PHYSICAL REVIEW B **82**, 153304 (2010)

Optical absorption measurements of electron quantum confinement in Si(111)-2×1 surface chains

G. Bussetti, A. Violante, B. Bonanni, S. Cirilli, C. Goletti, P. Chiaradia,* and G. Chiarotti
Dipartimento di Fisica, NAST and CNISM, Università di Roma "Tor Vergata," Roma, Italy

M. Rohlfing
Fachbereich Physik, Universität Osnabrück, Osnabrück, Germany

(Received 15 September 2010; published 13 October 2010)

Optical experiments on the Si(111)-2×1 surface show that the absorption peak due to dangling-bond transitions exhibits a blueshift upon oxygen exposure. The effect is interpreted as due to quantum confinement of surface electrons in π-bonded chains of atoms, whose length decreases with oxygen uptake (a particle-in-a-box effect, the box being one dimensional). This conclusion is supported by numerical simulation of the optical spectra.

DOI: 10.1103/PhysRevB.82.153304 PACS number(s): 78.40.Fy, 73.20.−r, 78.67.−n, 78.68.+m

The technological request of progressive miniaturization of electronic devices continues to stimulate the interest on confined structures. In particular, researches are focused on testing novel materials (inorganic semiconductor alloys, unusual organic materials) as well as on processing procedures. The latter topic includes conventional quantum wells, wires, and dots but also the very appealing one-dimensional/zero-dimensional (1D/0D) intermediate-regime structures (e.g., quantum rods[1,2]). In this respect, confined quantum wires may represent an appropriate starting system to go toward further three-dimensional confinement.[3] Nevertheless, there is still a lack of systematic investigation on the intermediate-size regime, caused by the experimental complexity in obtaining homogeneous and ordered 1D structures with well-defined lateral sizes and controlled length.[2,4]

The 1D character of Si(111)-2×1 π-bonded chains has been already assessed both experimentally and theoretically in the past three decades.[5] From an experimental point of view, the strong optical anisotropy observed when using light linearly polarized along the chains or in the orthogonal direction demonstrated the 1D character of its surface reconstruction[6] also confirmed by scanning tunneling microscopy experiments.[7] Recently, π-bonded chains have been viewed as a sort of "natural" semiconducting wires.[8] Moreover, taking advantage of the well established knowledge on this surface, Si(111)-2×1 has been often considered as a model system for theoretical calculations regarding exciton properties in 1D structures.[9–11]

In this Brief Report, we present experimental and theoretical results showing how silicon π-bonded chains can be reduced in their extension (chains of finite length) by controlled chemisorption of oxygen. The progressive blueshift of the surface-related peak observed in reflectance anisotropy spectroscopy (RAS) spectra as a function of the oxidation stage is consistent with exciton quantum confinement along the π-bonded chains due to their progressive shortening. This demonstrates that Si(111)-2×1 offers well-ordered "natural" wires which may represent a model to investigate the initial stages of three-dimensional confinement.

Si (111) crystals were cleaved in ultrahigh vacuum (UHV) at room temperature along the $[\bar{2}11]$ direction of the (111) face, providing the well-known 2×1 Pandey reconstruction.[12] *In situ* low-energy electron diffraction was used to check the domain structure after cleavage. Single-domain surfaces, with unidimensional chains along the $[0\bar{1}1]$ direction, were then exposed to a controlled flux of molecular oxygen introduced into the UHV chamber. For RAS measurements, a specifically built optical setup was used, operating in the near-infrared range (IR-RAS).[13] The polarization directions of IR-RAS were aligned along the two orthogonal symmetry axes, α and β, corresponding respectively to the chain axis ($[0\bar{1}1]$ direction) and its orthogonal direction ($[\bar{2}11]$). The RAS signal is defined as

$$\frac{\Delta R}{R} = 2\frac{R_\alpha - R_\beta}{R_\alpha + R_\beta},$$

where R_α and R_β are the intensities of reflected light for α and β polarizations.[13] Our IR-RAS setup has been employed here to highlight very small changes in the optical line shape thanks to its very high signal-to-noise ratio (more than one order of magnitude better than commercial apparatuses working in the visible-UV range). The excellent stability of RAS signal over time allowed monitoring oxidation with very low oxygen flux.

In Fig. 1, the IR-RAS spectrum of clean Si(111)-2×1 at room temperature is reported together with its evolution upon progressive exposure to oxygen, after 200, 500, 700, and 1200 L (1 L$=1\times10^{-6}$ Torr s). During each oxidation stage the RAS signal maximum intensity was continuously monitored to control the oxidation rate accurately. A detectable blueshift of the RAS peak, amounting to almost 20% of the clean surface peak energy, is observed. Besides this shift, the exposure to oxygen of the clean surface induces a decrease of the intensity of the bell-shaped curve, as expected when dangling-bonds are saturated. At the same time the width of the curves tends to increase. The final spectrum (measured after 1200 L) displays the residual background anisotropy of the optical system to be subtracted from the experimental curves.[13] No further variations have been detected at much larger exposure values.

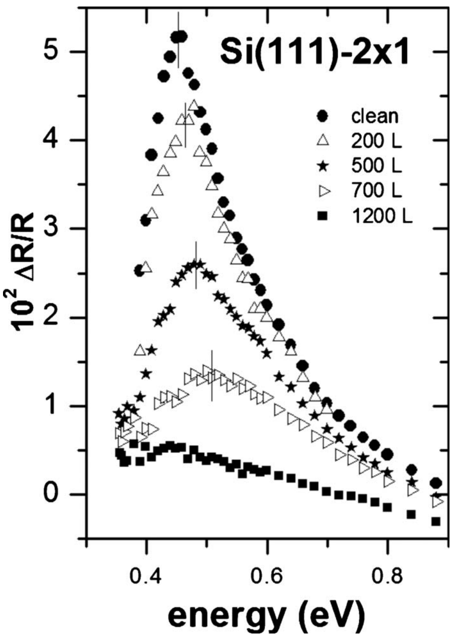

FIG. 1. Reflectance Anisotropy spectra of Si(111)-2×1 measured at the clean surface (circles) and at different oxidation stages. Data were taken at room temperature, starting from UHV conditions. The final curve (squares) has been measured at the completely oxidized surface and represents the residual optical anisotropy. Vertical bars are just a guide for the eye, to highlight the shift of the peak position.

The spectrum evolution (Fig. 1) is a general result that we observe in π-bonded Si(111)-2×1 surfaces. Indeed, within the experimental uncertainty, the same blueshift of the main peak is measured on samples of different doping, either at room and low temperatures (90 K). Such general finding suggests that some microscopic process related to oxidation affects the surface electronic levels.

Previous *ab initio* calculations of one of us (M.R.) have shown that the exciton, which is responsible for the optical response, is localized on the surface and has (quasi-) one-dimensional character.[9] In this calculation we have considered explicitly the shortening of chain length due to oxygen adsorption. Oxidation changes the local chemistry along the π-bonded chains, interrupting the conjugation of the electronic states. This constitutes a barrier for the 1D exciton. The blueshift of the excitonic peak would be due to a particle-in-a-box effect (the box being one-dimensional in this case), corresponding to a 1D/0D intermediate regime.

At the clean, perfect surface with infinite periodicity the optical response results exclusively from surface excitons with zero total momentum. At a surface with reduced periodicity nonzero momentum becomes relevant and the band dispersion of the surface exciton shows up. We have investigated this issue by a simplified tight-binding model, which was chosen to reproduce the single-particle dispersion on an infinite chain and the excitonic binding of the zero-momentum exciton. On a π-bonded chain of finite length L the exciton is confined and its energy rises. During the initial three-dimensional confinement, namely for not too short chains, this increase can be approximated by $E(L)=E(\infty)+h^2/8\pi^2m^*(L+L_0)^2$ with $E(\infty)$ being the free-exciton transition energy, m^* being the effective mass of the exciton, whereas L_0 accounts for some "spill-out" of the exciton wave function over the boundary of the chain due to the finite height of the potential barrier. We have assumed $L_0=7.6$ Å (2 surface sites) in the calculations. For the Si(111)-(2×1) surface, we take $E(\infty)=0.45$ eV and $m^*=0.11m_e$.[9,10]

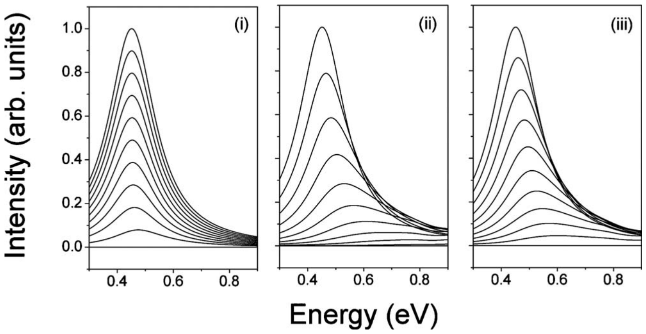

FIG. 2. Evolution of the simulated RAS optical response of the Si(111)-(2×1) surface from clean surface (highest curve, coverage=0) to a fully oxidized surface (zero signal, coverage=1) in coverage steps of 0.1. The data result from Monte-Carlo simulation, starting from an initial defect density $q=1\%$. The left panel refers to adsorption with *diffusion* and consequent oxide island formation [scenario (i)], the middle panel to *random* adsorption [scenario (ii)], and the right panel to a combination of both [scenario (iii), see text].

Initially, we consider two different, extreme scenarios for the oxidation process: (i) a "*hit and diffuse*" model, in which molecular oxygen is first physisorbed on the surface and it sticks after *diffusion* along the chains giving rise to oxide island formation at their ends, (ii) a "*hit and stick*" model in which oxygen is adsorbed where it hits, therefore in *random* positions.[14] In both processes two dangling bonds are saturated.

In the following we will show that the first model is totally inadequate to fit the experimental data, while the latter model qualitatively accounts for the experimental results. The above oxidation processes can be easily studied by Monte Carlo simulation. For the starting surface, we assume a random statistics of already existing defects limiting the chain length, with a certain initial density q (here 1%), yielding a Laplacian distribution of chain lengths with mean value a/q (a being the π bonded-chain lattice constant 3.8 Å).

The evolution of computed RAS spectra, for increasing oxygen coverage according to scenarios (i) and (ii), are reported in the left and middle panels of Fig. 2. It is seen that scenario (i) leads to a negligible blueshift of the optical peak, which becomes measurable only near the end of the process. A totally different trend results from scenario (ii), where a large blueshift results already at the very early stages of oxidation. However, this model overestimates the experimental blueshift and exhibits also a crossing of the curves on the high-energy side at variance with the experimental behavior.

Therefore, on a heuristic basis, we considered a third scenario, labeled (iii), including both random and diffusion processes, which turned out to be in better agreement with the experiment. Scenario (iii) is based on the following assumptions: (a) each chemisorbed oxygen molecule occupies two adjacent sites in the chain, as in the peroxide-bridge model; (b) an oxygen molecule hitting a clean segment of the chain chemisorbs without diffusion; and (c) an oxygen molecule hitting an already oxidized part of the chain diffuses until it finds the end of the oxidized chain, where it chemisorbs, increasing the size of the oxide island and reducing the remaining Pandey chain length.

The simulated spectra corresponding to this scenario are reported in panel (iii) of Fig. 2. As it will be shown in the following, this model is in excellent agreement with the experimental data of Fig. 1. In particular, we notice that the crossing of the curves has considerably reduced.

For a quantitative comparison of the simulated curves of Fig. 2 with the experimental results of Fig. 1 a small problem should be solved: the simulated curves have been obtained as a function of oxygen coverage while the experimental results refer to optical transitions as a function of oxygen exposure. It is reasonable to assume that the coverage is proportional to the area of the curves (both experimental and simulated). However, the simulated ones extend outside the measured interval (both to the high and low energy sides) because of the technique of calculation and the simplicity of the model. Such unphysical tails considerably alter the area of the curves. However, in the range of interest (0.3–0.9 eV) the areas of the theoretical curves are proportional to their heights, within 20% on the average.

Since the scope of this work is to prove the effect of confinement, we have neglected this small deviation and in Fig. 3 we plot the relative blueshifts as a function of the relative heights of the curves ($1-I/I_{\mathrm{clean}}$) for the three scenarios (i), (ii), and (iii).

Figure 3 shows a very good quantitative agreement between the simulation based on model (iii) and the experiment, suggesting that oxygen chemisorption on Si(111)-2×1 is essentially a random process, attenuated by some oxide island formation due to diffusion along the surface. A further refinement should include also parameters as temperature[15] and step density.[16] In addition, squeezing of the exciton by strong confinement ($I/I_0<0.2$) should also be considered. However, such difficult implementations are clearly beyond the scope of the present Brief Report.

We finally remark that the intention of the above simulations is mainly to support and to strengthen the interpretation of the experimental blueshift, observed for the first time in Si π-bonded chains, in terms of three-dimensional exciton confinement at the surface, rather than to provide a truly quantitative explanation. The simulations are based on the model assumption of a quadratic dependence of the blueshift on chain length, combined with random oxidation plus oxide island formation. The results point out the dependence of the exciton energy on quantum confinement and in turn the dependence of quantum confinement on the oxidation kinetics.[17]

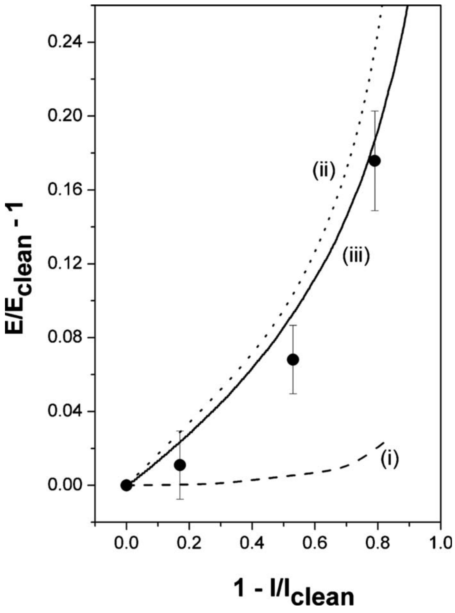

FIG. 3. Relative displacement of the peak position $E/E_{\mathrm{clean}}-1$ (blueshift) as a function of oxygen coverage, evaluated as $1-I/I_{\mathrm{clean}}$ (see text), for the three simulations of Fig. 2 [labeled (i), (ii), and (iii)]. The experimental results from Fig. 1 have been also reported (filled circles), with estimated error bars.

In conclusion, we report the first experimental evidence of a blueshift in the optical transitions between dangling-bond surface states in Si(111)-2×1, during the exposure to oxygen. The effect is interpreted and simulated in terms of a progressive electron confinement along the Pandey π-bonded chains. Our results implicitly confirm that Si(111)-2×1 can be regarded as an authentic 1D system and represents an intriguing model structure for further investigations in the new appealing 1D/0D regime physics.

The authors wish to acknowledge interesting discussions with Rodolfo Del Sole.

---

*Corresponding author.

[1] W. Buhro and V. l. Colvin, Nat. Mater. **2**, 138 (2003).

[2] L. H. Li, P. Ridha, G. Patriarche, N. Chauvin, and A. Fiore, Appl. Phys. Lett. **92**, 121102 (2008).

[3] Q. Zhu, K. F. Karlsson, E. Pelucchi, and E. Kapon, Nano Lett. **7**, 2227 (2007).

[4] Xue-Lun Wang and V. Voliotis, J. Appl. Phys. **99**, 121301 (2006) and references therein.

[5] G. Xu, B. Deng, Z. Yu, S. Y. Tong, M. A. Van Hove, F. Jona, and I. Zasada, Phys. Rev. B **70**, 045307 (2004) and references therein.

[6] P. Chiaradia, A. Cricenti, S. Selci, and G. Chiarotti, Phys. Rev. Lett. **52**, 1145 (1984).

[7] R. M. Feenstra, W. A. Thompson, and A. P. Fein, Phys. Rev. Lett. **56**, 608 (1986).

[8] J. K. Garleff, M. Wenderoth, R. G. Ulbrich, C. Sürgers, and H. v.

Löhneysen, Phys. Rev. B **72**, 073406 (2005).

[9] M. Rohlfing and S. G. Louie, Phys. Rev. Lett. **83**, 856 (1999).

[10] M. Rohlfing and J. Pollmann, Phys. Rev. Lett. **88**, 176801 (2002).

[11] L. Reining and R. Del Sole, Phys. Rev. Lett. **67**, 3816 (1991).

[12] K. C. Pandey, Phys. Rev. Lett. **47**, 1913 (1981).

[13] C. Goletti, G. Bussetti, F. Arciprete, P. Chiaradia, and G. Chiarotti, Phys. Rev. B **66**, 153307 (2002).

[14] We underline that the present calculations do not depend on the absolute value of the sticking coefficients (known to be on the order of 10^{-3} for oxygen on Si(111)-2×1) but only on the ratio between sticking on a free surface and on a surface already oxidized. In the present simple oxidation models we assume the same sticking coefficient on clean and oxidized surfaces.

[15] C. Goletti, P. Chiaradia, L. Moretti, W. Yian, G. Chiarotti, and S. Selci, Surf. Sci. **356**, 68 (1996).

[16] H. Ibach, K. Horn, R. Dorn, and H. Lüth, Surf. Sci. **38**, 433 (1973); K. D. Gronwald and M. Henzler, Appl. Phys. A: Mater. Sci. Process. **34**, 253 (1984).

[17] The blueshift may explain the slight variation ($<5\%$) of the surface optical gap in Si(111)-2×1, experimentally observed from cleave to cleave over the years, as due to different step densities resulting in different chain lengths.