

First Principles Studies of the Potential-Induced Lifting of the Au(100) Surface Reconstruction

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The potential-induced surface reconstruction of Au(100) has been studied by a combination of density functional theory and thermodynamic considerations. Surface free energies of reconstructed-(5×1) and unreconstructed-(1×1) surfaces were calculated as function of an external electric field using the extended *ab-initio* atomistic thermodynamics approach. After relating electric field and electrode potential by using capacitance measurements, we calculate lifting of the reconstruction to occur at 0.58 V in 0.01 M HClO₄ and 0.27 V in 0.01 M H₂SO₄, being in agreement with the experimental values of 0.60 V and 0.27 V (vs. SCE). Finally, the consequences of using experimental capacitance measurements for calculating surface free energies are discussed.

Keywords: Surface Reconstruction, Au(100), DFT, Thermodynamics, Sulfuric Acid, Perchloric Acid

1. Introduction

Surface reconstruction, which can be understood as a deviation from the bulk-truncated structure, is customarily observed under ultra high vacuum (UHV) conditions on the low-index faces of various noble metals such as Pt, Au or Ir [1]. Detailed investigations regarding this phenomenon for metal/solution interfaces [2] were performed by employing various *ex-situ* techniques [3,4] such as low-energy electron diffraction (LEED), reflection high-energy electron diffraction (RHEED), and structure-sensitive techniques such as *in-situ* scanning tunneling microscopy (STM) [5], *in-situ* X-ray diffraction (XRD) [6] and reflection anisotropy spectroscopy [7]. While studying reconstructed surfaces in an electrochemical environment, it was found that at electrode potentials positive of the potential of zero charge (E_{pzc}), the reconstruction is lifted and the surface morphology changes to the bulk-truncated structure [2,8]. For instance an Au(100) electrode, which in its ground-state is hexagonally reconstructed in the first surface layer, shows a *lifting* of the reconstruction in 0.01 M HClO₄ at $E_{SCE} > +0.60$ V (vs. SCE – saturated calomel electrode) [9] and transforms into unreconstructed Au(100)-(1×1). However, in

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contact with a 0.01 M H_2SO_4 solution, the same *lifting* occurs already at $E_{\text{SCE}} > +0.27 \text{ V}$ (vs. SCE). Besides changing the ions of the supporting electrolyte, it has been observed that adsorption of organic molecules such as pyridine, uracil, thymine, or adenine leads to similar modifications in the potential value at which lifting of the reconstruction is induced [10–12]. Therefore, the question arises whether the reconstruction is lifted due to the excess charge accumulated at the surface or the specific adsorption of ions (or molecules). Considering the Au(100) surface, which is of particular interest in the present work, current–potential curves in 0.1 M H_2SO_4 revealed that at 0.05 V, where the surface is still reconstructed, there are no specifically adsorbed anions on the surface. However, at 0.35 V, which is around the potential where lifting of the reconstruction appears, an ordered (1.4×3.6) sulfate adlayer is formed on the unreconstructed Au(100) [13]. Although this might indicate a substantial role of adsorbed ions in the process of changing the surface morphology, it does not answer the question whether specific adsorption of anions or a positive surface charge is the main cause of lifting of surface reconstruction.

So far, only few theoretical attempts have been made to better understand the potential-induced changes of the surface structure, ranging from tight binding studies [14] over simple glue models [15] to embedded atom simulations [16–18] and *ab initio* density functional theory calculations [19,20]. Focusing mainly on evaluating the surface free energies of the reconstructed and unreconstructed surfaces, the presence of the electrode potential was either neglected or treated in terms of an externally applied electric field, or by manually charging the electrode. Further explanations on the different methods to simulate the electrode potentials can be found in [21,22].

In this letter, we describe a combination of theoretical calculations and experimental measurements on the lifting of the Au(100) surface reconstruction in perchloric and sulfuric acid solutions at two different ion concentrations. While in the calculations the presence of an electrode potential has been modeled by applying an external electric field to the system, capacity measurements were used to evaluate the surface stabilities of unreconstructed Au(100)-(1×1) and hexagonally reconstructed Au(100)-hex as function of electrode potential.

2. Methods

2.1. Theoretical Calculations

In order to study the influence of an excess charge on the lifting of Au(100) surface reconstruction, we employed SeqQuest [23,24], a periodic DFT program with localized basis sets represented by a linear combination of Gaussian functions, together with the PBE [25] Generalized Gradient Approximation (GGA) exchange–correlation functional. A standard (non-local) norm-conserving pseudopotential [26] was applied to replace the 69 core electrons of each Au-atom, leaving the 5*d*- and 6*s*-electrons in the valence space and invoking a nonlinear core correction [27]. The basis sets were optimized "double zeta plus polarization" contracted Gaussian functions. All calculations were performed on a nine-layer slab, in which the lowest three layers were fixed to the calculated bulk crystal structure (with a lattice constant of $a_0=4.164 \text{ \AA}$), while the remaining six surface layers were allowed to fully optimize their geometry to $< 0.01 \text{ eV/\AA}$. Integrations in the reciprocal space were performed (and tested to be converged), using a Brillouin zone (BZ)

sampling of 12×12 k -points for the (1×1) unit cell. Finally, the electrode potential was modeled by applying a constant electric field of variable strength perpendicular to the surface plane such that the discontinuous potential drop occurred within the vacuum.

2.2. Experimental

Cyclic voltammetry and capacitance measurements were carried out in a conventional three-electrode glass cell with a home-made potentiostat and a lock-in amplifier (Stanford research systems SR 830 DSP) at 18 Hz and a 10 mV peak-to-peak sinusoidal perturbation, respectively. A saturated calomel electrode (SCE) and a platinum wire were used as reference and counter electrodes, respectively. The solutions were prepared from HClO_4 and H_2SO_4 (Merck, suprapur) and ultrapure water ($18.2 \text{ M}\Omega\text{cm}$ at 25°C , $\text{TOC} < 1 \text{ ppb}$). The Au(100) single crystal disc electrode has been oriented to better than 1° by MaTeCK (Jülich, Germany). It has a thickness of 2 mm and a diameter of 10 mm. Electrode surface preparation was done prior to each measurement by flame-annealing for 5 minutes and subsequent slow cooling in the nitrogen-purged electrochemical cell above the electrolyte. All measurements were done at room temperature. Figure 1 exemplarily shows the current density and differential capacitance curves as function of the potential for Au(100) in 0.01 M H_2SO_4 [28]. Equivalent measurements were performed at 0.1 M H_2SO_4 and with HClO_4 for both concentrations.

Furthermore, Tab. 1 provides an overview of measured potentials of zero charge for the reconstructed and the non-reconstructed Au(100) surface as been reported in literature.

3. Results and Discussion

Since the surface structures of Au(100)- (1×1) and Au(100)-hex as well as their geometrical changes when applying an electric field were discussed in detail earlier [21], in the following we will focus on the charge density distribution within these systems and the influence of different electrolytes on the stability of the surfaces.

In order to account for the electrode potential it is necessary to accumulate excess charge on the electrode surface. As already mentioned this was realized with an external electric field perpendicular to the surface, which was varied between $E_z = -3.85$ and $+3.85 \text{ V}/\text{\AA}$. Exemplarily, Fig. 2 shows the difference between the charge density distribution at $E_z = 0$ and $E_z = -3.85 \text{ V}/\text{\AA}$ for the reconstructed Au(100)-hex surface, reflecting the changes induced by the electric field. Although the electric field at $E_z = -3.85 \text{ V}/\text{\AA}$ is already relatively strong, the excess charge density near the surface is only $\approx 0.02 e/\text{\AA}^2$ (around $0.15 e$ per surface atom). The positive charge density distribution shown in Figs. 2a and b is mainly located in the topmost layer. Due to the electrostatic interaction between the excess charge, there is also a small part of the excess charge located in the second layer. This already indicates that not all excess charge is surface aligned but rather distributed over more than one surface layer. Interestingly, this also proves that there is no charge spill-out into the vacuum region, which could cause an unphysical behavior of the system.

In addition the positive charge density is delocalized over the entire surface plane, which implies that one might expect a prompt rearrangement of the excess charge in case of specific or non-specific adsorption accompanied by strong modifications in the local electric field. Furthermore, Figs. 2c and d show that as a result of the accumulated positive excess charge some negative charge is also attracted toward the topmost layer and

concentrates at the surface atoms, thus being much more localized. Although this somehow stabilizes the surface structure, the increasing ratio between positive and negative excess charge density at increasing electric field strengths, leads to a destabilization of the surface and a detachment of the topmost surface layer toward the vacuum by $\approx 0.2 \text{ \AA}$ (at $E_z = -3.85 \text{ V/\AA}$) [21].

The total density of states (DOS) of the surface and center layers of Au(100)-(1 \times 1) and Au(100)-hex are shown in Fig. 3. As expected, in absence of an electric field, the DOS of both the unreconstructed and reconstructed surfaces differ from their corresponding bulk-DOS (denoted as center layer). This is mainly due to a depletion of low-energy states accompanied by an occupation of high-energy states, which leads to an overall shift of the d -band center towards the Fermi-energy. Furthermore, the narrowing of the surface DOS indicates a localization of d -states at or near the surface. Comparing the surface DOS at $E_z=0 \text{ V/\AA}$ between both systems, shows that in case of the reconstructed surface smoothing of the peaks leads to a slight broadening of the band, which represents the delocalized nature of electrons over the reconstructed surface. As a consequence, applying an electric field influences the charge density distributions within the entire surface layer (see Fig. 2). Depending on the direction of the electric field vector, Fig. 3 shows that the surface DOS is either shifted upwards or downwards with respect to the Fermi-energy, which is a direct consequence of the accumulation or depletion at or near the surface. As expected for Au, further analysis of the corresponding projected DOS (PDOS) confirms that this shift is mainly due to the d -band.

In order to study the lifting of surface reconstruction the important quantity is the surface free energy, which for the present case where we assume a Au electrode in vacuum and under the influence of the electric field, can be written as (see Ref. [21] for details):

$$\gamma(E_z) = \frac{1}{A} \left[E_{\text{tot}}(E_z) - N_{\text{Au}} g_{\text{Au}}^{\text{bulk}} \right] - \sigma_e(E_z) \cdot \tilde{\mu}_e(E_z). \quad (1)$$

Here E_{tot} is the total energy of the particular system, which consists of N_{Au} gold atoms, and σ_e is the density (per area) of the excess charge with an electrochemical potential $\tilde{\mu}_e$. Furthermore, A is the surface area and $g_{\text{Au}}^{\text{bulk}}$ is the Gibbs free energy of Au-bulk, which is considered to be the reservoir the system is in contact with.

Fig. 4 shows the surface free energy as function of electric field for the reconstructed and unreconstructed Au(100) surface as evaluated by eq. (1). The plot makes apparent that the hexagonal-reconstructed surface is more stable over the entire range of applied electric fields, and that the difference between both maxima (around $E_z \approx 0 \text{ V/\AA}$) is only 0.002 eV/\AA^2 (0.04 J/m^2), which is within the error of the calculation. Interestingly, both maxima are not exactly at $E_z = 0 \text{ V/\AA}$, but slightly shifted to positive E_z -values. This reflects the fact that the potential of zero charge is usually required to remove or compensate the surface dipole. However, as Fig. 4 shows there is no crossing between both curves over the entire range of applied external electric fields, which would be necessary for a change of the preferred surface structure. This is caused by the fact that instead of $\gamma(\Delta\phi)$, which depends on the electrode potential $\Delta\phi$ and therefore allows comparison with experiments, we have used $\gamma(E_z)$ from eq. (1). As already mentioned above, to solve this problem we can use experimental information. While from our calculations we can extract the excess surface charge density as function of the applied electric field $\sigma_e(E_z)$,

integration of the experimental capacity measurements (Fig. 1) reveals the same quantity, but as function of the electrode potential $\sigma_e(\Delta\phi)$. By equating the calculated and the experimental surface charge densities, one is able to extract a relation between the electric field applied in the calculations and the experimentally applied electrode potential, giving $E_z(\Delta\phi)$. This relation can be used to plot $\gamma(E_z)$ from Fig. 4 as function of the electrode potential $\gamma(E_z(\Delta\phi))$ for the experimentally employed electrolytes and concentrations, depending on which experimental capacity-measurement has been used for the integration. Fig. 5 shows the resulting curves for HClO_4 and H_2SO_4 with the two concentrations 0.1 and 0.01 M. The curves now reveal the expected crossings at around 0.58 V for 0.01 M HClO_4 and 0.27 V for 0.01 M H_2SO_4 , both values being in good agreement with experiments. Since the reconstructed Au(100)-hex surface is stable at low electrode potentials, the crossings between the corresponding curves always indicate the lifting of surface reconstruction. Increasing the electrolyte concentrations from 0.01 M to 0.1 M lowers both potential values by approximately 0.05 V, which is consistent with calculations by Santos and Schmickler [32].

Since only electronic effects and no specific ion adsorption has been considered in our model, from the agreement of the calculated transition potentials with the experimentally measured values for both electrolytes one might conclude, that the lifting of the Au(100)-hex surface reconstruction is exclusively caused by surface charging. While this might be correct for HClO_4 , in case of H_2SO_4 adsorption of sulfate has been observed experimentally around the transition potential. This discrepancy can be interpreted in two ways. In the first scenario the surface excess charge first lifts the reconstruction and afterwards sulfate adsorbs on the unreconstructed Au(100)-(1 \times 1) surface. In this case the lifting is a purely electronic effect, which would support our theoretical model. However, in the second scenario first sulfate adsorbs and the lifting of the surface reconstruction is then caused by the adsorbate-induced changes in the surface stability. In this case the agreement between the theoretical and experimental transition potential can only be rationalized by the fact that experimentally determined CV-curves were required as external input for the theoretical evaluation of the surface free energy. Since those CV-curves automatically include the occurrence of any specific ion adsorption, the predictive abilities of these kinds of theoretical studies – having often been performed and described in literature – is reduced and specific adsorption as cause for the lifting cannot be fully excluded. Instead there only remains evidence that surface charging alone already plays an important role in destabilizing the hexagonal-reconstructed Au(100) surface at positive potentials.

From the previous discussion we finally conclude that one should be rather careful in not over-interpreting these kinds of calculations often used in literature. To shed further light on this problem, a self-consistent modeling of the entire electrode/electrolyte-interface and the electrode potential would be required.

4. Summary

In this letter we have presented theoretical studies on the potential-induced lifting of the hexagonal reconstruction of Au(100). The rather small energy difference between both surface structures required an explicit treatment of potential-dependent effects within our density functional theory calculations, which had been realized by applying an external

electric field to the system. By comparing the thus induced surface excess charges with those extracted from experimental CV-measurements, we were finally able to draw the surface stability as function of electrode potential. For both sulfuric and perchloric acids the resulting curves revealed the expected structural change at electrode potentials, which are in surprisingly good agreement with the experiments. Though adsorption of electrolyte ions had been omitted in our studies, in case of H_2SO_4 the formation of an ordered sulfate-layer at potentials around the transition-potential is experimentally well characterized. Therefore, we caution from over-interpreting these kind of theoretical studies.

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Table 1

Summary of literature-reported measurements of E_{pzc} for Au(100)-hex and Au(100)-(1×1) in contact with H₂SO₄ or HClO₄ at different concentrations.

Electrolyte	Conc. [M]	E_{pzc} [V]		Ref.
		Au(100)-hex	Au(100)-(1×1)	
H ₂ SO ₄	0.00032	–	0.00	[29]
	0.002	–	–0.01	[29]
	0.005	0.28	0.02	[30]
HClO ₄	0.01	–	0.01	[31]
	0.01	0.30	0.08	[28]
	0.03	–	0.00	[31]

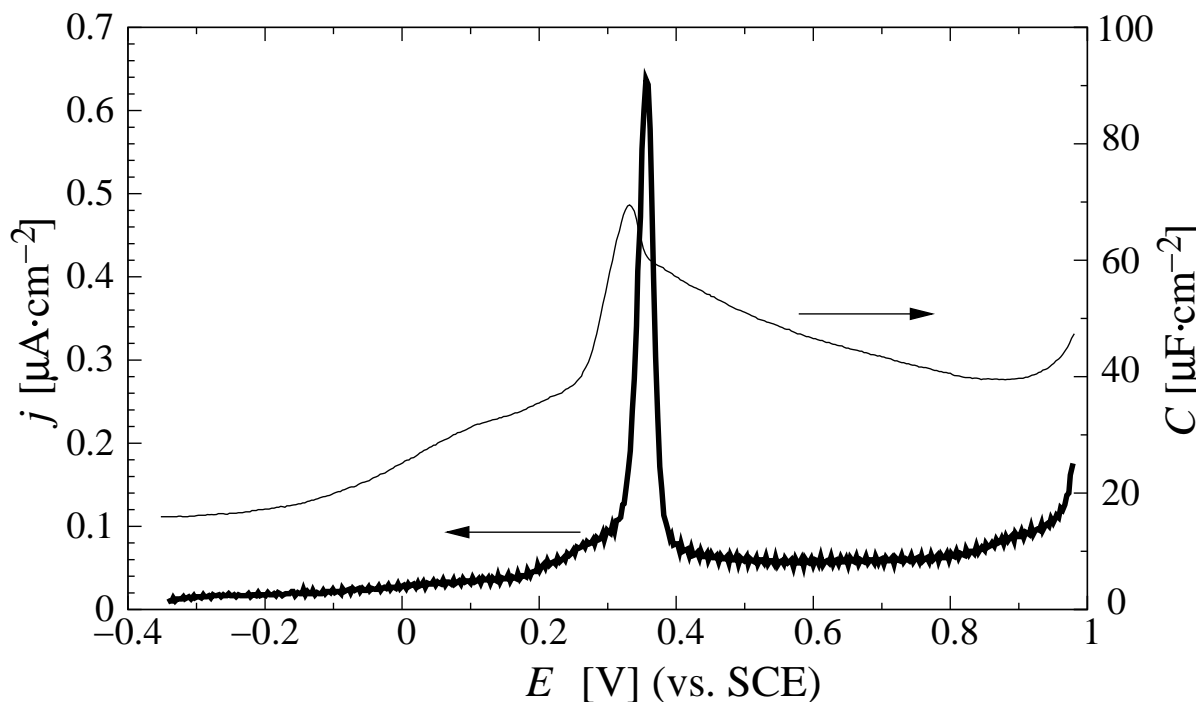


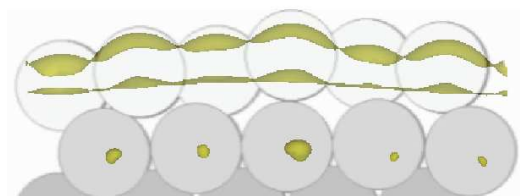
Figure 1. Positive-going first sweeps for the current–potential curve (thick line) and the differential capacitance curve (thin line) of freshly prepared Au(100) in 0.01 M H_2SO_4 after immersion at negative potentials. Scan rate: $1 \text{ mV}\cdot\text{s}^{-1}$.

Positive charge density (depletion)

a)

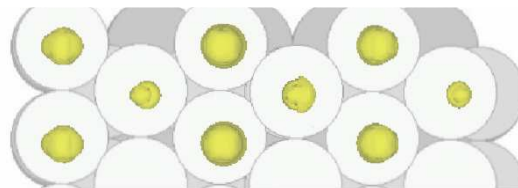


b)



Negative charge density (accumulation)

c)



d)

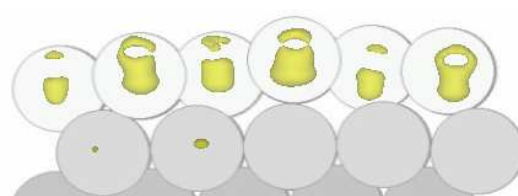


Figure 2. Difference in charge densities of Au(100)-hex (5×1 unitcell) at $E_z = 0$ and $E_z = -3.85 \text{ V}/\text{\AA}$. (a) and (c), respectively (b) and (d), represent the top and side views of the positive (depletion) and negative (accumulation) charge density distributions.

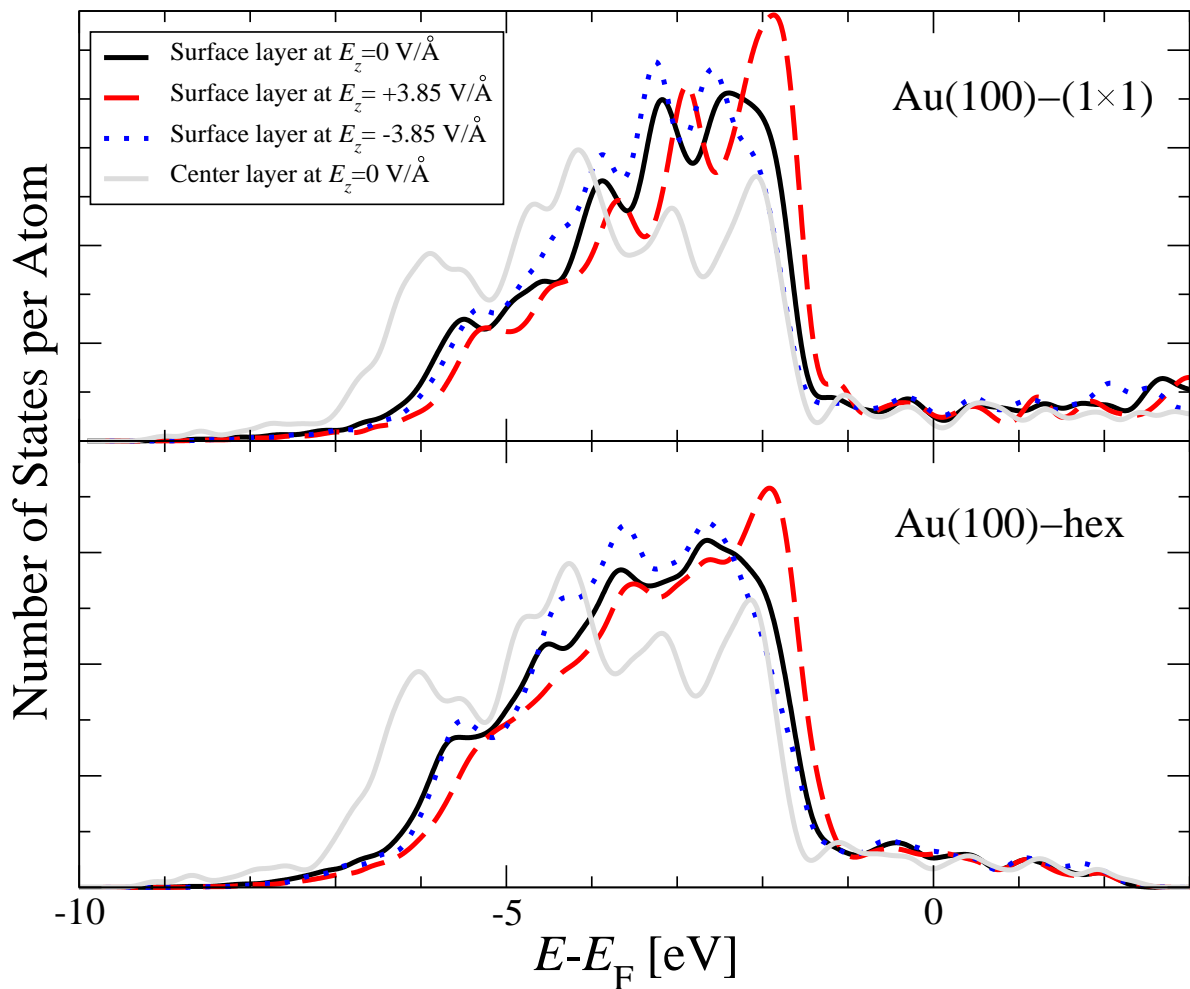


Figure 3. Total density of states (DOS) of Au(100)-(1 \times 1) and Au(100)-hex (5 \times 1 unitcell) for the center of the slab and the surfaces at three different electric fields (-3.85 , 0 , 3.85 V/ \AA). For the hexagonal-reconstructed surface the DOS had been averaged over all surface atoms of the unitcell. All energy scales have been referenced to the Fermi-Niveau.

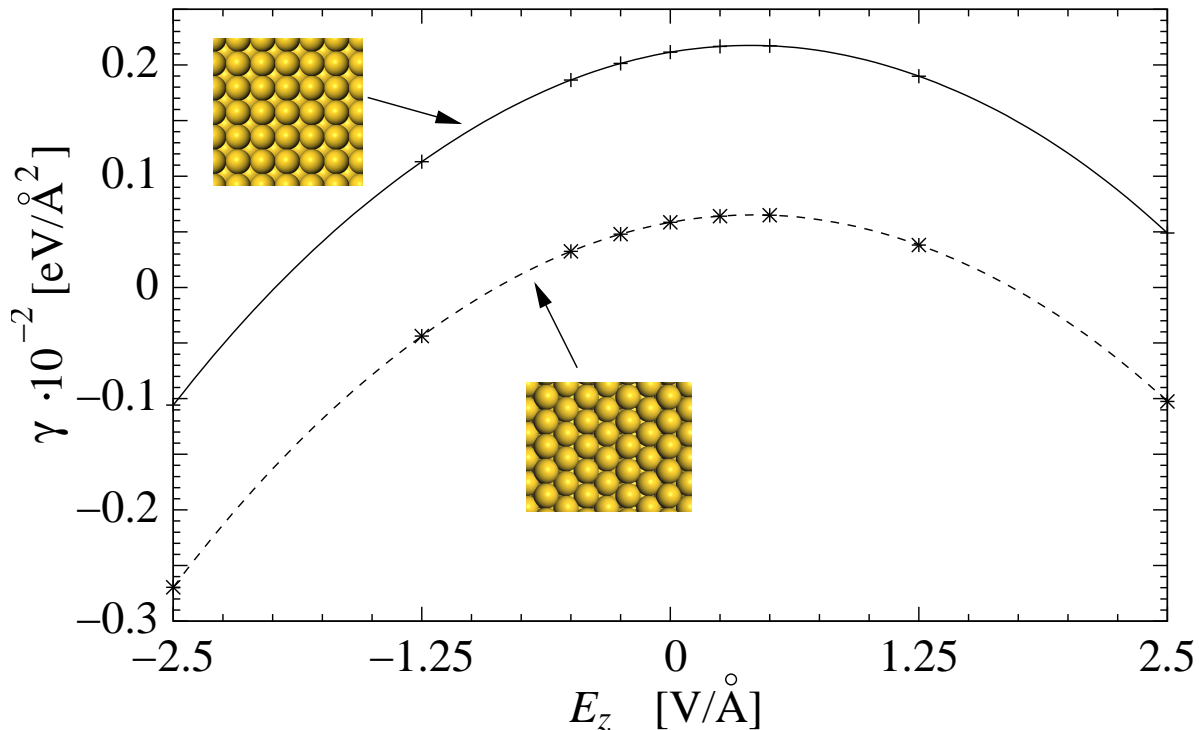


Figure 4. Calculated surface free energy γ as function of the electric field perpendicular to the surface (E_z) for unreconstructed and reconstructed Au(100).

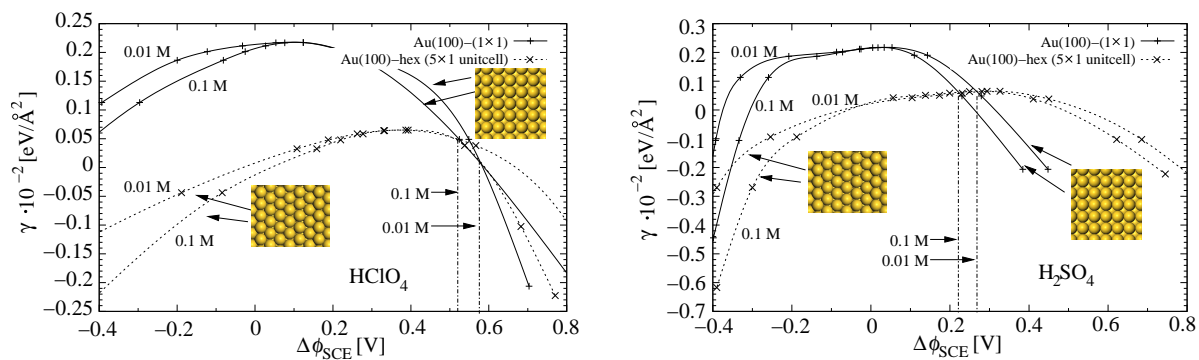


Figure 5. Calculated surface free energy γ as function of the electrode potential (referenced to SCE) for Au(100) in HClO_4 (left) and H_2SO_4 (right) at two different electrolyte concentrations: 10 and 100 mM. The crossing between the curves indicates the electrode potential at which the surface reconstruction is lifted (Au(100)-hex \rightarrow Au(100)-(1 \times 1)).