

# Role of Atomic Scale Roughness in Hot Electron Chemistry

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As already reported, the hydrogen evolution from neutral pH aqueous electrolytes by hot electrons in Al/Al<sub>2</sub>O<sub>3</sub>/Ag junctions at the silver/electrolyte interface is observed only when the silver electrode is weakly “activated” (roughened). After a short description of all relevant phenomena we present a simple model which is based on the increase of the average penetration depth of the hot electrons into the electrochemical double layer by scattering at the surface roughness of the silver(111) face. This leads to a more anodic onset of the hydrogen evolution from the dissociation of water, but only at an activated surface. The model also explains why activation does not reduce the overpotential of the normal hydrogen evolution.

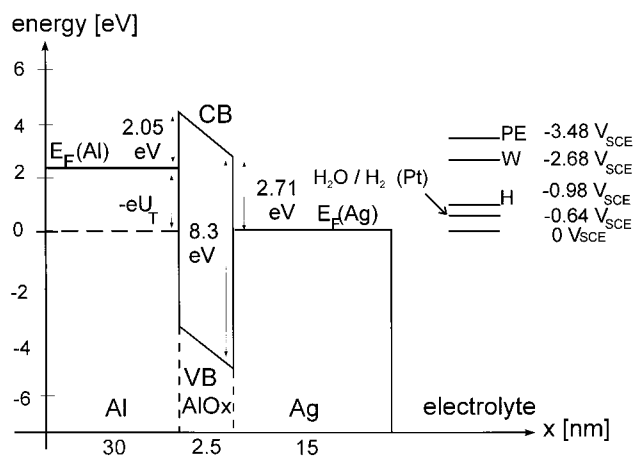
## 1. Introduction

In recent years, surface reactions of hot electrons at silver/UHV (ultrahigh vacuum) and silver/electrolyte interfaces have been reported.<sup>1</sup> A special subfield is the hydrogen evolution from neutral pH electrolytes by hot electrons.<sup>2–4</sup> In all these publications we could not give an explanation of why a weak “activation” (dissolution and redeposition of around 0.5 monolayers of silver) of the silver surface is needed to evolve hydrogen with hot electrons. In ref 3, we wrote: “It is not yet clear why the activation of the silver electrode reduces the overpotential of the hydrogen evolution of the hot electrons, but not of the electrons at the Fermi level”. Roughening is also important in hydrogen oxidation. Only when the surface of an Ag(111) film is slightly roughened can a strong anodic transient after switching from the hydrogen evolution to the nonfaradaic potential range be observed.<sup>5</sup> This was explained by the oxidation of adsorbed atomic hydrogen,<sup>5</sup> corresponding to a coverage of 0.7 monolayers (1 monolayer corresponds to one adsorbate per silver atom), as reported on Ag(111) at low temperatures in ultrahigh vacuum.<sup>6</sup>

In this contribution we propose an explanation of the electrocatalytic role of atomic scale roughness of silver electrodes of (111) orientation. To make this article more self-contained, we give a short review in section 2 of the experimental observations already published before we present the theoretical model in sections 4 and 5.

## 2. Review of Experiments

**(a) Hydrogen Evolution with Hot Electrons.** Electrons with the energy above the Fermi energy of silver exceeding several times  $kT$ , so-called hot electrons, are created in Al/aluminum oxide/Ag tunnel junctions by application of a negative voltage  $U_T$  between the Al and the Ag electrode, see Figure 1. A fraction of these hot electrons reach the outer surface of the silver top electrode as ballistic electrons (without loss of energy), the others are created by Coulomb interaction of the primarily tunneling electrons and the electrons below  $E_F(\text{Ag})$  (so-called secondary electrons). The top electrode is connected simultaneously as a working electrode for the electrolyte. Figure 1

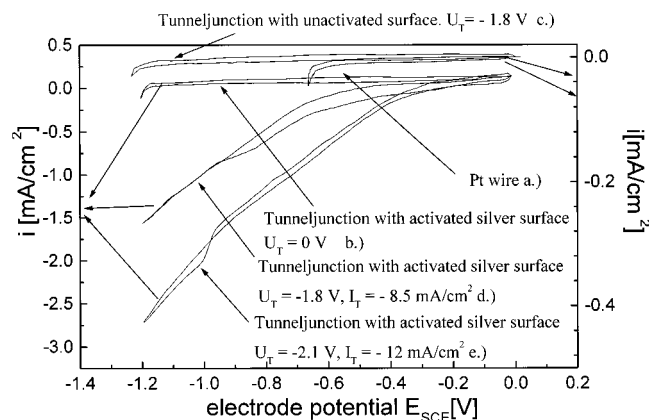


**Figure 1.** Energy scheme of the tunnel junctions (in eV) in contact with the electrolyte. PE = lower edge of the electron conduction band in H<sub>2</sub>O (= D state in ref 7, so-called dry electron), H<sub>2</sub>O/H<sub>2</sub> is the onset potential of hydrogen evolution at a platinum electrode both measured in 0.9 M acetate buffer (pH = 5.9) with 50% water and 50% ethylene glycol electrolyte,<sup>3</sup> W is the position of the lower edge of the so-called wet electron state, H is the center of the hydrated state of the electron in an aqueous electrolyte,<sup>7</sup> all levels at the electrochemical potential of the top silver electrode of 0 V<sub>SCE</sub>. (In this case the Fermi levels of the silver electrode and of the metallic mercury in the SCE ( $E_{F(\text{SCE})}$ ) are at the same level). CB: lower edge of conduction band of Al<sub>2</sub>O<sub>3</sub>. VB: upper edge of the valence band.  $U_T$  = tunnel voltage (the silver electrode is at ground level). From ref 4.

shows the levels of the electrons at the silver/electrolyte interface at an electrochemical potential of 0 V<sub>SCE</sub>. For an applied electrochemical potential negative of  $-0.64$  V<sub>SCE</sub>, the level H<sub>2</sub>/H<sub>2</sub>O (Pt) falls below the Fermi level of the Pt electrode and the hydrogen evolution sets in, see the voltammogram in Figure 2, scan a.

The comparison with the voltammogram of the activated silver electrode of the tunnel junction at  $U_T = 0$  V (Figure 2, scan b) shows the onset of the HER only at a cathodic overpotential of about  $-1.2$  V<sub>SCE</sub>. This behavior is nearly unchanged when a negative  $U_T$  is applied to the junction, provided this has not been “activated” or prepared rough intentionally, see scan c in Figure 2. However, when one prepares the junction on a rough CaF<sub>2</sub> substrate<sup>2</sup> or “activates”

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**Figure 2.** Cyclic voltammograms of tunnel junctions in 0.9 M NaAc buffer, (50% water, 50% ethyenglycole), (a) Pt wire, (b) activated top electrode  $U_T = 0$  V, (c) unactivated top electrode  $U_T = -1.8$  V, (d) activated top electrode  $U_T = -1.8$  V, (e) activated top electrode  $U_T = -2.1$  V.

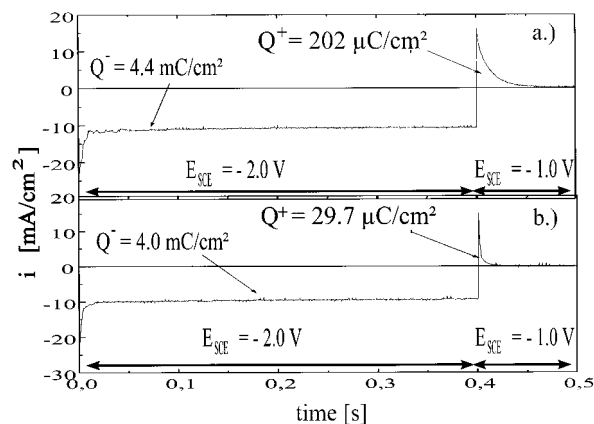
the silver electrode by a weak oxidation–reduction cycle ( $E_{SCE} = +0.5$  V,  $t = 0.2$  s), the HER sets in at more positive potential (see scan d in Figure 2).

Moreover, the onset potential of HER is shifted by 300 mV to positive potentials when the tunnel voltage is increased from  $-1.8$  to  $-2.1$  V (Figure 2, scans d and e). Detailed experiments under time resolution and at various values of  $U_T$  have demonstrated convincingly<sup>3,8</sup> that these reactions are not caused by ionic processes in the aluminum oxide film. One can safely exclude that the hot electrons first enter the levels PE or W (see Figure 1) before evolving hydrogen, because the HER is also observed when  $E_F(\text{Al})$  lies below the level W.<sup>4</sup> The role of the activation, given by the difference in scans c and d calls for an explanation.

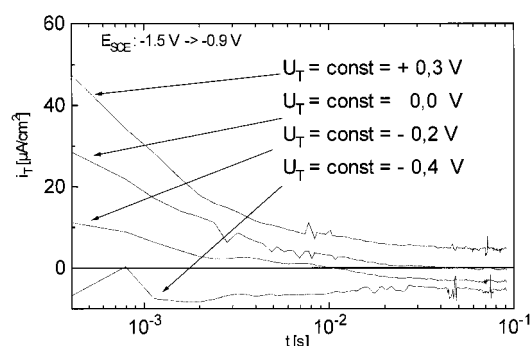
**(b) Hydrogen Oxidation at Activated MIMs<sup>3</sup> and Activated Ag(111) Electrodes.<sup>5</sup>** If the silver electrode of an activated MIM is set to  $E = -0.8$  V<sub>SCE</sub> and  $U_T$  is pulsed from 0 to  $-3.0$  V, the cathodic charge due to the HER by hot electrons exceeds several times a value of  $100 \mu\text{C}/\text{cm}^2$ . When  $U_T$  is pulsed back from  $-3.0$  to 0 V, one observes anodic current transients corresponding to a charge of  $120 \mu\text{C}/\text{cm}^2$ .<sup>5</sup> The most likely explanation is the oxidation of a submonolayer of adsorbed atomic hydrogen.<sup>5</sup> In this case the MIM contact can be used as an internal retarding field spectrometer. If the silver electrode of a MIM contact with adsorbed hydrogen atoms is set by a potential step to an electrochemical potential of for instance  $-0.9$  V<sub>SCE</sub>, i.e., 0.3 V above the onset of hydrogen evolution, one may expect the injection of hot electrons with an energy of up to 0.3 eV above the Fermi level of the silver electrode, a fraction of which may tunnel into the Al electrode.

In Figure 3 the tunnel voltage  $U_T$  is varied in steps from “accelerating” at 0.3 V to “retarding” at  $-0.4$  V. The transients in the tunnel current  $I_T$  after switching back to  $-0.9$  V<sub>SCE</sub> are obvious. At  $U_T = -0.2$  V, the transient is not yet fully suppressed, demonstrating that we do not observe a thermal effect. The constant tunnel currents induced by the application of  $U_T$  is seen at about 0.1 s after the end of the anodic transients.

As in the HER by hot electrons (section 2a) we also need for hydrogen oxidation an activated silver top electrode to observe the anodic transients in the tunneling current (Figure 3) and in the electrolyte current (Figure 7.27 in ref 1). The role of “activation” in oxidation of adsorbed atomic hydrogen may also be observed in the electrolyte current at a conventional silver electrode. Cathodic potential pulses from  $-1.0$  V<sub>SCE</sub> to  $-2.0$  V<sub>SCE</sub> were applied to an epitaxial Ag(111) film in neutral 0.1



**Figure 3.** Tunnel current at  $E_{SCE} = -0.9$  V directly after the end ( $t = 0$  s) of a cathodic pulse from  $-1.5$  V<sub>SCE</sub> to  $-0.9$  V<sub>SCE</sub> of 100 ms duration. The tunnel voltage is set from “accelerating” (+0.3 V) to “retarding” ( $-0.4$  V).



**Figure 4.** Current transients on activated Ag(111) (a) and smooth Ag(111) (b) surfaces in 0.1 M KClO<sub>4</sub> after potential pulses from  $E_{SCE} = -1.0$  V to  $E_{SCE} = -2.0$  V and back from  $E_{SCE} = -2.0$  V to  $E_{SCE} = -1.0$  V.

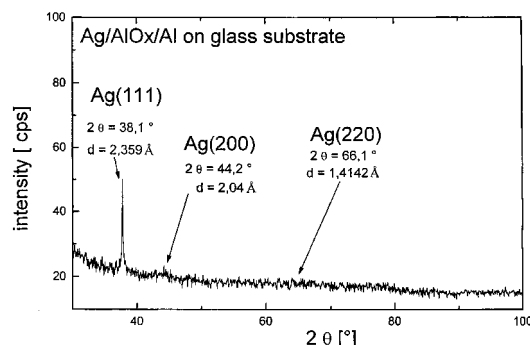
M KClO<sub>4</sub> aqueous electrolyte for 0.4 s, see Figure 3b. Also this reaction is related to hot electron chemistry, as demonstrated with a tunnel junction<sup>9</sup> (Figure 4).

During this time a faradaic cathodic charge  $Q^-$  of  $4 \text{ mC}/\text{cm}^2$  due to hydrogen evolution was accumulated, which corresponds to several monolayers (the charge corresponding to one electron per Ag surface atom of Ag(111) is  $222 \mu\text{C}/\text{cm}^2$ ).<sup>10</sup> The integral of the anodic transient after switching back to  $-1.0$  V<sub>SCE</sub> is just the charge  $Q^+$  involved in changing the voltage of the electrochemical double layer capacity.<sup>5</sup>

However, if the surface and the double layer capacity of this Ag(111) film is increased by about 10% (by a short anodic pulse, leading to silver oxidation and reduction), the charge in the anodic transient corresponds to about 0.7 monolayers on top of the charge to account for the reordering of the double layer. This charge has been assigned to the reoxidation of a layer of atomically adsorbed hydrogen.<sup>5</sup>

### 3. Crystallographic Orientation of the Silver Top Electrodes of the MIM Junctions on Glass Substrates

The crystallographic orientation can be obtained by the Bragg–Brentano method of X-ray scattering. The method delivers a signal from those lattice planes which are parallel to the macroscopic plane of the film. Of course, this method is applicable to the top electrodes of MIM junctions. The spectrum in Figure 5 shows preferentially a (111) orientation with presumably azimuthal randomness with what may be a small fraction of (100) orientation. Due to the limited penetration depth



**Figure 5.** X-ray diffraction on a tunnel junction with Ag top electrode (intensity versus  $2\theta$ ) ( $\lambda = 1.504 \text{ \AA}$ , Cu  $K\alpha_1, K\alpha_2$ ).

of the X-rays and the amorphous structure of the oxide and the glass substrate, all the discrete features are due to the silver top electrode.

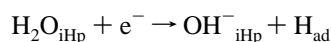
Therefore, the model presented in the next section is focused on hot electrons in Ag(111) films. In section 4, we discuss a model of the possible role of atomic scale roughness on Ag-(111) on the transfer of hot electrons to adsorbates. In section 5, we present our conjecture that the activation corresponds to creation of special sites of atomic scale roughness acting as pathways for the transfer of hot electrons.

#### 4. Model on the Role of Roughness in Hot Electron Transfer

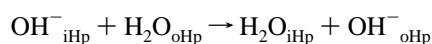
**(a) On Normal Hydrogen Evolution.** By X-ray scattering at the interface of Ag(111) with an NaF electrolyte, Toney et al.<sup>11</sup> evaluated the oxygen distribution in the inner Helmholtz layer. At a potential of  $-0.9 \text{ V}_{\text{Ag}/\text{AgCl}}$ , the maximum of the distribution was about 0.35 nm in front of the top (111) plane of the Ag ion cores. This distance changed to about 0.28 nm at the potential of  $-0.15 \text{ V}_{\text{Ag}/\text{AgCl}}$ . This difference was assigned to a reorientation of the water molecules in the inner Helmholtz plane, the oxygen end situated nearer to the interface at anodic potentials, and the hydrogen end nearer to the interface at cathodic potentials.

Theories of the hydrogen evolution in low pH electrolytes involve potential-dependent reorientations of the water molecules and hydronium ions in both Helmholtz layers and proton transfer (for instance ref 12, and references therein).

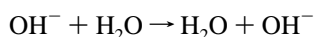
Hydrogen evolution in neutral to basic electrolytes probably involves tunneling of electrons from the metal into water  $\text{H}_2\text{O}_{\text{iHp}}$  in the inner Helmholtz plane (maybe into the empty O–H antibonding  $4a_1$  orbital of  $\text{H}_2\text{O}$ , see Figures 5, 6, and 8 in ref 13). This electron transfer can split the molecule and drive the Volmer reaction (for more details, see ref 5).



The further charge transport probably involves the steps of proton transfer between inner and outer Helmholtz plane



and a modified Grothuis mechanism in the bulk electrolyte by proton transfer



**(b) On Hydrogen Evolution by Hot Electrons.** Hydrogen evolution by hot electrons takes place at less cathodic potential than the usual hydrogen evolution which involves only “cold

electrons” of energy at and below the Fermi surface. In this case the ordering of the water molecules is probably not the same as at the onset of the usual “cold electron hydrogen evolution”.

The basis of our model of hydrogen evolution from  $\text{H}_2\text{O}$  by hot electrons is as follows. The tunneling probability grows quasi exponentially with the extension of the tail of the electronic wave functions into the double layer. At a certain threshold of the “penetration depth” the Volmer reaction starts. The penetration depth is a function of the electronic energy and momentum parallel to the surface and the applied electrochemical potential. The energy–momentum relation of the bulk electrons (which are involved in the observed transport processes) is given by the bulk band structure. The only information on the electron in the electrolyte we use is the energetic position PE of the lower band of the electronic conduction band in water, the so-called “dry electron”.

The penetration length of the bulk electrons of energy  $E$  into an electrolyte is calculated analogous to the penetration of free metal electrons into vacuum, with replacement of  $E_{\text{vacuum}}$  by PE. The electron wave function outside of the last layer of the cores of the silver surface atoms is assumed to be free-electron-like, (we neglect a possible increase of the mass because of interaction with the inner Helmholtz layer) with a relation between wavevector  $k$  and energy  $E$  given by

$$\hbar^2 k^2/2m = E - \text{PE} \quad (1)$$

The wavevector  $k = (k_x, k_y, k_z)$  has the normal component  $k_z$ , which is imaginary when

$$E < \text{PE}. \text{ In this case we set } k_z = ik.$$

In eq 1,  $E$  is the energy of the bulk electron and  $k_{\parallel} = (k_x, k_y)$  is the tangential component of the bulk part of the electronic wave functions, because of the continuity of the wave function across the metal/electrolyte interface. The decay length  $L$  of the wave function of electrons within the electrolyte is  $1/k$ . The difference  $\text{PE} - E_F$  varies with the electrochemical potential  $E_{\text{SCE}}$  according to refs 1 and 4:

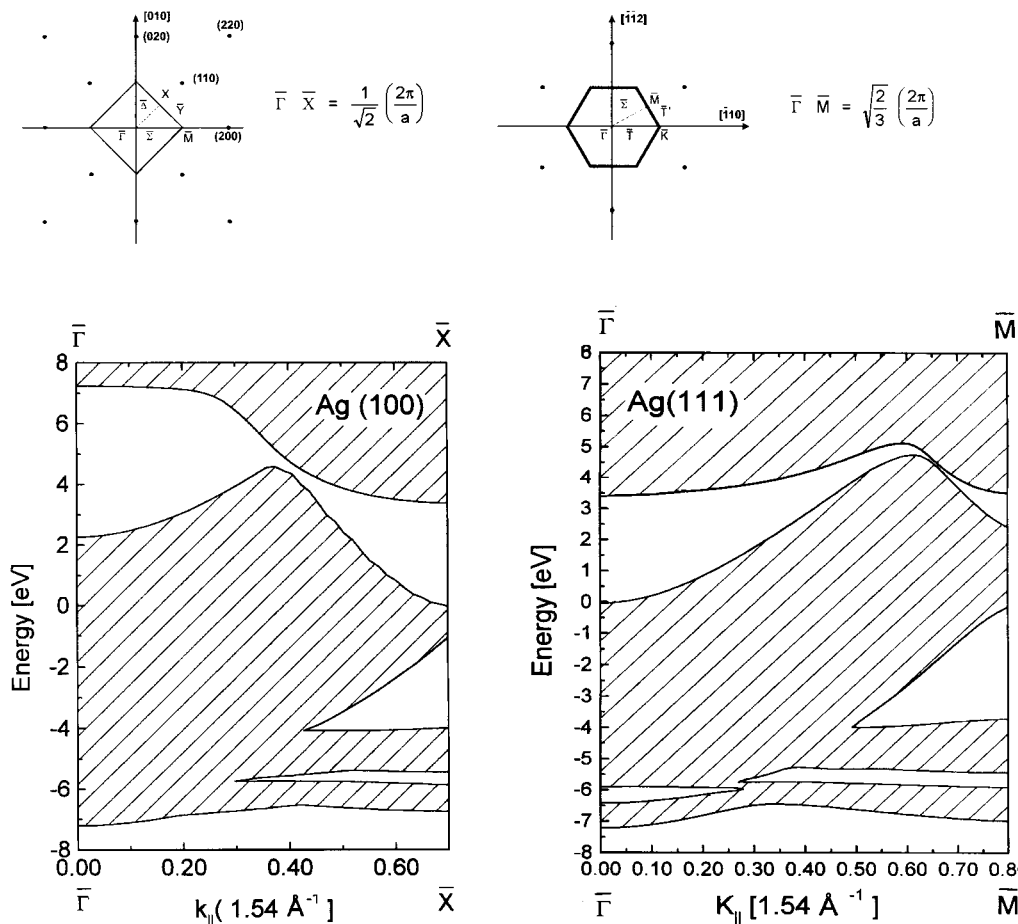
$$\text{PE} - E_F = 3.3 \text{ eV} + eE_{\text{SCE}} \quad (2)$$

At  $k_{\parallel} = 0$ ,  $L$  diverges when  $E$  reaches PE, because the electron can now enter the bulk electrolyte, as observed<sup>1,4</sup> by photoemission into the electrolyte (hence the abbreviation PE).

**(c) On the Role of Roughness.** Our general argument on the role of surface roughness is derived from the fact that there are gaps in the surface projected bulk electron density of states for the silver(111) and (100) surface.<sup>14</sup>

That means that for the (111) oriented electrodes there are only propagating bulk hot electrons at  $E - E_F \approx 2 \text{ eV}$  with components  $k_x$  and  $k_y$  of  $k$  above the minimum values. Consequently, hot electrons propagating normal to the surface do not exist. Related effects have been clearly observed in secondary-electron-emission and absorbed-current spectra of Ag-(111), (100), and (110).<sup>16</sup> The hot electrons arrive at (111) surfaces only at oblique incidence and therefore have a relative small decay length  $L$ . But when the surface is not perfect, these electrons may be scattered by atomic scale roughness into states with larger  $L$ . Larger  $L$  means that the tunneling probability to the lowest unoccupied molecular orbital (LUMO) of adsorbed molecules, atoms, and ions grows.

We try to quantify this for the Ag(111) surface. For hot electrons in silver films of (111) orientation there is because of a gap in the surface-projected density of bulk electronic states<sup>14</sup>



**Figure 6.** Surface-projected bulk electron density of states (shaded) of Ag(100) surface in  $\bar{\Gamma} - \bar{X}$  direction (left) and Ag(111) surface in  $\bar{\Gamma} - \bar{M}$  direction (right) from a self-consistent relativistic density functional calculation.<sup>15</sup> The  $k_{||}$  directions are indicated in the surface Brillouin zones above.

a minimum value  $k_m(E_{\text{hot}})$  of  $k_{||} = (k_x^2 + k_y^2)^{1/2}$  as a function of

$$E_{\text{hot}} = E - E_F = -eU_T \quad (3)$$

see Figure 6.

These conditions given, one easily derives:

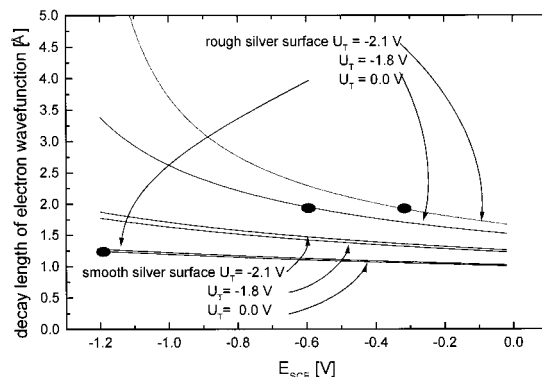
$$L \leq L_{\text{max,smooth}} = |2m/(-eU_T - 3.3 \text{ eV} - eE_{\text{SCE}}) - k_m(E_{\text{hot}})^2|^{-1/2} \quad (4)$$

Figure 7 shows  $L_{\text{max,smooth}}$  as a function of  $E_{\text{SCE}}$  for  $eU_T$  equal to 0, -1.8, and -2.1 V.

Our hypothesis is that there is elastic scattering of hot electrons by atomic scale surface roughness to laterally (parallel to the surface) and perpendicularly (versus the interior of the crystal) damped states with the real part of the parallel wavevector  $k_{||} < k_m(E_{\text{hot}})$ , so-called virtual states in the gap of the projected density of states in Figure 6. These virtual states may comprise the Shockley surface states which are at the clean surface at  $k_{||} = 0$  below the Fermi energy, but which may be pushed upward by the adsorbates. They are orthogonal to the bulk states at a perfect smooth low index surface, but atomic scale roughness (e.g. fuzzy steps, see section 5) may allow conversion of hot electrons into these virtual state electrons.

The scattering into virtual states will increase the right-hand side of relation 4, reaching its maximum at  $k_{||} = 0$ . The limit is given by

$$L \leq L_{\text{max,rough}} = |2m/(-eU_T - 3.3 \text{ eV} - eE_{\text{SCE}})|^{-1/2} \quad (5)$$



**Figure 7.** Maximum decay length  $L$  of the electron wave function within the electrolyte as a function of the electrochemical potential  $E_{\text{SCE}}$  for smooth and rough silver(111) electrodes according to eqs 4 and 5, respectively, for the indicated tunnel voltages  $U_T$ . For fat points, see text.

see also Figure 7 for  $eU_T$  equal to 0, -1.8, and -2.1 V. Note that  $L_{\text{max,rough}}$  depends only on  $(U_T + E_{\text{SCE}})$ .

The experimental onset of the hydrogen evolution at an activated surface by hot electrons at  $U_T = -1.8$  V is at about  $E_{\text{SCE}} = -0.6$  V (see Figure 2), where  $L_{\text{max,rough}} = 0.195$  nm, according to Figure 7 (fat point in the middle). We obtain the same value of  $L_{\text{max,rough}}$  for  $U_T = -2.1$  V at  $E_{\text{SCE}} = -0.3$  V (see left fat point in Figure 7), which corresponds with the observed onset of hydrogen evolution at  $U_T = -2.1$  V (see Figure 2). Equation 4, valid for the smooth surface, gives



$L_{\text{max,smooth}} = 0.144 \text{ nm}$  at  $U_T = -1.8 \text{ V}$  and  $E_{\text{SCE}} = -0.6 \text{ V}$  (see Figure 7).

The role of the roughness can thus be understood. When  $L \approx 0.195 \text{ nm}$ , this allows the hot electron to reach and dissociate the water molecules in the inner Helmholtz layer (with the structure of the double layer at  $E_{\text{SCE}} \approx -0.5 \text{ V}$ ), whereas the lower value of  $L_{\text{max,smooth}} = 0.144 \text{ nm}$  is not sufficient for this.

For  $U_T = 0 \text{ V}$ , the “normal, cold electron hydrogen evolution” is observed at  $E_{\text{SCE}} = -1.2 \text{ V}$  (see Figure 2). At this potential both the calculated values of  $L_{\text{max,rough}}$  and  $L_{\text{max,smooth}}$  are about  $0.124 \text{ nm}$  (see Figure 7, left fat point). We can understand why this relatively low value of  $L$  allows hydrogen evolution, if we assume that at this rather cathodic potential the water molecules in the double layer are reoriented.<sup>12</sup> This now allows the transfer of the “cold” electron into the inner Helmholtz layer with subsequent dissociation of water, as discussed above. Modeling of the metal/electrolyte interface by Pecina and Schmickler<sup>12</sup> shows a reorientation of the water O–H groups in the inner Helmholtz layer toward the surface by the strong electric fields in the double layer at cathodic potential which may allow the necessary electron transfer already at smaller values of  $L$ . The approximate agreement of  $L_{\text{max,rough}}$  and  $L_{\text{max,smooth}}$  at  $E = E_F$  may explain why roughness of the silver electrode reduces the overpotential of the normal hydrogen evolution only very little.

Our model would predict a less cathodic onset of hydrogen evolution by hot electrons at smooth silver electrodes, which is not indicated in Figure 2. However, there may be some experimental indication for this process in ref 17.

To our best knowledge, this is the first model of hydrogen evolution which involves not only orientational effects in the double layer, but also a potential dependent penetration of the metal electrons in the inner Helmholtz layer.

## 5. Conjectures on Activation

Our model above is based on the elastic scattering of hot electrons by atomic scale roughness of Ag(111) surfaces. This implies that two conditions must be fulfilled in order to observe the enhanced hydrogen evolution reaction by hot electrons: (1) a sufficiently high surface concentration of special atomic scale roughness sites at a surface of mainly 111 orientation, and (2) a sufficient overlap of bulk and virtual surface states at and near these special sites of atomic scale roughness to allow hot electron transfer.

The hydrogen evolution by hot electrons has been observed using tunnel junctions undercoated with a rough  $\text{CaF}_2$  film of  $100 \text{ nm}$  thickness. By measuring the electrochemical capacity of these samples and a silver(111) single-crystal one may define a roughness factor as the ratio of the capacities of the “rough” and “smooth” sample, both capacities normalized with respect to the apparent surface area. The roughness factor thus obtained ranged between 1.2 and 1.7. The layer of adsorbed hydrogen on an epitaxial Ag(111) film was observed after an increase of the surface by 10% by a fast oxidation–reduction cycle (ORC) (for experimental conditions, see section 2). Surprisingly, the activation of the tunnel junctions on glass substrates needed only the oxidation and subsequent reduction of half a monolayer of silver. The related increase in surface area is negligible. Therefore we think that the activation is needed to fulfill point 2) above. Maybe the activation reflects the cleaning of “active sites” from unknown adsorbates which prevent an efficient electron transfer. However “activation” was not necessary on the  $\text{CaF}_2$  roughened samples, to which these unknown adsorbates would probably stick as well. Therefore we envision the activation as a transformation of already-existing linear mona-

topic steps into static fuzzy steps with a high density of kink sites, by the partial dissolution of terraces, starting at steps and the subsequent redeposition of the material on the terraces, from which it migrates to the steps but does not diffuse length the steps. On the other hand, a silver film contouring the rough  $\text{CaF}_2$  substrate would have many stable kink sites, and therefore would not need “activation”.

Checking these conjectures will need careful scanning tunneling microscopy of the non-activated and of the activated surfaces.

Our model reflects the experimental observations only very approximately.

This is not surprising given the very simple theoretical assumptions made for a complicated problem. Since we see no other concept yet to explain the observed influence of the activation, we will resort to an experimental approach to check the concept of roughness-controlled penetration depths  $L$ . Experiments on Ag(111) electrodes with better-controlled roughness are under way.

We tentatively explain the role of roughness in the observed reoxidation of atomic hydrogen, see section 2b in an analogous way. Electrons in the virtual bound states, which extend farther out, can only hybridize with the bulk states in the presence of special roughness sites where the electron from adsorbed hydrogen can be released to Ag(111) bulk states. This process can be considered as the time-reversed reduction process discussed above. It should be noted that the critical penetration depths  $L$  necessary for the Volmer reaction and the oxidation of adsorbed atomic hydrogen are probably different. Without or with little activation, the electron-transfer rate from  $\text{H}_{\text{ad}}$  to the bulk will be low and the Tafel reaction



will have the higher reaction rate and will take over.

## 6. Summary

We present a simple model on the decay length of the wave function of bulk electronic states as a function of energy above the Fermi level of the metal, as a function of the bulk wavevector, and as a function of the electrochemical potential of an Ag(111) electrode. We propose how scattering of hot electrons by atomic scale surface roughness may increase the decay length of hot electrons, so that the hydrogen evolution by dissociation of water sets in at more anodic potentials than the normal hydrogen evolution (by “cold electrons”). The same model also implies that activation does not decrease the overpotential of the normal hydrogen evolution. With a further plausible assumption on the reorientation of the electrochemical double layer as a function of the potential, we can explain why the activation of the silver electrode reduces the overpotential of the hydrogen evolution by hot electrons, but not by the electrons at the Fermi level.

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