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MICROINDENTATION HARDNESS TESTING OF DIFFERENT COMPOSITE SYSTEMS WITH THIN ELECTRODEPOSITED NICKEL AND COPPER FILMS

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Abstract: *Thin Ni and Cu films with fine-grained structures have been electrodeposited from self-made sulphamate-based and sulphate-based electrolytes, respectively. DC electrodeposition of Ni films was performed on single crystal Si wafers with different orientations named (100) and (111), and electrodeposition of Cu films was performed on massive electrodeposited Ni films as the substrates. In order to investigate the influence of the microstructure of the substrates and Ni and Cu thin films on mechanical properties of these composite structures, Vickers microhardness testing for different loads was done. For any composite system of thin film on a substrate, there is a critical indentation depth,1 when 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. Composite hardness model of Chicot-Lesage was chosen and applied to the experimental data in order to analyse and determine the absolute film hardness. Further analysis of work hardening parameter* $(t/d)^m$*, that can express the difference in tendency of the composite hardness with the indentation load, was performed for the above-mentioned composite systems.*

Key words: *composite hardness, Vickers microhardness, composite hardness models, electrodeposition, thin films, work hardening parameter*

1. INTRODUCTION

Thin films obtained with electrodeposition technology on different substrates are often employed as components in microelectromechanical systems (MEMS) [1]. MEMS is the collective term for small integrated systems containing sensors, actuators, signal conditioning circuits and additional functions with physical dimensions ranging from a couple to a few hundred micrometers. MEMS can be found in systems ranging from consumer electronics, automotive, medical, communications to defence and homeland security applications.

Properly chosen materials and process technology, with emphasize on good mechanical properties of materials are critical for mechanical integrity of microsystems. Electrodeposition is a simple, inexpensive and versatile method to produce dense fine-grained films of many different metal and alloys. Electrodeposition is IC compatible as it is low-temperature and high rate deposition technology. Choice and optimization of the electrodeposition process parameters lead to ordered grain size and microstructure and because of that materials can be strengthened and hardened with little or no loss ductility.

Because electrodeposited thin films do not behave in the same manner as their bulk counterparts, there is a need for understanding and evaluation of their mechanical material properties, because of the mechanical integrity of the MEM systems.

Electrodeposited thin films of Ni and Cu are very well suited for microsystem applications. They have good mechanical properties such as high yield strength and hardness, and for MEMS devices, a high electrical and thermal conductivity are also very important for some aaplications [2,3,4].

The indentation hardness test is commonly used to estimate the mechanical properties of thin films. The evaluation of the absolute hardness of thin films is difficult, because the influence of the substrate must be taken into account. The measured hardness value varies continuously with the indentation depth, the film thickness and the hardness of the film and the substrate. The substrate starts to contribute to the measured hardness at indentation depths of the order of 0.07-0.2 times the film thickness. There is a critical penetration depth when the measured hardness named "composite hardness" includes, except film hardness, also a component of the substrate hardness [5,6].

There is a need to obtain the hardness of the film solely from the experimental composite hardness measurements and the model of Chicot and Lesage [7], was chosen and applied for analysis of the „soft film on hard substrate“ composite system type.

In the Section 2., theoretical model of Chicot-Lesage is shown with all important model parameters. Section 3. brings informations about chosen materials, process parameters and hardness measurements technique. In the Section 4., results and discussion on film and composite hardness measurements are given for two different composite systems of the same type („soft film on hard substrate“). Short analysis of experimental investigations and conclusion are given in the Section 5.

2. THE THEORETICAL MODEL

The model proposed by Chicot and Lesage (C-L) [8,9], avoids the knowledge or choice of any other data than that obtained easily from standard measurements (film thickness and apparent hardness). Their model is based on the analogy between the variation of the Young modulus of reinforced composites in function of the volume fraction of particles, and that of the composite hardness.

Hardness value deduced from an indentation test is not constant because hardness is load-dependent. 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**. Then 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:

$$\begin{aligned} H_C = (1-f)/\left(1/H_S + f\cdot\left(\frac{1}{H_F} - \frac{1}{H_S}\right)\right) + \\ + f\cdot\left(H_S + f\cdot\left(H_F - H_S\right)\right) \end{aligned} \tag{3}$$

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

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

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.

3. EXPERIMENTAL

The substrates for the electrodeposition of Ni and Cu thin films were monocrystalline Si wafers with (100) and (111) orientations and massive 50 µm-thick electrodeposited Ni films, respectively. The plating base for the Si wafers were sputtered layers of 100Å Cr and 1000Å Ni. Electrodeposition was carried out using DC galvanostate mode. Thin Ni films were deposited from self-made sulphamate electrolyte consisting of 300g/l $Ni(NH_2SO_3)_2\cdot 4H_2O$, 30g/l $NiCl_2\cdot 6H_2O$, 30g/l H_3BO_3, 1g/l saccharine, and thin Cu films were deposited from self-made sulphate electrolyte with the content of 240g/l $CuSO_4\cdot 5H_2O$, 60g/l H_2SO_4. The temperatures of the deposition processes were maintained at 50°C and 20°C respectively. According with plating surface, projected thickness of deposits and cathodic current efficiency, deposition time was determined.

The mechanical properties of the composite systems were characterized using Vickers microhardness tester "Leitz, Kleinharteprufer DURIMET I" using up to 15 loads ranging from 4.9N down to 0.049N. Three indentations were made at each load, yielding six indentation diagonals measurements, from which the average hardness could be calculated. Indentation was done at room temperature. The experimental data were fitted with GnuPlot, v.4.0 (http://www.gnuplot.info/).

The examination of samples microstructure by metallographic microscopy (Carl Zeiss microscope "Epival Interphako") was performed. Topographic details were investigated by means of AFM named "TM Microscopes-Veeco" operating in non-contact mode.

4. RESULTS AND DISCUSSION

4.1. Thin electrodeposited Ni films on monocrystalline Si wafers

Tests were performed with a Vickers diamond pyramidal indenter both on uncoated substrates and different coated substrates. Vickers microhardness indentation tests were carried out on Si monocrystalline substrates in such way that the indent diagonal was parallel with the prime flat, i.e. the diagonals were parallel with <110> direction for both substrate orientations. It is well known that mechanical properties of monocrystalline Si depend on the crystallographic orientation and this indenter orientation procedure was strictly applied during indentation [10,11].

The average values of impression diagonals *d*, were calculated from several independent measurements on every specimen for different applied loads, *P*. The composite hardness H_C, was calculated using the formula:

$$H_C = 1.8544 \cdot P \cdot d^{-2} \tag{6}$$

where 1.8544 is a constant, a geometrical factor for the Vickers pyramid.

At first, absolute hardness of the substrates were determined.

According to literature, the PSR (Proportional Specimen Resistance) model of Li and Bradt is suitable for analyzing load dependence hardness [12]. The indentation test load *P* is related to indentation size *d* as follows:

$$P = a_1 d + \left(P_C / d_0^2\right) \cdot d^2 \tag{7}$$

Here P_C is the critical applied test load above which microhardness becomes 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, and the slope gives the value of $P_C \cdot d_0^{-2}$ which when multiplied by the Vicker's conversion factor, 1.8544 from Eq.(6), gives the value of the load independent substrate microhardness, H_S. These calculated values of substrates microhardness are 6.49 GPa for the (100)-oriented Si substrate and 8.71 GPa for (111)-oriented Si substrate [13].

Fig.1. Uncoated substrate of silicon; Evidence of brittle response during indentation on Si(100) at 0.392 N load. The diagonals were parallel with <110> orientations.

Hardness response on indentation for the 5 µm - thick electrodeposited Ni film on Si(100) wafer as the substrate, with applied load of 0.25 N, is shown on Fig.2. For metallic materials, plasticity generally dominates, and nickel coatings reveals significant pileup around the indentation due to its relative softness in comparison to the harder silicon substrate („soft film on hard substrate" composite system type).

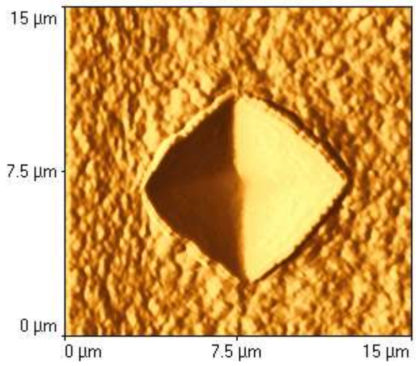
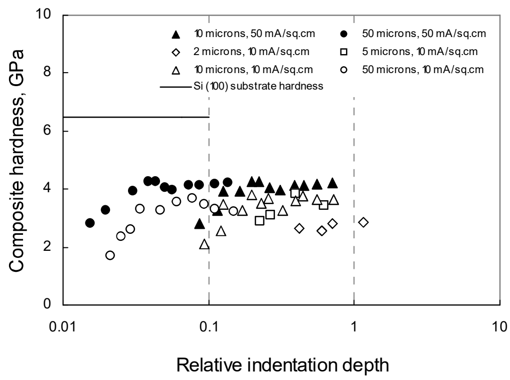


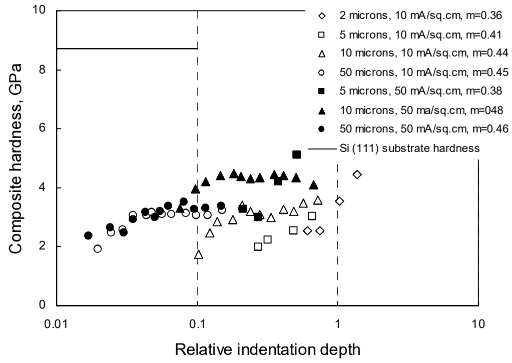
Fig.2. AFM image of indentation response of the system Ni film (5 µm) - Si(100) substrate using a 0.25-N applied load and a dwell time of 25 s.

Change of the composite hardness H_C, with relative indentation depth *h/t*, for electrodeposited Ni films of different thickness ranging from 2 to 50 µm on Si (100) and Si (111)-oriented substrates is shown on the Fig.3.

For shallow penetration depths ($h/t \leq 0.1$), it was found that the response was that of the film only. The hardness of the film increases until certain relative indentation depth (< 0.1). Films obtained with higher current density (50mA/cm^2) appear harder than others deposited with 10mA/cm^2.



(a)



(b)

Fig.3. Variation in composite hardness with normalised depth for a soft film of ED Ni on a hard substrate of: Si(100) (a), and Si(111) (b).

Chicot-Lesage model, based on the model for reinforced composites [9] was applied to the experimental data even for the thick coatings (50 µm) and the results are shown on Fig.4. The values obtained for the film hardness H_F, are not constant but influenced by the applied load. The composite system Ni film- Si substrate shows decreasing manner dependence of film hardness on relative indentation depth.

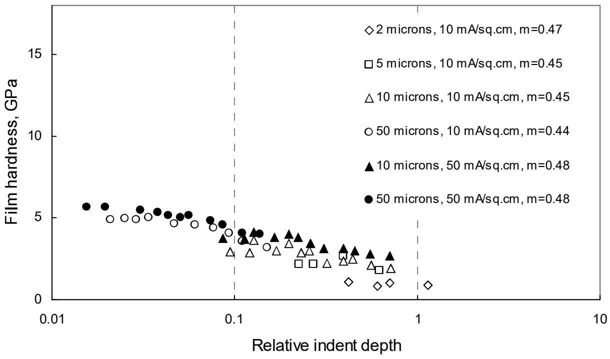


Fig.4. Variations in film hardness with relative indentation depths for the system which consists of electrodeposited Ni film on Si (100) substrate according to C-L model.

4.2. Thin electrodeposited Cu film on massive electrodeposited Ni film as the substrate

Composite system of electrodeposited thin film of Cu on massive electrodeposited Ni film as the substrate also belongs to the "soft film on hard substrate" type of the composite systems. Change of the composite hardness H_C with relative indentation depth *h/t*, is given on Fig.5. for different deposition parameters of the film and of the substrate. Absolute hardness of the 50 μm-thick electrodeposited Ni films as the substrates was determined as 4.08GPa and 4.63GPa for deposition current densities of 10 mA/cm^2 and 50 mA/cm^2, respectively [13].

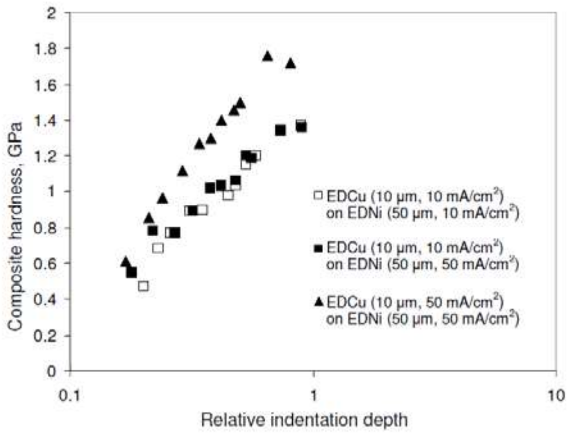


Fig.5. Variations of the composite hardness, H_C, with the relative indentation depth, *h/t*, for electrodeposited Cu films on ED Ni films as the substrates. Film thickness and deposition current densities are given in the diagram.

Composite microhardness value increases with the relative indentation depth and with increasing influence of the substrate.

Composite hardness values are most influenced by the deposition current densities of Cu and Ni films. Increase in current density leads to decrease in grain size and results in higher values of the composite microhardness.

On Fig.6., the composite hardness model of Chicot-Lesage (C-L) was applied to experimental data. The values obtained for the film hardness H_F, are not constant but influenced by the applied load.

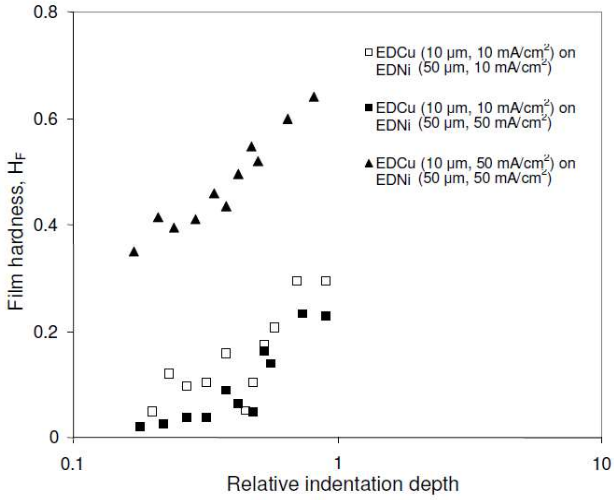


Fig.6. Variations in film hardness with relative indentation depths for the system which consists of electrodeposited Cu film on 50 μm thick ED Ni film substrate according to C-L model

Different physical phenomena such as indentation size effect, cracking of the film around the indent or the elastic contribution of the substrate for the lowest loads, may be the reasons for the film hardness variations. The composite system ED Cu film - ED Ni substrate shows increasing manner dependence of film hardness on relative indentation depth [8,9].

Film hardness response on indentation of various "soft film on hard substrate type" composite systems is shown on Fig.4. and Fig.6. Differences in hardness response stem from different microstructures and consequently different micromechanical properties of the composite systems, i.e. of the films and of the substrates. Hardness of the electrodeposited Ni films on Si substrates decreases with the applied load, but hardness of the electrodeposited Cu films on thick electrodeposited Ni films as the substrates increases with the relative indentation depth, because of these differences.

4.3. Comparison and analysis of the composite Meyer's index *(t/d)^m*

According to the Meyer's law, Eq.(1), which describes the variation of hardness with applied load (deformation hardening), n^* is known as the Meyer's exponent or index. Analogously, model of Chicot-Lesage (C-L) introduces a parameter *m*, named composite Meyer's index [8,9].

Table T.1. contains the values of the composite Meyer index for composite systems of ED Ni films on (100) and (111)- oriented Si substrates and ED Cu films on thick ED Ni -film substrates.

T.1. Values of the composite Meyer index, *m*, calculated according to the Chicot-Lesage model for different substrates and different thickness of electrodeposited Ni and Cu films obtained with different current density values

Film/Substrate	jf, mA/cm2	tf, µm	m
ED Ni / (100)Si	10	10	0.45
ED Ni / (100)Si	10	50	0.44
ED Ni / (100)Si	50	10	0.46
ED Ni / (100)Si	50	50	0.48
ED Ni / (111)Si	10	10	0.44
ED Ni / (111)Si	10	50	0.45
ED Ni / (111)Si	50	10	0.48
ED Ni / (111)Si	50	50	0.46
ED Cu / ED Ni (50µm, 10mA/cm2)	10	10	0.38
ED Cu / ED Ni (50µm, 50mA/cm2)	10	10	0.39
ED Cu / ED Ni (50µm, 50mA/cm2)	10	50	0.37

The composite Meyer index characterizes the manner in which the composite hardness varies with the load. On Fig.7. it is shown that *(t/d)^m^* is a parameter that can express the difference in tendency of the composite hardness with the indentation load, for different composite systems.

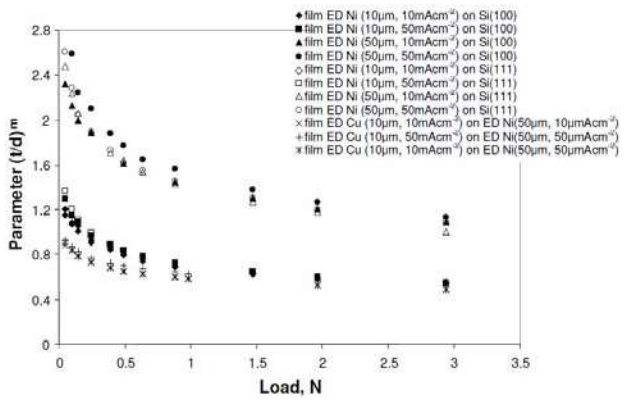


Fig.7. Comparison of the parameter $(t/d)^m$ with the indentation load, *P*, for electrodeposited Ni films on monocrystalline substrates and electrodeposited Cu films on ED Ni films as the substrates, with different film thickness (10 and 50 µm) and current density values (10 and 50 mA/cm^2).

For the low loads, the composite hardness tends to that of the film, and parameter $(t/d)^m$ is independent of the substrate type. For the loads when the influence of the film is dominant, parameter $(t/d)^m$ increases with increasing of the current density.

Parameter $(t/d)^m$ for different systems of the same type ("soft film on hard substrate" type) shows great sensitivity in low-load range (up to 50% of the thickness) and it depends on the microstructure and micromechanical properties of the film and of the substrate. It can be seen that increasing the film thickness above a critical thickness (for the systems of ED Ni on Si substrates, it is 50 µm), leads to insensitivity of this parameter on the substrate type.

With increasing of the relative indentation depth (especially when $h/t \geq 0.1$), the influence of the substrate becomes dominant and the tendency of the parameter $(t/d)^m$ dependes mostly on the substrate type (Fig.8.).

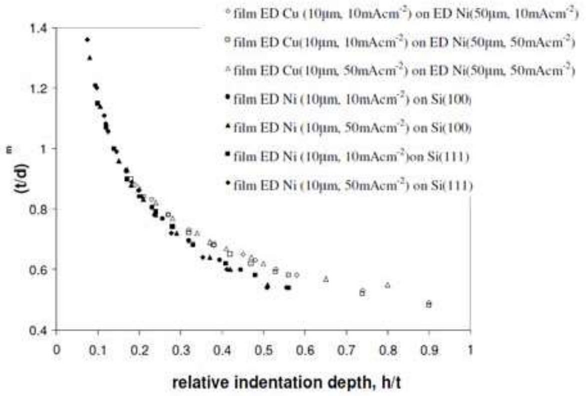


Fig.8. Comparison of the parameter $(t/d)^m$ with the relative indentation depth, h/t, for electrodeposited Ni films on single crystal Si substrates and electrodeposited Cu films on ED Ni films as the substrates, for the film thickness of 10 µm and current density values (10 and 50 mA/cm^2).

5. CONCLUSION

In order to analyze the hardness of different composite systems of the same type ("soft film on hard substrate"), nickel and copper films were electrodeposited on monocrystalline (100) and (111)-oriented Si and thick ED Ni films as the substrates, respectively.

It was shown that the tendency of the composite hardness depends on the type of the composite system, i.e. the differences in the mechanical properties of the film and of the substrate: the hardness of the substrate, the hardness of the film, their relative difference and the thickness of the film.

All of the analyzed composite systems can be considered as a soft film on a hard substrate. The Chicot-Lesage model (C-L model), based on the model for reinforced composites, was applied to the experimental data, even for the thick coatings (50 µm). The Chicot-Lesage model was chosen for all specimens and the film hardness was calculated for each indentation diagonal.

The values obtained for the film hardness, H_F, were influenced by the applied load. In case of the Cu films electrodeposited on thick electrodeposited Ni film as the substrate, the film hardness lines showed ascending character, but in case of the Ni films electrodeposited on monocrystalline Si substrates with different orientations, the film hardness lines had a descending character. According to the Chicot-Lesage model, explanation is that the variations should be related to different physical phenomena, such as the indentation size effect, cracking in the neighborhood of the indent, the elastic contribution of the substrate for the lowest loads or the crushing for the film for the highest loads.

The composite Meyer index, *m*, characterizes the way in which the composite hardness tends to that of the film (for the low loads), the parameter $(t/d)^m$ is almost independent of the substrate type. With increasing the load, the influence of the substrate became dominant and the parameter $(t/d)^m$ depended mostly on the type of the substrate.

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