current). This can be understood only in terms of electronic structure effects. Following up this study, STM images were computed within DFT for a half-covered surface [7]. In clear contradiction with experiments, the isolated molecules were found to appear brighter than the bare dimers. However, the experimental contrast could be recovered by taking into account the influence of the tip-induced electric field [8].

In this Letter, we present a study of the electronic properties of the C_2H_4/Si(001)-(2 × 1) surface using an accurate many-body formalism within a quasiparticle approach. The calculations are performed within the *GW* approximation [9]. To our knowledge, this is the first time that an accurate many-body study is conducted for a realistic molecular adsorbate system. We show that the quasiparticle band structure is in excellent agreement with photoemission spectra. The self-energy corrections for the adsorbate states are found to be about 1.5 eV larger than those for the bulk states, demonstrating the dependence of the self-energy correction on the localization and chemical nature of the wave functions. As a result, we show further that the calculated STM contrast between the bare Si dimers and the C_2H_4 molecules is significantly improved with respect to DFT.

We first relax the atomic positions and study the electronic properties for the fully covered and half-covered surfaces within the local-density approximation (LDA) to

DFT [10]. Exchange and correlation effects are calculated using the Ceperley-Alder electron gas data [11] and we use norm conserving pseudopotentials [12]. We adopt two tetragonal unit cells with 2×1 and 2×2 surfaces in the case of full and half coverage, respectively, with sides based on the theoretical equilibrium lattice constant of bulk Si ($a = 7.65$ Å). The unit cells consist of a six-layer Si slab [13] with the ethylene molecule adsorbed at the top [14], while the Si atoms at the bottom are saturated with hydrogen atoms. A vacuum region of 6 Å is kept between adjacent surfaces. The electronic wave functions are expanded in plane waves up to a kinetic energy cutoff of 36 Ry. The irreducible surface Brillouin zone is sampled using four and two special k points for the fully covered and half-covered surfaces, respectively. At the DFT-LDA level, our results are in excellent agreement with previous work [3,5]. In particular, among the seven ethylene states, four states are strongly localized on the adsorbate: the low-lying valence band orbitals $2a_g$ and $2b_{1u}$, which remain separated from the silicon valence band, and the $1b_{2g}$ and $1b_{3u}$ orbitals [5]. In Table I, we have reported the eigenvalues for these four states. The DFT-LDA eigenvalues present a systematic shift of about 1.5 eV with respect to the experimental data [4].

We now discuss our quasiparticle study for the fully covered surface. The DFT-LDA eigenstates and eigenvalues are used as zeroth order input in a perturbative fashion [15]. A cutoff of 9 Ry [16] is used to expand the dielectric matrices in reciprocal space and summations over the conduction bands include up to 320 bands. More technical details can be found elsewhere [17]. As shown in Table I, the GW eigenvalues for the ethylene states are in excellent agreement with the measurements. The band structures obtained within DFT-LDA and GW are compared in Fig. 1. The self-energy correction is clearly smaller for the substrate states (hatched region) than for the adsorbate states (solid circles), indicating a dependence of the magnitude of the self-energy correction on the localization and the chemical nature of the states. Such an effect has already been observed in the case of surface states [17,18]; however, the differential in correction is found to be as large as 1.5 eV in the present case.

Several arguments may explain this difference in the self-energy correction as a function of the localization and the chemical nature of the considered states. First, we note that the spurious self-interaction term present in DFT-LDA does not exist within the quasiparticle approach. The magnitude of this repulsive interaction and consequently of the self-energy correction strongly depends on the spatial localization of the considered states. Second, the DFT-LDA is expected to describe more accurately metallic "jellium-like" systems as compared to insulating systems, pointing out the dependence of the self-energy correction on the chemical nature of the considered states. While these two effects certainly account (nonexhaustively) for the large differential correction observed here, a detailed quantitative study of their respective contributions is a difficult issue, which will not be addressed here. However, based on these considerations, it can be predicted that the differential in self-energy correction might be even bigger in the case of an insulating adsorbate on a metallic surface.

The results obtained for the fully covered surface suggest that the self-energy corrections might affect the calculated STM images for the half-covered surface. Indeed, the adsorbate states are shifted to lower energies with respect to the substrate states while, on the contrary, the occupied quasiparticle states related to the Si dimers have been shown in the case of the bare Si(001) surface to be shifted up in energy [19]. As a result, the tunneling current associated with the adsorbate (the dimers) is expected to decrease (increase) within GW as compared to DFT-LDA,

TABLE I. Eigenvalues at Γ for four of the C_2H_4 states computed within DFT-LDA and GW for the fully covered surface. The eigenvalues are expressed in eV with respect to the top of the valence band. The experimental values are from Ref. [4]. For comparison, the GW correction for bulk Si states is found to range from −0.2 to −0.4 eV.

	LDA	GW	Expt.
$1b_{2g}$	−4.1	−5.1	−5.5
$1b_{3u}$	−6.6	−7.7	−8.0
$2b_{1u}$	−11.4	−13.1	−13.1
$2a_g$	−15.1	−16.7	−16.7

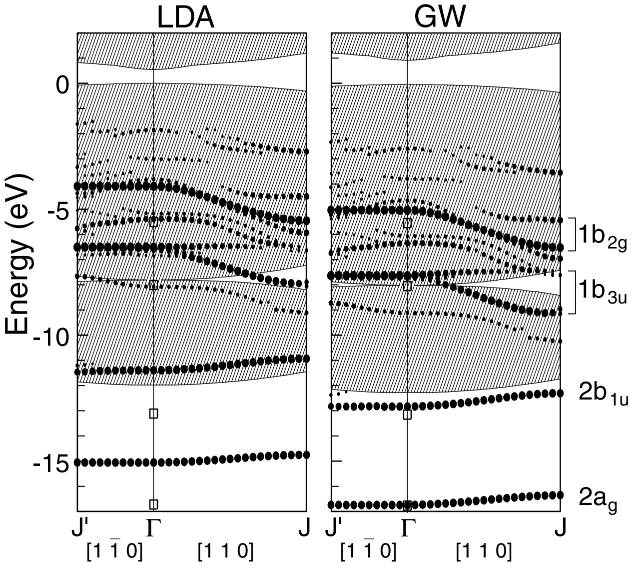

FIG. 1. Electronic band structure computed within DFT-LDA (left panel) and GW (right panel) for the fully covered surface. The eigenenergies are expressed in eV with respect to the top of the valence band. The experimental values are indicated by open squares and are taken from Ref. [4]. The ethylene states are indicated by solid circles whose diameter is proportional to the adsorbate population (e.g., at the Γ point, the biggest circles correspond to the states $2a_g$, $2b_{1u}$, $1b_{3u}$, $1b_{2g}$ which are localized at 85%–95% on the C_2H_4 molecule, while the smallest circles correspond to a 15%–20% population). The Si substrate continuum is indicated by the hatched region.

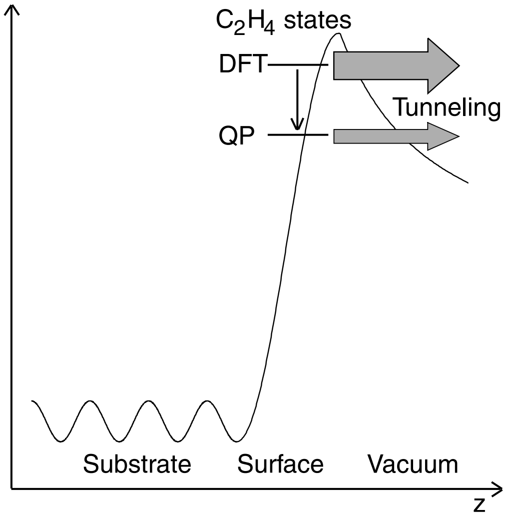

FIG. 2. Schematic representation of the quasiparticle effects on tunneling current associated with the C_2H_4 adsorbate.

as illustrated in Fig. 2. Therefore, the C_2H_4 might appear darker within *GW*.

In order to verify this, one should perform a full *GW* calculation on the half-covered surface. However, such a calculation is still too demanding nowadays. Therefore, we model the self-energy corrections using an extrapolation scheme which allows us to take the localization of the wave functions into account. Namely, for the fully covered surface we perform a weighted linear fit of the self-energy correction as a function of the quasiparticle energy:

$$w_X(E_{Qp} - E_{\mathrm{LDA}}) = \alpha_X E_{Qp} + \beta_X , \qquad (1)$$

where w_X (with $X = \mathrm{Si}$ and C_2H_4) are the weights of the wave functions on the bulk Si atoms and C_2H_4 molecule [20] with $w_{\mathrm{Si}} + w_{C_2H_4} = 1$. We verify that this scheme allows one to reproduce the quasiparticle correction at Γ and J within a 0.1 eV accuracy. From this set of equations, we extrapolate the self-energy correction to the half-covered surface. In this case, we also consider the population on the bare Si dimers besides the weight of the adsorbate and the substrate. Indeed, as in the case of the bare surface, the tilted dimers yield an occupied D_{up} band and an unoccupied D_{down} band. The qualitative agreement between the behavior of the D_{up} band in both systems allows us to extrapolate to the present case the quasiparticle corrections obtained in Ref. [19]. In calculating the *GW* STM current, we therefore apply a rigid shift correction to the D_{up} band of $+0.10$ eV with respect to the top of the valence bands [21].

From these extrapolated self-energy corrections, *GW* corrected STM images are calculated by replacing the DFT-LDA eigenvalues by the *GW* one [22] in the following equation for the tunneling current:

$$\bar{j} = V\bar{\sigma} = V \frac{2e^2}{h} \int_{\mu_f}^{\mu_i} dE \, \frac{\eta^2 |\psi_n|^2}{|E - E_n + i\eta|^2} . \qquad (2)$$

The integral is approximated by summing over a set of energies relevant for the experiments, i.e., in an energy window $\Delta E = \mu_i - \mu_f$ eV at the top of the valence band [23]. The DFT-LDA and *GW* results are presented in Fig. 3. Our DFT-LDA results agree well qualitatively with previous studies [7]: the C_2H_4 molecules appear brighter than the bare dimers. The self-energy corrections reduce the difference in the tip position above the bare dimer and the C_2H_4 molecule by ~33% (see Fig. 3). In other words, the *GW* C_2H_4 images are less bright than in DFT-LDA, though still brighter than the bare dimers.

To fully recover the experimental contrast, the influence of the tip-induced electric field should be further taken into account as in Ref. [7]. However, while the self-energy correction did not lead to an inversion of contrast, the change found here clearly shows that an accurate quantitative study of STM images should include quasiparticle effects. On more general grounds, we emphasize that accounting correctly for self-energy effects upon electron addition or removal should be of importance when calculating tunneling currents from or towards confined systems. We believe, in particular, that such effects should significantly show up in studying, for example, resonant tunneling devices, as the tunnel current in such systems

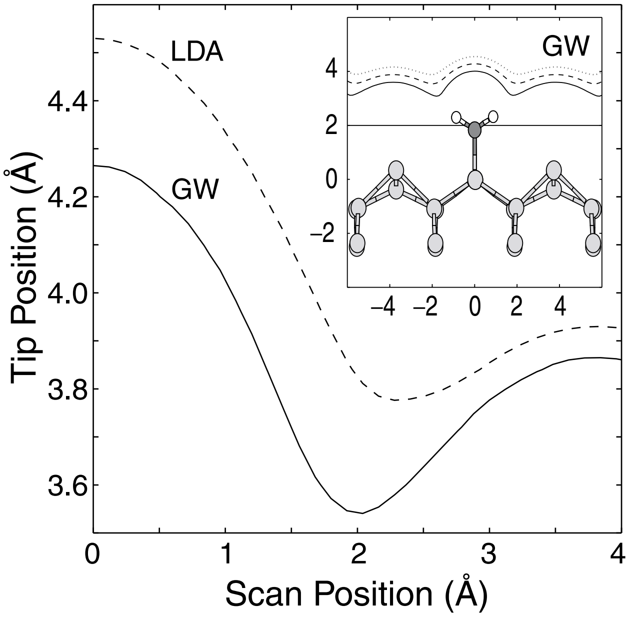

FIG. 3. Constant current $[\bar{\sigma}(2e^2/h) = 10^{-5}]$ scan along a dimer row passing above a molecule and a bare dimer (see atomic structure in the inset), calculated within DFT-LDA (dashed line) and *GW* (solid line). The center of the molecule corresponds to the scan position 0, while the center of the bare dimers are located at scan position ±8.84 Å. The tip position $Z = 0$ corresponds to the center of the Si dimer underlying the C_2H_4 molecule. The current is obtained by integration over the energy range $\Delta E = 0.9$ eV from the top of the valence bands. Inset: *GW* results for different values of the normalized current $\bar{\sigma}(2e^2/h)$ values: 2×10^{-5} (full line), 1×10^{-5} (dashed line), and 5×10^{-6} (dotted line).

sensitively depends on the alignment in energy of initial, intermediate, and final states.

In summary, we have presented a first-principles calculation of the quasiparticle electronic structure of ethylene adsorbed on the dimer reconstructed Si(001)-(2 × 1) surface within the *GW* approximation. For the fully covered surface, the self-energy corrections for the C_2H_4 states are found to be about 1.5 eV larger than those for the silicon states, bringing the band structure in excellent agreement with photoemission spectra. Taking into account the localization of the wave functions, the self-energy correction is extrapolated for the half-covered surface. For this geometry, we have shown that the differential in self-energy correction between the adsorbate and the substrate states significantly improves the STM image contrast between the bare Si dimers and the C_2H_4 molecule.

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[22] To calculate the STM images including the extrapolated self-interaction corrections, we consider that the quasiparticle wave functions do not differ significantly from the DFT-LDA ones. This could be checked by computing the so called off-diagonal elements within a full *GW* calculation.

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