

THE ANODIC DISSOLUTION OF THIN FILMS OF COPPER METAL FROM PYROLYTIC GRAPHITE

A STUDY OF THE MULTIPLE DISSOLUTION CURRENT PEAKS

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INTRODUCTION

When the technique of anodic stripping analysis¹⁻⁶ is employed in the determination of trace amounts (10^{-6} – 10^{-10} M) of a single metal ion in solution, the resulting current–potential stripping curve very often exhibits two or more distinct dissolution peaks rather than the single peak that would be expected for the dissolution of a single species⁷⁻¹¹. This effect which was often observed when solid electrodes such as platinum^{9,10}, gold^{9,10}, and graphite¹¹ were used, has also been observed when mercury films on platinum are used as electrodes⁸. It has been reported, for example for the stripping of nickel from platinum and gold electrodes¹¹, silver from graphite¹¹ and cadmium and zinc from mercury-plated platinum⁸.

It has been postulated that the *extra* current peaks arising at potentials more positive than the normal dissolution potential of the metal film, represent the oxidation of the first monolayer (*first* layer of the metal on the surface of the electrode) of the metal. This suggests that the first monolayer of a deposited metal on a different solid substrate (electrode) can have a considerably larger bonding energy with this different substrate than the normal bonding or lattice energy of the metal with itself (all subsequent layers of deposited metal beyond the first monolayer)^{9,11}. Thus considerably more positive potentials are required in order to oxidize the first monolayer. In cases where more than one *extra* dissolution current peak is observed, it has been postulated that the bonding energy of the atoms of the first monolayer with different sites of the electrode substrate differ markedly¹².

NICHOLSON⁹ has actually presented a theoretical treatment of the dissolution of the first monolayer, based on this model.

Several investigators have noted that the electrodeposition of carrier-free radioactive nuclides in tracer amounts occurs in measurable amounts at potentials which are several hundred millivolts more positive than the potentials observed in the deposition of macro amounts¹³⁻²⁰. These results, of course, contradict those predicted by the Nernst equation which predicts a negative shift of potential with dilution. This *underpotential* with regard to deposition corresponds to the more positive dissolution peaks (to the stronger bond between the metal and the different electrode material observed on stripping. ROGERS AND STEHNEY³⁰ made a careful study of the electrode position of carrier-free radioactive silver in free concentrations in order to determin

if the *underpotential* observed for tracer depositions corresponds to the deposition of the first monolayer and, hence, to increased bond interaction for the two different surfaces. Although the results indicated qualitatively that the amount deposited at the more negative potentials was roughly equivalent to a monolayer, they were inconclusive. First, it is difficult to estimate the true concentration of carrier-free radioactive tracer solutions because of adsorption on the surfaces of the cell; secondly and more important, it is impossible to distinguish between radioactive silver adsorbed on the electrode and actual reduced silver deposited on the electrode. Also, it is impossible to determine if this potential difference corresponds to massive deposition on certain active sites, crevices, etc. on the electrode rather than a uniform monolayer.

As previous work had not proved the existence of monolayer depositions of different interaction energy, this investigation was undertaken to try to determine the nature of the secondary more positive dissolution current peaks observed on stripping. This paper describes the results obtained from a study of the anodic dissolution of thin copper films on pyrolytic graphite electrodes. This system was chosen because of its reproducibility which made possible the deposition of surface films which correspond to the secondary or more positive *monolayer* films alone. The results of electron microprobe studies of the surfaces that correspond to deposited *monolayers* are also presented.

EXPERIMENTAL

The pyrolytic graphite electrode, electrode assembly, and electrolysis cell employed in this study were identical with those described previously^{12,31-32}. The electrodeposition-potential sweep apparatus was built around Philbrick UPA-2 and P-2 operational amplifiers (G. A. Philbrick Researches, Inc., Dedham, Mass.) employing the potentiostat, sweep generator, and current follower circuits of DEFORD^{12,34}. In all stripping experiments the rate of the voltage sweep was 0.5 V/min. The current-potential curves were recorded by means of a Sargent Model SR recorder. The cell was thermostatted and all experiments were run at $25 \pm 0.1^\circ$. All potentials are reported with reference to a saturated calomel electrode (S.C.E.). The electron microprobe studies of the surface composition and distribution were made with an Applied Research Laboratories X-ray microprobe. The apparent area of the electrode surface was 0.319 cm².

All chemicals and solvents employed were analytical or reagent grade and were further purified by massive electrolysis in the manner described previously^{12,33}. All solutions were de-aerated for 2 h with nitrogen gas purified according to standard practice³⁵. The water was triply distilled and then subjected to massive electrolysis.

In order to obtain reliable and reproducible *i-E* stripping curves, it is necessary to pre-treat each fresh pyrolytic graphite surface (all solutions, of course, must be free of surface-active agents). It was found necessary to polish the graphite surface prior to use. This was done using a metallurgical wheel with No. 600 carborundum paper, first, followed by Whatman No. 1 filter paper. The polished electrode was then chemically cleaned and electrochemically activated. The cleaning consisted of immersing the electrode surface in 70% phosphoric acid (alkaline solutions were found to de-activate the electrode in some way) for 30-60 sec and then rinsing repeatedly. The activation was accomplished by electrochemically *cycling* the electrode in the electro-

lysis solution used throughout the study, which was 0.1×10^{-3} – $5 \cdot 10^{-5}$ *M* $\text{Cu}(\text{NO}_3)_2$, 0.1 *M* KClO_4 , and 0.1 *M* HClO_4 . The electrode was first potentiostatted at -0.40 V *vs.* S.C.E. for 100 sec (this placed a relatively thick layer of copper metal on the surface). The potential was then stepped to -0.10 V *vs.* S.C.E. (approximately the threshold of the dissolution of the copper) and the $+0.50$ V/min anodic potential sweep begun. When the potential reached $+0.45$ V *vs.* S.C.E. (all copper oxidized) the sweep was stopped and the potential stepped back to -0.40 V *vs.* S.C.E. which began another cycle (any excursion of the potential to $+0.8$ to $+0.9$ V completely deactivates the surface). After about 20–30 cycles, all subsequent i – E stripping curves obtained during the anodic sweep were reproducible and also matched those obtained for any new electrode surface (pre-treated in this manner). The reproducibility was about ± 1 – 2% . A constant stirring rate of 200 rev./min by means of a synchronous motor was used throughout all experiments. The cyclic operation was carried out by an automated circuit which allowed for precise but variable deposition time^{1,2}.

RESULTS AND DISCUSSION

Figure 1 illustrates the typical characteristic shape of the current–potential stripping curves obtained. The electrode was plated with a thin copper-metal film by potentiostating at -0.40 V *vs.* S.C.E. for 100 sec with a 0.1×10^{-3} *M* $\text{Cu}(\text{NO}_3)_2$, 0.1 *M* KClO_4 , and 0.1 *M* HClO_4 solution. The i *vs.* E curve shown was recorded during the dissolution step (described above). Three distinct peaks are observed for the copper dissolution curve: peak *a* at $+0.015$ V *vs.* S.C.E., peak *b* at $+0.15$ V *vs.* S.C.E., and peak *c* at about $+0.35$ V *vs.* S.C.E. When the time of deposition (at $+0.40$ V *vs.*

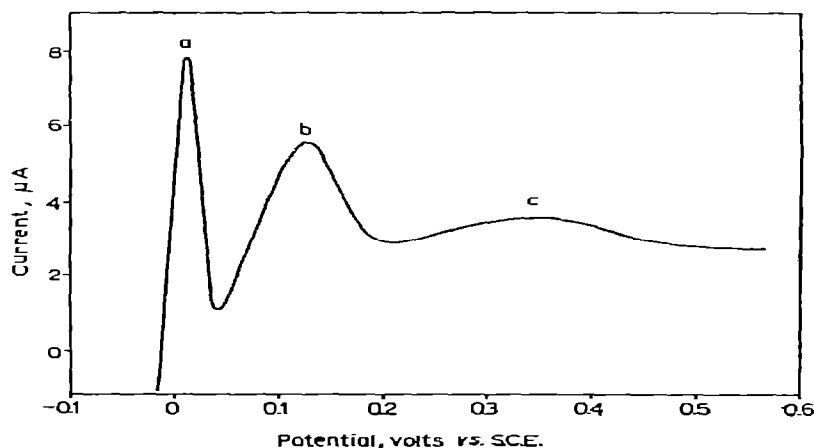


Fig. 1. Typical anodic stripping curves for a thin Cu film. Film plated from a 0.1×10^{-3} *M* $\text{Cu}(\text{NO}_3)_2$, 0.1 *M* KClO_4 , and 0.1 *M* HClO_4 soln. at -0.40 V *vs.* S.C.E. for 100 sec. Scanning rate: 0.50 V/min.

S.C.E.) was varied, it was found that all the areas under the three peaks (and, hence, amount on surface) increase approximately proportionally with time from 0 to about 50 sec. From 50 sec upwards, peaks *b* and *c* do not increase appreciably with time, but peak *a* continues to increase with deposition time. This, of course, indicates that peak *a* represents the normal copper deposition–dissolution which presumably represents layers of copper deposited on top of a layer(s) of copper. The fact that peaks *b* and *c*

cease to grow after a certain period of time (even when the total deposition times were several thousand seconds) (see below) indicates that these peaks represent either deposition of the monolayer (with at least two distinct energies of interaction with the electrode surface) or deposition at two specific types of active site such as crevasses, or crystal lattice defects on the graphite. In either case, the deposition of the copper corresponding to peaks *b* and *c* appears to cease as some area of the electrode is covered.

An investigation was made to determine the conditions under which the *b* and *c* peaks (a monolayer) could be deposited alone without any *a* peak (copper on copper) being present. It was found that by depositing copper at -0.40 V vs. S.C.E. as described above and then stepping the potential to 0.0 V vs. S.C.E. and holding for a period of time (the length of this hold period is not critical, but should be greater than 10^3 sec), the *a* peak was missing (copper-copper layer stripped), from the subsequent stripping curves (cyclic sweep carried out in same manner described above) and only the *b* and *c* peaks remain and are unchanged. A typical *i*-*E* curve obtained in this manner is shown in Fig. 2 which clearly shows both peaks *b* and *c*. The electrode was potentiostatted at -0.40 V vs. S.C.E. for 2000 sec in a solution that was 5.0×10^{-5} M $\text{Cu}(\text{NO}_3)_2$, 0.10 M KClO_4 and 0.10 M HClO_4 . The potential was then stepped to 0.0 V vs. S.C.E. and potentiostatted at this potential for 250 sec before the usual anodic potential scan was applied. The *i*-*E* stripping curve obtained for a copper deposit made in this manner *without* the potential hold at 0.0 V vs. S.C.E., is shown in Fig. 3.

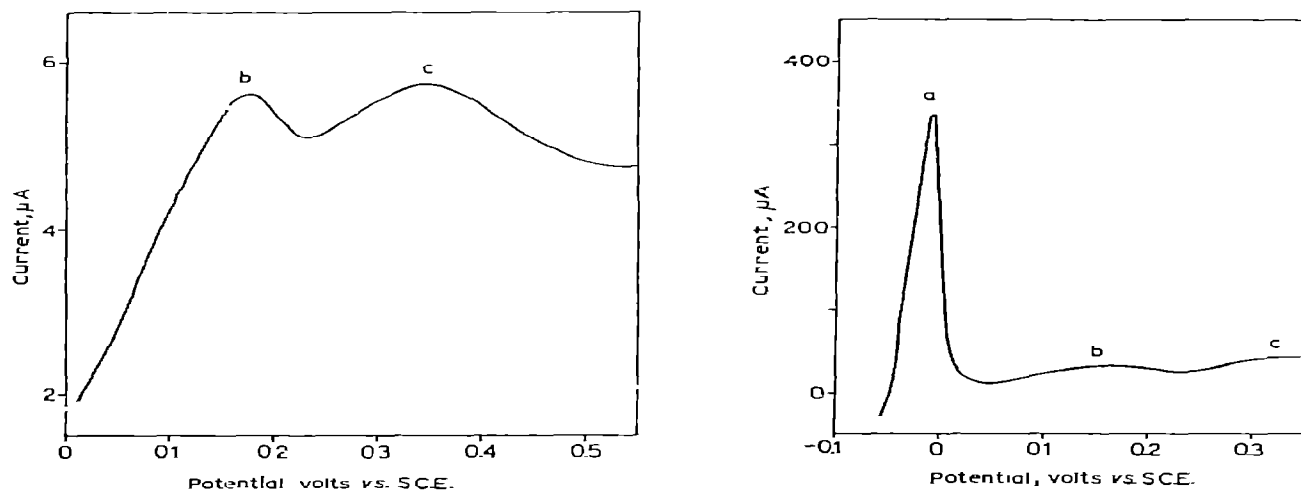


Fig. 2 Typical anodic stripping curve obtained after the *macro* Cu film was obtained by potentiostating at 0.0 V vs. S.C.E. for 250 sec after deposition. Soln. was $5 \cdot 10^{-5}$ M $\text{Cu}(\text{NO}_3)_2$, 0.1 M KClO_4 and 0.10 M HClO_4 . Scanning rate: 0.50 V/min.

Fig. 3. Typical anodic stripping curve obtained for a *macro* Cu film (deposited at -0.40 V vs. S.C.E. for 2000 sec using a 5.0×10^{-5} M $\text{Cu}(\text{NO}_3)_2$, 0.10 M KClO_4 , and 0.10 M HClO_4 soln. Scanning rate: 0.50 V/min.

The large *a* peak is clearly seen and essentially obscures the *b* and *c* secondary peaks. The curves shown in Figs. 2 and 3 were reproducible to within 1–2% for subsequent runs on a single electrode surface or from electrode surface to electrode surface when the activation procedure described above was employed.

Electron microprobe^{36–40} studies of pyrolytic graphite electrode surfaces con-

taining copper films prepared in exactly the same manner as described for the films that resulted in the $i-E$ stripping curves of Figs. 2 and 3, were also made. The only difference was that the electrodes were removed from the solution prior to the commencement of the anodic stripping sweep (the potential was held to 0.0 and -0.10 V, respectively, during removal). Thus, the films remained on the graphite surfaces. The surfaces were studied by two different techniques: the sample current technique (measures the electron adsorption current of the surface; the resulting oscilloscope image shows dark areas representing either holes in the surface or elements of high atomic weight and light areas representing level surfaces of low atomic weight) and the X-ray fluorescent emission technique (measures the intensity of the X-ray fluorescence at a specific wavelength emitted from the surface of the material on electron bombardment)³⁶⁻⁴⁰.

Figure 4 shows a typical sample current pattern obtained for a pyrolytic graphite electrode surface having a *heavy* or *macro* copper deposit plated from a solution of $5 \cdot 10^{-5}$ M $\text{Cu}(\text{NO}_3)_2$, 0.1 M KClO_4 and 0.1 M HClO_4 potentiostatted for 2000

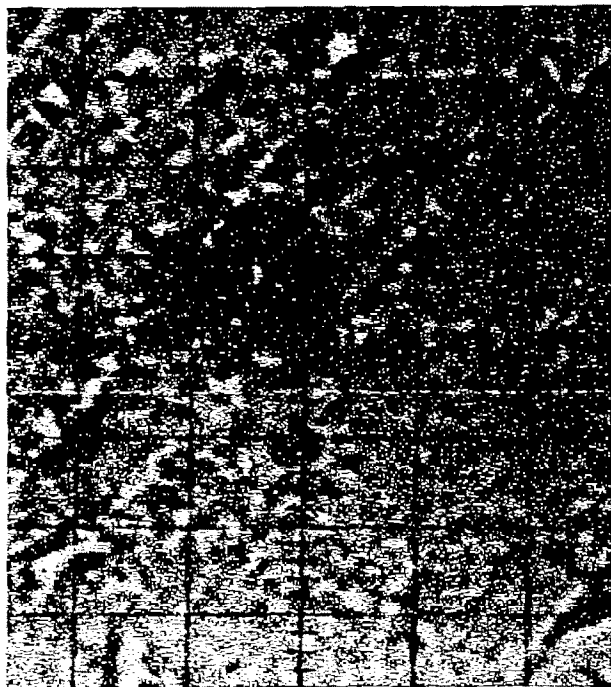


Fig. 4. Sample current pattern obtained with an electron microprobe for a Cu deposit of 1390 μC (deposited under exactly the same conditions as the film which gave the stripping curve illustrated in Fig. 3). One division on the photograph scale represents 18.5 μ .

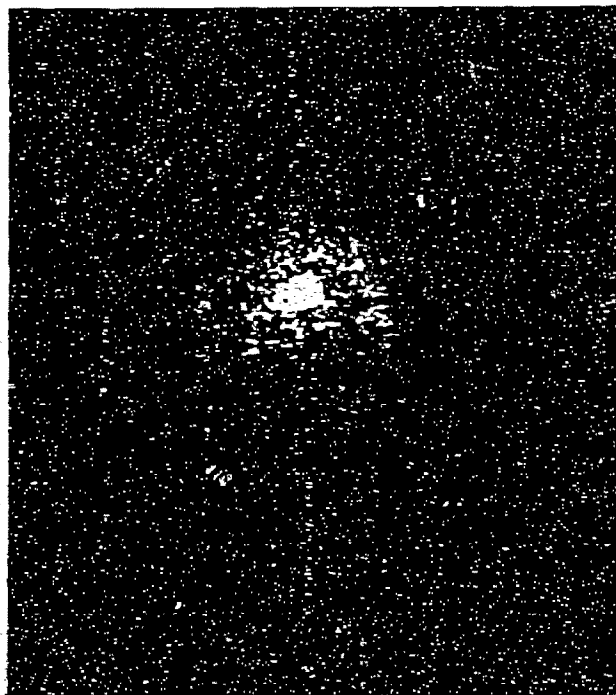


Fig. 5. X-ray fluorescence pattern of the electrode surface of Fig. 4 (same surface area). The X-ray wavelength measured was 1.542 Å (main Cu emission line).

sec at -0.40 V vs. S.C.E. (the anodic stripping curve for films deposited in this manner is shown in Fig. 3 which exhibits a predominant α peak; the amount of copper on the electrode was 1390 μC). It shows a dark-shaded region, presumably copper, slightly to the left and above the center co-ordinant. The very dark spots and light spots probably represent scratches and other defects on the surface. The black spots

are either holes or imbedded impurities. The area under the stripping peaks of films deposited in a similar manner (see Fig. 3) indicated that the deposit was about $1390 \mu\text{C}$ of copper which would correspond to 5–6 copper layers on the surface (if the deposit was uniformly distributed).

The X-ray fluorescence microprobe scan of the same electrode surface shown in Fig. 4 is given in Fig. 5 (the X-ray monochromator of the instrument was set for the main copper emission line at 1.542 \AA , as read on the instrument dial; a pure copper sample gave 36,500 counts/sec for a highly polished surface). The picture represents a 40-sec exposure. The large accumulation of light dots in the exact position of the dark-shaded area of Fig. 4 proves that this area represents a heavy copper deposit. The very centre of the cluster is estimated to be a copper deposit several microns in thickness. Thus, it appears that the main copper deposit, corresponding to the *a* peak, grows in spots and not uniformly. It was found, after examining several electrode surface areas, that the regions of heavy deposits were scarce and that the area between the heavy deposits was large but appeared to be covered with a uniform distribution of widely spaced spots (mostly copper but certainly some instrumental noise as well which could correspond to a very thin layer, one of two monolayers, uniformly distributed between the large concentrations).

Electrode surfaces deposited in the manner that gave the stripping curve of Fig. 2 (exhibits only the *b* and *c* peaks, or *mono-layer* peaks) were also studied with the electron microprobe. Figure 6 shows a sample current pattern for such an electrode surface. No dark areas are observed although several black and very light areas

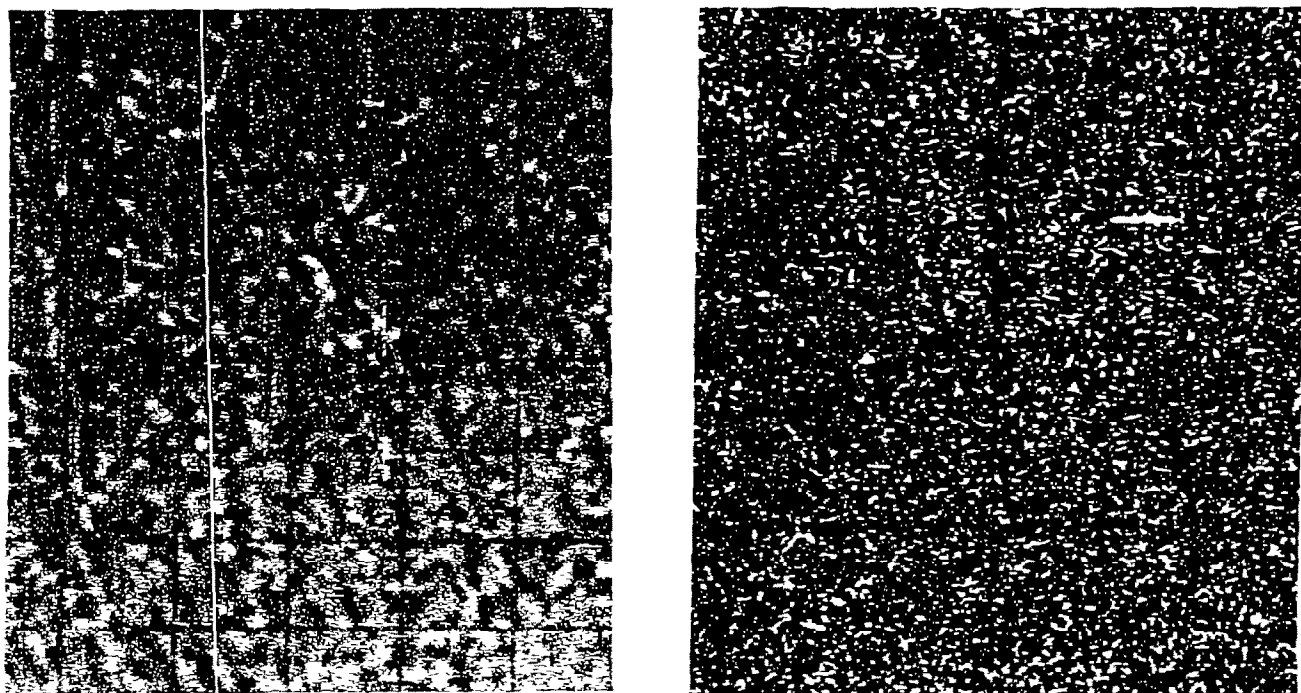


Fig. 6. Sample current pattern obtained for a *mono-layer* Cu deposit of $157 \mu\text{C}$ (deposited in the same manner as the film giving the anodic stripping curve shown in Fig. 2).

Fig. 7. X-ray fluorescence pattern of the electrode surface of Fig. 6.

representing holes and high points (or imbedded surface impurities) are observed. The X-ray fluorescence pattern obtained for the same surface (400-sec exposure), illustrated in Fig. 7, shows a uniform distribution of counts (no indication of the dark-shaded spots of Fig. 6 which are copper). The total copper on the electrode surface represents only about $157 \mu\text{C}$ (area under the stripping peaks of Fig. 2). This amount represents the lower limit of detectability of the instrument, and the counts observed contain a large background noise count as well as the smaller copper count. In order to show that this surface actually contained copper, *line reading* measurements were made of the surface (a repeated horizontal scan with no vertical motion of the electron beam, 2μ in diameter, was made over a length of 180μ on random areas on the surface for a period of 10 sec)⁴⁰. The average of twelve determinations at the copper emission line of 1.532 \AA was 3720 ± 55 counts/min. Moving the monochromator from the copper line in both directions yielded background counts of 3230 ± 57 and 3350 ± 56 counts/min respectively, for 12 measurements. It appears, therefore, that the surface does contain appreciable copper, and the fact that the pattern is uniform indicates that the copper is uniformly distributed (four 1-cm^2 areas were found to contain 132 ± 5 dots)¹². Thus, the copper is not found aggregated in specific spots such as the holes and scratches observed in the sample current pictures (Figs. 4 and 6) which would give a clear heavy light dot area on the X-ray fluorescence measurement.

CONCLUSIONS

The experimental evidence obtained by means of the electron microprobe studies indicates (but does not prove, however, because of the limitations of the instrument sensitivity) that the copper remaining on the electrode surface that corresponds to the *mono-layer* peaks, *b* and *c* peaks of Fig. 3, is uniformly distributed on the surface. Calculations also showed that a monolayer of copper atoms arranged as a face-centered lattice on the surface (0.319 cm^2) would amount to 0.81×10^{-9} moles or $160 \mu\text{C}$ ¹². The areas under the *b* and *c* *mono-layer* peaks amounted to approximately this value, usually $150\text{--}200 \mu\text{C}$ (the area under Fig. 2 was $157 \mu\text{C}$). Thus, the amount of copper on the surface corresponding to the *mono-layer* peaks is the right order of magnitude for a calculated monolayer. However, this result is qualitative as the roughness factor for the surface is not known. Also, the differences in surface conditions or interactions that yield the two *monolayer* peaks, *b* and *c*, is not understood.

It appears that the subsequent layers of copper on copper do grow at specific sites on the surface rather than as uniform layers. Further work is now in progress to determine the nature of these preferred sites.

It should be noted that freshly cleaved pyrolytic graphite surfaces were hard to activate in order to produce reproducible *mono-layer* peaks. Also, these peaks were generally smaller than those obtained for a polished surface. Unpolished surfaces were not studied extensively, however, as the electron microprobe requires flat, smooth surfaces and it was necessary, therefore, to polish the electrodes.

It should be noted also that as the electron microprobe sensitivity is insufficient to provide absolute proof of a uniform monolayer distribution, other methods have been examined. Autoradiography⁴¹ and neutron activation of the electrode plus monolayer film^{31,32} were much less sensitive and did not detect any surface distribution patterns. At present, a similar study of cobalt *mono-layer* films by means of Möss-

bauer spectroscopy is in progress; this technique appears to be sufficiently sensitive to detect different surface or lattice interaction⁴².

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SUMMARY

The anodic stripping curves of electrodeposited thin films of copper have been investigated. Three distinct current peaks were observed. The more negative peak corresponded to copper macrolayers (copper on copper); the smaller peaks, found at more positive potentials were interpreted as *mono-layer* peaks which indicates that the copper interaction with pyrolytic graphite is greater than that of the copper-copper interaction. A method for preparing the monolayer films is described. Electron-microprobe studies of the copper monolayer films indicated that the copper is uniformly distributed on the surface. These studies also showed that the *macro* layers started to grow at specific surface sites.

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