SERBIAN JOURNAL OF ELECTRICAL ENGINEERING
Vol. 14, No. 1, February 2017, 1-11
UDC: 669.245'779:621.793.3+669.782:669.3 DOI: 10.2298/SJEE1701001M

Synergetic Effect of Additives on the Hardness and Adhesion of Thin Electrodeposited Copper Films

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Abstract: Thin copper films were electrodeposited on a polycrystalline cold-rolled copper substrate. The composition of the laboratory-made copper sulphate electrolyte was changed by the addition of various additives. The influence of chloride ion (Cl^-), polyethylene glycol (PEG) and 3-mercapto-1-propane sulfonic acid (MPSA) on mechanical and adhesion properties of the electrodeposited copper films was investigated using Vickers microindentation technique. Calculations of the film hardness and adhesion were carried out using composite hardness models of Korsunsky and Chen-Gao. The hardness of the composite system is influenced by the adhesion of the copper film to the substrate. Increasing adhesion corresponds to increasing values of the calculated adhesion parameter b, named the critical reduced depth. When additives are added to a plating solution, the copper deposition mechanism is changed and fine-grained microstructure without the formation of microscopic nodules is obtained.

Keywords: Composite microhardness, Electrodeposition, PEG, MPS, Adhesion, Critical reduced depth.

1 Introduction

Electrochemical deposition (ED) of different metals plays an important role in the electronic industry and microelectromechanical systems (MEMS) technology. The galvanic application of copper coatings is a simple, fast and inexpensive process compatible with the existing MEM technologies. Selection and optimization of electrochemical deposition process parameters makes it possible to predict the microstructure (grain size) of the film [1]. The presence of even small amounts of adsorption compounds (chloride ions, PEG, MPS) in the plating bath, results in significant changes in the properties of the deposited films such as brightness, hardness, wear resistance and adhesiveness to the substarte.

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The systems of thin films on substrates, especially of copper thin films which are used in fabrication of different MEM devices, may be considered as the composite systems. Thin copper films have an important application in the electronic industry for the fabrication of contacts in integrated circuits and are the best choice when it is necessary to fill the HAR-channels (high aspect ratio trenches) [2]. Electrodeposited copper films are used as sacrificial layers for creating 3D microstructures with distinct chemical selectivity in silicon micromashining [3]. Thin Cu films alternately electrodeposited with Ni films may be considered as laminate composites with good mechanical properties such as high hardness and tensile strength, which is especially important for MEMS structures in terms of robustness and durability of the device [4 – 6].

The microhardness and adhesion test are very important and widely used for testing the structural and mechanical properties of composite systems. For a composite system of thin films on substrate, the influence of the substrate must be taken into account in composite and film hardness determination. It is possible to evaluate the adhesion of films on substrate by microhardness test method according to the model developed by Chen and Gao [7 – 13].

The effects of varying the deposition parameters and the combinations of additives in the electrolyte on the quality of the copper films electrodeposited on a copper foil were investigated. The presence of additives in the plating bath and their synergetic effect on copper deposition mechanism results in a change of the Cu thin film microstructure. The experimental data presented in this paper contribute to the understanding of the physical processes which control the deformation of the film-substrate system under indentation. The composite hardness model based on microhardness measurement is used to evaluate the adhesion of copper films on a copper foil substrate with and without additives in the plating bath. It is clear that the analysis of the hardness response of the composite system is an important step towards better understanding the control of MEMS wear properties. The film hardness and the adhesion of the ED copper coating on metallic substrates are responsible for the durability and the lifetime of the MEMS devices.

2 Hardness Determination of Thin Copper Films Using the Work-of-Indentation Model

The microindentation test is a known method for the analysis of mechanical properties of single or multilayer thin films. There is a need for the determination of the film hardness solely from the composite hardness measurements. The composite (H_c) and the film (H_f) hardness are load-dependent. It is not easy to measure thin film hardness because it is influenced by the total film thickness (t), the indentation depth (h) , the substrate hardness (H_s), the hardness ratio (H_s/H_f), adhesion, extension of the elastic-plastic zone

under the indent, the indentation size effect (ISE) and other phenomena. Experimental data were analyzed using the descriptive mathematical model named "work-of-indentation model" by Korsunsky et al. [14]. The total work of indentation is composed of the plastic work of deformation in the substrate (W_s) and the energy of deformation or fracture in the film (W_f) :

$$W_{tot} = W_s + W_f \,. \tag{1}$$

In the case where plastic deformation occurs in the film, the contribution of the overall work of an indentation may be expressed as:

$$W_f = \frac{\lambda H_F t^2 h}{3\kappa} \,. \tag{2}$$

The constant κ is a parameter that describes the geometry of the indenter, while λ describes the dependence of the length of the fracture on the type of the film-substrate system.

According to this model, the constant a is introduced as:

$$a = \frac{1}{1 + k\beta^2} \,. \tag{3}$$

The parameter k represents a dimensionless material parameter related to the composite response to indentation and β is the relative indentation depth (RID), given by the ratio between the indentation depth and the coating thickness. The range of the relative indentation depth between 0.1 and 1 is the most interesting for analysis from the point of view mechanics and mechanisms of the indentation process [15].

According to this model, the composite hardness H_c is given by:

$$H_c = H_s + \left[\frac{1}{1 + k'\left(\frac{d^2}{t} \right)} \right] \left(H_f - H_s \right), \tag{4}$$

where H_s represents the absolute hardness of the substrate, and k' is:

$$k' = \frac{k}{49t} \,. \tag{5}$$

It is not possible to calculate the variation of the film hardness with the indentation diagonal from the individual measurements of composite hardness. The values of k should be determined simultaneously from experimental measurements of the composite hardness. This model gives good results for the composite system of the type “hard film on soft substrate” [16].

3 Adhesion Model for Evaluation of Cohesive/Adhesive Properties of Thin Films by Microhardness Testing

Chen-Gao (C-G) method was chosen for the evaluation of the adhesion properties of thin electrodeposited films on substrate [8]. This method introduces the composite hardness as a function of the critical reduced depth beyond which the material has no effect on the measured hardness. They found that a large value of the critical reduced depth b (the ratio between the radius of the plastic zone under the indenter and the indentation depth) corresponds to good adhesion, while low values indicate poor adhesion of the films, as shown in Fig. 1.

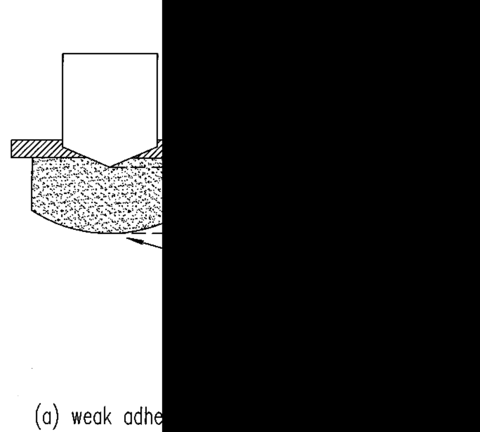


Fig. 1 –*Schematic representation of deformation associated with indentation in a coated substrate: (a) weak adhesion, (b) the effect of a strong film/substrate interface [7].*

The correlation between the composite hardness value and the critical reduced depth is found as:

$$\Delta H = \frac{7(m+1)(H_f - H_s)}{mb}\frac{t}{d}, \tag{6}$$

where m is the power index. The critical reduced depth has different values for various film/substrate systems. The power index is an empirical exponent and its value is in the range of 1÷2. For ED copper films, the value of m is 1.2 for the "hard film-soft substrates" composite system type, and 1.8 for the "soft film-hard substrates" composite system type [7 – 13].

4 Experimental Setup

We used a copper foil as substrate for electrodeposition of thin copper films. For each experiment, the samples were processed as follows: (1) substrate

preparation, (2) electrochemical reagents preparation, (3) ED process, (4) microhardness testing and (5) data processing.

4.1. Substrate preparation

Polycrystalline cold-rolled, 125μm thick copper foil for contact printing was used as the substrate for the copper electrodeposition. Before the ED process the substrate was washed, degreased and chemically polished in a mixture of acids $HNO_3 : H_3PO_4 : CH_3COOH = 4 : 11 : 5$ vol%.

4.2 Electrochemical reagents

The aqueous solution used for copper electrodeposition contained the following reagents: copper sulfate, sulphuric acid, and different additives. The copper films were electrodeposited from three different lab-made sulphate electrolytes with compositions given in **Table 1**. The ED process was carried out using the direct current (DC) galvanostatic mode. The working electrode was a cylindrical plate of electrochemical grade copper, washed and chemically etched in nitric acid (1:1 vol%) .

Table 1

Composition of the plating bath and deposition parameters.

Composition and working conditions			
Composition of bath, gL^{-1}	I	II	III
$CuSO_4{\cdot}5H_2O$	147	240	240
H_2SO_4	42	60	60
$CuCl_2$	0.0175		
NaCl		0.124	0.124
PEG		1	1
MPS			0.0015
Deposition conditions			
Temperature [°C]	25	25	25
Current density [$mA{\cdot}cm^{-2}$]	30	50	50
Deposition rate [$\mu m{\cdot}min^{-1}$]	1.14	1.10	1.04

The deposition time was determined according with plating surface and projected thickness of deposit (10 μm).

4.3 Microhardness testing and characterization

The microhardness of the composite systems was characterized using Vickers microhardness tester “Leitz Kleinharteprufer DURIMET I“. Different load values from 4.9 N down 0.049 N were used. Three indentations were made at each load and six indentation diagonals were obtained. Measurements were performed at room temperature. The microstructure of the samples was investigated by metallographic microscopy (Carl Zeiss microscope “Epival Interphako“).

5 Results and Discussion

5.1. Absolute hardness of substrates

Microhardness testing was performed both on uncoated substrates and on different composite systems. The model named PSR (Proportional Specimen Resistance) [17] was chosen for analyzing the variation of the substrate microhardness with the load.

The average values of the indent diagonal d [m], were calculated from several independent measurements on every specimen for different applied loads $P(N)$. The absolute and the composite hardness values H_0 and H_C were calculated using the formula:

$$H_c = 1.8544 P d^{-2} . \tag{7}$$

According to PSR model, the indentation test load P is related to the indentation size as:

$$P = a_1 d + \left(\frac{P_c}{d_0^2} \right) d^2 . \tag{8}$$

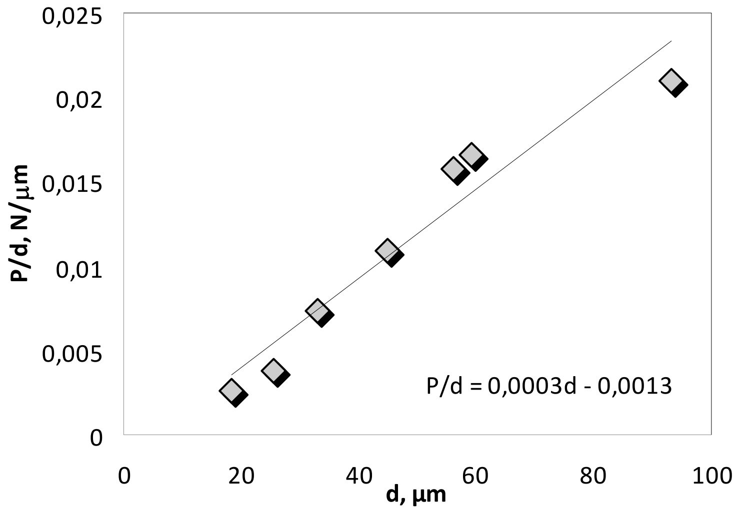
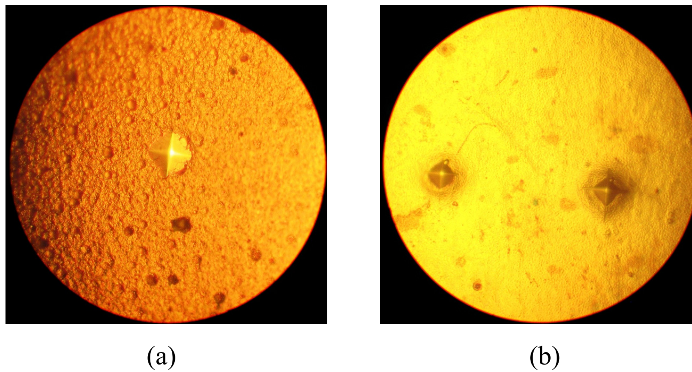


Fig.2 – *PSR plot of applied load (in* N*) through indent diagonal (in* μm*), P/d, versus indent diagonal, d, for different hard substrates.*

The value of P_c / d_0^2 for copper substrate was 0,0003 GPa/ μm^2. The absolute hardness of the copper substrate, H_s was calculated to be 0,56 GPa, as shown in Fig. 2.

5.2 Composite hardness of systems

According to **Table 1,** three different types of plating baths were employed in order to obtain various composite systems of thin copper film on copper substrate. The microstructure and microhardness of the copper films in presence of chloride ions only, chloride ions and polyethylene glycol (PEG), and chloride ions, polyethylene glycol and mercapto propane sulphonic acid (MPS) were studied. Fig. 3. represents Vickers the results of Vickers microhardness testing of composite systems with copper film whose microstructure was influenced by different additives.



(a) (b)

Fig. 3 – *Optical images of Vickers indent on 10 μm-thick copper films electrodeposited with* 50 mA/cm^2 *current density: (a) PEG + chloride ions; and (b) PEG + MPS + chloride ions.*

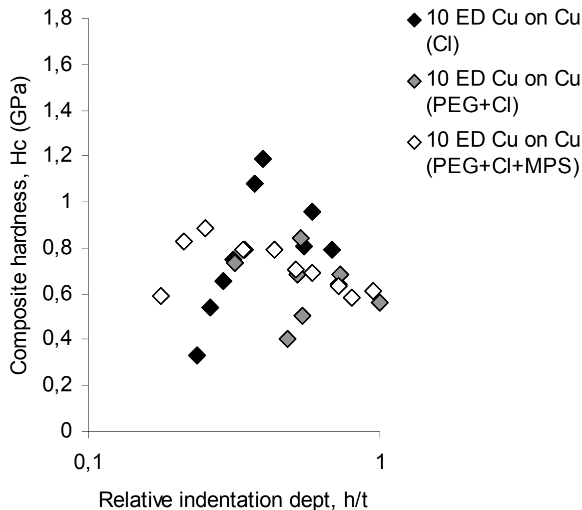


Fig. 4 – *Variation of composite hardness (Hc) with relative indentation depth (h/t) for* 10 μm *ED copper film electrodeposited with different additives.*

The change of the composite hardness (H_C) with relative indentation depth for different systems of copper film on copper substrate, expressed as the ratio of the indentation depth and the film thickness *h/t* is shown in Fig. 4.

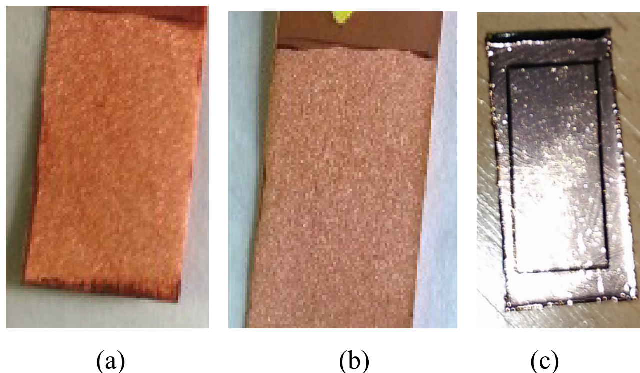
Copper films with a total thickness of 10 μm , were electrodeposited with 50 mA/cm^2 current density and with addition of different aditives: chloride ions and mercapto propane sulphonic acid as accelerators and polyethylene glicol as suppressor additive.

For the values of the relative indentation depths *h/t* between 0.1 and 1, the hardness response belongs to the whole composite systems and depends on the film and on the substrate hardness values. The shift of the composite hardness curve toward shallow penetration depths ($h/t \leq 0.1$) indicates a high influence of the film hardness in the composite hardness value.

The curve-fit data obtained by the Korsunsky composite hardness model are given in **Table 2**.

Table 2
The fitting results according to the model of Korsunsky for the electrodeposited Cu films of 10μm *thickness on a copper substrate.*

ED Cu film on copper, t = 10 μm, 50 mA·cm^{-2}, PEG+Cl+MPS	
H_F	0.8124
k'	2.98
ED Cu film on copper, t = 10 μm, 50 mA·cm^{-2}, PEG+Cl	
H_F	0.9845
k'	44.9
ED Cu film on copper, t = 10 μm, 50 mA·cm^{-2}, Cl	
H_F	0.7438
k'	9.73



(a) (b) (c)

Fig. 5 – *Images of copper films electrodeposited on copper substrate with (a) no additives, (b) chloride ions and (c) chloride ions + PEG + MPS addition.*

The copper films electrodeposited with PEG and MPS additives have fine-grained microstructure that leads to higher values of microhardness. The synergetic effect of additives, PEG, MPS and chloride ions is reflected in the resulting bright and uniform deposit shown in Fig. 5.

5.3 Adhesive properties of electrodeposited Cu films on different substrates

It is observed that adhesion influences the microhardness values of composite systems and films. For the evaluation of the adhesion properties of thin ED copper films on substrates, Chen-Gao (C-G) method was chosen. Equation (6) was used to calculate the critical reduced depth *b* for different systems of thin electrodeposited Cu films on Cu substrate.

In Fig. 6, the values of hardness difference, $\Delta H = H_C - H_S$, for ED Cu films on Cu substrate are plotted versus the ratio between the film thickness and the indentation diagonal, t/d . A linear fit of the data was performed and the calculated values of *b* are shown in the same figure. The substrate and the composite hardness, H_S and H_C, were obtained from microhardness measurements presented in Sections 4.1 and 4.2.

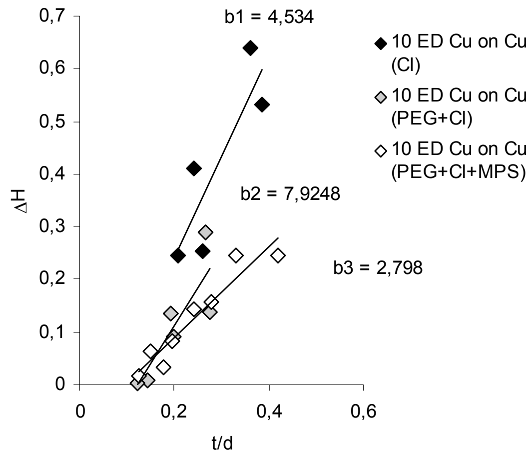


Fig. 6 – *Experimental values of hardness difference as a function of the ratio between the film thickness and the indentation diagonal, for ED Cu films on a copper foil deposited with different additives. The film thickness and the current density were* 10 μm *and* 50 mA/cm^2*, respectively. The critical reduced depth b is shown.*

For these systems it is obvious that the hardness of the composite and film and adhesion of the film on the substrate depend on the microstructure of the film. Synergetic effect of the additives (chloride ions + PEG + MPS) in the

plating solution contributes to obtaining the fine-grained film microstructure and high values of composite microhardness and adhesion.

6 Conclusion

We have presented a microhardness and adhesion analysis performed on copper films electrodeposited from plating baths with different additives on cold-rolled copper substrates: chloride ions only, chloride ions and polyethylene glycol (PEG) and chloride ions, PEG and mercapto propane sulphonic acid (MPS). The designed thickness of the films was 10 μm and the current density value was maintained at 50 mA/cm^2 for all the films.

The composite hardness model of Korsunsky was used for the analysis of the film hardness. The synergetic effect of additives is reflected in the copper film hardness value and the films electrodeposited with Cl^-, MPS and PEG have the highest hardness.

The adhesion influences the microhardness values of the composite systems. With increasing the indentation load, the composite hardness decreases more rapidly in the case of poor adhesion. The introduction of additives into the plating solution influences the adhesion properties of the metallic films on the substrate. When adhesion exists on the thin copper film-copper foil interface, the critical reduced depth, b , increases.

7 Acknowledgement

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

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