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MICROHARDNESS ANALYSIS OF THIN METALLIC MULTILAYER COMPOSITE FILMS ON COPPER SUBSTRATES

J. Lamovec[*,#], V. Jović[*], M. Vorkapić[*], B. Popović[*], V. Radojević[**] and R. Aleksić[**]

[*]Institute of Chemistry, Technology and Metallurgy – Department of Microelectronic Technologies and Single Crystals, Njegoseva 12, 11000 Belgrade, Serbia
[**]Faculty of Technology and Metallurgy, University of Belgrade, Karnegijeva 4, 11000 Belgrade, Serbia

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Abstract

Composite systems of alternately electrodeposited nanocrystalline Ni and Cu films on cold-rolled polycrystalline copper substrates were fabricated. Highly-densified parallel interfaces which can give rise to high strength of composites are obtained by depositing layers at a very narrow spacing. The hardness properties of the composite systems were characterized using Vickers microhardness testing with loads ranging from 1.96 N down to 0.049 N. Above a certain critical penetration depth, a measured hardness value is not the hardness of the electrodeposited film, but the so-called „composite hardness“, because the substrate also participates in the plastic deformations during the indentation process. Dependence of microhardness on layer thickness, Ni/Cu layer thickness ratio and total thickness of the film was investigated. Model of Korsunsky was applied to the experimental data in order to determine the composite film hardness. The microhardness increased with decreasing the layer thickness down to 30 nm and it is consistent with the Hall-Petch relation. Layer thickness and layer thickness ratio are the important parameters which are responsible for making decision of the total film thickness.

Keywords: Composite hardness; Vickers microhardness; Hardness models; Ni/Cu electrodeposition; Multilayers.

1. Introduction

Multilayered composite structures of different materials, with small layer thickness (less than 1 μm), have specific mechanical, magnetic and optical properties

[#] *Corresponding author: jejal@nanosys.ihtm.bg.ac.rs*

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[1, 2].

Development of the reliable techniques for growing of metal and magnetic layers is of great interest in the microsystem technologies [3- 5]. An interesting approach for growing of these layers is the use of electrochemical deposition technique. Electrochemical deposition (ED) is fully compatible with MicroElectroMechanical (MEMS) technologies and has several advantages in relation to another deposition processes: it is a low-temperature deposition technique with easy controlled high deposition rate allowing a wide thickness range, the easy control of thickness and residual stress, chemical composition of the layer, microstructure (grain size) of the deposits.

Copper and nickel are well suited for microsystem applications owing to their low resistivity, low cost and easy to grow electrochemically in a well-controlled way. Nickel has magnetic properties interesting for the development of magnetic sensors and actuators microsystems [4, 6, 7].

Multilayered Ni/Cu structures would allow the use of one of the electrodeposited layers as a sacrificial layer (selective etching technique) [8-10].

Indentation microhardness measurement is a well known and reliable test method for the evaluation of mechanical characteristics of coatings. During hardness determination of thin films and coatings by indentation method, the influence of the substrate must be considered. Above a certain critical penetration depth, the so-called „composite hardness“, which includes a component of the substrate hardness, will be measured. The measured hardness is a complex value depending on the relative indentation depth and structural and mechanical properties of both the composite film and the substrate [11, 12].

2. Composite Hardness Model

There is a need to obtain the hardness of the composite films alone from the experimental composite hardness measurements. Several models which operate on a number of different principles exist. According to earlier investigations, for the system „ hard film on soft substrate“, model Korsunsky et al. (K- model) gives good fitting results and will be examined for the multilayered-film composites [13, 14].

Descriptive model of Korsunsky et al. [13] is applicable to either plasticity- or fracture-dominated behaviour, with all scales measured relative to the film thickness. According to model, the total work-of-indentation during a hardness test is composed of two parts: the plastic work of deformation in the substrate and the deformation and/or fracture energy in the film. The composite hardness, H_C, according to this model is given by:

$$H_C = H_S + \left[\frac{1}{1 + k' \cdot \left(d^2 / t \right)} \right] \cdot \left(H_F - H_S \right); \; k' = \frac{k}{49 \cdot t} \quad ...(1)$$

where k represents a dimensionless materials parameter related to the composite response mode to indentation, d is indent diagonal and t is the thickness of the film.

This model doesn't allow computing the change in the film hardness with the indentation diagonal from the individual measurements of composite hardness. The magnitude of k should also be determined simultaneously from the experimental measurements of the composite hardness.

3. Experimental

3.1. Fabrication of electroplated Ni/Cu thin films

The substrates of rectangle cold-rolled polycrystalline copper pieces were prepared and chemically etched in a standard way [15]. Electrochemical deposition was carried out using direct current galvanostatic mode. Ni and Cu layers were alternately electrodeposited from two different electrolytes (dual bath technique, DBT) [16], Ni from a sulphamate bath consisting of 300 g/l $Ni(NH_2SO_3)_2 \cdot 4H_2O$, 30 g/l $NiCl_2 \cdot 6H_2O$, 30 g/l H_3BO_3, 1 g/l saccharine, and Cu from a sulphate bath consisting of 240 g/l $CuSO_4 \cdot 5H_2O$, 60 g/l H_2SO_4. The current density value was maintained at 10 mA/cm^2 and deposition time was determined according with plating surface and projected thickness of deposits.

3.2. Microindentation test of Ni/Cu thin films

The mechanical properties of the composite systems were characterized using Vickers microhardness tester „Leitz, Kleinharteprufer DURIMET I“ with loads ranging from 0.049 N up to 1.96 N. Three indentations were made at each load, yielding six indentation diagonals measurements, from which the average hardness value could be calculated. Indentation was performed at room temperature. The experimental data were fitted with GnuPlot, v 4.2 (http://www.gnuplot.info/).

3.3. Microstructure analysis of Ni/Cu thin films

After the mechanical testing, samples were prepared for the examination by metallografic microscopy (Carl Zeiss microscope „Epival Interphako“). Topographic details were investigated by means of atomic force microscope (AFM) named „TM Microscopes-Veeco“ operating in non-contact mode.

4. Results and Discussion

4.1. Microstructure of the substrate and ED films of copper and nickel

The substrate was polycrystalline cold-rolled copper which average grain size was a few microns. Optical image of the Cu substrate after revealing the grain boundaries is shown on Fig.1. [14, 16, 17]. The hardness of material is strong related to the material

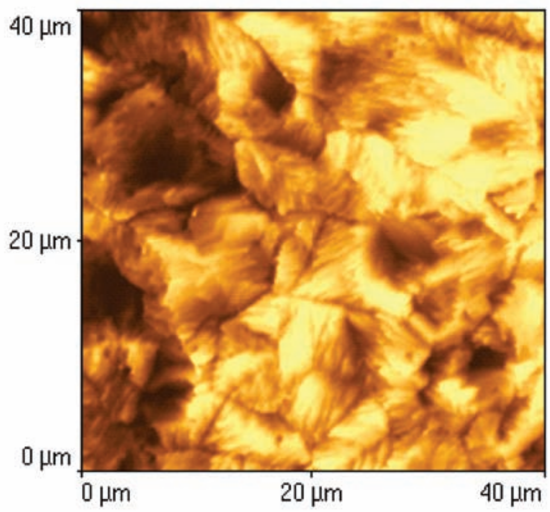

Fig.1. Optical image of polycrystalline copper substrate

structure and because of shown microstructure, the substrate belongs to the class of soft materials.

The structures of electrodeposited films of Ni and Cu are related to the plating variables such as: type of electrolyte bath, current density, pH value and temperature. For the above-mentioned experimental parameters, electrodeposited films of Cu and Ni are nanocrystalline materials [18-20].

With topographic AFM images shown on Fig.2. and Fig.3. it is possible to confirm the columnar structure of electrodeposited layers. According to literature [19], the plated structures consist of small substructures named „colonies“ and deep, large crevices among them. They were defined as series of very fine grains that tend to form groups. A colony boundary may be a grain boundary, but a grain boundary is not necessarily defined by a colony boundary, which may contain finer grains.

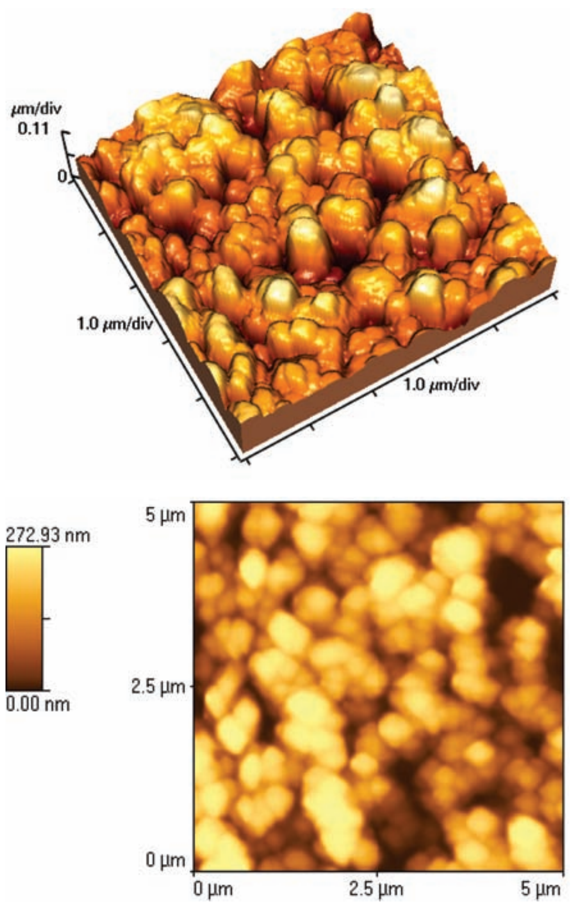

Fig.2. Topographic AFM image of ED Ni film (10 μm, 10 mA/cm^2), chemically etched for 60 s in solution for revealing grain boundaries showing structures of columnar grains.

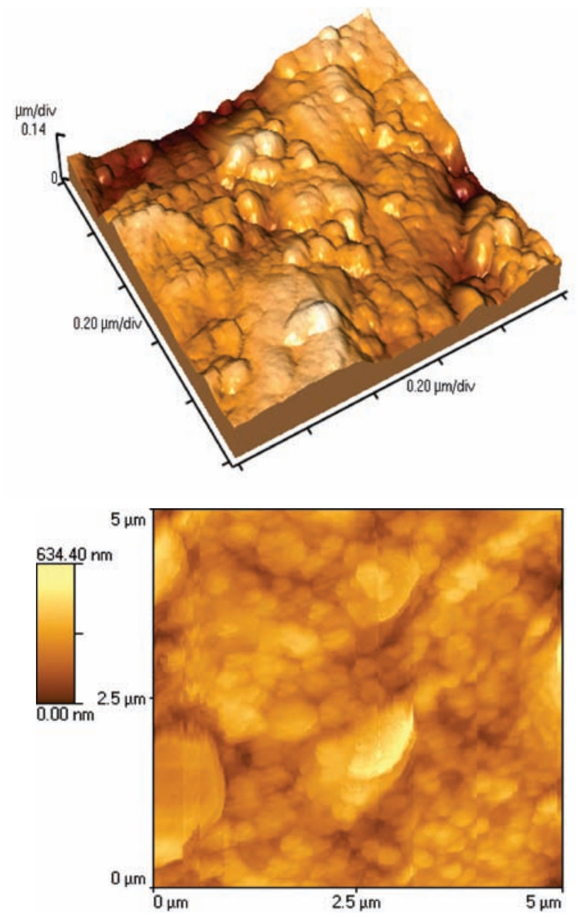

Fig. 3. Topographic AFM image of ED Cu film (10 μm, 50 mA/cm^2, chemically etched for 20 s in solution for revealing grain boundaries showing structures of columnar grains.

4.2. Determination of absolute hardness of the substrate

Proportional specimen resistance (PSR) model of Li and Bradt is suitable for analysing the variation of microhardness with load [21]. According to this model, the indentation test load P is related to indentation size d as follows:

$$P / d = a_1 + \left(P_C / d_0^2\right) \cdot d \qquad ...(2)$$

Here P_C is the critical applied test load above which microhardness become load independent and d_0 is the corresponding diagonal length of the indent. A plot of P/d against d will give a straight line, the slope of which give the value P_C / d_0^2. Load independent microhardness was calculated by multiplying the value of P_C / d_0^2 with the Vickers conversion factor 0.01854. For the cold-rolled copper material, the substrate hardness was determined as H_S = 0.37 GPa [14].

4.3. Composite hardness and film hardness

For the analysis of the multilayer composite system hardness, several parameters were chosen: dependence of Vickers composite microhardness on layer thickness (layer means one-component layer material, Ni or Cu), Ni/Cu layer thickness ratio and total thickness of the films. Fig.4. represents the topographic AFM image of the Vickers indent in the 5 μm-thick multilayer Ni/Cu film.

4.3.1 Dependence of composite microhardness on layer thickness

Change of the composite hardness (H_C) of the system of composite Ni/Cu film on Cu substrate with relative indentation depth expressed as indentation depth (h) through film thicknes (t), h/t, is shown on Fig.5. Composite films with total thickness of 5 μm, with different layer thickness (from 30 nm to 1 μm) were deposited with 10 mA/cm^2 current density.

It is found that with decreasing the layer thickness (and increasing the number of

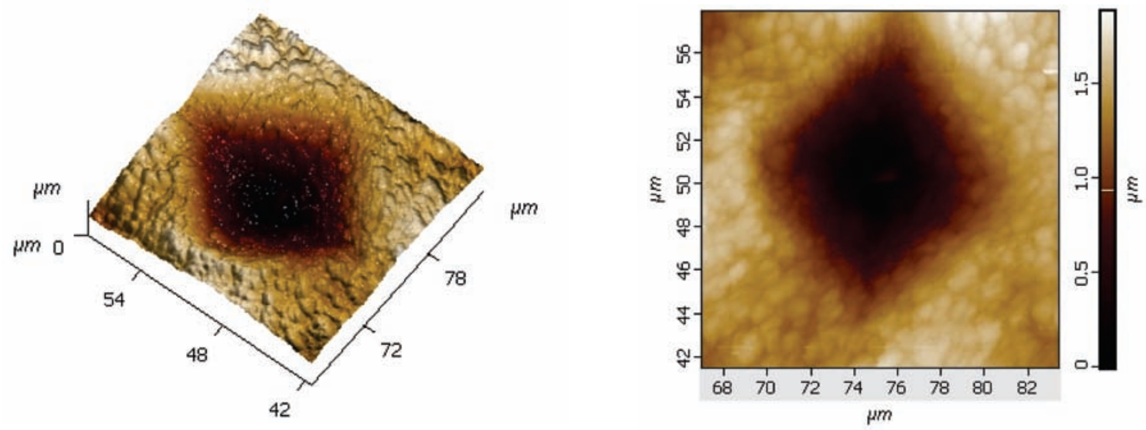

Fig.4. Topographic AFM images of electrodeposited 5 μm-thick Ni/Cu film on Cu substrate, layer thickness 300 nm.

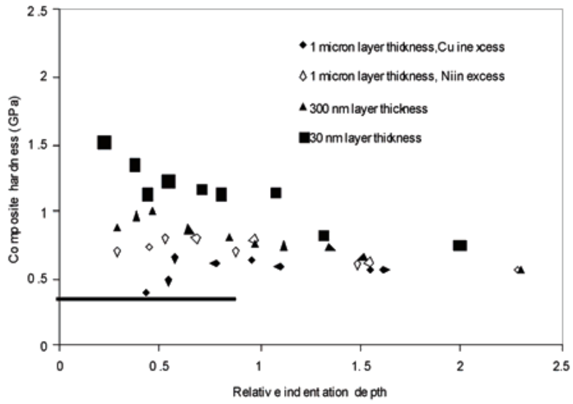

Fig.5. Variation in the composite hardness, H_C, with the relative indentation depth, h/t, for Ni/Cu 5 μm-thick films on Cu substrate. Thick line represents hardness of Cu substrate (H_S = 0.37 GPa).

interfaces) from 1 μm to 30 nm, the composite hardness of the systems (film and substrate) increases. The hardness of the ED Cu films is lower then that of the ED Ni films [17], and the composite system with Cu in excess and the same layer thickness has the lower value of the composite hardness.

For shallow penetration depths (h/t ≤ 0.1), the response is of the film only. With increasing of relative indentation depths, the composite hardness decreases until it reaches the substrate hardness H_S, indicated by solid line on Fig.5.

4.3.2 Dependence of composite microhardness on Ni/Cu layer thickness ratio

Change of the composite hardness (H_C) of the system Ni/Cu composite film on Cu substrate with different layer thickness ratio, with Ni in excess (Fig.6.) and with Cu in excess (Fig.7.) are shown.

With increasing the layer thickness ratio (300 nm Ni layer thickness and 300 nm, 150

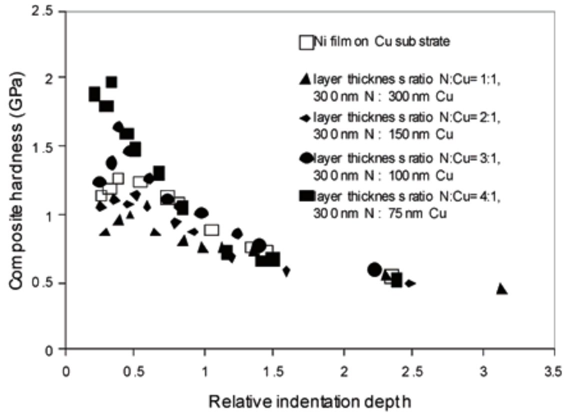

Fig.6. Variation in the composite harndess, H_C, with the relative indentation depth, h/t, for Ni/Cu 5 μm-thick films on Cu substrate with different layer thickness ratio Ni:Cu.

nm, 100 nm and 75 nm Cu layer thicknesses), the hardness of the composite increases and become higher than the hardness of monolayered Ni film (5 μm, 10 mA/cm2, H_F = 1.58 GPa) on Cu substrate [14, 17], for Ni:Cu layer thickness ratio 3:1 and 4:1.

On the contrary, with increasing the layer thickness ratio with Cu in excess (300 nm Cu layer thickness and 300 nm, 150 nm and 100

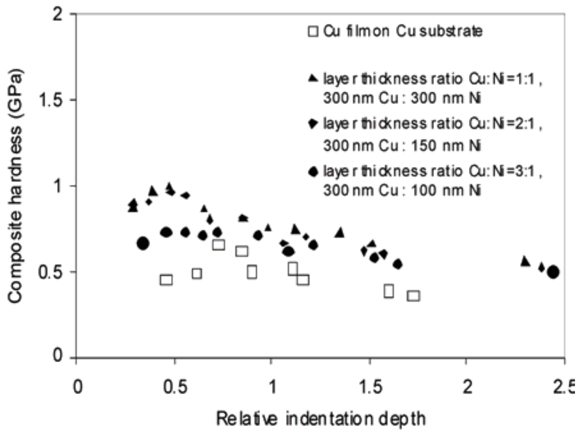

Fig.7. Change of the composite hardness, H_C, with the relative indentation depth, h/t, for Ni/Cu 5 μm-thick films on Cu substrate with different layer thickness ratio Cu:Ni.

nm Ni layer thickness), the composite hardness decreases, but in all cases it is higher than the hardness of the monolayered Cu film on Cu substrate (5 µm, 10 mA/cm^2, H_F = 0.58 GPa) [14].

4.3.3 Dependence of composite microhardness on total thickness of the Ni/Cu multilayered films

Change of the composite hardness H_C, with relative indentation depth, *h/t*, for different total thickness of the composite multilayered films is shown on Fig.8.

Composite hardness increases with increasing the total thickness of the films, but it is very sensitive to layer thickness parameter. 5 µm-thick film with 30 nm-layer thickness was appeared harder than 10 µm-thick film with 300 nm-layer thickness.

Below a certain critical layer thickness value (composite hardness of the 15 nm-layer thickness film was examined), composite microhardness value decreases and it is shown on Fig.8.

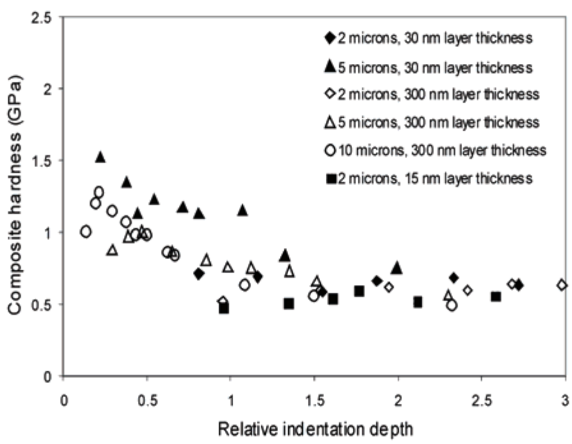

Fig.8. Change of the composite hardness, H_C, with the relative indentation depth, h/t, for Ni/Cu films of different thickness on Cu substrate.

Experimental data for chosen multilayered systems of Ni/Cu on Cu substrate (hard film on a soft substrate) were fitted with the composite hardness model of Korsunski et.al., Eq.(1). H_S was taken as 0.37 GPa, according to experimentally obtained value. The curve-fit data produced from the model validation process are given in Tab.I.

Table 1. The fitting results according to the model of Korsunsky for the Ni/Cu films of 5 µm thickness on a Cu substrate.

Quantity	K model	Asymptotic standard error
ED Ni/Cu film (5 µm, 10 mA/cm^2), layer thickness 300 nm		
H_F / GPa	0.97	±0.03 (3%)
k'	0.0018	±0.0004 (21.2%)
ED Ni/Cu film (5 µm, 10 mA/cm^2), layer thickness 30 nm		
H_F / GPa	1.39	±0.068 (4.9%)
k'	0.002	±0.0006 (31.1%)
ED Ni/Cu film (5 µm, 10 mA/cm^2), 300 nm Ni : 100 nm Cu		
H_F / GPa	1.61	±0.071 (4.4%)
k'	0.0042	±0.0008 (20.8%)
ED Ni/Cu film (5 µm, 10 mA/cm^2), 300 nm Ni : 75 nm Cu		
H_F / GPa	2.12	±0.008 (3.75%)
k'	0.0089	±0.001 (14.8%)

5. Conclusion

We have presented a microstructural and microhardness analysis performed on Ni/Cu multilayered films electrochemically grown on cold-rolled Cu substrates. AFM images confirmed fine-grained columnar structures of Ni and Cu layers, alternately electrodeposited from different electrolytes.

For the analysis of the composite system hardness, three parameters have been chosen: layer thickness, layer thickness ratio and total thickness of the film. With decreasing the layer thickness from 1 μm to 30 nm, composite system hardness increased more than two times, because of introducing the great number of interfaces, that are able to act as barriers to plastic deformation. Variation of the Ni/Cu layer thickness ratio has revealed the dependence of the composite hardness on structure and mechanical properties of any particular component of the film, i.e. Ni and Cu. It is possible to achieve high strength with properly chosen layer thickness ratio. Increasing the total thickness of the film leads to increasing in the composite hardness. Layer thickness and layer thickness ratio are the important parameters which are responsible for making decision of the total film thickness.

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