Coexistence of Negatively and Positively Buckled Isomers on n^+-Doped $\mathrm{Si}(111) - 2 \times 1$

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A long-standing puzzle regarding the $\mathrm{Si}(111) - 2 \times 1$ surface has been solved. The surface energy gap previously determined by photoemission on heavily n-doped crystals was not compatible with a strongly bound exciton known from other considerations to exist. New low-temperature angle-resolved photoemission and scanning tunneling microscopy data, together with theory, unambiguously reveal that isomers with opposite bucklings and different energy gaps coexist on such surfaces. The subtle energetics between the isomers, dependent on doping, leads to a reconciliation of all previous results.

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In recent years, a number of semiconductor systems, having slightly different configurations with energies close to the ground state, have been observed. For example the Si and Ge (001) surface dimers, tilting in different ways, produce different reconstructions such as the $c(4 \times 2)$ and $p(2 \times 2)$. These stacking arrangements of dimers are temperature dependent, and can be also changed in a controlled way by the bias voltage of a nearby probe-tip [1]. Indeed for these systems, theory has shown that injection of either electrons or holes may alter a delicate balance between electrostatic and elastic energies [2].

In this Letter we unambiguously demonstrate how on highly n-doped Si(111), two energetically very similar but different atomic reconstructions, coexist. We discuss how this finding resolves a long-standing puzzle concerning the value of the electronic and optical gap at the $\mathrm{Si}(111) - 2 \times 1$ surface. We reach these conclusions on the basis of low-temperature angle-resolved ultraviolet photoemission spectroscopy (ARUPS) and of scanning tunneling microscopy and spectroscopy (STM or STS) measurements, together with state-of-the-art first principles excited states calculations.

The atomic structure of the $\mathrm{Si}(111) - 2 \times 1$ surface has been known for decades to consist of π-bonded chains [3]. The chains can tilt (buckle), with two possible directions of buckling having very little energy difference. We refer to these two structures as isomers. It is currently believed that for Si(111) the chains have a particular buckling direction, known as positive (whereas it is opposite, or negative, for Ge(111) [4]). However, we report here that for highly n-doped Si(111) both positive and negative isomers coexist on the surface. Again, the difference in total energy between them is very small, but because of a difference in band gap energy between them we find that occupation of the normally empty states by the doping electrons makes it energetically favorable for the negative isomers to form.

Several years ago, ARUPS measurements from highly n-doped $\mathrm{Si}(111) - 2 \times 1$ permitted the observation of both filled and (normally) empty surface states [5], revealing an electronic energy gap of 0.45 eV which is nearly equal to the surface optical gap, thus implying a negligible binding energy for any surface-state exciton. On the other hand, the $\mathrm{Si}(111) - 2 \times 1$ surface has been employed as a prototypical one for theoretical and experimental studies of such excitons [6–8], as recently reviewed [9]. The binding energy of the exciton was estimated to be 250 meV, i.e., 10 times kT at room temperature, although the aforementioned ARUPS data was in conflict with that. However, with our observation of two coexisting isomers, the situation is resolved. We find that the empty state band seen in the ARUPS arises from the negative isomers, and this empty band is substantially lower in energy than the one from positive isomers. This is the first time that domains with both isomers have been unambiguously detected on the same surface.

Silicon samples, n type with doping concentrations 4 and 8×10^{18} donors/cm^3, were cleaved at the measurement temperature of 100 K for ARUPS, or at room temperature for STM and STS and then cooled to 8 K for study. Only single-domain 2×1 surfaces were studied with ARUPS. Electrons photoemitted after excitation by a He discharge lamp ($h\nu = 21.218$ eV) were analyzed with a hemispherical SCIENTA SES-200 analyzer (energy resolution 15 meV, angular resolution 0.16°). The edge of the surface Brillouin zone (SBZ) (at the $\bar{J}$ point) corresponded to about 24°, at a kinetic energy of about 16.3 eV. STM images were acquired with a constant current of 0.2 nA, and STS was performed as previously described [10].

Figure 1(a) shows a typical photoemission spectrum [energy distribution curve (EDC)] measured near the $\bar{J}$ point of the SBZ, at 100 K. Peaks A and B, separated by 0.45 eV, are identical with previous results [5], and also the dispersion of peak A along the $\bar{\Gamma}\bar{J}$ line [see panels (c) and (d)] exactly confirms the previous data. Peak B (at the Fermi level) is only visible near the $\bar{J}$ point, as already observed [5], since it is due to the filling of empty states by the excess electrons. Peak A', instead, has never been observed before. Its energy position is about 180 meV above the filled dangling-bond peak A.

It is important to emphasize that the new peak A' was exclusively observed on heavily n-doped samples while spectra acquired in the same experimental conditions from either intrinsic or p-type (even p^+) samples exhibited only peak A. While in Fig. 1(a) peak A' and B appear to have comparable areas, in other cases the areas are significantly different. Moreover, after a small residual-gas contamination we typically observed a sizeable decrease of peak B, until it vanishes, while neither A nor A' are significantly changed. The temperature is another crucial parameter, regarding peak A'. Figure 1(b) shows the evolution of curve (a) after raising the sample temperature to about 300 K. While (the areas of) A and B are essentially unchanged, A' is no longer visible by eye, although a change of slope is clearly seen in the energy region where it is supposed to be. Indeed by using a deconvolution routine, peak A' can be easily extracted from the curve, as shown in Fig. 1. It is clear that at room temperature its presence in the spectrum is masked by the increased broadening. The effect is reversible. Incidentally, we observe that since the old photoemission experiment was performed at room temperature [6], the spectroscopic signature of negative isomers (peak A') was not clearly detectable [see curve b in Fig. 1], although it is clear that minority isomers did play a role in the Fermi level pinning.

In panel (c) of Fig. 1 the experimental dispersion along the $\bar{\Gamma}\bar{J}$ line is shown, as given by a series of EDCs. In panel (d) the second derivatives of the same curves are plotted in a color scale. The extra peak A' is a distinct feature only near the $\bar{J}$ point, while it is entangled with the bulk bands in the surroundings of the $\bar{\Gamma}$ point. To interpret the new photoemission peak A' we made the hypothesis of isomers of the 2×1 reconstruction, with different energy gaps, and this hypothesis was tested using STM and STS.

Figure 2(a) shows a large-scale STM image obtained at 8 K. Domains of 2×1 reconstruction are seen, with typical lateral extent of 7 nm. There is a single corrugation maximum per unit cell, the well-known result for this surface [11,12]. Remarkably, however, a domain boundary extends through the image and, as seen in Fig. 2(b), the positions of the corrugation maxima are shifted by half a unit cell (0.192 nm) in the $[1\bar{1}0]$ direction between the two domains. Thus, the atomic arrangement on the two sides of the boundary must differ, and the observed shift is consistent with positive and negative isomers of π-bonded chains (at the imaging voltage of -1.0 V, the upper atom of the chain is imaged for both isomers). Voltage dependence of the images (not shown) is also consistent with this interpretation [13], and reveals that the "N" domain of Fig. 2(b) is composed of negative isomers and the "P" domain of

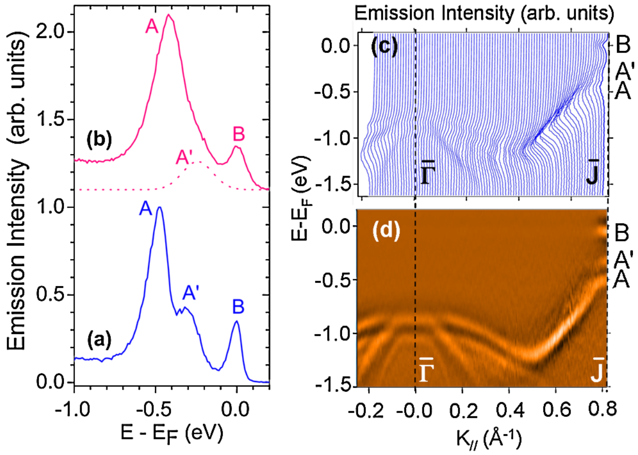

FIG. 1 (color online). Panels (a) and (b): EDCs near the $\bar{J}$ point of the SBZ, at (a) 100 K and (b) room temperature. When the temperature is raised, peak A' is hidden by the increased broadening, but it can be deconvolved and the result is shown below the curve. (c) A series of high angular and energy resolution EDCs (rotated by 90° counterclockwise) spanning the $\bar{\Gamma}\bar{J}$ direction of the SBZ, as a function of $k_{\|}$. Spectrum (a) is the first on the right-hand side. The dispersion of the dangling-bond related surface bands is clearly seen. (d) Second derivatives of curves reported in (c), plotted on a color scale.

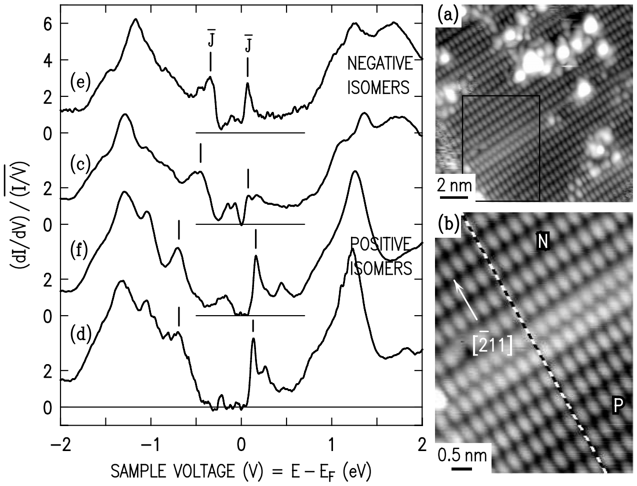

FIG. 2 (color online). (a) and (b) STM images from cleaved Si(111), acquired at 8 K and with sample-tip voltage of -1.0 V. Image (b) shows an expanded view of the area indicated in (a). Gray scale ranges are (a) 0.22 and (b) 0.12 nm. Tunneling spectra acquired from near the N and P symbols in image (b) are shown by curves (c) and (d), respectively. Spectra acquired from neighboring surface regions are shown by (e) and (f).

positive isomers. At 8 K the two types of isomers are found to have roughly equal abundance.

STS results obtained from the same spatial area as Fig. 2(b) are displayed in curves (c) and (d), and two additional spectra obtained from neighboring surface regions are shown in curves (e) and (f). In all the spectra we can identify peaks in both filled and empty states deriving from the $\bar{J}$ point of the surface band structure, as marked in Fig. 2. Examining first the filled states, we find $\bar{J}$-point peak positions of -0.69 and -0.40 V for positive and negative isomers, respectively, (all positions ± 0.05 V due to variation across the surface). For empty states the locations are 0.14 and 0.07 V, respectively. These voltages correspond to energies (in eV) of the respective states relative to the Fermi energy. The edge of the empty band for negative isomers is somewhat obscured by the presence of substantial conductance within the surface band gap, Figs. 2(c) and 2(e). This midgap conductance arises in part because of high electron concentration in the negative-isomer domains, so that the Fermi energy lies very near, or slightly above, the edge of the empty state band. Additional contributions to this midgap conductance arise from surface disorder, as discussed by Garleff *et al.* (for positive isomers)[12]. Those authors also identify a Coulomb gap at the Fermi energy, as is clearly apparent at 0 V in Figs. 2(c) and 2(e). Because of these effects, the actual position of the empty state for negative isomers might be slightly lower than marked in Fig. 2. In any case, using the marked positions, we deduce that the lowest empty surface state (LESS) is ~.07 eV lower for the negative isomers than the positive ones. This difference is near the accuracy limit of the STS spectra. However, the midgap conductance is found to be much higher for negative-isomer domains than positive ones, demonstrating that the electron concentration is significantly higher, and the LESS lower, for the former compared to the latter.

The results for the positive isomers are in good agreement with prior STS for the Si(111)2×1 surface [10]. We also find good agreement between our STS and ARUPS results for the filled state band edges, and moreover, the STS result reveals the bottom of the empty band of the negative isomers to be very near the Fermi energy, which is consistent with the ARUPS interpretation of this band onset [peak *B* of Fig. 1(a)] Energy minimization has been carried out according to density functional theory with the local density approximation (DFT-LDA), yielding two stable isomers with 2×1 periodicity, one with a positive buckling of 0.53 Å and another one with a negative buckling of 0.59 Å. We have found that the total energies of the two undoped isomers are nearly identical within the accuracy of the calculation, consistent with published results [14,15], and that their DFT-LDA gaps are in good agreement with previous work [15]. Then, the band structures have been corrected according to the many-body perturbation theory in the *GW* approximation for both isomers. All the computational details are the same as in Ref. [16], where only the positive isomer was considered. The resulting quasiparticle band structures of the two isomers near the $\bar{J}\bar{K}$ line, are shown in the right panel of Fig. 3. The quasiparticle gap at $\bar{J}$ is 0.79 eV for the positive isomer, and 0.62 eV for the negative one. These values must be compared with the STS experimental values: 0.83 eV (0.47 eV) for the positive (negative) isomer. The difference between the measured and calculated gaps is within the accuracy of the *GW* method.

According to many-body perturbation theory, the energy change when an extra electron is added is given by the empty band energy [17], which in our case is the LESS. Since the LESS of the negative isomer is lower than that of the positive isomer by 0.09 eV in our calculation (~ 0.07 eV by STS), it is clear that the extra electrons tend to create and occupy the negative isomer. We identify this as the *driving force* for the appearance of negative isomers in highly *n*-doped samples. Of course, the lowering of the negative-isomer total energy is proportional to the number of electrons populating its LESS. Interestingly, by DFT-LDA total-energy minimizations we calculate that at a filling of 1% (close to the experimental one), the negative-isomer total energy is lower than that of the positive isomer of 5 meV per 2×1 cell. The calculated STS curves are shown in Fig. 3. They are determined as the density of states projected on the upper and lower chains of the two isomers. The *GW* corrections have been described by a scissor operator of 0.5 eV, which avoids carrying out the corrections for all *k* points. This value is a compromise between the *GW* corrections at $\bar{J}$ and $\bar{K}$ (about 0.45 eV for both isomers) and those at $\bar{\Gamma}$ and $\bar{J}'$ (0.6–0.7 eV for the two isomers). The structures above and below the Fermi level well mimic the experimental ones: the structure at ~1.3 eV above the Fermi level is narrower (wider) in the case of the positive (negative) isomer, while the structure at ~1.3 eV below the Fermi level is similar for both isomers, as in the experiment.

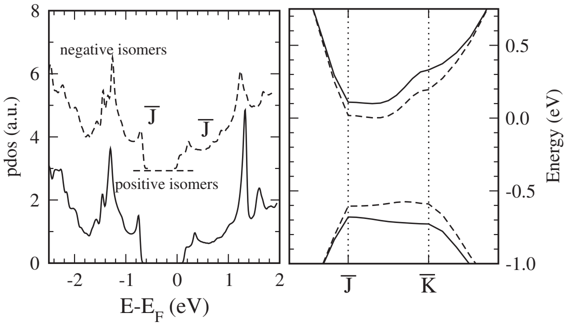

FIG. 3. Left panel: simulated STS of the isomers, calculated as the *GW* density of states projected on the upper and lower chains. Right panel: surface-state *GW* energies along $\bar{J}\bar{K}$ for the two isomers, aligned to a common vacuum level. Solid (dashed) line refers to the positive (negative) isomer.

Coming back to the original motivation of this work, in light of the present results there appear to be no contradiction between photoemission data from heavily n-doped samples and the existence of a large binding-energy exciton. Although it is true that the energy separation of peaks A and B in Fig. 1(a) is very close to the optical gap (0.45 eV) as noted in Ref. [5], the two peaks belong to different isomers and therefore have nothing to do with the optical gap. Peak B corresponds to the filled tail of the negative-isomer empty state, which is about 0.15 eV lower than the peak of the positive-isomer conduction band. A combination of the old direct and inverse photoemission results [7] and the present ARUPS data yield an estimate for the negative-isomer gap of 0.41 eV, and of the positive-isomer gap of 0.75 eV, in good agreement with STS results. The latter gap is well compatible with strong excitonic effects [6–8].

We emphasize that the solution of an old puzzling problem was made possible by the combined use of two powerful techniques (high-resolution ARUPS and STM and STS), backed up by state-of-the-art calculations. In light of the present result, also the pioneering surface-physics experiment of Allen and Gobeli [18] should be reconsidered.

Finally we notice that the simultaneous presence of both positive and negative isomer domains in heavily n-doped $\mathrm{Si}(111)-2\times 1$ surfaces, apart from explaining the above exciton-related controversy, is a new interesting result in itself. Although the atomic and electronic structures of the cleavage faces of the elemental semiconductors Si and Ge nowadays are well understood, some details have not been clarified yet. For instance, we do not know why in standard conditions $\mathrm{Si}(111)-2\times 1$ $(\mathrm{Ge}(111)-2\times 1)$ exhibits positive (negative) isomers, nor we can explain the crucial role of temperature in determining the fraction of surface covered with negative-isomer domains in heavily n-doped $\mathrm{Si}(111)-2\times 1$. Further investigation of this subject from the point of view of thermodynamics of surface phase transitions is needed. As mentioned at the start of this Letter, the existence of two types of isomers for $\mathrm{Si}(111)-2\times 1$ bears some resemblance with the case of the Si and Ge (001) surfaces, which in recent years have attracted attention for the potentiality of fabricating a rewritable nanoscale memory [19]. It would be interesting to investigate whether flipping of the buckling in $\mathrm{Si}(111)2\times 1$ can be artificially induced by an STM tip, either by applying a high voltage or by manipulating individual donor atoms. We believe that the present results will foster new investigations on isomer domains in $\mathrm{Si}(111)-2\times 1$ and $\mathrm{Ge}(111)-2\times 1$, leading to a deeper understanding of such systems with multiple configurations of nearly equal energies.

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