Hardness response and adhesion of thin copper films on alloy substrates

Ivana Mladenović, Jelena Lamovec, Vesna Jović, Bogdan Popović, Miloš Vorkapić and Vesna Radojević

***Abstract*—Microhardness test is the most commonly used method for assessing the mechanical properties of thin films. This testing method uses controlled contact at a single point of an indenter and chosen material which induces the plastic deformation in material under indenter. The measured hardness is considered as the composite hardness, because the substrate participates in the plastic deformation caused by indentation. This research has been carried out in order to analyze and compare the hardness response of different composite systems consist of monolayer electrodeposited copper thin film on brass and steel alloys as the substrates. The influence of the electrodeposition parameters and of the substrate on the hardness and interlayer adhesion were investigated by Vickers microhardness testing for different load.**

***Index Terms*— microhardness, composite system, thin film, adhesion, electrodeposition.**

I. Introduction

Copper electroplating is one of the oldest method for producing the protective and decorative coatings. Thin copper films are used to improve wear and corrosion resistance or used as diffusion barriers [1].

Thin copper films have various applications in the electronic industry for the fabrication of contacts in integrated circuits. They are the best choice when it is necessary to fulfil the HAR-channels (high aspect ratio trenches). Along with alternately electrodeposited thin Ni films, they may be considered as laminate composite structures with good mechanical properties such as high hardness and tensile strength, which is especially important for the MEMS structures fabrication [2-4].

Ivana Mladenović is with the Centre of Microelectronics Technology and Metallurgy, University of Belgrade, Njegoševa 12, 11 000 Belgrade, Serbia (e-mail: ivana@ nanosys.ihtm.bg.ac.rs).

Jelena Lamovec is with the Centre of Microelectronics Technology and Metallurgy, University of Belgrade, Njegoševa 12, 11 000 Belgtrade, Serbia (e-mail: jejal@ nanosys.ihtm.bg.ac.rs).

Vesna Jović is with the Centre of Microelectronics Technology and Metallurgy, University of Belgrade, Njegoševa 12, 11 000 Belgtrade, Serbia (e-mail: vjovic@ nanosys.ihtm.bg.ac.rs).

Bogdan Popović is with the Centre of Microelectronics Technology and Metallurgy, University of Belgrade, Njegoševa 12, 11 000 Belgtrade, Serbia (e-mail: bpopovic@ nanosys.ihtm.bg.ac.rs).

Miloš Vorkapić is with the Centre of Microelectronics Technology and Metallurgy, University of Belgrade, Njegoševa 12, 11 000 Belgrade, Serbia (e-mail: worcky@ nanosys.ihtm.bg.ac.rs).

Vesna Radojević is with the Faculty of Technology and Metallurgy, University of Belgrade, Karnegijeva 4, 11 000 Belgtrade, Serbia (e-mail: vesnar@ tmf.bg.ac.rs).

Electrochemical deposition (ED) is technique that is fully compatible with MEMS technologies. It is a low temperature and easy-controlled deposition technique with high deposition rate [5].

Electrolytes that are commonly used for the copper deposition are on the base of sulphate with content of various additives. Organic or nonorganic additives are added to electrolyte in purpose of change the film microstructure and improvement the mechanical properties such as higher hardness value, brightness and ductility [6]. Synergetic effect of the additives (chloride ions + polyethylene glycol (PEG) + MPSA) in the plating solution contributes to obtaining the fine-grained film microstructure and high values of composite hardness and adhesion [7-8].

Indentation testing is reliable test method for the evaluation of mechanical properties of bulk materials and thin films over a wide range of size scales. During hardness measurement of thin films by indentation method, the influence of the substrate must be considered. The measured composite hardness is a complex function which depends on the relative indentation depth and structural and mechanical properties of both the film and the substrate.

Change of the composite and film hardness with applied loads depends on the type of the system and structure of the film. Copper films electrodeposited on brass and steel substrates belong to “soft film on hard substrate” composite system type. The composite hardness model of Chicot-Lesage (C-L) [9] was chosen and applied to experimental data in order to calculate the film hardness. It is possible to assess the interlayer adhesion in the composite systems by microindentation test. The composite hardness model designed for the evaluation of thin film adhesion properties is developed by Chen and Gao [10-12].

II. Determination of Film Hardness

The model proposed by Chicot and Lesage (C-L) is developed on the analogy between the variation of the Young’s modulus of reinforced composite in function of the volume fraction of particles, and the variation of the composite hardness between the hardness of the substrate and the film.

Meyer’s law express the variation of the size of the indent in function of the applied load *P*. For the particular case of a film-substrate couple, the evolution of the measured diagonal and the applied load can be expressed by a similar relation as is Meyer's:

$$P = a^* \cdot d^{n^*} \tag{1}$$

The variation part of the hardness number with load is represented by the factor n^*. They adopted the following expression:

$$f\left(\frac{t}{d}\right)=\left(\frac{t}{d}\right)^{m}=f \quad where \;\; m=\frac{1}{n^*} \tag{2}$$

The composite hardness can be expressed by the following relation:

$$H_c=(1-f)/\left(1/H_s+f\cdot\left(\frac{1}{H_f}-\frac{1}{H_s}\right)\right)+ \\ +f\cdot\left(H_s+f\cdot\left(H_f-H_s\right)\right) \tag{3}$$

Hardness of the film is the positive root of the next equation:

$$A\cdot H_F^2+B\cdot H_F+C=0, \quad with \\ A=f^2\cdot(f-1) \\ B=\left(-2\cdot f^3+2\cdot f^2-1\right)\cdot H_S+(1-f)\cdot H_C \\ C=f\cdot H_C\cdot H_S+f^2\cdot(f-1)\cdot H_S^2 \tag{4}$$

The value of m (composite Meyer's index) is calculated by a linear regression performed on all of the experimental data obtained for a given film/substrate couple and deduced from the relation:

$$\ln d=m\cdot\ln P+b \tag{5}$$

With the known value of m, only the hardness of the films remains to be calculated.

III. Evaluation of Adhesion Properties of Thin Films in Composite Systems

For evaluation of the adhesion properties of thin films, Chen-Gao (C-G) method was chosen. This method introduces the composite hardness as a function of the critical reduced depth beyond which the material will have no effect on the measured hardness. They found that a large value of the critical reduced depth b (ratio between the radius of the plastic zone beneath the indentation and the indentation depth) corresponds to good adhesion, while low values indicate poor adhesion of the films, as shown in Fig.1. The correlation between composite hardness value H_C and the critical reduced depth are found as:

$$H_c=H_s+\left[(m+1)\cdot t/m\cdot b\cdot D\right]\cdot(H_f-H_s) \tag{6}$$

H_s and H_f are the hardness of the substrate and of the film, t is film thickness, D is indentation depth, m is the power index. Critical reduced depth has different values for various film-substrate systems. Even for the same film-substrate system, due to the different adhesion strength, b values are different.

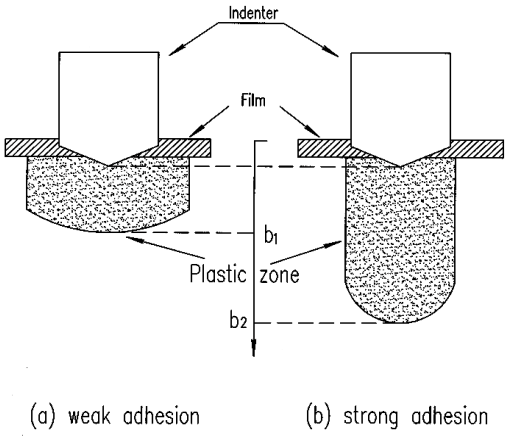

Fig.1. Schematic representation of deformation associated with indentation in a coated substrate (weak adhesion) (a); The effect of a strong film/substrate interface (b) [10].

IV. Experimental Procedure

4.1. Substrates and film deposition

For the composite hardness measurement two different substrates were chosen and prepared: brass foil 260 ½ hard, 250 μm-thick (ASTM B36, K&S Engineering) and stainless steel 316 L with a thickness of 200 μm. The α-brass has a FCC crystal structure as well as copper and constitutes a suitable surface for deposition in terms of crystal lattice match. Prior to deposition, the brass substrate requires the activation in 20% sulfuric acid solution. The stainless steel foil was degreased and mechanically polished with alumina powder. The set of starting samples is shown in Fig.2.

Electrochemical deposition was performed under DC galvanostatic mode . Copper films were electrodeposited from a sulphate bath consisting of 240 g/l $CuSO_4 \cdot 5\ H_2O$, 60 g/l H_2SO_4, 0.124 g/l NaCl, 1 mg/l PEG (polyethylene glycol), 1.5 mg/L MPSA (mercapto propane sulphonic acid) [13]. The current density values were maintained at 10 mA/cm^2 and 50 mA/cm^2. According to the plating surface and chosen process parameters, projected thickness of deposits was determined.

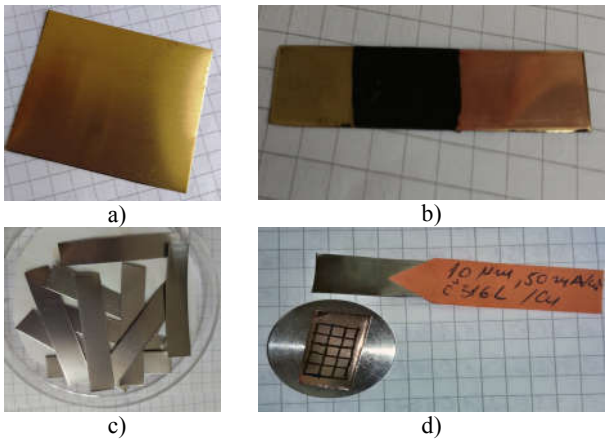

Fig.2. Prepared samples, brass foil (a) and steel foil (c); Electrodeposited copper film on brass (b), and ED Cu on steel (d).

4.2. Microindentation test

The mechanical properties of the composite systems were characterized using Vickers microhardness tester "Leitz, Kleinharteprufer DURIMET I " with loads ranging from 1.96 N down to 0.049 N. Three indentations were made at each indentation load from which the average composite hardness could be calculated. Topographic examination was done by the metallographic microscope (Carl Zeiss Epival Interphako) and optical images are shown in Fig.3.

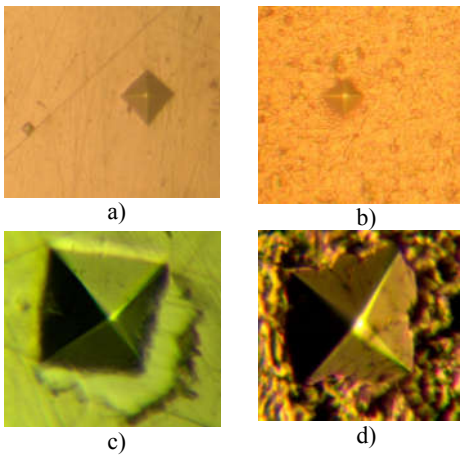

Fig.3. Optical images of Vicker's indent, on substrate steel and brass (a) and (c). The Vickers indent on 5 μm ED Cu film on steel b) and ED Cu film on brass, microetching in wather solution of $Na_2S_2O_8$ (ω=16.67 mas.%, time=10 min.) (d).

V. Results and Discussion

5.1. Absolute hardness of the substrates

Indentation tests were performed on uncoated substrates of brass 260 and steel 316 L in order to observe their response to indentation according to their different microstructure. Model proposed by Li and Bradt, Proportional Specimen Resistance (PSR) model [14], was chosen for analyzing the variation of substrate microhardness with the load:

$$P = a_1 \cdot d + (P_c / d_0^2) \cdot d^2 \qquad (7)$$

Here P_c is the critical applied test load above which microhardness becomes load independent and d_o is the corresponding diagonal length of the indent. A plot of P/d against d will give a straight line, and the slope gives the value of $P_c.d_0^{-2}$ which when multiplied by the Vicker's conversion factor 1.8544 gives the value of the load independent substrate microhardness, that is shown in Fig.4.

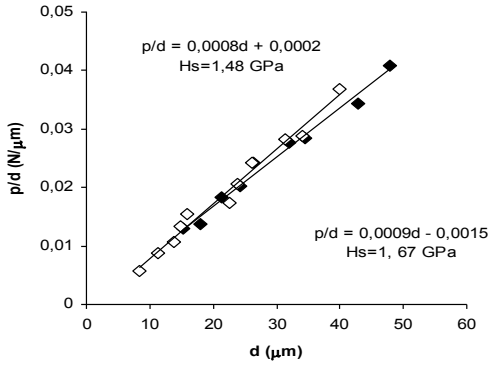

Fig.4. PSR plot of applied load (in N) through indent diagonal (in μm), P/d, versus indent diagonal, d, for different hard substrates. Absolute hardness of the substrates, Hs, is 1.483 GPa for brass and 1.67 GPa steel.

5.2. Composite and film hardness of monolayer thin film composite systems.

Composite systems of electrodeposited copper films on substrates of brass and stainless steel were fabricated. The average values of the indent diagonal d (in μm), were calculated from several independent measurements on every specimen for different applied loads P (in N). The absolute substrate hardness and composite hardness values, H (in GPa) were calculated using the formula:

$$H_c = 0.01854 \cdot P \cdot d^{-2} \qquad (8)$$

where 0.01854 is a constant, geometrical factor for the Vickers indenter.

Variation of the composite H_c, and film hardness H_f, of electrodeposited Cu films with different thickness (2 μm, 5 μm and 10 μm) on steel substrates, with relative indentation depth h/t, where h is indentation depth and t is total film thickness, is shown in Fig.5.

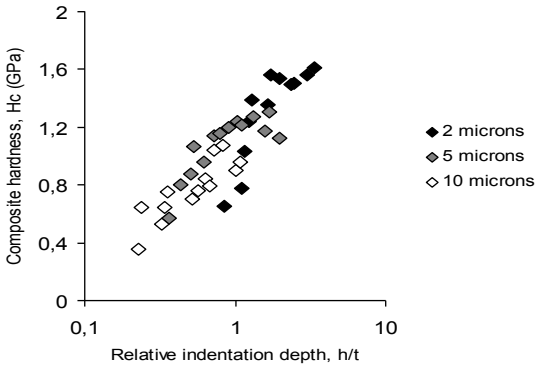

Fig.5. Composite hardness vs. relative indentation depth for the copper films deposited on steel substrate with variation film thickness, and 10 mA/sq.cm current density.

For relative indentation depth h/t, between 0.1 and 1, it was found that the hardness response is of the composite system (the film and the substrate together). The influence of the substrate is dominant for very thin films and the hardness curve is shifted to the right (for 2 μm-thick ED Cu film).

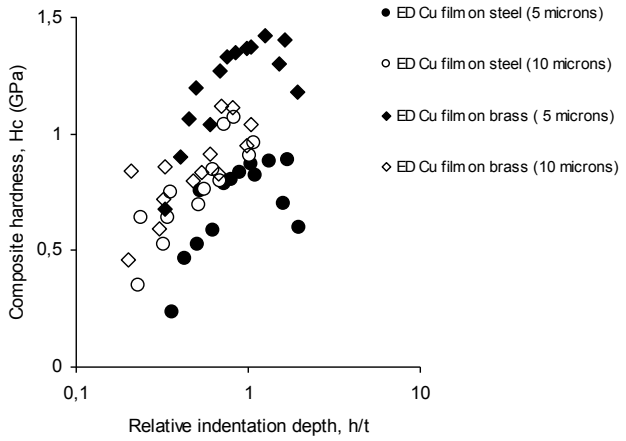

Fig.6. Variation in composite hardness with normalized depth *h/t*, for electrodeposited Cu film on alloy (brass and steel) with constant current density (j=10 mA/sq.cm).

Change of the composite hardness with relative indentation depth for ED Cu films with thickness 5 μm and 10 μm on different substrates is shown in Fig. 6. Composite hardness of ED Cu films on brass substrate is higher than the composite hardness of ED Cu films on steel substrate. A potential explanation can be found in analysis of the adhesion strength difference on the film-substrate interface [15].

The results of the calculated film hardness according to the Chicot-Lesage model for the system of ED Cu film on brass substrate were given in the Fig.7. The film thickness was 10 μm. The films obtained with higher current density (50 mA/cm^2) appear harder than films deposited with 10 mA/cm^2.

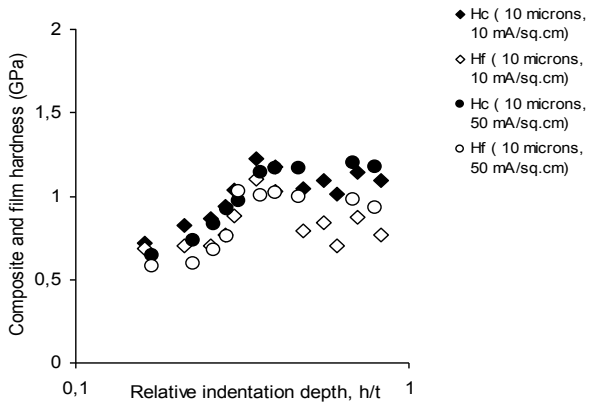

Fig.7. Variation in composite hardness H_c and film hardness H_f with relative indentation depth, h/t for 10 μm ED Cu films on brass as the substrate.

Change of the composite and film hardness, H_c and H_f, with relative indentation depth, *h/t*, for the system of soft ED Cu films on hard stainless steel and brass substrates, are shown in Fig.8. and Fig.9. The current density values were maintained at 10 mA/cm^2 and 50 mA/cm^2 and projected thickness of the films was 5 μm. Increase in current density value has led to grain size refinement and hardness increase [16].

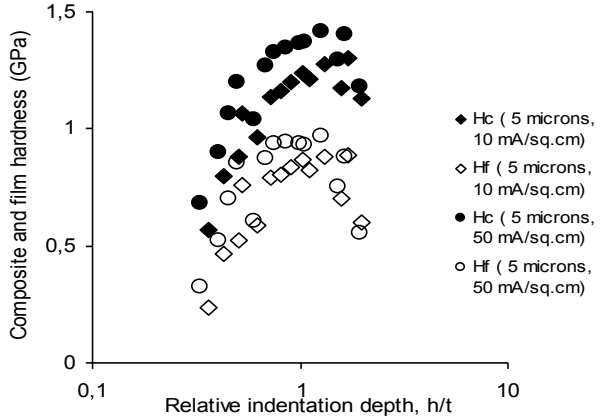

Fig.8. Variation in composite hardness *Hc* and film hardness *Hf*, with relative indentation depth, *h/t*, for 5 μm electrodeposited Cu films on stainless steel substrates.

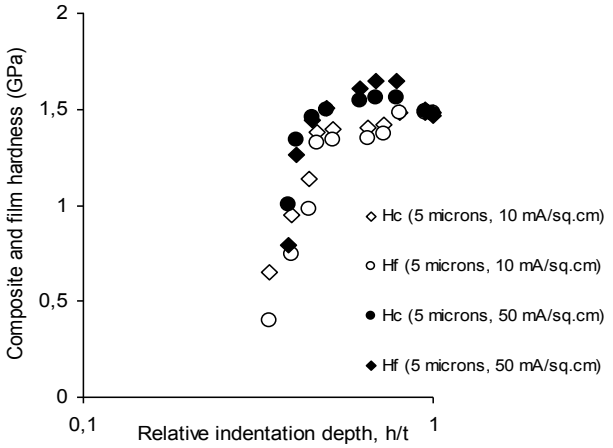

Fig.9. Variation in composite hardness H_c and film hardness H_f, with relative indentation depth, *h/t*, for 5 μm electrodeposited Cu films on brass substrate.

5.3. Composite hardness and adhesion

It is observed that adhesion influences the microhardness values of composite systems and films. Equation (6) was used to calculate the critical reduced depth *b* for the systems of thin ED Cu films on brass and stainless steel substrates. The hardness of the brass substrate was calculated and it is 1.483 GPa and of the stainless steel substrate is 1.67 GPa. The hardness of the copper film was calculated according to Chen-Gao (C-G) model. The calculated values of film hardness for 5 μm ED Cu film on steel substrates are 1.25 GPa (for current density 10 mA/cm^2), and 1.34 GPa (for current density 50 mA/cm^2). The copper film electrodeposited under the same process conditions on brass substrate has similar value of the film hardness and it is 1.24 GPa. It means that the model is appropriate for separation the film hardness value from the composite hardness. The indentation depth *D* is given by the indenter geometry ($D = d / 7$), and the film thickness was kept constant (5 μm). The appropriate value for power index, *m*, is found to be 1.8 for a soft film on a hard substrate [17].

The model of Chen-Gao was used to calculate the critical reduced depth, *b*, (the ratio between the radius of the plastic

zone beneath the indenter and the indentation depth) for 5 μm ED Cu films on steel substrate electrodeposited with different current density (10 and 50 mA/cm^2) as shown in Fig.10. The higher value of *b* is obtained for the films deposited with higher current density (50 mA/cm^2).

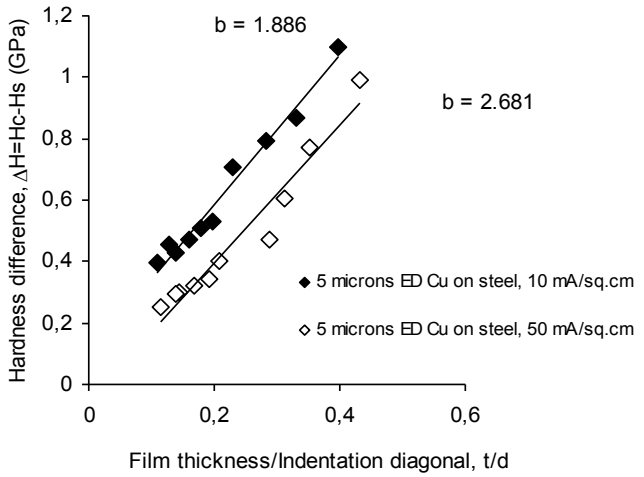

Fig.10. Hardness difference vs. ratio between the film thickness and the indentation diagonal for copper films on steel as a substrate. The critical reduced depth for 5 μm ED Cu films for different current density is shown.

Comparison of the adhesion parameter for the systems of ED Cu films on brass and stainless steel substrates show that critical reduced depth has higher value for the system of ED Cu on brass which corresponds to better adhesion properties. This behavior is shown in Fig.11.

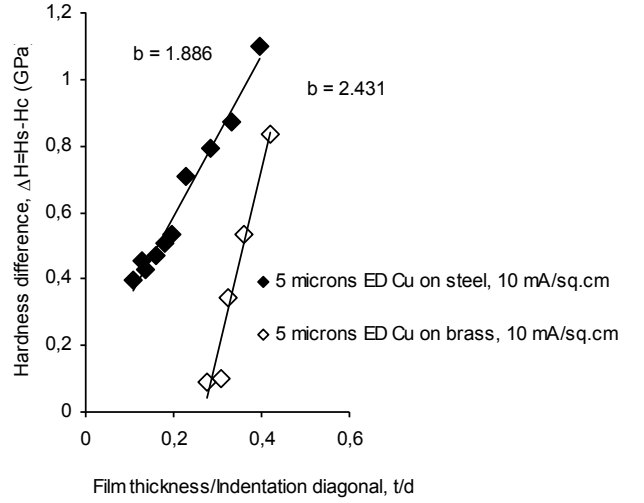

Fig.11. Hardness difference vs. ratio between the film thickness and the indentation diagonal for copper films on different substrates. The critical reduced depth b for 5 μm ED Cu films is shown.

In summary, adhesion influences the microhardness of films for soft films on hard substrates. With increasing the indentation load, the composite hardness decreases more rapidly for poor adhesion.

VI. CONCLUSION

Analysis of the composite and film hardness of ED Cu films on substrates of brass and stainless steel was studied. Microhardness measurements were performed on uncoated substrates and film-substrate composite systems to observe their hardness response. Composite hardness models of Chicot-Lesage and Chan-Gao were applied to experimental data in order to evaluate the film hardness and adhesion properties of the systems.

Composite and film hardness of ED Cu monolayer films on the brass and steel substrates were determined. Microhardness measurements indicated that the hardness response of the same film depends on type and contribution of the supportive substrate.

All test systems belong to "soft film on hard substrate" type of composite system (composite hardness values show ascending character). The copper films deposited on brass substrates have higher composite and film hardness then ED Cu films on steel substrates for the same deposition parameters and projected thickness.

A large value of critical reduced depth, corresponds to good adhesion properties of the film. For the same film-substrate system, critical reduced depth increases with increasing the current density. Systems of ED Cu film on brass substrate have better adhesion properties than the systems of ED Cu film on stainless steel substrate such as the critical reduced depth parameter shows.

ACKNOWLEDGMENT

This work was funded by Ministry of Education, science and Technological Development of Republic of Serbia through the orijects TR 32008, TR 34011 and III 45019.

REFERENCES

[1] S.S.Abd El Rehim, S.M.Sayyah, M.M.El Deeb, "Electroplating of copper films on steel substrates from acidic gluconate bath", Applied Surface Science, vol. *165,* no. *1,* pp. *249-254,* december, 1999.

[2] A.Ibanez, E.Fatas, "Mechanical and structural properties of electrodeposited copper and their relation with the electrodeposition parameters", Surf.&Coat. Technol., vol. *191,* no.*1*, pp. *7-16*, 2005.

[3] F.Ebrahimi, G.R.Boume, M.S.Kelly, T.E.Matthews, "Mechanical properties of nanocrystalline nickel produced by electrodeposition", Nanostructured materials, vol.*11*, no.*3*, pp. *343-350*, 1999.

[4] B.Zhang, Y.Kou, Y.Y.Xia, X.Zhang, "Modulation of strength and plasticity of multiscale Ni/Cu laminated composites", Materials Science & Engineering A, vol.*636*, pp. 216-220, june, 2015.

[5] J.Lamovec, V.Jović, I.Mladenović, M.Sarajlić, V.Radojević, "Micromechanical properties of composite systems obtained with electrodeposition of thin Ni and Cu films on different substrates", Proc. 57th ETRAN Conference, Zlatibor, Serbia, ISBN 978-86-80509-68-6,pp. *MO3.3*, 3-6 june, 2013.

[6] L.Bonou, M.Eyraud, Y.Massiani, "Influence of additives on Cu electrodeposition mechanisms in acid solution: direct current study supported by non-electrochemical measurements", Electrochemica Acta, vol. *47*, no. *26*, pp. *4139-4148*, 2002.

[7] I.Mladenovic, J.Lamovec, V.Jovic, V.Radojevic, "The synergetic effect of additives on the morphology and micromechanical properties of copper coatings on different substrates", Proc. 60th ETRAN Conference, Zlatibor, Serbia, ISBN 978-86-80509-68-6, pp. *MO3.3*, 3-6 june, 2016.

[8] I.Mladenovic, J. Lamovec, V. Jovic, V. Radojevic, "Synergetic effect of additives on the hardness and adhesion of thin electrodeposited copper

films ", Serbian Journal of electrical engineering, vol *14*, no. *1*, pp. *1-11*, February, 2017.
[9] D.Chicot, J.Lesage, "Absolute hardness of films and coatings", Thin Solid Films, vol *254*, no.*1*, pp. *123-130*, January, 1995.
[10] M.Chen, J.Gao, "The adhesion of copper films coated on silicon and glass substrates ", Modern Physics Letters B, vol. 14, no.3, pp. 103-108, *2000*.
[11] Q.R.Hou, J.Gao, S.J.Li, "Adhesion and its influence on micro-hardness of DLC and SiC films ", The European Physical Journal B, vol. *8*, pp. *493-496*, *1999*.
[12] J.L.He, W.Z.Li, H.D.Li, "Hardness measurement of thin films separation from composite hardness", Applied Physics Letters, vol. *69*, no.*10*, pp. *1402-1404*, *1996*.
[13] N.Nikolic, Z. Rakocevic, K.I.Popov, "Structural characteristics of bright copper surfaces", Journal of Electroanalytical Chemistry, vol. *514*, no. *1-2*, pp. *56-66*, november, *2001*.
[14] H.Li, L.Bradt, "The indentation load/size effect and the measurement of the hardness of vitreous silica", Journal of non-crystalline solids, no. *146*, pp. *197-212*, January, *1992.*
[15] D.S.Rickerby, P.J.Burnett, "Correlation of process and system parameters with structure and properties of physically vapor-deposited hard coatings", Thin Solid Films, vol. *157*, pp. *195-212*, september, *1998*.
[16] J.Lamovec, V.Jovic, I.Mladenovic, M.Vorkapic, B.Popovic, V. Radojevic, "Comparative microhardness analysis of various thin matallic multilayer composite films", Proc. 28th MIEL Conference, Niš, Serbia, ISBN 978-1-4673-0235-7/12, *13-16* may, *2012.*
[17] L.Magagnin, R.Maboudian, C.Carraro, "Adhesion evaluation of immersion plating copper films on silicon by microindentation measurements ", Thin Solid Films, vol. *434*, no.*1*, pp. *100-105*, february *2003*.