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CHARACTERIZATION OF NICKEL THIN MULTILAYER FILMS ELECTRODEPOSITED UNDER DIFFERENT AGITATION CONDITIONS

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Abstract: *Alternate electrodeposition of ordinary and ultrasonic-assisted Ni layers on polycrystalline copper substrates and single-crystal (100)-oriented silicon wafers was used for the formation of composite systems with nickel thin multilayer films. The hardness and adhesion properties of these composite systems were characterized using Vickers microhardness test, with different loads. Dependence of composite microhardness and film adhesion on type of substrate and layer thickness was investigated. Model of Korsunsky, Chicot-Lesage and Chen-Gao were chosen and applied to experimental data for obtaining the film hardness and adhesion evaluation, respectively. It is confirmed that in comparison with the conventional electrodeposited Ni films, the mechanical properties of the ultrasonic-assisted multilayer Ni films are improved. The microhardness and adhesion of the films are enhanced by introduction of ultrasound and by reducing the layer thickness in the film.*

Keywords: *Ni electrodeposition, Ultrasound agitation, Multilayers, Composite hardness, Film adhesion*

1. INTRODUCTION

Thin multilayer film/substrate laminated structures are usually used in production of microelectromechanical (MEMS) devices. Development of reliable and advanced techniques for growing of metal layers is of great interest in the microsystem technologies [1, 2].

Micromechanical properties of hardness and film adhesion depend on the film microstructure and interfacial structure of the film/substrate. There are various techniques used to change the interface structure by introducing a new layer between the substrate and the film or modifying the film into a multilayered structure [3, 4].

Electrochemical deposition (ED) is a well-known technique that provides the possibility of obtaining the nanostructured materials with controlled grain size and microstructure which will directly affect the mechanical properties [5].

In comparison with other materials, nickel and its alloys may have better chemical and mechanical properties for different microsystem applications.

Nickel nanostructured films obtained by electrochemical deposition have better mechanical properties such as high yield strength, lower wear ratings, high hardness values and better corrosion resistance compared with nickel of a standard grain size [6] .

Introduction of ultrasound into electrochemical deposition as a method of agitation, can improve the structural and mechanical properties of the films, such as hardness and brightness, better adhesion to the substrate, reduced internal stressand good wear resistance [7].

With the use of ultrasound, the multilayer structure of the film can be achieved, since it allows the structure of the film layer to change [8, 9].

Structures that comprise a film on the substrates can be observed as a composite laminate system. Indentation hardness testing is reliable method for evaluation of composite and film mechanical properties. The response of the system to the indentation is called “composite hardness“ and it depends on film thickness and microstructural properties of the film and the substrate. Microhardness measurements are a significant tool for assessing film adhesion on the substrates [10, 11, 12].

2. THEORY OF COMPOSITE HARDNESS AND ADHESION MODELS

A large number of mathematical models have been developed which are used to calculate the absolute hardness of films from experimental measurements of composite hardness. They operate on a number of different principles and according to previous research a selection of mathematical models for the systems being analyzed is made [13, 14, 15].

Model of Korsunsky (K-model) is suitable for the analysis of “hard film on soft substrate” composite systems [13]. This model introduces the “work-of-indentation” that is composed of two parts: the plastic work of deformation in the substrate and the deformation or fracture in the film. The composite hardness, H_C, according to this model, is expressed as follows:

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

A dimensionless material parameter k' is related to the composite response mode to indentation, d is indent diagonal and t is the thickness of the film. This model does not provide calculating the film hardness from the individual measurements of composite hardness for each measured indent diagonal.

Chicot and Lesage (C-L) constructed a mathematical model based on an analogy between the variation of the Young's modulus of reinforced composites in function of the volume fraction of particles and the variation of the composite hardness between the hardness of the substrate and hardness of the film [14, 15].

Hardness is load-dependent. Meyer's law is an empirical relation between change of the indentation diagonal d and the applied load P. The relation between the measured diagonal and the applied load and Meyer's relation are similar in appearance:

$$P = a^{*}\cdot d^{n^{*}} \qquad (2)$$

The variable part of the hardness number with load is represented by the factor n^*. By introducing the expression given by the Eq. (3), equation for the composite hardness (H_C) is derived (Eq. 4):

$$f\left(\frac{t}{d}\right) = \left(\frac{t}{d}\right)^{m} = f \quad where \quad m = \frac{1}{n^{*}} \qquad (3)$$

$$H_C = (1-f)/\left(1/H_S + f\cdot\left(\frac{1}{H_F} - \frac{1}{H_S}\right)\right) + \\ + f\cdot\left(H_S + f\cdot\left(H_F - H_S\right)\right) \qquad (4)$$

The value of m (composite Mayer's index) is determined by a linear regression performed on all experimental data obtained for a chosen composite system and deduced from the Eq. (5):

$$\ln d = m\cdot\ln P + b \qquad (5)$$

For each specific value of m, the hardness of the film was calculated.

Evaluation and comparison of the adhesion of Ni films electrodeposited on Cu and Si (100) substrates were performed using the Chen-Gao model [16]. This model introduces new relation, named a function of indentation depth weight factor, which describes the contribution of local hardness to composite hardness.

The composite hardness H_C of the film/substrate couple in its simplified form is given by the Eq. (6):

$$H_C = H_S + \left[\frac{(m+1)\cdot t}{m\cdot b\cdot D}\right]\cdot\left(H_F - H_S\right) \qquad (6)$$

H_S and H_F are the hardness of the substrate and the film respectively, t is the film thickness, D is indentation depth and b is the critical reduced depth (the ratio between the radius of the plastic zone beneath the indentation and the indentation depth) and m is the power index.

The appropriate value for the power index m is found to be 1.2 for ED Ni/Cu system (hard film on a soft substrate), and 1.8 for ED Ni/Si (100) system (soft film on a hard substrate) [16]. By replacing the Vickers indent diagonal d with $d = 7\cdot D$ and introducing the relation $\Delta H = H_S - H_C$, Eq. (6) may be reorganized as:

$$\Delta H = \left[\frac{7\cdot(m+1)\cdot(H_S - H_F)}{m\cdot b}\right]\cdot(t/d) \qquad (7)$$

The critical reduced depth, b, can be calculated by using Eq. (7), together with experimental values of H_C, H_F, t and d.

3. EXPERIMENTAL PROCEDURE

3.1. Preparation of the substrates and films

Cold-rolled polycrystalline Cu sheet and single crystal silicon Si (100) wafers were employed as the substrate materials. The samples of copper with dimensions 50 mm x 10 mm x 0.125 mm were cut and chemically polished in acidic solution ($HNO_3 : H_3PO_4 : CH_3COOH = 4 : 11 : 5$ vol. %). The plating base for the silicon wafers were sputtered layers of 10 nm Cr as the adhesion layer and 100 nm Au as the nucleation layer. Electrochemical deposition (ED) of Ni was performed under the DC - galvanostatic regime, without and with the assistance of agitation in ultrasonic bath (40 kHz). The composition of the Ni deposition solution and process parameters are given in Table 1.

Table 1. Composition of the electrolyte and the deposition parameters

$Ni(NH_2SO_3)_2\cdot 4H_2O$	300 g/l
$NiCl_2.6H_2O$	30 g/l
H_3BO_3	30 g/l
Saccharine	1 g/l
pH	4.0 - 4.4
Temperature	50°C
Current density	50 mA/cm^2

Projected thickness of deposited films was determined according to the selected deposit area and the current density value. In order to compare the properties of mono and multilayer films, monolayer thin films of Ni were electrodeposited on substrates with and without ultrasonic agitation. The multilayer Ni films were then obtained by alternate electrodeposition of ordinary (O-Ni) and ultrasonic-assisted nickel layers (U-Ni) for different deposition times for one layer (1 min, 30 s and 15 s) and constant film thickness of 10 µm.

3.2. Microstructure analysis

Observation of film microstructure was performed by optical microscopy. Cross-section of the multilayer O-Ni / U-Ni film with thickness of 25 µm was prepared by cutting the sample vertically to the deposit surface. After mechanical polishing, the sample was etched in acidic solution HNO_3 (konc.): CH_3COOH (glac.) = 1:1 for 20 s, followed by etching in HCl (konc.) for 1.5 hour [17].

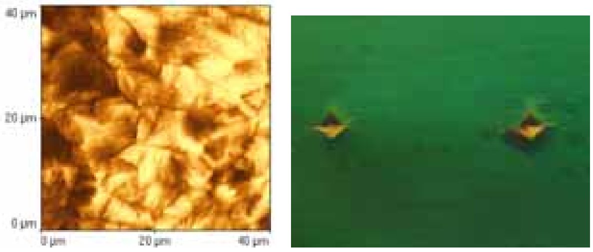
3.3. Microindentation test

The mechanical properties of electrodeposited monolayer and multilayer Ni films on different substrates were characterized using Vickers microindenter "Leitz, Kleinharteprufer DURIMET I" with loads ranging from 0.049 N up to 1.96 N. With the average value of six indentation diagonals measured, the average composite hardness value could be calculated. The experimental results were fitted with GnuPlot [18].

4. RESULTS AND DISCUSSION

4.1. Microstructural properties of the substrates and multilayer ED Ni films

Optical images of the soft polycrystalline copper and hard and brittle single crystal silicon substrates are given in Figures 1(a) and 1(b). As can be seen from Figure 1, the microstructure and therefore the mechanical properties of the substrates are completely different.



(a) (b)

Figure 1. Optical images of polycrystalline copper (a) and single crystal Si (100) (b) substrates

Optical image of the transverse cross-section of multilayer U-Ni / O-Ni film is shown in Figure 2. The multilayer structure of the film is confirmed and clearly visible. The bright ones are the nickel layers deposited under ultrasonic agitation (U-Ni) and the dark ones are the ordinary deposited nickel layers (O-Ni). According to literature, it is considered that the grains of the U-Ni layer grow preferentially in the manner parallel to the substrate surface unlike the O-Ni layer with columnar grains growth vertical to the substrate surface [9].

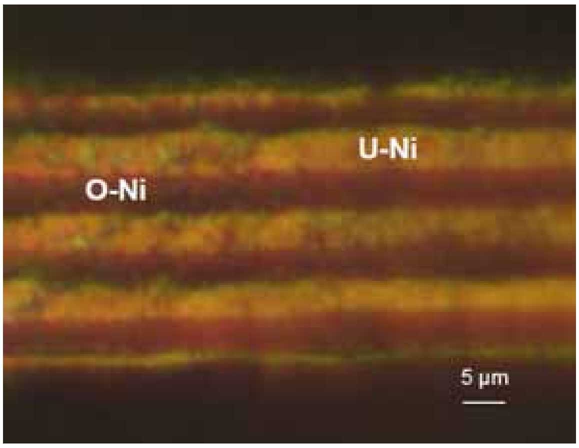


Figure 2. Optical image of cross-section of multilayer U-Ni / O-Ni film (layer thickness is 5 µm).

4.2. Composite and film hardness

Values of load-independent microhardness for the Cu and Si substrates were calculated according to the Proportional Specimen Resistance (PSR) model of Li and Bradt, as H_S = 0.37 GPa and H_S = 6.49 GPa, respectively [19, 6].

For the analysis and comparison of composite hardness value, eight samples were prepared. Monolayer Ni films electrodeposited on substrates with and without the ultrasonic agitation were first prepared. The others were multilayer composite systems with alternately electrodeposited O-Ni/U-Ni films with different layer thickness of 1 µm, 500 nm and 250 nm.

Change of the composite hardness (H_C) of different composite ED Ni/Cu and ED Ni/Si(100) substrate systems with relative indentation depth, *h/t* (indentation depth through film thickness) is given in Figure 3 and in Figure 4. All of the ED Ni films are with the total thickness of 10 µm and they were all electrodeposited with 50 mA/cm^2 current density.

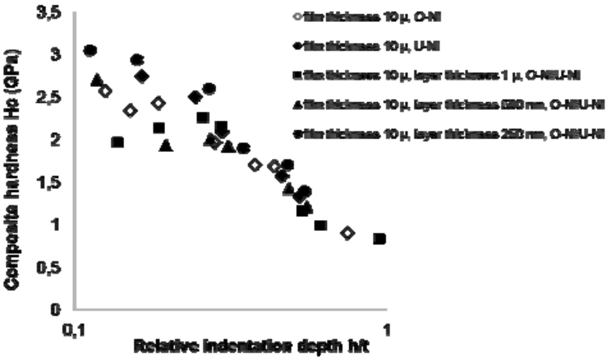


Figure 3. Variation in the composite hardness H_C, with relative indentation depth (*h/t*), for 10 µm-thick ED Ni films on Cu supstrate.

The difference in variation of the composite hardness with relative indentation depth indicates the different type and mechanical properties of these composite systems. For shallow penetration depths ($h/t \leq 0.1$), the response is that of the film only. As the relative indentation depths increase ($h/t > 0.1$), the composite hardness decrease or increase until it reaches the substrate hardness H_S.

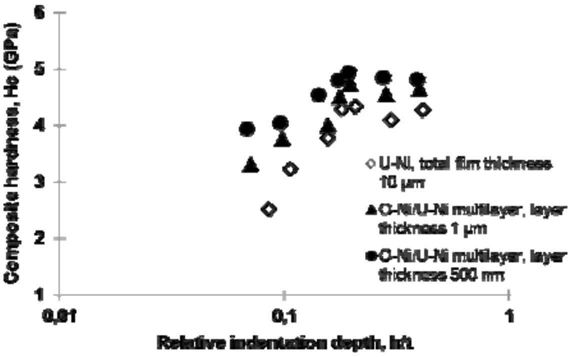


Figure 4. Variation in the composite hardness H_C, with relative indentation depth (h/t), for 10 µm-thick ED Ni films on Si (100) supstrate.

It is confirmed that electrodeposition supported by ultrasonic agitation leads to significant change in the microstructure and properties of the films. In comparison with the ordinary ED Ni films, higher values of the composite micro-hardness are obtained for the ultrasonic-assisted ED films. Decreasing the layer thickness and increasing the number of interfaces lead to increasing the composite hardness of the multilayer film composite systems.

For the system of ED Ni film /Cu substrate, experimental hardness measurements for chosen mono and multilayer systems were fitted with the composite model of Korsunsky [13]. The curve-fit data obtained from the model validation process are given in Table 2.

Table 2. The fitting results according to the composite model of Korsunsky for composite systems of mono and multilayer electrodeposited Ni films on Cu substrates

K model		Asymptotic standard error
Ordinary electrodeposited monolayer Ni film O-Ni [16]		
H_F (GPa)	2.68	± 0.11 (4.1%)
k’	0.0087	± 0.0017 (20%)
Ultrasound-assissted electrodeposited monolayer Ni film U-Ni (10 µm, 50 mA/cm^2)		
H_F (GPa)	2.82	± 0.0.28 (10.05%)
k’	0.012	± 0.0043 (34.17%)
Multilayer O-Ni/U-Ni film (layer thickness 1 µm, total film thickness 10 µm, 50 mA/cm^2)		
H_F (GPa)	2.23	± 0.1113 (4.98%)
k’	0.0091	± 0.001876 (20.48%)
Multilayer O-Ni/U-Ni film (layer thickness 500 nm, total film thickness 10 µm, 50 mA/cm^2)		
H_F (GPa)	2.72	± 0.1956 (7.47%)
k’	0.011	± 0.0033 (30.13%)
Multilayer O-Ni/U-Ni film (layer thickness 250 nm, total film thickness 10 µm, 50 mA/cm^2)		
H_F (GPa)	3.29	± 0.135 (4.11%)
k’	0.0169	± 0.1326 (14.78%)

Using the model of Chicot-Lesage [15] from measured indentation diagonal and calculated composite hardness, film hardness was calculated for the system consists of ED Ni film on Si (100) substrate. Dependence of film hardness on relative indentation depth according with applied C-L model is shown in Figure 5.

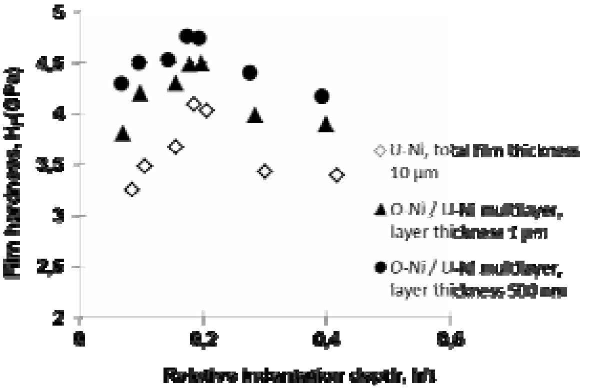


Figure 5. Variation in the film hardness H_F, with relative indentation depth (h/t), for 10 µm-thick ED Ni films on Si (100) supstrate.

As shown in Table 2 for the system of ED Ni/Cu, and in Figure 5 for the system of ED Ni/Si (100), the ultrasonic agitation increases the hardness of ED Ni films. By changing the thickness of the film layer it is possible to design the structure and mechanical properties of the films and of the composite systems. With decreasing the layer thickness within the film it is possible to achieve higher values of the film hardness.

Together with the current density value the ultrasonic agitation affects the film microstructure. The grain shape and grain size of the U-Ni films are different than of the O-Ni films. Smaller grain size can support a dislocation pileup. Also, a large number of the interfaces in multilayer film structure are considered to serve as a barrier to dislocations, obstructing dislocation movement between the layers.

4.3. Evaluation of film adhesion

A composite hardness model of Chen-Gao [16] was employed to evaluate the adhesion of ED Ni films on Cu and Si (100) substrates. The composite hardness of the film/substrate systems given in the form of Eq. (3) was used to calculate the critical reduced depth b. Indentation diagonals on the substrate and the films surfaces were measured and H_C and H_F were calculated. The hardness of the ED Ni films was obtained as result of the applied Korsunsky model (Table 1) for the system of ED Ni/Cu. For the system of ED Ni /Si (100) the film hardness results of applied Chicot-Lesage model were used. The values of critical reduced depth were calculated for every indent diagonal and then the average value was found. The results of calculation the critical reduced depth for ED Ni / Cu composite system are shown in Figure 6.

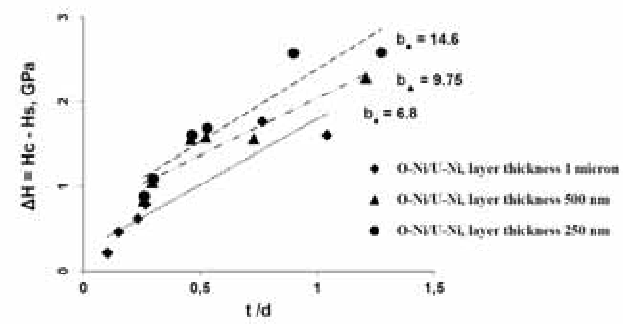


Figure 6. Hardness difference (Hc-Hs) vs. t/d (ratio between the film thickness and the indentation diagonal) for 10 µm-thick multilayer ED O-Ni/ U-Ni films on Cu substrates. The critical reduced depth b for each system is given.

In Table 3 results of the critical reduced depth calculation for the system ED Ni / Si (100) are given.

Table 3. Critical reduced depth values for the systems of electrodeposited Ni on Si (100) substrates with different layer thickness in the multilayer Ni film.

Sample	Critical reduced depth, b
U-Ni monolayer film	9.03
O-Ni/U-Ni multilayer film, layer thickness 1 µm	9.44
O-Ni/U-Ni multilayer film, layer thickness 500 nm	9.73

Increasing adhesion corresponds to increasing values of the plastic deformation zone around the indentation. It can be expressed numerically by critical reduced depth *b*. It is obvious that the microhardness difference decreases faster for a weaker adhesion when increasing the indentation load. It can be seen that decreasing the layer thickness leads to higher values of film hardness and better adhesion performance compared with the films electrodeposited under ordinary conditions. Using of multilayer films is effective way to release the stress across the interface of Ni films and the substrate. The distribution of stress at the interface is an important factor governing the adhesion of the film on the substrate.

5. CONCLUSION

Different composite systems of mono and multilayer Ni films electrodeposited on Cu and Si(100) substrates were prepared and analysed. Multilayer film structure was accomplished by alternation of ordinary and ultrasonic-assisted nickel electrodeposition.

Mechanical properties of the composite system are influenced by the microstructure of the substrate and the film. Tendency of composite hardness depends on the type of the composite system: hardness of the film, hardness of the substrate, their relative differences and also the thickness of the film.

Nickel film on Cu substrate represents the “hard film on soft substrate” composite system type. Model of Korsunsky gives the best fit of experimental data for the system Ni film-Cu substrate. Nickel films on Si substrate can be thought as “soft film on hard substrate” composite system type. Model of Chicot-Lesage for reinforced composites was chosen for the system Ni film-Si substrate for all samples and the film hardness was calculated, for each indentation diagonal.

The values obtained for the film hardness H_F are influenced by the applied load. Change of the film hardness with applied load depends on the substrate type. The variations should be related to physical phenomena such as the indentation size effect, the cracking in the neighborhood of the indent, the elastic contribution of the substrate for the lowest loads, or the crushing of the film for the highest loads.

The ultrasonic agitation changes the microstructure of Ni films. The grains of the U-Ni layer grow preferentially in the manner parallel to the substrate surface. It is confirmed that higher values of the composite and film hardness are obtained with the assistance of ultrasonic agitation in comparison with the ordinary electrodeposited films.

The multilayer film structure enables introducing new interfaces, changing the layer microstructure or/and thickness of the layers in the film.

Formation of the multilayer film structure, the reduction of layer thickness in the film, and introduction of ultrasonic agitation into the electrodeposition process led to increasing the composite and film hardness for all analyzed composite systems and better adhesion properties expressed through increased values of the critical reduced depth.

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