

CHAPTER 8:

SEQUENTIAL UPD OF CU AND AG ON AU(111)

The ability to control the architecture and chemical properties of surfaces at the atomic level is an active area of research for organic, inorganic, and hybrid systems and has produced catalysts^[74], electronic devices^[179], and ultra-thin films^[180] with enhanced properties. One way to control the chemical character of a surface is to produce monolayer of one kind or more than one kind of metals by UPD. Among the numerous UPD systems that have been characterized, the UPD of silver^[165-167, 169, 170, 174, 175] and the UPD of copper^[7, 47, 77, 117, 119, 147-149] on the Au(111) are the most thoroughly investigated ones.

It is well-known that no UPD is observed for Cu on Ag(hkl) in contrast to Au(hkl) (except for a few percent of a monolayer which are found for rough Ag electrodes positive of, but very close to the Nernst potential)^[181]. The reason behind this is probably the difference of work function and the potential of zero charge (PZC) of Ag(111) and those of Au(111)^[104, 176]. The PZC of Ag(111) is around -1.12 V versus Ag/Ag⁺ (0.1 M) while that of Au(111) is at -0.22 V versus Ag/Ag⁺ (0.1 M). While Cu UPD on Au(111) occurs at a negatively charged surface, Cu deposition on the Ag(111) takes place a highly positively charged surface.

In this chapter, we demonstrate the ability to prepare a well-defined composite or layered metal surface of Ag and Cu on the Au(111) surface in the absence and presence of thymine. The experimental techniques of cyclic voltammetry, chronoamperometry and XPS were used. The deposition of Cu on the Au(111)/Ag system was selected because the elements have relatively similar atomic diameters (0.256, 0.289, and 0.288 nm for Cu, Ag, and Au, respectively) and the overlayer elements, Ag and Cu, both form UPD layers on Au(111) and have little affinity for each other as noted in that Cu does not form an UPD layer on Ag^[181]. A similar study in the absence of thymine was formerly published by Takami and co-workers^[182]. They investigated

the formation of a composite monolayer with laterally mixed structure upon sequentially UPD of silver and copper on Au(111) in sulphuric acid solution.

The UPD of silver in perchlorate solution takes place in the potential range between 0.500 V and -0.120 V (Nernst potential of Ag), whereas, the UPD of Cu occurs between -0.220 and -0.490 V (Nernst potential of Cu) as shown in Fig. 8.1

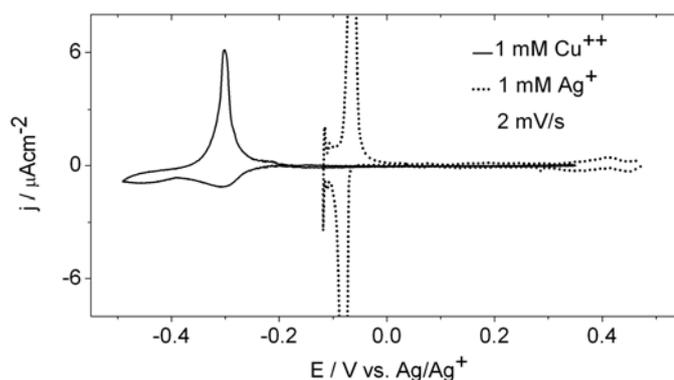


Figure 8.1: The cyclic voltammograms of Au(111) in 1 mM AgClO_4 (dotted) and 1 mM $\text{Cu}(\text{ClO}_4)_2$ (solid) electrolytes. Supporting electrolyte contains 1 M HClO_4 and 0.06 M NaClO_4 .

For sequential UPD experiments, Ag and Cu depositions were performed in separate electrochemical cells containing 0.1 M HClO_4 and 0.06 M NaClO_4 electrolytes. First, Ag was underpotentially deposited on the Au(111). Then the modified electrode was removed from the Ag^+ electrolyte under potential control, the (111) oriented surface of the electrode was immediately touched to three-distilled water 5-7 times. The used water was changed once and touched to the fresh water 3-5 times again. We changed the rinsing water due to the observation of some residue containing Ag^+ ions possibly deposited to the electrode. The rinsed single crystal was then dried under the flow of pure argon gas (especially the vertical side), and placed in the second cell filled with a Cu^{2+} electrolyte. Typically, the transfer time from the Ag^+ cell to the Cu^{2+} cell was 3 minutes. In the second cell (Cu^{2+}), the starting potential for the UPD of copper was chosen -0.18 V, which is 60 mV negative of the Nernst potential of silver (-0.120 V).

Different experimental conditions presented in Table 8.1 were combined during the sequential deposition studies. The combinations may be classified to two sections; in section 1,

the first cell does not contain thymine, however, in section 2 the cell contains 12 mM thymine in addition to 1 mM Ag^+ .

		1 st cell	→	2 nd cell
Section 1	a)	1 mM Ag^+		1 mM Cu^{++}
	b)	1 mM Ag^+		1 mM Cu^{++} / 12 mM Thymine
Section 2	a)	1 mM Ag^+ / 12 mM Thymine		1 mM Cu^{++}
	b)	1 mM Ag^+ / 12 mM Thymine		1 mM Cu^{++} / 12 mM Thymine

Table 8.1: The different experimental combinations performed during the sequential deposition studies.

8.1 In the absence of thymine in Ag^+ cell (section 1)

In this section, we demonstrate the copper deposition on the silver covered Au(111) prepared in 1 mM AgClO_4 solution containing no thymine. Au(111)/Ag was prepared scanning from 0.500 V to -0.085 V (peak position, Fig. 8.2) at the rate of 5 mV/s, afterwards 2 minutes were waited at this potential, then the silver deposited electrode was removed under potential control and transferred to the second cell. By this way, almost 2 ML of silver were deposited on the Au(111) electrode. For the experiments reported in this section, only this procedure was applied unless any other procedure is stated.

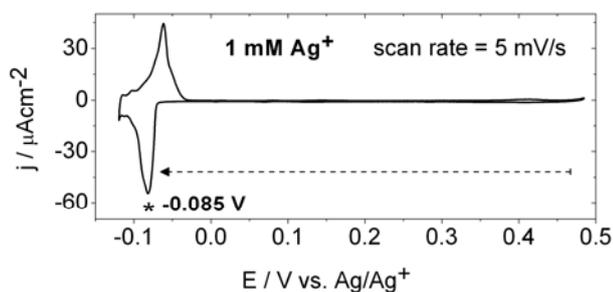


Figure 8.2: The cyclic voltammogram of Au(111) in 1 mM AgClO_4 at which based on the formation of Ag layer waiting at the peak potential of -0.085 V.

8.1.1 Electrochemical Results for Section 1a

Firstly, it should be noticed in this part that the results obtained from the Section 1a will be presented as representatives also for the other sections. In case of any significant difference between the sections, it will be stated.

The following voltammograms (Fig. 8.3) were measured in the Cu^{++} electrolyte starting from -0.180 V at the scan rate of 2 mV/s. As a reference, the CV (dotted curve) of copper UPD on Au(111) is included. The thin curve represents the CV of copper UPD on the bulk silver layer on Au(111). This layer, having 4-5 ML of silver, was obtained waiting 30 seconds at -0.150 V in Ag^+ electrolyte. The resulting voltammogram in Cu^{++} electrolyte reveals that the UPD of copper on bulk silver adlayer is very weak. This has also been observed on Ag(111) by Kolb et. al.^[181]. However, the UPD of copper on the silver adlayer having around 2 ML is clearly observed (thick curve). Comparing with the UPD of copper on Au(111), the main deposition of Cu on Au(111)/Ag(2 ML) takes place only around the second deposition peak (A_1).

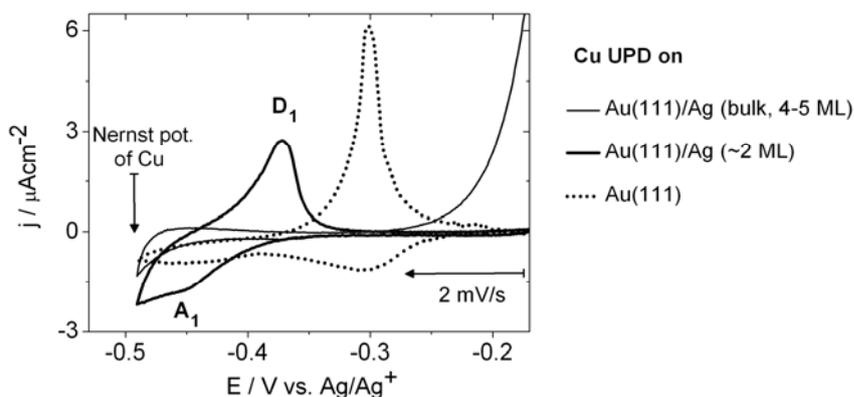


Figure 8.3: The cyclic voltammograms of Au(111) in 1 mM $\text{Cu}(\text{ClO}_4)_2$ at the scan rate of 2 mV/s. The silver modified Au(111) electrodes were prepared in 1 mM Ag^+ solution waiting 30 seconds at -0.150 V for bulk Ag (thin), waiting 2 minutes at -0.085 V for Ag UPD (thick). The dotted curve belongs to the unmodified electrode.

8.1.2 The influence of waiting in the UPD region

The following cyclic voltammograms (Fig. 8.4) on Au(111)/Ag measured in the Cu^{++} electrolyte show the changes upon waiting 30 minutes at -0.440 V (A_1). The voltammogram drawn as the thick curve reveals that waiting half an hour does not significantly increase the accumulated copper. The area under the stripping peak of the “thick” curve (thick) is 70 ± 5 $\mu\text{C}/\text{cm}^2$, which is close to the area under the corresponding “thin” curve (without waiting, but

scanned up to the Nernst potential of Cu). It should be remembered that the corresponding charge obtained using the bare Au(111) electrode after waiting half an hour is $305 \pm 5 \mu\text{C}/\text{cm}^2$.

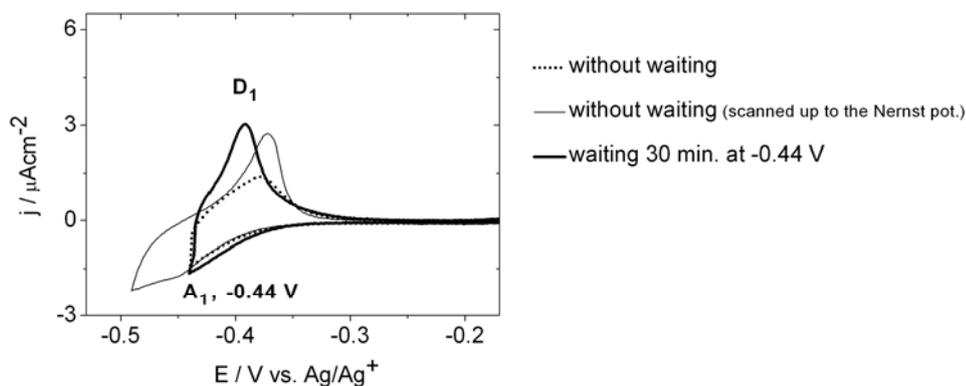


Figure 8.4: The cyclic voltammograms of Au(111)/Ag in 1 mM $\text{Cu}(\text{ClO}_4)_2$ solution at the scan rate of 2 mV/s.

8.1.3 Stability of Ag on Au(111) in Cu^{2+} Electrolyte

We investigated the electrochemical stability of the Ag adatoms on Au(111) in the Cu^{2+} electrolyte. In the case of cycling in the Cu-UPD region, the voltammetry of the Cu-UPD on Au(111)/Ag does not change markedly (not shown here). It reveals the silver layer is stable in the potential region negative of -0.200 V. However, in the other case, scanning to positive potentials ($E > -0.200$ V), the silver layer, as expected, stripes and diffuses into the Cu^{2+} solution. The cyclic voltammograms illustrated in Fig. 8.5 demonstrate the changes of Au(111)/Ag upon cycling in the potential range of the UPD of Cu as well as Ag. The first scan was started from -0.180 V to -0.440 V at which waited half an hour. Afterwards, cycling was continued. The deposited Cu is stripped at -0.400 V (D_1), and upon further scanning to positive potential, the stripping of silver adlayer is observed mainly at -0.060 V (D_2) and 0.300 V (D_3). At further scans, the CV around the Cu-UPD potential region resembles to the CV of the copper UPD on the bare Au(111) and the silver layer is almost be removed after 3 cycles.

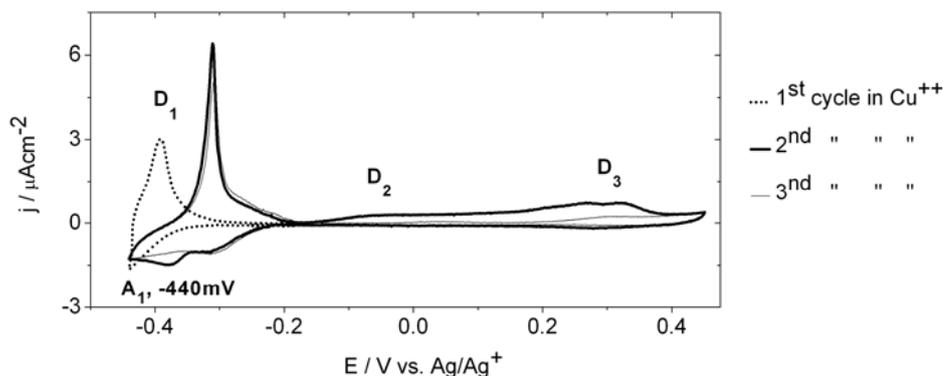


Figure 8.5: The cyclic voltammograms of Au(111)/Ag(2 ML) in 1 mM $\text{Cu}(\text{ClO}_4)_2$ at the scan rate of 2 mV/s. The silver modified Au(111) electrodes were prepared in 1 mM Ag^+ solution waiting 2 minutes at -0.085 V for Ag UPD.

8.1.4 Chronocoulometric Studies

During the waiting time at the formation potential (-0.085 V) the current-time evolution presented in Fig. 8.6 was obtained. It reveals that the formation of the Cu-UPD layer is fast at the first 5 minutes as compared to the further times. The deposition of Cu on Au(111)/Ag is almost completed in half an hour.

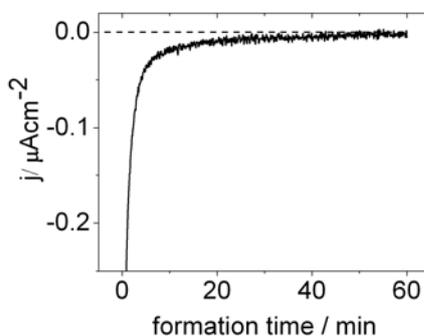


Figure 8.6: The current-time transient measured during waiting at the formation potential -0.440 V for Au(111)/Ag in Cu^{++} solution.

The transients obtained from the dissolution of copper from the Au(111)/Ag surface are shown in Fig. 8.7. The routine of those experiments are the same as stated in section 5.3.2. The typical minimum/maximum transients which were found formerly for the UPD of copper on Au(111) indicating a nucleation and growth process is not observed the present case. The charge density values have been calculated from the integration of the transients. They increase by a factor of almost four upon waiting half an hour and reaches to the value of $87 \pm 5 \mu\text{Ccm}^{-2}$.

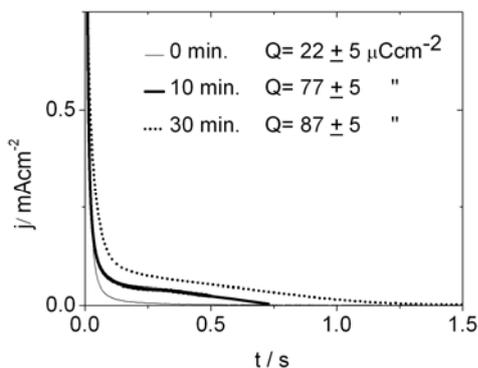


Figure 8.7: The dissolution transients and the charge density values for Au(111)/Ag obtained after waiting different times at the formation potential of -0.440 V in Cu^{++} solution.

8.1.5 The influence of thymine in the Cu^{++} cell (Section 1.b)

The voltammogram (bold curve) shown in Fig. 8.8 demonstrates the UPD of copper in the presence of thymine on Au(111)/Ag at the scan rate of 2 mV/s . As a better comparison, the CV for Au(111)/Ag from the thymine-free solution is included (dashed curve). The resulting CV (bold) taken in Cu^{++} /thymine solution shows that the UPD of copper starts $60\text{--}70\text{ mV}$ more positive potential (A_2) as compared to that obtained in thymine-free one (A_1). Additionally, the deposition/stripping peaks (A_2/D_2) are broader in the presence of thymine.

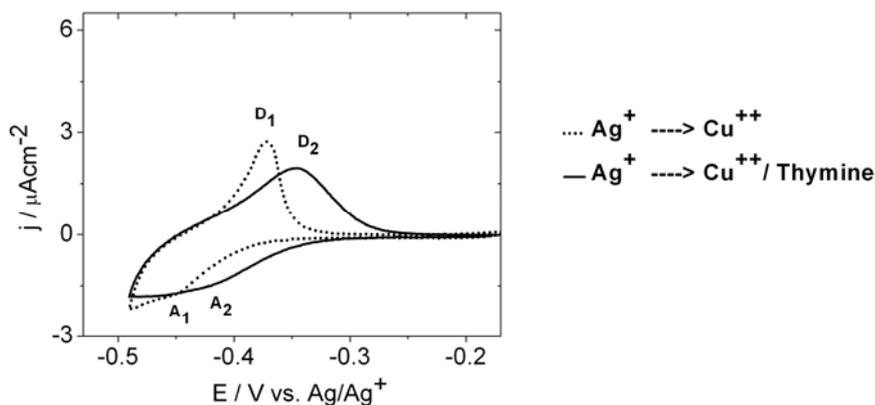


Figure 8.8: The cyclic voltammograms of Au(111)/Ag in $1\text{ mM Cu(ClO}_4)_2$ (thin) and in $1\text{ mM Cu(ClO}_4)_2 + 12\text{ mM thymine}$ (bold) solutions at the scan rate of 2 mV/s .

8.2 In the presence of thymine in the Ag^+ cell (section 2)

In this section, the deposition of copper on the silver/thymine coated Au(111) surface have been investigated. The solution in the first cell contains 12 mM thymine in addition to 1 mM Ag^+ . The preparation of Ag/thymine layer is followed considering the voltammogram shown in Fig. 8.9. Two different Ag/thymine adlayers were prepared as following: first scanning from 0.650 V to the formation potentials at the scan rate of 5 mV/s, afterwards waiting 5 minutes at +0.190 V (0.6 ± 0.05 ML of Ag) in addition to waiting 2 minutes at -0.085 V (0.9 ± 0.05 ML of Ag).

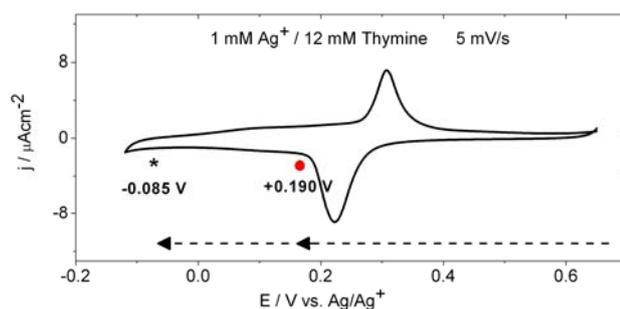


Figure 8.9: The cyclic voltammogram of Au(111) in 1 mM AgClO_4 + 12 mM thymine at which based on the formation of Ag layer waiting at the peak potentials of -0.085 V and 0.190 V.

i) Adjusting at -0.085 V

The following voltammograms represent the deposition-dissolution behaviour of Cu on the Au(111)/(Ag/thymine). As similar to the results observed in Section 1, also in this part the deposition of copper in thymine containing solution is more than that of the thymine-free one.

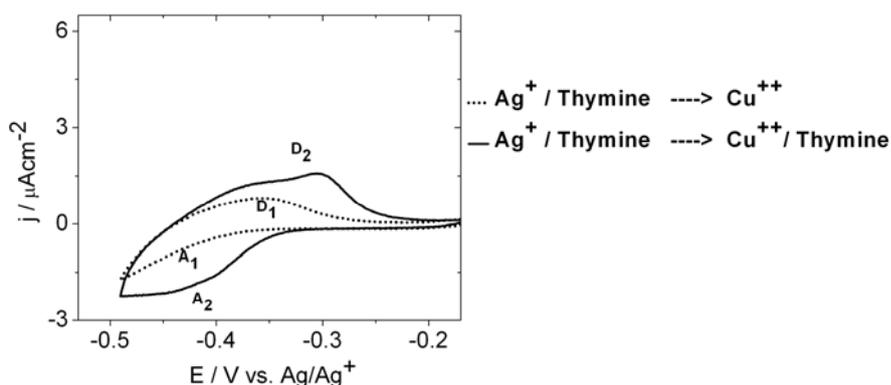


Figure 8.10: The cyclic voltammograms of Au(111)/(Ag + thymine) in 1 mM $\text{Cu}(\text{ClO}_4)_2$ (dotted) and in 1 mM $\text{Cu}(\text{ClO}_4)_2$ + 12 mM thymine (solid) solutions at the scan rate of 2 mV/s.

ii) *Adjusting at 0.190 V*

Upon adjusting the Au(111) electrode in Ag^+ /thymine solution by waiting 5 minutes at 0.190 V, the coverage of silver ($0.6 \pm 0.05 \text{ ML}$) becomes not condensed as much as the former cases. Apparently, there exists an open structure of silver. The open structure allows the interaction of thymine molecules with the surface gold atoms.

The voltammograms shown in Fig. 8.11 reflect the behaviour of the deposition of copper on the “open structure” Ag layer. The apparent feature of these voltammograms, which has not been observed at the former voltammograms in this chapter, is the closer similarity to the UPD of copper on the bare Au(111) (red curve). As similar to the former results, the deposition of copper in the presence of thymine in the solution starts at more positive potentials.

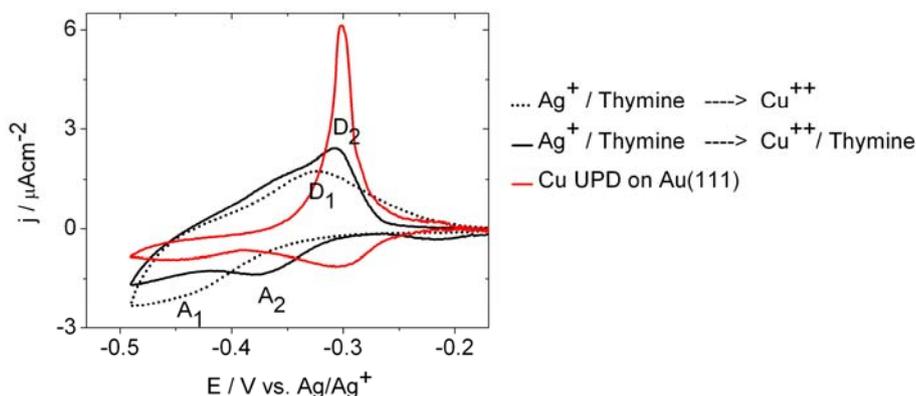


Figure 8.11: The cyclic voltammograms of Au(111)/(Ag + thymine) in 1 mM $\text{Cu}(\text{ClO}_4)_2$ (dotted) and in 1 mM $\text{Cu}(\text{ClO}_4)_2$ + 12 mM thymine (solid) solutions. The red curve: Cu-UPD on the bare Au(111). Scan rates: 2 mV/s.

8.3 The summary of all chronocoulometric studies

The evolution of the charge density with increased waiting time at the formation potentials upon the integration of the dissolution transients displays the diagram shown in Fig. 8.12. Due to that most of the transients are similar to those shown in Fig. 8.7, we do not present the others here. One small exception is observed in the transients obtained from the “open structure” Ag adlayer. Those transients have apparent minimum-maximum peaks, which are observed in the system of Cu-UPD on the bare Au(111). It also reveals that some copper adatoms interact with the surface gold atoms or chemisorbed thymine molecules in addition to silver adatoms.

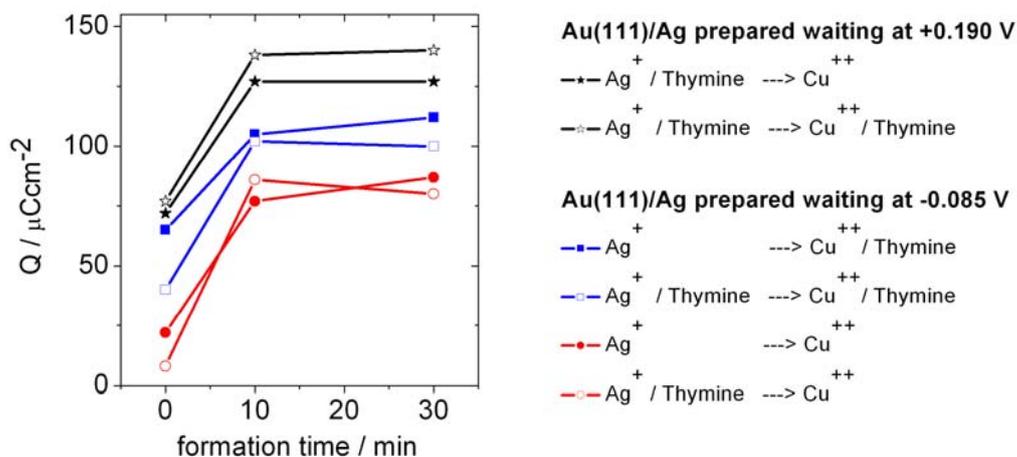


Figure 8.12: The charge density diagram obtained integrating the dissolution transients of copper at different conditions.

The diagram above indicates that the amount of the deposited copper strongly depends on two factors: one is the coverage of the silver adlayer and another is the presence of thymine in the Cu⁺⁺ cell. In the case of low coverage (0.6 ± 0.05 ML of Ag) of the silver adlayer (black curves), the deposition of copper reaches its maximum level compared to the others. The corresponding charge value is about $140 \pm 7 \mu\text{Ccm}^{-2}$ after waiting half an hour (empty star). This value corresponds to 0.3 ± 0.03 ML of copper considering 2-electron discharging per copper ions. In the case of higher surface coverage of the silver adlayer (1.7 ± 0.10 ML), the deposition of copper is lower (blue, red curves). The corresponding copper coverage is for red curves about 0.15 ± 0.03 ML after waiting half an hour.

The second factor influencing the copper deposition on the silver adlayer is the presence of thymine, especially in the second cell. In all cases, thymine increases the copper deposition about $10 \pm 5 \%$ compared to the absence of it. Therefore, it can be concluded again that thymine supports the UPD of copper on Au(111)/Ag as well as on Au(111).

These two factors probably compete with each other. However, the supporting of thymine in the second cell (Cu²⁺) to the copper deposition is most probably overcome to the negative effect which arises from the higher surface coverage of silver layer. The blue and the black (empty star) curves support this idea.

8.4 XPS Studies

Cu-2p

During the photoemission measurements on the sequential experiments, we could never observe a well-defined Cu-2p signal as formerly observed during the experiments of Cu-UPD on the bare Au(111) (Fig. 8.13.a). The most apparent spectrum we could observe is illustrated in Fig. 8.13.b. It belongs to the sample prepared as described in section 2.a (Ag/Thymine \rightarrow Cu/Thymine). The coverage of copper is 0.3 ± 0.05 ML, which is the highest one among all obtained from coulometric results. Even the spectrum of this probe suffers from very poor signal to noise ratio. Only the weak peaks around 933.2 eV and 934.8 eV can give us some hints about the existence of oxidized Cu^{n+} , probably $1 \ll n < 2$.

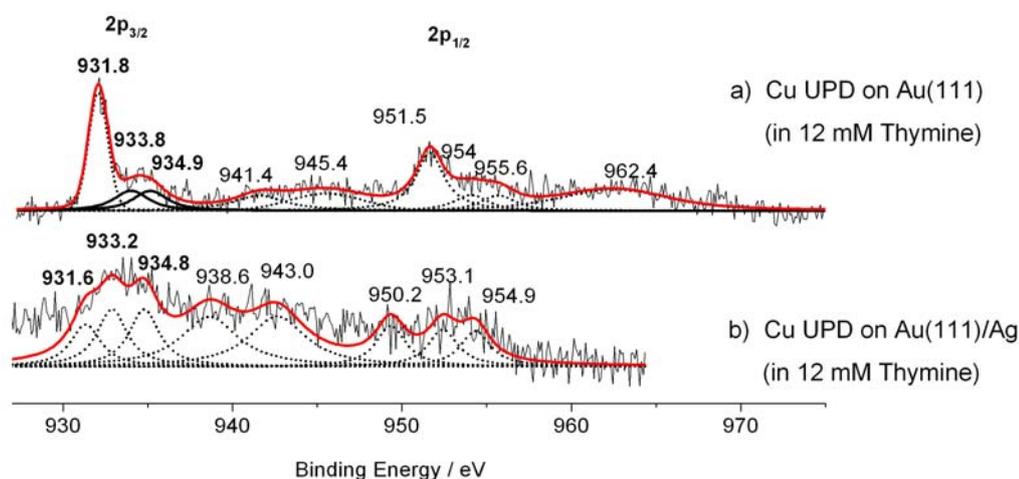


Figure 8.13: XPS Cu-2p spectra of copper/thymine deposited on Au(111) (a), and on Au(111)/Ag (b).

The reason for not observing a clear copper signal in the XPS might be the transfer procedure from the 2nd cell to the UHV. The rinsing of the probe with water may remove copper adatoms. This is possible only if the copper adatoms have very weak interaction with the silver adlayer on Au(111) and acquires that the oxidation state of copper is close to 2.

Ag-3d

The Ag-3d signals reflect any significant dependence neither to the transferring to a 2nd cell containing no silver, nor the change of chemical species in the solution (thymine, Cu^{++}). The chemical character of the atoms of the silver adlayer only depends on the preparation procedure

carried out in the Ag^+ cell. The $3d_{5/2}$ peak positions of the silver adlayer at different conditions are tabulated in Table 8.2.

As observed before, the $3d_{5/2}$ signals for Ag on Au(111) having monolayer or sub-monolayer structure are observed around 367.88 eV (red, green). Whereas, the Ag signals from 2 ML on Au(111) or bulk silver is observed at higher binding energies (368.13 eV).

	Ag(ML)	Ag(ML) → Cu^{++}	Ag(ML)/Thym.	Ag(ML)/Thym. → Cu^{++}	Ag(ML)/Thym. → Cu^{++} /Thym.	Ag(2ML)	Ag(2ML) → Cu^{++}
Ag- $3d_{5/2}$ (± 0.05 eV)	367.88	367.88	367.85	367.80	367.83	368.13	368.08

Table 8.2: The Ag $3d_{5/2}$ peak positions belong to the probes prepared at different conditions. The arrow shows the transfer of probe from the 1st electrochemical cell to the 2nd one.

N-1s

The N-1s core level investigations (Fig. 8.14) in the XPS studies have shown that thymine molecules exist in the silver layers. The first spectrum belongs to the probe having one ML silver incorporated with thymine on the Au(111) surface (from the section 7.2.3). Each spectrum has two signals located at different binding energies. It indicates that the thymine molecules are chemisorbed via N(3) as formerly proven by Nichols et.al [14]. This idea is also proven by the presence of N-1s signal even if the probe is transferred to thymine-free Cu^{2+} cell (Fig. 8.14.b).

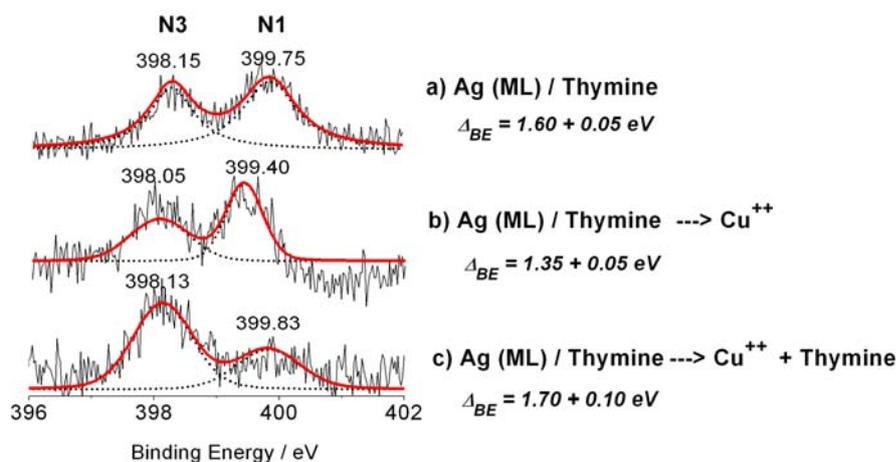


Figure 8.14: N-1s spectra for the bare Au(111) surface having silver monolayer and thymine (a), for the copper deposited on Au(111)/Ag in thymine-free electrolyte (b), for the copper deposited on Au(111)/Ag in thymine containing electrolyte (c). The emersion potentials are 0.00 V (a) and -0.47 V (b,c), respectively.

C-1s

The C-1s spectra shown in Fig. 8.15 also support the idea claimed above in N-1s part.

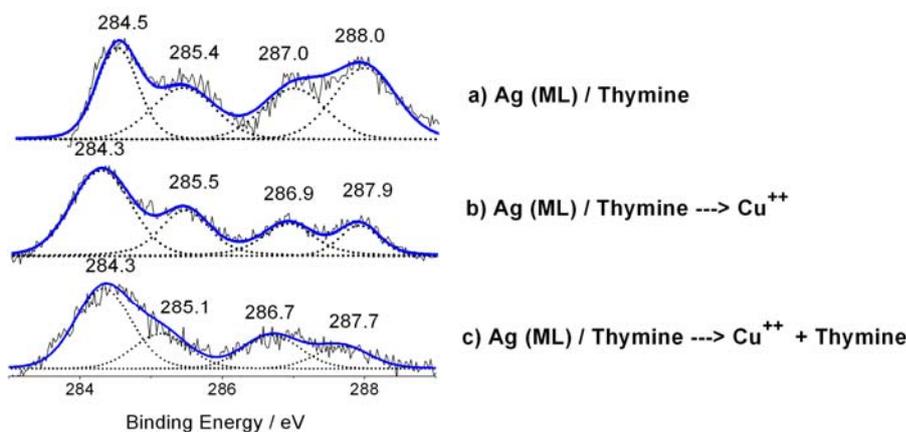


Figure 8.15: C-1s spectra for the bare Au(111) surface having silver monolayer and thymine (a), for the copper deposited on Au(111)/Ag in thymine-free electrolyte (b), for the copper deposited on Au(111)/Ag in thymine containing electrolyte (c). The emersion potentials are 0.00 V (a) and -0.47 V (b,c), respectively.

8.5 Summary

Despite observing a deposition/dissolution behaviour of copper on the silver modified Au(111) electrode during electrochemical studies, it has not been observed during the XPS experiments. Exceptionally, in the presence of thymine in the electrolyte (in Cu^{++} cell and/or Ag^+ cell), very poor XPS signal of copper was observed. However, we should not forget the transferring procedure during the *ex situ* XPS experiments. Because, the adatoms of Cu (even in thymine containing surfaces) are oxidized forming divalent species by adhesion of water and upon washing the the probe with water those divalent copper ions are removed from the surface.

Additionally, from electrochemical studies we observed that copper deposition on Au(111)/Ag was supported by thymine in electrolyte. It means that thymine leads to a relatively stronger interaction between copper and the silver adlayer. The following structural representations formed in thymine containing electrolytes can be introduced (Fig. 8.16). The first

structure (A) might represent the layer by layer deposition of copper and silver adatoms on Au(111). In this representation, partially discharged copper species are sandwiched between the deprotonated thymine molecules and partially charged silver species. The second probable structure (B) represents the composite formation between partially discharged Ag and Cu species. Deprotonated thymine molecules are on top of the composite monolayer.

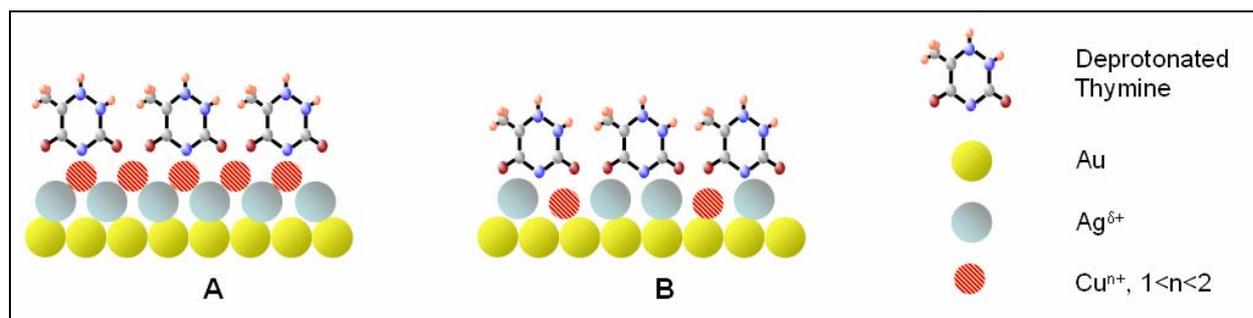


Figure 8.16: Schematic representation of copper deposition on the silver modified Au(111) in the presence of thymine. A: Layer by layer, B: Composite structure

In conclusion, in the absence of thymine, a layer by layer fashion of Cu on the Ag deposited Au(111) or a composite monolayer formation as formerly stated by Takami et. al^[182] most likely occurs but, the interaction between Cu species and Au(111)/Ag is very weak. Whereas, in the presence of thymine, formation of both kinds of adlayer structures are possible due to the relatively stronger interaction. Therefore, layer by layer deposition or composite formation at the first monolayer possibly occurs