Unoccupied electronic states in atomic chains on Si(557)-Au: Time-resolved two-photon photoemission investigation

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The prototypical one-dimensional Si(557)-Au surface is investigated with time-resolved two-photon photoemission. Three new states are found near $\Gamma$, two of them in the band gap of silicon. These states cannot be explained by existing band calculations. As a possible solution, we suggest a closer examination of the atomic and electronic structure near the step edge.

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In recent years, it has become possible to create one-dimensional (1D) structures at vicinal silicon surfaces that consist of atomic chains. Gold atoms produce metallic chains, which may be viewed as the ultimate nanowires.\(^1\) The electronic states at the Fermi level lie inside the band gap of silicon and thus cannot hybridize with three-dimensional states in the substrate, but the gold atoms are firmly locked to the surface lattice in substitutional sites. These surfaces can be used to systematically explore phases of electrons between one and two dimensions and to search for exotic new phenomena that are caused by the fact that the electron-electron interaction takes a qualitative leap in one dimension because all electrons are moving along the same line.\(^2\) As a consequence, the familiar Fermi liquid breaks down in one dimension and is replaced by a Tomonaga-Luttinger liquid, where single electron excitations are replaced by collective excitations.

The Si(557)-Au surface has become a prototype for atomic chain structures. It is one of the simplest chain structures with just a single Au chain per unit cell, and it has been investigated by many techniques, such as electron diffraction,\(^3\) x-ray diffraction,\(^4\) scanning tunneling microscopy (STM) and spectroscopy (STS),\(^5,7,12\) angle-resolved photoemission,\(^5,7,12\) inverse photoemission,\(^13\) electron-energy loss spectroscopy,\(^14\) surface conductivity,\(^15\) and first-principles calculations.\(^16-18\) The band structure is characterized by a closely spaced doublet of half-filled bands that is common to all Au-induced chain structures.\(^17\) This unusual doublet has been explained by a spin splitting induced by the spin-orbit interaction at a surface.\(^18,19\)

While the occupied bands have been mapped in detail by photoemission, the unoccupied part of the band structure has remained largely unexplored. An image-potential state has been found by inverse photoemission,\(^13\) reflecting the metallic nature of the surface. Theory\(^18\) predicts that the bands above $E_F$ differ dramatically from the occupied part below $E_F$: The metallic occupied band opens up a gap just above the Fermi level, which is assigned to the splitting between even and odd combinations of two equivalent Si bonds pointing toward a gold atom in the chain. In contrast to the strongly dispersing band below $E_F$, the calculation finds a flat, localized band just above $E_F$ which is associated with a graphitic Si chain at the step edge, not the Au chains in the middle of the terrace.

A wide open territory is the dynamics of carriers in 1D systems. Excited electrons are expected to interact strongly in 1D. Therefore it would be interesting to determine lifetimes and decay mechanisms on a short time scale. This study uses a femtosecond pump-probe technique to access the unoccupied electronic states of Si(557)-Au by bichromatic two-photon photoemission.\(^20\) To our knowledge, such studies have not yet been performed on 1D electron systems.}

Two-photon photoemission (2PPE) spectra were obtained using a Ti:sapphire oscillator at a center wavelength $\lambda_{\text{IR}} = 800$ nm ($h\nu_{\text{IR}}=1.55$ eV, pulse duration $\tau_{\text{IR}}\approx37$ fs). Part of the output intensity was frequency tripled ($h\nu_{\text{UV}}=4.65$ eV, $\tau_{\text{UV}}\approx55$ fs). Both beams were spatially overlapped on a beam splitter after the IR beam passed a delay stage. The polarizations of the IR and UV beams could be rotated to align the electric field vector either perpendicular to the plane of incidence (s-pol.) or parallel (p-pol.). Figure 1 depicts the experimental geometry. In normal emission the beams were incident on the sample at a glancing angle of 10°.

The p-type Si(557)-Au samples were prepared in an ultrahigh-vacuum chamber (base pressure $<5\times10^{-11}$ mbar) following a technique which was described earlier in the literature.\(^17\) Photoelectron spectra were recorded using an Omicron EA 125 HR spectrometer with seven channeltron detectors at an angle and energy resolution of 1.6° and 17 meV, respectively. Experiments were carried out at 300 K and 90 K. Apart from a photovoltage arising at low temperatures, no differences could be observed.

![FIG. 1. (Color online) Experimental geometry showing a sample with the chain direction vertical, the incident laser beams, and the direction toward the electron detector.](image_url)
A set of energy distribution curves (EDCs) at different pump-probe delays \( \Delta t = 0-150 \) fs is shown in Fig. 2 (upper panel). While the two peaks at kinetic energies \( E_{\text{kin}} = 0.71 \) eV and \( E_{\text{kin}} = 0.93 \) eV quickly lose intensity when increasing \( \Delta t \), a feature at \( E_{\text{kin}} = 0.32 \) eV emerges from the overall high background only at \( \Delta t = 100 \) fs.

Investigating the band dispersion by rotating the manipulator at fixed sample azimuths reveals the 1D nature of peaks B and C, which show a measurable dispersion only along the chains. The effective masses in units of the electron mass are \( m_B^* = +0.13 m_e \) and \( m_C^* = -0.17 m_e \), respectively.

Since peaks in 2PPE spectra can arise from initial or intermediate states, a careful separation of the possible processes is necessary. For that purpose our analysis makes use of the strong polarization dependence of peaks B and C. Figure 3 shows spectra recorded in normal emission for all eight possible combinations of the laser polarization and the azimuthal sample orientation.

The suppression of peaks in certain geometries is caused by optical dipole selection rules, which are applicable to each of the two transitions (short and long arrows in Fig. 4). Electronic states are either even or odd with respect to the \((1\bar{1}0)\) mirror plane, which is orthogonal to the chains (Fig. 1). Transitions between states with equal (opposite) parity are allowed for \( p \)-polarization (\( s \)-polarization). The final state has to be even for emission into the mirror plane. Although the exact mirror symmetry of the truncated bulk structure about the \((1\bar{1}0)\) mirror plane might be broken in the actual structure of Si(557)-Au, the strong polarization effects observed in Fig. 3 indicate that it is preserved at least locally around specific bond orbitals.

The appearance of peak C in all spectra with a \( p \)-polarized IR pulse indicates an even intermediate state which is pumped by UV (\( 3hv \)) and probed by IR (\( hv \)) pulses. We assign this peak to an \( n=1 \) image-potential state at \( E_C = E_{\text{vac}} - 0.62 \) eV. This value agrees with the energy obtained from the Rydberg-like formula for image-potential states when taking into account the dielectric constant of silicon, \( \varepsilon_r = 11.7^{21} \). Time-resolved experiments reveal a lifetime \( \tau_c < 10 \) fs. This small value can be understood considering the absence of a band gap in the band structure of silicon for the corresponding energies. Thus, the description as an image-potential resonance is more appropriate. This interpretation is in agreement with recent investigations by inverse photoemission.\(^{13} \) The resonance character of the image-potential

![Figure 2](image1.png)

**FIG. 2.** EDCs recorded in normal emission for various delays between the IR and UV pulses (both \( p \)-pol., \( T = 90 \) K). Peaks B and C are very short lived (<10 fs), while electrons in the band above A lose energy gradually.

![Figure 3](image2.png)

**FIG. 3.** Polarization-dependent EDCs recorded in normal emission for the chains oriented horizontally (dashed line, \( T = 90 \) K) and vertically (solid line, \( T = 300 \) K). See text and Fig. 1 for a detailed explanation of the experimental geometry. A strong dependence on the photon polarization is observed, for both IR (first \( p/s \)) and UV (second \( p/s \)) light.

![Figure 4](image3.png)

**FIG. 4.** (Color online) Summary of the observed 2PPE transitions together with the energy positions in eV referenced to the closest band edge (CBM and VBM). A possible scattering process accounting for the delayed occurrence of peak A is sketched schematically.
state broadens it so much that the band dispersion of peak C is dominated by the sharp initial states of negative effective mass. This is further corroborated by the dependence of the spectra on photon energy. From the polarization dependence we pinpoint two holelike occupied states of even and odd symmetry at an energy of 0.22 eV below the bulk valence-band maximum (VBM). A similar observation on clean Si(100):(4\times2) was explained as resonant excitation of the \( n=1 \) image-potential state from the \( D^\uparrow \) dangling bond state.\textsuperscript{22,23}

The polarization analysis finds that peak B originates from an even initial state and an odd intermediate state. It is highly anisotropic and requires the electric field vector of both transitions to be parallel to the chains. The intermediate state lies extremely close to the bulk conduction-band minimum (CBM) (cf. Fig. 4) and shows a lifetime \( \tau_B<10 \) fs. Symmetry reasons, however, forbid the interpretation in terms of the \( \Delta_I \)-like conduction-band minimum at the \( \bar{\Gamma} \) point of the Si(557) surface. Its anisotropy and the fact that it requires a highly accurate coverage seem to favor an interpretation in terms of a surface state resulting from the 1D reconstruction.

A very interesting feature is hidden in peak A—i.e., at very low kinetic energies \( E_{\text{kin}}<0.5 \) eV. While the EDC at \( \Delta t=0 \) is structureless in this region, a peak becomes clearly visible at \( \Delta t\approx 100 \) fs (Fig. 2). Our time-resolved experiments unambiguously show that the IR pulse comes first and therefore pumps electrons into states in the upper half of the bulk band gap. The occupation is probed with the UV pulse after a delay \( \Delta t \). The interpretation in terms of a single long-lived and exponentially decaying state can be ruled out. A comprehensive quantitative analysis including the dispersion and the determination of lifetimes, however, will require more experimental data.

Our findings are compared to recent band calculations\textsuperscript{18} in Fig. 5. The calculated bulk band gap appears to be only 0.92 eV, judging from the gap in the fine dots at \( \bar{\Gamma} \) and \( M^\bar{\gamma} \). This underestimated of the bulk band gap of semiconductors is a well-known phenomenon of DFT calculations. As indicated in Fig. 5, we therefore cut the energy scale right above \( E_F \) and shift the experimental bands down by 0.24 eV, such that the calculated and the experimental CBMs line up (an experimental band gap of 1.16 eV at \( T=90 \) K is assumed).

We feel that this is the most accurate way to compare experimental energies of occupied and unoccupied states to calculations. After adjusting the energy scales properly, one can seek possible assignments from the comparison to the band calculation. Band B lies close to the unoccupied adatom band (open triangles in Fig. 5). However, the polarization dependence requires an odd band, while one would expect the adatom state to be even, because it corresponds to a \( \sigma \) orbital. Band A lies in the middle of the gap far from any calculated band. Band C lies close to the occupied adatom band (open triangles). However, the strong experimental band dispersion needs an explanation.

Compared to previous photoemission results,\textsuperscript{5,7,12} the calculation\textsuperscript{18} explains the split band near \( \bar{K} \) remarkably well (solid circles in Fig. 5), including the spin-orbit character of the splitting.\textsuperscript{19} The unoccupied part of the spin-split band is far too far in \( k \) space to be accessible by our two-photon photoemission experiments. Other features such as the flat-band straddling \( E_F \) (open squares) have never been observed in photoemission and are not seen in our 2PPE experiments, either.

These detailed comparisons can be connected to a larger picture: The features that are captured well by the calculation originate from the Au chains at the center of the (111) terrace. The step state at \( E_F \) and the adatom states, however, might require a refinement of the calculation. In fact, the step geometry is the least understood part of the structure,\textsuperscript{4} and it is open to a large variety of modifications. It could be that the optimum structure finds a way to avoid a narrow band at \( E_F \), which piles up density of states at \( E_F \) and leads to an unstable situation. This might be accomplished by rearranging the step atoms or adding extra Si atoms.

In conclusion, we use two-photon photoemission to shed light on the unoccupied electronic states of atomic chain structures. Two unexpected states are observed in the gap, and time-resolved measurements provide insight into the dynamics. These results provide a stimulus for theoretical efforts to pinpoint the origin of the newly found states and their connection to one-dimensional electron physics.

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