**The Structure and Stability of Underpotentially Deposited Ag on Au(111) in Alkaline Electrolyte**

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**Abstract**

 A combination of *in-situ* surface x-ray scattering (SXS) and cyclic voltammetry (CV) measurements have been performed to understand the structure and behaviour of underpotentially deposited (UPD) Ag layers on Au(111) following transfer of the electrode to alkaline electrolyte (0.1 M KOH). UPD of Ag from 0.05 M H2SO4 + 1 mm Ag2SO4 electrolyte was used to form a monolayer and bilayer film of Ag on Au(111) before immersion into 0.1 M KOH electrolyte. Analysis of the SXS data shows that, while the bilayer Ag film is stable upon transfer to the alkaline electrolyte, the Ag monolayer film re-orders to a partial bilayer structure upon or during the transfer process. The Ag-modified Au(111) electrode shows a potential response for OH- adsorption that is similar to that of Ag single crystal electrode surfaces.

**1. Introduction**

 The adsorption of oxygen and hydroxide species onto metal surfaces is key to understanding surface reactivity and catalytic behavior, both in the high pressure gas environment and at the electrochemical interface. In an electrochemical environment, while there has been widespread study of multilayer oxide growth on Ag electrode surfaces [1-2](#_ENREF_1), there has been less study of the underpotential region of oxidation, in spite of the fact that this is the potential region of the oxygen reduction reaction (ORR) [3](#_ENREF_3). The adsorption of hydroxide species is of particular interest as it is involved in many surface processes such as the ORR and the oxidation of glucose [4-5](#_ENREF_4). It is also the precursor state of surface oxide formation which is of fundamental importance in both electrochemical and gaseous environments as it is the oxide surface that plays the key role in many applications in heterogeneous catalysis and electrocatalysis [4](#_ENREF_4), [6](#_ENREF_6). Furthermore, the formation and properties of supported metal multilayers on a metallic substrate and core-shell nanoparticles, in which the surface atomic layer is a different element to the core, are of particular interest as the surface metal can greatly affect the properties and reactivity of the material [7-10](#_ENREF_7). Much research has been done on the underpotential deposition (UPD) of Ag on Au(111) [11-14](#_ENREF_11) and the synthesis of gold-silver core-shell nanoparticles [15-18](#_ENREF_15), the latter have been found to have enhanced antibacterial activity [19](#_ENREF_19) and some research has also been done to study the catalytic properties of these systems [20](#_ENREF_20).

 In this special issue paper, we present an *in-situ* surface X-ray scattering (SXS) [21](#_ENREF_21) study of the UPD of Ag onto a Au(111) electrode surface, both during the UPD process and after transfer of the Ag-modified Au(111) electrode into alkaline electrolyte (0.1 M KOH). This special issue of the Journal of Physical Chemistry is dedicated to the work of Professor Kohei Uosaki who has previously published SXS studies of the Ag/Au(111) UPD system that form the basis for the new research presented in this article [11](#_ENREF_11), [14](#_ENREF_14). The outline of the paper is as follows; the UPD process and the *in-situ* study by SXS is briefly explained in Section 3.1. In Section 3.2, a detailed analysis of the Ag monolayer and bilayer thin film structures on Au(111) after transfer to Ag-free alkaline electrolyte is presented. Transferring the Ag-modified Au(111) electrode to Ag-free 0.1 M KOH allows the applied potential to be cycled without further deposition of Ag. This enables a detailed study of the potential region of hydroxide (OH-) adsorption. Measurements and modelling of the crystal truncation rod (CTR) data gives an atomic-scale picture of the interface, i.e. the Au/Ag interface, the Ag thin film structure and any ordering in the electrochemical double layer. Potentiodynamic x-ray voltammetry (XRV) measurements, which involve the monitoring of the x-ray diffraction signal at key reciprocal lattice positions as a function of the applied electric potential, are used to determine the potential dependent structural changes induced by the deposition of Ag and subsequent adsorption of hydroxide species onto the Ag surface. The results indicate that in addition to ordering of the electrolyte at the Ag surface, as observed on single crystal Ag electrodes [22](#_ENREF_22), there can also be penetration of the hydroxide species into the Ag thin film structure.

**2. Experimental Methods**

 The Au(111) single crystal (miscut< 0.1°) was prepared by sputtering and annealing in a UHV system for several days. After a sharp low-energy electron diffraction (LEED) pattern was observed the sample was removed from UHV. Prior to each experiment the crystal was flame annealed in a butane flame before cooling in air. Once cool a drop of ultrapure water was used to protect the surface whilst the crystal was transferred to either the x-ray electrochemical cell or a hanging meniscus electrochemical cell. For *in-situ* studies of the Ag deposition process the Au(111) crystal was transferred directly to the electrochemical x-ray cell and was immersed at open circuit potential into 0.05 M H2SO4 + 1 mm Ag2SO4 electrolyte. For studies of the UPD-formed Ag films in alkaline electrolyte the following methodology was used; first the crystal was immersed at open circuit potential in a hanging meniscus electrochemical cell containing 0.05 M H2SO4 + 1 mm Ag2SO4. This enabled precise control of the UPD of Ag layers onto the Au(111) surface as the measured current in the cyclic voltammetry is due only to the (111) surface which is contacted with the electrolyte droplet. After Ag deposition, the crystal was emersed at the deposition potential and transferred to the electrochemical x-ray cell with a drop of ultrapure water protecting the surface. It was then immersed at open circuit potential into 0.1 M KOH electrolyte. The outer chamber of the x-ray cell was continuously purged with nitrogen to protect the surface from oxygen. The reference electrode used in both the hanging meniscus and x-ray cells was leak free Ag/AgCl against which all potentials are quoted.

 X-ray measurements were performed on beamline I07, at the Diamond Light Source, UK and on beamline ID32 (since decommissioned), at the European Synchotron Radiation Facility, France using focused incident x-rays of energy 11 keV and 21.3 keV respectively. Due to the configuration of the diffractometer on each beamline two kinds of x-ray electrochemical cells were used. A ‘thin-layer’ x-ray cell was used on beamline I07, mounted on the hexapod on the (2+3)-circle diffractometer with surface normal horizontal. The thin layer cell uses a polypropylene film to trap the electrolyte solution and, for the x-ray measurements, is operated with an electrolyte layer of ~10 m in thickness. An electrochemical ‘droplet’ x-ray cell was used on beamline ID32, mounted on the Huber tower on the 6-circle diffractometer with surface normal vertical and an incidence angle of 0.6°. The droplet cell is similar to a hanging meniscus cell in that a droplet of electrolyte is contacted with the crystal surface and the x-rays must penetrate the entire droplet. In both experiments the Au(111) crystal was indexed to a conventional hexagonal unit cell for the *fcc* surface where the surface normal is along the (0, 0, *l*)hex direction and the (*h,* 0, 0)hex and (0, *k,* 0)hex vectors lie in the plane of the surface and subtend 60°. The units for *h*, *k* and *l* are a\*=b\*=4/√3aNN and c\*=2 /√6aNN, where aNN is the nearest-neighbour distance in the crystal (aNN = 2.884 Å). Due to the ABC stacking along the surface normal direction, the unit cell contains three atomic layers and the Bragg reflections are spaced apart by multiples of three in L. More details of the experimental set-ups and procedures followed have been reported previously in related studies [21](#_ENREF_21), [23](#_ENREF_23).

**3. Results**

**3.1 Underpotential Deposition of Ag on Au(111)**

 There have been numerous studies of the underpotential deposition (UPD) of Ag onto Au(111) [11-13](#_ENREF_11). These studies have shown that there are different potential regions for monolayer, bilayer (both UPD processes) and bulk deposition, hence electrochemical deposition can allow fine control of the Ag thin film structure that is formed. Figure 1(a) shows the cyclic voltammetry (CV) for the Au(111) electrode in 0.05 M H2SO4 + 1 mm Ag2SO4 performed in a hanging meniscus cell at a sweep rate of 5 mV/s. The three cathodic peaks at 0.95 V (C1), 0.57 V (C2) and 0.46 V (C3) are due to the deposition of Ag. C1 and C2 correspond to the deposition of an incomplete Ag monolayer and C3 for the deposition of a Ag bilayer [11](#_ENREF_11). At potentials negative of C3 bulk deposition of Ag occurs. The completion of the Ag monolayer occurs between C2 and C3. Although the charge of the first two cathodic peaks corresponds to 0.72 of a monolayer, Uosaki and co-workers found, using x-ray diffraction, that the monolayer is actually complete at 0.48 V (vs Ag/AgCl) [11](#_ENREF_11).

 Ag UPD was also performed in the electrochemical x-ray cell so that x-ray diffraction measurements could be made *in-situ* during the Ag deposition process. The scattered x-ray intensity at key reciprocal lattice positions was measured as a function of the applied electrode potential, a technique termed x-ray voltammetry (XRV). Figure 1(b,c,d) shows the XRV measured at a sweep rate of 2 mV/s at the reciprocal space positions (0 0 1.5), (1 0 3.7) and (0 1 0.5). The background signal, obtained from a rocking curve performed prior to the XRV measurements, has been subtracted from the data points and they have then been normalized to the highest intensity data point. This procedure was followed for all of the XRV data presented in this paper. (0, 0, 1.5) is an ‘anti-Bragg’ position on the specular CTR sensitive to any layer ordering at the interface, including that of the electrolyte, (1, 0, 3.7) is a position on the non-specular CTR sensitive to lattice relaxation of the Au surface and (0, 1, 0.5) is an ‘anti-Bragg’ position on the non-specular CTR, (0, 1, L), and is sensitive to Ag deposition, particularly if the deposited Ag atoms are commensurate with the Au lattice. To discuss the XRV we will start at 1.06 V where the surface is free of Ag; the potential is scanned cathodically (open symbols) and just before reaching C1 (Figure 1(a)) a partial monolayer of Ag is deposited on the surface, thus causing the decay in intensity at all of the CTR positions shown in Figure 1 at this potential. The intensity is then stable until reaching C2 where further UPD occurs. This is only apparent in Figure 1(d) as further silver completing the monolayer reduces the intensity at the anti-Bragg position. In the other two XRV’s there is no change in the intensity but at the (0, 1, 0.5) position the intensity decays further until the monolayer is completed. Finally just before reaching C3 the monolayer completes and the bilayer starts to form. This is signified by a change in intensity at all three reciprocal lattice positions. It is important to note that the XRV measures the ordering at the surface so features may not always correlate exactly with those in the CV. The UPD process is fully reversible over this potential range as shown in both the CV and XRV.

 Following XRV studies of the deposition process the potential was scanned anodically from 0.44 V, where a bilayer would be present, to 0.47 V (which is between peaks C2 and C3 on Figure 1(a)) in order to leave nominally a single monolayer thick film of Ag deposited on the surface. The potential was then held at 0.47 V so that detailed CTR measurements could be made. In order to obtain a structural model for the Ag-Au(111) interface, non-specular CTR’s, (1, 0, L) and (0, 1, L), were measured by performing rocking scans at successive L values to obtain background subtracted integrated intensities and the results are shown in Figure 2. The data points (black circles) have been corrected for the instrumental resolution [24-25](#_ENREF_24). Error bars shown were calculated from the statistical error on the fits to the individual rocking scans at each L value, plus a systematic error of 10% which is an estimate based on the measurement of intensity at symmetry equivalent reciprocal lattice positions and is typical in such measurements. The green dashed line in Figure 2 shows a calculation for a clean unrelaxed Au(111) surface, the red dashed line for an ideal Ag monolayer on Ag(111) and the dotted black line for a 2 monolayer thick Ag film. These simulations help to understand the XRV data in Figure 1, particularly Figure 1d, i.e. the completion of the Ag monolayer corresponds to the minimum in the measured intensity (at ~0.5 V). The measured data points, obtained at 0.47 V, in Figure 2, however, indicate that the monolayer is not complete and this is confirmed by the fit to the data. The best fit to the CTR data (black line) was obtained using a structural model in which the variable structural parameters were the coverage (θ) of the Ag monolayer, the surface normal atomic layer spacing's of the topmost Au layer and the Ag layer and a root-mean-square (*rms*) surface roughness (σ) for each surface layer (modelled by a static Debye-Waller factor). The best fit to the data ($ χ^{2}= $2.6) gives a Ag coverage of 0.6 monolayer (ML) (fraction of Ag atoms per surface Au atom), a Ag-Au spacing of 2.36 Å and a slight expansion of the topmost Au layer by ~0.5% (the bulk Au(111) spacing is 2.355 Å). A full list of the structural parameters is given in Table 1. Although the Ag monolayer should be complete at this potential as indicated by the CV data and previous studies, the coverage obtained in our measurements (=0.6) is rather low. In a previous study of the effects of small temperature changes in electrochemistry it was shown that ordering in the UPD Ag monolayer on Au(111) was increased at higher temperatures [26](#_ENREF_26). Using SXS, Uosaki and co-workers [11](#_ENREF_11) found that the Ag monolayer was complete and recorded CTR data that was similar to the simulated data (red dashed line) in Figure 2. In fact the XRV data in Figure 1b, measured at the anti-Bragg position on the specular CTR, is also consistent with formation of a complete Ag monolayer as the intensity is reduced by more than an order of magnitude in the UPD monolayer potential range. As the XRV data (Figure 1) was measured in the droplet x-ray electrochemical cell, this implies that the UPD process in the thin layer x-ray electrochemical cell (in which the data shown in Figure 2 was obtained) may not be complete. The principal new results presented in this paper, however, refer to the transfer of the Ag UPD films on Au(111) to alkaline electrolyte and not to the UPD process itself. In this case Ag UPD is performed in a hanging meniscus cell before transfer to the x-ray cell.

**3.2 Transfer to 0.1M KOH**

 Transferring the Ag-modified Au(111) electrode to a Ag-free alkaline electrolyte (0.1 M KOH) enables potential dependent measurements to be made without further deposition of Ag. As noted above, separate electrochemical cells were used for the deposition and subsequent x-ray measurements in alkaline electrolyte. First the hanging meniscus electrochemical cell containing 0.05 M H2SO4 + 1 mm Ag2SO4 was used to enable precise control of the Ag UPD process. A monolayer or bilayer of Ag was formed, by holding the potential at 0.47 V and 0.44 V respectively. For clarity the monolayer and bilayer Ag films are referred to as 1 ML Ag film and 2 ML Ag film throughout the rest of this article. Once the Ag layers were formed the electrode was emersed at the deposition potential, rinsed with ultrapure water and transferred to the electrochemical x-ray cell with a droplet of 0.1 M KOH electrolyte protecting the surface. It was then immersed at open circuit potential into alkaline electrolyte, 0.1 M KOH, in the thin layer x-ray electrochemical cell. A series of CTR and XRV measurements were then made to fully characterise the surface and understand the potential dependence of the UPD structures in alkaline electrolyte. Corresponding CV measurements were also made in the hanging meniscus cell.

**3.2.1 Cyclic Voltammetry (CV) of Ag-modified Au(111) in 0.1 M KOH**

 The CV measured in 0.1 M KOH of the 1 ML Ag film (deposited at 0.47 V) and 2 ML Ag film (deposited at 0.44 V) are shown in Figure 3 together with the CV measured for a clean Au(111) electrode. Upon immersion of the electrode into the 0.1 M KOH electrolyte the measured open circuit potentials were -0.2 V, -0.36 V and -0.45 V for bare Au(111), the 1 ML Ag film and the 2 ML Ag film respectively. For the Au(111) electrode the potential region -0.9 V to -0.6 V corresponds to charging/discharging of the double layer and the potential region -0.6V to 0 V corresponds to the reversible adsorption/desorption of oxygenated species, hereafter called OH-[23](#_ENREF_23). As would be expected, the CV for both the 1 ML Ag film and 2 ML Ag film show additional features which are characteristic of Ag single crystal electrode surfaces. A detailed study of the low-index surfaces of single crystal Ag electrodes in 0.1 M NaOH has been reported previously [3](#_ENREF_3), [27-28](#_ENREF_27) and sets of peaks similar to those labelled A4 and C4 in Figure 3 have been attributed to the specific adsorption and desorption of OH- anions. In addition Savinova *et al*. attributed the peaks labelled as C5 in Figure 3 to the sub-surface incorporation of OH- species into both Ag(111) [29-30](#_ENREF_29) and a polycrystalline Ag electrode [31](#_ENREF_31). These studies showed that the potential region for OH- adsorption onto Ag(*hkl*) is dependent on the atomic geometry of the single crystal surface and correlates directly with the potential of zero charge (*pzc*) [3](#_ENREF_3). Hence the shift in the peaks labelled A4/C4 in Figure 3 may be expected to correlate with the crystallographic morphology of the Ag film. This is discussed further in section 4.

**3.2.2 Ag Bilayer on Au(111)**

 As shown by the CV in Figure 1a, the reversible peak in the CV corresponding to deposition/desorption of the second Ag UPD monolayer (labelled A3/C3) is very close to the onset of bulk Ag deposition. In order to form the Ag bilayer structure (2 ML Ag film) the potential was scanned to 0.44 V and held before immersion of the electrode and transfer to the electrochemical x-ray cell containing alkaline electrolyte, 0.1 M KOH. Specular CTR (0, 0, L) measurements of the 2 ML Ag film were then obtained at fixed potentials of -0.9 V and -0.1 V.

 Figure 4(a) shows the specular CTR (0, 0, L) obtained for the 2 ML Ag film at -0.9 V (black circles) and -0.1 V (red squares). As described in section 3.1, the data points correspond to background subtracted integrated intensities obtained from rocking scans at successive L values and have been corrected for the instrumental resolution. Figure 4(b) shows the ratio between the two data sets-such data are useful to highlight systematic changes and test the reliability of the structural models that are used to simulate the CTR data. In order to fit the CTR data in Figure 4, a structural model consisting of two Ag monolayers on top of the Au(111) substrate was used. In fitting the data the variable structural parameters for each layer were the coverage (), the surface normal atomic layer spacing (d-spacing) and a roughness factor (). The best fits to the data are shown by the solid lines in Figure 4 with the corresponding structural parameters listed in Table 2. The specular CTR is of particular interest as it is sensitive to any layer ordering at the interface, including that of the electrolyte [22](#_ENREF_22). In order to get a reasonable fit to the data measured at -0.1 V it was necessary to include an additional layer of OH- in the structural model. This layer mostly affects the calculated CTR at low L values and reproduces the systematic decrease in intensity for the data measured at -0.1 V below L~3.

 At -0.9 V the best fit to the data ($ χ^{2}= $3.5) consists of two Ag layers on Au(111) surface each with an occupation of 1 ML. Inclusion of a third Ag layer did not improve the fit to the data. The d-spacing's in the Ag bilayer indicate a ~6% expansion of the Ag-Ag layer spacing compared to the bulk Ag(111) lattice spacing (2.359 Å) and a slight contraction at the Au-Ag interface (~3%) compared to the value expected on the basis of a hard sphere model (2.356 Å). The fit to the data measured at -0.1 V ($ χ^{2}= $3.3) indicates that is little change in the relaxation in the metal film although there is an increase in the  values which represent static surface disorder (albeit within the statistical error). Figure 4(b) shows the ratio of the set of specular CTR’s (R = I -0.1 V / I -0.9 V) (black squares), which highlights the difference between the -0.9 V and -0.1 V data, together with the calculated ratio (black line) based on the fits to the CTR data shown in Figure 4(a).

**3.2.3 Ag Monolayer on Au(111)**

 After repreparation of the Au(111) surface, a nominally 1 monolayer (ML) thick Ag film (1 ML Ag film) was deposited on the Au(111) electrode by cycling the potential to 0.47 V in 0.05 M H2SO4 + 1 mm Ag2SO4 electrolyte, followed by emersion and transfer to 0.1 M KOH. After potential contact at the OCP, the potential was cycled over the range -0.2 V to -1.0 V and then held at these two potentials for detailed CTR measurements to be performed. Figure 5 shows the specular CTR (a) (0, 0, L) and the non-specular CTR’s (b) (1, 0, L) and (c) (0, 1, L) for the 1 ML Ag film on Au(111) measured at -1 V (black circles) and -0.2 V (red squares). By comparison with the data shown in Figures 2 and 4 it is clear from the CTR data in Figure 5, that during transfer of the sample to 0.1 M KOH, the morphology of the Ag deposit had changed from that of a single monolayer (Figure 2) to a partial coverage of a bilayer structure, i.e. a weak oscillation between the Bragg reflections is evident in the CTR data although the amplitude of the oscillation is damped compared to the data from the 2 ML thick Ag deposit shown in Figure 4a. This conclusion is supported by previous studies which found that on exposure to ambient atmosphere the Ag monolayer on the Au(111) surface transforms to a partial bilayer [14](#_ENREF_14). It appears likely that the structural transformation occurred during the transfer of the electrode and is a process that is not reversed upon immersion into the alkaline electrolyte. The same structural model, used to fit the CTR data in Figure 4, was used to fit the CTR data shown in Figure 5. The corresponding best fit parameters for the data at -1 V and -0.2 V are given in Table 3. The fit to the data measured at -1.0 V is shown by the solid lines in Figure 5a,b,c ($ χ^{2}= $2.8) and confirms that the Ag monolayer has reordered into a bilayer film structure covering ~50% of the Au(111) surface. In order to get a good fit to the data it was necessary to include a third Ag layer in the model with very low coverage (=0.15). The d-spacing's in the Ag bilayer are similar to those observed for the 2 ML Ag film (Table 2) indicating a slight contraction at the Au-Ag interface (~3%) compared to the value expected on the basis of a hard sphere model (2.356 Å), although the Ag-Ag d-spacing is close to that expected in bulk Ag(111). In order to fit the CTR data measured at -0.2 V, the ratio of the data compared to that measured at -1.0 V was calculated, R = I -0.2 V / I -1 V and is shown by black squares in Figure 5 (d) (0, 0, L), (e) (1, 0, L) and (f) (0, 1, L). A fit to the ratio data set was then calculated ($ χ^{2}= $1.9) and is shown by the solid lines in Figure 5d,e,f according to the structural parameters in Table 3. The systematic changes in the CTR data are highlighted in the ratio data sets and the calculations show that these are due to very subtle changes in the surface coverage and relaxations in the Ag film structure (Table 3).

**3.2.4 Potential dependence in 0.1M KOH**

 In addition to the CTR measurements, XRV measurements were performed on the 1 ML and 2 ML Ag films in 0.1 M KOH and the results are shown in Figure 6 (data points in red correspond to the 2 ML Ag film and data points in black to the 1 ML Ag film). The XRV measurements were made at the same CTR positions used to monitor Ag UPD (shown in Figure 1), i.e. (a) (0, 0, 1.5), (b) (1, 0 3.7) and (c) (0, 1, 0.5). The changes in the intensity at the specular ‘anti-Bragg’ position are quite significant, ~30%. A similar effect was observed in the study of a bulk Ag(111) electrode in alkaline electrolyte where the changes were attributed to layering in the electrolyte side of the interface [22](#_ENREF_22). Comparison with the CV data shown in Figure 3 indicates that the changes in the x-ray intensity correlate directly with the peaks A4/C4 in the CV and are related to the adsorption and desorption of hydroxide species. The observed changes are fully reproduced in the potentiostatic CTR measurements, i.e. the data in Figure 6 is consistent with the CTR data in Figures 4 and 5. We note also that the XRV measurements for the 1 ML Ag film were reproducible throughout the experiment, i.e. directly after potential contact in the 0.1 M KOH electrolyte. This confirms that the change in Ag film morphology occurs during the transfer of the electrode and is not induced by potential cycling.

**4. Discussion**

 In the electrodeposition of Ag onto Au(111) the supporting sulfate anions in the electrolyte play an important role. To fully understand this effect the deposition of Ag on Au(111) in UHV conditions is first considered. Here the first Ag layer deposits as fingerlike rows locked to the Au(111) (23x√3) reconstruction [32-33](#_ENREF_32). The growth is not layer by layer, instead the second layer commences before the first is complete [34](#_ENREF_34). In contrast the electrodeposition of less than 1 monolayer of Ag onto the Au(111) surface produces open structures as previously shown [35-40](#_ENREF_35). However a series of first-principle calculations by Sanchez *et al*. showed that no structure more expanded than a (1x1) compact monolayer is more stable than a bulk Ag deposit and hence UPD of Ag should not occur on Au(111) [41](#_ENREF_41). In order to explain the discrepancy between the calculations and experimental results it was suggested that adsorbed Ag may generate a large shift in the work function thus inducing a negative shift in the potential of zero charge (*pzc*) and resulting in the additional adsorption of anions and a change in the Au-Ag binding energy. The open structures observed during the electrodeposition of Ag onto Au(111) are dependent on the anion present; for example in the presence of sulfate the Ag UPD overlayer exhibits a (3x3) structure, in the presence of nitrate a (4x4) structure and in pure perchlorate electrolyte another open structure [35-40](#_ENREF_35). These open structures imply that there is an increased Ag-Ag repulsion due to the presence of the anions. In the presence of sulfate, as the coverage of the Ag deposit is increased the Ag structure transitions from an expanded (3x3) structure to a close-packed pseudomorphic monolayer of Ag. STM images have revealed that before the initial Ag deposition (bi)sulfate forms an ordered (√3 x √7)R19.1° structure on the Au(111) surface. It is also suspected that (bi)sulfate is adsorbed onto the Ag monolayer, but the exact nature of this is unknown [39](#_ENREF_39). On a bulk Ag(111) electrode surface sulfate forms an ordered (3 x 3√3) structure [42](#_ENREF_42).

 It is clear from the CTR measurements presented in section 3.2.3 that on transfer to 0.1 M KOH the Ag monolayer reorders to a partial Ag bilayer structure. Marinkovic *et al* found that in an electrolyte containing both OH- and sulfate (0.1 M K2SO4 + 0.01 M NaOH) the adsorption of sulfate on Ag(111) surface is inhibited by the more strongly specifically adsorbed OH- ions [43](#_ENREF_43). It is therefore likely that for the Ag monolayer on Au(111) the sulfate anions which are stabilising the monolayer structure [44](#_ENREF_44) are replaced by OH- anions causing the silver to rearrange into the bilayer structure. An almost identical effect was observed when the UPD-formed Ag monolayer on Au(111) was removed from the supporting electrolyte and exposed to ambient atmosphere [14](#_ENREF_14). In our experiments, during the transfer to alkaline electrolyte the sample is not exposed to ambient atmosphere, however, potential contact to the sample is not maintained. It is impossible to determine precisely at which point the reordering of the Ag film occurs, however, the reordering process is not reversible once the sample is immersed into the alkaline electrolyte.

 As shown in Figure 3 the potential at which OH- adsorption/desorption occurs (attributed to the peaks A4/C4) on the Ag/Au(111) surface is dependent on the silver coverage. It has been shown that for Ag single crystals the potential for OH- adsorption/desorption is dependent on the single crystal surface, with the OH- adsorption/desorption potential decreasing in the order Ag(111) > Ag(100) > Ag(110) [3](#_ENREF_3), [28](#_ENREF_28). Horswell *et al*. showed that this effect is related to the *pzc* for each surface as when the CV’s are plotted with respect to the *pzc* (on a rational potential scale) the potential of OH- adsorption/desorption for the different faces coincide [3](#_ENREF_3). It was concluded that the onset of OH- adsorption on the different Ag single-crystal planes is related to the work function and atomic density of the surface [3](#_ENREF_3). The *pzc* of the low-index Au and Ag surfaces decreases in the order Au(111) < Au(100) < Au(110) < Ag(111) < Ag(100) < Ag(110) [39](#_ENREF_39), [45](#_ENREF_45). For sub monolayer coverages of Ag on Au(111) the *pzc* stays close to that of Au(111), shifting from -0.55 V for clean Au(111) to -0.75 V (vs Ag/AgCl/KCl (sat) in 0.1M NaOH) after the deposition of 1/3 ML of Ag [46](#_ENREF_46). As the monolayer is completed the *pzc* shifts close to that of Ag(111), becoming almost identical to that of a single crystal Ag(111) electrode after the deposition of the second Ag monolayer [39](#_ENREF_39), [47-48](#_ENREF_47).

 By considering all of the above it possible to conclude that the 2 ML Ag bilayer on Au(111) is stable upon transfer to 0.1 M KOH and has a similar potential response to that of a bulk Ag(111) electrode. The 1 ML Ag monolayer on the other hand is not stable and, although a Ag surface structure with a (111) close packed structure is initially formed, on transfer to 0.1 M KOH, the Ag film undergoes a structural transition to a partial Ag bilayer. The new partial bilayer surface results in the creation of Ag (100) and (110) step sites, which have a lower *pzc* and as a result lowers the potential for the onset of OH- adsorption. This accounts for the lower potential of OH- adsorption/desorption for the monolayer compared to the bilayer, as indicated both by the CV data in Figure 3 and the XRV data in Figure 6(a).

 Savinova *et al*. observed a cathodic peak in the CV of Ag(111) and polycrystalline Ag in alkaline electrolytes that is similar to peak labelled C5 in Figure 3 and suggested this was due to the formation of subsurface hydroxide species [29-31](#_ENREF_29). The diffusion of hydroxide species into the bulk Ag lattice is a slow process on the close-packed Ag(111) surface, but is much faster for polycrystalline Ag due to the higher concentration of grain boundaries and other defects. This would explain why the peak C5 in Figure 3 is so pronounced for the supported Ag multilayers, as these UPD films would be expected to contain many grain boundaries and other defects. The amount of subsurface hydroxide is not expected to exceed 0.04 monolayers [29](#_ENREF_29). The effect of subsurface hydroxide would therefore be impossible to detect directly using the SXS technique, however it may lead to an decrease in the surface order in the Ag film. Indeed at the positive potential limit a slight increase in the Ag layer  values is observed for the 2 ML Ag film and a slight decrease in the Ag coverage's in the 1 ML Ag film (which could also be representative of disorder). A summary of the structural changes for both the 1 ML Ag and 2 ML Ag films is shown as a schematic illustration in Figure 7.

 The electrocatalytic activity of Ag overlayers on Au(111) for the oxidation of glucose in 0.1 M NaOH has been investigated by Soliman *et al*. [5](#_ENREF_5). The highest activity was found for Ag adlayers with a coverage of less than two monolayers, whereas the Ag bilayer was a poor catalyst. The specific activity was explained by the influence of OH- adsorption and the difference in *pzc*, assuming a closed packed Ag(1x1) overlayer for deposits higher than one monolayer. Earlier studies of the system [4](#_ENREF_4), however, argued that the specific high activity for Ag adlayers up to 2 ML of coverage was due to the presence of AuOH sites which are more active for glucose oxidation than AgOH sites. Our studies support the presence of free Au sites when the deposited Ag is less than a full bilayer in alkaline solution as the Ag deposit reorders into a partial bilayer. In contrast the 2 ML Ag film forms a stable bilayer with no free Au sites for OH adsorption.

**5. Conclusions**

 The structure and electrochemical behaviour of Ag monolayer and bilayer films electrodeposited onto Au(111) have been studied using SXS and CV. Figure 7 shows a schematic illustration of the structural changes for both the Ag monolayer and bilayer films on Au(111). On transfer to the alkaline electrolyte the Ag bilayer on Au(111) was stable, conversely the Ag monolayer re-orders to a partial bilayer structure. This is due to the absence of adsorbed sulfate anions, which stabilise the monolayer in the electrolyte in which the Ag film is electrodeposited. The CV for the Ag-modified Au(111) electrode shows OH- adsorption behaviour similar to that of Ag single crystals with the bilayer behaving as Ag(111). The potential for OH- adsorption for the partial bilayer suggests that Ag (100) and (110) steps are present. This is further supported by the CTR measurements which indicate an increase in the Ag surface roughness at the more positive potential. The results also help to explain the specific electrocatalytic effects observed in studies of glucose oxidation, for example, on bimetallic Au-Ag electrode surfaces.

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**Tables**

**Table 1.** Structural parameters used to obtain the fit to the CTR data shown by the solid lines in Figure 2, measured on the Au(111) electrode in 0.05 M H2SO4 + 1 mm Ag2SO4 electrolyte at a potential of 0.47 V where a monolayer of Ag UPD is expected to be deposited onto the Au(111) surface.

|  |  |  |  |
| --- | --- | --- | --- |
|   | θ | d-spacing (Å) | σ (Å) |
| Au | 1.0 ± 0.1 | 2.359 ± 0.006 | 0.12 ± 0.07 |
| Ag | 0.6 ± 0.1 | 2.38 ± 0.03 | 0.12 ± 0.07 |

**Table 2.** Structural parameters used to obtain the fit to the CTR data shown by the solid lines in Figure 4, measured on the 2 ML Ag/Au(111) electrode in 0.1 M KOH at -0.9 V and -0.1 V.

|  |  |  |
| --- | --- | --- |
|   |  -0.9 V |  -0.1 V |
|   | θ | d-spacing (Å) | σ (Å) |  | d-spacing (Å) | σ (Å) |
| Au | 0.96 ± 0.14 | 2.389 ± 0.014 | 0.12 ± 0.08 | 0.96 ± 0.14 | 2.397 ± 0.014 | 0.12 ± 0.08 |
| Ag 1  | 1 ± 0.1 | 2.28 ± 0.04 | 0.07 ± 0.04 | 1 ± 0.1 | 2.28 ± 0.04 | 0.2 ± 0.05 |
| Ag 2  | 1 ± 0.1 | 2.50 ± 0.07 | 0.29 ± 0.15 | 1 ± 0.1 | 2.50 ± 0.07 | 0.4 ± 0.2 |
| OH- |  |  |  | 0.6 ± 0.2 | 3.1 ± 0.5 | 0.3 ± 0.3 |

**Table 3.** Structural parameters used to obtain the fit to the CTR data shown by the solid lines in Figure 5, measured on the 1 ML Ag/Au(111) electrode in 0.1 M KOH at -1.0 V and -0.2 V.

|  |  |  |
| --- | --- | --- |
|   |  -1 V |  -0.2 V |
|   | θ | d-spacing (Å) | σ (Å) | q | d-spacing (Å) | σ (Å) |
| Au | 1.0 ± 0.07 | 2.347 ± 0.007 | 0.15 ± 0.1 | 1.0 ± 0.07 | 2.347 ± 0.010 | 0.15 ± 0.1 |
| Ag 1  | 0.5 ± 0.06 | 2.30 ± 0.06 | 0.1 ± 0.1 | 0.5 ± 0.06 | 2.33 ± 0.06 | 0.1 ± 0.1 |
| Ag 2  | 0.46 ± 0.06 | 2.33 ± 0.06 | 0.2 ± 0.1 | 0.41 ± 0.06 | 2.39 ± 0.06 | 0.2 ± 0.1 |
| Ag 3  | 0.15 ± 0.05 | 2.4 ± 0.2 | 0.2 ± 0.1 | 0.14 ± 0.05 | 2.2 ± 0.2 | 0.2 ± 0.1 |

**Figure captions**

**Figure 1. (a)** Cyclic voltammetry of Au(111) in 0.05 M H2SO4 + 1 mm Ag2SO4 recorded at a sweep rate of 5 mV/s. X-ray voltammetry (XRV) measured at **(b)** (0, 0, 1.5), **(c)** (1, 0, 3.7) and **(d)** (0, 1, 0.5) at a sweep rate of 2 mV/s . All data is plotted versus a Ag/AgCl reference electrode. The XRV data shown has been background subtracted and normalised to the highest intensity data point.

**Figure 2.** Crystal Truncation Rod (CTR) data (black circles) of a Au(111) electrode measured in 0.05 M H2SO4 + 1 mm Ag2SO4 at 0.47 V (where 1 monolayer of UPD Ag is expected) **(a)** (1, 0, L) and **(b)** (0, 1, L). A fit to the data is shown by the black solid lines according to the structural model described in the text and the parameters listed in Table 1. Dashed lines correspond to calculated CTR profiles for an ideal clean Au(111) surface (green), a full Ag monolayer on Au(111) (red) and a Ag bilayer on Au(111) (blue).

**Figure 3.** Cyclic voltammetry of clean Au(111) (blue dotted line), a 1 ML Ag film on Au(111) (black line) and a 2 ML Ag film on Au(111) (red line). Data were measured in 0.1 M KOH electrolyte at a sweep rate of 20 mV/s.

**Figure 4.** **(a)** Specular crystal truncation rod (CTR) data, (0, 0, L), for a 2 ML Ag film on Au(111) measured in 0.1 M KOH electrolyte at -0.9 V (black circles) and -0.1 V (red squares). The solid lines are fits to the data according to the structural model described in the text and the parameters listed in Table 2. **(b)** The ratio of the two CTR data sets, I-0.1 V/ I-0.9 V . The solid line is calculated from the fits to the data shown in Figure 4a.

**Figure 5.** Crystal Truncation Rod (CTR) data of the 1 ML Ag film on Au(111) measured in 0.1 M KOH at -1.0 V (black circles) and -0.2 V (red squares) **(a)** the specular CTR (0, 0, L) and the non-specular CTR’s **(b)** (1, 0, L) and **(c)** (0, 1, L). The ratio I-0.2 V / I-1.0 V of the CTR data **(d)** (0, 0, L), **(e)** (1, 0, L) and **(f)** (0, 1, L). The solid lines are fits to the data according to the structural model described in the text and the parameters listed in Table 3.

**Figure 6.** X-ray voltammetry (XRV) for a 1 ML Ag film on Au(111) (black lines) and 2 ML Ag film on Au(111) (red lines) measured in 0.1 M KOH electrolyte at **(a)** (0, 0, 1.5), **(b)** (1, 0, 3.7) and **(c)** (0, 1, 0.5) reciprocal lattice positions at a sweep rate of 5 mV/s. The data has been background subtracted and normalised to the highest intensity data point.

**Figure 7.** Schematic illustration summarizing the structural changes that occur for underpotentially deposited 1 ML Ag and 2 ML Ag films on Au(111) both before and after transfer to alkaline electrolyte (0.1 M KOH).

Figure 1



Figure 2



Figure 3



Figure 4



Figure 5



Figure 6



Figure 7



TOC Graphic

