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ON THE CORRELATION OF MICROHARDNESS WITH THE FILM ADHESION FOR "SOFT FILM ON HARD SUBSTRATE" COMPOSITE SYSTEM

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Abstract: *Composite systems of monolayered electrodeposited Ni and Cu thin films (5-10 μm) on monocrystalline Si wafers and 50 μm-thick electrodeposited Ni film as the substrates were fabricated.* On the basis of their difference in hardness, these systems can be *thought of as "soft film on hard substrate" composite systems.*

Adhesion of electrodeposited films on different substrates was investigated by Vickers microindentation hardness testing. Strong adhesion corresponds to extended plastic deformation zone at the film/substrate interface. Interfacial tension effects contribute to the measured hardness. Composite hardness models of Chicot-Lesage (C-L) and Chen-Gao (C-G) were applied in order to investigate the influence of adhesion on microhardness test results. When adhesion exists between the film and the substrate, the critical reduced depth (the ratio between the radius of the plastic zone beneath the indent and the indentation depth) increases.

Microhardness measurements are useful tool for assessment and quantification of the film/substrate interface strength.

Keywords: *Vickers microhardness, adhesion, composite system, composite hardness model, critical reduced depth.*

1. INTRODUCTION

Complex structures of thin films on substrates are often used in fabrication of different microelectromechanical devices. A thin film on a substrate can be considered as a composite system whose properties depend not only on particular material properties of the film and the substrate but also on the composite parameters such as good adhesion, controlled residual stresses, good corrosion resistance, etc.

Hardness and adhesion testing are the most important and widely used techniques for assessing the structural and mechanical properties of the composite systems. As the thickness of the film is very small, the influence of the substrate must be considered during the hardness determination.

The measured hardness is influenced by a number of factors such as film thickness, indentation depth, film and substrate hardness and hardness ratio as well as adhesion. It has been shown that the microhardness testing can be a useful technique in assessing the adhesion of thin films to the substrate [1-7].

2. THEORY OF COMPOSITE HARDNESS AND ADHESION MODELS

There is a need for determination of the film hardness solely from the composite hardness measurements. The composite and the film hardness are load-dependent. Change of the composite and the film hardness with load depends on the composite system structure [5, 8].

The composite hardness model of Chicot-Lesage (C-L) was found to be appropriate for experimental data analysis and film hardness determination [9]. The model is based on the analogy between the variation of the Young modulus of the reinforced composites in function of the volume fraction of particles and that of the composite hardness.

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:

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

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.

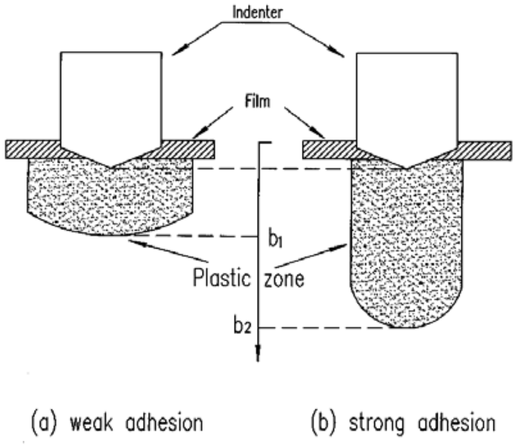
For the evaluation of the adhesion properties of thin films, Chen-Gao (C-G) method was chosen [2]. This method introduces the composite hardness as the function of the critical reduced depth beyond which the material will have no effect on the measured hardness. They found that a large value of the critical reduced depth (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 Picture 1. The correlation between composite hardness value H_C and the critical reduced depth *b* is found as:

$$Hc = Hs + [(m+1)\cdot t/m\cdot b\cdot D - t^{m+1}/m\cdot b^{m+1}\cdot \\ \cdot D^{m+1}]\cdot(Hf - Hs)$$

$t^{m+1}/m\cdot b^{m+1}\cdot D^{m+1} \to 0$, then is

$$Hc = Hs + [(m+1)\cdot t/m\cdot b\cdot D]\cdot(Hf - Hs) \tag{6}$$

where 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 and *b* is the critical reduced depth. Critical reduced depth *b* has different values for various film-substrate systems. Even for the same film-substrate system, due to the different adhesions, *b* values are different.



Picture 1. (a) Schematic representation of deformation associated with indentation in a coated substrate (weak adhesion), (b) the effect of a strong film/substrate interface [2]

3. EXPERIMENTAL

3.1. Substrates and film deposition

The substrates for the electrodeposition of Ni and Cu thin films were monocrystalline Si wafers with (100) and (111) orientations and 50μm-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 galvanostatic mode. Thin and thick Ni coatings were deposited from proprietary 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 to plating surface, projected thickness of deposits and cathodic current efficiency, deposition time was determined.

3.2. Microhardness testing and characterization

The mechanical properties of the composite systems were characterized using Vickers microhardness tester "Leitz, Kleinharteprufer DURIMET I”. Different loads ranging from 4.9N down to 0.049N were used. 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 examination of samples microstructure by metallographic microscopy (Carl Zeiss microscope “Epival Interphako”) was performed.

4. RESULTS AND DISCUSSION

4.1. Absolute hardness of the substrates

Microhardness testing was performed both on uncoated substrates and on different composite systems. Model named PSR (Proportional Specimen Resistance) [10] was chosen for analyzing the variation of 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 composite hardness values H_0 and H_C were calculated using the formula:

$$Hc = 0{,}01854 \cdot P \cdot d^{-2} \tag{7}$$

where 0.01854 is geometrical factor for the Vickers indenter.

Absolute hardness of the substrates Hs was calculated as 6.49GPa and 8.71GPa for (100) and (111)-oriented single-crystal Si substrates respectively, and 3.89GPa for thick electrodeposited Ni film as the substrates [11, 12].

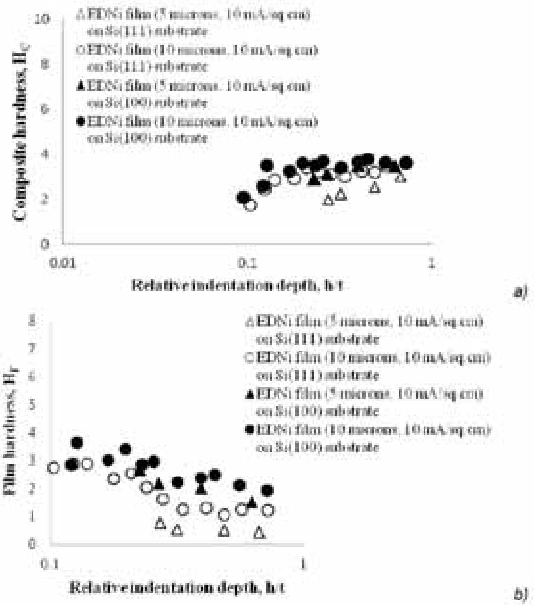
4.2. Composite and film hardness tendency of various “soft film on hard substrate” composite systems

Two different composite systems were investigated: thin electrodeposited Ni films on Si(100) and Si(111)-oriented wafers and thin electrodeposited Cu films on thick and harder electrodeposited Ni films as the substrates. There is an essential difference between the two above-mentioned systems; the first system requires the existence of sputtered adhesion layer because of the hard and brittle semiconductor Si substrate; the second system consists of two metals with similar crystallographic structure.

Variation of the composite hardness H_C and film hardness H_F of electrodeposited Ni films with different thickness on single-crystalline Si substrate, with relative indentation depth h/t, where h is indentation depth and t is total thickness of the film, is shown in Picture 2.

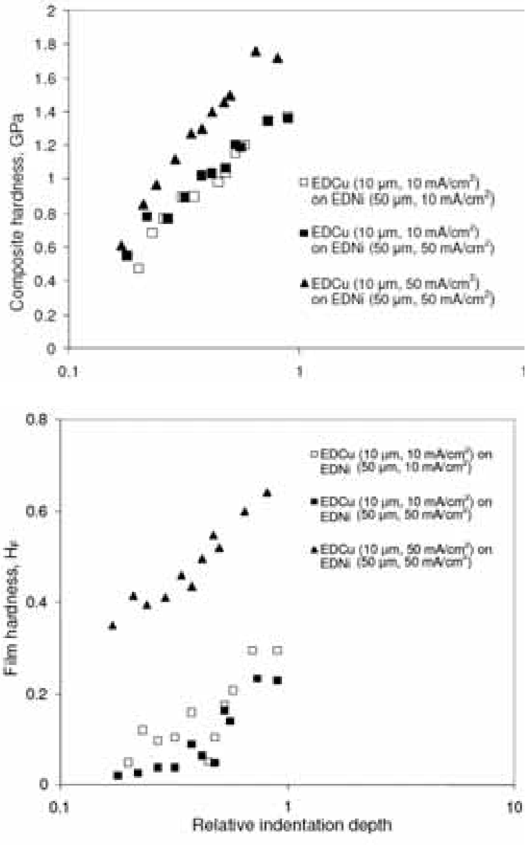
For low indentation depths ($h/t \leq 0.1$), the response of the system is mostly response of the film. For indentation depths between 0.1 and 1, the hardness response belongs to the whole composite system and depends on the film and on the substrate hardness values.

The system of ED Ni film on Si(100) substrate has slightly higher values of composite and film hardness than the system of ED Ni film on Si(111) substrate. Hard but brittle single-crystalline Si substrates facilitated cracks formation and for these systems film hardness has descending character.



Picture 2. Variation in composite hardness H_C (a) and film hardness H_F according to C-L model (b) with normalized depth *h/t* for ED Ni film on Si substrate

Change of the composite and film hardness with relative indentation depth for the system of soft ED Cu film on thick and harder ED Ni film as the substrate is shown in Picture 3.



Picture 3. Variations of the composite and film hardness (according to C-L model) with the relative indentation depth for electrodeposited Cu films on ED Ni films as the substrates. Film thickness and deposition current densities are given in the diagram

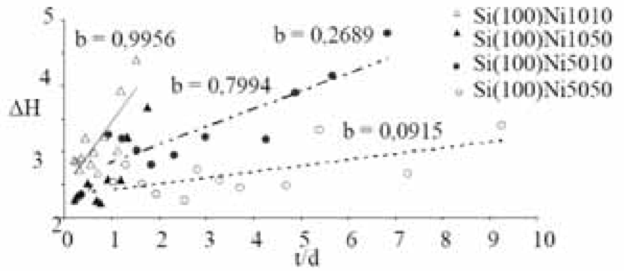
Increase in current density has led to grain size refinement and hardness increase. In distinction from the system of ED Ni film on single-crystal Si substrate, both composite and film hardness have ascending characters. The deformation hardening of the polycrystalline fine-grained ED Ni substrate occurred.

4.3. Composite hardness and adhesion of various "soft film on hard substrate" composite systems

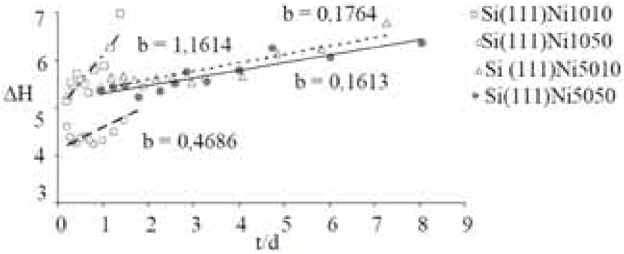
It is observed that adhesion influences the microhardness values of composite systems and films. Equation (6) was used to calculate the critical reduced depth *b* for the system of thin electrodeposited Ni films on Si(100) and Si(111) substrates and for the system of thin electrodeposited Cu films on thick electrodeposited Ni film as the substrate.

All of the systems belong to the „soft film on hard substrate“ composite system type. The substrate and composite hardness, H_S and H_C respectively, were obtained from the microhardness measurements and reported in the previous section.

In Pictures 4 and 5, values of $\Delta H = H_S - H_C$, for ED Ni films on (100) and (111)–oriented Si substrates are plotted vs. 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 reported in the same figure.



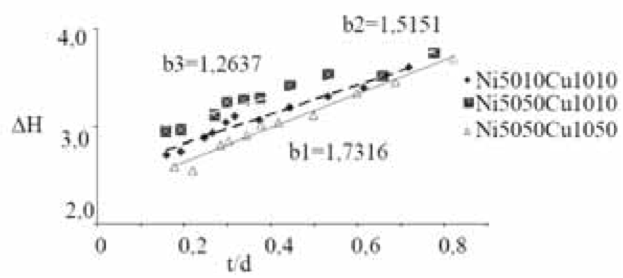
Picture 4. Experimental values of hardness difference as function of ratio between film thickness and the indentation diagonal, for ED Ni films on Si (100) substrate deposited under different conditions (Ni1010 denotes the film thickness of 10μm and the current density of 10 mA/cm^2). The film deposition parameters and critical reduced depth *b* are reported



Picture 5. Experimental data of hardness difference as function of ratio between film thickness and the indentation diagonal for different ED Ni films on Si (111) substrate

With increasing ED Ni film thickness, decreasing values of the critical reduced depth *b* corresponds to decreasing adhesion in both cases.

In Picture 6., values of $\Delta H = H_S - H_C$, for ED Cu films on thick ED Ni film as the substrate are plotted vs. 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 reported in the same picture.

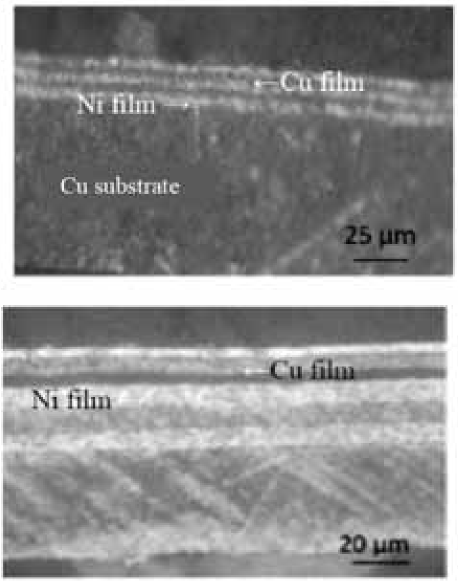


Picture 6. Experimental data of hardness difference as a function of ratio between film thickness and the indentation diagonal for thin films of Cu electrodeposited on thick film of Ni. The critical reduced depth *b* is reported

The values of the critical reduced depth *b*, which correspond to good adhesion of the film on substrate, are significantly higher for the "ED Cu film on thick ED Ni film as the substrate" composite system, than for the system of ED Ni film on Si substrates. Adhesion of metallic films to semiconductors is usually poor even if there is an adhesive layer.

In assessment of the adhesion of particular film/substrate combination, all possible factors that may influence the adhesion between film and substrate must be considered and some of them are deposition technique, critical film thickness, crystallographic structure and compatibility.

Cross-section images obtained with optical microscopy of ED Cu/ED Ni contact interfaces are given. Evidence of poor adhesion on the ED Ni / ED Cu interface is shown.



Picture 7. Cross-section of the Cu/Ni film with different layer thickness (a) Ni and Cu sublayer thickness in the film is 5 μm and total thickness of the film is 25 μm, (b) sublayer thickness is 20 μm and the total thickness of the film is 85 μm [12]

With increasing thickness of the film and the substrate for the EDNi / EDCu system, adhesion decreases. Experiments have shown good adhesion characteristics for the ED Cu film thickness up to 10 µm. The great quantity of hydrogen bubbles, captured on the ED Ni/ED Cu interface as the side-reaction of mentioned electrodeposition process, is the reason for poor adhesion.

5. CONCLUSION

Analysis of the composite hardness and film hardness and adhesion of different composite systems of the same type (“soft film on hard substrate”) was given. Thin films of Ni and Cu were electrodeposited on single-crystal Si substrates and thick polycrystalline ED Ni films as the substrates, respectively.

Microindentation measurements were performed on uncoated substrates and film-substrate composite systems in order to observe their hardness response according to their different structures. The composite hardness model of Chicot-Lesage was found to be appropriate for calculation of film hardness of different composite systems.

Different microstructures and deformation response and consequently, different hardness values of the substrate and the film, as their relative difference are the most important parameters that influence the composite hardness value.

Adhesion influences the microhardness of the films. A composite hardness model was used for the evaluation of the adhesion of the Ni and Cu films on different substrates. When adhesion exists between the film and the substrate, the critical reduced depth b (the ratio of the plastic zone radius to the indentation depth) increases.

The system of thin EDCu film on thick EDNi substrate has higher values of critical reduced depth b than the system of EDNi film on Si substrate and it corresponds to better adhesion properties.

For the same film/substrate combinations, a large value of b usually corresponds to a good adhesion of the films. When increasing the indentation load, the hardness difference $(\Delta H = H_S - H_C)$ decreases faster for poor adhesion. Increasing of the film thickness leads to loss of adhesion properties and possible delamination of the film.

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