Excitons and Optical Spectrum of the Si(111)-(2 × 1) Surface

Michael Rohlfing[1] and Steven G. Louie[2]
[1]*Institut für Theoretische Physik II–Festkörperphysik, Universität Münster, Wilhelm-Klemm-Straße 10, 48149 Münster, Germany*
[2]*Department of Physics, University of California, Berkeley, California 94720-7300*
and Materials Science Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720
(Received 6 April 1999)

We investigate excitons at the Si(111)-(2 × 1) surface and their optical spectrum from first principles. This is done by solving the Bethe-Salpeter equation for the two-particle Green's function, including the electron-hole interaction. The optical spectrum of the surface is dominated by a surface exciton formed from the π-bonded surface states. The excitonic binding energy is more than 1 order of magnitude larger than in bulk Si. The two-particle wave function of the exciton state is strongly localized at the surface and exhibits distinct anisotropy due to the surface reconstruction.

PACS numbers: 78.66.Db, 71.35.Cc, 73.20.At, 78.40.Fy

Optical excitations play a major role in surface science. Optical techniques, such as reflectance anisotropy or second-harmonic generation, are employed to characterize surfaces. Light absorption is also used to modify surface behavior, for instance, to promote chemical reactions of molecules at surfaces or for photodesorption. In order to arrive at a deeper understanding of such processes, it is necessary to first fully understand the optical properties of the underlying surface. The properties of a clean surface can already be very complicated due to the interrelation between its geometric structure, surface-state band structure, and excitonic effects arising from electron-hole interaction. All these quantities can deviate strongly from bulklike behavior and should be described within an *ab initio* framework.

The occurrence of excitons at the Si(111)-(2 × 1) surface and their role in the optical spectrum of the surface have been the subject of an ongoing debate for more than a decade [1–8]. A number of experimental studies have been carried out, leading to contradictory conclusions for the excitonic binding energy. In differential reflectivity spectroscopy [1,2] and photothermal deflection [3] an optical gap of 0.45 eV was observed. From a combination of direct and inverse photoemission spectroscopy, a quasiparticle (QP) surface gap of about 0.75 eV was obtained [9]. The difference between the two gaps was interpreted as an indication that the optical gap is given by a surface exciton at 0.45 eV with a large exciton binding energy of about 0.3 eV (i.e., more than 1 order of magnitude larger than the binding energy of 0.015 eV in bulk Si). In a photoemission study of a highly n-type doped sample [4], however, a surface gap of only about 0.5 eV was obtained which would be in agreement with the optical gap. This would indicate that the excitonic binding energy at the surface is comparable to that of bulk Si, and no strong enhancement of excitonic effects occurs at the surface. On the other hand, recent reanalysis of scanning-tunneling spectroscopy data yielded a surface state gap of 0.60 ± 0.05 eV [5,6].

The formation of surface excitons has been addressed in two theoretical studies, reporting different results for the binding energy. Northrup, Hybertsen, and Louie [7] carried out a *GW* calculation (yielding a QP surface gap of 0.62 eV), included a model electron-hole interaction, and obtained a surface exciton with a binding energy of 0.13 eV. Reining and Del Sole [8], on the other hand, observed a much larger binding energy of 0.3 eV. Both studies, however, had to make simplifying assumptions. Northrup *et al.* employed a crude expression for the electron-hole interaction which is responsible for the excitonic binding. Reining and Del Sole calculated the interaction in a more realistic way, but they also had to model the dielectric response and the dangling-bond surface states by a tight-binding Hamiltonian, and assumed that the excitons are fully confined to only one of the π-bonded chains that terminate the Si(111)-(2 × 1) surface.

The entity of all these studies does not give a consistent picture. The reported excitonic binding energies range from negligible to 0.3 eV. Furthermore, no detailed information on the shape, size, and properties of the surface exciton is available. It is not clear, e.g., to what extent the exciton is confined to the surface or to the surface atom chains (as was assumed in Ref. [8]), which, in turn, would be very important for the excitonic binding energy.

The aim of the present work is to resolve these questions within a state-of-the-art *ab initio* framework which enables us to investigate the QP and the optical spectrum in a highly reliable and consistent way. This is done by calculating the electronic one-particle and two-particle Green's function of the system, including all relevant aspects of electronic correlation. The electron-hole interaction, which is responsible for the formation of the excitons, is fully calculated. The approach has yielded excellent results for the optical spectra and bound excitons of bulk semiconductors [10–12], as well as, for lower-dimensional systems such as clusters and polymers [13,14].

In this study, we first calculate the geometric structure and QP band structure of the surface. It is generally

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agreed that the Si(111)-(2 × 1) surface is terminated by buckled π-bonded chains of Si atoms, as proposed by Pandey [15,16] (see Figs. 2, 4, and 5). Within local density approximation we find that one surface atom (which we will call *up*) relaxes towards the vacuum by 0.29 Å while the other one (called *down*) relaxes towards the bulk by 0.22 Å. Figure 1 shows the QP band structure of the surface, as calculated within the *GW* approximation [17]. It exhibits one occupied and one empty surface band (D_{up} and D_{down}) inside the bulk band gap. Figure 2 depicts the charge densities of the corresponding states (calculated for the J point of the surface Brillouin zone) in a plane perpendicular to the chains. The occupied (empty) state D_{up} (D_{down}) is formed from the p_z-like dangling-bond orbitals of the up (down) atoms. For both states, the charge density is strongly localized at the surface atom layer.

The Pandey chain geometry leads to a strong coupling of the dangling-bond orbitals along the chain while the coupling is much weaker between the chains due to the large chain-chain distance of 6.6 Å. Consequently, in **k** space, the surface bands have strong dispersion along the $\overline{\Gamma J}$ and $\overline{KJ'}$ lines in the direction of the chains while the dispersion is very weak along the $\overline{JK}$ line perpendicular to the chain. The maximum of the occupied D_{up} band is at the J point. The minimum of the empty D_{down} band is about half way between J and K. Between J and $\overline{JK}/2$ the two surface bands are nearly parallel with a direct fundamental surface gap of 0.69 eV. Our QP results are basically the same as those of Ref. [7].

Our calculated QP surface band structure is in very good agreement with the direct and inverse photoemission data of Ref. [9] (included as dots in Fig. 1). Both our calculated and the measured photoemission data disagree, however, with the experimental results of Ref. [4] which show a much smaller gap of only 0.5 eV. We believe that the discrepancy is of real physical origin. In Ref. [4], a heavily n-type doped Si sample was used to occupy the D_{down} state and make it show up in the photoemission spectrum. The occupation of D_{down} was estimated to be ∼1% in the surface Brillouin zone. This partial occupation of the D_{down} state has a significant influence on its electronic self-energy and thus on its band-structure energy and the surface band gap. In bulk Si, such a high conduction-band occupation of 1% of the Brillouin zone (corresponding to a carrier density of $\sim 5 \times 10^{20}$ cm^{-3}) would lead to a band-gap narrowing of as much as 0.2 eV [18]. Although the effect of charging at the surface is certainly different from that in bulk Si, it seems possible that a similar band-gap narrowing may occur at the surface which would account for the difference between our calculated and the measured gap. The indirect minimum QP surface gap has also been measured in scanning-tunneling spectroscopy [5]. From a recent reanalysis of his data, Feenstra [6] obtains a value of 0.6 eV for the gap. Our calculated minimum indirect gap of 0.65 eV is in good agreement with this value.

Based on the *GW* calculation, we can now calculate the electron-hole interaction and solve the Bethe-Salpeter equation for coupled electron-hole excitations [10,19]. This yields both bound and unbound, i.e., resonant excitations, and allows us to evaluate the entire excitation spectrum. In Fig. 3 we show our calculated differential reflectivity spectrum [20] of the surface. The dashed line depicts the spectrum when we neglect the electron-hole interaction; i.e., the spectrum is given by vertical transitions within the QP band structure. The onset of the spectrum is at the minimum direct surface gap of 0.69 eV. Because of the electron-hole interaction, however, the spectrum is drastically changed (now given by the solid line). Above the surface QP gap, the differential reflectivity is much reduced due to a destructive coupling of dipole oscillator strength caused by the interaction. Below the surface QP gap, a number of discrete exciton states are formed (see Table I). The optical oscillator strength is, however, nearly completely concentrated in the lowest-energy exciton at 0.43 eV, which now dominates the spectrum. The oscillator strengths of the other exciton states are much lower and transitions to these states contribute only weakly to

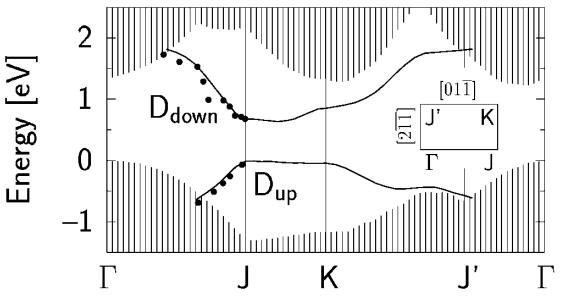

FIG. 1. *GW* quasiparticle band structure of the Si(111)-(2 × 1) surface. The shaded areas denote Si bulk states. The dots denote experimental data [9].

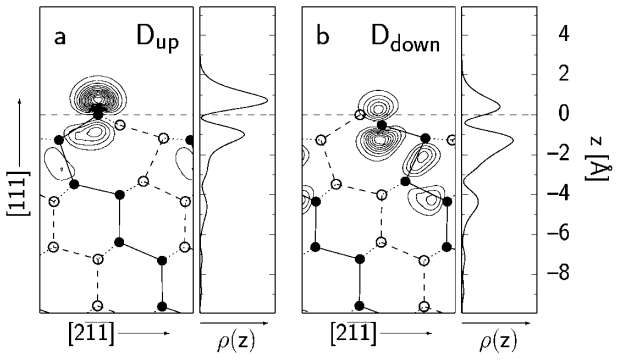

FIG. 2. Charge densities $|\psi(\mathbf{r})|^2$ of the occupied D_{up} state (a) and of the empty D_{down} state (b) at the J point, plotted in two different $(0\bar{1}1)$ planes containing the up atom (a) and the down atom (b), respectively. The full circles denote atoms in the drawing plane. The line plot next to each panel depicts the same quantity as averaged over a plane perpendicular to the [111] surface normal.

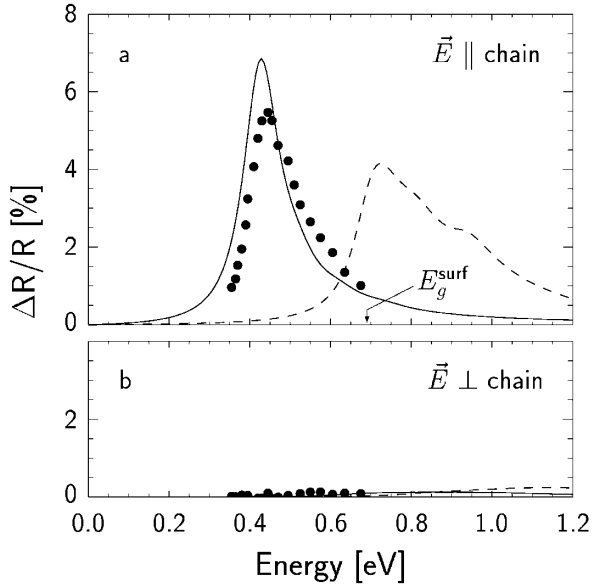

FIG. 3. Differential reflectivity spectrum of the Si(111)-(2 × 1) surface, calculated for normal incidence. The solid (dashed) curves include (neglect) electron-hole interaction. Panel a (b) is for the electric field vector parallel (perpendicular) to the Pandey chains. An artificial broadening of 0.05 eV is included. The dots denote experimental data by Chiaradia *et al.* [1].

the spectrum, giving rise to the slightly higher right-hand shoulder of the main peak. This agrees very well with the experimental results of Chiaradia *et al.* (included as dots in Fig. 3) which also show a single peak with a slightly asymmetric tail structure at higher energies. For the lowest-energy exciton we find a transition energy of 0.43 eV in comparison with the measured value of 0.45 eV.

The dipole oscillator strengths of the excitations are highly anisotropic. While the spectra show a large signal for the electric field vector in the direction of the Pandey chains (Fig. 3a), the oscillator strength is 2 orders of magnitude smaller for the electric field vector perpendicular to the chains (Fig. 3b). This behavior, which is also found in experiment, adds to the many existing evidences that the surface is terminated by Pandey chains [1].

Only spin-singlet excitations contribute to the optical spectrum shown in Fig. 3. For the sake of completeness we have also calculated the spin-triplet excitations (see Table I). They form a similar set of levels but with the lowest transition at 0.37 eV. The excitonic binding energy of 0.26 eV (0.32 eV) of the lowest spin-singlet (spin-triplet) exciton state is more than 1 order of magnitude larger than in bulk Si (15 meV). The main reason for this increased binding is the spatial confinement of both the electron and the hole to the surface (see below), leading to a strong overlap of the single-particle wave functions and a large electron-hole interaction. In fact, this individual localization of both particles leads to much stronger electron-hole correlation as could ever be caused by the interaction itself in three dimensions. Our result of 0.26 eV for the binding energy of the spin-singlet exciton is larger than the model result of Northrup *et al.* (0.13 eV) [7] and is in agreement with that of Reining and Del Sole (0.3 eV) [8].

TABLE I. Calculated excitation energies (in eV) of the lowest spin-singlet and spin-triplet excitons on the Si(111)-(2 × 1) surface.

	Singlet	Triplet
E_1	0.43	0.37
E_2	0.51	0.51
E_3	0.53	0.53
E_4	0.55	0.55
	...	...
E_{gap}^{dir}	0.69	

We now discuss in more detail the properties of the lowest-energy exciton at 0.43 eV which dominates the optical spectrum. In particular, we analyze its electron-hole wave function $\psi(\mathbf{r}_h, \mathbf{r}_e)$ in real space [10] to visualize the electron-hole correlation at the surface. In Fig. 4, we have placed the hole ($\mathbf{r}_h$) slightly above one of the up atoms, i.e., at a position where the amplitude of the D_{up} hole state (which contributes strongly to the exciton) is very high (cf. Fig. 2a). The contour plot shows the distribution of the excited electron relative to the fixed hole, in a $(0\bar{1}1)$ plane perpendicular to the Pandey chain. The electron is strongly localized at the surface; i.e., its distribution decays rapidly when going towards the bulk region. The reason for this behavior is the confinement of the D_{down} electron state to the surface. Another interesting feature is the strong lateral localization of the exciton. The amplitude of the electron is very large on the same Pandey chain where the hole is located. On the neighboring Pandey chains to the left and to the right, the amplitude is already much weaker. On the second-neighbor Pandey chains, the amplitude is very close to zero. This can be seen in more detail in Fig. 5a which shows the same electron distribution as Fig. 4, but on a different drawing plane, i.e., on a (111) plane parallel to and slightly above the surface, showing the zigzaglike Pandey chains. The

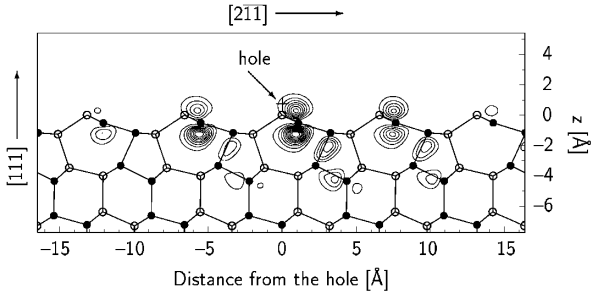

FIG. 4. The electron-hole wave function of the lowest-energy spin-singlet surface exciton in real space. The plot shows the distribution of the electron relative to the hole position (which is indicated as +). The plotting plane is the same as in Fig. 2b.

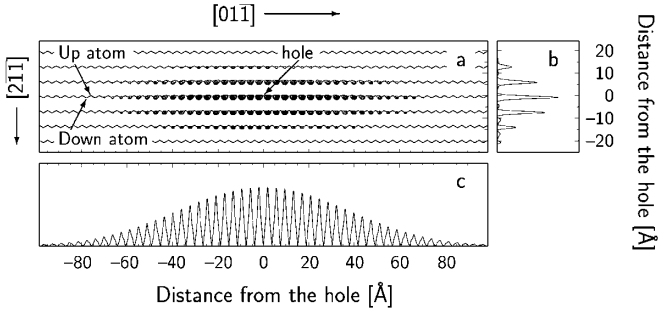

FIG. 5. (a) Same as Fig. 4, but in a (111) plotting plane slightly above the surface plane. The hole is fixed at the up atom in the center of the plot. Panels (b) and (c) show the same quantity along the [2$\bar{1}\bar{1}$] and the [01$\bar{1}$] directions, respectively.

hole is placed in the center of the panel. Figure 5b shows the same distribution, averaged over the [01$\bar{1}$] direction and projected on the [2$\bar{1}\bar{1}$] direction. The rapid decay of the electron distribution when going to the neighboring Pandey chains is clearly visible. The mean square distance $\sqrt{\langle \hat{x}^2 \rangle}$ of the electron from the hole amounts to 8 Å in this direction. Figure 5c, on the other hand, shows the electron distribution projected on the [01$\bar{1}$] direction along the chain. In this direction, the distribution ranges over a much larger distance with a mean square distance of 40 Å of the electron from the hole. This distinct anisotropy of the exciton wave function results from the atomic structure of the surface and the corresponding QP surface band dispersion. As discussed above, the electronic coupling is very strong along the Pandey chains, leading to strong band dispersion of the surface states with small effective masses and to the distinct delocalization of the electron-hole correlation. Perpendicular to the chains, on the other hand, the electronic coupling is weak, leading to weak band dispersion with large effective masses and a strong localization of the electron-hole wave function. Nevertheless, the extent of the exciton in this direction is much more delocalized than in the model study by Reining and Del Sole [8] who assumed that the exciton is fully confined to one chain.

In summary, we have investigated surface excitons on the Si(111)-(2 × 1) surface using an *ab initio* approach. We obtain a direct QP surface gap of 0.69 eV, in good agreement with experiment and a previous calculation. Because of the electron-hole interaction between the dangling-bond surface states, surface excitons with binding energies as large as 0.26 and 0.32 eV are formed for singlet and triplet excitons, respectively. The optical spectrum is dominated by the lowest-energy spin-singlet exciton, having an excitation energy of 0.43 eV. Our calculated differential reflectivity spectrum is in good agreement with experimental data. We have analyzed the real-space wave function of the lowest-energy exciton, yielding detailed information on the nature of electron-hole correlation. The exciton exhibits strong spatial anisotropy.

We thank L. Reining and R. M. Feenstra for fruitful discussions. This work was supported by the Deutsche Forschungsgemeinschaft (Bonn, Germany) under Grant No. Ro-1318/2-1, by National Science Foundation Grant No. DMR-9520554, and by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098. Computational resources have been provided by the Bundes-Höchstleistungsrechenzentrum Stuttgart (HLRS).

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