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Determination of the absolute hardness of electrolytically produced copper coatings by application of the Chicot–Lesage composite hardness model

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Abstract: In this study, a novel procedure, based on application of the Chicot–Lesage (C–L) composite hardness model, was proposed for the determination of an absolute hardness of electrolytically produced copper coatings. The Cu coatings were electrodeposited on the Si(111) substrate by the pulsating current (PC) regime with a variation of the following parameters: the pause duration, the current density amplitude and the coating thickness. The topography of produced coatings was characterized by atomic force microscope (AFM), while a hardness of the coatings was examined by Vickers microindentation test. Applying the C–L model, the critical relative indentation depth $(RID)_c$ of 0.14 was determined, which is independent of all examined parameters of the PC regime. This *RID* value separated the area in which the composite hardness of the Cu coating corresponded to its absolute hardness ($RID < 0.14$) from the area in which the application of the C–L model was necessary for a determination of the absolute coating hardness ($RID \geq 0.14$). The obtained value was in a good agreement with the value already published in the literature.

Keywords: electrodeposition; the pulsating current; topography; hardness; relative indentation depth.

INTRODUCTION

According to its unique combination of properties, such as high thermal and electrical conductivity, malleability, corrosion resistance, and good adhesiveness with a substrate, copper found wide application in many industrial branches such as aerospace, automotive, electronics and telecommunications.[1] Due to its anti-

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microbial characteristics, Cu also found application in a medicine in a control of healthcare-associated infections.[2] The methods including electrodeposition, electroless plating, chemical vapour deposition (CVD), physical vapour deposition (PVD), thermal spray and sputtering techniques are widely used for the production of Cu in a form of coatings on various conductive or non-conductive substrates.[2] The choice of a method for a production of Cu coatings is closely related to a desired application of the coating.

The main advantages of electrodeposition processes over the other production techniques are the obtaining of coatings of desired quality and thickness by an easy control of parameters and regime of electrodeposition.[3] The both constant (galvanostatic) and periodically changing (the PC and the reversing current (RC)) regimes are used in a production of Cu coatings for commercial purposes. The main parameters affecting a quality of coatings are: type and composition of electrolyte, temperature, stirring of electrolyte, the type of cathode, time of electrodeposition, *etc*.[3]

Mechanical properties of metal coatings are closely related with their morphological and structural characteristics determining a quality of any coating. Hardness is one of the most important mechanical properties of coatings, and indentation techniques are widely used to determine it.[4] The main challenge in hardness analysis of any coating is a determination of its absolute (or real) hardness which exclude a contribution of substrate (cathode) in measured hardness value. It can be done either by the use of relatively small indentation loads which enable that a critical indentation depth after which a substrate begins to affect hardness is not exceeded, or by the application of various composite hardness models which in calculations predict contributions from both substrate and coating in measured hardness value. The first way is usually suitable for the thick coatings, because it enables the use of larger indentation loads. The Chicot–Lesage (C–L),[5–8] Chen–Gao (C–G)[9–11] and Korsunsky (K-model)[12–15] are most often used composite hardness models for a determination of an absolute hardness of coating. The choice of models depends on substrate/coating hardness ratio, and some of them give optimum results for „hard film on soft substrate“ systems like Korsunsky model,[12–15] while some other models like the Chen–Gao[9–11] and the Chicot–Lesage[5–8] are suitable for the analysis of "soft film on hard substrate" systems.

For a long time was adopted so-called Buckle's one-tenth rule,[4] which predicts that a critical indentation depth above which a substrate begins to affect a coating hardness is 0.1 of a coating thickness value. However, this rule has not an universal character, and the beginning of effect of a substrate on a coating hardness depends on substrate/coating hardness ratio,[4] and it depends on the indenter geometry, plastic pile-up effect, film/substrate adhesion, elastic properties of the film and substrate and the friction between the indenter and film.[4,16–20] For example, for „soft film on hard substrate“ systems, this rule is too strong, while for systems like „hard film on soft substrate“, more restrictive limitations than the one-tenth rule can be valid.

In this study, the try to determine an absolute (or real) hardness of Cu coatings obtained by the PC regime on very hard Si(111) cathodes is made by the analysis of data obtained by applying the C–L model. The idea for this study was based on our recently published results,[8,21] in which extremely high values for the hardness of the Cu coatings on Si(111) were observed using the application of the C–L model.[8] The solution of this problem, through an establishment of the limiting (or critical) relative indentation depth $(RID)_c$ of 0.14 for the Cu coatings of various thicknesses, was obtained the same way, but on the brass cathode.[21] The aim of this study is to resolve some of the main dilemmas related to an application of the C–L model in a determination of absolute (or real) hardness of the Cu coatings on the hard substrates.

EXPERIMENTAL

The copper coatings were electrolytically produced by the electrodeposition of Cu on the Si(111) hard substrate. The electrodeposition of copper was performed by the pulsating current (PC) regime from 240 g L^{-1} $CuSO_4\cdot5H_2O$ in 60 g L^{-1} H_2SO_4, at the room temperature in an open cell of a prismatic shape.

The parameters of the applied PC regime for electrodeposition of Cu coatings are given in Table I.

TABLE I. The parameters of the PC regime used for electrodeposition of copper coatings on the Si(111). j_A – the current density amplitude; j_{av} – the average current density; t_p – pause duration; ν – frequency; δ – thickness of coating; deposition pulse, t_c = 5 ms

No.	t_p / ms	j_A / mA cm^{-2}	j_{av} / mA cm^{-2}	ν / Hz	δ / μm
1	5	100	50	100	40
2	7.5	100	40	80	40
3	15	100	25	50	40
4	28.3	100	15	30	40
5	5	120	60	100	40
6	5	140	70	100	40
7	5	100	50	100	20
8	5	100	50	100	60

Analytical grade chemicals (p.a.) and double distilled water were used for a preparation of the electrolyte. The two parallel Cu sheets placed close to the wall of cell were used as the anodes. The Si(111) orientation of (1.0×1.0) cm^2 surface area is used as a cathode, and it was placed in the middle of the cell between two parallel Cu anodes. The preparation of the Si(111) cathodes for electrodeposition was described elsewhere.[8]

Topography of the Cu coatings was examined by the atomic force microscope (AFM) using model auto probe CP research; TM microscopes, Veeco Instruments, in the contact mode. The scan area was (70×70) μm^2. The R_q (root mean square roughness) value of the same coatings was determined using the software WSxM 4.0 beta 9.3 version.[22]

Vickers microhardness tester Leitz Kleinert Prufer DURIMET I was used for the measurements and determination of an absolute (or real) hardness of the Cu coatings. The dwell time of 25 s, and loads in the 0.049–2.942 N range were used for this purpose. The rest of the experimental procedure for a determination of a composite hardness of the Cu coatings is presented in literature.[8]

RESULTS AND DISCUSSION

Basic facts

The regime of pulsating current (PC) is defined by periodic repetitions of current square wave and pause, and it can be presented as:[3]

$$j_{\mathrm{av}} = j_{\mathrm{A}} \frac{t_{\mathrm{c}}}{t_{\mathrm{c}} + t_{\mathrm{p}}} \tag{1}$$

where j_{av} is the average current density, j_{A} is the current density amplitude, and t_{c} and t_{p} are durations of deposition pulse and pause, respectively.

For the PC regime, frequency, ν, is another important parameter, and it is defined as:

$$\nu = \frac{1}{t_{\mathrm{c}} + t_{\mathrm{p}}} \tag{2}$$

The PC regime gives optimum results in the range of frequencies between 10 and 100 Hz, and electrodeposition process in this range of frequency (the ms range) occurs at the average current density.[3]

Topography and roughness of the Cu coatings produced by the various PC regimes

Morphology and roughness of the electrolytically produced Cu coatings were characterized by AFM. Fig. 1 shows the 2D (two dimensional) AFM images of the Cu coatings obtained with various parameters of the PC regime, *i.e.*, at various average current density values.

The decrease of both size and regularity of Cu grains is observed with increasing the j_{av} values. It is necessary to note that the fine-grained coatings were obtained starting from an average current density of 40 mA cm^{-2}. This change in surface morphology can be attributed to a decrease of contribution of the activation control and an increase of contribution of the diffusion control with increasing j_{av} value, since a formation of all these Cu coatings occurred in the mixed activation-diffusion control.[8]

The decrease of grain size was accompanied by an increase of uniformity of the Cu coatings, which is confirmed by roughness analysis of the obtained coatings. The values of R_{q} roughness parameters for the same Cu coatings are given in Table II. The presence of the larger grains in the Cu coatings obtained using j_{av} of 15 and 25 mA cm^{-2} (Fig. 1a and b, respectively) induced an increased nonuniformity, and hence, larger roughness of these coatings relative to those obtained with the larger j_{av} values, when fine-grained coatings are formed. The slight increase in a roughness of the Cu coatings with j_{av} of 60 and 70 mA cm^{-2} is due to a beginning of dominant effect of the diffusion control of the electrodeposition process, characterizing a formation of rougher deposits and the obtaining of various disperse or irregulars forms.[3,8]

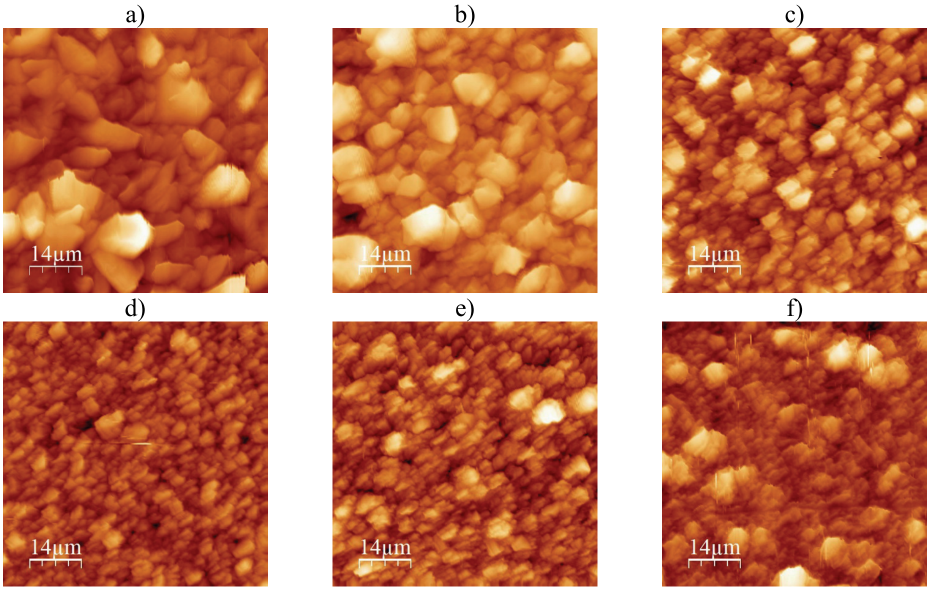


Fig. 1. The 2D AFM images of the Cu coatings obtained by the PC regime at j_{av} of: a) 15, b) 25, c) 40, d) 50, e) 60 and f) 70 mA cm^{-2}. The thickness of coatings, δ = 40 μm.

TABLE II. The values of R_q roughness obtained by application of AFM software from (70×70) μm^2 scan area, and Meyer's index m for the Cu coatings produced by various PC regimes

j_{av} / mA cm^{-2}	15	25	40	50	60	70
R_q / nm	677.2	599.2	490.8	318.0	326.3	359.9
m	0.4288	0.4372	0.4770	0.4979	0.4346	0.3447

The same technique is used to analyse the effect of thickness of coatings on their roughness. Fig. 2 shows 2D AFM images of the Cu coatings, obtained at j_{av} of 50 mA cm^{-2}, with thicknesses of 20 (Fig. 2a) and 60 μm (Fig. 2b). Although the uniform fine-grained coatings were obtained with the both thicknesses, it is necessary to note that size of grains enlarged with increasing the coating thickness. This was in accordance with theory considering a mechanism of electrodeposition by the PC regime on morphology of metal deposits.[3] For the Cu coatings thicknesses from 20 and 60 μm, the values of R_q roughness were 131.1 and

367.2 nm, respectively. This increase in roughness of the coatings is just a consequence of the growing size of grains with the thickness of coating.

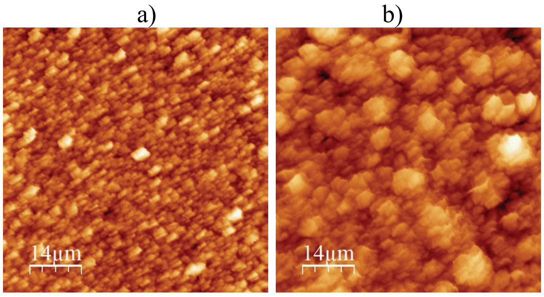


Fig. 2. The 2D AFM images of the Cu coatings obtained by the PC regimes at *j*av of 50 mA cm^{-2}. The thicknesses of coatings, *δ*, a) 20 and b) 60 μm.

Hardness analysis of the Cu coatings produced by the various the PC regimes

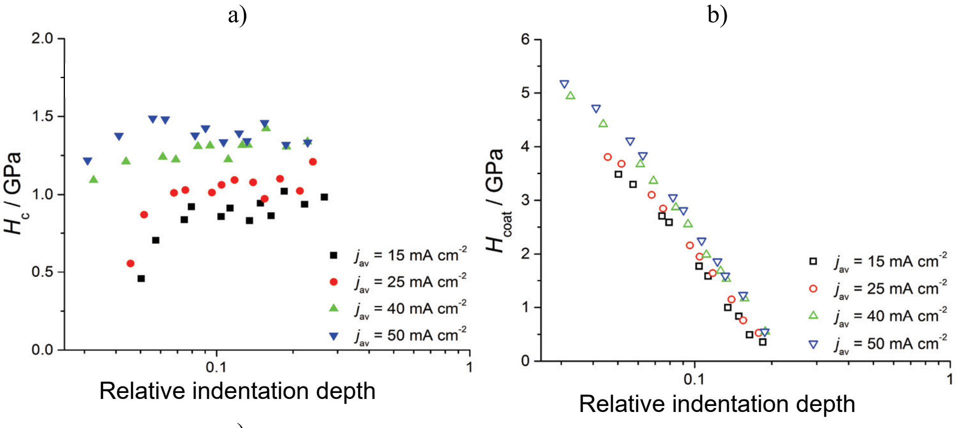
The measured (also known as composite) hardness, H_c / Pa, of any coating depends on applied load, *P* / N, and size of a diagonal, *d* / m, made by indenter in a coating, and it is defined as:[8]

$$H_c = 1.8544\frac{P}{d^2} \tag{3}$$

This value often includes a contribution of substrate (cathode), and for that reason, it is necessary to eliminate this contribution in order to obtain absolute (or real) hardness of a coating. The application of various composite hardness models represents valuable way to achieve it.[8,11,14,15,21]

Fig. 3a shows the dependencies of the composite hardness (H_c) on the relative indentation depth (*RID*) for the Cu coatings obtained on the Si(111) cathodes at the various average current densities (*i.e.*, frequencies). *RID* is defined as a ratio between an indentation depth (*h*) and a thickness of coating (*δ*) as *RID* = $= h/\delta$, where an indentation depth is related with a diagonal size as $h = d/7$. The indentation depth increases a contribution of a substrate to the measured composite hardness with the growth of *RID* values. At the high *RID* values the composite hardness corresponded to a hardness of substrate.[8] Although there is no precise boundary where a contribution of substrate to measured hardness begins, as well as where measured hardness begins to correspond to a substrate hardness, the *RID* values of 0.1 and 1, respectively, are usually taken as the limiting values for these boundaries.[8] The fact that a significant number of H_c values is situated in a zone where the substrate affects hardness (Fig. 3a) indicated a necessity of application of the composite hardness models in a determination of the absolute hardness of the Cu coatings.

With the hardness of 7.42 GPa,[8] Si(111) belongs to a group of very hard substrates, while the Cu coatings on the Si(111) electrodes belong to a group of "soft film on hard substrate" type of a composite system. The C–L composite model showed as very valuable for a determination of the absolute hardness of such coatings,[8] and the dependencies of the coating hardness, H_{coat} on the *RID*, calculated by this model,for the given Cu coatings, are presented in Fig. 3b. The detailed description of the C–L composite hardness model can be found in literature.[8] At the first sight, it can be noticed that the calculated H_{coat} values were much larger than the measured H_{c} values at the smaller *RID* values. Anyway, it is illogical and an additional analysis of the obtained dependencies was necessary in order to determine the absolute (real) values of the coating hardness in the whole range of the *RID* values.



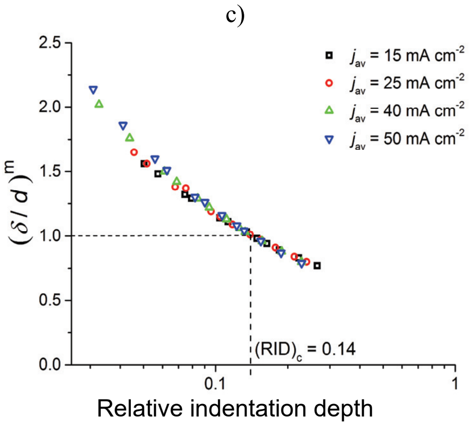


Fig. 3. The dependencies of: a) H_{c} and b) H_{coat} values calculated by the C–L model on the relative indentation depth for the Cu coatings obtained by the PC regime at j_{av} of 15, 25, 40 and 50 mA cm^{-2} (according to literature[8]) and c) the dependencies of $(\delta/d)^{\mathrm{m}}$ on the relative indentation depth for the same Cu coatings. The thickness of coatings, $\delta = 40$ µm.

For that reason, the following analysis of the obtained dependencies was performed using the C–L model. Fig. 3c shows the dependencies of the $(\delta/d)^{\mathrm{m}}$ on the *RID* values for the Cu coatings obtained on the various average current densities (*i.e.*, frequencies). In these dependencies, an exponent *m* is the composite Meyer's index, calculated by a linear regression performed on all experimental points for the given coating–substrate system.[6,14] The values of this exponent calculated for the Cu coatings are given in Table II. The composite Meyer's index defines a way of change of the composite hardness with the applied load. The detailed explanation of the composite Meyer's index can be found in literature.[6,14] The increase of the Meyer's composite index with the increase of j_{av} from 15 to 50 mA cm^{-2} can be explained by the strain hardening effect.

Assuming that the C–L model is valid up to $(\delta/d)^m = 1$,[7] the limiting or critical *RID* value of 0.14 ($(RID)_c = 0.14$) was determined (Fig. 3c). It is clear that for *RID* values larger than 0.14 it is necessary to apply the C–L model in order to determine an absolute hardness of the Cu coatings. On the other hand, for the *RID* values smaller than this value, the measured composite hardness corresponded to the coating hardness. In this way a precise boundary where begins an effect of substrate (cathode) on the measured hardness of Cu coatings is determined. The additional analysis of the data shown in Fig. 3a and b can confirm this assumption. Namely, the careful analysis of these data showed that the *RID* value of 0.14 represents the limiting value after which the measured H_c values become larger than the calculated H_{coat} values. For the *RID* values smaller than 0.14, the calculated H_{coat} values are larger than the measured H_c values, and this difference increased with the decrease of *RID* values, so that at the small *RID* values, they became much larger than the H_c values. It is necessary to note that this critical *RID* value was independent of the applied average current density.

That way was confirmed the *RID* limiting value of 0.14, previously observed for the Cu coatings of various thicknesses, obtained by the same regime on the brass substrate.[21] In the next step, the Cu coatings noted at a frequency of 100 Hz, but at j_{av} of 60 and 70 mA cm^{-2} were analyzed. Simultaneously, the Cu coatings obtained at ν of 100 Hz and j_{av} of 50 mA cm^{-2}, but with the thicknesses of 20 and 60 μm are also analyzed. The H_c and H_{coat} dependencies on the *RID* for these coatings are given in Fig. 4a and b, respectively. These figures also include the same dependencies for the 40 μm thick Cu coating obtained at j_{av} of 50 mA cm^{-2}, which have been already given in Fig. 3.

The dependencies of the $(\delta/d)^m$ on the *RID* for the analyzed Cu coatings are shown in Fig. 4c. The values of *m* exponent for the Cu coatings obtained at j_{av} of 60 and 70 mA cm^{-2} are given in Table II, while *m* values for 20 and 60 μm thick Cu coatings were 0.3591 and 0.4286, respectively. The increase of the Meyer's composite index with the growing coating thickness is due to a decrease of influence of substrate with the thickness of coating.

Applying the same procedure, which takes into consideration of a validity of the C–L model up to $(\delta/d)^m = 1$, the critical *RID* value of 0.14 was also determined for these Cu coatings. The analysis of these dependencies also showed that for *RID* < 0.14 the calculated H_{coat} values were larger than the measured H_c values, strongly proving that *RID* of 0.14 represents the limiting (or critical) value separating an area in which the measured composite hardness can be equal to an absolute hardness of the coating, from that in which the application of the C–L model was necessary for a determination of the absolute hardness. It is very clear that the critical *RID* value is not affected by the average current density and the thickness of coating.

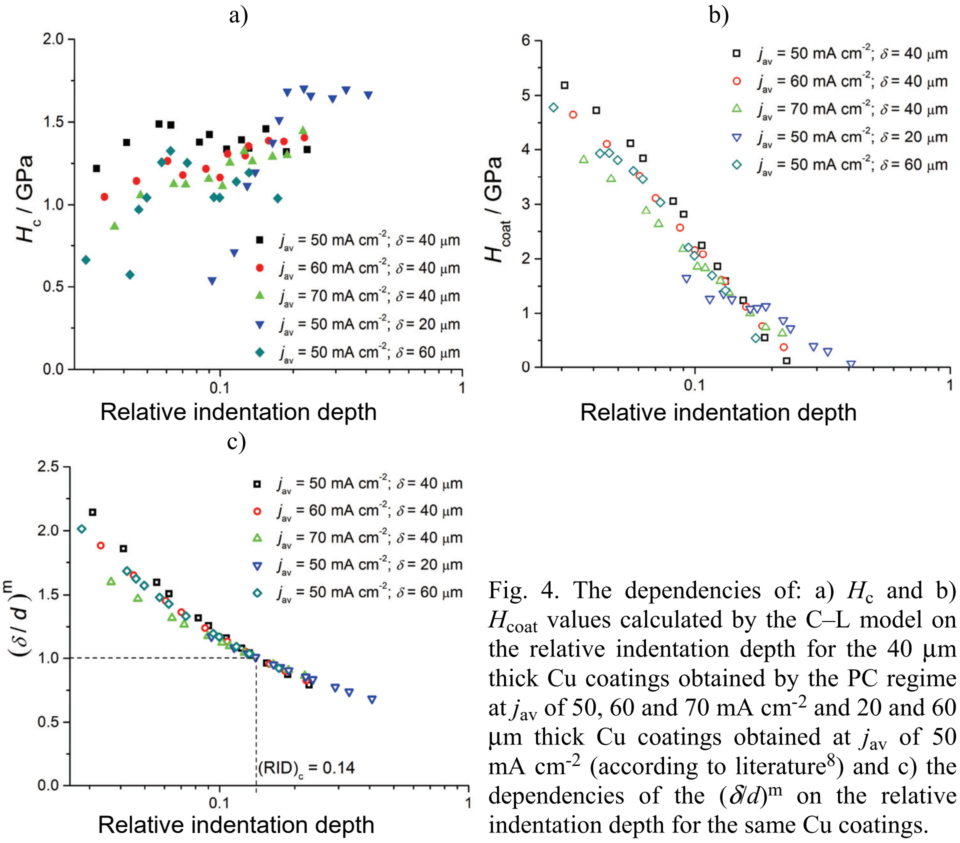


Fig. 4. The dependencies of: a) H_c and b) H_{coat} values calculated by the C–L model on the relative indentation depth for the 40 μm thick Cu coatings obtained by the PC regime at j_{av} of 50, 60 and 70 mA cm^{-2} and 20 and 60 μm thick Cu coatings obtained at j_{av} of 50 mA cm^{-2} (according to literature[8]) and c) the dependencies of the $(\delta/d)^m$ on the relative indentation depth for the same Cu coatings.

Hence, the critical (or limiting) *RID* value of 0.14 separating the zone of the absolute coating hardness from the zone of strong effect of substrate was determined. This value was independent of parameters of the PC regime, such as pause duration and the current density amplitude (*i.e.*, independent of frequency and the average current density). Also, this value was independent of the coating thickness and the type of cathode. This clearly indicates that the *RID* value of 0.14 can represent a general characteristic of Cu coatings.

The obtained *RID* value of 0.14 was in excellent agreement with the results of an estimation of effect of a substrate on coating hardness found in the literature.[4,23] Namely, for a polycrystalline soft films on hard substrate like the coatings of Cu on Si(111), a critical indentation depth, h_c above which a substrate achieves a strong effect on a hardness is related with a coating thickness as $h_c > 0.20\delta$. For $h_c < 0.20\delta$, a substrate has a negligible effect on the hardness. Hence, the critical *RID* value which separates area of absolute hardness of coating from that one where an effect of substrate cannot be neglected on measured hardness is 0.20. This clearly indicates that the here obtained value of 0.14 was inside this zone. The advantage of the proposed procedure in this study is that it is not necessary to do a cross section analysis of coating in order to establish whether a critical indentation depth, with maximum value of 20 % of the overall thickness of coating, is exceeded. In this proposed procedure, based on the application of the C–L model, considering the existing relation between a diagonal size and an indentation depth, it is possible to define a maximum load for any coating thickness, which can be applied to ensure that a measured composite hardness corresponds to a coating hardness. In this moment, the proposed *RID* value of 0.14 is valid for the electrolytically obtained copper coatings on the hard substrates like brass and Si(111). For any other metals and substrates, it will be a subject of future investigations.

CONCLUSIONS

The coatings of copper were electrolytically produced by electrodeposition of Cu on the Si(111) hard substrate, under the regime of the pulsating current (PC) varying a duration of pause (5, 7.5, 15 and 28.3 ms) and the current density amplitude (100, 120 and 140 mA cm^{-2}) values. The corresponding average current densities were in the 15–70 mA cm^{-2} range, and the frequencies were in the 30–100 Hz range. The examined thicknesses of the coatings were 20, 40 and 60 μm. The topography and the hardness of Cu coatings were characterized by AFM and by Vickers microindentation test using the C–L composite hardness model for data processing.

By the application of the C–L model, it is established the critical (or limiting) relative indentation depth $(RID)_c$, of 0.14, which is independent of the parameters of the PC regime and of the thickness of the coatings. This value separated the zone in which the measured hardness corresponds to a hardness of the coating from the zone which requires an application of the C–L model for a determination of an absolute hardness of the coating.

This critical *RID* value was in excellent agreement with the *RID* value of 0.20 found in the literature for the same type “soft film on hard substrate” composite system.

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ИЗВОД

ОДРЕЂИВАЊЕ АПСОЛУТНЕ ТВРДОЋЕ ЕЛЕКТРОЛИТИЧКИ ДОБИЈЕНИХ ПРЕВЛАКА БАКРА ПРИМЕНОМ CHICOT–LESAGE КОМПОЗИТНОГ МОДЕЛА ТВРДОЋЕ

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Предложен је нови поступак заснован на примени Chicot–Lesage (C–L) композитног модела тврдоће за одређивање апсолутне тврдоће електролитички добијених превлака бакра. Превлаке бакра су електрохемијски исталожене на силицијуму (111) оријентације режимом пулсирајуће струје варирањем следећих параметара: трајање паузе, амплитудна густина струје и дебљина превлаке. Топографија произведених превлака је окарактерисана микроскопијом атомских сила, док је тврдоћа превлака испитивана Викерсовим тестом утискивања. Применом C–L композитног модела тврдоће, одређена је критична релативна дубина утискивања (*RID*), од 0,14, која је независна од свих испитиваних параметара режима пулсирајуће струје. Ова вредност раздваја област у којој композитна тврдоћа превлаке може да се изједначи са њеном апсолутном тврдоћом ($RID < 0,14$) од области у којој је неопходно применити C–L модел за одређивање апсолутне тврдоће превлаке ($RID \geq 0,14$). Добијена вредност *RID* показује добро слагање са вредностима публикованим у литератури.

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