Spin pairing versus spin chains at Si(553)-Au surfaces

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Density-functional theory is used to probe the spin structure of the Si(553)-Au surface. A diamagnetic $sp^2$ + $p$ rehybridized structure, where the dangling bonds are either filled with two spin-paired electrons or are empty, is more favorable and in better agreement with experiment than the generally accepted spin-chain model. The shallow potential energy surface of Si(553)-Au, together with the ordered array of empty dangling bonds, suggests this surface as susceptible for spin polarization by doping, however.

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The integration of single-spin magnetoelectronics into standard silicon technology is crucial for technologies involving spin-based computation and storage. Typically, magnetic order in nonmagnetic materials relies on the inclusion of magnetic transition metals, elements with a large atomic magnetic moment, or rare earths. Therefore, the creation of intrinsic magnetism at silicon surfaces by nanostructuring—as reported for the Si(553)-Au surface [1]—has found much resonance in the scientific community. It not only promises to provide an entry point for combining magnetoelectronics based on single spins with standard electronics technology, it is also of fundamental interest: While some arguments suggest the formation of an exotic spin quantum liquid at this surface [2], quantum fluctuations should prevent any magnetic ordering in strictly one- or two-dimensional systems [3].

Consequently, the Si(553)-Au surface has found much interest. It is formed by Si(111) terraces separated by single atomic steps and is stabilized by a submonolayer of Au. Its main geometrical building blocks, i.e., the double Au chain running in the middle of the terrace and the Si honeycomb chain at the step edge (cf. Fig. 1), have been established by scanning tunneling microscopy (STM) [2,4–11], x-ray diffraction [12], low-energy electron diffraction (LEED) [2,6], and density-functional theory (DFT) [1,2,4,9,13,14]. Au chain dimerization lowers the surface energy [14] and gives rise to a $\times 2$ periodicity along the steps [see Fig. 1(a)]. A further energy reduction is believed to result from the formation of an antiferromagnetic spin chain [1]. It is formed by spin-polarized electrons that singly occupy every third Si dangling bond (db) along the Si step edge. Figure 1(b) shows this spin-chain (SC) model. It accounts naturally for the $\times 2$ and $\times 3$ periodicities found by LEED [2] as well as STM [6,7,10,11] and nicely explains the metallic Au bands observed by angle-resolved photoemission spectroscopy (ARPES) [4,6,15–17].

At the same time, there is no direct experimental evidence for the appearance of spin chains at Si(553)-Au, e.g., by spin-polarized STM, nor for the existence of half-occupied Si dangling bonds. Surfaces of covalent materials typically undergo relaxation or reconstruction, which allows the broken bonds to be either eliminated, emptied, or doubly occupied with spin-paired electrons [18–25].

This somehow questions the formation of spin chains at Si(553)-Au. Their existence is probed in the present study by means of DFT calculations. It is found that a $sp^3 \rightarrow sp^2 + p$ rehybridization and the emptying of the $p$ orbital for every third Si edge atom is energetically favored over spin-chain formation. The rehybridization leads to a diamagnetic structure that very well accounts for all experimental data.

The Vienna ab initio simulation package (VASP) [26] implementation of DFT is used to study the Si(553)-Au surface. The structure is modeled within periodic supercells, consisting of five essentially bulklike Si bilayers stacked along the surface normal. An additional layer contains the Au and Si surface atoms. The bottom layer Si atoms are hydrogen passivated. A vacuum region of 15 Å decouples the slab from its periodic images along the surface normal. The lowest two Si bilayers

![FIG. 1. Structure models of Si(553)-Au: (a) Model proposed by Krawiec (K) [14], (b) spin-chain (SC) structure due to Erwin and Himpsel [1], and (c) rehybridized (R) surface proposed here. Yellow and (dark) gray balls indicate Au and (honeycomb chain) Si atoms. The structurally and electronically salient step-edge Si$_{\times 3}$ atoms characteristic for the SC and R surfaces are red. Arrows indicate spin polarization.](image-url)
are kept fixed in ideal bulk positions during structural relaxation, while all remaining atoms are free to move. The electron orbitals are expanded into plane waves up to an energy cutoff of 450 eV. The Brillouin zone is sampled using a $2 \times 5 \times 1$ k-point mesh. Collinear spin orientation is assumed for the spin-polarized calculations. The Tersoff-Hamann model [27] is used to simulate STM images.

The electron-electron exchange and correlation (XC) effects are treated within the generalized-gradient approximation (GGA) using the revised Perdew-Burke-Ernzerhof (PBEsol) functional [28]. Energy differences between competing structure models for large surface reconstructions often depend sensitively on XC effects [29]. This can be expected to be particularly relevant in the case of strongly localized electrons in weakly interacting Si db’s. Therefore, we use hybrid DFT to verify the energy order of the minima on the potential energy surface. The Heyd-Scuseria-Ernzerhof (HSE) functional [30] with 11% exact Hartree-Fock exchange is used. This value has been found to well describe the Si db [31] and has been used earlier for Si(553)-Au [32]. In order to compare with previous work, and for the sake of completeness, GGA calculations using the standard PBE functional [33] as well as local-density approximation (LDA) calculations [34] are performed, too.

The Au chain at Si(553)-Au acts as an electron reservoir that readily provides and accepts charge, as recently established by hydrogen adsorption studies [35]. This finding suggests a surface energy lowering due to $sp^3 \rightarrow sp^2 + p$ rehybridization of every third Si edge atom, and subsequent charge transfer from the Si p orbital to the Au chain. A similar rehybridization gives rise to asymmetric dimers at the Si(001) surface [20].

In order to probe that mechanism for Si(553)-Au, we start from the Krawiec (K) structure [cf. Fig. 1(a)] and gradually lower the vertical height of every third Si edge atom (Si$_{3 \times 3}$). The energy profile of this reaction path along with the corresponding surface magnetization is shown in Fig. 2. The lowering of Si$_{3 \times 3}$ reduces the surface energy and increases the surface magnetization, which assumes its maximum when the Si$_{3 \times 3}$ atoms are about 0.3 Å below the neighboring step-edge atoms. In this configuration, a charge redistribution along the Si step edge takes place: The Si$_{3 \times 3}$ db carries about one electron and the neighboring step-edge atom db’s are fully occupied. The surface is stabilized by an antiferromagnetic spin order along the chain of Si$_{3 \times 3}$ db electrons. The resulting structure, shown in Fig. 1(b), corresponds to the spin-chain model proposed by Erwin and Himpsel [1]. According to the present calculations it is a local, but not the global, minimum on the potential-energy surface (cf. Fig. 2 and Table I). The latter is reached upon passing an energy barrier of about 5 meV and is characterized by Si$_{3 \times 3}$ atoms about 0.8 Å below the neighboring step-edge atoms. In this configuration, they assume a planar, $sp^2$-like bonding configuration with respect to their Si neighbors [cf. Fig. 1(c)].

The formation of this rehybridized structure is accompanied by a surface charge transfer. About 1.6 electrons per $1 \times 6$ surface cell are shifted from the Si step edge to the Au chain. This corresponds to the magnetization calculated for the SC model, i.e., it is equivalent to the spin-polarized charge in the Si$_{3 \times 3}$ db’s. The charge redistribution is visualized in Fig. 3(a), where we plot the electron density difference between the SC and the K model. The electron transfer from the Si$_{3 \times 3}$ db’s to the Au dimers is clearly seen. The additional charge at the Au chain strengthens its dimerization, which increases from 5% to 14%. We note than an increase in Au

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<td>R</td>
<td>$-114$</td>
<td>$+191^*$</td>
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**FIG. 2.** Calculated (DFT-PBEsol) surface energy (solid line) and surface magnetization (dashed line) per $1 \times 6$ surface unit cell vs the reaction coordinate given by the Si$_{3 \times 3}$ vertical position. Its respective position for the Krawiec (K), spin-chain (SC), and rehybridized model (R) is indicated.

**FIG. 3.** (a) Difference between the charge densities calculated for the spin-chain (SC) and the rehybridized (R) surface. The relative electron accumulation/depletion at the R surface is shown in red/blue. (b) Schematic model for the parity breaking of the Si step edge due the Au dimers (see text and Fig. 5).
The spin-spin exchange constant along the chains is estimated to be about 15 meV [2]. This is roughly two orders of magnitude smaller than the Si hybridization energy. Therefore it might at first seem obvious that the energy gain due to rehybridization and emptying the Si$_{3} \times 3$ orbitals outweighs the stabilization due to the antiferromagnetic spin order. However, the energy balance is as well affected by the charge transfer and strain accompanying the rehybridization. In fact, we find the energy difference between the R and the SC model (cf. Table I) to be small and to depend on the treatment of the XC effects: PBEsol and HSE calculations predict a lower surface energy for the spin-paired compared to the spin-chain surface. The PBE calculations, in contrast, failed to identify a local energy minimum for the R model. PBE calculations based on frozen PBEsol geometries yield a higher surface energy for the R than for the SC structure. On the other hand, LDA calculations predict the rehybridization to lower the surface energy, but fail to provide an antiferromagnetically ordered state. In summary, the total-energy calculations suggest the rehybridization of the surface, but they are not fully conclusive. Obviously, the energy landscape is rather flat. In order to arrive at a conclusive picture, the calculated electronic properties of the SC and R model are now compared with the available experimental data.

The different electron distributions of the SC and R models lead to somewhat different surface band structures, as shown in Fig. 4. The SC model is characterized by spin-polarized states at the singly occupied Si$_{3} \times 3$ db’s that form two very flat bands about 0.1 eV below and 0.2 eV above the Si valence-band maximum (VBM), respectively. These bands are pushed away from the VBM upon rehybridization, accompanying the electron transfer from the Si$_{3} \times 3$ db’s towards the Au chain. At the same time, the strongly dispersive, partially occupied Au bands shift down in energy and are now below the empty Si db band throughout the Brillouin zone.

Although the calculated Au bands seem to match the experimental data slightly better in the case of the rehybridized compared to the spin-chain structure, their modification is not sufficiently strong to allow for discriminating between the models. This holds also with respect to the nondispersing unoccupied state 0.62 eV above the Fermi level observed by two-photon photoemission [32]. Given the DFT band-gap underestimation, this state is well explained by the Si db states predicted for both the R and the SC geometry. The situation is different in the case of the prominent flatband assigned to the single electrons at the Si$_{3} \times 3$ atoms, calculated for the SC model. This band, about 0.1 eV below the VBM, has not been detected experimentally. The disappearance of this state for the R model supports the spin-paired structure.

Additional support for the spin-paired structure is provided by the comparison between recent high-resolution low-temperature STM data [11] and simulations, as shown in Fig. 5. Both models clearly account for the $\times 2$ and $\times 3$ periodicities observed experimentally for voltages of 0.7 V. These periodicities are due to the Au chain dimerization and the Si$_{3} \times 3$ atoms that stand out structurally and electronically. For biases
close to the Fermi level, at 0.2 V, however, the measurements show a ×6 periodic structure reminiscent of “bones” linked by bright “joints” (see labels in Fig. 5). Aulbach et al. [11] suggest these features to be related to the parity breaking of the Si step edge due to the Au dimers. This interpretation is corroborated by the present calculations, as shown schematically in Fig. 3(b): The charge accumulation in the Au dimers affects the electron localization at the Si step-edge atoms in their vicinity. This effect increases with increasing dimerization. Therefore it should be more pronounced and better visible for the R than for the SC model. This is in fact what can be clearly seen in the simulated STM images. The experiment at intermediate voltages corresponds roughly to a superposition of the low and high tunneling bias appearance: The bones and joints are still visible, while the Si$_{3}$-$\lambda$ atoms start to become prominent, but with different intensities (“darker” and “brighter spots” in Fig. 5). This intensity variation is again excellently reproduced by the simulations based on the diamagnetic surface, but not accounted for by the spin-chain model. This shows that the ideal Si(553)-Au surface—considered a prototypical example for intrinsic magnetism at silicon surfaces—is in fact diamagnetic: The present calculations demonstrate that a structure, where all Si dangling bonds either host spin-paired electrons or are empty, is more favorable and in better agreement with experiment than antiferromagnetically ordered spin chains. The electron affinity of the Au chain in conjunction with the energy release upon depopulating the Si $p$ orbitals quenches the magnetism. The shallow potential energy surface of Si(553)-Au in conjunction with the existence of evenly placed Si empty dangling bonds, however, suggest the Si(553)-Au as a promising candidate for the creation of surface spins by nanostructure engineering. In particular, Si adsorbate-induced electron doping [37–39] can be expected to induce intrinsic magnetism at Si(553)-Au. Also, an enhanced spin-spin interaction resulting from smaller dangling bond distances as well as a reduced Au coverage—both realized, e.g., at Si(557)-Au—may shift the energy balance in favor of intrinsic magnetism. In fact, our PBEsol calculation for Si(557)-Au indicates a slightly reduced energy gain upon rehybridization compared to Si(553)-Au: We calculate a reduction from 68 to 43 meV per rehybridized Si surface atom. At the same time, the energy gain due to spin polarization increases considerably from 13 to 56 meV per surface spin. Thus, at least within DFT-PBEsol, the spin-chain structure proposed by Erwin and Himpsel is stable for Si(557)-Au, in contrast to the present findings for Si(553)-Au.

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