Determination of the Step Dipole Moment and the Step Line Tension on Ag(001) Electrodes

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Abstract

Using impedance spectroscopy, we determined the step dipole moment and the potential dependence of the step line tension of silver electrodes in contact with an electrolyte: (001) and vicinal surfaces (11*n*) with *n* = 5, 7, 11 in 10 mM ClO_4^--solutions were investigated. The step dipole moment is determined from the shift of the potential of zero charge (*pzc*) as a function of the surface step density. The dipole moment per step atom was found to be 3.5±0.5 *e*Å. From the *pzc* and the potential dependence of the capacitance curves, the potential dependence of the surface tension of the vicinal surfaces is determined. The line tension of the steps is then calculated from the difference between the surface tensions of stepped (11*n*) and the nominally step free (001) surface. The results are compared to a previous study on Au(11*n*)-surfaces. For gold, the step line tension decreases roughly linear with potential, whereas a parabolic shape is observed for silver.

1. Introduction

The stability of surface structures against diffusive processes decreases with the second to the forth power of the size scale. Hence, the question of stability becomes more and more significant as research follows the road of device minimization into the nanometer range and even further down to atomic dimensions. Single crystal surfaces with two- and three-dimensional deposits are frequently used as model system for the investigation of diffusion processes. Diffusion processes follow a path that leads to a smaller number of atoms in low nearest neighbor configuration. On most rough or nanostructured surfaces, the by far largest number of atoms with a lower coordination than the surface atoms resides at monatomic steps. Monatomic steps are therefore objects of particular interest in this context.

In order to describe the literary zillions of processes which are involved in the decay of nanoscale structures on surfaces a coarse-grained description in a thermodynamic approach has proved useful. The thermodynamic quantity that is the driving force for diffusion and coarsening phenomena in general is the work per step length required to form a step, the step line tension [1]. For surfaces in vacuum, this step line tension is equal to the Helmholtz free energy per step length which in turn is nearly equal to the step energy, save for a small term due to the phonon entropy [2]. In an electrochemical environment where surfaces are held at constant potential rather than at constant (i.e. zero) charge, the step line tension involves an additional term comprising of the product of the potential and the extra charge associated with the step. Since surfaces in an electrolyte are substantially charged, the step line tension differs considerably from the free energy and becomes potential dependent [3], just as the surface tension does [2, 4]. Key to the potential dependence of the step line tension is the step dipole moment. This dipole moment has its origin in the rearrangement of the electronic charge at the surface [5]. For metal surfaces, the step dipole moment is of the order of 0.01 eÅ [2]. The orientation of the dipole moment is such that it reduces the work function of vicinal surfaces [6]. The reduction in the work function has its equivalent at the solid/liquid interface in the shift of the potential of zero charge (*pzc*) towards negative potentials [2, 4, 7]. We have shown recently that this shift in the *pzc* by itself gives rise to a linear dependence of the step line tension on the surface charge density while additional quadratic terms are due to the capacitance associated with the steps [7]. In the same paper, we have shown that step dipole moments can be extracted experimentally from the shift in the *pzc* with step density of vicinal surfaces.

The present work is an extension of that previous work on unreconstructed vicinal Au(001) surfaces [7] to vicinal Ag(001) surfaces in 10 mM $KClO_4$ using impedance spectroscopy. For the Ag(11*n*) surfaces we find step dipole moments of $3.5\pm0.5\times10^{-3}\,e$Å, slightly smaller than the dipole moments on Au(11*n*) vicinals ($5\times10^{-3}e$Å). The reduction of the capacitance due to the presence of steps is larger than for gold surfaces. Because of the small step dipole moment and the large change in the capacitance, the line tension of steps on Ag(001) surfaces exhibits a quadratic dependence on the electrode potential.

2. Experimental and Theory

The experiments were performed on stepped Ag(001) single crystals. The samples were cut by spark erosion from a single crystal rod. The electrodes were oriented by diffractometry and polished to the desired orientation to within 0.1°, the limit determined by the mosaic structure of high-quality single crystals. The samples had Miller indices (11*n*) with $n = 5$, 7, and 11. These surfaces are vicinal to the (001)-plane, with a miscut angle θ along the atomically dense $[\bar{1}\,\bar{1}\,0]$-direction, where $\tan\theta = \sqrt{2}/n$ [1]. The geometrically ideal surface consists of equally spaced, monatomic high and parallel steps separated by (001)-oriented terraces. The mean terrace width is $L = na_{\perp}/2$ [1], with $a_{\perp}$ the distance between densely packed atomic rows along $[\bar{1}\,\bar{1}\,0]$ ($a_{\perp} = 2.89$ Å). The real surface, however, reveals a distribution of step-step distances. In the case of stable vicinal surfaces, the step-step distance probability distribution is close to a Gaussian with the peak shifted to slightly smaller terrace widths compared to the nominal value $L = na_\perp/2$. This is due to a small asymmetry in the distribution slightly favoring large step-step distances compared to a Gaussian distribution [8]. In an electrolyte, the step-step distance distribution depends on the electrode potential [9, 10]. It could be shown that on the long time scale stepped Ag(111) [9, 10] and stepped Au(001) [11] vicinal surfaces may undergo a step bunching transition [12] for large potentials. We note that this transition is different from a surface faceting, since the steps remain well separated with the step-step distance distribution broadened or even bifurcated. Because of the considerable mass transport involved, the potential induced step bunching is kinetically slow (30 min up to 2 h [9]). The time scale is much longer than the typical time for collecting impedance spectroscopy data and for a cyclic voltammogram, which is of the order of minutes. Hence, in the studies presented here, we may assume that the electrodes consist of well-separated steps and that the step-step distance distribution is reasonably close to a Gaussian distribution. In any case, since merely the mean step-step distance enters our analysis, even a possible step bunching would be of no consequence for the conclusions of our study.

Prior to each experiment, the single crystals were prepared by etching in a KCN-H_2O_2 solution, annealed in a H_2 flame, and cooled down to room temperature in Ar atmosphere. Afterwards, the samples were transferred to the cell under the protection of a droplet of deoxygenated water [13]. As electrolytes, we used suprapure $KClO_4$ (Merck) twice recrystallized, and Milli-Q water (Millipore, 18.2 MΩ cm^{-1}). The crystal surface was brought in contact with the electrolyte under potential control at values well below the *pzc*. The contact between the electrode surface and the solution was made by means of the hanging meniscus method [13]. A saturated calomel electrode (SCE) served as reference electrodes and a platinum foil as counter electrode. Cyclic voltammetry and capacitance curves were recorded using a Zahner IM5 impedance potentiostat.

By definition, the step line tension is

$$\beta_{(11n)}(E) = \lim_{L\to\infty} L\left\{\gamma_{(11\mathrm{n})}(E) - \gamma_{(001)}(E)\right\} \tag{1}$$

where L is the distance between steps on the $(11n)$ surfaces and $\gamma_{(11\mathrm{n})}(E)$ and $\gamma_{(001)}(E)$ are the surface tensions of the $(11n)$ and (001) surfaces, and E is the electrode potential. The surface tensions can be calculated from the surface charge density $\sigma(E)$ by integrating the Lippmann equation

$$\gamma(E) = \gamma(E_{pzc}) - \int_{E_{pzc}}^{E} \sigma(E')\mathrm{d}E' \tag{2}$$

Here, E_{pzc} is the potential of zero charge. The determination of the step line tension $\beta(E)$ thus requires the measurement of *pzc* and the capacitance $C(E)$ on vicinal surfaces and the (nominally) step free (001) surface.

For a qualitative understanding of the potential dependence of the step line tension it is useful to consider the case where the capacitance of a stepped surface is shifted on the potential scale according to the shift in the *pzc*, ΔE_{pzc}, and corrected by a factor that accounts heuristically for the different screening and polarizability at step sites [14]:

$$C_{(11n)}(E) = C_{(001)}(E - \Delta E_{\mathrm{pzc}})(1 + \frac{l_c}{L}) \tag{3}$$

Here, l_c is a length that characterizes the line capacitance of a step. The contribution of steps to the surface capacitance (line capacitance) is positive (negative) if $l_c > 0$ ($l_c < 0$). Taking l_c as independent of the potential requires that the isotherm for specific adsorption of ions is identical for step and terrace sites except for the shift in the *pzc*. As will be demonstrated and discussed in more detail in a forthcoming publication [15], steps exclusively influence the Helmholtz capacitance and leave the Gouy Chapman capacitance unchanged. Therefore, l_c as defined in eq. (3) becomes concentration dependent and has not a direct physical interpretation. Nevertheless, for a given electrolyte concentration, it nicely parameterizes the effect of steps on the capacitance in the entire potential range [7].

The shift in the *pzc*, ΔE_{pzc}, can be expressed in terms of the dipole moment per step atom p_z

$$\Delta E_{\mathrm{pzc}} = -\frac{p_z}{\varepsilon_0 a_{\|} L} \tag{4}$$

with $a_{\|}$ the atom length unit along the step edge ($a_{\|} = a_{\perp} = 2.89$ Å for Ag(001)) and ε_0 the dielectric permeability. The shift in *pzc* is towards negative potentials as experimentally well documented [2, 7, 16, 17]. Hence, the dipole moments of steps (and also adatoms and vacancies) point with their positive ends away from the metal surface [18].

With eq. (4) the charge density can be expanded as

$$\begin{aligned} \sigma_{(11n)}(E) &\cong \left[\sigma_{(001)}(E - \Delta E_{\mathrm{pzc}})\right](1 + \frac{l_c}{L}) \\ &\cong \sigma_{(001)}(E) - \frac{\partial \sigma_{(001)}}{\partial E} \Delta E_{\mathrm{pzc}} + \sigma_{(001)}(E)\frac{l_c}{L} \end{aligned}. \tag{5}$$

Inserting (5), (4) and (2) into (1) yields the approximation

$$\beta(E) \cong \beta(E_{\mathrm{pzc}}) - \frac{p_z}{\varepsilon_0 a_{\|}} \sigma_{(001)}(E) + \left[\gamma_{(001)}(E) - \gamma_{\mathrm{pzc},(001)}\right] l_{\mathrm{c}} \tag{6}$$

The experimental determination of the potential dependence of the step line tension therefore requires measurements of the capacitance vs. the potential E on vicinal surfaces and the flat surface. E_{pzc} is determined from the minimum in the capacitance $C(E)$ vs. the potential in sufficiently dilute electrolytes.

3. Results and Discussion

The cyclic voltammogram of Ag(001) is similar to those reported in the literature [17, 19, 20]. The double layer region is limited by the hydrogen evolution at negative potentials (< – 1.2 V) and by silver dissolution at positives potentials (> – 0.2 V). The cyclic voltammogram shows a minimum (in the positive or negative potential sweep) around the *pzc*. The voltammograms of the stepped surfaces (*n*=5, 7 and 11) are similar to those of Ag(001) save for a slight shift of the *pzc* towards negative potentials.

Fig. 1a shows the capacitance curves of Ag(001) and Ag(117) in 10 mM $KClO_4$ as solid and dashed line, respectively. These capacitance curves have a similar shape compared to those obtained for Au crystals (Fig. 1b). The minimum in the capacitance curve, and hence the *pzc*, for Ag(117) is shifted to more negative potentials compared to Ag(001). Compared to Au(117) (Fig. 1b) the capacitance curve of Ag(117) is slightly broadened around *pzc*, which indicates that the potential dependence of the capacitance near steps may differ from the flat surface. For Ag(11*n*), *n*=5, 11, the capacitance curves look similar to that of Ag(117) and are not plotted here.

The *pzc* values obtained from the capacitance curves in Fig. 1 (a) and from the equivalent curves for *n* = 5, 7, and 11 are plotted in Fig. 2a. Fig. 2b shows the corresponding results for Au electrodes as publsihed previously [7]. Within the limits of error, the *pzc* depends linearly on the step density, in agreement with eq. (4). Note that the step density for Ag(001) and Au(001) is set to zero. The typical step density of a high-quality single-crystal electrode after flame annealing is of the order of 10^{-3} Å^{-1}. Assuming the step density to be zero for the (001) surfaces therefore has merely a negligible effect on the slope of the solid lines in Fig. 2.

Fig. 3 displays the capacitance at *pzc* $C(E_{\mathrm{pzc}})$ versus the step density for Ag(11*n*) in 10mM $KClO_4$ (triangles) together with the results for Au(11*n*) in 5mM $HClO_4$ (squares) [7]. In both cases, the capacitance decreases with increasing step density and the decrease appears to be approximately linear in L^{-1} in agreement with eq. (3). A step density-independent characteristic length l_{c} can therefore be assigned to both the gold and the silver surfaces. For both materials, the characteristic length l_{c} is negative, i.e. the capacitance is reduced by the presence of steps.

Table 1 summarizes the dipole moments per step atom, the step capacitance $C(E_{pzc})$ and the characteristic length l_{c} at *pzc* for Ag(11*n*) in 10 mM $KClO_4$. For comparison we have added the previously published data for Au(11*n*) in 5 mM $HClO_4$ [7]. The errors are taken as the single variance obtained from fitting a straight line through the data points as for instance shown in Figs. 2 and 3. According to Table 1, the step dipole moment for Ag(11*n*) is even smaller than for Au(11*n*) surfaces. The capacitance at *pzc* is somewhat larger for silver than for gold. The difference is mostly to be attributed to the higher electrolyte concentration [4]. The characteristic length l_{c} for Ag(11*n*) electrodes (l_{c} = 1.1±0.1Å) is twice as large as for Au(11*n*). This difference cannot be attributed to the difference in the concentrations.

Fig. 4a displays the step line tension $\beta a_{\|}$ calculated using the definition (eq. (1)) for Ag(1 1 5), Ag(1 1 7) and Ag(1 1 11) as solid, dashed and dash-dotted line respectively. The approximate dependence calculated from eq. (6) with the dipole moments p_z and the characteristic length l_{c} taken from Table 1 is shown as a dotted line with estimated error bars. The data are referenced to the (unknown) line tension at *pzc*. The respective results as reported for Au(11*n*), *n*=5,7,11, in a previous paper [7] are shown for comparison in Fig. 4b.

We begin our discussion with the step dipole moments p_z for silver and gold. Table 2 compares our results on the dipole moments to previously published data for various silver and gold surfaces. In the case of Ag(11*n*) we find $p_z = 3.5 \pm 0.5 \times 10^{-3}$ *e*Å which is in reasonable agreement with the value obtained by Hamelin et al. (5.4×10^{-3} *e*Å) [17]. It seems that the step dipole moment is considerably larger on (111) compared to (001) metal surfaces. The larger step height on the (111)- compared to the (001)-terraces, 2.36 and 2.05 Å, respectively[1] may contribute to the larger dipole moments on the (111)-surfaces. However, the main effect must arise from the different local environment of atoms on the two surfaces. The importance of the local atomic structure at the steps is emphasized by the fact that on (111)-surfaces the dipole moments of A-steps ((001)-microfacets) and B-steps ((111)-microfacets) may differ by as much as a factor of two [6, 16, 17]. Further interpretation of the larger differences in the dipole moments must await an analysis of the problem by first principle methods.

The characteristic length l_c that describes the change of the interface capacitance at *pzc* due to steps is negative; hence, the interface capacitance is reduced near steps. Theoretical results in [21] proposed a negative step capacitance, however, the values reported there are incorrect, as the results proved to be not fully converged. The theory will be revisited in the course of a detailed discussion of the potential and concentration dependence of the step capacitance on Au(001) electrodes in a forthcoming publication [15].

Moving to the discussion of the results for the step line tension as presented in Fig. 4, we note that the data for the various Ag(11*n*) surfaces with $n = 5, 7, 11$ agree well among each other for negatively and slightly positively charged surfaces. The increasing deviations for larger positive or negatively charged surfaces are attributed to the increasing errors in the integration procedures (eq. (2)) and the smallness of the difference $\gamma_{(11\mathrm{n})}(E) - \gamma_{(001)}(E)$ (eq. (1)).

As for the gold surfaces (Fig. 4b) the approximation of eq. (6) describes the overall trend of the data reasonably well, even far away from *pzc*. Because of the lower step dipole moment of

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[1] Note that the lattice constants for Ag (4.09 Å) and Au (4.08 Å) are almost identical.

the Ag-surfaces, on the one hand, and the larger value of l_c, on the other, the shape of the line tension for the silver surfaces (Fig. 4a) resembles more a parabola than a straight line, as is the case on gold surfaces.

For both the Ag(001) and the Au(001) steps the potential dependence of the step line tension is rather small compared to the absolute values at *pzc*. At *pzc*, the step line tension should be approximately equal to the step formation energy at the solid/vacuum interface for which 130 meV and 170 meV have been determined theoretically for Ag(001) [22] and experimentally for Au(001) [23] surfaces. Insofar as the step line tension is considered as the driving force for the decay of nanostructures on surfaces, the decay rate should merely weakly depend on the potential. However, the actual decay rate depends also on the speed of the diffusion processes, hence on the activation energies for diffusion. Just as the potential dependence of the step line tension depends on the dipole moment of the step atoms the formation energy of adatoms carrying the diffusion current depends on the dipole moment of the adatoms [24, 25] which amounts to 0.075 *e*Å and 0.095 *e*Å on Ag(001) and Au(001), respectively [18]. These dipole moments are about a factor of 20 larger than the step dipole moments and will dominate the potential dependence of decay process on (001) surfaces. The situation is different for the (111) surfaces of silver and gold for which the step dipole moments are a factor of 5-10 higher than for the (001) surfaces. The resulting dramatic consequences for the potential dependence of the defect formation energies and also the activation energies for atom migration and thus for the process of *electrochemical annealing* have been discussed recently in the context of Ostwald ripening on Au(001) surfaces [24, 25].

4. Conclusions

In the present work, we determined the relative step line tension of stepped Ag(001) surfaces in contact with an electrolyte. By measuring the shift in the potential of zero charge and the slope of the step line tension versus surface charge, we deduce the step dipole moment per atom to 0.0035 eÅ for Ag(001). Furthermore, we measured the potential dependence of the step line tension on silver surfaces. Contrary to Au(001) surfaces where the step line tension is essentially a linear function of the potential, the step line tension on Ag reveals a quadratic dependence. This is due to the larger (negative) step line capacitance of silver.

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Captions

Fig. 1: Capacitance curves for (001) (solid lines) and (117) (dot-dashed lines) surfaces of (a) Ag electrodes in 10 mM $KClO_4$ and (b) for Au electrodes in 5 mM $HClO_4$ as published previously [7]. The capacitance curves were obtained using a frequency 20Hz and a 5mV amplitude.

Fig. 2: Potential of zero charge vs. step density determined from the capacitance curves in Fig. 1 for (a) Ag(11*n*) in 10 mM $KClO_4$ and (b) Au(11*n*) in 5 mM $HClO_4$ (data taken from ref. [7]).

Fig. 3: Capacitance $C(E_{\mathrm{pzc}})$ at the potential of zero charge vs. step density determined from the capacitance curves for Ag in 10 mM $KClO_4$ (triangles) and for Au in 5 mM $HClO_4$ (squares) [7].

Fig. 4: The step line tension per step atom, $\beta a_{||}$, for Ag(11*n*) surfaces is shown as solid, dashed and dash-dotted line for $n = 5$, 7, and 11, respectively. The curves are calculated using the definition (eq. (1)). The approximate dependence calculated from eq. (6) with the dipole moments p_z and the characteristic length l_c taken from Table 1 is shown as a dotted line with estimated error bars. The data are referenced to the (unknown) line tension at *pzc*. Fig. 4b shows the corresponding results for Au(11*n*) surfaces in 5 mM $HClO_4$ [7].

Tables

Table 1:

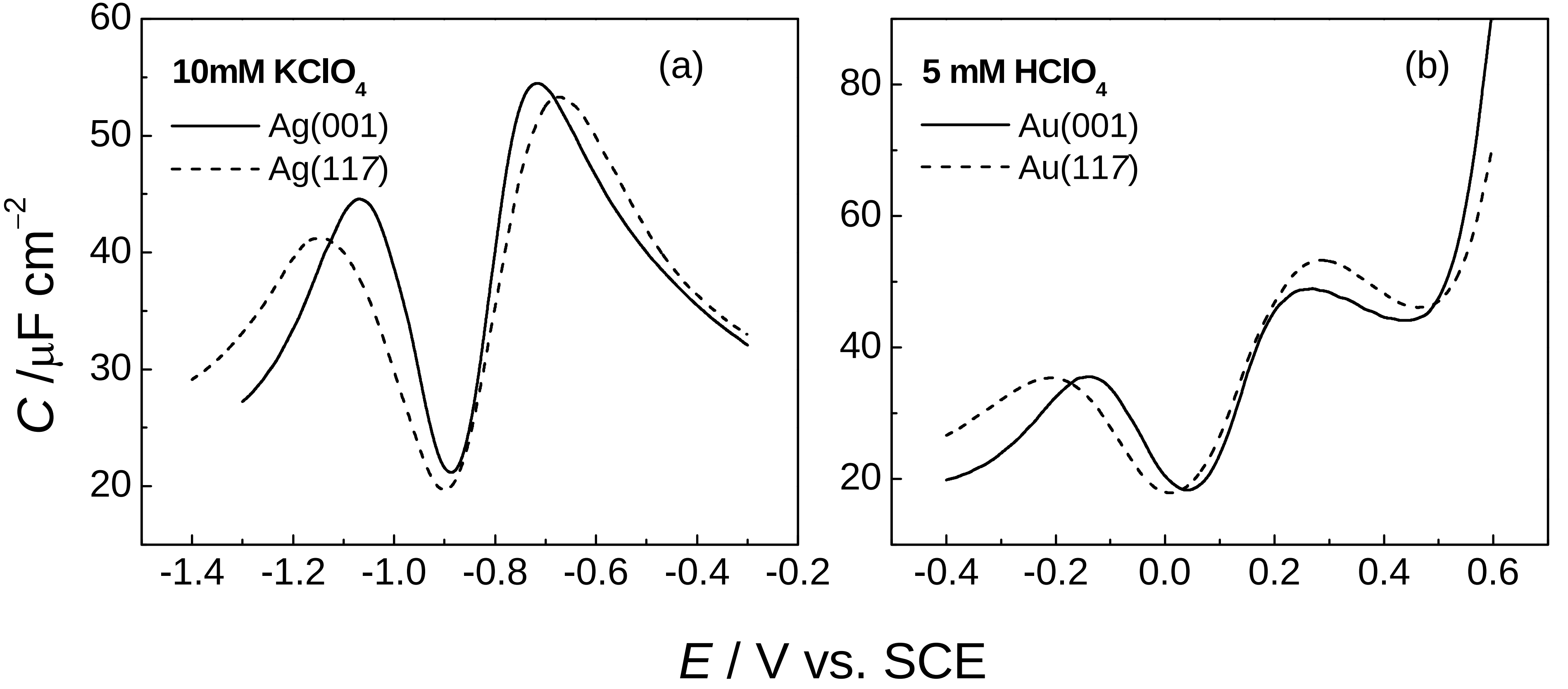
	Ag(11n) 10 mM $KClO_4$	Au(11n) [7] 5 mM $HClO_4$
p_z / $10^{-3} e$Å	3.5±0.5	5.2±0.4
$C(E_{\mathrm{pzc}})$ / µF cm^{-2}	22.0±0.9	18.6±0.3
l_c / Å	−1.1±0.1	−0.5±0.2

Table 1: Values of the step dipole moment per atom p_z, the capacitance $C(E_{\mathrm{pzc}})$, and the characteristic length l_c according to eq. (3) for Ag(11n) and Au(11n) vicinal surfaces.

Table 2:

Vicinal Surfaces	p_z /10^{-3} eÅ	
	Ag	Au
(111) - A sites [16, 17]	23.8	42
(111) - B sites [16, 17]	13.8	60
(001) [17]	5.4	
(001)	3.5±0.5 (this work)	5.2±0.4 [7]

Table 2: Dipole moment per step atom of steps on silver and gold surfaces calculated from the experimental data on the *pzc*.



60
50
40
30
20
C /μF cm−2
10mM KClO4
Ag(001)
Ag(117)
(a)
-1.4
-1.2
-1.0
-0.8
-0.6
-0.4
-0.2
80
60
40
20
5 mM HClO4
Au(001)
Au(117)
(b)
-0.4
-0.2
0.0
0.2
0.4
0.6
E / V vs. SCE

Fig. 1

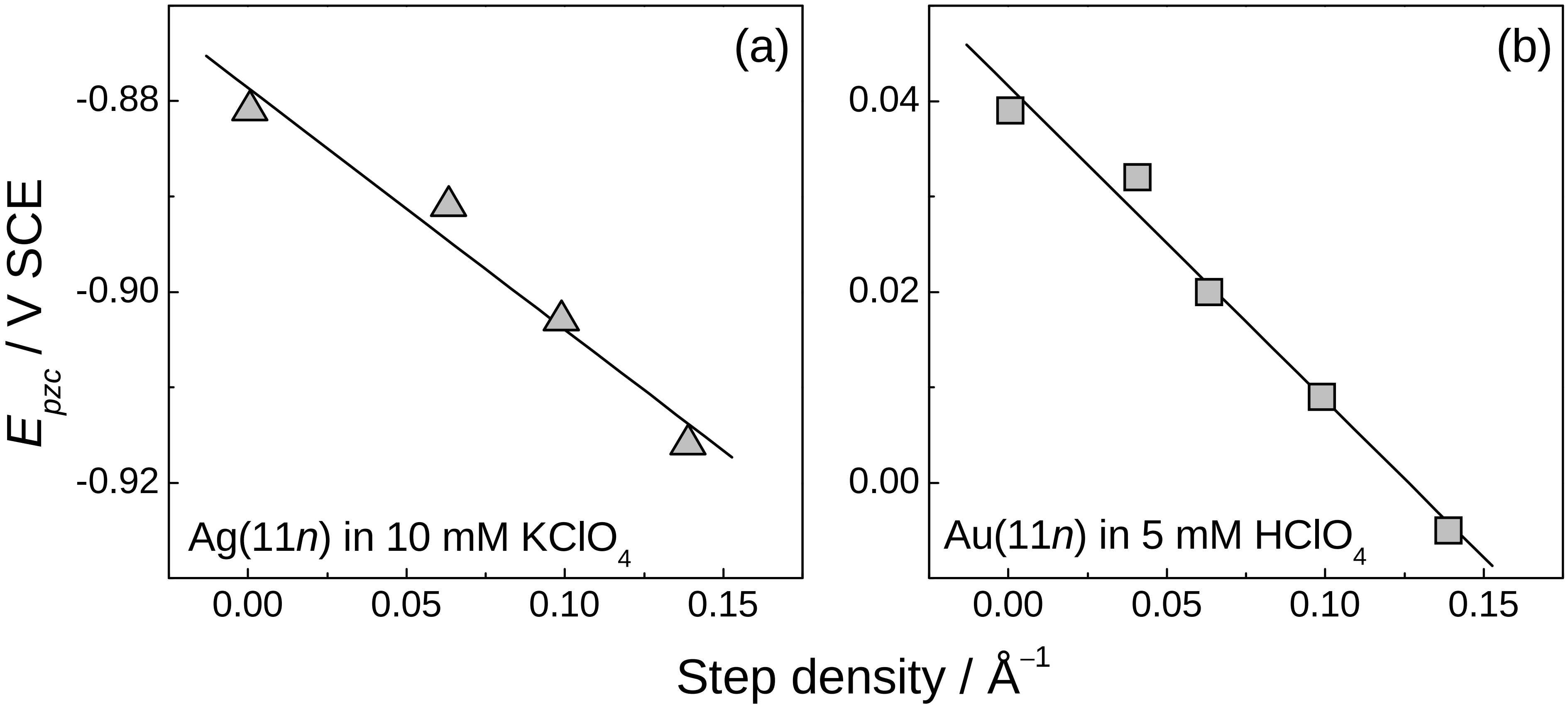

(a)
(b)
-0.88
-0.90
-0.92
0.04
0.02
0.00
0.00
0.05
0.10
0.15
E_{pzc} / V SCE
Ag(11n) in 10 mM $KClO_4$
Au(11n) in 5 mM $HClO_4$
Step density / Å^{-1}

Fig. 2

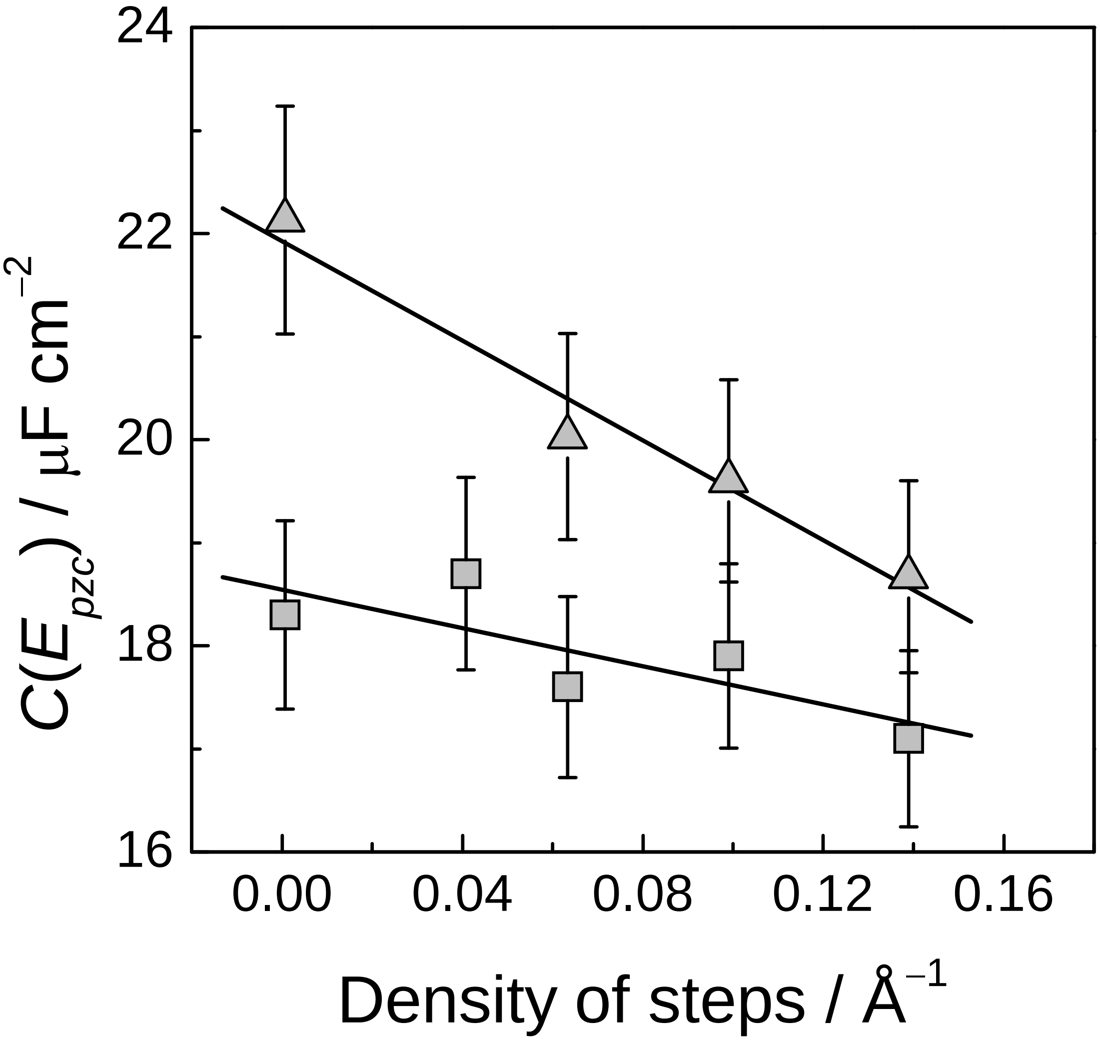
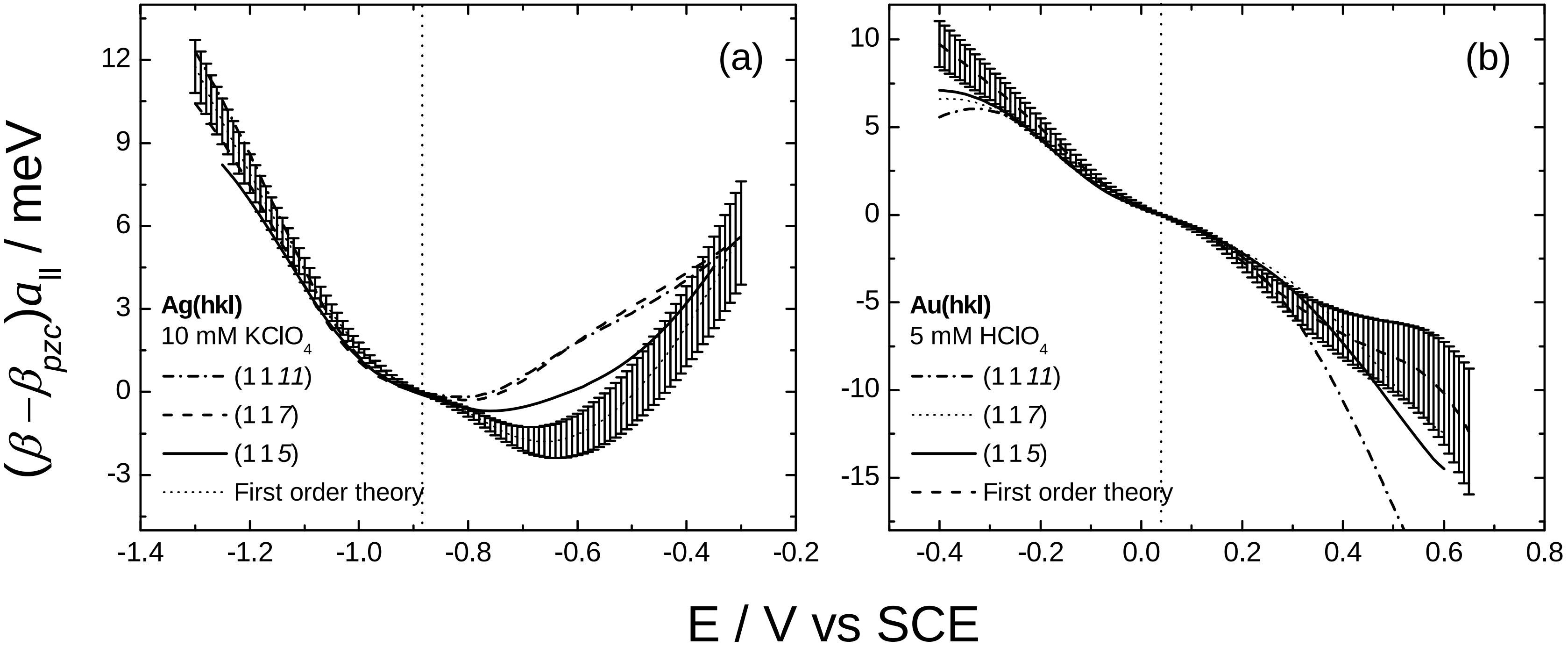

24
22
20
18
16
0.00
0.04
0.08
0.12
0.16
$C(E_{pzc})$ / μF cm^{-2}
Density of steps / Å^{-1}

Fig. 3



$(\beta - \beta_{pzc}) a_{||}$ / meV
(a)
Ag(hkl)
10 mM $KClO_4$
(1 1 11)
(1 1 7)
(1 1 5)
First order theory
12
9
6
3
0
-3
-1.4
-1.2
-1.0
-0.8
-0.6
-0.4
-0.2
(b)
Au(hkl)
5 mM $HClO_4$
(1 1 11)
(1 1 7)
(1 1 5)
First order theory
10
5
0
-5
-10
-15
-0.4
-0.2
0.0
0.2
0.4
0.6
0.8
E / V vs SCE

Fig. 4