Electrochemical and Ultrahigh Vacuum Characterization of 
Ultrathin Cu Films on Pt(111)

Lam-Wing H. Leung, Thomas W. Gregg, and D. Wayne Goodman

Department of Chemistry, Texas A&M University, College Station, Texas 77843-3255

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Submonolayer to multilayer coverages of Cu electrodeposited and vapor-deposited onto a well-characterized Pt(111) surface were studied in both ultrahigh vacuum (UHV) and electrochemical environments by use of a combined UHV–electrochemical transfer apparatus. Linear sweep voltamograms obtained in 0.2 M HClO₄ for both types of surfaces displayed very similar electrochemical stripping profiles. The potential difference between the multilayer and the underpotential deposited (UPD) monolayer stripping peaks is \( \sim 0.43 \) V, which is equivalent to an absolute energy difference of 19.8 kcal/mol. In addition, these voltammetric results demonstrated that simple site blocking for hydrogen chemisorption on Pt(111) by both electrodeposited and vapor-deposited Cu occurs linearly with chemisorption being essentially eliminated at \( \theta = 1.0 \) ML, much similar to analogous studies performed in a UHV environment. Although the charge measured for the monolayer Cu stripping peak in both cases is lower than the theoretically expected value for a Cu monolayer in registry with the Pt(111) substrate surface, UHV studies of Cu overlayers on Pt(111) based on low-energy diffraction (LEED) analysis, Auger electron spectroscopy (AES) analysis, work function measurements, and photoemission studies have shown that a complete Cu monolayer is formed prior to the formation of Cu multilayers. To account for the discrepancy between these two values, we believe that the UPD Cu monolayers in the electrochemical environment near their stripping potentials are partially charged as a consequence of transfer of electronic charge from the metal adlayer to the Pt(111) substrate.

I. Introduction

It is now well-known that the modification of metal surfaces by deliberate addition of another metal component can lead to selective improvement or degradation in catalytic activity, selectivity, and resistance to poisoning of such surfaces in both gas-phase and liquid-phase environments. The modification of the metal substrate at the gas–solid interface is usually accomplished by vapor deposition of the second metal, while at the liquid–solid interface, controlled submonolayer and monolayer deposits of a second metal can be electrochemically deposited onto the metal substrate by underpotential deposition (UPD). This UPD phenomenon in general involves monolayer or submonolayer formation of various metals on foreign metal substrates at electrode potentials anodic to that for the reversible electrodeposition of the bulk metal. As a result, UPD is clearly the result of a relatively strong interaction between the monolayer and the substrate, very similar to that observed following the vapor deposition of a second metal onto a metal substrate.

While studies performed using modern techniques of surface science give a detailed atomic-level picture of the chemistry occurring at the gas–solid interface, the corresponding information is not easily obtained in the analogous electrochemical environment. In an effort to correlate the properties of these bimetallic surfaces at the gas–solid and liquid–solid (or electrolyte–electrode) interfaces, we have specifically constructed a combined ultrahigh vacuum (UHV) and electrochemical apparatus that allows easy and rapid controlled transfer of a well-characterized single-crystal surface between UHV and atmospheric liquid electrochemical environments. This type of apparatus is essential since it enables the powerful UHV surface science techniques to be applied to study and characterize the electrode surface before and after electrochemical measurements.

In this paper we report on studies of the electrochemical stripping of both vapor-deposited and electrochemically deposited copper on Pt(111) and an investigation of how copper affects the adsorption of hydrogen on Pt(111) in the electrochemical environment. We will demonstrate that specific comparisons can be drawn between the present electrochemical data and that reported in the surface science literature. Furthermore, on the basis of the charge measured from our electrochemical stripping experiments, the present results strongly suggest that the polarization of the copper overlay is altered significantly when the Cu/Pt(111) surface is placed in contact with the

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electrolyte solution. Likewise, our recent study of the Ag/Pr(111) system shows analogous behavior.

II. Experimental Section

The experiments were conducted in an apparatus consisting of an electrochemical (EC) chamber attached directly to a UHV chamber with a base pressure of \( \sim 2 \times 10^{-10} \) Torr. This combined UHV–EC apparatus is more fully described in another publication and will only be briefly discussed below.

The Pt(111) sample, 10 mm in diameter and 1.5 mm thick, was heated resistively by tantalum leads spot-welded to the edge of the crystal while the temperature measurement was made by using a W-5% Re/W-26% Re thermocouple spot-welded to the backside. The Pt(111) sample was cleaned by heating the sample to 1300 K in \( 10^{-6} \) Torr O\(_2\) followed by annealing in vacuum to 1500 K to remove traces of oxygen. Surface cleanliness was verified by Auger electron spectroscopy (AES) and the order of the Pt(111) sample was confirmed by low-energy electron diffraction (LEED). The Pt(111) sample was mounted onto a sample manipulator allowing 20 in. of travel in the horizontal direction and \( \pm 0.5 \) in. in the perpendicular plane.

Following characterization in the UHV chamber, the sample was moved to an antechamber by sliding the manipulator through a pair of differentially pumped, spring-loaded Teflon seals. The major purpose of the antechamber, which is completely isolated from the EC chamber by a gate valve, is to serve as an intermediate vessel in which the pressure can be varied between UHV and atmospheric. The antechamber was then pressurized with ultrapure N\(_2\) gas, the gate valve opened, and the sample translated to the EC chamber. For postelectrochemical surface analysis of the sample, the antechamber was evacuated from atmospheric pressure following closure of the gate valve by a 100 L/s turbomolecular pump. Pumpdown from atmospheric pressure to low (\( 10^{-5} \)) or high (\( 10^{-9} \)) Torr requires \( \sim 15 \) min.

A PAR Model 273 potentiostat was used for the electrochemical measurements. The electrochemical cell is of a conventional three-electrode configuration consisting of a platinum counter electrode, an Ag/AgCl reference electrode, and the Pt(111) sample as the working electrode. The entire electrochemical cell setup is attached to a XYZ manipulator and can be easily maneuvered with respect to the sample to form a meniscus-type sample–solution contact. Water was purified by means of a Milli-Q system (Millipore). Copper perchlorate and perchloric acid (doubly distilled) were used as the electrolyte solution. Likewise, our recent study of the Ag/Pr(111) system shows analogous behavior.

III. Results

A. Cu-Free Pt Surface. To demonstrate the capability of our combined UHV–EC apparatus, the Auger spectra of an initially clean Pt(111) sample before and after electrochemical measurements were performed in the EC chamber are displayed in Figure 1a (upper and lower spectra, respectively). As shown in the lower spectrum in Figure 1a, Auger peaks due to Cl and O are present, which can be attributed to residual electrolyte on the surface following evaporation of perchloric acid. More importantly, no contamination due to C is observed, as evidenced by the absence of an Auger peak at 270 eV. In addition, the cleanliness and order of the Pt(111) surface upon transfer from the UHV chamber is demonstrated in Figure 1b by the cyclic voltammogram observed in 0.2 M HClO\(_4\). The characteristic voltammetric features obtained in the present measurement are in excellent agreement with those reported previously for clean Pt(111) in HClO\(_4\).

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The cyclic voltammogram obtained at 0.05 V s\(^{-1}\) in the Cu\(^{2+}\) solution shown in Figure 2 is in reasonably good agreement with earlier observations.\(^{22-26}\) Thus, the cathodic peaks at \(\sim 0.4\) and \(\sim 0.2\) V correspond to the deposition of the UPD copper layer while a rather featureless cathodic wave observed at potentials negative of 0 V represents the electrodeposition of copper multilayers on Pt(111). When the electrode potential is reversed and swept in the positive direction, two anodic peaks are observed at \(\sim 0.05\) and \(\sim 0.5\) V, as shown in Figure 2. The anodic peak at \(\sim 0.05\) V, whose faradaic charge varies as a function of the turnaround potential as well as the holding time at \(-0.2\) V, arises from the desorption of Cu multilayers (i.e., Cu\(^+(aq)\) \(\rightarrow\) Cu\(^{2+}(aq)\) + 2e\(^-\)). The relatively more positive anodic peak at \(\sim 0.5\) V, whose faradaic charge is independent of the potential at 0 V as well as the holding time at \(-0.2\) V, can be attributed to the electrochemical stripping of UPD copper layers from Pt(111) (to form solution Cu\(^{2+}\)). Interestingly, the voltammogram seems to indicate that the electrodeposition of the UPD Cu layer takes place in two distinct steps while the stripping of this UPD layer involved only a single step, as illustrated in Figure 2. We also note that the total amount of underpotentially deposited Cu, based on the faradaic charge measured from the stripping peak at \(\sim 0.5\) V, is approximately 340 ± 25 \(\mu\)C cm\(^{-2}\). Although this value is substantially lower than the theoretically expected value for a monolayer in registry with the substrate surface (480 \(\mu\)C cm\(^{-2}\) for the present Pt(111) surface), we are confident that a full monolayer indeed is formed in this UPD process (see below). In addition, similar values of faradaic charge for the stripping of UPD Cu on Pt(111) have been reported.\(^{26,27}\)

Also of interest is the current–potential stripping profiles for various amount of UPD Cu on Pt(111). Figure 3 shows the linear sweep voltammograms for various coverages of UPD Cu on Pt(111) in 0.2 M HClO\(_4\) at 0.05 V s\(^{-1}\). The UPD Cu layers were prepared by setting the electrode potential at \(-0.2\) V at various time intervals in a very dilute Cu\(^{2+}\) solution. The Cu\(^{2+}\) solution was then replaced with Cu\(^{2+}\)-free 0.2 M HClO\(_4\) solution prior to the stripping process. The Cu coverages, \(\theta_{\text{Cu}}\), depicted in Figure 3 were determined by assuming the faradaic charge measured under a saturated UPD stripping peak is a full monolayer (ML). As shown in Figure 3, the shape of the UPD stripping peak remains essentially unchanged as a function of \(\theta_{\text{Cu}}\), although a slight upshift in peak potential can be observed at increasing \(\theta_{\text{Cu}}\). Close inspection of Figure 3 reveals that the voltammetric wave, corresponding to the removal (oxidation) of adsorbed hydrogen on Pt(111) within the electrode potential region between \(-0.2\) and 0.1 V, is increasingly suppressed as \(\theta_{\text{Cu}}\) is progressively increased. Eventually, this adsorbed hydrogen wave is completely suppressed at \(\theta_{\text{Cu}} \geq 1\) ML.

**C. Electrochemical Stripping of Vacuum-Deposited Cu Films on Pt(111).** Figure 4 displays a series of linear sweep voltammograms at 0.05 V s\(^{-1}\) in 0.2 M HClO\(_4\) for vacuum-deposited Cu films on Pt(111) at various Cu coverages. The \(\theta_{\text{Cu}}\) values depicted in Figure 4 were estimated in the same manner as mentioned in the previous section. It is important to note that following vacuum deposition of a given coverage of Cu, the Pt(111) electrode was introduced into the electrochemical cell under a controlled potential of \(-0.2\) V to avoid any loss of Cu to the electrolyte. The voltammetric profiles of Figure 4 from a series of vacuum-deposited Cu films of coverage similar to those of Figure 3 (which were deposited electrochemically) display striking similarities. Furthermore, the faradaic charge for the 1.0 ML Cu stripping peak shown in Figure 4 yields a value of 335 ± 25 \(\mu\)C cm\(^{-2}\) (compared to the theoretical value of 480 \(\mu\)C cm\(^{-2}\) for a full mono-

![Figure 3](image3.png)

**Figure 3.** Linear sweep voltammograms for various coverages of electrodeposited Cu on a well-characterized Pt(111) surface in 0.2 M HClO\(_4\) at 0.05 V s\(^{-1}\).

![Figure 4](image4.png)

**Figure 4.** As for Figure 3, but obtained for various coverages of vapor-deposited Cu on Pt(111).
layers linearly attenuate the hydrogen adsorption capacity of the clean Pt(111) surface is assumed to be 1.0 ML.\) The data points plotted in Figure 5 were obtained from the corresponding linear sweep voltammograms for electrodeposited (filled circles) and vacuum-deposited (open squares) Cu overlayers on Pt(111). Figure 5 clearly demonstrates that both electrodeposited and vacuum-deposited Cu overlayers linearly attenuate the hydrogen adsorption capacity of the Pt(111) electrode in a 0.2 M HClO₄ environment with chemisorption being essentially eliminated at \( d_{H} = 1.0 \).\) In addition, this linear attenuation of the hydrogen adsorption capacity resembles closely that reported in a recent UHV study in which hydrogen adsorption on Pt-\((111)\) was blocked linearly by vapor-deposited copper layers.\(^{15}\)

**IV. Discussion**

We start the discussion by justifying our assignment of a full monolayer of Cu for the UPD Cu stripping peak even though the faradaic charge measured under this peak (340 \( \mu \)C cm\(^{-2}\)) is well below the theoretically expected value for a Cu monolayer in registry with the Pt(111) substrate surface (480 \( \mu \)C cm\(^{-2}\)).\(^{29}\) There are several important pieces of data obtained in the present and previous studies that support this assignment. First, UHV studies of Cu overlayers on Pt(111)\(^{15,18,28,29}\) based on LEED analysis, AES analysis, work function measurements, and photoemission studies have shown that a complete monolayer is formed prior to the formation of Cu multilayers. The fact that our linear sweep voltammetric results for vacuum-deposited Cu films on Pt(111) yielded a faradaic charge for the UPD stripping peak well below the expected monolayer value strongly suggests that the polarization of the vacuum-deposited Cu monolayer has been altered significantly when placed in contact with the electrolyte solution. Although the similar appearance in the electrochemical stripping profiles for both electrodeposited and vacuum-deposited Cu overlayers (Figures 3 and 4) is not surprising, the almost identical values of faradaic charge obtained for both UPD Cu stripping peaks clearly imply that the nature of the Cu monolayer in both cases is virtually identical.

Second, it has long been recognized that hydrogen chemisorbs strongly on Pt both in UHV environment\(^{15,28,29}\) and in acidic electrolyte solution.\(^{16,17,30,31}\) In addition, both UHV\(^{32}\) and electrochemical\(^{28,29}\) studies have demonstrated that total blockage of hydrogen chemisorption on this surface requires a full monolayer of Cu. The data of Figure 5 clearly illustrate that a simple linear relation exists between the amount of adsorbed hydrogen and the Cu coverage in 0.2 M HClO₄. The fact that there was complete blocking of hydrogen adsorption on the Pt(111) electrode at the completion of the UPD Cu layer deposited electrochemically or in vacuum strongly indicates that this UPD Cu layer represents a complete Cu monolayer. UHV studies of the site blocking of adsorbed CO on Pt(111) by Cu overlayers have been reported\(^{18,28,29}\) and could serve as an additional test to calibrate the Cu coverage. Unfortunately, however, the potential region at which adsorbed CO is electrooxidatively removed from the Pt(111) electrode\(^{17,33}\) significantly overlaps the UPD Cu stripping peak.

Finally, comparisons of the AES [Cu(920 eV)/Pt(237 eV)] ratios for the vacuum-deposited Cu monolayer before and after immersion in the electrolyte under controlled potential (-0.2 V) reveal no measurable loss of Cu. In addition, the observed AES ratio is in close agreement (within 5-10%) with that found for the electrodeposited UPD Cu layer. Moreover, both aforementioned Cu monolayers displayed \((1 \times 1)\) LEED patterns at room temperature, confirming the pseudomorphic structure of each. The above observations imply that the UPD Cu layers deposited electrochemically or in vacuum are essentially identical and therefore represent a complete Cu monolayer. Although in many cases\(^{7,10,16,31}\) a more accurate overlap-layer coverage calibration can be obtained by means of temperature-programmed desorption (TPD), the Cu/Pt(111) surface, when annealed to temperatures above 520 K, forms a strong Cu/Pt(111) alloy.\(^{28,29}\) The onset of desorption of Cu from this alloyed substrate takes place at temperatures above 1350 K.\(^{34}\) Nevertheless, interesting electrochemical properties of the Cu/Pt(111) alloy surfaces have been observed and the results will be presented elsewhere.\(^{34}\)

Having justified our Cu coverage calibration for the UPD monolayer, it is of interest to discuss the origin of the discrepancy between the faradaic charge measured for the UPD Cu stripping peak and the theoretically expected value for a complete monolayer. One simple explanation is that the monolayer Cu adatoms are significantly partially

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**Figure 5.** Plots of saturation coverages of adsorbed hydrogen, \( \theta_H \), as a function of Cu precoverage, \( \theta_{Cu} \), in 0.2 M HClO₄. The Cu overlayers were prepared electrochemically (closed circles) and under vacuum conditions (open squares).
charged under the electrochemical conditions near their stripping potentials. As a result, the charge measured for the UPD stripping peak will lead to a lower value than the theoretically expected value, which assumes a full two-electron-transfer process to occur within the UPD peak potential region. Two factors could contribute to the presence of a partially charged Cu monolayer at the Pt/solution interface: (1) a charge transfer from Cu to Pt in the first monolayer is expected based upon the lowering of the work function upon the vapor-deposition of Cu onto Pt(111) in UHV studies; and (2) the adsorption of solution anions near the stripping potential of monolayer Cu should facilitate charge transfer from the Cu overlayer to the Pt substrate. From the work function difference between monolayer Cu on Pt and bulk Cu, the contribution of (1) to the development of the partial Cu charge is estimated to be relatively minor. The contribution of (2), then, clearly is seen to dominate the development of the partial charge on the Cu prior to the onset of the UPD stripping peak. In this regard it is noteworthy that a partially charged UPD Cu adlayer electrodeposited on a polycrystalline platinum electrode, using thermodynamic and kinetic arguments, has been proposed. In addition, a recent radiochemical study has provided direct evidence that, in the presence of submonolayer and monolayer coverages of electrodeposited Cu on polycrystalline gold, an enhanced adsorption of (bi)sulfate is induced by the Cu adatoms. This enhanced anion adsorption likely is a consequence of the positive charge developed at the Cu sites via transfer of electronic charge from the Cu to the metal substrate. An "electrosorption valency" of Cu that is significantly less than 2 can be ascribed to a polarization of the Cu to optimize the destabilizing Cu-anion electronic interactions, which involve primarily occupied orbitals, and the stabilizing Cu2+-anion electrostatic interactions. In this regard, we have recently obtained convincing evidence, based on AES and coulometric measurements, that strongly suggest that the polarization of the Cu atoms is highly coverage dependent. Moreover, it is also of interest to note that recent X-ray photoelectron spectroscopy (XPS) studies have demonstrated that chemisorption of CO onto bimetallic surfaces, in general, induces a large positive shift in the core level of the metal overlayer. The mechanism by which the metal overlayers become partially charged has been ascribed to an adsorbate-induced charge transfer from the overlayer metal to the substrate.

Based on the above considerations, a significant decrease in the electron density of the UPD Cu overlayers in the present electrochemical environment is expected. This is a consequence of charge transfer from the metal adlayer to the Pt(111) substrate. This type of charge transfer very likely is a major contributor to the observed low charge value measured for the UPD Cu stripping peak in the present study, and as well in the Ag/Pt(111) system. These preliminary studies imply that coulometric determination of UPD Cu and Ag coverage on Pt(111) using simple peak areas can lead to substantial error (~30% for 1 ML Cu and Ag/Pt(111)). It is of interest to note that recent in situ scanning tunneling microscopy (STM) studies for the electrodeposition of Cu onto Au(111) have also suggested that metal overlayer coverage evaluations from current–potential curves can lead to significant error. Whether this is generic to other UPD overlayers and to other adsorbates is of considerable interest and is the focus of studies in progress.

Close agreement has been found for the relative stabilities of monolayer versus multilayer Cu on Ru(0001) determined both electrochemically and in a UHV environment by use of TPD. Whether this observation can be generalized to other metal–overlayer systems is unclear; thus, it was believed important to undertake such a comparison for the Cu/Pt(111) system. However, as mentioned earlier, a strong Cu/Pt(111) alloy surface is formed at sample temperatures above 520 K such that the initial desorption of Cu from the substrate surface occurs at temperatures above 1350 K. As a result, no meaningful TPD spectra were obtained for the thermal desorption of Cu on Pt(111). However, the cyclic voltammogram displayed in Figure 2 for the electrochemical stripping of approximately 3 ML of Cu on Pt(111) (solid trace) provides useful information concerning the difference in desorption energies between multilayer and monolayer Cu on Pt(111) in the electrochemical environment. As shown in Figure 2, the potential difference between the multilayer and the monolayer stripping peaks is ~0.43 V, which is equivalent to an absolute energy difference of 19.8 kcal/mol. To a first approximation, this represents the free energy change for Cu bound to Pt versus Cu bound to Cu. Although solvation effects could contribute to this free energy difference, this relatively large value does correlate with the ease of alloy formation for the Cu/Pt(111) surface at temperatures above 520 K.

Finally, we have shown in Figures 3–5 that both electrodeposited and vapor-deposited Cu adlayers display identical behavior for the linear attenuation of the total hydrogen adsorption capacity with $\theta_{Cu}$ in an electrochemical environment. This behavior, together with the reported site blocking of hydrogen adsorption on Pt(111) by Cu adlayers in UHV environment, suggests that the properties of these bimetallic surfaces in the two drastically different environments are very similar. It is therefore of great interest to study catalytic reactions on these bimetallic surfaces (prepared electrochemically or by vapor-deposition) in the electrochemical environment and compare the results with those obtained in analogous gas-solid catalytic studies. Such studies are in progress.

V. Summary

(1) Both electrodeposited and vapor-deposited Cu at various coverages on a well-characterized Pt(111) surface display remarkably similar electrochemical stripping profiles in 0.2 M HClO$_4$.

(2) From the potential difference between the multilayer and the UPD stripping peaks, we have estimated that the desorption energies between multilayer and monolayer Cu on Pt(111) in the present electrochemical environment is ~19.8 kcal/mol.

(3) Similar to that reported in UHV studies, simple site blocking of hydrogen chemisorption on Pt(111) by both electrodeposited and vapor-deposited Cu occurs linearly with chemisorption being essentially eliminated at $\theta_{Cu} \sim 1.0$ ML.

(4) The apparent discrepancy between the measured faradic charge for the UPD Cu stripping peak and the theoretically expected value for a complete monolayer is

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likely due to the partially charged nature of the Cu monolayer. This partial charge arises as a consequence of the transfer of electrons from the metal overlayer to the Pt-(111) substrate.

(5) These preliminary studies imply that coulometric determination of UPD Cu and Ag coverage on Pt(111) can lead to substantial error. Whether this is generic to other UPD overlayers and to other adsorbates is of considerable interest and is the focus of studies in progress.

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Registry No. Cu, 7440-50-8; Pt, 7440-06-4; HClO₄, 7001-90-3; H₂, 1333-74-0.