

## A study of the morphological aspects\* of the indium electrorefining process

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The cathodic deposition of In was performed under conditions suitable for electrorefining purposes. The main goal of the study was: i) to determine the possibilities for In ultrapurification through multiple electrorefining with controlled parameters and ii) to study the regularities of the morphology of the In deposit as influenced by the electrodeposition conditions. Without application of special high purity techniques, it was possible to obtain an In purity level of 99.997 %, by repeating the refining procedure in a set of modular electrolysis cells with forced electrolyte circulation and applying modified current regimes. Irregular (non planparallel) migration of indium from the anode to the cathode and *vice versa*, as well as dendrite formation at the edges of the electrode prevented further repetition necessary for the achievement of higher purification levels. This provoked the need to study the morphology of the In-deposits. The phenomena and some regularities of In nucleation and grain growth, as influenced by the applied overpotential and quantity of current passed through the cell, were studied. Electrodeposition was performed onto a stationary Pt-electrode from a mixed sulfate–chloride solution. SEM with magnification up to 1000 × was used to identify the morphology of the deposits. Granular grains were dominant at overpotentials of 85 and 110 mV, while at 160 and 185 mV, needle-like and nonbranched dendrites were visible. The deposit became less compact as its thickness advanced. The apparent thickness of the In layer increased from 20–25 to 320–380 μm when the amount of charge was increased from 1 to 10 mA h cm<sup>-2</sup>.

*Keywords:* In, electrorefining, ultrapurification, SEM, morphology, dendrites.

### INTRODUCTION

In our previous papers,<sup>1–4</sup> the results of a study of the morphology of silver electrodeposits, as influenced by the electrolysis regime, *i.e.*, the value of the applied overpotential, the hydrodynamic regime and the electrolyte composition were presented. Surprisingly, favorable conditions for the deposition of thick, smooth and al-

\* Dedicated to Professor Dragutin M. Dražić on the occasion of his 70th birthday.

most dendriteless silver layers were achieved when phosphate ions were added to the electrolyte, composed to meet the requirements of silver electrorefining.<sup>5</sup> The whole course of the silver deposition was visualized by use of SEM, so that it was possible to distinguish the initial step (nucleation) from the subsequent steps of crystal growth. The measured density and regularity of nuclei formation was successfully attributed to and explained in terms of the existence of zones at the cathode surface where nucleation was not possible due to the screening effect of protruding crystallites.<sup>1</sup>

The knowledge and understanding of the restrictions existing in nuclei formation were further improved and confirmed when the phenomenon of phosphate ions addition was explained in terms of its effect on the  $i_o/i_L$  ratio. Experimental evidence was obtained that showed that  $\text{PO}_4^{3-}$ -ions lower the exchange current density,  $i_o$ , and proportionally squeeze the radius of the zones of zero probability of nucleation.

In this study, the same procedure was applied to study the morphology of indium electrodeposited under conditions suitable for electrorefining purposes.<sup>7</sup> In doing so, our previous interest in the ultrapurification of In,<sup>8</sup> a process manifold dependent on the morphology of the deposit, was continued.

#### EXPERIMENTAL

Electrorefining of indium was performed from both sulfate and chloride electrolytes in a variety of three different cells (a cell with monopolar electrodes only and a stationary electrolyte, a cell with bipolar electrodes and a stationary electrolyte and a set of modular cells connected in series with forced electrolyte circulation). In order to achieve higher purification, the refining procedure was repeated up to 6 times by switching the cell polarity. A current density of only  $15 \text{ mA cm}^{-2}$  was applied, a value achievable with minor displacement from the equilibrium potential (less than 50 mV, see Fig. 1), so that anodic dissolution of more noble impurities and cathodic deposition of less noble cations, is expected to take place with a rather limited number of metallic species. Modified current regimes, pulsating and reversing ones, were applied in some cases, as specified. Different techniques for the stirring or circulation of the electrolyte were applied.

The morphology was studied on In deposited onto a Pt electrode (wire, 0.5 mm in diameter) from a  $0.5 \text{ mol dm}^{-3} \text{ In}_2(\text{SO}_4)_3$  in  $80 \text{ g dm}^{-3} \text{ NaCl}$  solution. Open cells at room temperature were used, as well as analytical grade chemicals and doubly distilled water. Indium was deposited under potentiostatic conditions at overpotentials of 85 to 185 mV, using a counter electrode of pure indium and a SCE as the reference one. Constant quantities of electricity ( $1$  or  $10 \text{ mA h cm}^{-2}$ ) were passed through the cell at the given overpotential. Scanning electron microscopy (JOEL 35 CF) was used for microstructure observation and documentation.

#### RESULTS

##### *General features of the morphology of In deposits*

The general shape of a polarization curve, taken in  $0.5 \text{ mol dm}^{-3} \text{ In}^{3+}$ -ions under quasistationary conditions, is shown in Fig. 1. The most important feature of In deposition is that it occurs under activation control over a rather limited potential range of *ca.* 200 mV, followed by diffusion control. This phenomenon is obviously due to the fact that the difference between the exchange current density and the limiting current density under the applied conditions is rather small. Thus, in order to control dendrite formation, the cathodic deposition of In has to be performed over a narrow potential range, before the onset of significant diffusion limitations.

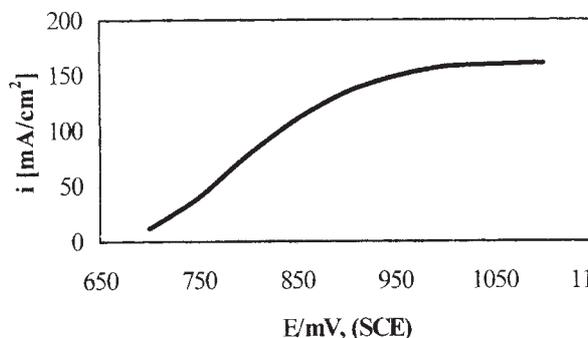


Fig. 1. Polarization curve for In deposition onto a Pt substrate from  $0.5 \text{ mol dm}^{-3} \text{ In}_2(\text{SO}_4)_3 + 80 \text{ g dm}^{-3} \text{ NaCl}$ .

Nevertheless, when deposition occurs under constant current conditions, as is usually the case when performing technical electrolysis, dendritic growth occurs even at small values of the current density.<sup>9</sup> In order to improve the compactness of the deposit, modified DC regimes and/or stirring were applied, both of which lead to higher values of the In-ion concentration at the cathode.

Indium deposits produced by reversed current (applying an AC of 50 Hz on top of a cathodic DC, so that the ratio of the voltage peaks is  $U_c:U_a = 7:1$ ) are shown in Fig. 2. Current reversal helps a great deal in reducing the growth of dendrites, as can be seen in Fig. 2a, which was taken at a current density of  $15 \text{ mA cm}^{-2}$ . When  $30 \text{ mA cm}^{-2}$  were applied, dendritic growth was again evidenced, as shown in Fig. 2b.

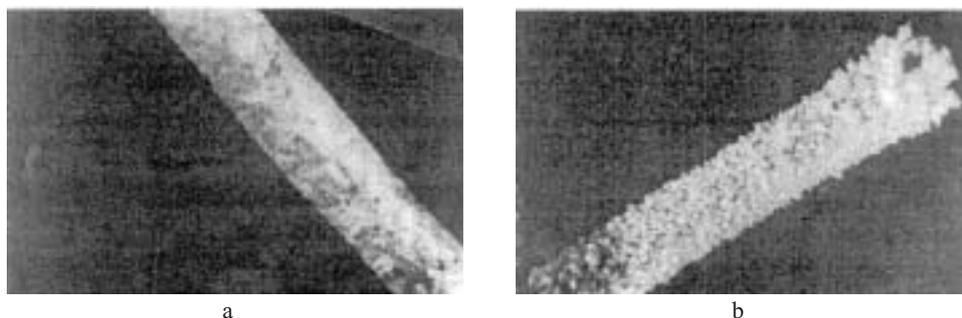


Fig. 2. In deposited from  $0.5 \text{ mol dm}^{-3} \text{ In}_2(\text{SO}_4)_3$  using reversed AC with  $U_c:U_a = 7:1$ , magnetic stirrer,  $20^\circ \text{C}$ : a)  $15 \text{ mA cm}^{-2}$ ; b)  $30 \text{ mA cm}^{-2}$ .

A further decrease of the  $U_c:U_a$  ratio, as well as of the current density, favors the formation of more smooth In deposits (Fig. 3). In this case multiple (2 to 4-ply) electrolysis with bipolar electrodes was applied. Problems, such as electrode perforation (Fig. 3a), or even non-uniform dissolution and (re)deposition (Fig. 3b) are evident, corresponding to lower and higher cathodic to anodic pulse voltage ratios, respectively.

Finally, when the electrorefining procedure was repeated in a set of moduled cells where forced electrolyte circulation is feasible, the morphology of the deposit was further improved towards more compact and smoother deposits, as shown in Fig. 4 taken at  $20 \text{ mA cm}^{-2}$  at  $U_c:U_a = 4:1$  and  $5:1$ , respectively. The achieved level of purity (99.997

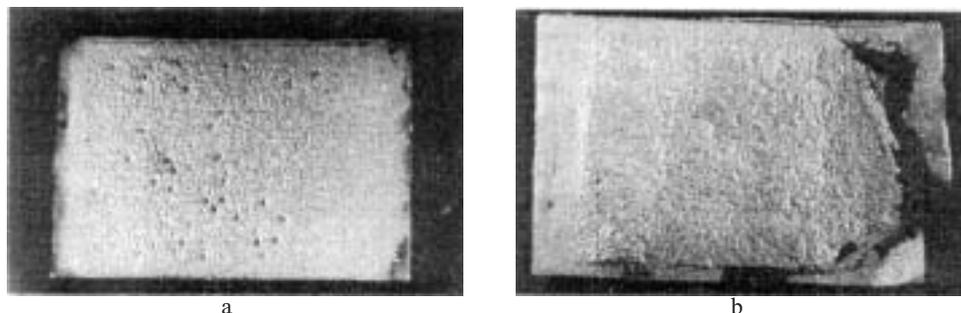


Fig. 3. In deposited from  $0.5 \text{ mol dm}^{-3} \text{ In}_2(\text{SO}_4)_3$  at  $8 \text{ mA cm}^{-2}$  reversed current,  $20^\circ\text{C}$ , without stirring in a cell with bipolar electrodes: a)  $U_c:U_a = 5:1$ ; b)  $U_c:U_a = 1.5:1$ .

% In), identified by glow-discharge mass spectrometry, after triple refining starting with anodes of *ca.* 99 % In is shown in Table I.

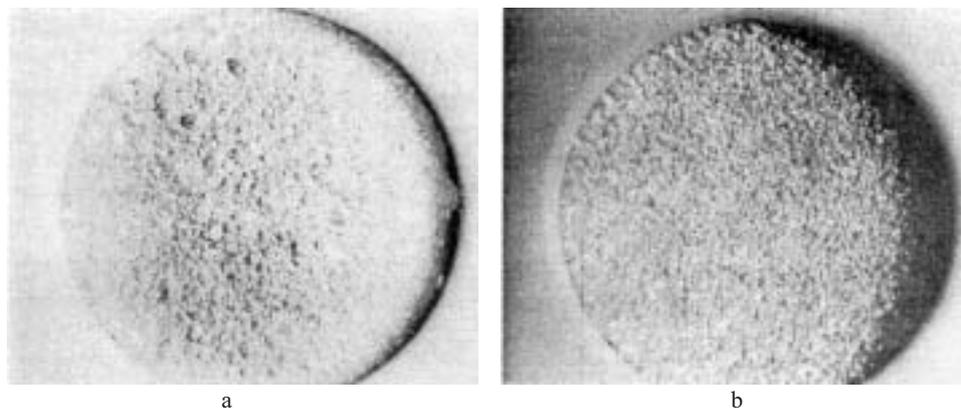


Fig. 4. In deposited from  $0.5 \text{ mol dm}^{-3} \text{ In}_2(\text{SO}_4)_3$  in a modular cell with forced electrolyte circulation at  $20 \text{ mA cm}^{-2}$  and  $20^\circ\text{C}$ : a)  $U_c:U_a = 4:1$ ; b)  $U_c:U_a = 5:1$ .

TABLE I. Composition of In-deposits after triple electrorefining

Impurity	Pb	Sn	Fe	Ni	Tl	Mg	O	F	Si	Cd	Co	Cu	Zr	Ag	In
Content/ppm	11	7	3	2	1	1	1	0.9	0.9	0.8	0.6	0.5	0.5	0.3	major

#### *Some regularities in the formation of In-nuclei*

It is obvious that results presented in Figs. 2–4 are rather qualitative ones, demonstrating some general trends in the morphology of the deposits. In order to obtain a more precise and, possibly, quantitative insight into the parameters defining the morphology of produced deposits, experiments were conducted aimed at demonstrating the very first step in the deposition of In, *i.e.*, the formation of In-nuclei.

A series of microphotographs aimed at demonstrating the effect of increasing the In-deposition overpotential on the electronucleation when In was deposited from  $0.5 \text{ mol dm}^{-3} \text{ In}^{3+}$  ions onto a Pt substrate are shown in Fig. 5.  $1 \text{ mA h cm}^{-2}$  is the quantity

of electricity large enough to deposit a layer of In crystallites covering the substrate almost uniformly, except on the spot where bubbles of co-deposited  $H_2$  blocked the cathode surface. Increasing the overpotential from 85 to 185 mV causes the crystallites to become sharper and even to transform into needles (possibly dendrite precursors). The size of the bubble traces changes irregularly with increasing overpotential, but their number grows without any doubt. In order to observe the individual grain shape better, a magnification of 1000 $\times$  instead of the previous 150 $\times$  is needed, as is shown in Fig. 6 (to be compared with Fig. 5d, taken at 185 mV overpotential). Pyramids are the most frequent crystallite shape. It is important to stress that the pore bottom in this case is not bare, but covered with crystallites much smaller than the neighboring visible ones.

Further growth of the so formed grains was studied after 10 times more electricity had been passed through the cell, as is shown in Fig. 7, for the same overpotentials as in Fig. 5. The deposits are much thicker than the ones in Fig. 5 (typically 320 to 380  $\mu m$  with 10 mA h  $cm^{-2}$ , as compared with only 20 to 25  $\mu m$  with 1 mA h  $cm^{-2}$ ). They are bulky, shallow and composed of mixed crystals of different crystallographic origin. Pores are less visible, probably due to the overlapping of randomly grown neighboring crystals or to their real disappearance due to subsequent nucleation and growth of nuclei (Fig. 6). The grains formed at overpotentials up to 160 mV are granular in shape. Needle-like crystals are visible in deposits formed at 185 mV.

Again, the structure of the deposits is better visible at larger magnifications. Crystals deposited at 160 and 185 mV (200 $\times$ , Fig. 8) form needles and carrots. Higher

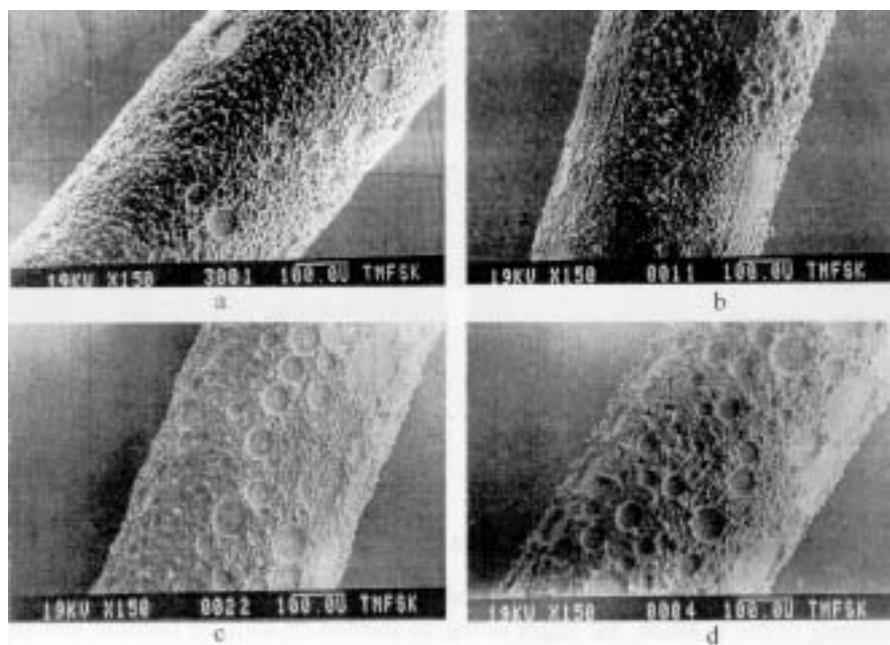


Fig. 5. In deposited on a Pt wire from  $0.5 \text{ mol dm}^{-3} \text{ In}_2(\text{SO}_4)_3 + 80 \text{ g dm}^{-3} \text{ NaCl}$  at  $20^\circ \text{C}$  with  $1 \text{ mA h cm}^{-2}$  at an overpotential of: a) 85 mV; b) 135 mV; c) 160 mV and d) 185 mV. Magnification 150 $\times$ .



Fig. 6. Same as Fig. 5d, but magnification: 1000 $\times$ .

overpotentials are probably needed for the appearance of branched dendrites. At higher magnification (500 $\times$ , Fig. 9), the transition from granular to dendritic and needle-like growth can be seen to occur between 135 and 160 mV, while the random growth of sharp needles is visible at 210 mV.

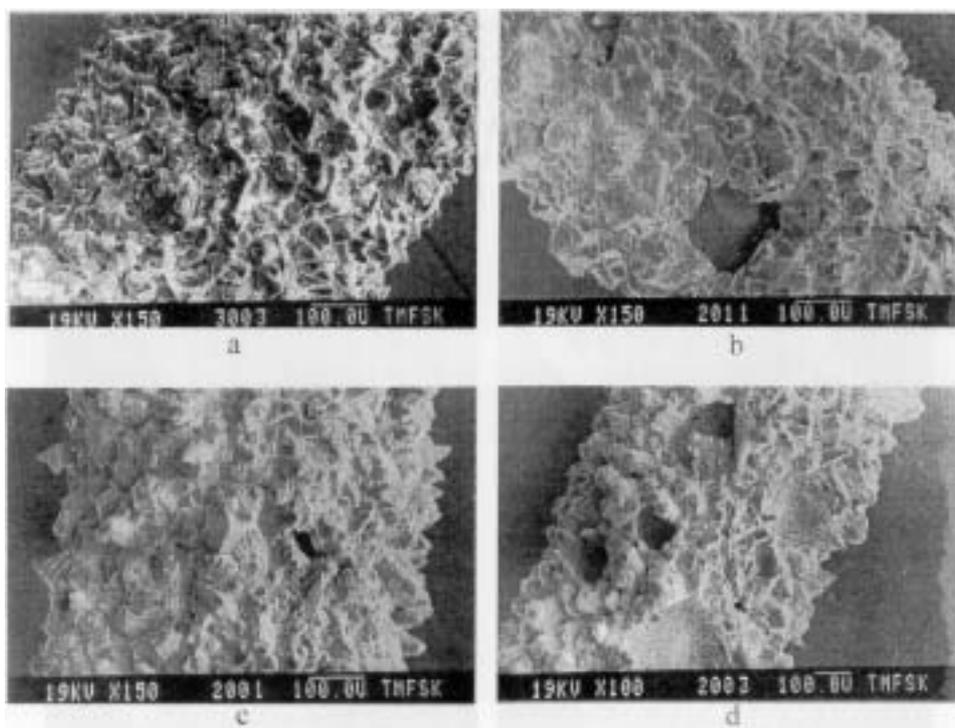


Fig. 7. Same as Fig. 5, but with 10 mA h cm<sup>-2</sup>: a), b) and c) magnification 150 $\times$ ; d) magnification 100 $\times$

When the in depositions were repeated under the same conditions, but with intensive stirring of the solution, the edges of the so-formed crystallites become less sharp and the number of pores between the crystallites becomes smaller. There is a sound reason to believe that this is due to the increase in the  $i_L/i_0$  ratio when stirring is applied, as

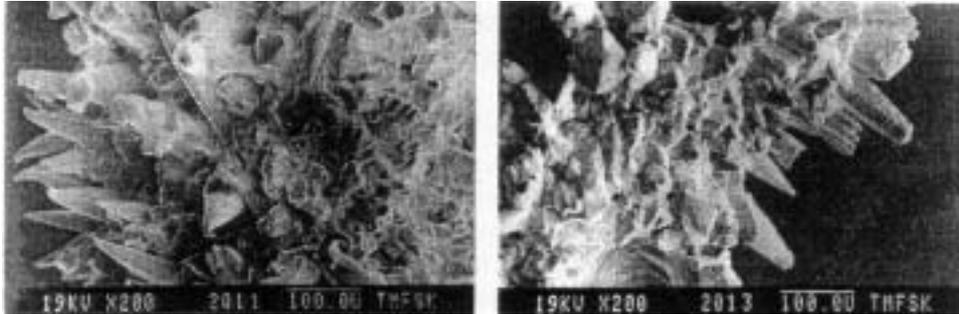


Fig. 8. Same as Fig. 7 but at an overpotential of: a) 160 mV and b) 185 mV. Magnification 200 $\times$ .

was the case with the morphology of silver deposits but experimental proof for such a statement still has to be produced.

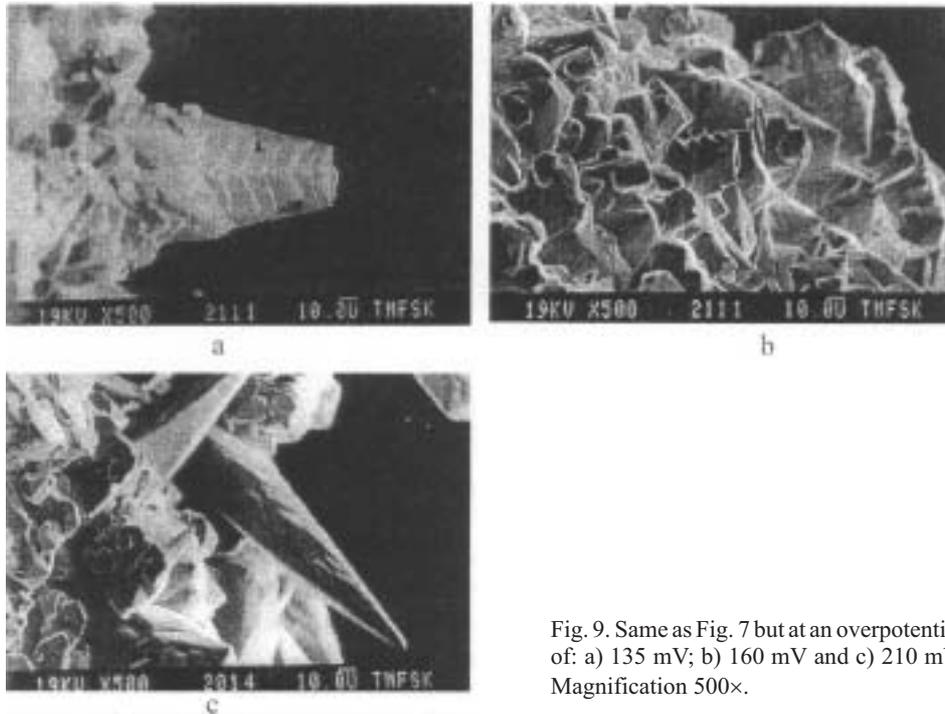


Fig. 9. Same as Fig. 7 but at an overpotential of: a) 135 mV; b) 160 mV and c) 210 mV. Magnification 500 $\times$ .

The explanation of observed changes in In-deposits morphology, *i.e.*, that the shape of In-grains passes from granular into needle-like and finally into flat dendritic forms and that the nucleation's surface density changes with the rise of overpotential, together with the mentioned effect of electrolyte stirring, is the same as in the case of silver deposition. Zones of zero nucleation probability exist around each growing crystal, their radius being defined by the expression proposed by Markov *et al.*<sup>10</sup> The situation

with In deposits is further complicated by the inclusion of hydrogen bubbles in the deposit, thus forming macropores besides the micro ones.

#### CONCLUSIONS

The morphology phenomena observed during the In-electrodeposition from sulfate-chloride solution are described. When indium is deposited under conditions similar to those for electrorefining, different grain shapes appear the nature of which are influenced by the applied overpotential, the In-ion concentration at the cathode surface and hydrodynamic conditions of the electrolyte.

When the total course of the electrolysis was followed, it was possible to diminish dendritic growth of the deposit by applying current reversal and effective electrolyte stirring/circulation. When only small amounts of current were passed through the cell, it was possible to create relatively smooth granular films, 20 to 25  $\mu\text{m}$  in thickness, but with ten times higher quantities of current, the thickness of the layers increased unproportionally to values of 320 to 380  $\mu\text{m}$ . We succeeded in visualizing a part of the morphology of the In deposits, but we did not succeed in producing smooth In deposits with the applied set of experimental conditions. It could be expected that a combination of both applied techniques (modification of the current pulses and intensive stirring, as well as control of the applied overpotential) would be more effective in achieving the desired goal – the creation of smooth and dendriteless surface of In-deposits, which would be advantageous for In ultrapurification purposes.

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#### ИЗВОД

##### ПРОУЧАВАЊЕ МОРФОЛОШКИХ АСПЕКТА У ПРОЦЕСУ ЕЛЕКТРОРАФИНАЦИЈЕ ИНДИЈУМА

СВЕТОМИР ХАЦИ ЈОРДАНОВ, АЛЕКСАНДАР ДИМИТРОВ, ПЕРИЦА ПАУНОВИЋ  
и ДРАГАН СЛАВКОВ

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Катодно таложење In извођено је у условима погодним за сврхе електрорафинације. Циљ проучавања био је 1) одређивање могућности за ултрапречишћавање In вишеструком електрорафинацијом при контролисаним параметрима и 2) проучавање правилности морфологије талога In под утицајем услова електроталожења. Постигнут је квалитет In 99,997 % без примене специјалних техника високе чистоће понављањем процеса рафинације у сету модуларних електролитичких ћелија са принудном циркулацијом електролита и применом модификованих струјних режима. Нерегуларна миграција In од аноде ка катоди и обратно, као и стварање дендрита на ивицама електроде ограничили су понављање и постизање већег степена чистоће, намећући потребу за проучавањем морфологије талога In. Проучаван је утицај пренапетости и протекле количине наелектрисања на нуклеацију и раст зрна In. Електроталожење је вршено на

стационарној Pt електроди из мешаног раствора сулфата и хлорида. Морфологија талога је испитивана техником SEM са увећањем до хиљаду пута. На пренапетостима од 85 и 110 mV у талогу су доминирала грануларна зрна, док су на пренапетостима 160 и 185 mV виђени игличасти и негрануларни дендрити. Са повећањем дебљине талога смањивала се његова компактност. Пропуштањем количине наелектрисања између 1 и 10 mA h cm<sup>-2</sup> повећавала се привидна дебљина слоја In од 20–25 на 320–380 μm.

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