Vibration-Driven Self-Doping of Dangling-Bond Wires on Si(553)-Au Surfaces

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(Received 16 October 2019; accepted 21 February 2020; published 7 April 2020)

Density-functional theory is used to explore the Si(553)-Au surface dynamics. Our study (i) reveals a complex two-stage order-disorder phase transition where with rising temperature first the $\times 3$ order along the Si step edges and, subsequently, the $\times 2$ order of the Au chains is lost, (ii) identifies the transient modification of the electron chemical potential during soft Au chain vibrations as instrumental for disorder at the step edge, and (iii) shows that the transition leads to a self-doping of the Si dangling-bond wire at the step edge. The calculations are corroborated by Raman measurements of surface phonon modes and explain previous electron diffraction, scanning tunneling microscopy, and surface transport data.

DFT calculations were performed using the Vienna ab initio simulation package (VASP) [26] and the PBEsol functional [27]. Collinear spin polarization is assumed. This methodology was recently shown to correctly describe the ground state of the $1 \times 6$ reconstructed Si(553)-Au surface [20]. A supercell containing six Si bilayers (H passivated at the bottom), a 450 eV plane-wave energy cutoff, and a $2 \times 3 \times 1$ Brillouin-zone sampling ensure numerical convergence. The Nosé-Hoover thermostat was used for ab initio molecular dynamics (AIMD) calculations.

A soft Au chain phonon mode is identified that facilitates—via Au $\rightarrow$ Si db charge transfer—an order-disorder transition at the Si step edge starting below 100 K. At higher temperatures, the Au chain order is quenched.

In detail, DFT calculations were performed using the Vienna ab initio simulation package (VASP) [26] and the PBEsol functional [27]. Collinear spin polarization is assumed. This methodology was recently shown to correctly describe the ground state of the $1 \times 6$ reconstructed Si(553)-Au surface [20]. A supercell containing six Si bilayers (H passivated at the bottom), a 450 eV plane-wave energy cutoff, and a $2 \times 3 \times 1$ Brillouin-zone sampling ensure numerical convergence. The Nosé-Hoover thermostat was used for ab initio molecular dynamics (AIMD) calculations.

FIG. 1. Atomic structure of the $1 \times 6$ reconstructed Si(553)-Au surface. Yellow, (dark) gray, and blue balls indicate Au, (honeycomb) Si, and Si atoms with empty dangling bonds, respectively. Filled and empty dangling bonds in the ground state (2,2,0) configuration are shown (only at one step edge) in red and blue, respectively.
Surfàce Raman measurements were performed in backscattering geometry using a triple Dilor-xy spectrometer with a high-efficiency Si-based CCD detector from Andor iDus. A Kr$^+$ laser operated at 647 nm is used as light source. This setup allows for the registration of Raman intensity down to 15 cm$^{-1}$ with a spectral resolution below 3 cm$^{-1}$. The sample temperature was controlled with a PID control loop, combining the operation of a closed-cycle He cryostat with a heating wire system.

Tegenkamp and co-authors [25] attribute the surface conductivity increase above 65 K to an Au $\rightarrow$ Si db charge transfer. Such a charge redistribution characterizes the spin-liquid structure suggested by Erwin et al. [14,24] for Si(553)-Au: It has a (2,2,1) electron configuration, i.e., two fully occupied dbs alternate with one singly occupied db along the step edge. The occupation of the formerly empty Si $p$ orbital causes a $sp^2 + p \rightarrow sp^3$ rehybridization and moves the respective Si atom out of the planar $sp^2$ configuration [20].

How likely is a local transition to such an electron-doped (2,2,1) configuration? In order to answer this question we first calculate the total energy along the reaction path where—within the $1 \times 6$ surface unit cell—a single Si atom with an originally empty db is raised from the flat $sp^2$ coordination to the $sp^3$ configuration, see Fig. 2. Here the Au chain dimerization is fixed at its average value at 100 K. The movement of the Si edge atom is accompanied by Au $\rightarrow$ Si db charge transfer, see the Supplemental Material [28] for band structures. Along the reaction path a metastable structure appears that locally corresponds to the (2,2,1) structure [14]. The energy barrier hindering such a local (2,2,0) $\rightarrow$ (2,2,1) transformation amounts to 58 meV, far above the thermal energy at 65 K, i.e., about 6 meV. The energy barrier may be reduced at finite temperatures due to entropy effects [30]. In order to assess their magnitude, free-energy calculations were performed within the adiabatic approximation [31] based on surface vibrational modes determined in harmonic approximations by frozen-phonon calculations. As shown in Fig. 2, entropy effects indeed ease the (2,2,0) $\rightarrow$ (2,2,1) transition, but not sufficiently enough to explain a transition close to 65 K.

In order to probe the possibility that a concerted movement involving a variety of atoms causes the $sp^2 + p \rightarrow sp^3$ rehybridization and the accompanying charge transfer, AIMD is performed. The time evolution (after equilibration) of the Si step edge atom vertical positions is shown in Fig. 3. Here it is discriminated between three configurations: $sp^2$ hybridized Si with an empty $p$ orbital db, partially $sp^3$ hybridized Si hosting a single electron in its db, and completely $sp^3$ hybridized Si with fully occupied db. The $1 \times 6$ surface unit cell considered in the calculations is nearly entirely characterized by (2,2,0) structures at 50 K. In fact, there are only two very short occurrences of singly occupied Si dbs. These occurrences get more frequent and last longer at 100 K. Also an emptying of the originally doubly occupied dbs is observed at this temperature. Still, the (2,2,0) configuration is the most dominant structural motif at 100 K. However, strong vertical vibrations of the Si step edge atoms occur. These vibrations get more pronounced for higher temperatures and quench the dominance of the (2,2,0) structure. Increasing disorder is observed and singly occupied dbs occur frequently for
temperatures in excess of 200 K. The AIMD results clearly show an order-disorder type phase transition.

The distribution function of the Si edge atom vertical positions in Fig. 4(a) provides additional details. At 50 K the distribution is bimodal, with cluster points for completely filled and empty Si dbs. A third, very weak accumulation point is observed for T > 50 K. It corresponds to the occupation of the local energy minimum of the reaction path shown in Fig. 2, i.e., singly occupied dbs. For higher temperatures, the distribution gets broader and the Si vertical positions scatter broadly. This shows that the description of the phase transition in terms of solitons and antisolitons [32], i.e., binary occupancy shifts along the db wire, simplifies the actual surface dynamics.

Why does the order-disorder transition start at far lower temperatures than expected from the rehybridization barrier (black line in Fig. 2)? The answer is related to the electron chemical potential of the Au chain. A strongly dimerized chain has a stronger electron affinity than a weakly or undimerized chain [33]. Therefore, a reduced dimerization favors the Au → Si charge transfer required for the rehybridization. In Fig. 2 it can be seen that a reduction of the dimerization from 12.8% (average value at 100 K) to 10.0% reduces the $sp^2 + p \rightarrow sp^3$ transition barrier (blue line) as strongly as doping the $1 \times 6$ unit cell with 0.4 electrons (red line). While the average dimerization is larger than 10.0% even at 400 K, it already drops below 50 K Au chain segments with 10.0% dimerization occur temporarily, cf. distribution in Fig. 4(b). With increasing temperature, even lower dimerization values occur and reduce locally the energy barrier for the Si $sp^2 + p \rightarrow sp^3$ rehybridization. Because of the nonlinear dependence of the reaction rate on the energy barrier, the rehybridization probability depends not only on the average dimerization, but on its entire distribution function. The probability for the occurrence of self-doped (2,2,1) structures derived from the temperature-dependent dimerization distribution under the assumption of thermodynamic equilibrium between (2,2,0) and (2,2,1) surface domains is shown in Fig. 4(c). Its rise for temperatures above 50 K is—even quantitatively—consistent with the AIMD findings discussed above and explains the disorder along the Si step edge already at moderate temperatures.

Are these computational findings in agreement with the actual surface dynamics? First the temperature dependence of the surface Raman signatures is explored. Two signatures that are particularly strongly affected by temperature are shown in Fig. 5(a): There is a low-frequency phonon mode at around 41 cm$^{-1}$ that softens considerably with rising temperature. A phonon mode at around 415 cm$^{-1}$ appears slightly below 100 K and strongly gains intensity with rising temperature. Both signatures show a continuous rather than an abrupt change in energy or intensity, respectively. This supports the interpretation of the AIMD results in terms of an order-disorder transition.

Frozen-phonon calculations for Si(553)-Au surfaces allow for a microscopic interpretation of the Raman data. The calculations show the existence of a Au chain dimerization mode at 41 cm$^{-1}$ for the (2,2,0) ground state, see Fig. 5(d). Its thermal frequency shift—obtained by projecting the AIMD atomic velocities on the phonon eigenvector—is in close agreement with the low-energy Raman signature described above, see Fig. 5(c). The phonon-mode softening with rising temperature roughly

![Figure 4](image4.png)

**FIG. 4.** (a) Distribution of the Si step edge atom vertical positions for various temperatures. Equilibrium positions of Si with empty (0), singly (1), and doubly (2) occupied dbs are indicated. (b) Temperature dependent distribution of Au chain dimerization. Color coding as shown left. (c) Probability of (2,2,1) ordered surface domains derived from the dimerization distributions shown in (b), see text.

![Figure 5](image5.png)

**FIG. 5.** (a) Temperature-dependent Raman spectra, focusing on a Raman mode located at the step edge at 415 cm$^{-1}$ depicted in (b) and one located at the Au chain at 41 cm$^{-1}$ depicted in (d). The measured frequency shift of the 41 cm$^{-1}$ mode is in (c) compared with the calculated shift and the relative change in dimerization.
FIG. 7. Calculated average number of (unpaired) electrons per dangling bond.

Both the total number of electrons as well as the number of unpaired electrons in the db wires strongly increase for temperatures in excess of 50 K, see Fig. 7. This reflects the increasing probability for \((2,2,0) \rightarrow (2,2,1)\) surface structure transitions, i.e., the temperature induced self-doping of the surface. Similar to other activated atomic wire systems \([34–36]\), the structural transition is accompanied by strong band structure modifications. As shown in the Supplemental Material \([28]\), the weakly dispersing Si step edge states do not only shift in energy, they also hybridize with the Au chain states for thermally activated surface structures. This reduces drastically the effective masses characteristic for the Au bands \([28]\). The measured increase of the surface conductivity for temperatures above 65 K \([25]\) is thus probably related to Si-modified Au states. This interpretation is supported by the experimental finding that toward higher temperatures the surface conductivity decreases again, which is a hallmark of metallic transport \([25]\).

To conclude, the present DFT calculations and Raman measurements do not only provide for the first time a consistent description of the experimentally observed two-stage Si(553)-Au surface phase transition, they also reveal a novel mechanism for the self-doping of db nanostructures: Thermally excited vibrations of the Au charge reservoir lead to transient changes of its electron affinity and thus facilitate electron doping at low temperatures. This mechanism can be expected to be relevant beyond the family of gold-stabilized Si surfaces, and to be conveniently tuned by modifying the species of the charge reservoir, the metal coverage, and the db density.

Financial support by DFG (FOR1700, SCHM1361/25, SCHM1361/26, TRR142 Project No. 231447078), Senatskanzlei Berlin, MKW NRW, BMBF, and EFRE (Project No. 1.8/07) is acknowledged. We thank the Paderborn Center for Parallel Computing (PC²) and the Höchstleistungs-Rechenzentrum Stuttgart (HLRS) for grants of high-performance computer time.

parallels the reduction of the dimer strength, i.e., is caused by the reduction of the average Au-Au bond strength. Because of its very low frequency, the Au chain mode is occupied already at a low temperature. It reduces temporarily the Au chain dimerization and thus lowers—as discussed above—the \(sp^2 + p \rightarrow sp^3\) activation energy.

Frozen-phonon calculations for the \((2,2,1)\) surface predict a transversal shear mode along the Si honeycomb chain with a frequency of 415 cm\(^{-1}\), see Fig. 5(b). Its frequency coincides with that of the high-temperature mode seen by Raman spectroscopy. This mode is replaced by localized Si vibrations for the \((2,2,0)\) structure, due to the stronger variation of the force constants along a step edge where \(sp^3\) and \(sp^2\) hybridized Si atoms alternate. This explains, why the measured mode disappears upon cooling the sample below 100 K.

The calculated surface geometries are furthermore consistent with the evolution of the LEED data, see Fig. 6. Here the \(\times 3\) and \(\times 2\) LEED intensities measured in Ref. \([25]\) are compared with the squared structure factors including Debye-Waller effects obtained from AIMD. Both the measured data and the calculations show a gradual loss of order starting below 100 K, which first affects the \(\times 3\) signatures and subsequently the \(\times 2\) features, in agreement with earlier STM observations \([22,23]\). The quenching of the \(\times 3\) signals is well reproduced by the calculated order-disorder transition at the Si step edge, whereas the measured disappearance of the \(\times 2\) intensities clearly precedes the calculated Au chain order-disorder transition. This is, however, to be expected: While the AIMD calculations find a broadening of the dimerization distribution, cf. Fig. 4(b), they cannot correctly account for disorder arising from dimerization phase shifts. The relatively small \(1 \times 6\) unit cell leads to an overestimation of the defect or antidefect interaction that blueshifts the calculated critical temperature. Since the Au atoms are directly bonded, this effect is more relevant for the Au chain than for indirectly interacting step edge Si.
In Figure 1 the evolution of the unfolded Si(553)-Au surface band structure along the reaction path corresponding to the $sp^2 + p \rightarrow sp^3$ rehybridization of a single Si step-edge atom within a 1×6 surface unit cell is shown. Along the reaction path, one originally empty Si $p$ orbital is transformed into a singly occupied $sp^3$ hybridized Si dangling bond. The reaction coordinate $q$ describes the local transition from the (2,2,0) ground-state configuration to the (2,2,1) excited state. The transition is accompanied by an energy down shift of the corresponding band: The rather weakly dispersive Si state is pushed below the Fermi energy. As obvious from Fig. 1, also the metallic Au bands are affected. A strong hybridization of Si and Au states occurs. This does not only lead to a substantial increase of the electronic density of states close to the Fermi level (a 70% increase is calculated for $q = 0.55$), but also modifies the curvature of the Au bands at the Fermi energy, i.e., the effective masses of the respective charge carriers. They are calculated according to

$$\frac{1}{m_{\text{eff}}} = \frac{1}{S_F} \int_{FS} \frac{1}{\hbar^2} \frac{\partial^2 E(k)}{\partial k^2} dS_k,$$

(1)

where $S_F$ denotes the area of the (here nearly one-dimensional) Fermi surface (FS). The calculated values are contained in Tab. I. A strong increase of the absolute total inverse mass for Au band charge carriers is observed for structures in-between the (2,2,0) and (2,2,1) configurations. The calculated band structures thus indicate that Si-induced modifications of Au states are largely responsible for the conductivity increase observed for the structural phase transition onset.

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TABLE I: The inverse effective mass of the $S_{1/2}$ and $S_3$ band electrons (relative to the free electron mass $m_e$) of Si(553)-Au along the reaction path from local (2,2,0) ($q = 0.0$) to (2,2,1) ($q = 1.0$) configurations.

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FIG. 1: Si(553)-Au surface band structures calculated along the reaction path from local (2,2,0) \((q=0.0)\) to (2,2,1) \((q=1.0)\) configurations. To ease the interpretation, the bands are unfolded into the \(1\times1\) Brillouin zone (see inset) following Medeiros et al. [1]. Yellow and red colors denote electron localization at Au and Si step edge atoms, respectively.