Atomic and electronic structures of Si(111)-(\(\sqrt{3}\times\sqrt{3}\))R30°-Au and (6x6)-Au surfaces

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Si(111)-Au surfaces with around one monolayer of Au exhibit ordered structures and structures containing disordered domain walls. Atomic and electronic structures of Si(111)-Au surfaces with \((1\times1), (\sqrt{3}\times\sqrt{3})R30^\circ, (\sqrt{2}\times\sqrt{2})R30^\circ\) and \((6x6)\) unit cells and a supercell with a domain wall are investigated using hybrid density functional theory. The \(\sqrt{3}\)-Au surface is metallic and has a large density of states at the Fermi level. Si adatoms adsorbed on the \(\sqrt{3}\)-Au surface induce a gapped surface. The metallic character of the \(\sqrt{3}\)-Au surface arises from a strongly dispersing quasi-particle state whose orbital character is identified. Adsorption of extra Au atoms in interstitial sites of the \(\sqrt{3}\)-Au surface is stabilized by interaction with these orbitals and leads to higher coverage ordered structures including the (6x6)-Au phase. Extra Au atoms bound in interstitial sites of the \(\sqrt{3}\)-Au surface result in top layer Si atoms with an SiAu4 butterfly wing configuration. The structure of a (6x6)-Au phase, whose in-plane top atomic layer positions were previously determined by an electron holography technique [Grozea et al. Surf. Sci. 418, 32 (1998)], is calculated using total energy minimization. The Patterson function for this structure is calculated and is in good agreement with data from an in-plane x-ray diffraction study [Dornisch et al. Phys. Rev. B 44, 11221 (1991)]. Filled and empty state scanning tunneling microscopy (STM) images are calculated for domain walls and the (6x6)-Au structure. The (6x6)-Au phase is 2D chiral and this is evident in computed and actual STM images. The (6x6)-Au and domain wall structures contain the SiAu4 motif with a butterfly wing shape. Chemical bonding within the Si-Au top layers of the \(\sqrt{3}\)-Au and (6x6)-Au surfaces is analyzed and an explanation for the SiAu4 motif structure is given.

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I. INTRODUCTION

Adsorption of Au on the Si(111) surface up to 1 monolayer (ML) Au coverage leads to the \((5x2)\)-Au[1–5] and \((\sqrt{3}\times\sqrt{3})R30^\circ\)-Au[6–11] surface reconstructions, which have been extensively studied experimentally and also using density functional theory (DFT) [12–16]. The Si(111)-Au system is particularly complex, especially as the Au coverage reaches 1 ML. The \(\alpha\sqrt{3}\)-Au phase, which forms initially below 1 ML Au coverage [17], transforms into \(\beta\sqrt{3}\)-Au [10, 11] and (6x6) [7, 18–21] phases as the coverage increases further. Scanning tunneling microscopy (STM) has shown that the \(\alpha\sqrt{3}\)-Au surface contains a dense network of domain walls [8, 10, 22, 23]. Additional periodicities including \((2\sqrt{3}\times2\sqrt{3})R10.9^\circ\)-Au and \((3\sqrt{3}\times3\sqrt{3})\)-Au phases above 1 ML coverage [23, 24] have also been observed by STM. The ground state of the Si(111)-Au surface in the range 1.1 to 1.4 ML coverage appears to be the (6x6)-Au phase [20, 25]. A surface displaying a \(\beta\sqrt{3}\)-Au low energy electron diffraction (LEED) pattern with an Au coverage of around 1 ML was heated from room temperature to 923K [10]. A LEED spot profile analysis and STM showed that at 893K the surface consists of large \(\sqrt{3}\)-Au domains and that quench cooling resulted in recovery of the \(\beta\sqrt{3}\)-Au phase while slow cooling resulted in formation of a (6x6) phase. The (6x6) structure has been interpreted as a domain wall crystal and the \(\beta\sqrt{3}\)-Au phase as a domain wall glass by Nagao and coworkers [10], while Grozea and coworkers [20] interpreted the (6x6) structure as a glass containing pseudo-pentagonal, five-membered Au rings.

Recent work has shown that a range of adsorbates, notably In, adsorbed on Si(111)-Au surfaces can transform the \(\alpha\sqrt{3}\)-Au surface with a disordered domain network into a structure which is nearly free of domain walls [16, 26–31]. The coverages of these adsorbates, which include In [16, 26–29], Tl [29], Na [29, 30] and Cs [29], are typically in the range 0.1 to 0.15 ML.

The Si(111)-Au system has been extensively studied by angle resolved photoelectron spectroscopy (ARPES). The Fermi surface of the (5x2)-Au system has been studied by ARPES [32, 33]. Adsorption of Si on top of the (5x2)-Au surface has been shown by scanning tunneling spectroscopy (STS) to yield a gapped state [34–36]. Early ARPES measurements on Si(111)-Au systems with around 1 ML Au coverage were carried out on the \(\alpha\sqrt{3}\)-Au and \(\beta\sqrt{3}\)-Au states [11, 37] whose disordered domain walls limit quasi-particle lifetimes and ARPES peak widths. When ARPES is performed after adsorbates which remove domain walls have been deposited and annealed, a sharp quasi-particle feature close to the Fermi level is observed [27, 29, 30].

The conjugate honeycomb chain trimer (CHCT) structure [12] (Fig. 1) is the fundamental short range order in the \(\sqrt{3}\)-Au structure. A honeycomb Au-trimer structure at the Si(111)-Au surface was initially found by low energy alkali ion scattering [6] and medium energy ion scattering (MEIS) [38] and more precise measurements of the local Au arrangement were later made using x-ray standing waves [8, 9]. The CHCT structure contains Si\(_5\)Au\(_3\) triangles which bond to the underlying Si bulk via Si atoms in the top layer and which bond to each other through interaction between Si atoms at apexes of
Si$_3$Au$_3$ triangles and Au atoms in adjacent triangles (Fig. 1). There are two possible orientations of the CHCT layer on the Si(111) surface. Centers of Si$_3$Au$_3$ triangles may be located over an Si atom in the top bilayer of bulk Si (a T$_4$ site) or over an Si atom in the second bulk bilayer (an H$_3$ site). One structure transforms into the other if the top layer is rotated by $\pi$ and there is a shift in registry of $2/\sqrt{3}$ in the [112] direction (in units of the (1x1) surface lattice constant).

Beginning from a (1x1) structure, displacements of bonded pairs of Si and Au atoms along bond directions in the coherent fashion shown in Fig. 1 lead to formation of a $\sqrt{3}$-Au structure in which small Au$_3$ triangles are part of larger Si$_3$Au$_3$ triangles centered over T$_4$ sites of the Si(111) bulk lattice. The CHCT structure adopted by Si(111)-Au surfaces differs from the honeycomb chain trimer (HCT) structure adopted by Si(111)-Ag surfaces around 1 ML coverage in a $\sqrt{3}$-Ag structure [39]. In that case occupation of atomic sites in Si$_3$Ag$_3$ triangles is opposite to that in the $\sqrt{3}$-Au surface and there is a slight rotation of Si$_3$Ag$_3$ triangles to give an inequivalent triangle (IET) structure. This reversal of site occupation can be understood in terms of displacements of Si-Ag atomic pairs in the opposite sense to displacements shown in Fig.

1. Previous DFT calculations on the $\sqrt{3}$-Au system [14–16] have considered variations in total energies of HCT and CHCT structures over T$_4$ sites and found the difference to be small (0.05 eV Ref. [15], 0.083 eV Ref. [16]) with the CHCT structure favored. In this work the energy difference between CHCT structures with Si$_3$Au$_3$ triangles over T$_4$ versus H$_3$ sites was found to be 0.26 eV per $\sqrt{3}$-Au unit cell, with the T$_4$ site favored.

The remainder of this paper is organized as follows: firstly the electronic structure of the hypothetical (1x1)-Au surface is considered. Relaxation of the (1x1)-Au phase to the $\sqrt{3}$-Au structure results in a reduced Fermi surface length and a more stable structure. Dispersion of a quasi-particle state found in hybrid DFT calculations is in excellent agreement with recent ARPES data [29]. The change in electronic structure of the $\sqrt{3}$-Au unit cell when Si adatoms are adsorbed over the interstitial sites between Si$_3$Au$_3$ triangles is investigated. The quasi-particle state on the adatom-free $\sqrt{3}$-Au surface is extinguished by adatoms, leaving a gapped surface electronic structure.

Creation of H$_3$ domain walls between T$_4$ $\sqrt{3}$-Au domains and insertion of extra Au atoms into interstitial sites between Si$_3$Au$_3$ triangles are two ways of increasing Au coverage above 1 ML in the $\sqrt{3}$-Au structure. The relative stability of H$_3$ domain walls between T$_4$ domains and chains of Au atoms inserted into a T$_4$ $\sqrt{3}$-Au monodomain is estimated using calculations on large supercells.

The structure of the (6x6)-Au phase is determined using total energy minimization calculations on the structure obtained by Grozea and coworkers by an electron holography technique [20]. Experimental data for in-plane positions of top layer Si and Au atoms are available and hybrid DFT calculations presented here allow z heights to be determined. The Au coverage for this structure ranges from 1.16 to 1.25 ML, depending on filling of sites which have been found to have partial occupancy [20, 21], and is consistent with experimental estimates for the coverage in the (6x6)-Au phase, which range from 1.1 to 1.4 ML [20, 25]. The Patterson function is calculated for this relaxed structure at a z height of 0.0 Å and found to be in agreement with the Patterson function for this surface determined from in-plane x-ray diffraction measurements [18]. All of the structures which contain Au atoms added to the $\sqrt{3}$-Au T$_4$ structure contain a common SiAu$_4$ structural motif. This is a five-coordinate Si atom with four Au neighbors in the top layer in a butterfly wing shape and one Si atom in the layer underneath the top layer.

II. COMPUTATIONAL DETAILS

All self-consistent field calculations were performed using the Crystal program [40] and a modified B3LYP hybrid DFT functional described in Ref. [41]. The all-electron basis set used for Si in all cases (except the (6x6)

![FIG. 1: (Color online) Top panel (left) (1x1) unit cell showing Au displacements which lead to a ($\sqrt{3}$x$\sqrt{3}$)R30° unit cell. (right) Equilibrium structure of ($\sqrt{3}$x$\sqrt{3}$)R30° unit cell showing Si$_3$Au$_3$ triangles in the CHCT structure. Bottom panel (left) Reciprocal lattice points and primitive lattice vectors for the (1x1) (blue) and ($\sqrt{3}$x$\sqrt{3}$)R30° (red) reciprocal space unit cells. (right) Fragment of (6x6) structure showing that Au atoms inserted into the ($\sqrt{3}$x$\sqrt{3}$)R30° unit cell (enlarged blue circles) form SiAu$_4$ butterfly wing configurations (circled). Au atoms (blue spheres), top layer Si atoms (red spheres), lower layer Si atoms (grey spheres).]
unit cell) is described in Ref. [42]. Calculations on the (6x6) system used the ECP10MWB pseudopotential [43] together with the four outermost sp and d shells of the basis in Ref. [42]. The basis set and pseudopotential for Au is a version of the Hay-Wadt small core pseudopotential and basis [44] for Au modified by Weihrich and Anusca [45]. Back surfaces of slabs used in this work were terminated by pseudo-hydrogen atoms. The pseudo-H atom basis set and Si-H distance were modified so that Mulliken populations of Si atoms at the H-terminated surface were close to the bulk value.

Slabs used for surface electronic structure calculations contained Si/Au top layers and between 3 and 6 Si bulk bilayers. All atom positions in slab unit cells, with the exception of terminating H atoms and their Si nearest neighbors, were allowed to relax in energy minimization calculations. Slabs with a (1x1) or (5x√3)R30° unit cell used for projected band structure calculations had 6 bulk bilayers and the (5x√3) slab used to obtain the projected band structure calculation for the domain wall had 4 bulk bilayers. The slab used for determination of the structure of the (6x6) phase had 3 bulk bilayers. A (6x6) Monkhorst-Pack net [46] of k-points was used for all self-consistent field calculations.

Densities of states (DOS) and dielectric susceptibilities were calculated using the Exciton code [47] using a 24 x 24 grid of points in the surface Brillouin zones (SBZ) for the (1x1) and (5x√3)R30° unit cells, a 10 x 30 grid for the (5x√3) domain wall supercell and a 10 x 10 grid for the (6x6) unit cell. The Exciton code [47] was also used to calculate projected band structures, surface state wave function plots and simulated STM images using Bloch functions and energy eigenvalues from Crystal calculations. Simulated STM images were generated by plotting |Ψ|^2 in a plane 4 Å above the top atomic layer. A Gaussian filter, centered at the sample bias potential with respect to the Fermi energy and of width 0.1 eV, was applied to the density matrix to generate these plots.

The VESTA code [48] was used to display atomic structures and to calculate the Patterson function for the (6x6) structure using superposed atomic Au and Si electron densities.

III. RESULTS

A. Instability of the (1x1)-Au phase

The atom-projected band structure of the (1x1)-Au phase is shown in Fig. 2. The surface band structure in the ΓM direction consists of a strongly dispersing surface state band, which disperses down from the Γ point and crosses the Fermi level and another band, which remains in the conduction band energy range. There are two downward dispersing surface state bands in the ΓK direction which cross the Fermi level. The top of the Au 5d band lies just above -5 eV. The Fermi surface is approximately a circle centered on the Γ point and others centered on \( \overline{K} \) points of the SBZ.

FIG. 2: (Color online) Atom-projected band structure for the T\(_4\) (1x1) surface structure. Symbol sizes reflect the degree of localization on surface atoms. Red circles top layer Si, blue squares Au. Surface projected bulk Si bands are shown as grey shading.

The large Fermi surface of the (1x1)-Au phase is unstable and a (5x√3)R30° supercell with Au in (1x1) sites relaxes to the CHCT structure shown in Fig. 1. Removal of a pair of electrons from the T\(_4\) CHCT relaxed structure unit cell results in lifting of the \( \sqrt{3} \)-Au reconstruction and relaxation back to the (1x1)-Au structure.

B. (5x√3)R30°-Au phase

The atom-projected band structure for the T\(_4\) \( \sqrt{3} \)-Au structure is shown in Fig. 3. A surface state disperses sharply upward from Γ to K and another surface state just crosses the Fermi level in the middle of the ΓK direction. Similar dispersions are found for these states in the ΓM direction. Two occupied surface states exist on the SBZ boundary between K and M. Moduli squared for these surface states are shown in Fig. 4. An early ARPES study [11] of this system showed a state denoted S\(_1\) dispersing strongly upward from the Γ point along the ΓM direction. The S\(_1\) state was 0.3 eV below the Fermi level at the Γ point. That study used the \( \alpha\sqrt{3} \)-Au phase which has a high domain wall density. Domain walls limit quasi-particle mean free paths and therefore experimental observation of this state. The calculated band structure closely matches that observed in more recent ARPES measurements [29] where domain wall density is very low owing to coadsorption of 0.15 ML of In. The
The experimentally measured surface state dispersion is also indicated in Fig. 3. The Fermi level in this experimental data lies about 0.5 eV above the Fermi level in this work. The sample in the experimental work was n-type [29].

\[ dp - \pi \] bonding character of the strongly dispersing quasi-particle surface state at \( \Gamma \) can clearly be seen in Fig. 4 between the Au atom in one \( \sqrt{3} \) triangle and an Si atom in a neighboring triangle - not within an \( \sqrt{3} \) triangle. \( \sigma \) bonding character between Si and Au atoms in neighboring triangles can be seen in the surface state wave function \( M_1 \). \( \sigma \) bonding character between Si and Au atoms within triangles can be seen in the surface state wave function at \( M_2 \). The \( M_1 \) state has a higher energy than the \( M_2 \) state. They correspond to states denoted \( S_2 \) and \( S_3 \) in Ref. [11]. The Si-Au distance within an \( \sqrt{3} \) triangle is 2.44 Å while it is 2.40 Å between Si and Au in neighboring triangles, showing that the strongest interactions between top layer Si and Au atoms are between those in neighboring triangles, not within triangles. The character of surface states is mainly Si 3s and 3p with a lesser participation of Au 5d states in surface state bands within 2 eV of the Fermi level.

The \( \sqrt{3} \)-Au unit cell contains an even number of electrons and since the system is metallic (because of the quasi-particle state dispersing upwards from \( \Gamma \)), more than one band must cross the Fermi level. Fig. 3 shows the \( S_2 \) and \( S_3 \) surface states dispersing upward in the \( \Gamma K \) and \( \Gamma M \) directions of the SBZ. These states cross the Fermi level over a small range of the SBZ so that the Fermi surface for the neutral system consists of three concentric rings about the \( \Gamma \) point. This is obviously an unstable state and any electron source is expected to fill the surface state bands which just cross the Fermi level. This would leave the quasi-particle band which disperses upward from \( \Gamma \) as the only partly filled band.

![FIG. 3: (Color online) Atom-projected band structure for the \( \sqrt{3} \)-Au surface without (top) and with (bottom) a Si adatom. Symbol sizes reflect the degree of localization on surface atoms. Red circles top layer Si, blue squares Au, black circles Si adatoms. Surface projected bulk Si bands are shown as grey shading. ARPES data redrawn from Fig. 2 of Ref. [29] are shown as hollow squares.](image)

![FIG. 4: (Color online) Modulus squared of surface states at the \( \Gamma \) and \( M \) points of the SBZ for the \( \sqrt{3} \)-Au surface. Red spheres (Au atoms), blue spheres (top layer Si atoms), grey spheres (second layer Si atoms).](image)

The need to fill partly filled surface states \( S_2 \) and \( S_3 \) in the \( \sqrt{3} \)-Au phase to achieve a stable electronic structure may explain the tendency for domain walls to form in the...
Orbitals of the quasi-particle surface band (shown at the \( \Gamma \) point in Fig. 4) are 2\( p \) orbitals localized mainly on Si atoms which are oriented towards centers of interstitial sites between Si\( _3 \)Au\( _3 \) triangles. Adding electron donor Au atoms to interstitial sites allows electrons to be transferred to surface states. Strong interaction between Au atoms and these orbitals results in the SiAu\( _3 \) butterfly wing motif observed in all structures with Au coverages exceeding 1 ML.

C. Domain walls and interstitial Au atoms

STM images of the Si(111)-Au surface with around 1 ML Au coverage exhibit dense networks of features which zig-zag across the surface in [11\( \sqrt{2} \)] directions and subtend angles of 2\( \pi \)/3 at three-fold junctions [26]. These features, generally called domain walls, tend to avoid crossing but may form closed loops [7, 8, 23, 26] and have a (2x\( \sqrt{3} \)) local structure [26]. Fig. 1 in Ref. [26] shows a clear mirror symmetry about the center of the domain wall while Fig. 2 in Ref. [8] shows zig-zag chains which lack mirror symmetry about the wall centers. The appearance of domain wall features in STM does, of course, depend on sample bias, tip shape, etc. Some reports of these STM images note a shift of registry of the top layer of atoms across domain walls with a shift vector of \( a_0/\sqrt{2} \) in the [1\( \bar{1} \)0] direction [7, 49], where \( a_0 \) is the bulk lattice constant. These have been interpreted as boundaries between \( T_4 \) domains separated by chains of Si\( _3 \)Au\( _3 \) triangles centered over H\( _3 \) sites [8, 23, 26].

FIG. 5: (Color online) Atomic configurations around a \( T_4 H_3 T_4 \) domain wall and a row of extra Au atoms in a \( \sqrt{3} \)-Au monodomain. Dotted lines outline the domain wall and extra row of atoms. (Left panel) Displacements of Au atoms from (1x1) sites (indicated by arrows) lead to formation of \( T_4 \) Si\( _3 \)Au\( _3 \) triangles in two domains. A domain wall exists because the coherent displacements to the right of the wall are shifted with respect to those on the left by the vector indicated by the red arrow. A vertical chain of Si-Au bonds exists on the domain wall. The Au at the site marked A and at equivalent sites in the wall are replaced by a triple of Au atoms centered over H\( _3 \) sites and indicated by large blue circles. (Right panel) Zig-zag line of Au atoms (shown as large blue circles) inserted into interstices in a \( \sqrt{3} \)-Au monodomain. Au atoms in interstices cause adjacent Si atoms to have four Au neighbors in a butterfly wing configuration.

Domain walls in the \( \sqrt{3} \)-Au phase must exist because coherent patterns of atomic displacements illustrated in Fig. 1 can lead to one of three possible domains. Shifts of origin by \( a_0/\sqrt{2} \) along [1\( \bar{1} \)0] or [01\( \bar{1} \)] directions generate two other domains. The structure of a \( T_4 H_3 T_4 \) domain wall (i.e. \( T_4 \) domains separated by a continuous line of H\( _3 \) Si\( _3 \)Au\( _3 \) triangles), as suggested by Falta and coworkers [8], is shown schematically in the left panel of Fig. 5. The vector generating the \( a_0/\sqrt{2} \) shift of origin of the domain on the right is shown as a red arrow. Displacements of Au atoms at domain edges lead to broken Si-Au bonds, where the Si is located in the center of the wall. Replacement of Au atoms located in the center of the wall by Au triples, around the site marked A and equivalent sites elsewhere in the wall, generates H\( _3 \) Si\( _3 \)Au\( _3 \) triangles in the wall.

A simulated STM image of the relaxed domain wall structure is shown on the left of Fig. 6. Si and Au atoms in H\( _3 \) triangles retain a nearly hexagonal configuration while those in \( T_4 \) triangles at the domain edge retain their usual shape. Each Si atom at each domain edge has four Au neighbors in a butterfly wing configuration. The simulated STM image is for a sample bias of +1.0 V. It shows V shaped bright features centred on Au atoms at the domain edge. These Au atoms are bonded to only two Si neighbors. Bright features in simulated STM images with positive sample biases are also found in the other structure in Fig. 6 where Au atoms are bonded to only two Si neighbors. These simulated STM image features have a local (2x\( \sqrt{3} \)) structure and resemble those reported by, e.g. Gruznev and coworkers [26], where the V shaped images were recorded with a sample bias of +0.8 V.

An alternative explanation for bright features in a ‘domain wall’ with no shift of origin is a line of Au atoms inserted into the \( \sqrt{3} \)-Au lattice. This structure is shown schematically in Fig. 5 and the relaxed structure and simulated STM image at a sample bias of 1.0 eV is shown in Fig. 6. This structure shows bright features in the simulated STM image on atoms in the \( T_4 \) domain adjacent to
inserted atoms, not the inserted atoms themselves. This shows that there is a high density of unoccupied states on these atoms 1 eV above the Fermi level. These atoms are bonded to two adjacent Si atoms only and resemble atoms which produce bright features in the domain wall in this way. Si atoms bonded to inserted Au atoms have four Au neighbors in a similar butterfly wing configuration to those in the $T_4H_3T_4$ domain wall.

Both domain walls and extra Au atoms inserted into a $T_4$ monodomain increase the Au coverage above 1 ML. In order to test the relative stability of inserted Au atoms versus domain walls, $(15x\sqrt{3})$ supercells containing either three domain walls or three zig-zag rows of extra Au atoms were set up and their structures were relaxed. This supercell size was chosen as insertion of three parallel domain walls results in a structure which is commensurate with one with no domain walls. Both supercells contained the same number of each atom type (including terminating pseudo-H atoms) and six more Au atoms than a $\sqrt{3}$-Au monodomain. The supercell with Au atoms inserted within the monodomain was 0.20 eV per inserted atom lower in energy than the supercell with three domain walls. This shows that insertion of extra Au atoms into monodomain areas is energetically more favorable than creation of domain walls as a way of increasing the Au coverage above 1 ML. The preponderance of domain walls observed in STM images is presumably due to nucleation and growth of small domains, which inevitably have domain walls. It is worth noting that the $(6x6)$-Au phase has only $T_4$ microdomains and no $H_3$ domains.

The electronic band structure for a $(5x\sqrt{3})$ supercell containing one domain wall, whose structure is shown in the left panel of Fig. 6, is shown in Fig. 7. There is one surface state band which is weakly dispersing and which is partly occupied and there are four strongly dispersing, unoccupied surface states which resemble the quasi-particle state dispersion in the monodomain $\sqrt{3}$-Au surface. Localization of these states on the $T_4$ domain region and on the $H_3$ wall region is indicated.

D. Si(111)-(6x6)-Au phase

Several ordered phases, including $(3\sqrt{3}x3\sqrt{3})$-Au [23], $(2\sqrt{11}x2\sqrt{11})R10.9°$-Au [23] and $(6x6)$ [7, 10, 11, 18, 20, 21, 50] structures have been reported in the literature for Au coverages above 1 ML. STM images of the latter structure [7, 10, 21, 25, 50] show small, bright triangular features with a $(6x6)$ periodicity. Estimates of the Au coverage of the $(6x6)$ phase range from 1.1 to 1.4 ML [25, 51]. Ordering and disordering of the $\alpha\sqrt{3}$-Au and $\beta\sqrt{3}$-Au phases with temperature has been studied by STM and LEED spot profile analysis[10]. At an Au coverage of 0.79 ML, LEED spot profile analysis showed that $(1/3, 1/3)$ diffracted beams, which are broad at room temperature, sharpen considerably on heating above 700 K and remain sharp up to 923 K. At 1 ML, annealing at 600 K followed by slow cooling to room temperature results in a $(6x6)$ pattern, while heating at 823 K and quench cooling results in a $\beta\sqrt{3}$-Au ring pattern in LEED. LEED evidence for an ordered state at high temperature and a disordered state on quenching was confirmed by STM [10].

The Si(111)-(6x6)Au structure may be the ground state for Au coverages above 1 ML. An early surface x-ray diffraction experiment [18] obtained the Patterson function for the $(6x6)$ phase, but models used to fit this data were not successful. A subsequent reanalysis of the data using so-called direct, electron holography methods [20] was successful in establishing a structure for the $(6x6)$ phase containing 42 Au atoms per unit cell. The structure was described as a pseudo-glass with short-range order but varying degrees of long-range order [20].

A schematic model for the structure of Grozea and coworkers is shown in Fig. 8. The $P_3$ symmetry structure which they refined can be rationalized as follows: each $(6x6)$ unit cell has three groups of four Au atoms inserted into the $(1x1)$-Au lattice in $Y$ configurations. Each Y is surrounded by three $Si_3Au_3$ triangles, indicated by Au displacement arrows in Fig. 8, which form local $T_4$ microdomains. The two $T_4$ microdomains centered on Y’s at (0,0) and (1/3, 2/3) would belong to the same domain, if the surface were covered by a $T_4$ monodomain. The $T_4$ microdomain centered on the Y at (2/3, 1/3) belongs to a different $T_4$ domain and its four Au atom Y is rotated.

![FIG. 7: (Color online) Atom-projected bandstructure for a $(5x\sqrt{3})$ unit cell containing a $T_4H_3T_4$ domain wall. Bands are plotted for dispersion in a direction corresponding to the $\Gamma$ and $\overline{\Gamma}$ directions of a monodomain $\sqrt{3}$-Au surface. Bands were projected onto Au atoms (blue squares), Si atoms in the domain wall (green circles) and in the $T_4$ domain (red circles).](image-url)
by \( \pi \) with respect to the other Y’s in the unit cell. Each four Au atom Y and adjacent Si\(_3\)Au\(_3\) triangles are connected to its three neighbors by a bridging Au atom. In Fig. 8 these are the atoms in ideal (1x1) positions. They occur as three pairs of Au atoms (marked P) and three single Au atoms (marked S). One of each pair, P, of these atoms is removed, allowing Si dimers to form. Note that this structure is 2D chiral and that the choice of primitive cell vectors in this work results in the opposite chirality to that shown in Ref. [20].

Grozea and coworkers reported 14 independent sites in the \( P_3 \) structure [20], giving 42 Au atoms per unit cell overall. Au sites at (0, 0), (1/3, 2/3) and (2/3, 1/3) positions, which are included in Fig. 8 and our DFT calculations, were found to have an occupancy of about 0.5 [20] and are not included in the list of 14 sites in Ref. [20]. There are 45 Au atoms in the unit cell in Fig. 8, including the sites with partial occupancy, and the Au coverage is 5/4 ML.

In-plane coordinates from Table 1 in Ref. [20] were used in a DFT energy minimization calculation for the (6x6) structure. The slab unit cell had three Si bilayers, Si and Au top layers and terminating pseudo-hydrogen atoms. Bottom Si layer and pseudo-hydrogen atom positions were held fixed in the relaxation process. Relaxed atom coordinates are given in Supplementary Information. The structure is shown in Fig. 9, where Si-Si, Si-Au and Au-Au bonds are highlighted separately. Si atoms are colored green or red, depending on whether they belong to Si dimers or not. Au atoms which are inserted into a (1x1)-Au lattice in the manner shown in Fig. 8 are enlarged in Fig. 9. Panel (a) of Fig. 9 shows Si-Au bonds.

![Figure 8](image1)

**FIG. 8:** (Color online) Model structure for the Si(111)-(6x6)Au structure after Grozea et al. [20]. Three triangular groups (Y’s) of four Au atoms (indicated by large blue circles) are inserted into each (6x6) unit cell with a 1 ML Au coverage (indicated by small blue circles), resulting in an Au coverage of 4/3 ML. Si\(_3\)Au\(_3\) triangles form T\(_4\) microdomains around the added atoms as indicated by Au displacement arrows. Nine Au atoms which are originally in (1x1) positions remain and occur as pairs, marked P, or single atoms, marked S. One Au atom is removed from each pair, P, leaving 45 Au atoms per unit cell and a net coverage of 5/4 ML.

![Figure 9](image2)

**FIG. 9:** (Color online) Plan view of the top layers of the (6x6) structure showing various interatomic contacts. The (6x6) unit cell is also shown. Top layer Si atoms in Si dimers (small green spheres), top layer Si atoms not in dimers (small red spheres), top layer Au atoms (blue spheres), top layer Au atoms in Y’s (large blue spheres), second bilayer Si atoms (small grey spheres). (a) Si-Au contacts up to 2.65 Å. (b) Si-Au contacts up to 2.65 Å and Si in dimers. (c) Au-Au contacts up to 2.80 Å. (d) Au-Au contacts up to 3.05 Å.
bonds. 27 Si atoms in the top layer belong to a Si$_3$Au$_3$ triangle and 9 Si atoms do not. Panel (b) shows Si-Au bonds where the Si atom is not part of a Si dimer and Si dimer bonds. Viewed in this way, the (6x6) structure consists of a Y of Au atoms at the (2/3, 1/3) position which is surrounded by Si dimers and two Y’s (at (1/3, 2/3) and (0, 0) positions) which form $2\pi/3$ junctions in a continuous ‘domain wall’. In this case, the domain wall is composed of connected chains of SiAu$_4$ units in the butterfly wing configuration also found in H$_3$ domain walls in Fig. 6. Panel (c) shows Au-Au contacts where the bond length is less than or equal to 2.80 Å as well as Si dimers. Panel (d) shows Au-Au contacts where the bond length is up to 3.05 Å. The interatomic distance in bulk Au is 2.88 Å. Panel (d) shows pentagonal Au rings with adjacent Si$_3$Au$_3$ triangles, referred to as a pseudo-pentagonal glass in Ref. [20].

Simulated STM images of the (6x6) structure (Fig. 10) show bright features associated with Au Y’s (large blue circles) in Fig. 9. Au atoms at the (0, 0), (1/3, 2/3) and (2/3, 1/3) positions sit 0.2, 0.1 and 0.3 Å higher than the mean height of the other Au atoms. The bright feature in the top panel coincides with the Au atom at the (2/3, 1/3) position and its three Si nearest neighbors. The Au atom at the (1/3, 2/3) position and its Si nearest neighbors can also be seen in this image. Bright features in the lower panel, which shows an occupied state image, are found on Si atoms neighboring the Au atom at the (2/3, 1/3) position and nearby Si atoms. A spiral feature in the other half of the unit cell is centered on the (1/3, 2/3) position. Comparing these simulated images with published STM images for the (6x6) structure, we find that image recorded with a bias voltage of -0.8 V shows similar small, bright features [7]. Fig. 3 in Ref. [21] shows similar small, bright features in an occupied state image recorded with a bias voltage of +0.8 V. The authors of that work label sites A, B and C, which correspond to the (0, 0), (1/3, 2/3) and (2/3, 1/3) positions in this work. Sites A and C have Y’s with the same orientation and the Y at site B is rotated by $\pi$ with respect to sites A and C. Whether one of these sites appears bright or dark will depend on whether the Au atom at the center of the Y is present or not (Grozea and coworkers [20] estimated the occupancies of these sites to be 0.5). By counting on a large area STM image, Higashiyama and coworkers [21] found these positions to be 1/3 filled. Fig. 4b in Ref. [21] shows an empty state image recorded with a bias voltage of +1 V which shows spiral features similar to those for a filled state image in Fig. 10. The 2D chirality of both computed and experimental images is evident. The authors of Ref. [21] did not state whether the bias voltage referred to the tip or sample. The calculated and experimental results agree well if the voltages refer to tip bias in the experiment.

The Patterson function for the (6x6) structure has been measured by in-plane x-ray diffraction [18]. Only superstructure reflections were included in the analysis of this data and only differences from the (1x1) structure are observed [18]. Consequently a contour plot of the Patterson function has positive and negative features. More generally, Patterson functions have the same...
period as the crystal unit cell, are positive definite and contain peaks at interatomic distances. A contour plot of the Patterson function calculated using the structure shown in Fig. 9 for a $z = 0.0$ Å is compared to the Patterson function from x-ray diffraction in Fig. 11 and a surface plot of the function is shown in Supplementary Information, Fig. 1. Peaks appear at bond lengths between atoms which are approximately at the same $z$-height in the unit cell. Since x-ray scattering by heavier Au atoms is much stronger than scattering by Si atoms, the peaks in the function mainly indicate in-plane Au-Au distances.

**TABLE I:** Peak positions in the Patterson function for the (6x6) structure at $z = 0$ Å and corresponding interatomic separations.

<table>
<thead>
<tr>
<th>Peak positions</th>
<th>Origin</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1/6, 1/6), (1/6, 0)</td>
<td>Au in small triangles 2.9 Å apart (0, 1/6) (1 in Ref.[18] and Fig. 11)</td>
</tr>
<tr>
<td>(1/6, 1/3), (1/3, 1/6)</td>
<td>$\sqrt{3}$ distances in $T_4$ regions</td>
</tr>
<tr>
<td>(1/6, 5/6), (5/6, 1/6)</td>
<td>(2 in Ref.[18] and Fig. 11)</td>
</tr>
<tr>
<td>(2/3, 5/6), (5/6, 2/3)</td>
<td></td>
</tr>
<tr>
<td>(1/3, 1/3), (1/3, 0)</td>
<td>Au in $Y$'s and neighboring $T_4$ regions (0, 1/3) (Unmarked in Ref.[18])</td>
</tr>
<tr>
<td>(1/3, 2/3), (2/3, 1/3)</td>
<td>$2\sqrt{3}$ distances between $Y$ centers (A in Ref.[18] and Fig. 11)</td>
</tr>
<tr>
<td>(1/6, 2/3), (2/3, 1/6)</td>
<td>Centers of $Y$'s to neighboring $Y$ edges (1/6, 1/2), (1/2, 1/6) (1/3, 1/2), (1/2, 1/3) (1/3, 5/6), (5/6, 1/3) (1/2, 5/6), (5/6, 1/2) (1/3, 1/3), (2/3, 2/3)</td>
</tr>
</tbody>
</table>

Strong features in the simulated Patterson function in Fig. 11 and their corresponding interatomic separations are summarized in Table I. The strongest features are six peaks at approximately (1/6, 1/3) and equivalent positions, which correspond to distances between Au atoms in small triangles in one $T_4$ microdomain, labelled 2 in Ref. [18]. The next most important features are peaks at (1/3, 2/3) and (2/3, 1/3) which correspond to distances between Au atoms at centers of neighboring Y’s. These are labelled ‘A’ in Ref.[18], where they are surrounded by six additional features with positive and negative contours in a hexagonal pattern. These features correspond to peaks at (1/6, 2/3) and equivalent positions. They correspond to distances between the Au atom at the center of a $Y$ and those on the periphery of neighboring Y’s.

There are additional features in the (6x6) Patterson function, notably at (1/3, 1/3) and features labelled 3 and 4 in Fig. 11. Grozea and coworkers used a technique in which atomic positions are determined iteratively. Presumably atoms in positions which are most strongly correlated appear at earliest iterations. The initial cluster of atoms found by this technique contained 20 Au atoms (Fig. 2a, Ref. [20]). 13 of these Au atoms are the four atoms in the $Y$ at the unit cell origin plus the 9 nearest Au in the associated $T_4$ microdomain. These additional features are also present in the calculated Patterson function and mainly arise from interatomic distances within the 13 atom Au cluster around $Y$’s.

**E. Densities of states and optical transitions**

Atom-projected DOS and the imaginary parts of dielectric functions are shown in Figs. 13 and 14. All DOS are normalized to states per (1x1) surface unit cell area and so surface layer DOS can be compared directly. Slabs used for domain wall and (6x6) calculations contained fewer bulk Si layers (see Section II), hence there is a lower total DOS in these cases. The (1x1) phase has a peak in the surface layer DOS around -1.5 eV which corresponds to the minimum of the strongly dispersing surface states at the $M$ and $K$ points of the SBZ (Fig. 1). This peak is broadened in the $\sqrt{3}$-Au and $\sqrt{3}$-Au Si adatom surfaces. The large DOS at the Fermi level of the $\sqrt{3}$-Au phase is removed by adsorbing a 1/3 ML of Si adatoms.

The electronic structure and DOS of the Si(111)-Au system in the ideal (1x1) structure is that of a metal with a Fermi surface containing two circles in the SBZ centered on the $\Gamma$ and $K$ points. Fig. 13A shows that it has a large DOS at the Fermi level owing to the strongly dispersing bands which define the Fermi level (Fig. 2). Once this structure has relaxed to the $\sqrt{3}$-Au structure, the DOS at the Fermi level increases more than two-fold. One strongly dispersive surface state in the (1x1) phase is replaced by a surface state which just crosses the Fermi surface (Fig. 3) in the $\sqrt{3}$-Au phase, leading to a strong increase in DOS at the Fermi level (Fig. 13B). Addition of an Si adatom above interstitial regions between Si$_3$Au$_3$...
triangles results in opening of a band gap of 0.4 eV (Fig. 13C).

Creation of a $T_4H_3T_4$ domain wall between $\sqrt{3}$-Au domains results in a nearly dispersionless band which contains the Fermi level and a corresponding peak in the surface layer DOS (Fig. 13D). There are also several unoccupied, strongly dispersive bands in this system which are localized on either the $T_4$ domain or $H_3$ wall regions. There is a marked change in electronic structure on going from the linear $T_4H_3T_4$ domain wall (Fig. 7) to the complex, intersecting domain wall structure of the $(6x6)$ phase (Fig. 9). Strongly dispersing surface states in the domain wall are replaced by weakly dispersing surface states in the $(6x6)$ phase which are delocalized over the whole surface.

The DOS for the $(6x6)$ phase (Fig. 13 E and F) is dominated by surface states in the energy range between -0.7 eV and 1.0 eV. The DOS is projected onto Au and Si atoms in $T_4$ microdomains, Au Y’s, Au bridging atoms, Si dimers and Si atoms which do not belong to one of the $T_4$ microdomain regions. The DOS shows that these surface states are strongly delocalized over the surface layer within 1 eV of the Fermi level. Measurements of the surface conductivity of the $\beta\sqrt{3}$-Au and $(6x6)$ phases showed weakly activated hopping conductivity in these phases at low temperature [50]. A fit to data showed activation energies of 0.45 and 1.1 meV for the $(6x6)$ and $\beta\sqrt{3}$-Au phases, respectively.

Imaginary parts of dielectric functions in Fig. 14, calculated using interband transitions only, show a marked increase in optical conductivity at low energy on going from the $\sqrt{3}$-Au phase with 1 ML Au to the domain wall and $(6x6)$ phases, which have more than 1 ML Au. As noted above for the DOS in Fig. 13, the slabs used for the domain wall and $(6x6)$ slabs contained fewer layers of bulk Si than the $\sqrt{3}$-Au slab. Consequently the dielectric function above the bulk Si optical band gap energy (over 3 eV) is reduced for those slabs compared to the dielectric functions for the $\sqrt{3}$-Au slabs. However, the dielectric functions below 3 eV, which only have contributions from interband transitions between surface states, are directly comparable. The scale of the ordinate axis in Fig. 13 is adjusted appropriately for the thicker $\sqrt{3}$-Au and $\sqrt{3}$-Au Si adatom calculations.

The $\sqrt{3}$-Au-Si adatom phase is gapped. Removal of the Si adatoms from this surface leads to a metallic state, interband transitions in that system only begin around 0.4 eV. When the Au coverage is increased to 1.25 ML in the $(6x6)$ phase, interband transitions extend down to 70 meV and when it is increased further to 1.38 ML in the domain wall phase, the dielectric function diverges at
IV. DISCUSSION

In this section chemical bonding in the $\sqrt{3}$-Au and (6x6) structures is discussed and especially the local orbital arrangement which stabilizes the SiAu$_4$ butterfly wing atomic configuration that appears in all structures considered except $\sqrt{3}$-Au. Band structures presented in this work are compared to experimental data from ARPES.

Some insight into the local order in the Si(111)-Au system may be obtained by considering chemical bonding in Si$_3$Au$_3$ triangles and the SiAu$_4$ butterfly wing atomic configuration. At 1 ML coverage, the Si(111)-Au system contains one Si and one Au atom per (1x1) unit cell. Si atoms in the outer bilayer are bonded directly to Si atoms in the bilayer beneath, which requires one valence electron from each of these Si atoms, leaving three valence electrons per surface layer Si for bonding with Au atoms. Each Au atom contributes one valence electron so that there is a total of two valence electron pairs per top layer Si atom for bonding within that layer.

Au chemistry is dominated by Au(I) and Au(III) valence states [52]. Au(I) compounds are typically linear with a $d^9$ electronic configuration while Au(III) compounds are square-planar with a $d^5$ electronic configuration. AuCl$_3$ exists as a dimer in the gas phase [53] and in the solid state. A calculation on the AuCl$_3$ monomer using the Hamiltonian used in this work found three Cl $3s$ lone pairs and five Au $5d$ states to be the lowest-lying valence electron states. In addition, six Cl $3p$ orbitals donate electrons into vacant Au $6d$ orbitals forming $dp-\pi$ bonds and two further occupied molecular orbitals exist which constitute $\sigma$ bonds to Cl atoms.

The T ground state geometry of AuCl$_3$ is similar to that adopted by Au at the Si(111) surface. The T consists of an Si-Au-Si unit in one Si$_3$Au$_3$ triangle and the Si atom bonded to that Au atom (Fig. 15). Bond lengths and angles within the T are: 2.44 Å between Si and Au within an Si$_3$Au$_3$ triangle (bond length $a$ in Fig. 15) and 2.40 Å between Si and Au in neighboring triangles (bond length $b$). Si and Au in neighboring triangles. The bond angle within a triangle is 72° (bond angle $\alpha$). The bond angle subtended by an Au atom and Si atoms in neighboring triangles is 95° (bond angle $\beta$), very close to the 96° angle in AuCl$_3$. There are three surface states in $\sqrt{3}$-Au which are occupied or vacant in different parts of the SBZ. These are predominantly of Si 3p character. The state which disperses strongly across the Fermi level from the $\Gamma$ point is of Si 3p$_{x,y}$ character and in-plane Au 5d character. These states constitute $dp-\pi$ bonds between Au and Si in neighboring triangles.

Surface states which are most prominent around the $\overline{M}$ point of the SBZ are Si 3p$_{x,y}$ and in-plane 5d in character and correspond to bonds between Si and Au within one Si$_3$Au$_3$ triangle (Fig. 4).

Understanding the SiAu$_4$ butterfly wing unit is clearly a key to the structure of the Si(111)-Au system for coverages above 1 ML Au, and probably the (5x2)-Au phase at a coverage of 0.6 to 0.7 ML [5, 17] as well. Addition of Au atoms into interstitial sites leads to SiAu$_4$ units with the butterfly wing configuration, in each system studied in this work. The quasi-particle state in the $\sqrt{3}$-Au phase, which is filled at the $\overline{F}$ point of the SBZ but empty for most of the rest of the SBZ, has an in-plane Si 2p orbital (Fig. 4) which is ideally oriented to allow an Au atom inserted into an interstitial site to donate charge into the Si bonding network. Bond lengths between the Si atom at the center of an Si$_3$Au$_3$ unit and Au atoms within Si$_3$Au$_3$ triangles in the (6x6) structure average 2.52 Å (bond length $d$) and are longer than equivalent bond lengths in $\sqrt{3}$-Au (2.44 Å). Bond lengths to Au atoms in interstitial sites are short, averaging 2.42 Å (bond length $e$) and indicate a strong interaction with Au in interstitial sites. The Si-Au bond between the Au atom in one Si$_3$Au$_3$ triangle and the Si atom at the apex of an adjacent triangle is short (2.40 Å) in the $\sqrt{3}$-Au phase, but this becomes elongated to an average value of 2.61 Å in the (6x6) structure (bond length $e$). Hence insertion of extra Au atoms into interstitial sites disrupts the $dp-\pi$ bonding of the $\sqrt{3}$-Au phase. Bond angles at butterfly wing Si atoms in the (6x6) structure subtended by Au atoms within Si$_3$Au$_3$ triangles range from 67° to 75° (bond angle $\delta$). Compared with 72° in $\sqrt{3}$-Au, and those subtended by Au atoms in interstices range from 129° to 134° (bond angle $\delta$).

In the Erwin, Barke and Himpel (EBH) model [55] for the (5x2) phase, where the Au coverage is 0.6 ML,
Si atoms occur in silicene chains, or have three or four Au neighbors. Two of the four Si atoms which are not in silicene chains are in the SiAu4 butterfly wing configuration. The Kwon and Kang (KK) model [5] is formed by adding one more Au atom to the Au rich region of the EBH model to give an Au coverage of 0.7 ML. In this structure three of the four Si atoms which are not in the silicene chain are in the SiAu4 butterfly wing configuration.

Au coverages of the $\sqrt{3}$-Au, (6x6) and (5x$\sqrt{3}$) domain wall phases are 1.00, 1.25 and 1.38 ML, respectively. Insertion of Au atoms into interstitial regions in the (6x6) or (5x$\sqrt{3}$) domain wall phases increases the surface electron concentration and this is reflected in surface atom charge populations and metallic character of those phases. Si atoms in the top layer of the $\sqrt{3}$-Au phase have an excess electronic charge of 0.40 $e$ (according to a Mulliken population analysis) which is transferred from Au atoms. When Si adatoms are adsorbed, 0.20 $e$ of the excess charge on the three surface Si atoms is transferred to the adatom. In the (6x6) phase, top layer Si atoms have between 0.46 and 0.65 $e$ of excess charge and in the (5x$\sqrt{3}$) linear domain wall phase, surface Si atoms have an excess charge of between 0.37 and 0.50 $e$, with a monotonic increasing trend from the T4 domain region into the domain wall. This increased excess of about 0.1 $e$ per surface Si, when about 1/4 to 1/3 ML of Au is added in interstitial sites, is sufficient to yield a metallic state with delocalized surface states. The degree of metallicity, indicated by the imaginary parts of dielectric functions of (6x6) and domain wall phases at low energy, also increases substantially when Au atoms are inserted in interstitial sites.

Electronic structures of the clean $\alpha\sqrt{3}$-Au surface [11, 27, 37] and the $\alpha\sqrt{3}$-Au surface with various adsorbates [29, 30] have been determined by ARPES. Zhang and coworkers found four surface states for the $\alpha\sqrt{3}$-Au surface, which they denoted S1 to S4. The S1 state is a strongly dispersing state centered at the $\Gamma$ point, which they find to be 0.3 eV below the Fermi level and corresponds to the state illustrated at the $\Gamma$ point of the SBZ in Fig. 4. States S2 and S3 at the $M$ point are likely to be the states shown along the $\Gamma - M - \Gamma$ direction in Fig. 3 and labelled $M_1$ and $M_2$ in Fig. 4. Zhang and coworkers found the S4 state about 2 eV below the Fermi level at the $\Gamma$ point. Fig. 3 shows a surface state around this energy in the $\Gamma - M - \Gamma$ direction. Grain and coworkers [37] found the S1 state around the $\Gamma$ point of the SBZ to have a band minimum 0.32 eV below the Fermi level.

Zhang and coworkers also found eight dispersionless surface states at the (6x6) surface in the energy range down to 2.5 eV below the Fermi level[11]. Fig. 12 shows a number of surface states in this energy range, but without ARPES cross-section information it is difficult to assess which states produce the strongest features in ARPES. The large change in electronic structure with respect to the $\sqrt{3}$-Au structure, found in both theory and experiment, is consistent with a major change in surface structure.

More recently, Kim and coworkers [27] and Bondarenko and coworkers [29, 30] have used ARPES to study the dispersion of the S1 quasi-particle band on the $\sqrt{3}$-Au surface. Unlike adsorption of 1/3 ML Si, adsorption of lower coverages of adsorbates with odd numbers of valence electrons, such as In [27, 29] or Na [29, 30], leads to removal of domain walls from the $\alpha\sqrt{3}$-Au phase and a considerable sharpening of quasi-particle band dispersion and the Fermi surface measured in ARPES. Kim and coworkers find that the S1 state is shifted down by coadsorption of Au and In, so that the S1 band minimum occurs 0.6 eV below the Fermi level. They deduced that this band contains 0.3 $e$ after In adsorption. Bondarenko and coworkers [29] find the S1 state band minimum at 0.6 eV below the Fermi level, following In adsorption and 1.0 eV below the Fermi level following Tl adsorption. Fig. 3 compares the dispersion of the quasi-particle band from this work with the data from Ref. [29] for Tl. There is excellent agreement between theory and experiment for the quasi-particle effective mass (as shown in Fig. 3), but the extra band filling occurs only in the Tl-coadsorbed system. Increased filling of this band leads to filling of the S2 surface state and a Fermi surface which is closely approximated by a circle [29]. Competition between filling of the quasi-particle band by donor coadsorbate species (In, Tl, Na, etc.) and donation of electrons by Au in interstitial sites may explain how these coadsorbates remove domain walls from $\alpha\sqrt{3}$-Au and $\beta\sqrt{3}$-Au phases.

STM studies of the Si(111)-Au system have shown that a number of ordered structures can form for more than 1 ML Au coverage. These include the (2$\sqrt{2}$x2$\sqrt{2}$)R10.9°-Au and (3$\sqrt{3}$x3$\sqrt{3}$)-Au structures mentioned above. Total energy calculations reported above have shown that when Au is added to the $\sqrt{3}$-Au structure it enters interstitial sites and it prefers to enter in an ordered way, e.g. as Au Y’s. The surface Au concentration can be increased by adding Au in interstitial sites or by introducing T4H3T4 domain walls. It was shown that adding Au into a single T4 domain is a significantly lower energy route to increasing the Au coverage than introducing T4H3T4 domain walls. Notably, annealing the $\beta\sqrt{3}$-Au surface and cooling slowly results in the ordered (6x6) phase [10]. The structure for the (6x6) phase presented here does not contain any Au in H4 sites - the ordered structure contains only T4 microdomains. Calculated STM images for the T4H3T4 domain walls in Fig. 6 agree well with experimental STM images, e.g. in Ref. [26]. It is therefore likely that these are kinetically stabilized by nucleation of the three domain types. The (2$\sqrt{2}$x2$\sqrt{2}$)R10.9°-Au and (3$\sqrt{3}$x3$\sqrt{3}$)-Au structures observed in STM by Seifert and coworkers [23] and others are likely to be composed of T4 microdomains clustered around Au atoms inserted into interstitial sites. The (6x6)-Au surface has a 2D chiral structure which is evident from STM images and especially in short Au-Au bond distances (Fig. 9c).
V. SUMMARY AND CONCLUSIONS

The electronic structures of the (1x1), √3-Au, √3-Au/Si adatom, T4H3T4 linear domain wall and (6x6) phases have been calculated using a hybrid DFT method. Results are compared to ARPES data for the √3-Au phase and calculated STM images are compared to experimental STM images for a domain wall. Au atoms inserted into interstitial sites in a single √3-Au domain and the (6x6) phase. A strongly dispersive quasi-particle state observed in experiment [29, 30] is also found in our hybrid DFT calculations and there is excellent agreement between predicted and measured band dispersion. In contrast to adsorption of In or Na [29], which transforms the α√3-Au surface with dense domain walls into a domain wall-free √3-Au state with a strong quasi-particle state, adsorption of Si is found to extinguish the quasi-particle state and results in a gapped state.

STM features resembling T4H3T4 domain walls were investigated by inserting extra Au atoms into interstitial regions between large Si3Au3 triangles or by inserting an Au3 triangle over an H3 site, instead of the more energetically favorable T4 site. The T4 √3-Au structure is 0.4 eV per √3-Au unit cell more stable than the H3 structure. Insertion of Au atoms into interstitial sites within a single T4 domain was found to be more stable than insertion of a T4H3T4 domain wall by 0.20 eV per extra Au atom. STM images for both T4H3T4 domain walls and atoms inserted into a T4 monodomain were found to agree well with STM images reported in Refs. [26] and [8].

The structure of the (6x6) phase was calculated using in-plane coordinates of top-layer Si and Au atoms generated using so-called direct methods [20]. The structure was relaxed using a hybrid DFT method and atomic coordinates are available in the Supplementary Information section. The Patterson function for the relaxed structure was compared to the Patterson function derived from in-plane x-ray scattering data [18] and found to be in good agreement. The (6x6) phase unit cell can be described as consisting of three T4 microdomains, each of which surrounds a group of four Au atoms inserted into T4 interstitial sites in a Y shape. One of these Y’s is 0.3 Å above the mean Au height above the surface and results in a very bright, small triangle in the simulated STM image of the (6x6) surface. These and other spiral features are also clearly seen in experimental STM images [21].

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