

Infrared reflectance anisotropy spectroscopy of Si(111)- 2×1 : Surface excitons and polarons

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The experimental data regarding the energy distribution of dangling-bond electronic states at the Si(111)- 2×1 surface, with special attention to the gap between filled and empty states, are revisited. Clearly some of the results are not compatible. Theorists almost unanimously conclude in favor of a strong (about 0.25 eV) excitonic energy in the optical transitions between surface states. On the experimental side, on the other hand, conflicting results seem to support either large or negligible exciton energy. In order to reconcile all available data, it has been suggested that in highly doped samples a sizeable gap shrinking should occur. We have performed a reflectance anisotropy spectroscopy experiment in order to verify this hypothesis. The optical peak at 0.45 eV associated to dangling-bond transitions does not shift, in highly doped crystals ($N_D=4\times 10^{18}\text{ cm}^{-3}$), within the experimental accuracy of 20 meV, thereby ruling out the hypothesis of a shrinking of the gap. Under the assumption that all experimental results are correct, an alternative explanation of this puzzling problem, based on the existence of *surface polarons* together with *surface excitons*, is suggested. Although very difficult to detect spectroscopically in a direct way, it is argued that polaronic states could play an important role in highly doped samples. A number of possible experiments to clarify the last point are suggested. Accurate theoretical calculations of the polaron energy would also be helpful.

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I. INTRODUCTION

Si(111)- 2×1 is by far the best studied clean semiconductor surface, both experimentally and theoretically.¹⁻³ Consequently one may think that this surface conceals no more secrets to the investigators except maybe minor details of little importance. This article is meant to show that the above statement is not true (at least for the connection between optical excitation and electronic structure) and that interesting aspects of the physics of Si(111)- 2×1 surface are still unknown.

In recent and less recent years a number of theoretical articles have appeared⁴⁻⁷ claiming that optical transitions between dangling-bond type surface states have a strong excitonic character with an unusually large binding energy, at least one order of magnitude larger than that observed in bulk Silicon (14 meV).

However, the experimental results are controversial and do not clearly converge towards either relevant or negligible exciton energy. Evidence for a large binding energy comes from combined measurements of angularly resolved photoemission⁸ (ARUPS) and *k*-resolved inverse photoemission⁹ (KRIPES) that show a surface gap of approximately 0.75 eV considerably larger than the optical gap of 0.45 eV.¹

On the contrary, evidence for a negligibly small binding energy comes from ARUPS experiments in highly *n*-doped Si ($N_D\cong 8\times 10^{18}\text{ cm}^{-3}$)¹⁰; because of the high doping, ARUPS can detect transitions both from the ground and excited states. The energy difference between these states is practically coincident with that of the optical gap. Less clearcut results come from STM spectroscopy¹¹⁻¹⁴ (STS) and pump-and-probe photoemission¹⁵ (see below for a discussion).

In order to overcome this difficulty Rohlfing and Louie,⁵ following an earlier suggestion,⁷ proposed that, in highly

doped samples the surface gap is narrowed because of a larger screening, as occurs in bulk semiconductors.¹⁶ If this were true the optical gap should be correspondingly reduced.

We have then performed infrared reflectance anisotropy spectroscopy¹⁷ experiments (IR-RAS) at the (111)- 2×1 surface of highly doped Si crystals, finding essentially no differences with respect to undoped samples.

II. EXPERIMENTAL METHODS AND RESULTS

Silicon samples with fairly high *n*-type doping ($P, 4\times 10^{18}\text{ cm}^{-3}$) were cleaved in UHV (high 10^{-11} mbar) in order to obtain a (111) surface with a 2×1 reconstruction. By properly orienting the crystal (cleaves propagating along the $[\bar{2}11]$ direction) single-domain surfaces exhibiting extra spots in the $[0\bar{1}1]$ direction have been obtained, or at least surfaces with one prevalent domain. This fact, together with the strong anisotropy of the Si(111)- 2×1 surface,¹⁸ allowed us to use RAS to study the optical transitions of surface electronic states.

In the RAS technique the polarization of light impinging on the sample at near-normal incidence is periodically modulated between two orthogonal directions coincident with the symmetry axes of the surface (here the $[\bar{2}11]$ and $[0\bar{1}1]$ directions, as resulting from the chain model of the 2×1 reconstruction¹⁹). Since the bulk is isotropic, modulation of the light polarization generates a signal proportional to the anisotropy of the surface dielectric function $\Delta\epsilon_s$.²⁰ In the spectral region where the bulk is transparent, only the imaginary part of $\Delta\epsilon_s$ ($\Delta\epsilon_s''$) contributes to the signal.²⁰ In the case of Si(111)- 2×1 in the near IR $\Delta\epsilon_s''$ is equivalent to ϵ_s'' , because the optical transitions between dangling-bond states are 100% anisotropic.¹⁸ Therefore in this case the same line

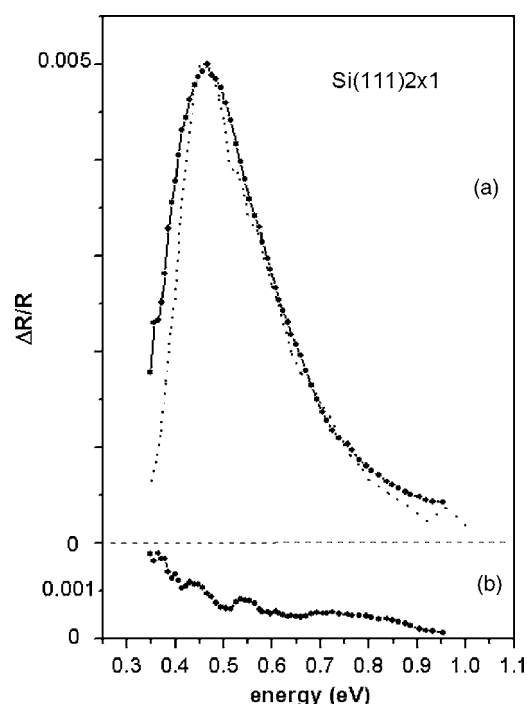


FIG. 1. Panel (a): Reflectance anisotropy spectrum (RAS) in highly doped n -type samples of Si(111)- 2×1 (full line curve and experimental points), compared to the spectrum of a nearly intrinsic sample (dashed curve). The vertical scale refers to the doped sample, while the data for the intrinsic material have been normalized (see the text). Panel (b): Background spectrum obtained for the fully oxidized highly doped sample. In the curves of panel (a) the background has been subtracted.

shape is expected for RAS and SDR (surface differential reflectivity). We recall that with the latter method the reflectance spectra of the clean and oxidized surfaces are compared, for each of the two light polarizations.^{18,21} The equivalence of the results obtained with RAS and SDR in the case of Si(111)- 2×1 has been recently demonstrated experimentally, by extending the range of RAS to the near-IR region of the spectrum.²² The RAS experimental apparatus has been described previously.²²

We have empirically observed that, in highly doped samples, the occurrence of a single-domain surface is less frequent (presumably because of local variations of disorder). However, after cleavage one of the three possible domains usually prevails, allowing the use of the RAS method. This does not hamper the measurements, given the high sensitivity of RAS ($\Delta R/R$ down to 10^{-4} can be detected).

Figure 1 (part a) shows the RAS signal in the range 0.3 eV to 1.0 eV obtained on highly n -doped samples of silicon (full line curve). The bottom curve (part b) shows the residual signal after oxidation, presumably originating from instrumental anisotropy. For comparison, a typical^{22,23} curve obtained by RAS on intrinsic or moderately doped samples is also reported (dashed curve). For the reasons outlined before the intensities of the two curves have been normalized at the peak position.

As it is seen from Fig. 1 there is no evidence of a shift of the optical peak with doping, within the experimental accuracy of about 20 meV. A slightly larger half width is observed in doped crystals, presumably associated to a larger amount of lattice disorder. Similar results were obtained with SDR in similarly doped samples.

Of course the reported results do not exclude that higher doping could induce some sizeable effect on the optical spectrum. However, such an investigation is beyond the scope of the present work.

III. DISCUSSION

The experimental results of Fig. 1 rule out the hypothesis of a shrinking of the gap with doping that was put forward^{5,7} to rationalize the discrepancies between the experimental results.^{8–10} A possible concomitant reduction of the exciton binding energy with doping seems highly improbable because of the high accuracy of the optical results that would require a perfect cancellation of two opposite effects. This conclusion is enforced by the experimental result showing that the position of the inverse photoemission peak is independent of doping.²⁴

Therefore the contradiction between the photoemission gap in highly n -doped samples (0.45 eV) and the gap inferred from the combination of ARUPS and KRIPES (about 0.75 eV) calls for a different explanation.

In principle, one may argue that the comparison of direct and inverse photoemission (which is based on the alignment of the Fermi levels in spectra obtained with these two techniques) is possibly affected by large errors. In fact the Fermi level position at the surface is frequently determined by extrinsic rather than intrinsic electronic states. However, this objection is ruled out in the present case since data collected *on the same sample* (highly doped) yield the same results as data on *different samples*.²⁵

Of course KRIPES spectra are affected by a much larger experimental error than ARUPS's, on the order of 0.35 eV in the case at issue.^{9,24} However, the peak position is not expected to vary appreciably with the instrumental broadening, unless the density of states near the critical point is highly asymmetric. In such a case a slight reduction of the surface gap has been inferred.²⁴

Another experimental determination of the gap between surface states comes from STS. Unfortunately, the available STS data on Si(111)- 2×1 do not agree as far as surface gap and density of (empty) states are concerned. In fact, a previous work pointed to a surface gap of about 0.45–0.50 eV,^{11,12} subsequently corrected to 0.6 eV by the authors.¹³ On the other hand more recent STS data coupled to theoretical calculations have indicated a much larger value of the gap, 0.75 eV.¹⁴ The reasons for such discrepancies have not been elucidated yet. The latter finding is apparently in good agreement with the results of direct and inverse photoemission. However, it should be noted that in the case of STS¹⁴ the 0.75 eV gap comes by taking the onset of the empty state

distribution, rather than the peak (as done for the filled states). Instead, in the case of empty states probed by inverse photoemission^{9,24} the peak value rather than the onset has been considered.

It is worthwhile to mention also the results of another interesting experiment on Si(111)- 2×1 , namely pump-and-probe photoemission.¹⁵ By dynamically populating the empty surface states (with a laser pump at 0.45 eV), electrons in these states can be photoemitted by a second laser (the probe synchronized with the first). Analysis of the energy of the electrons photoemitted from the excited surface state as well as from the ground state seems to confirm the presence of an energy gap of approximately 0.5 eV.

However, the experiment cannot exclude the hypothesis of a strongly bound exciton. In such a case the energy of the probe photon is spent to break the exciton (producing a free electron at the bottom of the surface conduction band) and to impart to this electron the energy necessary to overcome the surface barrier and acquire the external kinetic energy. The energy balance of this process is the same as that of a direct transition from a state approximately 0.45 eV above the surface valence band.

By delaying the probe with respect to the pump the authors determine the dynamics of the decay of the excited electron (or exciton) and find a lifetime of approximately 300 ps. The experimental results demonstrate that in this relatively long time the relaxation of the excited electron (or the exciton) is quantitatively negligible, at variance with theoretical evaluations based on the Huang and Rhys theory.²⁶

Therefore the exciton puzzle remains unsolved and it seems hard to reconcile the various experiments, in particular those on the determination of the surface gap by ARUPS/KRIPES^{8,9} and by ARUPS in highly doped silicon.¹⁰

Assuming that all the previous experimental results⁸⁻¹⁰ and of course those of the present article are correct, we propose a different tentative explanation, based on the concept of surface polaron.

In the experiments on highly doped samples, the photoemitted electrons near the Fermi level come from a steady population in the surface conduction band.²⁷ The electron-lattice interaction (whose time characteristics cannot affect the optical transitions or the isochromats of KRIPES) may form a trough around the electron, significantly reducing its energy. This process is well known and is called surface polaron.²⁶ Under this hypothesis a polaronic band splits off from the surface conduction band. By its nature, this band is always completely filled and cannot be the final state of the optical transitions of Fig. 1.

On the other hand, it is precisely this band that is the initial state of the photoemission process in highly doped materials. It gives rise to the peak B of Fig. 3 of Ref. 10, which is separated from that due to photoemission from the surface valence band (peak A) by 0.45 eV. The coincidence of this value with the energy of the optical peak of Fig. 1 has suggested the conclusion that one-electron theories satisfactorily explain both results without (or with negligible) excitonic effects.¹⁰ In the polaron hypothesis, on the contrary, the two energies are related to different processes and cannot be directly compared.

The problem in this interpretation is the fortuitous coincidence of the polaron energy and the exciton binding energy,

necessary to reconcile the various experimental results on the surface gap. Moreover, this coincidence exists also for Ge(111)- 2×1 .^{28,29} A theoretical evaluation of the polaron problem as well as further experiments (as outlined in the next Section) seem necessary before drawing definite conclusions.

As already mentioned, theoretical evaluations of the polaronic shift for surface states are present in the literature.²⁶ Though many of these results depend on the reconstruction model and some of them have not been confirmed by experiments, nevertheless a general conclusion is worth mentioning. According to Tosatti *et al.*,²⁶ the polaron energy at the surface is “more than an order of magnitude larger than in bulk silicon or about as important as in a three-dimensional ionic crystal.” This rather high energy is presumably associated to the partially ionic character of the 2×1 surface, in which the buckling along the chains displaces the electron into the “up” position.³⁰

IV. CONCLUDING REMARKS AND PERSPECTIVES

The controversy on the strength of the exciton binding energy rests on theoretical grounds as well as on the discrepancy of the surface gap values obtained by direct/inverse photoemission and by direct photoemission in highly doped samples. The explanation based on the shrinking of the surface gap has been ruled out by the present experiment.

We have proposed an alternative explanation based on the presence of a polaron band in highly doped silicon. Though any direct method for solving the controversy cannot at present be envisaged, a number of experiments and theoretical evaluations may clarify this intriguing problem.

(i) Revisit the old inverse photoemission experiments^{9,24} with an improved resolution and possibly by using a Bremsstrahlung technique (instead of the isochromat mode). As a matter of fact, in GaAs(110) very different values of the empty surface state energies have been obtained with the two methods.^{31,32}

(ii) Revisit the old photoemission experiments on highly doped samples^{10,28} searching for small details in the spectra possibly related to a polaronic structure under the ground state peak.

(iii) Since the main problem with the polaron hypothesis is the apparent coincidence of the exciton binding energy and the polaron relaxation energy, revisit (i) and (ii) with the aim of evaluating errors, accuracies and general reliability of the figures given. Perform the same analysis also for Ge(111)- 2×1 .

(iv) Try to understand the discrepancies between the old¹¹⁻¹³ and the new¹⁴ STS values of the surface gap in Si.

(v) Revisit the classical Allen and Gobeli's experiment³³ with modern techniques and with a better control of the surface. Allen and Gobeli's data on the surface gap do not seem to fit with those considered before (especially the largest ones). Check whether the polaron hypothesis can relieve some of the discrepancies.

(vi) Evaluate theoretically the polaron relaxation energies for Si and Ge.

(vii) Extend the range of doping to higher concentrations to see whether a shrinking of the surface gap is observed. Though this may not have a direct consequence for the exciton/polaron puzzle, it is an interesting problem in itself.

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