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In-Situ Laser Raman Spectroscopy of Copper Annodization in Alkaline Media

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Ext. Abstract

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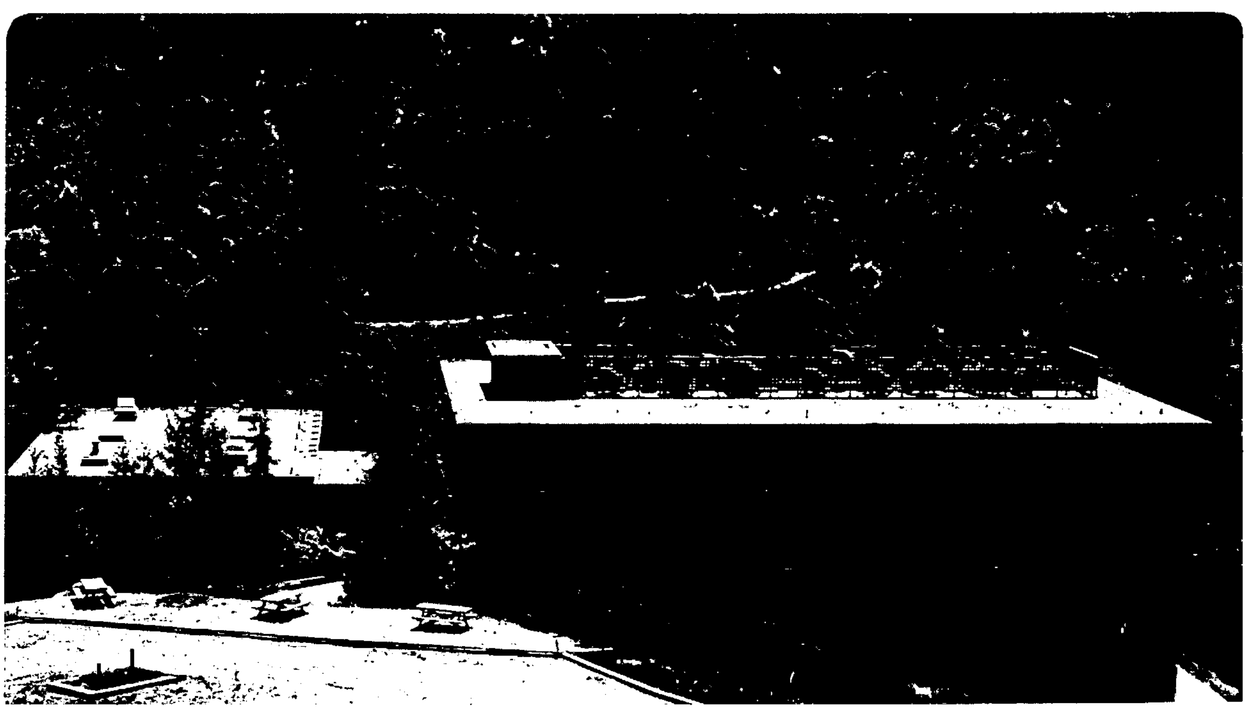

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IN-SITU LASER RAMAN SPECTROSCOPY OF COPPER ANODIZATION IN ALKALINE MEDIA

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SHORT ABSTRACT

Anodic surface films formed on copper in 1M KOH were studied using Raman Spectroscopy. During a potential sweep, Cu_2O was observed to form at the potentials of the first current wave, and $Cu(OH)_2$ near the second wave. Evidence for the formation of a trivalent solid near the potential of oxygen evolution has been obtained. The mechanism of reduction of these species to copper metal is complex, and is affected by illumination.

INTRODUCTION

Much of our understanding of electrochemically formed anodic films has been derived from electrochemical measurements. Additional information on the physical nature of the film can be presented by *in-situ* techniques. In recent years, the identification of surface species and the study of photo-induced transformations has been performed by Raman spectroscopy. In the present study, laser Raman spectroscopy, in conjunction with electrochemical measurement, was used to explore the physical and chemical nature of anodic films on copper in 1M KOH.

Two major anodic peaks prior to oxygen evolution are obtained in the cyclic voltammetry of copper in alkaline solutions The first peak, at around -350 mV vs. Hg/HgO, appears with a peak current density of about 50 $\mu A/cm^2$. This peak has been associated with a monovalent oxidation process. The second anodic peak (0 mV vs. Hg/HgO) is at least an order of magnitude larger than the first and is associated with divalent oxidation processes [1,2]. The voltammetric wave of this peak exhibits a complex dependence on sweep rate. Thermodynamic calculations show that the divalent oxide CuO is thermodynamically more stable than the hydroxide $Cu(OH)_2$ [3]. It has been suggested that at least these two species and a dissolved divalent compound form at potentials near the second anodic peak.

RESULTS

Figures 1-3 show the change in Raman scattering during a potential sweep experiment with an initial potential of -700 mV vs. Hg/HgO, an anodic peak potential of +700 mV, and a cathodic peak potential of -1000 mV. Standard Raman spectra of Cu_2O, CuO, and $Cu(OH)_2$ have been presented before [4]. Near the first anodic peak potential a Raman band associated with the formation of Cu_2O is clearly observed around 633 cm^{-1}. This finding should be compared to the previous results at pH 13, where the Cu_2O peak was not observed until 300 mV anodic of the first oxidation peak [4]. Figure 1 also shows that at a potential of around -100 mV vs. Hg/HgO, $Cu(OH)_2$ is identified by a band at 488 cm^{-1}. This observation coincides with the beginning of the second anodic voltammetry peak. As the potential is increased further, the Cu_2O band intensity slowly diminishes and the $Cu(OH)_2$ band increases slightly. Figure 2 compares the Raman spectra taken at 450 and 650 mV. At the latter potential, oxygen evolution begins and a broad Raman band centered around 550 cm^{-1} is observed together with the 488 cm^{-1} band. The Cu_2O band is not seen. Figure 3 shows the Raman spectra collected for the cathodic scan in this experiments. The broad band at 550 cm^{-1} completely disappears at a potential of 450 mV, accompanied by a decrease in the size of the $Cu(OH)_2$ band and the reappearance of a weak 633 cm^{-1} Cu_2O band. Further decreases in potential result in an increase in both the the $Cu(OH)_2$ and Cu_2O band intensities. The Cu_2O band disappears at a potential of -700 mV which follows the disappearance of the 488 cm^{-1} $Cu(OH)_2$ band at -450 mV.

The broad band observed at 550 cm^{-1} and found at potentials far above that of the divalent copper oxidation, has previously been interpreted as being due to either the presence of $Cu(OH)_2$ or a polymeric form of the hydroxide [4]. Our results clearly show that at potentials near the second anodic voltammetric peak a sharp 488 cm^{-1} $Cu(OH)_2$ band is observed. Miller's ring/disk experiments demonstrated the existence of a trivalent soluble species in this potential range [1]. We believe that the appearance of the broad 550 cm^{-1} band may be due to the formation of a trivalent copper surface species, possibly Cu_2O_3. The reappearance and later disappearance of Cu_2O (and to a lesser degree, $Cu(OH)_2$), during the cathodic sweep does not coincide with the potentials of the observed cathodic currents. The contrast of this and other Raman data with voltammetry results appears to be connected with a photoelectrochemical process. The Cu_2O underlayer acts as a p-type semiconductor Schottky-barrier, whose resistance decreases under illumination. A series of potential sweep and step experiments will be presented to support this conclusion.

ACKNOWLEDGMENTS

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FIGURES

Figure 1. Laser Raman spectra observed during a 1 mV/sec anodic potential sweep of Cu in 1M KOH at various potentials (vs Hg/HgO). Spectra are offset to allow readability. Detector exposure time: 100 sec/scan. (XBL 891-346)

Figure 2. Laser Raman spectra observed during a 1 mV/sec anodic potential sweep of Cu in 1M KOH at potentials near that of oxygen evolution. Detector exposure time: 100 sec/scan. (XBL 891-347)

Figure 3. Laser Raman spectra observed during a 1 mV/sec cathodic potential sweep of Cu in 1M KOH at various potentials (vs Hg/HgO). Spectra are offset to allow readability. Detector exposure time: 100 sec/scan. (XBL 891-348)

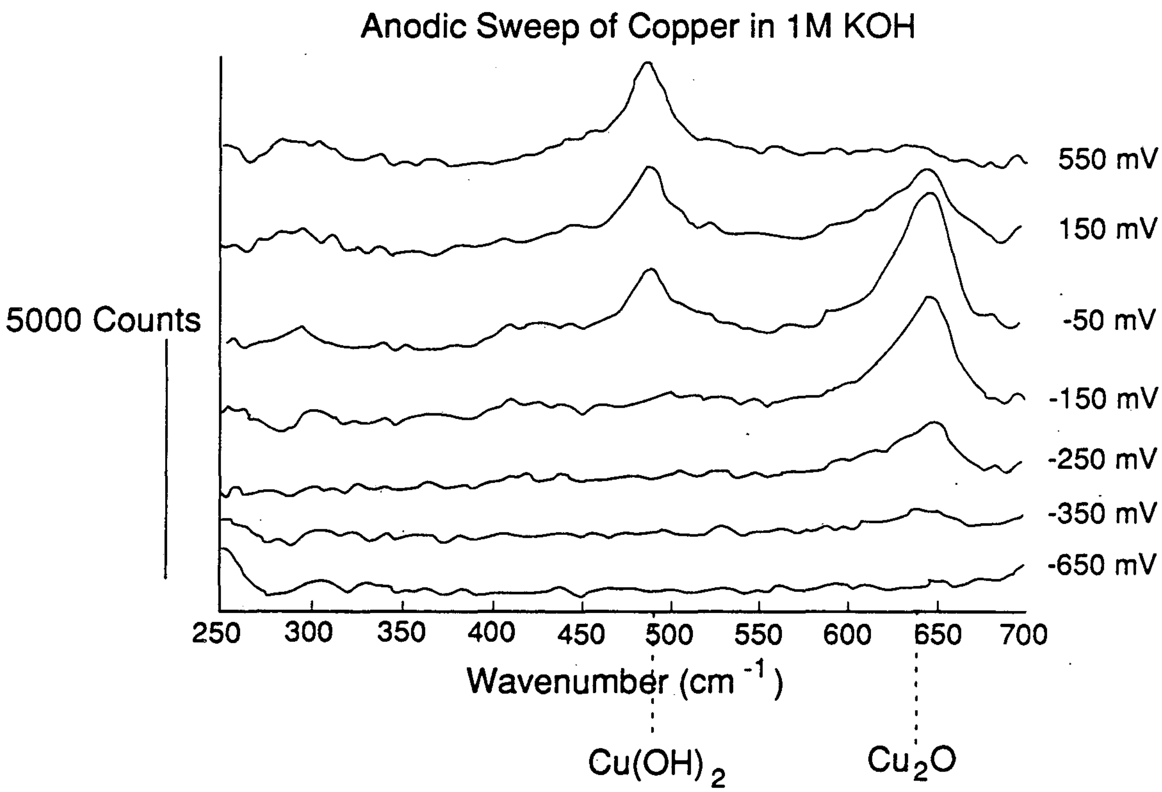

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Figure 1

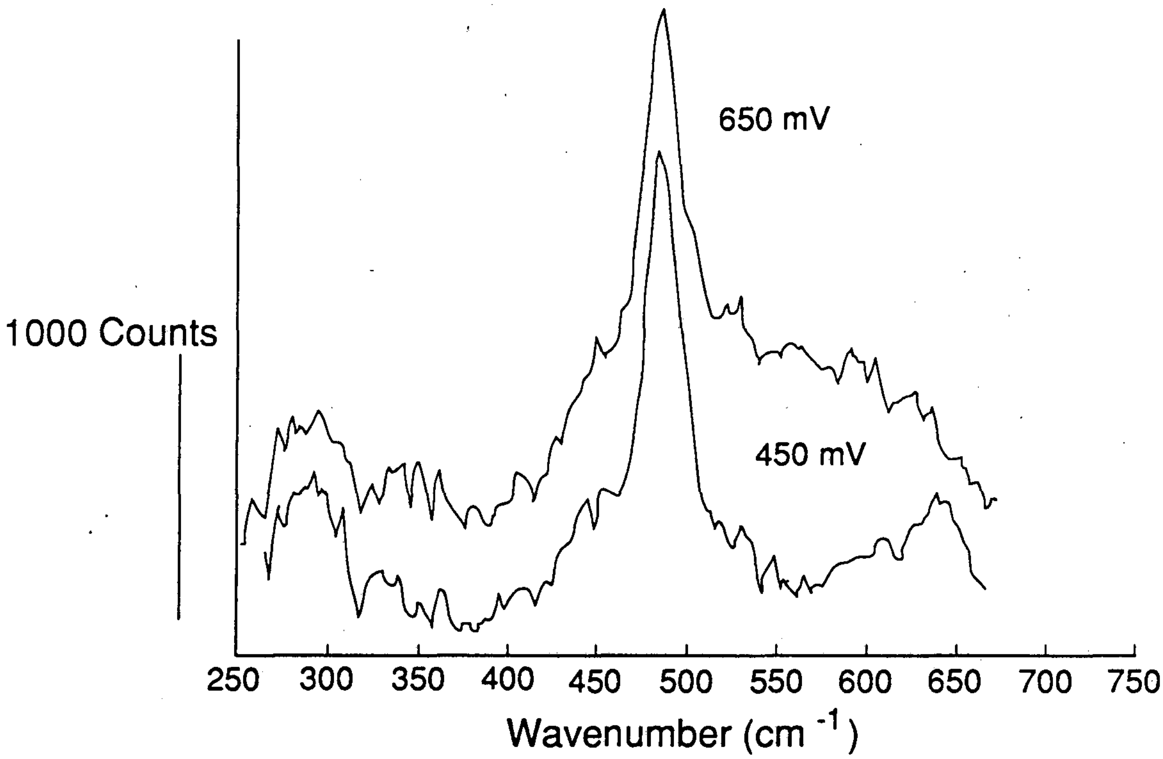

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Figure 2

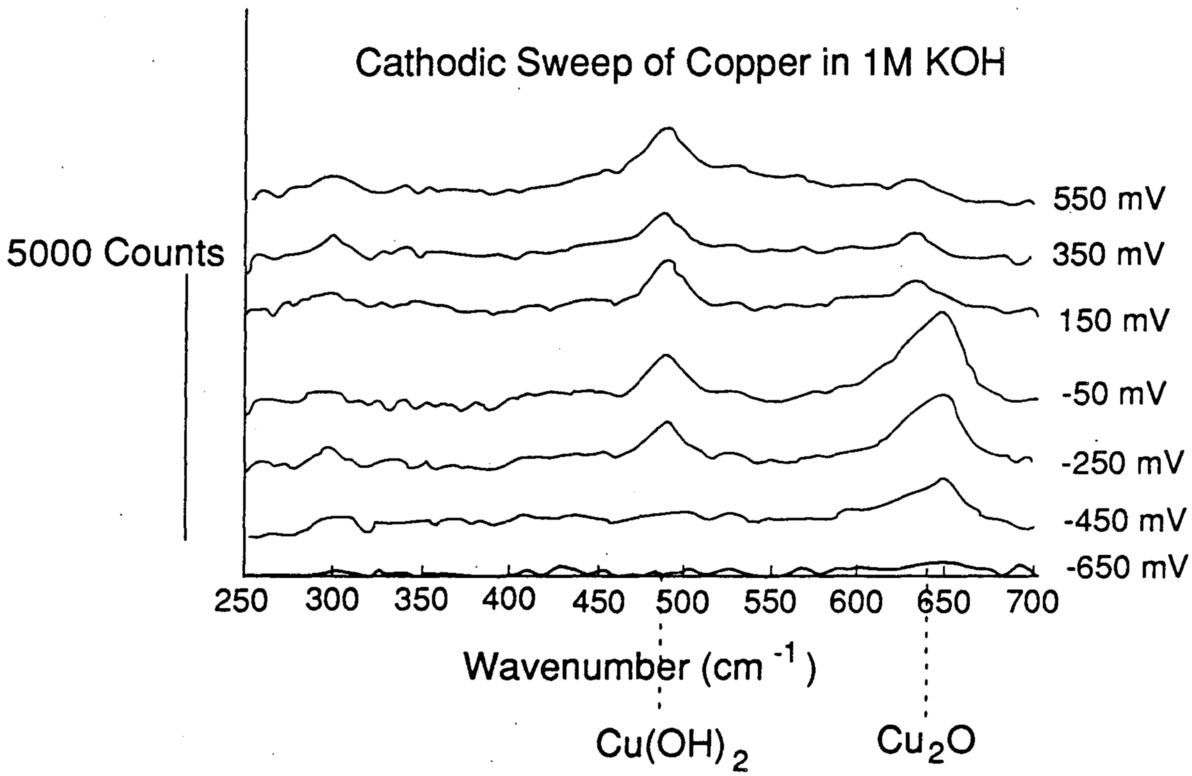

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Figure 3

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