

**A STUDY OF THE INITIAL STAGES OF THE
ELECTROCHEMICAL DEPOSITION OF THALLIUM ON COPPER –
PART IV
THE POTENTIAL STEP RESULTS: UNDERPOTENTIAL
DEPOSITION ON (111), (110) AND (100) ORIENTED COPPER
SINGLE CRYSTAL ELECTRODE**

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Abstract. *The underpotential deposition and dissolution of thallium onto carefully chemically polished single crystal copper (111), (110) and (100) electrode surfaces from acetate, sulphate and perchlorate solutions have been investigated using single and double potential step techniques. It appeared that the different anions used did not change the current-time response characteristics significantly.*

Current-time responses to the potential steps applied strongly resemble those observed in the case of thallium underpotential deposition on silver single crystals [1].

The characteristics of i-t transients obtained by single potential step suggest very fast 2D crystal growth processes taking place. Sharp linear voltammetry peaks, which are observed for both thallium and lead deposition on Cu(111) [3,8] and on Ag(111) [1,3], probably always indicate nucleative phase formation processes, but the rate of the lattice growth step will vary from system to system. Comparison of the obtained results with those for lead underpotential deposition [8-13] on Cu(111), (110) and (100) suggests that, in the present case, the rate of the 2D lattice building process for both thallium underpotential monolayers formed on three copper single crystal surfaces examined is so fast that it becomes controlled by diffusive processes; this will probably be surface diffusion [24,25] initially and, at longer times, planar bulk diffusion.

Double pulse experiments did not help significantly in attempts to obtain i-t transients capable of providing data suitable for showing conclusively the occurrence of 2D crystal formation processes. A similar situation occurred also with silver substrates [1].

Key words: *Underpotential deposition, Potentiostatic step, Cu, Tl, Phase formation, Single crystal*

INTRODUCTION

Despite extensive studies of metal underpotential deposition [1-19] there have been some important problems still unresolved. These related principally to the nature of the monolayer (adsorbed or crystalline), the interpretation of the linear sweep voltammogram peaks, phase changes within the monolayer, the kinetics of the crystalline monolayer formation, if any, and the relevance of the UPD monolayer to the overpotential deposition process.

The system selected for the study was thallium on copper (111), (110) and (100) oriented single crystal surfaces. The underpotential as well as overpotential deposition and their possible mutual interdependence were investigated. Chosen substrates possess high hydrogen evolution overvoltage and therefore hydrogen co-adsorption processes do not complicate deposition of lead.

Linear sweep voltammetry [15-17], however carefully and successfully performed, is not sufficiently diagnostic tool to characterise underpotential monolayers and the possible phase changes taking part within them. Therefore help from potential step techniques, which are known to provide clear information on the mechanism of phase formation, was required. The analysis of the current against time transients, observed after initiating phase formation at constant potential using a potential step should yield additional data on the formation of 2D phase films during UPD.

MATERIALS AND METHODS

The experimental work described in this paper was done using single, double and triple potential pulses.

All potential programming of the working electrode was supplied either from a potentiostat ("Hi-Tek Instruments" model DT2101, or two "Chemical Electronics" models V150/1.5A, TR70/2A) in conjunction with a "Chemical Electronics" waveform generator (type R.B.1), or two "H.Tinsley and Co." potentiometer (type 3387B). The waveform generator provided single/double potential step.

The cell currents were recorded as voltages on an XY recorder (types "Bryans 26000" or "Hewlett Packard 7015A"). In potential step experiments of longer duration, a Yt recorder ("Servoscribe 1s" RE 541.20) was used to record i-t transients. To observe and record the current-time transients and other functions too rapid to be followed on an XY or Yt recorder, oscilloscopes ("Tektronix" 547 or 5030) were employed. However, permanent records of such transients were obtained using a "Hi-Tek Instruments" signal averager (type AA1) as a transient recorder in conjunction with an XY recorder. This instrument has the ability to sample the signal-input voltage; converting it into digital form and storing it in memory having one location for each sample (256 locations). Since the time between the samples (e.g. points on an i-t curve) memorised can be altered at will, very fast transients could be reproduced from the instrument's memory on a longer time scale than used for the input of the data, thus enabling an XY recorder coupled with the signal averager to record them.

The signal averager was used in the averaging mode when i-t transients taken in the region of very small current densities (10^{-6} to 10^{-5} A cm⁻²) showed noise levels big enough to obscure the true picture of the process. This technique relies on the fact that the time average resulting from the superposition of a number of identical signals (e.g. i-t transients) each of which has some random or periodic noise associated with it, will be the original signal but with the signal to noise ratio improved. This statement is valid provided that any periodic noise on the

signal is not time locked to the repetition rate of pulsing (e.g. as would be the case if the beginning of each pulse coincided with the same point on the 50Hz mains frequency noise). On each cycle of the signal, the averager samples the signal input at fixed time intervals, converts the sampled voltages into digital form and stores the information in a memory having one location for each sample. This sampling process is repeated a pre-set number of times "n"; a trigger signal from the waveform generator ensures that samples are taken at equivalent points on each signal. Each new sample is added algebraically to the value already accumulated in the memory location, so that the final value stored is equal to "n" multiples of the average value of the sample taken at that point. If one assumes that the electrochemical process itself produces no random fluctuations in the signal level, signal content of each sample point is constant and therefore its contribution to the value stored will increase linearly with "n". However, as "n" increases, the average value of the noise will approach zero.

The overall signal to noise improvement, $(SN)_n$, is given by $(SN)_n = n^{1/2}$. Typically in the pulse experiments described here the value of "n" used was 16 or 32.

Two types of cell were used, Fig.1. a) and b). The cell given in Fig.1.a) was used for most of the potential step experiments and was made entirely of glass. The working electrode, C, and Luggin capillary, L, were positioned in syringe barrels to enable adjustment to give the best positions and mutual distances of the two. The counter electrode, A, was either a platinum disc or a platinum mesh disc $\approx 1.5 \text{ cm}^2$ in area, positioned parallel to the working electrode.

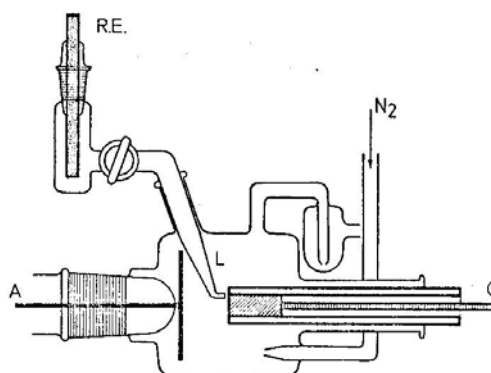


Fig. 1a. The cell used for most of the L.S.V. and potential step experiments

The cell in Fig.1.b) was used for potential step experiments controlled by potentiometers. This cell was also made entirely of glass. The counter electrode, A, however, was made of the metal deposited (surface area 4.5 cm^2 ; lead "Koch-Light Laboratories Ltd.", 99.999%) and served as a reference electrode at the same time. The lead disc was pressed into a glass tube of slightly larger diameter after being wrapped with very thin ($1 \cdot 10^{-4} \text{ cm}$) Teflon foil.

Working electrodes were small cylinders of single crystal copper ("Metal Research Ltd.", 99.999%) $\approx 0.8 \text{ cm}$ in diameter. These were sealed into Kel-F rod such that only the top surface of the metal cylinder was exposed to the solution. Great care was taken to ensure that no leakage occurred around the side of the metal crystal. This was achieved by cooling the cylinder of copper in liquid nitrogen before mounting in the hollow Kel-F rod (drilled for a tight fit at room temperature), which had been placed in boiling water so that insertion of the metal and contraction of the plastic housing ensured a very tight fit. Electrical contact was made via

brass soldered to the copper cylinder. The reference electrodes housed at the end of the Luggin capillary were either a saturated calomel (S.C.E. "Radiometer K401") or lead wire ("Koch - Light Laboratories Ltd.", 99.999%) sealed into the glass holder.

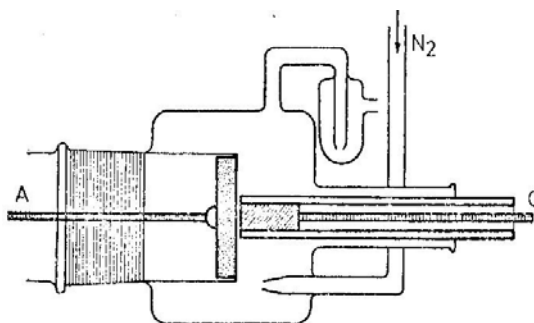


Fig. 1b. The cell used for potential step experiments on a very long time scale.

Prior to use all glass-ware was soaked in a mixture containing equal volumes of concentrated nitric and sulphuric acids to remove any possible traces of grease, then it was rinsed thoroughly in tap water, singly distilled and finally triply distilled water. The latter was prepared by slow distillation from a weakly alkaline solution of KMnO_4 and then from solution containing a trace amount of ortho- H_3PO_4 .

All solutions were made up from Analar grade chemicals ("B.D.H. Chemicals Ltd." and "Hopkin and Williams Company", without further purification) in triply distilled water. Prior to experiment, solutions were deaerated inside the cell by purging with a stream of purified oxygen-free nitrogen, for about 30-35 minutes. Nitrogen was purified by purging it through a solution of ammonia metavanadate, hydrochloric acid and distilled water lying on top of $\approx 25\text{g}$, of amalgamated zinc [20].

The importance of electrode surface preparation cannot be overstressed in connection with the metal deposition work. The surface preparation procedures finally adopted for copper single crystal electrodes were result of investigating a number of other methods. Criteria used to judge the success of each method was based on the best reproducibility of experimental data and the clearest delineation of various features on the voltammetric characteristics. The polishing process consisted of two stages, the first mechanical and the second chemical.

Firstly, the electrodes were polished on selvyt cloths ("Buchler Ltd.") impregnated with alumina ("Buchler Ltd." $5 \cdot 10^{-4}\text{cm}$ and $3 \cdot 10^{-4}\text{cm}$ grade, and "Banner scientific Ltd." $1 \cdot 10^{-5}\text{cm}$ and $3 \cdot 10^{-5}\text{cm}$ grade). Initially the largest grade was used and then progressively smaller ones down to the smallest, until the electrode had a mirror-like appearance free from scratches or blemishes. These mechanical polishing steps were always performed manually rather than on a polishing machine, which was less convenient to use. Before each experiment copper single crystal electrodes were chemically polished using a modified version of a process described elsewhere [2,21].

The (111) oriented single crystal was immersed for 3 seconds in the acid mixture heated to over 75°C while stirring, left without stirring for another 3 seconds, then stirred and again left still for 3 seconds, finally the solution was stirred, the electrode removed and washed under a strong stream of tap water and eventually in triply distilled water. The whole procedure was repeated a second time. Then the electrode would be immersed in 30 vol.% solution of ortho-

phosphoric acid and stirred for 10 seconds, washed in tap water and finally with plenty of triply distilled water. If gas evolution occurred on the electrode immersed in the polishing mixture earlier than 3 seconds, then the time which the electrode spent standing still was made shorter.

The (110) oriented single crystal was immersed in the acid mixture heated to 65°C, alternately standing still and stirred every 4 seconds for 4 times. Then it was rinsed with tap water and eventually with triply distilled water. Thereafter the procedure was the same as that previously described for the (111) orientation.

The (100) oriented single crystal was immersed in the acid mixture heated to 70°C, and alternately kept still and stirred every 3 seconds four times. Then it was rinsed with tap water and eventually with triply distilled water. Thereafter the procedure was the same as that previously described for the (111) and (110) copper surface orientation.

Examinations of the polished electrode surfaces under microscope and with X-ray emission spectroscopy revealed no contaminating elements except very minute particles of alumina, but these were very few in number (on the sample investigated one particle of alumina was found in an area of about 0.25cm²).

The amount of the copper dissolved in this chemical polishing process was relatively small. A single crystal polished several hundred times would lose 35% of its volume. The investigation of a particular electrode solution combination always started with linear sweep voltammetry.

The voltammogram itself was a direct indication of the nature of the electrode surface and consequently could be used to assess the degree to which the polishing had been successful in producing a well-defined surface. For any particular system, repeated linear sweep experiments were performed before any additional measurements were made in order to establish an arbiter to which all future voltammetry could be referred. Potential step measurements were made only if the linear sweep voltammetry was identical or very close to the accepted arbitrary standard, which was the clearest delineation of the voltammetric features.

The cell complete with working electrode (not yet finally mechanically polished) was rinsed thoroughly in tap, and triply distilled water. Then the cell was rinsed with the solution being used and finally filled with it. This was followed by deaeration with a rapid stream of nitrogen (scrubbed by a vanadous ion mixture) for about 35 minutes. During this process the working electrode was polarised at a potential somewhat positive to that where U.P.D. began. After the deaeration period, the working electrode was removed from the cell and finally mechanically polished as described earlier and after thorough rinsing was placed back in the cell. Gas purging was continued in the cell sealed with a syringe piston while the final mechanical polishing was performed. It was resumed for an additional 5-10 minutes after the freshly polished working electrode had been put into the cell. The process of polarising the electrode during the gas purging acted as a mild pre-electrolysis method and impurities were removed from the solution. That this was the case could be seen by carrying out voltammetry with the electrode at the end of the degassing period without chemical polishing, when markedly inferior results were obtained. Before the actual L.S.V. was recorded the cell was sealed off from the air by tight rubber covers being placed on the gas inlet and outlet.

Single and double potential steps could be applied to the working electrode, both in the UPD and the OPD regions, either by switching from channel A to channel B or on the "Hi-Tek Instruments" potentiostat (if the potential steps were of longer duration), or with the waveform generator RB1 in conjunction with a potentiostat. If the pulse train was employed, the dissolution pulse was always at least ten times the length of the deposition one, to ensure steady state conditions.

The fact that both the "Hi-Tek Instruments" potentiostat and the waveform generator had a facility for providing double step, allowed triple step experiments to be performed when the two were connected.

If potential step responses were not varying rapidly with time, the transients were recorded directly onto a Yt or XY recorder with time base supplied from the signal averager. When this was not possible, the averager was used to store and average current transients that could then be played back onto recorder.

When long duration potential step experiments in the UPD region were performed, two potentiometers with stable battery power supplies ("EXIDE" LCP13) were used to provide the working electrode with the desired potential. Potentiometers were connected to the electrode through a make-before-break switch, which enabled the choice of two pre-set potentials. The cell current was monitored with a battery driven Current picoammeter ("Level" D.C. Multimeter type TM 9B) and recorded on a Yt recorder.

RESULTS

As already explained earlier [1,2,11-13], on the basis of the linear sweep voltammograms for each of the electrode surface orientations the potential E_s (starting potential) and η (deposition potential) were chosen, such that when the first was applied no underpotential deposition occurred, but when the second was performed depending on its location within L.S.V. spectrum, deposition of the first or the second thallium layer could be recorded.

However, it should be said immediately, that pulse experiments in this system did not produce results that could be readily analysed in contrast to the analogous results for lead [3,11-13].

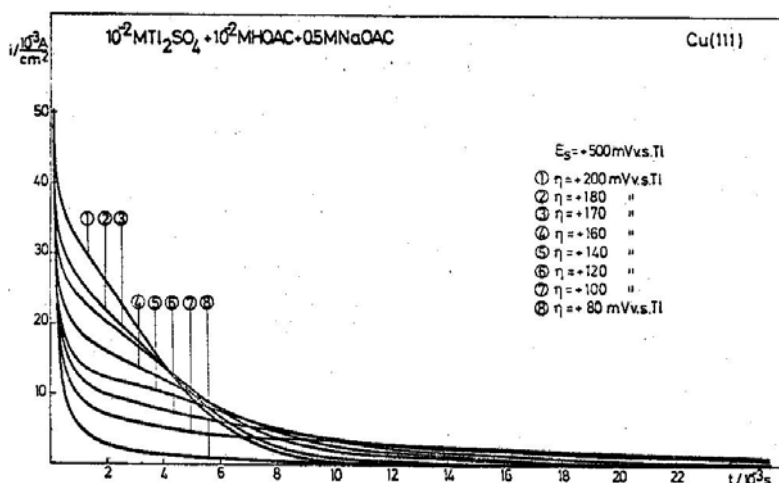


Fig. 2a. Current-time responses to single potential steps on Cu(111).

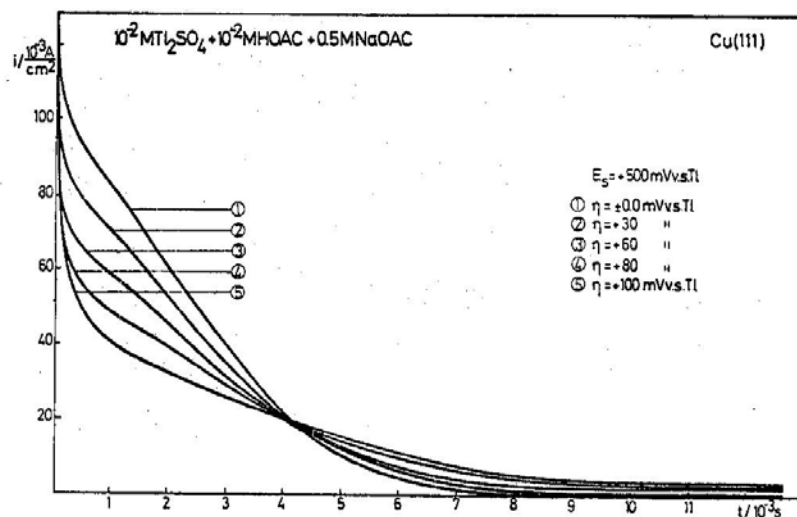


Fig. 2b. Current-time responses to single potential steps on Cu(111).

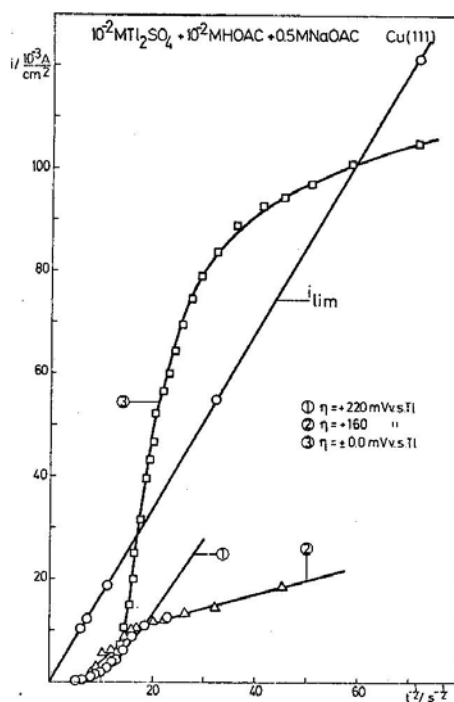
The (111) oriented electrode surface

Pulsing into the region slightly negative to the first peak, K_1 , produced falling transients of a characteristic shape, curve 8 in Fig. 2.a. Pulsing into potential region negative to the peak potential of the second peak, K_2 , and to the reversible potential of thallium, yielded i - t transients with a hump, Fig. 2.a. and b., respectively.

Pulsing to potential more negative than the K_2 peak potential produced in all cases a change in shape of the transient. A hump develops at very short times, Fig. 2.a., but soon it appears that current runs into planar diffusion control (curve 2 in Fig. 3.)

The (110) oriented electrode surface

Potential steps to potentials slightly negative to the K_1 peak potential produced monotonously falling current-time transients (curve 6 in Fig. 4.). Pulsing into the potential region more negative than the K_2 peak potential and to the reversible thallium potential produced i - t transients characterised by a hump, curves 1-3 in Fig. 4.

Fig. 3. Plots of i vs. $t^{1/2}$ for the transients from potential step experiments, (Fig. 2)

The (100) oriented electrode surface

Potential steps applied into the region of the peaks K_1 , K_2 and the reversible potential, produced the current-time relationships presented in Fig. 5.a. (curve 1), Fig. 5.b (curves 1,2) and Fig. 5.b. (curves 3-6 respectively).

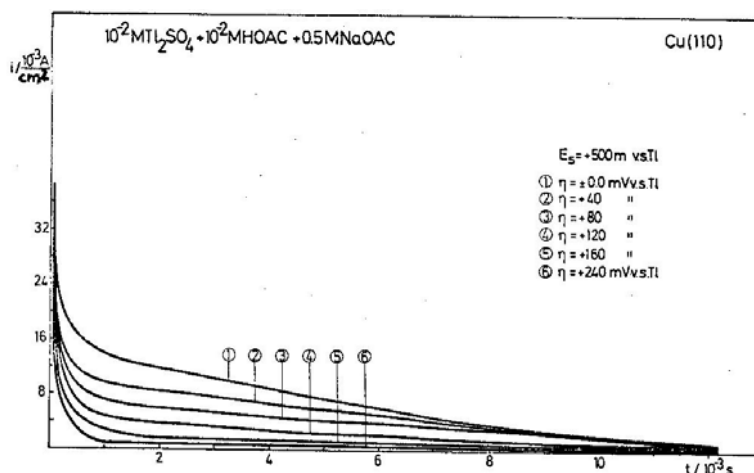


Fig. 4. Current-time responses to single potential steps on Cu(110).

DISCUSSION

The (111) oriented electrode surface

Analysis of the transients obtained for η more negative than the K_1 peak potential showed a linear i vs. $t^{1/2}$ relationship [22,23] for the initial part and this was maintained for most of the transient. At longer times the plots were curved, but the initial linear portion could be extrapolated to intersect the $t^{1/2}$ axis at positive values (curve 1 in Fig. 3.)

Pulsing to the reversible thallium potential, which is negative to the K_4 peak potential, does not change the character of an i - t transient. It does however, shift the hump to higher currents and even shorter times, Fig. 3.b. The plot of i vs. $t^{1/2}$ shows (curve 3 in Fig. 3.) that the currents in this case are very close indeed to the planar diffusion limiting currents calculated for these conditions.

Current-time transients exhibiting these characteristics have already been observed in the case of thallium underpotential deposition on silver single crystals [1].

Such transients present a strong indication of a fast 2D crystal growth process. The sharp K_1 peak which is observed for both thallium and lead deposition on Cu(111) and on Ag(111) probably always indicates a nucleative phase formation process but the rate of the lattice growth step will vary from system to system. Comparison of obtained results with the those for lead underpotential deposition on Cu(111) suggests that, in the present case, the rate of the 2D lattice building process is so fast that it becomes controlled by diffusive processes; this will probably be surface diffusion [24,25] initially and, at longer times, planar bulk diffusion.

Unfortunately, this obliterates those features observed in the case of lead UPD on copper single crystals, in particular, the rising portions of the i - t transients, which present conclusive proof for the participation of the crystal growth process and make the final conclusions rather tentative.

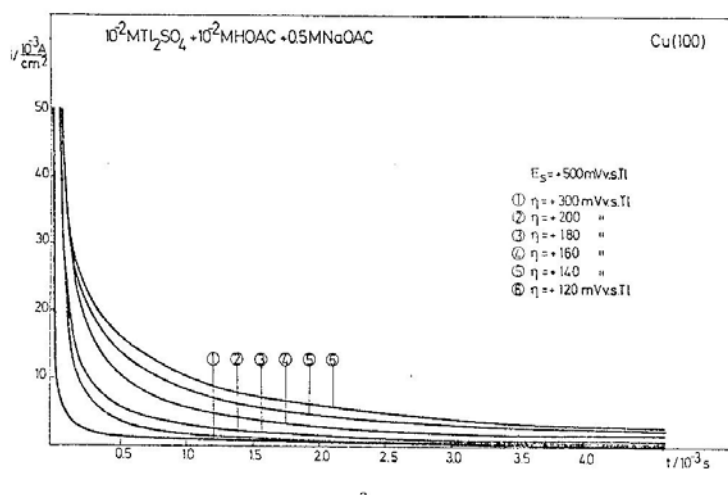


Fig. 5a. Current-time responses to single potential steps on Cu(100).

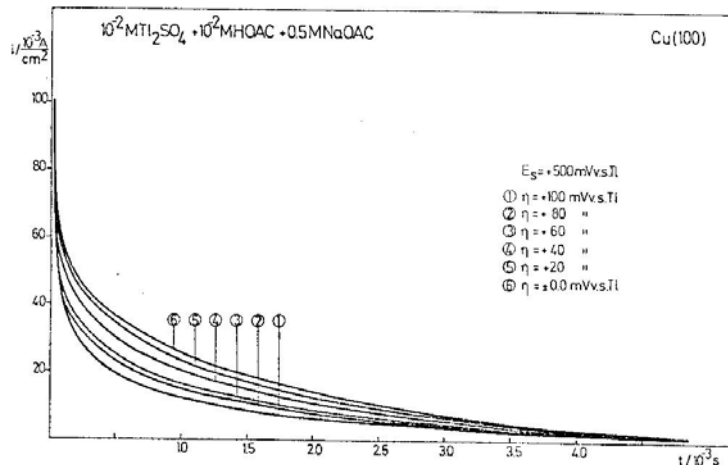


Fig. 5b. Current-time responses to single potential steps on Cu(100).

Double pulse experiments with the first pulse, η_1 , to a potential just prior to the second monolayer formation, and the second, η_2 , to the reversible potential produced transients which showed that, at 10^{-2} M Tl concentrations, the rate of the second monolayer phase formation was also dominated initially by surface diffusion.

The (110) oriented electrode surface

Relatively high current densities and the short times needed for the deposition of thallium monolayers suggest very fast crystal building processes.

Plotting these as i vs. $t^{-1/2}$ shows that planar bulk diffusion takes over rather quickly from surface diffusion control of the initial monolayer deposition stages, Fig. 6.

The (100) oriented electrode surface

Once again it is shown that thallium underpotential deposition on copper is a very fast process, and therefore the initial stages of 2D crystal growth are most probably surface diffusion controlled. It also appears that planar bulk diffusion control takes over rather quickly at longer times, Fig. 7, particularly in cases where both monolayers are deposited (curve 3).

Double pulse experiments did not help significantly in attempts to obtain i - t transients capable of providing data suitable for showing conclusively the occurrence of 2D crystal formation processes. A similar situation occurred also with silver substrates [1].

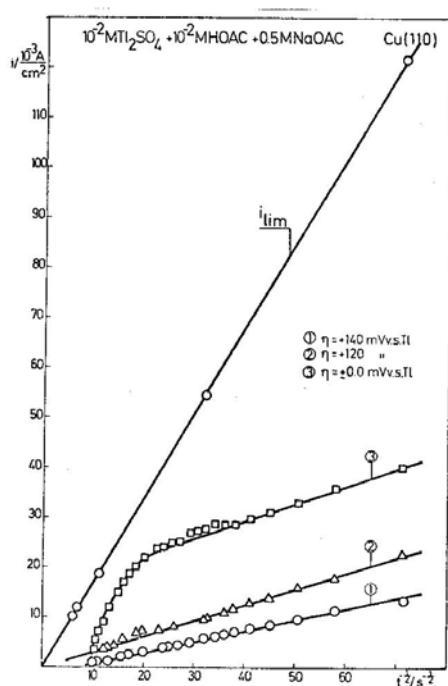


Fig. 6. Plots i vs. $t^{-1/2}$ for the transients in Fig. 4.

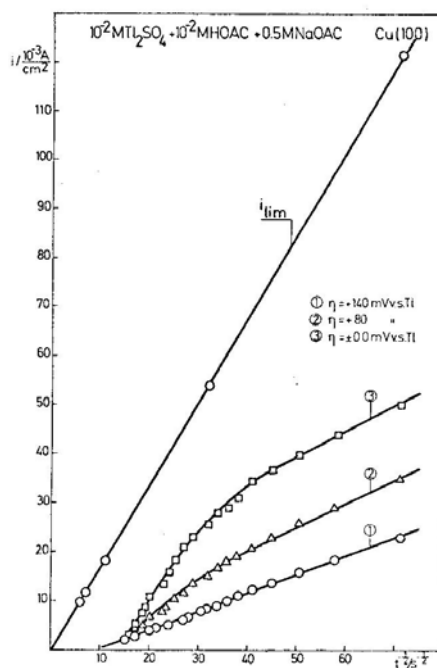


Fig. 7. Plots i vs. $t^{-1/2}$ for some of the transients in Fig. 5.a. and b.

CONCLUSION

Analysis of the transients obtained for η more negative than the K_1 peak potential showed a linear i vs. $t^{1/2}$ relationship [22,23] for the initial part and this was maintained for most of the transient. At longer times the plots were curved, but the initial linear portion could be extrapolated to intersect the $t^{1/2}$ axis at positive values.

Pulsing to the reversible thallium potential, which is negative to the K_4 peak potential, does not change the character of an i - t transient. It does however, shift the hump to higher currents and even shorter times. The plot of i vs. $t^{1/2}$ shows that the currents in this case are very close indeed to the planar diffusion limiting currents calculated for these conditions.

Current-time transients exhibiting these characteristics have already been observed in the case of thallium underpotential deposition on silver single crystals [1].

Such transients present a strong indication of a fast 2D crystal growth process. The sharp K_1 peak which is observed for both thallium and lead deposition on Cu(111) and on Ag(111) probably always indicates a nucleative phase formation process but the rate of the lattice growth step will vary from system to system. Comparison of obtained results with the those for lead underpotential deposition on Cu(111) suggests that, in the present case, the rate of the 2D lattice building process is so fast that it becomes controlled by diffusive processes; this will probably be surface diffusion [24,25] initially and, at longer times, planar bulk diffusion.

It appears that thallium underpotential deposition on copper is a very fast process, and therefore the initial stages of 2D crystal growth are most probably surface diffusion controlled. It also appears that planar bulk diffusion control takes over rather quickly at longer times, particularly in cases where both monolayers are deposited.

Double pulse experiments did not help significantly in attempts to obtain i - t transients capable of providing data suitable for showing conclusively the occurrence of 2D crystal formation processes. A similar situation occurred also with silver substrates [1].

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STUDIJA POČETNOG STADIJUMA ELEKTROTALOŽENJA TALIJUMA NA BAKRU – IV DIO REZULTATI DOBIJENI POTENCIOSTATSKIM PULSEVIMA: ELEKTROTALOŽENJE PRI POTENCIJALIMA POZITIVNIJIM OD REVERZIBILNOG NA BAKARNOJ MONOKRISTALNOJ POVRŠINI KRISTALOGRAFSKE ORIJENTACIJE (111), (110) I (100)

Jovan N. Jovićević, Alan Bewick

Ovo je četvrti iz serije radova u kojima se iznose rezultati istraživanja početnih stadijuma elektrotaloženja talijuma (iz acetatnih, sulfatnih i perhloratnih rastvora) na polikristalnom i monokristalnom bakru.

Rad predstavlja rezultate dobijene potenciostatskom metodom jednostrukog i dvostrukog pulsa na monokristalnoj elektrodi površinske kristalografske orijentacije (111), (110) i (100) u području potencijala pozitivnijih od reverzibilnog potencijala talijuma u datoj sredini.

Još jednom se uvjerljivo pokazalo da je pažljivo i uspješno poliranje površine radne elektrode od najvećeg značaja pri ispitivanjima područja potencijala pozitivnijih od reverzibilnog potencijala taloženja/rastvaranja ispitivanog metala, ukoliko se žele dobiti pouzdani kvantitativni i kvalitativni podaci. Različiti upotrebljeni anjoni ne utiču značajnije na karakteristike eksperimentalno dobijenih podataka.

Analiza i-t odgovora na potenciostatske pulseve u područje potencijala negativnijih od potencijala vrha najmanjeg voltametrijskog katodnog strujnog talasa K_1 , pokazuje linearnu zavisnost i od $t^{1/2}$ kako za početni, tako i za najveći preostali dio odgovora. Za duža vremena funkcija $i-t^{1/2}$ odstupa od linearnosti, ali početni linearni dio ekstrapolacijom na $t^{1/2}$ osi pravi odsječak pozitivne vrijednosti.

Primjena potenciostatskih pulseva čija amplituda ima vrijednost reverzibilnog potencijala talijuma u datome rastvoru, što je naravno vrijednost negativnija od potencijala vrha najkatodnijeg voltametrijskog katodnog talasa K_2 , ne mijenja osobine dobijenih i-t odgovora, mada pomjera karakteristično rame u područja viših gustina struje i kraćih vremena pojave. Vrijednosti $i-t^{1/2}$ zavisnosti pokazuju da su gustine struja kojima se odigravaju procesi formiranja oba talijumova monosloja veoma blizu izračunatim vrijednostima gustina difuzijom kontrolisanih graničnih struja za date uslove. Veoma slični i-t odgovori na potenciostatske pulseve u području potencijala pozitivnijih od reverzibilnog zabilježeni su i u slučaju elektrotaloženja talijuma na srebnim monokristalnim površinama iste kristalografske orijentacije. Strujni odgovori na potenciostatske pulseve ovakvih karakteristika predstavljaju odraz brzih procesa rasta dvodimenzionih kristalnih struktura. Poređenje dobijenih rezultata sa rezultatima dobijenim za slučajeve elektrotaloženja olova na istim bakarnim površinama i olova i talijuma na istim kristalografskim orijentacijama na srebru pri potencijalima pozitivnijim od reverzibilnog potencijala posmatranog metala, navodi na zaključak da je proces formiranja i rasta dvodimenzionih struktura oba talijumova monosloja na ispitivanim bakarnim monokristalnim površinama toliko brz da vrlo brzo postaje kontrolisan procesima difuzije; u početku vjerovatno brzinom površinske difuzije, a kasnije brzinom planarne difuzije.

Eksperimenti rađeni sa dvostrukim potenciostatskim pulsom nisu omogućili značajniji napredak u pokušaju da se dobiju i-t odgovori koji bi po svojim osobinama dali podatke za nedvosmisleni potvrdu odigravanja procesa formiranja dvodimenzioni kristalnih struktura talijuma na ispitivanim bakarnim površinama.