

## The role of surface defects in HOPG on the electrochemical and physical deposition of Ag

S. ŠTRBAC,<sup>1</sup> Z. RAKOČEVIĆ,<sup>2</sup> K. I. POPOV,<sup>3</sup> M. G. PAVLOVIĆ<sup>1</sup> and R. PETROVIĆ<sup>4</sup>

<sup>1</sup>ICTM-Institute of Electrochemistry, University of Belgrade, P.O.Box 815, YU-11001 Belgrade, <sup>2</sup>Vinča Institute of Nuclear Sciences, P.O.Box 522, YU-11001 Belgrade, <sup>3</sup>Faculty of Technology and Metallurgy, University of Belgrade, P.O.Box 3503, YU-11020 Belgrade and <sup>4</sup>ICTM-Institute of Microelectronic Technologies and Single Crystals, University of Belgrade, P.O.Box 815, YU-11001 Belgrade, Yugoslavia

(Received 26 February 1999)

The role of defects on a substrate surface during the initial stages of nucleation and growth of Ag deposited electrochemically and physically on highly oriented pyrolytic graphite (HOPG) has been observed *ex situ* by scanning tunneling microscopy (STM). The silver was electrodeposited under current controlled electrochemical conditions at  $26 \mu\text{A}/\text{cm}^2$ , which corresponded to a deposition rate of 0.1 monolayers (ML) per second. For comparison, physical deposition of Ag on HOPG was performed by DC  $\text{Ar}^+$  ion sputtering, at the same deposition rate and for the same deposition times. In both cases, Ag grows in an island growth mode, but the distribution of the islands appears to be quite different. In physical deposition, the Ag islands are almost homogeneously distributed over the substrate surface and a slight accumulation of islands on steps does not contribute significantly to the overall morphology. This indicates the crucial role of point defects on the substrate in the initial stages of nucleation. In electrochemical deposition, more line defects are observed after a flow of current, and their role in the beginning of the nucleation is more pronounced. Lined defects are responsible for the string-like shaped domains of deposited atoms. Also, the existence of string-like shaped nucleation exclusion zones is indicated. The problem of the formation of nucleation exclusion zones, which appear only in electrochemical deposition, has been reconsidered and a new explanation of their formation is given. A mathematical model for the calculation of the radius of the nucleation exclusion zone has been developed.

*Key words:* surface defects, electrodeposition, silver, HOPG, scanning tunneling microscopy.

The process of nucleation during electrochemical metal deposition on a foreign substrate occurs at active surface sites, which are supposed to be defects. Preferential nucleation at steps has been directly evidenced by the STM technique<sup>1</sup> for a number of investigated systems. Also, it has been proved experimentally by different techniques that, in physical deposition, surface defects take part in the beginning of the nucleation process.<sup>2-6</sup>

We will focus here on the role of defects on the substrate surface during the electrochemical deposition of Ag on a HOPG surface. The Ag/HOPG system is convenient for such studies due to the weak substrate-deposit interaction and the different types of easily recognizable defects on the mainly flat substrate surface.

Previous *in situ* STM observations under potential controlled electrochemical conditions have shown that at low overpotentials Ag is deposited preferentially at step edges and other surface defects, and that three-dimensional (3D) clusters are formed at the surface defects during the initial stages of Ag deposition.<sup>7,8</sup> The initial deposition kinetics, whose evolution was based on electrochemical measurements, has been described by a model involving progressive nucleation on active sites and diffusion controlled three-dimensional growth.<sup>8</sup>

A crucial task of this work was to observe the influence of the type and size of defects on the distribution of clusters created in the initial stages of nucleation and growth of Ag on electrochemically deposited HOPG and to compare it with Ag physically deposited on HOPG. Therefore, the electrodeposition of Ag was performed under current controlled conditions since the current density can be regarded as a parameter corresponding to the deposition rate. The surface morphologies were compared for Ag deposited by the two methods at the same deposition rate and for the same deposition time.

The first efforts to obtain *in situ* STM images of Ag on HOPG under potential<sup>9</sup> and current<sup>10</sup> controlled electrochemical conditions, showed that the tip could affect the deposition morphology. Therefore, the morphology of the deposit was observed by STM *ex situ*, after each galvanostatic pulse applied on a freshly cleaved HOPG substrate. The nucleation and growth of the electrochemically deposited Ag was followed up to the formation of a grain. We have also tried to explain the formation of nucleation exclusion zones, which appear only during electrochemical deposition.

## EXPERIMENTAL

Silver was electrodeposited on freshly cleaved HOPG surfaces from silver nitrate solutions (0.1 M AgNO<sub>3</sub>+0.5 M NaNO<sub>3</sub>). The electrodeposition was carried out galvanostatically with a very low current density (0.26 μA/cm<sup>2</sup>), which corresponded to a deposition rate of 0.1 ML/s for various pulse durations (5–60 s) (ML = monolayer).

Physical deposition of Ag on freshly cleaved HOPG surfaces was performed by DC Ar<sup>+</sup> ion sputtering in a commercial vacuum system Perkin-Elmer 2400. The partial pressure of Ar during the deposition was  $p = 2 \times 10^{-6}$  mbar. The deposition rate was  $R = 0.1$  ML/s or about  $1.1 \times 10^{14}$  species/cm<sup>2</sup> s. The temperature of the holder was estimated to be 19 °C.

The samples were analyzed by STM in air at room temperature. The microscope used was a commercial Nanoscope III instrument (Digital Instruments, Inc.). The STM images were obtained in the constant-height mode using a Pt–Ir tip. A set-point current  $I_t$  ranging from 4.0 nA to 20.0 nA and bias voltages  $V_b$  from 13.0 mV to 26.0 mV were used.

## RESULTS

*The electrochemical deposition of Ag on HOPG*

The initial freshly cleaved HOPG surface, as well as the HOPG surface in nitrate solution before current flow appeared to be mainly flat. Lined defects present on the HOPG surface were steps usually present at the initial surface and corrugations which were observed only after the deposition process. Figure 1 shows the corrugations on part of the HOPG surface a subjected to a flow of current for the shortest deposition time but not covered with a deposit. The origin of such corrugations will be the subject of separate investigations.

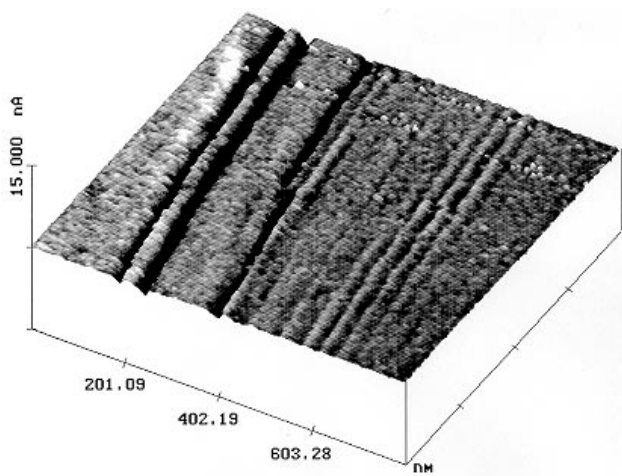


Fig. 1. Corrugations at a part of the HOPG surface not covered with depositing atoms obtained after a current flow.

Larger scale STM images showing the various stages of growth obtained after current pulses of different duration are presented in Fig. 2.

After shorter deposition times (5–15 s), the clusters created occupy small domains of the surface, while the major part of the initial surface remains uncovered. In Fig. 2a, a typical STM image is presented. The observed clusters are mainly aligned in the same direction and arranged into string-like domains of the deposit with the elongation of the strings in different directions, Fig. 2a, while in the surrounding region several randomly distributed 3D clusters are observed. The further growth and coalescence of strings into ensembles is obtained after 30 s of the deposition, Fig. 2b. Longer deposition leads to the formation of grains surrounded by empty domains, Fig. 2c.

We suppose that the ensembles of strings are active sites for the formation of the new metal phase on the foreign substrate, which means that more nucleation centers are required for the formation of a grain around which the zones are being formed, where practically no nucleation occurs. The appearance of these zones during nuclei growth on a foreign substrate is well known and they are called nucleation exclusion zones.<sup>11</sup> A possible explanation for their appearance will be given below.

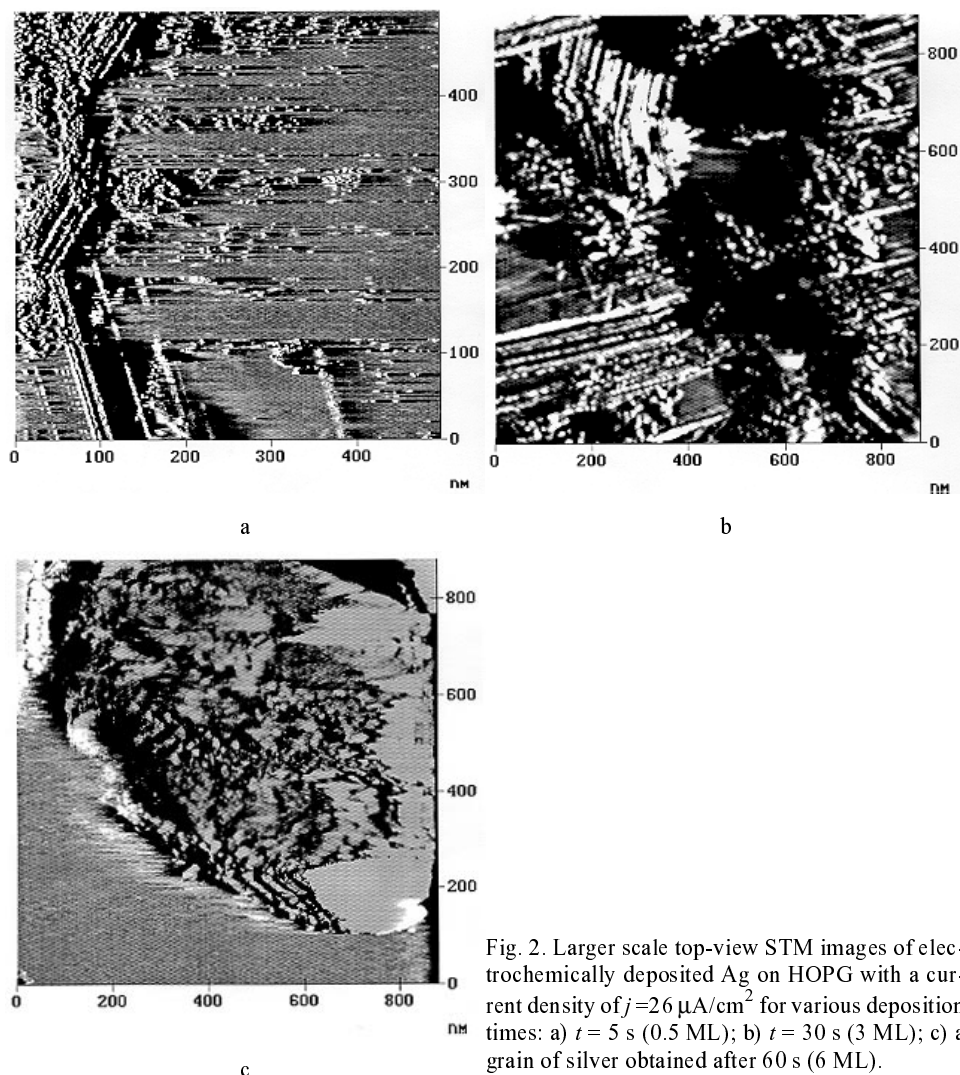


Fig. 2. Larger scale top-view STM images of electrochemically deposited Ag on HOPG with a current density of  $j=26 \mu\text{A}/\text{cm}^2$  for various deposition times: a)  $t = 5 \text{ s}$  (0.5 ML); b)  $t = 30 \text{ s}$  (3 ML); c) a grain of silver obtained after 60 s (6 ML).

The alignment of 3D clusters in the same direction and their coalescence into strings indicates the importance of lined defects during the nucleation process. The smaller-scale STM image, shown in Fig. 3, was obtained after a deposition time of 5 s, by scanning over the areas where a string like deposit was obtained. One can see that these areas consist of separated 3D clusters situated along lined defects, which gives rise to the pearl like structure of the strings. However, from such top-view images, the real nature of the lined defects cannot be clearly resolved.

From atomic-resolution surface plot STM images, Fig. 4, the condensed 3D clusters situated along the steps, (Fig. 4a), and along the corrugations, (Fig. 4b), can be easily distinguished. It should be pointed out that nucleation does not occur

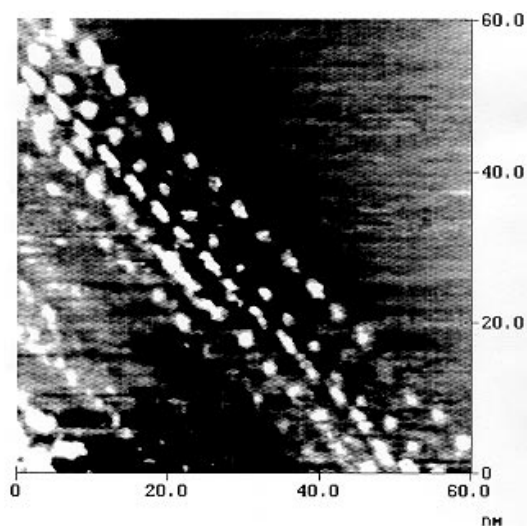


Fig. 3. Smaller-scale top-view STM image obtained after a deposition time of 5 s by scanning over the string-like shaped domains of depositing atoms showing the pearl-like arrangement of 3D Ag clusters..

among the strings which could be regarded as lined nucleation exclusion zones. Also, 3D islands, grown on a flat part of the surface nucleate in the vicinity of point defects, can be easily recognised on such images. Therefore, lined defects on the substrate surface are responsible for the string-like shaped domains of deposited atoms which are separated by string-like shaped nucleation exclusion zones.

#### *The physical deposition of Ag on HOPG*

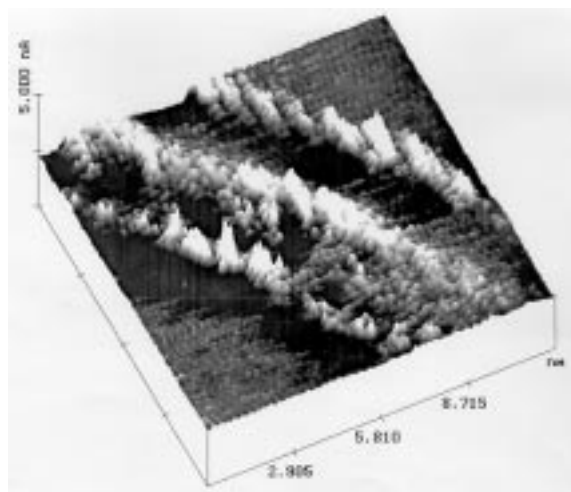
Larger scale ( $200 \times 200$ ) nm<sup>2</sup> STM images of physically deposited Ag on HOPG, obtained after a deposition time of 30 s, are presented in Fig. 5. It is important to note that the silver grows in an island growth mode with the islands almost homogeneously distributed over the substrate surface, Fig. 5a, while a slight accumulation of clusters on the steps, Fig. 5b, does not contribute significantly to the overall morphology. No exclusion nucleation zones were observed.

### DISCUSSION

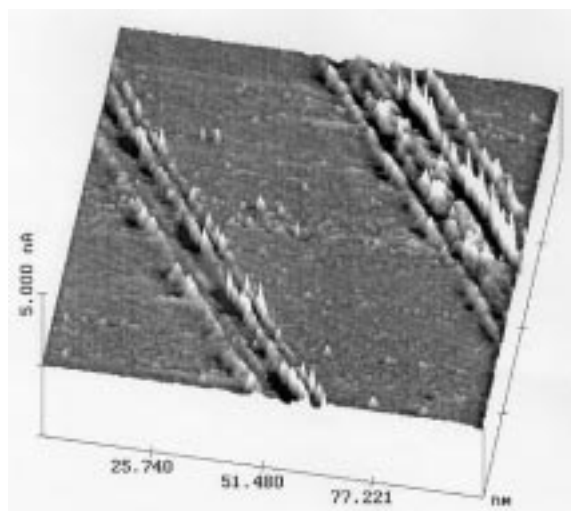
According to the presented results, one can see that, although deposited Ag grows on HOPG in an island growth mode in both electrochemical and physical deposition, there is a significant difference in the distribution of islands over the surface. Possible reasons for such behavior will be considered below.

#### *Surface defects as active sites in physical deposition*

In physical deposition, the sputtered Ag atoms reach the substrate surface equally from all directions. Once they are on the surface, the process of surface diffusion of the Ag adatoms is responsible for their further distribution over the surface and for the creation of clusters. The nucleation processes occur according to a previously presented model,<sup>4</sup> which assumes that all defects present on the surface are active sites for nucleation to begin.



a



b

Fig. 4. Atomic-resolution surface-plot STM images showing: a) 3D Ag clusters situated along the steps; b) 3D Ag clusters situated along the corrugations.

#### *The influence of surface defects on the deposition rate in electrochemical deposition*

In electrochemical deposition, the flow of depositing ions is governed by the potential difference between the electrodes. Let us assume that the electrical field between the electrodes is not homogeneous, *i.e.*, that the equipotential surfaces in the vicinity of the electrode are not straight lines and that they follow the surface morphology. As a consequence, the current lines, which are normal to the equipotential surfaces, deviate from straight lines in the vicinity of the electrode surface, which affects the local deposition rate. For low overpotentials, or low current densities, Fig. 6a, the equipotential surfaces follow the shape of the largest defects on the surface. Around the defects, the density of the current lines is very high (the tip effect), while in the surrounding space their density is much lower or equal to

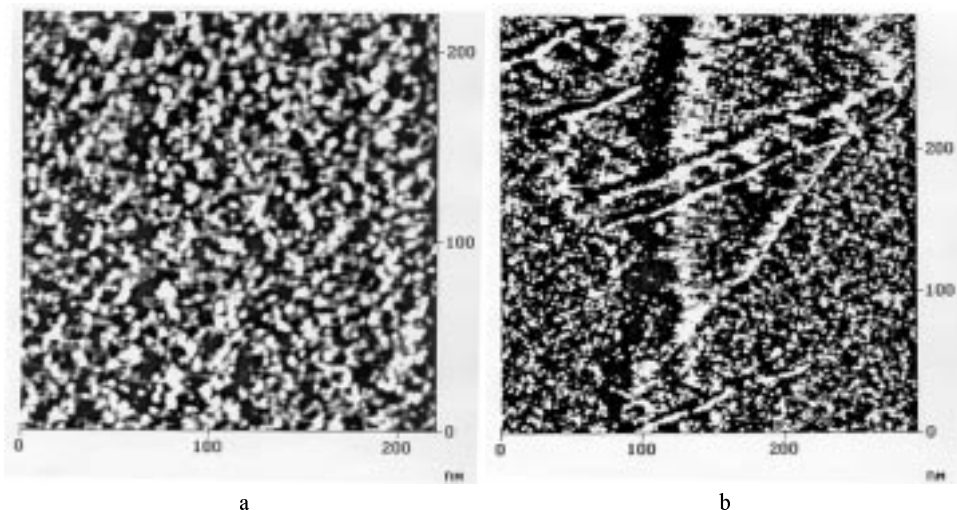


Fig. 5. Larger scale STM images of physically deposited Ag on HOPG after a deposition time of 30 s (3ML): a) on a flat part of the HOPG surface; b) on a part of the surface containing step defects.

zero. This means that on the electrode surface there are some regions where the deposition rate is higher than the average deposition rate (deposition zones), while in the surrounding regions the deposition rate is zero or very low (the nucleation exclusion zones). With increasing overpotential, the current lines become even more deformed since the influence of the smaller defects on the surface becomes significant, Fig. 6b. As a consequence, the number of deposition zones increases and the radii of the nucleation exclusion zones decrease. At a high enough overpotential, the equipotential surfaces completely follow the surface topography, so that the current lines tend to homogeneity in the vicinity of the electrode surface and radii of the nucleation exclusion zones tend to zero.

This discussion points to the crucial role of the size of surface defects at the beginning of nucleation for the formation of clusters and nucleation exclusion zones.

#### *The calculation of the radius of the nucleation exclusion zone*

The radius of a nucleation exclusion zone can be calculated on the basis of the discussion presented above. If, on a flat electrode, there is a half-spherical defect, the extent of the deviation in the shape of equipotential surfaces which occurs around it depends on the potential  $E$  applied to the electrode, on the anode-cathode distance,  $L$ , and on the radius of a defect,  $R$ . If the distance from the flat part of the substrate surface to the equipotential surface which corresponds to the critical nucleation overpotential,  $E_k$ , is  $l$  then this changes around defect to the extent  $kR$ , as it is presented in Fig. 7. Therefore, in this region the current lines deviate from a straight lines towards a defect thus causing an increase in the deposition rate, while in the surrounding region nucleation does not occur, *i.e.*, a nucleation exclusion zone is being formed. The radius of the nucleation exclusion zone,  $r$ , corresponds to the

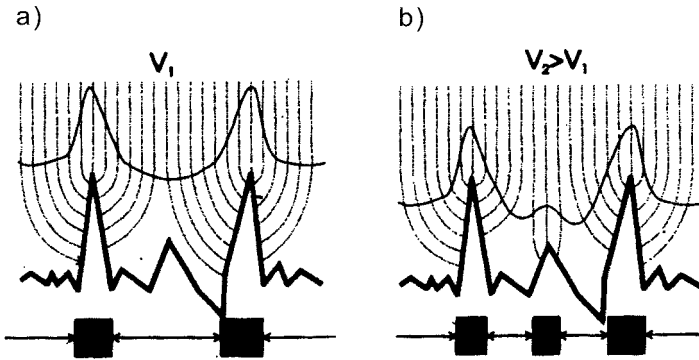


Fig. 6. The deviation of the current field due to defects present on the surface for: a) a low electrode potential; b) a high electrode potential.

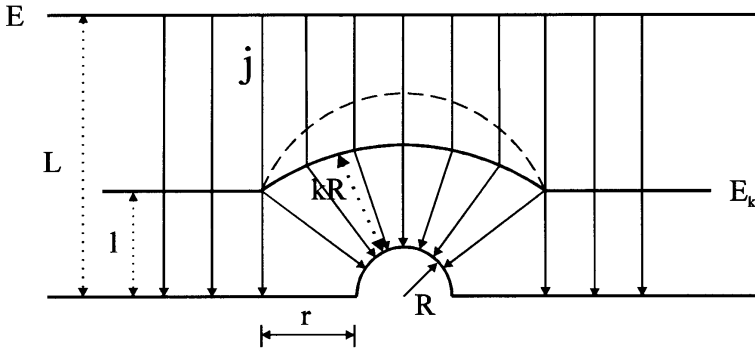


Fig. 7. A schematic presentation of the deformation of the current field around a defect or a grain grown on a foreign substrate. For an explanation of the symbols see the text.

distance between the edge of a defect and the last current line which deviates (when  $kR$  becomes equal to  $l$ ). Accordingly, nucleation will occur at distances from the edge of a defect higher than  $r$ , which can be calculated as:

$$r = R (\sqrt{2k + 1} - 1) \tag{1}$$

If one takes into account that:

$$\rho j l = E_k \tag{2}$$

$$\rho j L = E$$

where  $j$  is the current density along current lines and  $\rho$  is the electrolyte conductivity, one obtains:

$$r = R (\sqrt{2E_k L / ER + 1} - 1) , \tag{3}$$

According to this equation, new nucleation is possible in the vicinity of a defect if  $E \gg E_k$ , i.e.,  $E_k \rightarrow 0$ , and supposing that  $L \gg R$  and  $R$  has a finite value.



In the case of lined defects, such as steps or corrugations on the surface, the same calculation can be applied if one regard  $R$  as the height of a terrace, and  $r$  as the distance from the edge of the lower terrace where nucleation could occur. As the deviation of current lines extends along the step defect, this causes the formation of the string-like shaped deposition zones and string-like shaped nucleation exclusion zones. For lower deposition times, Ag atoms deposited on lined defects create 3D clusters by surface diffusion along the lined defects, which gives rise to the formation of perl-like structures of the string deposits (see Fig. 3).

This approach is also valid during nuclei growth as they take on the role of surface defects. It has to be noted that during current controlled deposition, when  $R$  is attributed to the radius of a growing grain, its value changes with the time as does the radius of the nucleation exclusion zone.

The previous model for the calculation of the radius of a nucleation exclusion zone was based on the change in the ohmic drop in the vicinity of a growing grain, and it was evaluated for a flat surface. According to that model, the radius of the nucleation exclusion zone was estimated as:

$$r = \frac{E}{E - E_k} R \quad (4)$$

where  $E$  is the cell potential,  $E_k$  is the critical nucleation overpotential, and  $R$  is the radius of a grain. For  $E \gg E_k$ , the nucleation exclusion zone disappears, *i.e.*,  $r \rightarrow R$ .<sup>11</sup>

Experimental evidences indicate that this is mainly true in the case of Hg electrocrystallisation on Hg, as well as for silver electrodeposition from concentrated aqueous solutions and molten salts.<sup>11-15</sup> However, this approach does not take into account the influence of the anode-cathode distance and the presence of defects on the surface.

The role of  $E_k$  in the formation of the nucleation exclusion zones has only recently been considered.<sup>16</sup> According to Klapka,<sup>17</sup>  $E_k$  is considerably dependent on the exchange current density,  $j_0$ . In the case of very fast processes,  $E_k$  is the highest, but with decreasing  $j_0$ , it very soon becomes negligible. This is in agreement with the previous considerations according to which the given mathematical model is valid for total ohmic control, this is the case with concentrated metal ion solutions (when diffusion polarisation is negligible), when the deposition process is characterised with a very high exchange current density (activation control is negligible).

It is important to mention that an such explanation of the behavior of  $E_k$ , according to Klapka, satisfies both the presented models. Besides, the measured overpotential at the moment of nucleation, according to Klapka, is the sum of both the activation and the crystallisation overpotentials, so that all speculation is obviously valid, also for processes where the activation fraction of the overpotential can not be neglected. This is because charge transfer occurs on the grain during its growth, as well as on the foreign substrate before nucleation. Which of these models and under which conditions explain the observed phenomena better will be solved in the future.

And in addition, we would like to stress that in the beginning of nucleation on a foreign substrate, when  $j_0$  has no real meaning (it is defined for a substrate in a solution of the corresponding ions), the deviation of the current lines leads to preferential nucleation on the larger surface defects. Once the nucleus is formed, preferential deposition occurs on the growing grains, again due to the deviation of the current lines. This means that the growing grains take over the role of the substrate even before a full coverage. Therefore, at this stage of the deposition,  $j_0$  achieves its real meaning, which explains the growth of grains in a layer by layer mode.<sup>12</sup> From this stage of the deposition, which is achieved very quickly when the deposition is carried out with higher current densities, the above-mentioned consideration of the dependence of  $E_k$  on  $j_0$  has sense.

### CONCLUSIONS

According to the presented results the following conclusions can be drawn. In both, electrochemical and physical deposition of Ag on HOPG, Ag grows in an island growth mode, but with significantly different distributions of the islands over the substrate surface.

In the case of physical deposition, the islands, *i.e.*, 3D clusters, are almost homogeneously distributed over the substrate surface, which indicates the crucial role of point defects. The slight accumulation of clusters on steps, does not contribute significantly to the overall distribution of the clusters. Nucleation exclusion zones do not exist, which can be explained by the homogeneity of the flux of incoming Ag atoms reaching the substrate surface.

In the case of electrochemical deposition, more lined defects were observed after a flow of current. The lined defects are responsible for the string-like shape of the domains of deposited species. Also, the existence of lined nucleation exclusion zones along the lined defects is indicated. We suppose that an ensemble of islands arranged into strings is the basis for the formation of a grain. We also assume that surface defects cause a deviation of the current lines which affects the local deposition rate. This leads to the preferential deposition on larger surface defects and to the appearance of nucleation exclusion zones.

### ИЗВОД

#### УЛОГА ПОВРШИНСКИХ ДЕФЕКТА НА НОРГ-у У ЕЛЕКТРОХЕМИЈСКОЈ И ФИЗИЧКОЈ ДЕПОЗИЦИЈИ Ag

С. ШТРБАЦ,<sup>1</sup> З. РАКОЧЕВИЋ,<sup>2</sup> К. И. ПОПОВ,<sup>3</sup> М.Г. ПАВЛОВИЋ<sup>1</sup> И Р. ПЕТРОВИЋ<sup>4</sup>

<sup>1</sup>ИХТМ-Центар за електрoхемију, Универзитет у Београду, б.бр. 815, 11001 Београд,

<sup>2</sup>Институт за нуклеарне науке "Винча", б.бр. 522, 11001 Београд, <sup>3</sup>Технолошко-металуршки факултет, Универзитет у Београду, б.бр. 3503, 11020 Београд и <sup>4</sup>ИХТМ-Центар за микроелектронске технологије и монокрисјале, Универзитет у Београду б.бр. 815, 11001 Београд

Улога дефеката на површини супстрата у почетним стадијумима нуклеације и раста Ag депонованог електрохемијски и физички на високо оријентисани графит (НОРГ) је испитивана *ex situ* техником сканирајуће тунелирајуће микроскопије (STM). Елек-

трoдепозиција сребра је изведена галваностатски, са густином струје од  $26 \mu\text{A}/\text{cm}^2$ , што је одговарало брзини депозиције од 0,1 монослоја (ML) по секунди. Поређења ради, физичка депозиција Ag на HOPG је изведена спатеровањем са DC  $\text{Ag}^+$  јонима, са истом брзином депозиције и за иста времена депозиције. У оба случаја је запажен острвски раст Ag, али се испоставило да је расподела острва по површини сасвим различита. Након физичке депозиције, острва сребра су скоро хомогено распоређена по површини, и слаба акумулација острва на степеницама не доприноси значајно укупној морфологији. Ово указује на пресудан значај тачкастих дефеката на површини супстрата на почетне стадијуме нуклеације. Након електрохемијске депозиције, примећено је више линијских дефеката на самој површини супстрата, и показано је да је њихова улога у почетку нуклеације много израженија. Линијски дефекти су одговорни за настајање тракастих области са депонованим атомима. Такође, указано је на постојање тракастих зона искључења. Проблем зона искључења у току електрохемијске депозиције је поново разматран и понуђено је ново објашњење за њихово настајање. Дат је математички модел за израчунавање пречника зоне искључења.

(Примљено 26. фебруара 1999)

#### REFERENCES

1. A. A. Grewirth, B. K. Niece, *Chem. Rev.* **97** (1997) 1129
2. J. A. Venables, G. D. T. Spiller, in Vu Thein Bink (Ed.), *Surface Mobilities on Solid Materials*, Plenum, New York, 1981
3. K. Reichelt, *Thin Solid Films* **25** (1975) 539
4. Z. Rakočević, S. Štrbac, N. Bibić, D. Perusko, T. Nenadović, *Thin Solid Films* **257** (1995) 83
5. Z. Rakočević, S. Štrbac, N. Bibić, T. Nenadović, *Surf. Sci.* **343** (1995) 247
6. Z. Rakočević, S. Štrbac, D. Perusko, N. Bibić, T. Nenadović, *Thin. Solid. Films* **288** (1996) 212
7. F. Endres, W. Freyland, B. Gilbert, *Ber.Bunsenges.Phys. Chem.* **101** (1997) 1075
8. R. T. Potzschke, A. Gervasi, S. Vinzelberg, G. Staikov, W. J. Lorenz, *Electrochim. Acta* **10** (1995) 1469
9. R. Sonnenfeld, B. Schardt, *Appl. Phys. Lett.* **49** (1986) 1172
10. R. S. Robinson, *J. Vac. Sci. Technol. A* **8** (1990) 511
11. I. Markov, A. Boynov, S. Toshev, *Electrochim. Acta* **18** (1973) 377
12. G. Adžić, *PhD Thesis*, University of Belgrade, Belgrade, 1992
13. J. Malinowski, E. Budewski, *Bull. Bulg. Acad. Sci. (Phys.)* **2** (1951) 205
14. A. Scheludko, G. Bliznakov, *Bull. Bulg. Acad. Sci. (Phys.)* **2** (1951) 239
15. A. N. Baraboshkin, A. T. Kosikhin, N. A. Saltikova, *Tr. Inst. Po Elektrokhemii, UF AN SSSR* **7** (1965) 47
16. K. I. Popov, B. N. Grgur, E. R. Stojiljković, M. G. Pavlović, B. N. Nikolić, *J. Serb. Chem. Soc.* **62** (1997) 43
17. Y. Klapka, *Collection Czechoslov. Chem. Commun.* **35** (1970) 899.