Au/TiO$_2$(110) interfacial reconstruction stability from

\textit{ab initio}

Min Yu$\dagger$ and Dallas R. Trinkle$^*,\ddagger$

\textit{Department of Physics, University of Illinois at Urbana-Champaign, Urbana, IL 61801, and Department of Materials Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, IL 61801}

E-mail: dtrinkle@illinois.edu

*To whom correspondence should be addressed
$\dagger$Department of Physics, University of Illinois at Urbana-Champaign, Urbana, IL 61801
$\ddagger$Department of Materials Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, IL 61801
Abstract

We determine the stability and properties of interfaces of low-index Au surfaces adhered to TiO$_2$(110), using density functional theory energy density calculations. We consider Au(100) and Au(111) epitaxies on rutile TiO$_2$(110) surface, as observed in experiments. For each epitaxy, we consider several different interfaces: Au(111)//TiO$_2$(110) and Au(100)//TiO$_2$(110), with and without bridging oxygen, Au(111) on 1×2 added-row TiO$_2$(110) reconstruction, and Au(111) on a proposed 1×2 TiO reconstruction. The density functional theory energy density method computes the energy changes on each of the atoms while forming the interface, and evaluates the work of adhesion to determine the equilibrium interfacial structure.

Introduction

Bulk metallic Au is chemically inert and catalytically inactive as a consequence of combination of valence $d$ orbitals and diffused valence $s$ and $p$ orbitals. Recently, Au nanoparticles have been found to be catalytically active when supported on metal oxides such as TiO$_2$, SiO$_2$, Fe$_2$O$_3$, Co$_3$O$_4$, NiO, Al$_2$O$_3$, MgO, etc. For example, Au nanoparticles supported on a TiO$_2$(110) surface demonstrate catalytic activity to promote the reaction between CO and O$_2$ to form CO$_2$ at $T < 40$K with 3.5 nm Au nanoparticles maximizing activity. The catalytic activity is remarkably sensitive to the support material, Au particle size and Au-support interaction; in addition, the reaction mechanism of CO oxidation over Au/TiO$_2$ system remains under debate. High-resolution transmission electron microscopy (HRTEM) and high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) have characterized the atomic structure of nanocrystal interface. However, the atomic structure of Au/TiO$_2$ interface is difficult to determine in HRTEM image simulations due to several issues, such as the thickness of nanoparticles and metal oxide substrates are not determined, and the positions of atoms in the direction parallel to the electron beam are not determined, and the very low contrast for oxygen atoms. New HRTEM experiments observed Au nanoparticles on TiO$_2$(110) surfaces with both the Au(111) and Au(100) epitaxies, with the Au(111) epitaxy more frequently observed than Au(100). Their
analysis with HAADF-STEM analyzed the reconstructed interface of epitaxial Au(111) sitting on a TiO$_2$(110) $1 \times 2$ surface, and extracted important geometric information such as interlayer separations, the presence of Au in the interface of a $1 \times 2$ reconstruction, and estimates of the work of adhesion.

Density functional theory (DFT) calculations\textsuperscript{13} have studied the optimum size and stable adsorption of Au nanoparticles on rutile TiO$_2$(110). Single Au atom is energetically favorable on the atop site above five-fold coordinated (5c) Ti atom on a stoichiometric TiO$_2$ surface,\textsuperscript{14} and is most stable on the two-fold coordinated (2c) bridging O vacancy site on a reduced surface.\textsuperscript{15-17} Oxygen vacancies cause a stronger binding of Au atoms,\textsuperscript{18} nanoclusters\textsuperscript{19-21} and nanorows\textsuperscript{20} to the reduced TiO$_2$ surface than to the stoichiometric surface. Apart from the stoichiometric and reduced TiO$_2$ surfaces, Shi \textit{et al.} found the O-rich interface is the most stable at low temperature of catalytic reaction after examining the Au-rod/TiO$_2$(110) in the orientation Au(111)//TiO$_2$(110) with different interface stoichiometry and various rigid-body translations.\textsuperscript{22} Recently, Shibata \textit{et al.} examined two and nine Au(110) atomic layers supported on reduced TiO$_2$(110), and demonstrated that both the atomic and electronic structure of two-layer Au are reconstructed, while the lattice coherency decays rapidly across the interface for nine-layer Au.\textsuperscript{23} We compare different Au/TiO$_2$ interfaces: Au(111)//TiO$_2$(110) and Au(100)//TiO$_2$(110), with and without bridging oxygen, Au(111) on $1 \times 2$ added-row TiO$_2$(110) reconstruction,\textsuperscript{24} and Au(111) on a new proposed $1 \times 2$ TiO reconstruction.\textsuperscript{11} We use the newly-reformulated\textsuperscript{25,26} density functional theory energy density method to evaluate energy for each atom in the interfacial reconstruction. This provides insight into interfacial stability from the changes in atomic energy from the formed interface, and corrects for spurious errors in the work of adhesion from the remaining free surfaces in the computational cell. The new information of atomic energies extracted from density functional theory shows the response to bonding environment changes in interfaces. The comparison with experimental geometry\textsuperscript{11} and work of adhesion\textsuperscript{27} allows us to validate our predicted structures.
We perform DFT calculations on the Au/TiO\textsubscript{2} interfaces using the projector augmented wave (PAW) method with the Vienna ab initio simulation package (VASP). The exchange-correlation energy is treated in the Perdew-Burke-Ernzerhof version of the generalized gradient approximation functional (PBE-GGA). Elements Au, Ti, and O are given by [Xe]6\textsuperscript{1}5\textsuperscript{d}\textsuperscript{10}, [Ne]3\textsuperscript{s}\textsuperscript{2}3\textsuperscript{p}\textsuperscript{6}4\textsuperscript{s}\textsuperscript{2}3\textsuperscript{d}\textsuperscript{2}, [He]2\textsuperscript{s}\textsuperscript{2}\textsuperscript{p}\textsuperscript{4} atomic configurations; this requires a plane-wave basis set cut-off at 900 eV. We use Monkhorst-Pack k-point meshes of 1 \times 6 \times 1 for interface supercells; Brillouin-zone integration uses the Methfessel-Paxton method with \( k_B T = 0.2 \) eV for electronic occupancies, and the total energy extrapolated to \( k_B T = 0 \) eV. The calculated lattice constant for Au in the FCC phase is 4.171 Å, and for TiO\textsubscript{2} in the rutile phase \( a = 4.649 \) Å, \( c = 2.970 \) Å, and \( u = 0.305 \). These calculated values compare well with the experimental values of 4.08 Å for Au and \( a = 4.584 \) Å, \( c = 2.953 \) Å, \( u = 0.305 \) for TiO\textsubscript{2}.

The work of adhesion of forming an interface from two individual surfaces can be determined from total energy calculations:

\[ E_{\text{adh}} = \frac{1}{A} (E_{\text{Au}} + E_{\text{TiO}_2} - E_{\text{Au/TiO}_2}), \]

where \( E_{\text{Au}} \) and \( E_{\text{TiO}_2} \) are the energy of relaxed Au surface and relaxed TiO\textsubscript{2} surface and \( E_{\text{Au/TiO}_2} \) is the energy of the interface system. To avoid differences in grid densities or the planewave basis, the surfaces are computed with the same supercell as the interface system. In addition to total energies, the energy density method proposed by Chetty and Martin provides the formation energy for more than one surface or interface in one calculation, and a picture of the distribution of energy among the surrounding atoms. We use a new reformulation of the energy density method with VASP for PAW method. Moreover, we compute atomic energies by integrating the local energy density over gauge independent integration volumes. The data allows us to identify the spatial range of the interface and gives insight into the nature of interfacial stability. The integration of the energy density over these volumes produces a small integration error, that can be estimated from
the extent to which gauge-invariance is broken; we include that error as a ± range in all of our reported energy density calculations. For the Au/TiO$_2$ interfaces, the supercell configurations in the calculations are periodic parallel to the interface, and contain six layers of Au, eight trilayers of TiO$_2$, and 10.5 Å vacuum region. Due to the lattice mismatch, Au layers are strained to lattice match the TiO$_2$ according to the supercell periodicity; strained Au surfaces are used as references for energy differences. Atomic relaxation is allowed for all six layer Au atoms and for three interfacial layers of TiO$_2$ for all geometries considered. In addition, different translations of Au relative to TiO$_2$ are attempted in order to determine the minimum energy configuration. The equilibrium positions of the atoms are determined by requiring the force on each relaxed atom to be smaller than 0.02 eV/Å.

**Interfaces**

![Interfaces](image)

Figure 1: Geometry for four different TiO$_2$(110) surface structures. Upper two are stoichiometric 1 × 1 and reduced 1 × 1; bottom two are added-row 1 × 2 reconstruction and TiO 1 × 2 reconstruction. The stoichiometric structure has bridging oxygen (2c)$_h$ atoms above the flat titanium (5c) / (6c) and oxygen (3c) plane. Removal of the bridging oxygens produces a reduced surface, with four- and five-fold coordinated titanium. The added-row reconstruction removes every other row of Ti (4c) atoms with subsurface bridging oxygens (3c)$_{sub}$ for a 1 × 2 reconstruction, with two-fold coordinated oxygen. Finally, additional reduction of the added-row reconstruction, by removing the oxygen (2c) atoms neighboring the removed row, produces the TiO reconstruction with three-fold coordinated titanium.

Figure 1 shows the four different configurations of rutile TiO$_2$(110) substrates we consider. We start
with a stoichiometric surface, and then reduce the surface by removing all bridging O atoms; both are \(1 \times 1\) surfaces. Pang et al. proposed an added-row \(1 \times 2\) reconstruction for the rutile (110) surface, where one row of Ti atom with its sub-bridging O row are removed per \(1 \times 2\) cell for a fully reduced surface.\(^{24}\) Finally, removing the two-fold coordinated O atoms from the added-row reconstruction gives a TiO reconstruction. While this reconstruction is not the lowest in energy, it provides the most stable Au/TiO\(_2\) interface that also matches the experimentally observed geometry.

**Au(111)/TiO\(_2\)(110) \(1 \times 1\): Stoichiometric and reduced interfaces**

Both interfaces on \(1 \times 1\) surfaces use a similar geometry for relaxation. Along the direction Au[\(\bar{1}10\)]//TiO\(_2\)[001], a single repeat length of Au and TiO\(_2\) gives a 1\% lattice mismatch. This agrees with STEM measurements showing registry even up to 10 layers from the interface.\(^{11}\) Along the direction Au[\(\bar{1}12\)]//TiO\(_2\)[\(\bar{1}10\)], a repeat length of 4 for Au matches with a repeat length of 3 for TiO\(_2\), producing a total 3.6\% lattice mismatch strain at the interface. The supercells contain 48 Au, 48 Ti, and 96 O atoms in the interface configuration with stoichiometric TiO\(_2\) surface, and 3 fewer O atoms for the reduced TiO\(_2\) surface. After relaxation, we determine the interlayer spacing at the interface; with energy density calculations, we can ignore any spurious energy changes due to the opposing Au and TiO\(_2\) surfaces.

\(^{2}\) and \(^{3}\) show the geometry of the relaxed Au(111) on stoichiometric and reduced TiO\(_2\)(110) surfaces. The interfacial distance between Au and Ti layers relaxed to 3.90 Å with stoichiometric TiO\(_2\) surface, and 2.79 Å in the configuration with reduced TiO\(_2\) surface. From total energy, the work of adhesion of the interface with stoichiometric TiO\(_2\) surface is 7 meV/Å\(^2\), while the work of adhesion of the interface with the reduced TiO\(_2\) surface is 54 meV/Å\(^2\). The differences in interlayer spacing and energy is due to the presence or absence of bridging oxygen atoms on the TiO\(_2\) surface. Energy density shows that TiO\(_2\) layers reach bulk behavior by the fifth layer from the interface. We integrate the energy density over two Au layers and four TiO\(_2\) layers to evaluate the work of adhesion strictly from changes in energy near the interface. This gives a work of adhesion of
Figure 2: Geometry and energy of Au(111) on the stoichiometric TiO$_2$(110) surface following relaxation. The atomic energy on each layer is referenced to the bulk, and shown before (orange) and after (blue) forming the interface. The interfacial distance relaxes to 3.90 Å between Au and Ti layers, and 2.63 Å between Au and bridging-O layers.

Figure 3: Geometry and energy of Au(111) on the reduced TiO$_2$(110) surface following relaxation. Energy per layer in the reference of bulk value is given before (orange) and after (blue) forming the interface. The interfacial distance relaxes to 2.79 Å between Au and Ti layers; and 2.70 Å between Au and in-plane O layers. The geometry reduces the energy of the surface Au layer to a more stable configuration than the stoichiometric TiO$_2$ surface.
4 ± 2 meV/Å² to the stoichiometric TiO₂ surface, and 53 ± 1 meV/Å² to the reduced TiO₂ surface. The work of adhesion is primarily due to a decrease in energy of the Au surface layer at the reduced TiO₂ surface. This suggests that the main effect of removing bridging oxygen is to provide a flat surface for Au(111) layers to adhere, and that the TiO₂ surface energy change is significantly less than the Au surface energy change.

\textbf{Au(111)/TiO₂(110) 1 × 2: Added-row and TiO reconstructions}

Both interfacial reconstructions on 1 × 2 surfaces use a similar geometry for relaxation. Along the direction Au[1Ī0]/TiO₂[001], a single repeat length of Au and TiO₂ gives a 1% lattice mismatch as for the 1 × 1 reconstructions. Along the direction Au[ĪĪ2]/TiO₂[ī10], a repeat length of 5 for Au matches with a repeat length of 4 for TiO₂, producing a total 2.9% lattice mismatch strain at the interface; the different periodicity is required for a 1 × 2 reconstruction. The supercells contain 62 Au, 62 Ti, and 122 O atoms in the interface configuration with added-row TiO₂ reconstruction, and 4 fewer O atoms for the TiO reconstruction. After relaxation, we determine the interlayer spacing at the interface; with energy density calculations, we can ignore any spurious energy changes due to the opposing Au and TiO₂ surfaces.

\textbf{Added-row reconstruction}

The added-row reconstruction for the 1 × 2 rutile (110) surface removes one row of Ti atom with its sub-bridging O row per 1 × 2 cell for a fully reduced surfaces.\textsuperscript{24} Experimental observations of the interface find a mixed TiO₂-Au layer with 1 × 2 periodicity.\textsuperscript{11} to build our interface and compute the work of adhesion, we consider different configurations to attach a row of Au atoms on added-row reconstruction in 4. After geometry relaxation, the configuration of each Au atom sitting on the top of two Ti atoms with 4 neighboring O atoms is the most stable; there is an energy cost of 15.7 meV/Å² to place a Au row into the missing row of TiO₂. This is similar to the adhesion of Au rows to bridging oxygen vacancies in a TiO₂(110) “missing row” reconstruction.\textsuperscript{20} The energy density shows that the energy of Au dominates the stability.
Figure 4: Three different configurations of a single Au row on the TiO$_2$ added-row reconstruction: (a) in the missing Ti row with 4 nearest neighboring O atoms; (b) on top of the TiO$_2$ surface directly above a Ti atom; (c) on top of the TiO$_2$ surface bridging between two Ti atoms. Au atoms are in gold, and the wireframe shows the supercell. Opaque atoms are on the top layer while transparent atoms are on lower layers. The (c) configuration has lowest total energy, 6.3 meV/Å$^2$ lower than (b) configuration, and 15.7 meV/Å$^2$ lower than (a) configuration. From the energy calculations, the Au row controls the total energy, with the largest increase in energy from filling the missing Ti-O row in the surface layer; hence, we expect to see a mixing of the TiO$_2$ surface with Au only after coverage by a gold nanoparticle.

Figure 5: Geometry and energy of the Au(111)//TiO$_2$ added-row reconstruction following relaxation. Atomic energy per layer in the reference of bulk value is given before (orange) and after (blue) forming the interface. The interfacial distance between Au layer with mixed layer is about 3.4 Å, and the work of adhesion is –9 meV/Å$^2$. While the Au surface layer reduces its energy, the TiO$_2$ layer increases in energy as the oxygen atoms that neighbor the in-surface Au rows are unable to relax out of the (110) plane; hence, the Ti$_6$O$_{10}$ layer increases in energy.
shows the geometry of the relaxed Au(111) on added-row TiO$_2$ reconstruction. The interfacial distance between Au and the mixed interfacial layer is 3.4 Å. This larger distance is due to the displacement of oxygen atoms neighboring the interfacial Au rows. From total energy, the work of adhesion of the interface is $-9 \text{ meV/Å}^2$ after accounting for the $16 \text{ meV/Å}^2$ increase in energy due to the addition of Au into the subsurface (c.f. 4). We integrate the energy density over two Au interfacial layers, one mixed interfacial layer and three next TiO$_2$ interfacial layers and subtract the corresponding energy density integration in Au layers and the ground-state configuration of an Au row on TiO$_2$, 4(a). This energy density calculation gives a work of adhesion of $6 \pm 1 \text{ meV/Å}^2$ before subtracting $16 \text{ meV/Å}^2$. After forming interface, the atomic energy of Au interfacial layer drops, while the atomic energy of TiO$_2$ in the mixed layer increases. The increase in the energy of the surface Ti$_6$O$_{10}$ layer is due to the constraint placed on oxygen atoms neighboring to the intermixed Au row in the mixed layer.

**TiO reconstruction**

![Figure 6](image_url)  
Figure 6: Two different configurations of a single Au row on the TiO reconstruction: (a) in the missing Ti row; (b) on top of the TiO$_2$ surface bridging between two Ti atoms. Au atoms are in gold, and the wireframe shows the supercell. Opaque atoms are on the top layer while transparent atoms are on lower layers. The energy of the (b) configuration is $0.8 \text{ meV/Å}^2$ lower than (a) configuration. Adding Au into the missing row only slightly increases the energy of the Au row; this increase is much less than for the TiO$_2$ added-row reconstruction. However, the TiO reconstruction is a higher energy surface than the added-row reconstruction.

The added-row reconstruction can be further reduced by removing the two-fold coordinated
O atoms on the TiO$_2$ surface layer to form a TiO $1 \times 2$ reconstruction. This reconstruction is suggested by the energy density calculations above as a possible route to increase the work of adhesion. We build our interface in a similar manner as for the added-row reconstruction, and consider different configurations to attach one row of Au atoms on the reconstruction in 6. After geometry relaxation, both the Au row in the missing row of Ti and on the surface have large, but similar, energies (a difference of 0.8 meV/Å$^2$). The increase in surface energy is entirely due to the first TiO$_2$ layer, suggesting that further reduction to TiO is unfavorable without an interfacial layer of gold to “protect” the surface.

Figure 7: Geometry and energy of the Au(111)/TiO reconstruction following relaxation. Atomic energy per layer in the reference of bulk value is given before (orange) and after (blue) forming the interface. The interfacial distance between Au layer with mixed layer is 2.45 Å, compared with experimental observation of 2.35 ± 0.16 Å. The work of adhesion is 107 meV/Å$^2$ from energy density integration compared with the Au(111) and TiO reconstruction filled with a Au row. The stability of the interface comes from a reduction in the Au surface energy with no penalty in the mixed layer, as occurs with the added-row reconstruction.

shows the geometry of the relaxed Au(111)/TiO reconstruction interface. Despite the higher energy of the TiO reconstruction, it produces an attractive interface configuration with Au(111). The interfacial distance between the Au layer and mixed interfacial layer is 2.44–2.45 Å; the closer attachment distance compared with the added-row reconstruction is due to the removed oxygen atoms in the interfacial layer. From total energy, the work of adhesion of the interface is 99 meV/Å$^2$. We integrate the energy density over two Au interfacial layers, one mixed interfacial layer and three next TiO$_2$ interfacial layers and subtract the corresponding energy density integration in Au layers and the ground-state configuration of an Au row on TiO$_2$. This energy density
calculation gives a work of adhesion of 107 ± 1 meV/Å²; the difference with the total energy calculation is due to spurious changes in the free TiO₂ surface that the energy density calculation removes. We observe a remarkable drop of atomic energy on Au interfacial layer. In addition, the mixed layer energy sees only a small change leading to a stabilized interface. To compute the true work of adhesion, however, we must account for the energy change due to a further reduction from the added-row reconstruction to the TiO reconstruction.

shows the changes in local electronic density of states for atoms in the Au(111)//TiO interface compared with other atomic configurations in Au and TiO₂. In the interface, the Au atom mixed in the TiO₂ layer has a narrower width, indicating reduced bonding to neighbors than even Au atoms in the interfacial layer above. Moreover, the Au d states are pushed towards the Fermi level, even compared with atoms on a free surface. The widening of the density of states for Au atoms in the interface compared with the free surface corresponds to changes in atomic energy in Titanium has a downward shift in unoccupied states pulling them below the Fermi energy in the interface. Finally, the oxygen atom in the surface next to Au (c.f., 5) that is removed in the new reconstruction sees its density of states narrow and produce a peak; this increase in energy corresponds to the atomic energy changes also seen for this atom. After removal, the remaining oxygen neighbors have bonding environments that are less disturbed by the presence of Au in the interfacial layer.

Work of adhesion

shows the relative energies for the different configurations to produce the two different 1 × 2 reconstructions of Au(111)//TiO₂(110). Au(111) adhered to the TiO reconstruction is the most stable interface configuration with an interfacial distance 2.45 Å that agrees with the STEM observed 2.35 ± 0.16 Å. However, the work of adhesion of 107 meV/Å² is relative to the higher energy TiO surface with the introduced Au into the subsurface. The difference between the added-row reconstruction and the TiO reconstruction means that a single Au row on the TiO reconstruction is less stable by 62meV/Å², plus 16meV/Å² to place Au in the subsurface (c.f. 4); hence, the TiO
Figure 8: Partial electronic density of states for Au, Ti, and O in the relaxed Au(111)//TiO reconstruction. The panels show, from top to bottom: total density of states for three types of Au atoms, and Ti and O atoms that neighbor Au in the interface; $d$ density of states for several different Au atomic environments; $d$ density of states for different Ti atomic environments; and $p$ density of states for different O atomic environments.
Figure 9: Evaluation of work of adhesion for Au(111) on $1 \times 2$ TiO$_2$(110) reconstructions. The top two energies are changes in the surface energy before the interface is formed, and are relative to the stable $1 \times 2$ TiO$_2$(110) added-row reconstruction; hence, we start by adding 16 meV/Å$^2$ when Au is added into the surface (c.f., [4]). The bottom two energies are relative to the Au(111) surface and the TiO$_2$(110) surface—the negative work of adhesion. The TiO reconstruction leads to a stable interface after Au deposition as the energy required to remove additional oxygen atoms from the added-row reconstruction is offset by a larger reduction in energy when forming the interface. This is an interesting example of an interfacial reconstruction that is stabilized solely in the presence of the interface. Compared with the other simple added-row reconstruction which produces a small work of adhesion due to distortions in the mixed layer, the TiO interfacial reconstruction explains the observed $1 \times 2$ reconstruction, the interlayer spacing, and is energetically favorable.
reconstruction produces a stable configuration with work of adhesion of 29 meV/Å² after Au deposition. Note that we have computed our work of adhesion relative to the stable Au(111) surface with energy 43meV/Å² (38 ± 1meV/Å² for the strained surface) and the 1 × 2 added-row reconstruction for TiO₂(110) with an energy of 80 ± 1meV/Å². This is lower than simply adhering to the added-row reconstruction, which has a work of adhesion of −9 meV/Å². It should be noted that the intermediate configuration of TiO without Au(111) is unstable, and is needed to compute relative energies; given the higher surface energy, it is unlikely that further oxygen reduction occurs before the growth of Au(111) layers.

**Au(100)//TiO₂(110) 1 × 1: Stoichiometric and reduced interfaces**

Both interfaces on 1 × 1 surfaces use a similar geometry for relaxation. Along the direction Au[01̅1]/TiO₂[001], a single repeat length of Au and TiO₂ gives a 1% lattice mismatch. Along the direction Au[011]/TiO₂[1̅10], a repeat length of 9 for Au matches with a repeat length of 4 for TiO₂, producing a 0.9% lattice mismatch. The supercell contains 54 Au, 64 Ti, and 128 O atoms for stoichiometric case, and 4 fewer O atoms for reduced case. As before, we determine the interlayer spacing at the interface following relaxation; with energy density calculations, we can ignore any spurious energy changes due to the opposing Au and TiO₂ surfaces.

![Figure 10: Geometry and energy of Au(100) on the stoichiometric TiO₂(110) surface following relaxation. The atomic energy on each layer is referenced to the bulk, and shown before (orange) and after (blue) forming the interface. The interfacial distance is 3.63 Å between Au and Ti layers, and 2.33 Å between Au and bridging O layers.](image)
Figure 11: Geometry and energy of Au(100) on the reduced TiO$_2$(110) surface following relaxation. The atomic energy on each layer is referenced to the bulk, and shown before (orange) and after (blue) forming the interface. The interfacial distance is 2.64 Å between Au and Ti layers, and 2.55 Å between Au and in-plane O layers. The Au layer energy is reduced while the TiO$_2$ layer energy increases for a work of adhesion of 64 ± 1 meV/Å$^2$.

[10] and [11] show the geometry of the relaxed Au(100) on stoichiometric and reduced TiO$_2$(110) surfaces. The interfacial distance between Au and Ti layers relaxed to 3.63 Å with stoichiometric TiO$_2$ surface, and 2.64 Å in the configuration with reduced TiO$_2$ surface. From total energy, the work of adhesion is 3 meV/Å$^2$ of the interface with stoichiometric TiO$_2$, while the work of adhesion of the interface with the reduced TiO$_2$ surface is 55 meV/Å$^2$. The differences in interlayer spacing and energy is due to the presence or absence of bridging oxygen atoms on the TiO$_2$ surface. Energy density shows that TiO$_2$ layers reach bulk behavior by the fifth layer from interfaces. We integrate the energy density over two Au layers and four TiO$_2$ layers to evaluate the work of adhesion strictly from changes in energy near the interface. This gives a work of adhesion of 1 ± 1 meV/Å$^2$ to the stoichiometric TiO$_2$ surface, and 64 ± 1 meV/Å$^2$ to the reduced TiO$_2$ surface. Similar to Au(111)//TiO$_2$(110) reduced interface, atomic energy at the interface decreases in the Au surface, and increases in the TiO$_2$ surface in the reduced case during forming the interface, to stabilize the structure more than the stoichiometric case. The energy of TiO$_2$ free surface away from the interface experiences a spurious energy changes during the interface formation. Therefore, the integration of energy density over interfacial region reduces the finite-size error, and provides more accurate work of adhesion or interfacial energy.
Conclusions

Table 1: Comparison of different Au(111)//TiO$_2$(110) interfaces. The two different work of adhesions are from the total energy calculation of ??, and the energy density integration; the latter accounts for finite-size errors in the supercell calculation. The Au(111)//TiO reconstruction agrees with experimental observation in three factors: the $1 \times 2$ symmetry, the work of adhesion $E_{\text{adh}}$, and the Au-Ti separation distance $d_{\text{Au-Ti}}$. The work of adhesion $29 \pm 1$ meV/$\text{Å}^2$ compares well with $28 \pm 7$ meV/$\text{Å}^2$; the experimental value comes from the Wulff-Kaishew theorem, where $\Delta h/\gamma = E_{\text{adh}}/\gamma_{\text{Au(111)}}$, and the geometry parameter $\Delta h/\gamma$ characterizes various equilibrium shapes of supported Au nanoparticles in experiments. The surface energy $\gamma_{\text{Au(111)}}$ is 43 meV/$\text{Å}^2$ from our PAW-GGA-PBE calculation.

|                | $E_{\text{adh}}$ [meV/$\text{Å}^2$] | $d_{\text{Au-Ti}}$ [Å] | misfit |
|----------------|-----------------------------------|--------------------------|--------|
| Stoichiometric | $1 \times 1$                      | 7 | 4 ± 1 | 3.90 | 3.6% |
| Reduced        | $1 \times 1$                      | 54 | 53 ± 1 | 2.79 | 3.6% |
| Added-row      | $1 \times 2$                      | $-9$ | $-9 \pm 1$ | 3.00 | 2.9% |
| TiO            | $1 \times 2$                      | 22 | 49 ± 1 | 2.45 | 2.9% |
| Experiment     |                                   | 28 | 28 ± 7 | 2.35 ± 0.16 |

summarizes the geometric and energy comparison of proposed Au(111)//TiO$_2$(110) interfaces and the experimental observations. Density functional theory energy density calculations of several Au/TiO$_2$ interfacial reconstructions determines the equilibrium structure that matches experimental measurements. Both Au(111) and (100) prefer attaching to reduced rutile TiO$_2$(110) surfaces over stoichiometric surfaces. Comparison of Au(111) attaching on two TiO$_2$(110) $1 \times 2$ reconstruction cells shows that the TiO reconstruction leads to the most stable interface configuration with interfacial distance 2.45 Å, and work of adhesion 29 meV/$\text{Å}^2$. Atomic energy variation during interface formation demonstrates that the attraction of top Au interfacial layer leads to a stable structure. The energy density computation also identifies spurious changes to atomic energies on the free-surfaces during the formation of an interface, which affect the computation of work of adhesion from total energy calculations; these finite-size errors are removed. Our calculations provide an atomistic-level explanation of the stability of the unusual TiO reconstruction, where further reduction of the interface is possible when “protected” by an epitaxial gold layer, and demonstrates the power of energy density computation to guide the identification of stable defect structures.
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