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13. ABSTRACT (Maximum 200 words) The final report contains a brief summary of research findings: The basic aim of this contract was to investigate structural and dynamical aspects of electrochemical phase formation. In these investigations researchers have emphasized the underpotential deposition of metal mono and multilayers employing electrochemical, x-ray based and ultra high vacuum surface spectroscopic techniques. They have been able to study: 1. The underpotential deposition of silver on a Pt(111) electrode as function of a. concentration b. potential sweep rate c. the presence of co-adsorbates (continued on reverse side)				6pf	
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From these studies it was possible to determine that two monolayers of silver are deposited at underpotentials and that the stability of the second layer is a strong function of the concentration of silver in solution and the potential sweep rate. The presence of co-adsorbates can have a profound influence in the deposition and the magnitude of this effect(s) is strongly dependent on the type of adsorbate employed.

2. The underpotential deposition of copper on an iodine covered platinum surface by x-ray based techniques with emphasis on:
 - a. isotherms derived from electrochemical and x-ray based measurements
 - b. mode of deposition
 - c. structure of the copper layer

Researchers have found that isotherms derived from x-ray based measurements consistently yield a significantly higher coverage (relative to electrochemically derived isotherms) that they ascribe to copper species weakly associated with the interface. The deposition appears to obey a mechanism where sites deeper in the platinum surface are occupied first and that sites further up are the progressively occupied. The structure of the copper appears to be strongly influenced by the chemisorbed iodine. The copper atoms appear to occupy bridge sites on the surface.

Final Report for ARO Proposal No. 27502-CH
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Structural and Dynamical Aspects of Electrodeposition

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A. Brief Summary of Research Findings:

The basic aim of this contract was to investigate structural and dynamical aspects of electrochemical phase formation. In these investigations we have emphasized the underpotential deposition of metal mono and multilayers employing electrochemical, x-ray based and ultra high vacuum surface spectroscopic techniques.

We have been able to study:

1. The underpotential deposition of silver on a Pt(111) electrode as function of
 - a. concentration
 - b. potential sweep rate
 - c. the presence of co-adsorbates

From these studies we have been able to determine that two monolayers of silver are deposited at underpotentials and that the stability of the second layer is a strong function of the concentration of silver in solution and the potential sweep rate. The presence of co-adsorbates can have a profound influence in the deposition and the magnitude of this effect(s) is strongly dependent on the type of adsorbate employed.

2. The underpotential deposition of copper on an iodine covered platinum surface by x-ray based techniques with emphasis on:

- a. isotherms derived from electrochemical and x-ray based measurements
- b. mode of deposition
- c. structure of the copper layer

We have found that isotherms derived from x-ray based measurements consistently yield a significantly higher coverage (relative to electrochemically derived isotherms) that we ascribe to copper species weakly associated with the interface. We have also found that the deposition appears to obey a mechanism where sites deeper in the platinum surface are occupied first and that sites further up are progressively occupied. The structure of the copper appears to be strongly influenced by the chemisorbed iodine. The copper atoms appear to occupy bridge sites on the surface.

B. Publications acknowledging support by the Army Research Office

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5. Abruña, H.D.; Bedzyk, M.J.; "Probing Interfacial Structure and Composition with X-ray Standing Waves"; *Chem. Rev.* (in preparation)
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11. Bommarito, G. M.; Acevedo, D.; Rodríguez, J. F.; Abruña, H. D.; "In-Situ X-Ray Standing Wave Study of Cu UPD on an Iodine Covered Platinum Surface" in "Symposium on X-ray Methods in Electrochemistry" Gordon, J. G.; Davenport, A. eds. The Electrochemical Society, Pennigton, N.J. 1992 p. 125
12. Bommarito, G. M.; Acevedo, D.; Rodríguez, J. F.; Abruña, H. D.; "In-Situ X-Ray Standing Wave Study of Cu UPD on an Iodine Treated Platinum Surface" In: *Proc. Workshop on Structural Effects in Electrocatalysis and Oxygen*

Electrochemistry, D. Scherson, M. Daroux, D. Tryk, X. Xing, Eds. The Electrochemical Society Inc. Pennington, N.J. 1992

13. Bommarito, G. M.; Acevedo, D. ; Rodríguez, J. F.; Abruña, H. D.; "Potential Dependent Structural Changes of Underpotentially Deposited Copper on an Iodine Treated Platinum Surface Determined In-Situ by Surface EXAFS and Its Polarization Dependence" J. Phys. Chem. (submitted)
14. Bommarito, G. M.; Acevedo, D. ; Rodríguez, J. F.; Abruña, H. D.; "In-Situ Structural Studies of the Underpotential Deposition of Copper onto an Iodine Covered Platinum Surface Using X-ray Standing Waves:" J. Phys. Chem. (submitted)

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