# Quasi-One-Dimensional Excitons and the Optical Properties of Si(111)2×1

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We present theoretical evidence for strong excitonic effects at Si(111)2×1. On the basis of a self-consistent calculation of electronic states, excitons, and optical properties, which involves for the first time a realistic treatment of the screened electron-hole interaction, we find a gap between surface states of 0.75 eV, and an optical spectrum in quantitative agreement with experiment. The exciton binding energy turns out to be $E_b = 0.3$ eV. Higher excitonic states are not visible, due to the quasi-one-dimensionality of the surface states.

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For many years, the excitonic—or single-particle—origin of the main peak in the optical spectrum of the Si(111)2×1 surface, at 0.47 eV [1], has been an object of discussion [2-5]. Theoretical predictions of strongly bound (~0.3 eV) surface-state excitons were contradicted by the lack of experimental evidence, until, very recently, evidence was given [6-8] of a gap between filled and empty surface states larger than the energy of the optical peak. We present in this Letter a realistic exciton calculation, where the screened electron-hole interaction has been correctly determined, including the surface-state contribution to screening and central-cell corrections, yielding a binding energy of 0.3 eV and optical properties in good agreement with experiment. The one-dimensional character of the exciton shows up in the large binding energy and oscillator strength of the lowest state, while higher states give nearly no contribution to the optical spectrum.

These results lead to an interpretation of the optical properties of Si(111)2×1 which differs fundamentally from previous attempts to explain the absorption spectrum within the one-electron picture [9]: In that picture, the peak of lowest energy in the optical spectrum of Si(111)2×1 corresponds to the gap between dangling-bond- (DB-) like surface states, because these states are nearly one dimensional [10]. In fact, scanning tunneling microscopy (STM) spectroscopy [11] and photoemission from highly *n*-doped samples [12], where the upper surface state is populated, yielded a gap of about 0.5 eV, in agreement with the optical peak at 0.47 eV. Therefore, no space was left for the strongly bound excitons predicted by the theory [3,4]. Those latter calculations, however, were based on the assumption that the screening of the electron-hole pair at the surface was of the order of the classical image potential result, i.e., $(\epsilon_b+1)/2=6.5$ for silicon. By way of contrast, the small optical gap between surface states, and the large oscillator strength of transitions across it [13,14], implied that surface states might give a big contribution to the screening [4], leading to a reduction of the electron-hole (*e-h*) interaction and to smaller exciton binding energies. An accurate study of surface screening [15,16], however, has led us to discard the occurrence of large screening, as a consequence of quantum effects, which strongly reduce screening at short distances with respect to classical predictions. Moreover, the one-dimensional character of the chains of atoms at Si(111)2×1 [10] leads to an antiscreening contribution of surface states at intermediate distances. The resulting position-dependent screening of the *e-h* interaction ranges between 4 and 10, and is hence even smaller than in the bulk. Therefore, no explanation was found for the absence of strong excitonic effects. A first hint to the solution of the puzzle has been given by a recent inverse photoemission experiment [6], which found a gap between surface states of 0.75 eV (or 0.6 eV, according to a more critical interpretation [17]). Moreover, a similar value of the gap has been suggested by a model calculation of the self-energy correction to the local-density-approximation (LDA) eigenvalues [8], and has also been confirmed independently by an *ab initio* many-body perturbative *GW* calculation, which yielded 0.62 eV [7]. Such values are consistent with an exciton binding energy ranging from 0.15 to 0.3 eV, in qualitative agreement with the theory [3,4]. Hence, the question to be addressed here is: Does a calculation, which treats the screened *e-h* interaction in a realistic and self-consistent way, actually lead to *quantitative* agreement with the experiments?

We determine the dielectric response of the surface within a model, that—although simplified—embodies the basic features of surface states. We expand these states in the DB orbitals and perform tight-binding calculations including first ($t$) and second ($V$) neighbor $\pi$ interactions [9]. In this model, which has worked well in the interpretation of the anisotropy of optical and electron-energy-loss spectra [9,18], electrons belonging to different chains do not interact, so that the electron dynamics is essentially one dimensional. Fitting the dispersion of the lower band and the LDA gap [7,19] yields $t=-1.1$ eV, $V=0.35$ eV, and $E_{22}-E_{11}=0.27$ eV, where $E_{ii}=\langle i|H|i\rangle$, $i=1,2$ labeling the two DB orbitals in the surface 2×1 unit cell. The inverse dielectric function reads [16]

$$\epsilon^{-1}(\mathbf{q},z,z';\omega)_{\mathbf{G},\mathbf{G}'}=\delta_{\mathbf{GG}'}f_b^{-1}(\mathbf{q}+\mathbf{G},z,z')+e^2\frac{(2\pi)^3}{A_0}\int\int dz_1\,dz_2\,v_b(\mathbf{q}+\mathbf{G},z,z_1)f_b^{-1}(\mathbf{q}+\mathbf{G}',z_2,z')\times\sum_{ss'}A_s(\mathbf{q}+\mathbf{G},z_1)M_{ss'}(\mathbf{q};\omega)A_{s'}(-\mathbf{q}-\mathbf{G}',z_2)\,, \tag{1}$$

where the $M_{ss'}$ obey the matrix equation [20]

$$M_{ss'}(\mathbf{q};\omega)=S_{ss'}(-\mathbf{q};\omega)+\sum_{tt'}M_{st}(\mathbf{q};\omega)[V_{tt'}(\mathbf{q})-\tfrac{1}{2}V_{tt'}^{\text{ex}}(\mathbf{q})]S_{t's'}(-\mathbf{q};\omega)\,. \tag{2}$$

**q** is a vector in the first two-dimensional (2D) Brillouin zone, **G**,**G**′ are reciprocal-lattice vectors, $z$ is the direction perpendicular to the surface, and $A_0$ is the area of the 2D unit cell. $f_b$ is the dielectric susceptibility of the substrate, which we treat as a semi-infinite classical dielectric, and $v_b$ is the substrate-screened Coulomb interaction. $A_s$ is the Fourier transform of a pair of DB orbitals, characterized by the index $s$. $S$ is the random-phase approximation (RPA) polarizability matrix [21], and $V_{ss'}$ is the lattice Fourier transform of the substrate-screened Coulomb interaction between two pairs ($s$ and $s'$) of DB orbitals. This matrix $V$ contains the information about local field effects. $V^{\text{ex}}$ is the lattice Fourier transform of the exchange interaction between pairs of DB orbitals. The exchange interaction is screened self-consistently by both the substrate and the surface states.

In previous work [15,16], we have evaluated the static screening, which follows from (1) by setting $\omega=0$. Self-consistency in the screened exchange was obtained by consecutive iteration of the calculation. The results serve here as an input for the calculation of the quasiparticle (QP) gap, according to the approaches of Bechstedt and Del Sole [22] and Gygi and Baldereschi [23]: The difference between the self-energy $\Sigma(r,r',E)$ and the exchange-correlation potential $V_{\text{xc}}(r)$ of the LDA is written in terms of the difference between the screening functions of the real system and of the homogeneous electron gas with the local density, neglecting dynamical-screening effects. Since large gap corrections are expected, we avoid the use of perturbation theory, and determine the self-consistent *GW* wave functions $|\psi_{n\mathbf{k}}\rangle$ in the DB basis. The details of the calculation will be given elsewhere [24]. The resulting self-consistent gap is 0.66 eV, in very good agreement with the *ab initio* result (0.62 eV).

These calculations confirm that a gap larger than the optical one should be expected. However, the precision in determining electron levels, even using *ab initio* methods, cannot be better than 0.1 or 0.2 eV. This is not sufficient, when one is looking at excitonic shifts, which are of the same order of magnitude, or smaller. In the present case, it is even difficult to determine the gap on the basis of the experimental results [6,11,12,25], since they are contradictory. In order to obtain a well-defined value of the gap we determine from Eq. (1) the static dielectric constant $\epsilon^{\text{opt},s}$ of the surface,

$$\epsilon^{\text{opt},s}=\lim_{\mathbf{q}\to 0}\int\int dz\,dz'\,\epsilon^{\text{mac}}(\mathbf{q},z,z')\,, \tag{3}$$

where

$$\int d\tilde{z}\,\epsilon^{\text{mac}}(\mathbf{q},z,\tilde{z})\,\epsilon^{-1}(\mathbf{q},\tilde{z},z';\omega=0)_{\mathbf{G}=\mathbf{G}'=0}=\delta(z-z')\,. \tag{4}$$

According to (3), this quantity has the dimension of length: Roughly speaking, it is the dielectric constant of the surface layer times its thickness [4]. $\epsilon^{\text{opt},s}$ can be obtained from the measured optical spectrum [14] via a Kramers-Kronig transform. If only transitions involving DB orbitals (i.e., up to 1 eV) are considered in the experimental spectrum, a value of $\bar{\epsilon}^{\text{opt},s}=102$ Å is obtained for the average over the directions parallel to the surface. The integration over $z$ and $z'$ in (3) arises from the long wavelength of the light. By way of contrast, in the calculation of screening the values $z$ and $z'$ are weighted with the DB orbitals: This causes the difference between the large value of $\epsilon^{\text{opt},s}/d_s$ (about 67, for an assumed thickness $d_s$ of the surface region of $d_s=1.5$ Å) and the small value of the effective screening (from 4 to 10). Figure 1 shows the calculated static dielectric constant as a function of the gap. Agreement with experiment is obtained for a gap of $E_g=0.75\pm0.06$ eV, where the indetermination of 0.06 eV arises from a supposed uncertainty of 20%

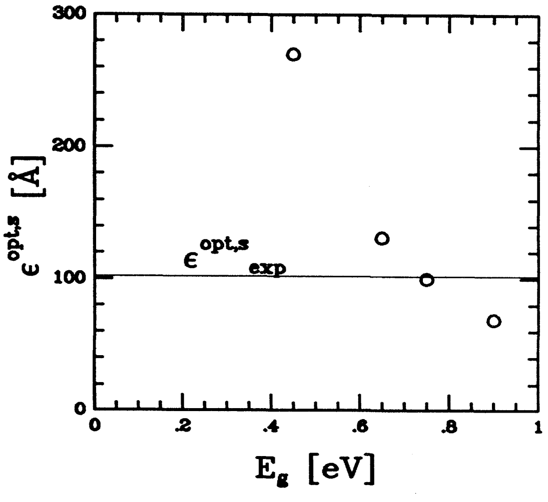

FIG. 1. Calculated average surface dielectric constant $\bar{\epsilon}^{\text{opt},s}$, as a function of the gap $E_g$. Local field and excitonic effects are included in the calculation. From experiment, a value of $\bar{\epsilon}^{\text{opt},s}_{\text{expt}}=102$ Å is extracted.

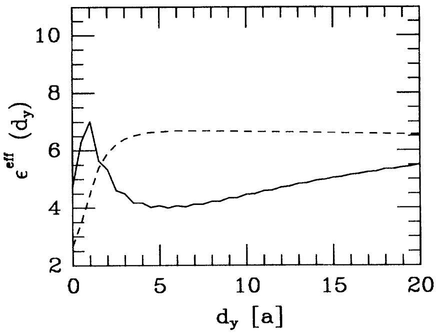

FIG. 2. Effective dielectric function $\epsilon^{\text{eff}}(d_y)$ ($d_y$ is given in units of the periodicity along the chains, $a$). Dashed curve: screening of the semi-infinite classical substrate. Continuous curve: screening of both substrate and surface states, including local field and excitonic effects.

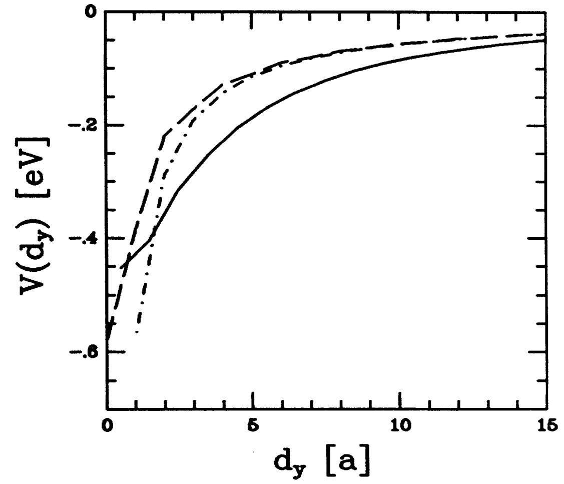

FIG. 3. Electron-hole interaction. Continuous curve: diagonal elements of the $e$-$h$ interaction matrix, as used in the present calculation. Dashed curve: model interaction used in Ref. [7]. Dash-dotted curve: classical image potential result $V(\mathbf{d}) = e^2/6.5|\mathbf{d}|$. ($d$ is given in units of the periodicity along the chains, $a$).

in the optical-peak height.

We can now compute the optical response, including excitonic and local-field effects, by assuming that the gap is 0.75 eV. We calculate the differential reflectivity, starting from the dielectric function given in Eq. (1) and generalizing Eq. (3) for the whole range of frequencies. In order to include self-consistently the excitonic effects, the screened interactions obtained in the previous calculation of static screening [16] are used (see Fig. 2). It is convenient to switch from the local-orbital to a Wannier basis. The $e$-$h$ interaction, which corresponds to the expression used in Eq. (2), is hence given by the matrix

$$V^{e\text{-}h\,mm'}_{(n\bar{n})(n'\bar{n}')} := V^{mm'}_{(n\bar{n})(n'\bar{n}')} - \tfrac{1}{2}\, V^{\text{ex}\,mm'}_{(n\bar{n})(n'\bar{n}')} ,$$

where the index $m$ labels a distance associated to the lattice vector $\mathbf{R}_m$, and $(n\bar{n})$ is a pair of one valence-band ($v$) and one conduction-band ($c$) Wannier function. The strongest contribution arises from the diagonal elements $V^{e\text{-}h\,mm}_{(cv)(cv)}$, which may be compared to the simple screened monopole-monopole Coulomb interaction. This comparison is shown in Fig. 3: The continuous curve is our result for $2V^{e\text{-}h\,mm}_{(cv)(cv)}$. The dashed curve is the model $e$-$h$ interaction which is used in Ref. [7]. (In that work, the position of the optical absorption peak is *fitted* to the experimental result by a suitable choice of the parameter $\beta$, which describes the penetration of surface states in the bulk, as explained by the authors of Ref. [7] in their Ref. [24]. On the other hand, we actually *calculate* the spectrum.) The dash-dotted curve is the classical image potential result $V(\mathbf{d}) = e^2/\epsilon|\mathbf{d}|$, with $\epsilon = 6.5$. Apart from the divergence of this curve at short distances, it is identical to the model interaction of Ref. [7]. In our calculation the antiscreening effect of the surface states enhances the electron-hole interaction at intermediate distances with respect to the $1/r$ behavior. Of course, this comparison is rather qualitative, since it does not consider the off-diagonal elements of the matrices (included, however, in our calculation), which have no classical counterpart.

The resulting differential reflectivity is shown in Fig. 4, together with the one-electron calculation. It is evident that the latter (dashed curve) is quite different from experiment [5], since the peak value coincides with the assumed gap, 0.75 eV. On the other hand, the continuous curve, which includes the $e$-$h$ interaction, has a peak at 0.45 eV, in very good agreement with experiment. This peak corresponds to the lowest exciton state, with a binding energy of 0.3 eV. The quasi-one-dimensional character of the exciton shows up in the large binding energy

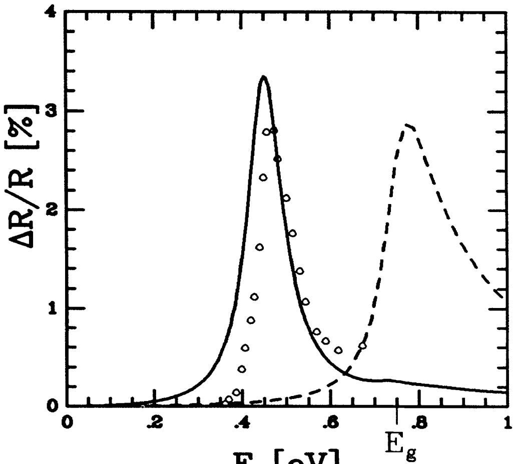

FIG. 4. Contribution of the surface states to the reflectivity, averaged over the directions parallel to the surface. Circles: experimental result. Dashed curve: one-electron calculation. Continuous curve: local field and excitonic effects are included.

and oscillator strength of the lowest-energy state, and in the vanishing oscillator strength of higher states. In fact, the lowest state of the one-dimensional hydrogen atom [26] is a delta function localized at the nucleus, with infinite binding energy, while the wave functions of the excited states vanish there. In our case, the central-cell corrections, which depend on the DB extension, yield a finite value of the binding energy of the lowest state, but only weakly affect the more extended higher-lying states, which maintain their one-dimensional character, with vanishing wave functions for zero *e-h* separation.

In conclusion, we have given a coherent account of the screened *e-h* interaction, of the gap correction to LDA, of excitons, and of the optical properties at Si(111)2×1, in terms of the dielectric response. In particular, we have presented the first calculation of surface excitons carried out on the basis of a realistic shape of the *e-h* interaction. Our findings are in agreement with photoemission [6,25] and optical measurements [5], but at variance with STM spectroscopy [11] and photoemission from highly *n*-doped samples [12]. This latter discrepancy might be explained in terms of the electron-lattice coupling: When an electron fills an empty surface state, a huge outward relaxation of the surface atom may occur, which lowers the DB energy and can trap the electron. In fact, inverse photoemission experiments [17], which are carried out on *n*-doped samples similar to the ones of Ref. [12], yield an empty DB-like surface state (at $\bar{J}$), 0.3 eV above the Fermi level, while the same state (always at $\bar{J}$, but filled) is seen at $E_F$ in direct photoemission. The explanation is that populated initial states of direct photoemission lower their energies, upon relaxation, by 0.3 eV with respect to the unrelaxed final states of inverse photoemission. This cannot occur in optical measurements, because the lattice cannot move in the short time of an electronic transition. In the case of STM, it is possible that the electron (hole)—after tunneling to the surface state—can lower (increase) its energy by inducing a screening charge in the nearby highly polarizable metal tip. The definite confirmation of the occurrence of strong excitonic effects at this surface might hence arise from the study of polaronic effects and of the theory of STM.

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[1] G. Chiarotti, S. Nannarone, R. Pastore, and P. Chiaradia, Phys. Rev. B **4**, 3398 (1971).
[2] K. C. Pandey and J. C. Phillips, Phys. Rev. Lett. **34**, 1450 (1975).
[3] R. Del Sole and E. Tosatti, Solid State Commun. **22**, 307 (1977).
[4] R. Del Sole and A. Selloni, Phys. Rev. B **30**, 883 (1984).
[5] F. Ciccacci, S. Selci, G. Chiarotti, and P. Chiaradia, Phys. Rev. Lett. **56**, 2411 (1986).
[6] P. Perfetti, J. M. Nicholls, and B. Reihl, Phys. Rev. B **36**, 6160 (1987).
[7] J. E. Northrup, M. S. Hybertsen, and S. G. Louie, Phys. Rev. Lett. **66**, 500 (1991).
[8] L. Reining and R. Del Sole, in *Proceedings of the Twentieth International Conference on the Physics of Semiconductors,* edited by E. M. Anastassakis and J. D. Joannopoulos (World Scientific, Singapore, 1990), p. 187.
[9] R. Del Sole and A. Selloni, Solid State Commun. **50**, 825 (1984).
[10] K. C. Pandey, Phys. Rev. Lett. **47**, 1913 (1981); **49**, 223 (1982).
[11] R. M. Feenstra, W. A. Thompson, and A. P. Fein, Phys. Rev. Lett. **56**, 608 (1986).
[12] P. Martensson, A. Cricenti, and G. V. Hansson, Phys. Rev. B **32**, 6959 (1985).
[13] P. Chiaradia, A. Cricenti, S. Selci, and G. Chiarotti, Phys. Rev. Lett. **52**, 1145 (1984).
[14] A. Cricenti, S. Selci, F. Ciccacci, A. C. Felici, C. Goletti, Zhu Yong, and G. Chiarotti, Phys. Scr. **38**, 199 (1988).
[15] L. Reining and R. Del Sole, Phys. Rev. B **38**, 12768 (1988).
[16] L. Reining and R. Del Sole, Phys. Rev. B **44**, 12918 (1991).
[17] A. Cricenti, S. Selci, K. O. Magnusson, and B. Reihl, Phys. Rev. B **41**, 12908 (1990).
[18] A. Selloni and R. Del Sole, Surf. Sci. **168**, 35 (1986).
[19] F. Ancilotto, W. Andreoni, A. Selloni, R. Car, and M. Parrinello, Phys. Rev. Lett. **65**, 3148 (1990).
[20] W. Hanke and L. J. Sham, Phys. Rev. B **21**, 4656 (1980).
[21] R. Del Sole and E. Fiorino, Phys. Rev. B **29**, 4631 (1984).
[22] F. Bechstedt and R. Del Sole, Phys. Rev. B **38**, 7710 (1988).
[23] F. Gygi and A. Baldereschi, Phys. Rev. Lett. **62**, 2160 (1989).
[24] L. Reining and R. Del Sole (to be published).
[25] F. J. Himpsel, P. Heiman, and D. E. Eastman, Phys. Rev. B **24**, 2003 (1981); R. I. G. Uhrberg, G. V. Hansson, J. M. Nicholls, and S. A. Flodstrom, Phys. Rev. Lett. **48**, 1032 (1982).
[26] R. Loudon, Am. J. Phys. **27**, 649 (1959).