

A STUDY OF THE INITIAL STAGES OF THE ELECTROCHEMICAL DEPOSITION OF METALS ON FOREIGN SUBSTRATES: LEAD AND THALLIUM ON COPPER AND SILVER SURFACES – GENERAL DISCUSSION

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Abstract. *The basic applicability of the UPD theory of Gerischer et al. has been confirmed in the case of lead and thallium deposition on copper and silver single crystals, but it was shown also that this is only one of the important factors.*

It was established that the effect of substrate structure on the mechanism of the UPD monolayer formation plays an important role in the addition to the effect of electronegativity difference between the substrate and depositing atoms. An effect of changing the concentration of depositing metal and specifically adsorbing anion were found and attributed to the changes in the electronegativity of the substrate and underpotential layer as a result of changing the electrode potential. It was conclusively proven by the analysis of the peaked current-time transients obtained by potential step measurements and the very sharp voltammetry peaks, that first order 2D phase transformations are possible in UPD systems. It was also found that the L.S.V. peaks reflecting such processes must not be expected to be free from the influence of slow kinetics. It was established that the 2D crystalline metal-like phases with the closest-packed epitaxial structure exist as a stable, final product in UPD. Moreover, the possibility of higher order 2D transformations in UPD has been given strong support by the evidence of gradual monolayer density change with increasing driving force. Lead UPD on vitreous carbon was found to be the result of substrate reconstruction induced by the repeated deposition and dissolution leading to surface condition changes favoring deposition of the first layer. UPD monolayers on copper and silver surfaces always preceded OPD and had a profound effect on its nucleation overpotential (making it very small indeed) or even changing its character from 3D into 2D (in the case of vitreous carbon substrate). It was also shown that lead and thallium OPD on copper and silver single crystals starts off by charge transfer controlled instantaneous 3D nucleation and subsequent growth of 3D centers. Finally, the results obtained in the experiments performed have shown that electrochemical techniques can prove very suitable in the study of 2D phase transformation kinetics and that their further employment in this field should prove particularly rewarding.

Key words: *Underpotential deposition, Overpotential deposition, Ag, Cu, Tl, Pb, Phase formation, Single crystal surfaces*

1. INTRODUCTION

The history of electrochemical metal deposition is no younger than the history of electrochemistry. It was a subject of theoretical as well as experimental research as early as 1834 [1]. Nevertheless, explanations for many of the phenomena involved are still not available. This is still particularly true for the deposition of metals on foreign substrates, where only relatively recently the phenomenon of a deposition occurring at more positive potentials than that of the bulk of the deposited metal/metal ion electrode - underpotential deposition, has been closely investigated.

The principles governing metal deposition and electrocrystallisation on similar substrates basically apply to most of the deposition on foreign substrates. Naturally, certain specific features of the latter process, arising from the differences between the two crystal structures (deposit and substrate) meeting and coexisting, were expected. Therefore, for a long time 3D nucleation was considered a necessary step for starting a lattice of a new kind on a foreign substrate [2-9]. Of course, any process of nucleation and its rate is markedly dependent on supersaturation and in many cases it occurs at a measurable rate only at overpotentials in excess of 100mV.

It was only relatively recently that it was found that certain amounts of metal are being deposited at potentials well anoxic to the reversible potential [10-23]. The earliest explanation [11] of this phenomenon argued that the small number of lattice sites on the electrode have adsorption energies for metal atom deposition so high as to be equal to the substrate work function, the rest of the sites available being associated with adsorption energies smaller than this. Because of that, deposition of a given metal would always start at the same potential irrespective of the substrate electrode material.

Soon, however, it was established that deposition of fractional monolayers was very sensitive to the substrate material, and an attempt to interpret the observed underpotential deposition on a thermodynamic basis was initiated [16,17]. It relied on Herzfeld's [24] concept according to which the activity of metal in a fractional monolayer of a deposit, $a_{m(s)}$, should vary with the fraction of the surface covered, Z/Z_0 (Z_0 and Z , number of moles amounting to one monolayer of deposit and number of moles deposited, respectively, $f_{m(s)}$ being the activity coefficient of the metal deposit):

$$a_{m(s)} = f_{m(s)} \frac{Z}{Z_0} . \quad (1)$$

At approximately the same time, the first indication of a strong dependence of the underpotential deposition (UPD) on the state of the electrode surface was found [25].

Soon underpotential deposition became a well recognised phenomenon of particular interest to deposition on foreign substrates and a topic of extensive investigation [26]. The results obtained in these experiments led some authors [27] to believe that the UPD process produces neutral atom adsorbed on the substrate electrode. Coupling an appropriate adsorption isotherm to the bulk diffusion conditions therefore could reproduce experimental current-voltage curves, in their view. Other workers [26] preferred to assume the involvement of 2D crystal plane formation in UPD processes although there was no

experimental evidence following this explanation. According to them, large differences in the lattice parameters of the deposited and substrate metal would preclude UPD in certain systems, whereas, a similarity of crystal structure and lattice parameters would lead to UPD.

While the former theoretical approach was still very much alive, mainly among the groups around its authors and workers using the same technique, the latter did not gain widespread acceptance.

Then, in 1974, Gerischer, Kolb and Przasnyski [28,29] had put forward the theory to explain the origin of UPD. Their investigations on UPD phenomena showed that the potential difference between monolayer and bulk deposition was closely related to the difference in work functions of substrate and deposit. This led them to assume that the work function difference is a measure of the electronegativity difference between a substrate atom and a deposited atom bonded together. The distortion of the electronic distribution arising from this electronegativity difference would give an ionic contribution to the bond energy enabling the first layer to be deposited at an underpotential and particles within the layer should possess a small partial charge (10-20%). The correlation between UPD shift and work function difference plays a major role in determining the onset of UPD. However, the theory did not consider the possible importance of structural effects, neither did it explain the underpotential deposition of several layer.

Meanwhile a modification of the above theory was proposed by Vijn [30,31]: he proposed that for UPD to occur the electrode surface atoms must possess significant "d" character and the heat of adsorption of the metal atom on a given substrate, as calculated from the Pauling-Eley equations, must be exothermic. The correlation of UPD shifts and heats of adsorption gave a linear plot similar to the plot by Gerischer *et al.*

The views put forward by Gerischer *et al.* and Vijn were generally accepted as describing one of the important factors controlling UPD but it was recognised also that other structurally related factors are also significant.

From the beginning of seventies both theoretical and experimental work on UPD was basically concerned with the following questions:

- a) What is the state of charge of the species within the monolayer?
- b) Does the layer consist of adsorbed species or is it a crystal plane?
- c) What is the origin of the multi-peak structures observed in the linear sweep voltammetry of many UPD systems?
- d) To what extent does the UPD influence subsequent overpotential deposition?

Partial charge on adsorbed species has been a topic of particular interest to several authors [27,32-35]. The result was the definition of the electrosorption valency [36], γ , as a quantity dependent on geometrical factors, the partial transfer coefficient, λ , dipole factors and a capacitive term, through:

$$\gamma = \frac{1}{F} \left(\frac{\partial q_m}{\partial \Gamma_{ad}} \right)_{\Delta\psi} \quad (2)$$

where q_m is the electrode charge, Γ_{ad} is the surface concentration of specifically adsorbed substance, and $\Delta\psi$ the potential difference of the compact double layer.

In the case of γ values approximately equal to z it seemed plausible that the adsorbed metal atom would be only slightly charged and bonded to the substrate by a covalent bond bearing small partial character.

From the work published earlier, there emerge two possible structures for UPD monolayers:

- a) an adsorbed layer of neutral or partially charged atoms,
- b) a 2D crystal plane.

Although strong indications supporting each of the above views exist in the literature and although both views had strong support among workers in the field, no really convincing evidence to prove either of the cases was produced before the completion of the work described in this papers [51,78-92].

The originators of the first case, a), were looking upon the monolayer as consisting of neutral atoms [27], the deposition of which at an underpotential would be governed by Langmuir isotherm. More recently, to describe UPD, they used the term "cation adsorption" [37,38], and have treated it in an analogous manner to the specific adsorption of anions. This has caused some confusion, because in some work [28,29] it has been interpreted literally as implying the presence of cations in the inner Helmholtz plane bearing full ionic charge. Later, however [39,40], the authors did not imply that the charge flowing when UPD takes place is purely capacitive, but considered charge transfer being even rate determining in "metal ion adsorption" processes.

To support their own idea of UPD deposits existing as adsorbed layers these authors considered the fact that deposition in many systems, then investigated, occurs over a wide range of potential with the activity of the deposit varying with coverage (which is consistent with an adsorption isotherm), and this is sufficient evidence for lack of any phase formation process. This view, of course, could be challenged because change of state can be of several types [41], and thus phase transformations can occur over a range of values of the variable causing the transformation.

They also argued that the fact that measured charges in many UPD systems correspond just to a monolayer [42] is strong evidence for the lack of crystallisation process taking place, which would be more dependent on pretreatment of electrodes and purity of solutions. However, the surface coverage corresponding to a complete adsorbed layer are dependent on whether adsorbed atoms are restricted to interstitial sites between surface atoms in the electrode or whether a close-packed structure. In addition, a roughness factor which has rarely been determined in UPD studies, but does represent the electrode surface and is known to be high, surely must have an influence on the measured charges, particularly on polycrystalline electrodes.

Other workers [36,43], while discussing the electrosorption valency of the "adsorbed state" in UPD, considered these systems in a manner analogous to the known systems of specific anion or neutral organic adsorption.

Meanwhile some authors [26,44-46] gathered experimental evidence, which led them to propose that some of the systems a crystalline phase in UPD may be involved [26]. After publication of works of Bewick, Thomas and Jovićević [47-51] this approach to UPD metal layers gained wider support [52-56]. Their results proved conclusively how important it is to perform UPD experiments on single crystal well defined substrates and how much the structure of UPD monolayer depends on crystallographic orientation of the substrate and the ratio between atom dimensions of deposit and substrate. Also, for the first time a strong indication of the 2D nucleation and crystal growth of the 2D crystalline

monolayer (in a form of a very sharp linear sweep voltammetry peaks with a crystallisation overpotential existing between deposition and stripping peaks, current-time transients from potential step experiments as well as reflectance spectroscopy results) were produced. In addition the possibility of phase transformations occurring within the UPD monolayer during the underpotential deposition process was introduced and discussed.

However, the work of some other authors [57-63] performed in the same systems, which soon followed, disputed these conclusions and showed that some of the peaked *i-t* transients could alternatively result from adsorption processes, although the experimental results were more or less confirmed. The main objection was that no really conclusive evidence for phase transformation through 2D nucleation and subsequent crystal growth.

Multipeak structure during linear sweep induced UPD on single crystals became a topic of investigation relatively recently [42,46,64,65] and immediately invited controversy. Some authors [64] claimed that no dependence of the deposition peak potential on substrate orientation was observed (indeed that only single deposition peak was increasing in the order $Q_{(100)} \geq Q_{(110)} \geq Q_{(111)}$) and the phenomenon was explained through the superlattice model of adsorption. In contrast, other workers found that L.S.V. for the deposition of lead in single crystal gold substrate was markedly dependent on orientation, but the total charge under the L.S.V. peak for each crystal face was identical. Very similar effects were found for several other UPD systems [65] on single crystal gold substrate, and the variety of peaks was thought to arise from different adsorbed states.

Authors of the work done on UPD of lead and thallium on carefully prepared silver single crystals [47-51,57-63] although differing in explanation of the monolayer structure, do agree on the following:

- a) the L.S.V. peak potentials depend on crystal orientation of the substrate,
- b) the charge associated with the monolayer depends on the substrate,
- c) the multipeak structure arises from different states of the atoms, i.e. from different phases of the monolayer.

For a long time many studies of bulk deposition and electrocrystallisation as well as reviews on the subject have completely ignored the possibility of a monolayer formation [66-71].

However, the view that UPD was the very initial stage of metal deposition on foreign substrates has already been suggested [42,72] but until recently there were no attempts to correlate underpotential monolayer formation with the subsequent electrocrystallisation of the bulk deposit.

Some authors [73] suggested that the presence of an adsorbed metal monolayer might promote nuclei formation in the overpotential region, the others [42,72] agreed that the low ($\leq 10\text{mV}$) overvoltage required for the initiation of the bulk growth indicated the formation of the 2D rather than 3D nuclei. The fact that the optical properties of thin metal deposited on top of the UPD monolayer reach those of the bulk metal at much lower thickness than is the case for evaporated films has been explained as due to the monolayer promoting the growth of subsequent deposits in regular rather than 3D islands.

In this context it seems relevant that some authors [74,75] as early as 1962 while discussing the implications of the expression relating the radius of a critical nucleus, r^* , to the relevant surface energy parameters (σ_1 , σ_2 , σ_3 , the free surface energies of the electrode solution, electrode-film and film-solution interfaces respectively) showed that:

$$r^* = \frac{a\sigma_3}{-a\Delta G_v - (\sigma_2 + \sigma_3 + \sigma_1)} \quad (3)$$

a being the height of the patch and, ΔG_v the free energy change per unit volume accompanying formation of the film. Even when the bulk phase is unstable, i.e. for somewhat positive values of ΔG_v , r^* becomes positive and finite if $(\Delta\sigma = \sigma_2 + \sigma_3 + \sigma_1)$ is negative. Therefore the electrode could become covered with a monolayer of an anodic reaction product even at a potential more negative than the equilibrium potential for the reaction. This might provide a surface on which subsequent (anodic) deposition could occur with small overpotential.

Although 3D systems, and especially films on solid surfaces, have been a subject of interest in the last three decades of last century, there have only relatively recently been major advances in the experimental and theoretical areas of surface physics involving 2D layers on solid surfaces. Knowledge accumulated through years of experimental and theoretical research on 3D systems is being intensively modified and applied to 2D systems. This has led to novel results as far as the analogy between 2D and 3D systems is concerned.

Knowledge on the subject has been reviewed [41,76,77].

Despite extensive studies of metal underpotential deposition there have been some important problems still unresolved. These related principally to the nature of the monolayer (adsorbed or crystalline), the interpretation of the kinetics of the crystalline monolayer formation, if any, and the relevance of the UPD monolayer to the overpotential deposition process.

The systems selected for the study were: lead on vitreous carbon [78,79]; lead on polycrystalline and single crystalline copper [51,78,80-87] substrates; thallium on polycrystalline and single crystalline copper [88-92] substrates. 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 and thallium from acetate, sulphate, nitrate and perchlorate aqueous solutions.

MATERIALS AND METHODS

The techniques employed were linear sweep voltammetry (L.S.V.) [51,80-82,88-90] and potential step (single, double and triple potential pulses were used) [84-86,91,92].

Lead electrochemical deposition and dissolution on copper single crystals with (111), (110) and (100) oriented surface, was examined in solutions containing three different anions (perchlorate, acetate and nitrate), and four different lead concentrations:

xM Pb(OAC) ₂ + 10 ⁻² M HOAC + 0.5M NaOAC	10 ⁻⁴ M ≤ x ≤ 10 ⁻¹ M
xM PbO + 10 ⁻³ M HClO ₄ + 0.5M NaClO ₄	10 ⁻³ M ≤ x ≤ 10 ⁻¹ M
xM Pb(OAC) ₂ + 10 ⁻³ M HClO ₄ + 0.5M NaClO ₄	0 ⁻⁴ M ≤ x ≤ 10 ⁻¹ M
xM Pb(OAC) ₂ + 10 ⁻³ M HClO ₄ + 0.5M NaNO ₃	10 ⁻³ M ≤ x ≤ 10 ⁻¹ M

and on silver (111) oriented surfaces in:

$x\text{M Pb}^{+2} + 5 \cdot 10^{-3}\text{M HClO}_4 + 0.5\text{M NaClO}_4$	$10^{-4}\text{M} \leq x \leq 10^{-1}\text{M}$
$x\text{M Pb}(\text{CH}_3\text{COO})_2 + 10^{-2}\text{M CH}_3\text{COOH} + 0.5\text{M CH}_3\text{COONa}$	$10^{-4}\text{M} \leq x \leq 10^{-1}\text{M}$
$x\text{M Pb}^{+2} + 0.5\text{M Na}_2\text{C}_6\text{H}_5\text{O}_7$	$10^{-5}\text{M} \leq x \leq 10^{-2}\text{M}$
$5 \cdot 10^{-2}\text{M Pb}^{+2} + 5 \cdot 10^{-3}\text{HClO}_4 + y\text{M NaClO}_4 + y\text{M NH}_2\text{SCNH}_2$	$10^{-5}\text{M} \leq y \leq 10^{-3}\text{M}$
$5 \cdot 10^{-2}\text{M Pb}^{+2} + 5 \cdot 10^{-3}\text{HClO}_4 + 0.5\text{M NaClO}_4 + z\text{M CH}_3\text{COONa}$	$10^{-5}\text{M} \leq z \leq 10^{-3}\text{M}$
$5 \cdot 10^{-2}\text{M Pb}^{+2} + 5 \cdot 10^{-3}\text{HClO}_4 + 0.5\text{M NaClO}_4 + k\text{M Na}_2\text{C}_6\text{H}_5\text{O}_7$	$10^{-5}\text{M} \leq k \leq 10^{-3}\text{M}$

The underpotential deposition (UPD) and overpotential deposition (OPD) of thallium were carried out from solutions containing following anions and thallium concentrations:

$x\text{M Tl}_2\text{SO}_4 + 10^{-3}\text{M HClO}_4 + 0.5\text{M NaClO}_4$	$10^{-3}\text{M} \leq x \leq 10^{-1}\text{M}$
$x\text{M Tl}_2\text{SO}_4 + 10^{-3}\text{M HClO}_4 + 0.5\text{M Na}_2\text{SO}_4$	$10^{-3}\text{M} \leq x \leq 10^{-1}\text{M}$
$x\text{M Tl}_2\text{SO}_4 + 10^{-3}\text{M HOAC} + 0.5\text{M NaOAC}$	$10^{-3}\text{M} \leq x \leq 10^{-1}\text{M}$

This relatively wide variation in solution composition and concentration was necessary to understand all the variables affecting the UPD and OPD, and their mutual interdependence.

Three types of cells (specially designed for this experiments [78,79,93,94]) were used in the experiments. One cell was used for electrochemical preparation of lead perchlorate and citrate, by galvanostatically or potentiostatically controlled dissolution of lead ("Koch-Light Laboratories Ltd.", 99.999%) in a chosen solution.

The second cell 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.

The third cell 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 vitreous carbon ("Le Carbone", France) $\approx 0.6\text{ cm}$ in diameter; single crystal copper ("Metal Research Ltd.", 99.999%) $\approx 0.8\text{ cm}$ in diameter and single crystal silver ("Metal Research Ltd.", 99.999%) $\approx 0.67\text{ cm}$ 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 or thallium wire ("Koch - Light Laboratories Ltd.", 99.999%) sealed into the glass holder.

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.

The importance of electrode surface preparation cannot be overstressed in connection with the metal deposition work. The surface preparation procedures finally adopted for vitreous carbon, copper and silver single crystal electrodes were result of investigating a number of 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.

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 0.25cm^2).

The amount of the copper and silver dissolved in this chemical polishing process was relatively small. A single crystal polished several hundred times would lose 35% of its volume.

Further details concerning electronic equipment and methods used, including glassware and solution preparations are available elsewhere [78-98].

RESULTS

Subjects of interest in this paper are experimental results obtained by the authors on initial stages of Pb and Tl electrodeposition on different foreign substrates in an attempt to contribute to the general understanding of UPD and OPD phenomena and their interdependence. Detailed presentation of the experimental results are published [78-98] and available elsewhere.

DISCUSSION

Phase formation and transformation in underpotential deposition

In earlier studies it was assumed that underpotential deposition (UPD) was simply the formation of an adsorbed layer of partially charged atoms [99,100], although the epitaxial features of the process were recognised [64]. The multi-peak voltammograms were there-upon explained accordingly.

However, more recently [47-51,78-98] it was shown that there is a strong possibility of phase formation and transformation processes taking place in UPD and therefore that the current peaks obtained in L.S.V. reflect the spectrum of such processes.

Generally speaking, surface phases are the result of complex interactions [77] with the substrate and therefore none of these systems is entirely two-dimensional. This is particularly true for electrochemically produced UPD monolayers, where all three major components of the system (solution, UPD deposit and underlying substrate) play important roles in the overall arrangement.

It has been shown [28-31] that a large factor in the free energy difference between the bulk phase and the UPD deposit is the partial ionic character of the bond energy between

the two dissimilar metal atoms in contact at the substrate surface, arising from the difference in their electronegativities. This theory, however, did not predict multilayer UPD, neither did it take into account the possible influence of several other important factors, e.g. the structure of the underlying substrate, the solution concentration of the deposited metal, the degree of crystalline organisation of the monolayer, etc.

If the work function values are correlated with potential of zero charge [102] in the usual way [103] for each of the single crystals examined, copper [78-92] or silver [47-51,93-98], then the UPD of lead, for example, should commence at the most cathodic potentials on the (110) face and the least cathodic on the (111) face. The linear sweep voltammetry results for lead [79-82] and thallium [88-90] UPD on copper and silver [93-98] however show that the (110) and (100) faces have exchanged their places in the series (110), (100), (111). In the same time, the UPD shifts towards the bulk lead and thallium reversible potentials on both copper and silver single crystals, appear to be smaller than would be expected from the plot obtained by the treatment of Gerischer *et al.* [28,29].

The coordination number of an atom within a monolayer and the coordination number with atoms of the substrate also decreases in the series (110), (100), (111). Since it is to be expected that the deposition will be most favoured when a deposited atom can interact with the greatest number of its neighbours, the recorded UPD potentials for different Cu single crystal surfaces appear to show the change in series of the same kind as above, contrary to the trend predicted by the zero charge potentials.

The structures of underpotentially deposited metal monolayers and the way in which they change with substrate orientation [79-98] have shown a variety of phases. Moreover, the transformations from one to the other monolayer structure depend markedly upon the degree of registration to the underlying substrate.

Related studies of adsorption onto well-defined solid surfaces from the gas phase [101] have also shown that the registration of the films to the substrate promotes and preserves long range order [77]. In addition, it was suggested [77] that a variety of interesting phase transition processes taking place in these systems is strongly dependent on the degree of the registration.

It must be concluded, therefore, that any model pretending to describe successfully and quantitatively the variations of UPD shifts for the different metal couples must consider structural interactions in addition to work function differences.

In many instances the UPD in the first layer takes place in the form of an appreciable amount of adsorption. Charge values due to these processes, as indicated by the L.S.V. and potential step measurements [78,79,91-94], are often not enough to account for a full, close-packed monolayer but are in good agreement with the charges needed for one of the superlattice models [42,64,72,47-51,93,94]. These are explained by assuming that the adsorption of depositing atoms occurs on the interstitial sites between the surface atoms, a structure well known from LEED investigations of gas phase adsorption phenomena [104]. However, such structures are usually not the final form of the UPD monolayers (Pb on Cu(110) and Tl on all three copper single crystal orientations in the present work, as well as Pb and Tl on Ag single crystals [47-51]), and when the potential is changed to more cathodic values additional material is usually deposited. The free energy change imposed in this way requires structural and therefore phase transformation from the initially existing form into a more stable configuration of the monolayer. These processes are reflected in the voltammograms in broad and very sharp peaks, respectively.

Some workers [40,59] have continuously disputed that phase formation processes take place during UPD in spite of the work [47-51] done on the UPD of lead and thallium on Ag, attributing the sharp peaks to adsorption processes following a Frumkin isotherm with a large attractive interaction parameter. They also insisted on finding a discontinuous isotherm indicative of a first order phase transition before accepting the participation of a nucleative process although it was suggested [47-51,77] that higher order transformations might be taking place.

Performed work [78-98] has provided data for the UPD of lead onto Cu(111) oriented surface and lead onto Ag(111) which allowed the construction of isotherms approaching very closely to this ideal form. This has an almost discontinuous rise, changing from coverage of about 10% to that of a complete layer within an interval of 1mV. These measurements as well as the results from L.S.V. and other potential step measurements on the same systems, have shown that in general L.S.V. voltammograms obtained at realistic sweep speeds must not be expected [80,93] to show the characteristics of a first order phase change free from the effects of the limitations of slow kinetics.

In addition, it is conclusively proven that UPD monolayer phases not only do exist in a form of a crystal lattice when a close-packed structure is achieved (e.g. Pb on Cu(110) and Tl on all three copper single crystal orientations), but also that the closest-packed epitaxial layers exhibit well pronounced crystalline phase characteristics (Pb and Tl on Cu(111), and Pb on Cu(110), if the substrate structure and atomic size ratio between deposit and substrate, enables lateral distances and interactions within the monolayer to be of a suitable value. The comparison between the results obtained from the work on Ag single crystals [47,93,94] and the work on copper single crystals lead to conclusion that it is only when such UPD monolayer configurations are not sufficiently energetically stable at potential closer to the bulk, the transformation into an energetically favourable structure, such as a close-packed monolayer, is required. The differences in behaviour on copper and on silver substrates, can therefore be accounted for by the higher electronegativity of copper which will lead to stronger bonding to the lead and thallium, and by the significantly smaller atomic radius ($r_{\text{Cu}} = 1.28 \cdot 10^{-8} \text{ cm}$ compared with $r_{\text{Ag}} = 1.42 \cdot 10^{-8} \text{ cm}$).

It should be noted, however, that the transformation taking place in any system need not necessarily be of the first order, but may indeed be of a second or higher order as in the case of Pb UPD on Cu(110), Cu(100) and most probably in all cases of Tl UPD on the three Cu single crystal surfaces examined [88-92].

In all these cases the strong effect of the correlation between the substrate structure and the UPD monolayer on the final product was very pronounced. In fact, the influence of substrate structure is still strongly felt by the second UPD monolayer in the case of Tl on both Ag and Cu single crystals. This indicates that the first close-packed phase layer is partially distorted and moulded by the substrate structure, a process that would be most likely on the (110) substrate, and this is probably one of the causes for the second lead UPD layer in the case of Ag(110) substrate.

In general it seems that the appearance of the second monolayer could be attributed to the effect of the electronegativity difference between the first thallium monolayer – a crystalline phase but definitely not yet a bulk phase; and thallium atoms occupying especially active adsorption sites in it – a result of the first monolayer crystalline structure.

The results obtained, although not giving sufficient data for the kinetic analysis of the second layer UPD process, strongly indicate that this proceeds in a fashion similar to the formation of the first monolayer. The shape and the number of the voltammetry peaks

reflecting the processes is usually the same and it is to be expected that the mechanism is similar. On (100) and (110) planes, the second layer crystal phase formation is preceded by an appreciable amount of adsorption and it is possible to envisage the existence of adsorption sites similar to those in the original copper substrate, because of the distorted structure of the first layer. At the same time, the second monolayer on the Cu(111) face appears to undergo phase formation directly without comparable adsorption, which would be expected on account of the first monolayer being the least moulded by the original substrate. Similar conclusions have been reached for Tl UPD on silver single crystal electrodes.

Finally, there appears to be a correlation between the observed order of the phase formations and the structure of the underlying substrate: it was always a first order for (111) surface where no different adsorption sites exist and the adsorption energy is comparatively lower: while it was of second or higher order on the (100) and (110) surfaces which have a choice of different adsorption sites and comparatively higher adsorption energies.

These results and the fact that higher order transitions occur at more cathodic potentials suggest that string registration (e.g. on Cu and Ag surfaces) contrary to some predictions [77] favours higher order transformation. This is most probably due to additional energy needed to pull out deposited atoms from very stable positions in strong adsorption sites and need to provide, at the same time, a large enough free energy change to induce and sustain the more or less planar configuration of the forming close-packed monolayer (the situation occurring on the Cu(110) substrate for example), which would account for the exchange of places between (110) and (100) in the series for UPD shifts on different orientations taking into account electronegativity differences only ((100), (110), (111)).

The results from the work presented here have shown that electrochemical techniques are suitable for following the dynamics of phase formation and transformation processes in 2D systems of this kind and their further employment in this field should prove particularly rewarding.

UPD potential variation due to solution concentration changes

There is one interesting experimental phenomenon, which requires some explanation. It can be seen from the results obtained [78-98] that the potentials of the underpotential voltammogram peaks, E_p , move with respect to the bulk reversible potentials, E_r , when the concentration of the deposited metal ion is varied at constant ionic strength. Two simple possible explanations can be readily discarded: the constraint of constant ionic strength removes the effect of simple changes in the electrical double layer, and a possible explanation in terms of changing anion adsorption as the electrode potential changes can be ruled out by the observation that a similar concentration dependence is found for solutions using the acetate anion, the nitrate anion, the sulphate anion and the perchlorate anion. It is particularly interesting to note that the adsorption peak potentials show an opposite concentration dependence to that of the phase peak potentials, ΔE_p becoming larger for the former and smaller for the latter as the bulk concentration of the metal ion is increased (where $\Delta E_p = E_r - E_p$). This general rule is true for all three single crystal substrates and both for lead and for thallium deposition. On thermodynamic grounds one can write a simple Nernst expression for the potential of the underpotential layer as a function of the coverage, θ :

$$E_u = E_u^0 + \frac{RT}{zF} \ln \frac{a_{M^{+z}}}{a_\theta} \quad (4)$$

were a_θ and $a_{M^{+z}}$ are the activities of the layer and the metal ion in the solution, respectively. Thus variations in ΔE_p with changes in $a_{M^{+z}}$ require that a_θ should vary since,

$$E_r = E^0 + \frac{RT}{zF} \ln a_{M^{+z}} \quad (5)$$

The ΔE_p values effectively measure shifts at constant coverage since the peak shapes are independent of concentration. Thus a_θ must vary with changing $a_{M^{+z}}$ at constant θ , and the essential question involves the reason for this change. A simple answer can be formulated by the following arguments.

It has been demonstrated that a large factor in the energy difference between the bulk metal and the underpotential layer, ($e \cdot \Delta E_p$), is due to the difference in electronegativity, $\Delta \chi$, between the substrate metal and the depositing metal. The experimental data was found to give a reasonable fit to [28,29]:

$$e \cdot \Delta E_p = 0.5 \Delta \phi \quad (6)$$

where $\Delta \phi$ is the work function difference of the two metals. The well known interdependence evidence of work function and electronegativity:

$$\chi = 0.5 \phi + \text{const.} \quad (7)$$

completes the relationship between $e \cdot \Delta E_p$ and $\Delta \chi$. It is also well established that there is a linear correlation between the point of zero charge, E_{pzc} , of metal and its work function:

$$e E_{pzc} = \phi + \text{const.} \quad (8)$$

When $a_{M^{+z}}$ is increased, E_r moves in positive direction with respect to E_{pzc} and thus the effective work function and electronegativity of the metal electrode increases. In view of Eq. (6), (7) and (8) one should write:

$$\Delta E_p = \pm 0.5 (E_r - E_{pzc}) + \text{const.} = \pm \frac{RT}{2zF} \ln a_{M^{+z}} + \text{const.} \quad (9)$$

The sign of the right hand side of Eq. (9) will depend upon the location of the charge on the electrode, q_m , when it has an underpotential layer on its surface. If this layer does not electrically screen the substrate, i.e., q_m on the substrate surface, then the sign will be positive because the substrate becomes more electronegative as the concentration increases. On the other hand, if the layer completely screens the substrate, then q_m will reside on the layer and the sign will be negative. It should be remembered that the Thomas-Fermi screening length for a metal is about 0.07nm. The actual situation will probably lie in between these two limits any vary with the structure of the underpotential layer. Thus it is not surprising to find that the sign of the effect is positive for adsorption peaks, indicating inefficient screening, and negative for the phase peaks, indicating efficient screening. The limiting gradients from Eq.(9) are $\pm 30\text{mV}$ for thallium and $\pm 15\text{mV}$ for

lead. It can be seen from the Table. 1., that the experimental values lie nicely within this range and the values for thallium are larger than those for lead.

Table. 1. Average values of $\left(\frac{dE_p}{d \log C_{M^{+z}}}\right)$ for underpotential deposition of Pb and Tl on copper single crystals [78-92].

Cu substrate Orientation	Depositing metal	Calculated concentration dependence of the UPD peak potential	Measured concentration Dependence of the phase peaks	Measured Concentration dependence of the adsorption peaks
(111)	Lead	-15mV	-15mV	Not applicable
	Thallium	-30mV	-30mV	Not applicable
(110)	Lead	-15mV	-10mV	+5mV
	Thallium	-30mV	-20mV	+15mV
(100)	Lead	-15mV	-15mV	Small positive values
	Thallium	-30mV	-20mV	Small positive values

Influence of adsorbing substances on underpotential deposition

Until very recently little systematic attention has been given to the role of anions in the overall process of the UPD, particularly in the case of single crystal substrates and anion other than halogenides.

It has been recognized that anions can have strong influence on the UPD. The UPD potential shift was found to decrease (Pb on Ag for example [93,94]) and the area under the monolayer LSV deposition peak to increase in the sequence $\text{ClO}_4^- \leq \text{F}^- \leq \text{SO}_4^{2-} \leq \text{Cl}^- \leq \text{Br}^- \leq \text{SCN}^- \leq \text{I}^-$.

While former can imply reduction in the bond strength between metal adatom and substrate surface or change of substrate electronegativity due to anion's stronger interaction with substrate then with adsorbate, the latter can be attributed to atom deposition being accompanied probably by anion desorption contributing to the current in the same direction.

Experimental evidence presented [78-98] leaves no doubt that adsorbing substances affect both the thermodynamics and the kinetics of the UPD monolayer formation. Moreover, through their adsorptive quality different anions cause substantial difference in the structure of the adsorbed monolayers and thus influence kinetics of the UPD monolayer formation.

Effect of solution composition on thermodynamics of the UPD can be easily followed by the changes in the standard potential of the UPD^I, with respect to the bulk metal:

$$\Delta U = E_{\text{MS}} - E_{\text{MM}} = E_{\text{MS}}^0 - E_{\text{MM}}^0 + \frac{RT}{F} \left(\frac{1}{\gamma_{\text{MS}}} - \frac{1}{z} \right) \ln a_{\text{M}^{+z}} - \frac{RT}{\gamma_{\text{MS}} F} \ln a_{\text{MS}} \quad (10)$$

where E_{MS} stands for the UPD monolayer Nernst potential [9] of atoms M on foreign substrate S (γ_{MS} being electrosorption valency of the same adatoms):

$$E_{MS} = E_{MS}^0 + \frac{RT}{\gamma_{MS}} \ln \frac{a_{M^{+z}}}{a_{MS}} \quad (11)$$

and E_{MM} for the Nernst potential of the substrate made of bulk metal M:

$$E_{MM} = E_{MM}^0 + \frac{RT}{zF} \ln a_{M^{+z}} \quad (12)$$

The values of E_{MS} are taken at the middle potential between the main cathodic and anodic peak on a voltammogram recorded, because in the case of kinetic control of the L.S.V. shifting the potential on either side of it provokes a cathodic or anodic process (cathodic or anodic "overpotential"). The fact that it is seen to be independent of the sweep rate strengthens its thermodynamic character and justifies the term "reversible potential of the UPD".

The observed shift of the standard potential of the UPD [93,94], see Table. 2., with changing solution composition in the given sequence, must reflect the change in the effect of adsorption of the anions and of thiourea on lead crystalline monolayer, compared to silver (111) surface. For, inasmuch as the reversible potential of the bulk phase cannot depend on adsorption, that of 2D phases must be susceptible to it. On one side some of the energy liberated in the deposition of lead adatoms must be used to desorb the substances previously present at the silver substrate. On the other side, bonding of lead adatoms does not depend only on the attractive forces of the silver substrate but also on the forces acting from the solution side. If one takes the difference in adsorption energy of perchlorate on lead and silver as an arbitrary zero, the potential difference between the UPD metal layer in a solution with a more strongly adsorbing substances and in the perchlorate solution must be due to the difference in the energy of adsorption of the substance and of perchlorate ions at (111) silver substrate and that on the UPD layer on lead, e.g., in the case of acetate solutions:

$$\Delta U^0_{(OAC^-/ClO_4^-)} = \{[{}^b\Delta^s G_{OAC^-(adsAg)} - {}^b\Delta^s G_{ClO_4^-(adsAg)}] - [{}^b\Delta^s G_{OAC^-(adsPb)} - {}^b\Delta^s G_{ClO_4^-(adsPb)}]\} \left(\frac{1}{2F}\right) \quad (13)$$

where ${}^b\Delta^s G$ denotes the difference in the free energy of the given substance in the bulk of solution and at the surface. It is seen that the differences are smallest in the case of acetate and increase going to citrate and onto thiourea.

Table. 2. Standard potentials and free energy differences for the UPD of lead on (111) silver substrate in different solutions.

Solution	Perchlorate	Acetate	Citrate	Thiourea
ΔU^0 (V)	0.152	0.136	0.129	0.111
ΔG^0 (kJ)	-29.2	-26.2	-24.8	-21.4

In the cases particularly studied [93,94], the steep portion of Frumkin's isotherm started in the perchlorate solution at coverage around 0.11. in acetate around 0.045 and in the case of citrate around 0.035. These findings would indicate the interaction parameters of 5.5, 6.8 and 7.2, respectively [93]. It was only in the case of solution containing thio-

urea that Frumkin's isotherm with $g=3.34$ fits the isotherm obtained experimentally. It appears that thiourea prevents the formation of 2D solid phase, while instead keeping adatoms in a state of 2D gas not far from the condensation point.

Since in the case of perchlorate solutions experimental Frumkin's isotherm fits experimental one up to approximately 0.55 of the theoretical coverage it must be concluded that "solid phase" lead UPD monolayer on Ag(111) substrate builds closest-packed epitaxial superstructure to start with. It is only when the potential is driven to more negative values that this layer is transformed into close-packed full compact lead UPD monolayer. This phase transition is kinetically controlled, as shown by its dependence on the sweep speeds applied [93,94].

Acetate and citrate seem to stimulate the formation of the close-packed compact UPD monolayer directly; acetate causing such a fast phase formation that one can maintain to be in the reversible domain, while in citrate this is approached only at the lowest sweep speeds (less than 0.2mVs^{-1}).

These conclusions are in accordance with the fact that adhesion with which the 2D phases are held against substrate decreases in the sequence perchlorate $\geq$ acetate $\geq$ citrate $\geq$ thiourea as was shown earlier.

Temperature dependence of underpotential deposition of metals

Linear sweep experiments designed to establish temperature dependence [97] of UPD monolayer formation, for lead UPD on Ag(111) electrode surface from perchlorate and acetate solutions have shown that:

- "reversible UPD monolayer potential" becomes more positive with increasing temperature,
- peak potential of adsorption UPD monolayer formation becomes more negative with increasing temperature,
- potential difference between cathodic and complementary anodic voltammetry UPD peaks becomes smaller with increasing temperature,
- reversible potential of the bulk lead does not change with changing temperature.

Thermodynamics of UPD monolayer formation process is reflected in temperature dependence of reversible UPD monolayer potential through well known thermodynamic relation:

$$\frac{\partial(\Delta G)}{\partial T} = -\Delta S \quad (14)$$

Since:

$$E_{\text{rev}} = -\frac{\Delta G}{zF} \quad (15)$$

then:

$$\Delta S = zF \frac{\partial E_{\text{rev}}}{\partial T} \quad (16)$$

or:

$$\frac{\partial E_{\text{rev}}}{\partial T} = \frac{\Delta S}{zF} \quad (17)$$

Reversible lead UPD monolayer potential being defined by:

$$E_{\text{Pb,mon/Pb}^{+2}} = E_{\text{Pb,mon/Pb}^{+2}}^0 + \frac{RT}{zF} \ln a_{\text{Pb}^{+2}} \quad (18)$$

and reversible bulk lead potential by:

$$E_{\text{Pb,bulk/Pb}^{+2}} = E_{\text{Pb,bulk/Pb}^{+2}}^0 + \frac{RT}{zF} \ln a_{\text{Pb}^{+2}} \quad (19)$$

and activity of lead ions being the same, the difference between two reversible potentials is given by:

$$\Delta E_{\text{rev}} = E_{\text{Pb,mon/Pb}^{+2}}^0 - E_{\text{Pb,bulk/Pb}^{+2}}^0 \quad (20)$$

It was this very potential difference which was measured as a function of changing system temperature and therefore according to Eq. (17):

$$\begin{aligned} \frac{\partial(\Delta E_{\text{rev}})}{\partial T} &= \left\{ \left(\frac{\partial E_{\text{Pb,mon/Pb}^{+2}}^0}{\partial T} \right) - \left(\frac{\partial E_{\text{Pb,bulk/Pb}^{+2}}^0}{\partial T} \right) zF \right\} = \\ &= \Delta S_{\text{Pb,mon/Pb}^{+2}}^0 - \Delta S_{\text{Pb,bulk/Pb}^{+2}}^0 = \Delta(\Delta S^0) \end{aligned} \quad (21)$$

Furthermore:

$$\begin{aligned} \Delta S_{\text{Pb,bulk/Pb}^{+2}}^0 &= S_{\text{soln,Pb}^{+2}}^0 - S_{\text{Pb,bulk}}^0 \\ \Delta S_{\text{Pb,mon/Pb}^{+2}}^0 &= S_{\text{soln,Pb}^{+2}}^0 - S_{\text{Pb,mon}}^0 \end{aligned} \quad (22)$$

and:

$$\begin{aligned} \Delta(\Delta S^0) &= S_{\text{soln,Pb}^{+2}}^0 - S_{\text{Pb,mon}}^0 - S_{\text{soln,Pb}^{+2}}^0 + S_{\text{Pb,bulk}}^0 \\ \Delta(\Delta S^0) &= S_{\text{Pb,bulk}}^0 - S_{\text{Pb,mon}}^0 \end{aligned} \quad (23)$$

Temperature dependence of $\Delta(\Delta S^0)$ evaluated [97] has shown only positive values decreasing with increasing temperature. It must be concluded therefore that since:

$$a_{\text{m(s)}} = f_{\text{m(s)}} \frac{Z}{Z_0} \quad (1)$$

$$\Delta(\Delta S^0) > 0; \text{ then } (S_{\text{Pb,mon}}^0) < (S_{\text{Pb,bulk}}^0)$$

It is difficult to speculate on the structure of the UPD monolayer formed (amorphous or crystalline) relying solely on the absolute value of the entropy change evaluated [97]. However, remains strong evidence that entropy of monolayer formation is smaller than entropy change for bulk lead formation, and that both 3D bulk lead lattice formation and 2D lead UPD monolayer formation are influenced by water molecules release from the lead ion solvation sphere and anion desorption from the silver electrode surface prior to phase formations.

Interdependence of under and overpotential depositions

The results obtained in the work on the UPD and OPD of lead and thallium on copper [80-92], silver [93-98] and vitreous carbon [79] substrates have shown a profound effect of the UPD on subsequent bulk deposition.

The underpotential deposition, UPD process on the copper substrate was a necessary initial stage for lead and thallium deposition and was completed always before the onset of bulk deposition.

This, however, was not the case with the vitreous carbon substrate [79]. Here the extent of the lead UPD was a function of the substrate surface reconstruction induced by the repeated deposition and dissolution of lead, which due to alloying effects increased the number of surface active deposition sites.

In all cases where UPD was present, the nucleation overpotential for the bulk deposition was very small indeed.

It appears that UPD brings about changes in the interfacial energy term governing the rate of the nucleation process [73,108], large enough to make it a predominant factor of influence on the nucleation overpotential. This would lead to higher nucleation rates at very low negative overpotentials observed in this work as well as by some other authors [105-107].

It is interesting to note that surface conditions due to UPD on carbon can be changed so much as to favor 2D instead of 3D nucleation in the case of lead deposition at very low negative overpotentials. That, of course, could be expected on account of the higher dependence of 3D nucleation [68,69,109] on the overpotential applied.

In the case of copper substrate, this effect was not observed but changed surface conditions appeared to be favorable enough to make 3D bulk nucleation proceed at exceptionally low overpotentials [26,47,80-92]. The process of bulk deposition of both lead and thallium on copper obeyed the laws of 3D instantaneous nucleation and growth which confirmed the suggestions made from the results in UPD region about the distortion and molding of the monolayers by the underlying substrate. It appears that the UPD monolayers already present at the substrate before the onset of bulk deposition are to a certain extent still preserving the activity of the nucleation sites existing in the original substrate.

CONCLUSION

The basic applicability of the UPD theory of Gerischer *et al.* [28,29] has been confirmed in the case of lead and thallium deposition on copper and silver single crystals, but it was shown also that this is only one of the important factors.

It was established that the effect of substrate structure on the mechanism of the UPD monolayer formation plays an important role in the addition to the effect of electronegativity difference between the substrate and depositing atoms.

An effect of changing the concentration of depositing metal and specifically adsorbing anion were found and attributed to the changes in the electronegativity of the substrate and underpotential layer as a result of changing the electrode potential.

It was conclusively proven by the analysis of the peaked current-time transients obtained by potential step measurements and the very sharp voltammetry peaks, that first order 2D phase transformations are possible in UPD systems. It was also found that the

L.S.V. peaks reflecting such processes must not be expected to be free from the influence of slow kinetics.

It was established that the 2D crystalline metal-like phases with the closest-packed epitaxial structure exist as a stable, final product in UPD. Moreover, the possibility of higher order 2D transformations in UPD has been given strong support by the evidence of gradual monolayer density change with increasing driving force.

Lead UPD on vitreous carbon was found to be the result of substrate reconstruction induced by the repeated deposition and dissolution leading to surface condition changes favoring deposition of the first layer.

UPD monolayers on copper and silver surfaces always preceded OPD and had a profound effect on its nucleation overpotential (making it very small indeed) or even changing its character from 3D into 2D (in the case of vitreous carbon substrate). It was also shown that lead and thallium OPD on copper and silver single crystals starts off by charge transfer controlled instantaneous 3D nucleation and subsequent growth of 3D centers.

Finally, the results obtained in the experiments performed have shown that electrochemical techniques can prove very suitable in the study of 2D phase transformation kinetics and that their further employment in this field should prove particularly rewarding.

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STUDIJA POČETNOG STADIJUMA ELEKTROTALOŽENJA METALA NA STRANIM METALNIM PODLOGAMA: OLOVO I TALIJUM NA BAKRU I SREBRU - OPŠTA DISKUSIJA

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Ovo je petnaesti iz serije radova u kojima se iznose rezultati istraživanja početnih stadijuma elektrotaloženja olova i talijuma (iz sulfatnih, perhloratnih, acetatnih, nitratnih, citratnih rastvora uz i bez dodatka tiouree) na polikristalnom i monokristalnom bakru, srebru i staklastom grafitu. Rad predstavlja diskusiju već objavljenih rezultata dobijenih metodama ciklične voltametrije, jednostrukog, dvostrukog i trostrukog potenciostatskog pulsa na polikristalnim i monokristalnim bakarnim i srebrnim elektrodama površinske kristalografske orijentacije (111), (110) i (100).

Potvrđena je osnovna primjenjivost teorije Gerischer et al. o elektrotaloženju metala pri potencijalima pozitivnijim od reverzibilnog na elektrotaloženje olova i talijuma na srebrnim i

bakarnim polikristalima i monokristalima, ali je također pokazano da je činilac od uticaja dat tom teorijom samo jedan od važnih faktora. Ustanovljeno je da je pored razlike u elektronegativnosti između metala koji se taloži i metala na koji se taloži (što predviđa pomenuta teorija) i struktura površine podloge od velikog uticaja na mehanizam formiranja monosloja nastalog pri potencijalima pozitivnijim od reverzibilnog. Ustanovljen je efekat promjene koncentracije elektrotaloženog metala i uticaj specifično adsorbovanih aniona na termodinamiku i kinetiku formiranja monosloja pri potencijalima pozitivnijim od reverzibilnog i pripisani promjeni elektronegativnosti podloge i monosloja uslijed promjene elektrodnog potencijala. Ustanovljena je zavisnost formiranja monoslojeva pri taloženju metala pri potencijalima pozitivnijim od reverzibilnog od temperature i objašnjena promjenama do kojih dolazi u termodinamici procesa uslijed promjene solvatacionog omotača taloženog jona i solvatacionog sloja podloge (adsorbovani anioni i rastvarač). Uvjedljivo je dokazano, analizom rastućih odgovora struje = $f(t)$ na potenciostatske pulsne izazove i veoma oštih voltametrijskih strujnih talasa, da su dvodimenzionalne fazne transformacije prve vrste moguće u sistemima nastalim taloženjem pri potencijalima pozitivnijim od reverzibilnog. Također je pokazano da se od strujnih talasa koji pri cikličkoj voltametriji odražavaju takve procese ne može očekivati da budu potpuno neosjetljivi na uticaj spore kinetike tih procesa. Ustanovljeno je i da dvodimenzionalne kristalne metalu-slične faze sa najgušće pakovanom epitaksijalnom strukturom postoje kao stabilan i krajnji proizvod elektrotaloženja pri potencijalima pozitivnijim od reverzibilnog, čak šta više, mogućnost dvodimenzionalnih transformacija višeg reda u strukturama nastalim pri potencijalima pozitivnijim od reverzibilnog dobila je snažnu podršku u eksperimentalnim dokazima o postepenoj promjeni gustine monosloja sa povećanjem vučne sile procesa. Ustanovljeno je također, da elektrotaloženje olova pri potencijalima pozitivnijim od reverzibilnog na staklastom grafitu predstavlja rezultat rekonstrukcije površine podloge uslijed ponovljenog taloženja i rastvaranja olova koje vodi promjeni površinskih uslova u pravcu favorizovanja taloženja prvog sloja olova. Monoslojevi olova i talijuma formirani pri potencijalima pozitivnijim od reverzibilnog uvijek predhode elektrotaloženju istog metala uz katodne prenapetosti i od suštinskog su uticaja na njihovu prenapetost nukleacije (značajno je smanjujući) ili čak mijenjajući njen karakter iz 3D u 2D (u slučaju podloge od staklastog grafita). Rezultati dobijeni u razmatranim eksperimentima pokazali su da elektrohemijske tehnike mogu biti veoma primjerene proučavanjima formiranja 2D faza i njihovih transformacija, posebno ukoliko se podloge na koje se vrši elektrotaloženje pažljivo pripreme.