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EFFECT OF SUBSTRATE TYPE ON MICROHARDNESS OF MULTILAYER THIN FILM COMPOSITE SYSTEM

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Abstract: *Thin metallic multilayer films consisting of nanometer layer thickness deposited on different substrates have shown promising mechanical, electrical and magnetical properties, especially for applications in fabrication of microelectromechanical (MEMS) structures and wear-resistant applications.*

Electrodeposition of Ni/Cu multilayer films on substrates of (111)-oriented single crystal Si and 100μm-thick electrodeposited Ni film was carried out using dual-bath technique (DBT). The current density values was maintained at 10 mA·cm^{-2} and projected thickness of deposit was 5μm. Vickers microhardness of Ni/Cu thin multilayer films was investigated. The substrate starts to contribute the measured hardness at penetration depths of the order of 0.07 - 0.20 times the film thickness. The measured "composite hardness" is a complex value that depends on the microstructure and the hardness of the film and the substrate and their relative differences.

Ni/Cu films on (111)-oriented Si wafer and 100μm-thick electrodeposited Ni film as the substrates can be thought as "soft film on hard substrate" composite systems. Chicot-Lesage model based on the model for reinforced composites can be applied to experimental data for all specimen and the film hardness was calculated for each indentation diagonal. The values obtained for the film hardness H_F are not constant for all types of these composite systems, but influenced by the applied load.

Keywords: *Composite metallic multilayer films, Vickers microhardness, Composite hardness models.*

1. INTRODUCTION

The metallic monolayer or multilayer thin film structures are in wide use in fabrication of different microelectronic and micromechanical devices. Thin film and substrate constitute a composite system which properties depend on material parameters of the film and of the substrate and of the composite parameters such as the residual stress and adhesion [1,2,3].

Thin Ni/Cu multilayer films have attracted great interest owing to their high mechanical strength, high wear and corrosion resistance and giant magnetoresistance behavior. Multilayer film of Ni/Cu sublayers is a technologically interesting system, because of the simplicity with which coherent multilayers of Ni/Cu can be fabricated and the fact that both, Ni and Cu have a fcc structure with lattice mismatch only 2.5%.

Electrodeposition technology (ED) is fully compatible with microsystem technologies (MEMS). This technology has several advantages compares to available deposition technologies: it is a low-temperature deposition technology with easy control of high deposition rate, film thickness and residual stresses and easy control of chemical composition and microstructure od the films. Electrodeposition is an inexpensive and versatile method and with optimized process parameters it is possible to produce dense fine-grained films of many different metals and alloys [4].

The Vickers indentation hardness test is commonly used as a guide of a material deformation resist ability, especially for the evaluation of mechanical properties of thin films. Calculation of the absolute hardness of thin films in composite systems is difficult because the substrate participates in measured hardness value. The measured hardness values vary continuously with the indentation depth, the film thickness and the hardness of the film and of the substrate. The composite hardness model of Chicot- Lesage (C-L) was chosen and applied to experimental data in order to analyse the influence of the substrate for different composite systems.

Change of the composite and film hardness with applied loads dependes on the composite structure (especially of the substrate type). Composite Meyers index m (composite work hardening exponent) characterizes the way in which the composite hardness varies with load and $(t/d)^m$ is a parameter that can express the difference in tendency of the composite hardness with the indentation load (t is film thickness, d is indent diagonal and m is work hardening exponent) [5,6].

In the Section 2, theoretical composite hardness model of Chicot-Lesage (C-L) is given with important model parameters. Section 3 gives informations about experimental details, such as chosen materials for films and substrates, deposition techniques and hardness measurement technique. In the Section 4, results and discussion on composite and film hardness measurements for two different composite systems of the same type ("soft film on hard substrate" are given. Short analysis and conclusion are given in the Section 5.

2. COMPOSITE HARDNESS MODEL

For the analysis of experimental hardness results, the model of Chicot-Lesage (C-L) was chosen [5,6]. The model uses data obtained from standard measurements, thickness of the film and apparent hardness. This model is constructed on the 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 that of the film.

Hardness value calculated from an indentation test is load-dependent. Meyer's law is used to express the variation of the indent size in function of applied load. Chicot and Lesage proposed a hardness model with a similar relation as is Meyer's:

$$P = a^* \cdot d^{n^*} \quad (1)$$

Factor n^* represents the variational part of the hardness number with load and is given with the following expresion:

$$f\left(\frac{t}{d}\right) = \left(\frac{t}{d}\right)^m = f \quad where \ \ m = \frac{1}{n^*} \quad (2)$$

Composite hardness H_C, can be expressed through next equation:

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

Hardness of the film H_F, is the positive root of the equation:

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

The value of composite Meyers index m is calculated by a linear regression performed on all experimental points obtained for a given film-substrate couple and deduced from the relation:

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

Now it is possible to calculate the hardness of the film with known value of m.

3. EXPERIMENTAL

Two different substrates were prepared for the experiments: single-crystal Si(111)-oriented wafers and 100-μm thick nanocrystalline films of electrodeposited Ni.

The plating base for the Si wafers were sputtered layers of 100Å Cr as the adhesion film and 800Å Ti as the nucleation film. Electrochemical deposition (ED) was performed in the DC galvanostatic regime. Nickel was electrodeposited 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 sacharine and copper layers were electrodeposited from a sulfate bath consisting of 240 g/l $CuSO_4 \cdot 5H_2O$, 60 g/l H_2SO_4 and 40 mg/l thiourea. The process temperature were maintained at 40ºC for the sulfate and 50ºC for the sulphamate bath.

The current density values were maintained at 10 mA/cm^2 for the electrodeposition of thin Ni/Cu films and 50 mA/cm^2 for the thick films of Ni. According to the plating surface, projected thickness of deposits was determined.

The mechanical properties of the films were characterized using Vickers microhardness tester "Leitz Kleinharteprufer DURIMET I" with load range from 1.96N down to 0.049N. Three indentations were made at each indentation load from which the average composite hardness could be calculated. Experimental data were fitted with GnuPlot v.4.0.

4. RESULTS AND DISCUSSION

Absolute hardness of the substrates

Indentations were performed with Vickers diamond pyramidal indenter both on uncoated substrates and on different composite systems. Model of Li and Bradt (Proportional specimen resistance model-PSR) is suitable for analyzing the variation of substrate microhardness with the load [7]:

$$P = a_1 d + (P_c / d_0^2) d^2 \quad (6)$$

Value of P_C is the critical applied 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, the slope of which gives the value for the calculation of load independent microhardness.

The average values of the indent diagonal *d* (in m), were calculated from several independent measurements on every specimen for different applied loads *P* (in N). The absolute substrate hardness and composite hardness values, *H* (in GPa), were calculated using the formula:

$$H = 0.01854 \cdot P \cdot d^{-2} \quad (7)$$

where 0.01854 is a constant, geometrical factor for the Vickers pyramid.

On Figure 1, *P/d* values are plotted against *d* for two tested substrates: single-crystal Si(111)-oriented and 100-µm thick Ni film electrodeposited with 50mA/cm^2 current density. Substrate hardness H_S is calculated as 8.71 GPa for Si(111)-oriented single crystal wafer and 5.38 GPa for thick ED Ni film as the substrate.

Composite hardness and film hardness

Two composite systems that have been investigated belong to the “soft film on hard substrate” composite system type. Our intention was to analyse the composite hardness response of above-mentioned systems, according to different substrate type and different structure of metallic multilayer films.

Change of the composite hardness *Hc* with relative indentation depth, *h/t* (*h* is indentation depth and *t* is total thickness of the film) is shown on the Figure 2.

For shallow indentation depth, when relative indentation depth is $h/t \leq 0.1$, the response is of the film only, and for the large indentation depths ($h/t \geq$)1, the response is of the substrate mostly. The composite hardness region is region for the values of relative indentation depths between 0.1 and 1 [8].

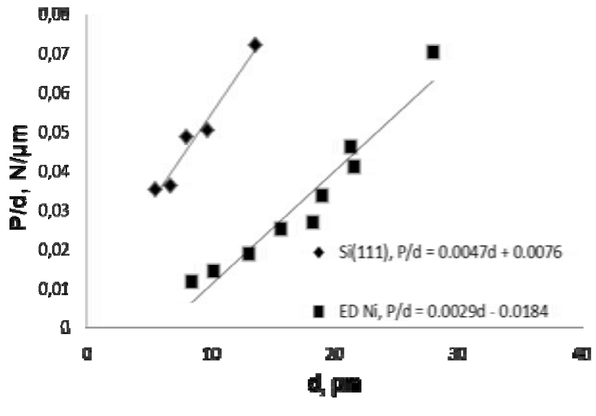

Figure 1. PSR plot of applied load (in N) through indent diagonal (in µm), *P/d*, versus indent diagonal, *d*, for Si(111)-oriented single crystal wafer and thick ED Ni films as examples of the hard substrates

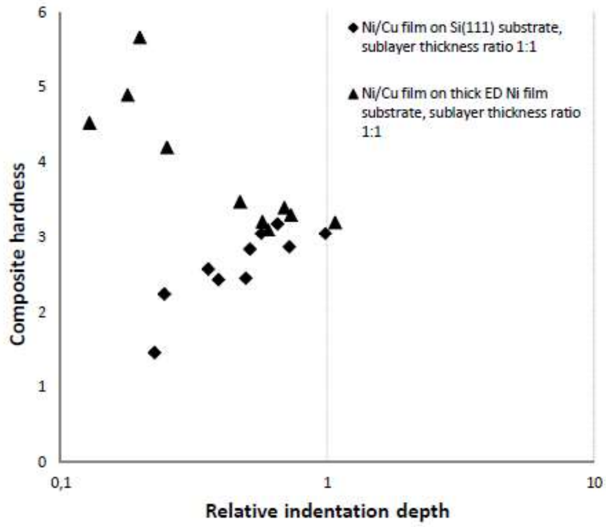

Figure 2. Change in composite hardness with relative indentation depth for different composite systems. Total film thickness of the film is 5 µm, sublayer thickness is 100 nm and current density value was 10 mA/cm^2

The microstructure of the substrate plays key role for the composite hardness response. Because of the work hardening of the ED Ni substrate and according to Chicot –Lesage (C-L) model, the system ED Ni/Cu on ED Ni substrate has the highest values of composite and film hardness of all the analysed systems and has the most expressive composite character.

Increasing the sublayer thickness ratio in the Ni/Cu film from 1:1 to 1.4, leads to increase of the composite and film hardness of the composite systems [9]. The influence of change of the sublayer thickness ratio on composite and film hardness (calculated according to C-L model) for different composite systems is shown on Figure 3.

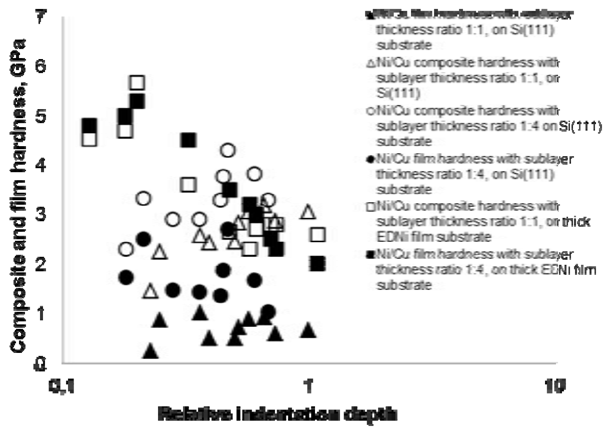

Figure 3. Change in composite and film hardness with relative indentation depth for different composite systems. Total film thickness of the film is 5 µm, and the sublayer thickness ratio Ni:Cu is 1:1 and 1:4

The difference in tendency of the composite hardness *Hc* with load can be expressed through $(t/d)^m$ parameter. When the composite hardness tends to that of the film (for the low load values), parameter $(t/d)^m$ is almost independent of the substrate type. With increasing load, influence of the substrate becomes dominant and parameter $(t/d)^m$ depends mostly on the substrate type. It is shown on Figure 4.

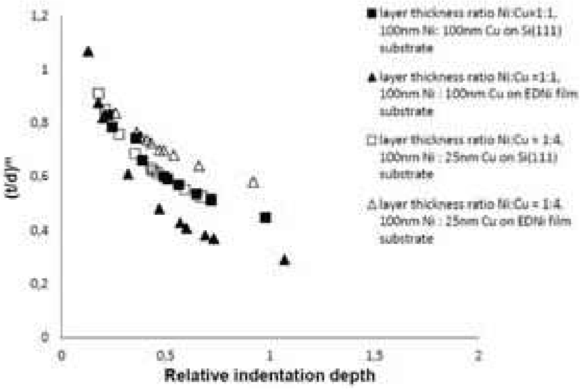

Figure 4. Comparison of the parameter $(t/d)^m$ with relative indentation depth, h/t, for 5-µm thick ED Ni/Cu multilayer films on single crystal Si(111)-oriented wafer and 100-µm thick ED Ni film as the substrates

The composite system of ED Ni/Cu on thick ED Ni film as the substrate is more sensitive on composite parameter $(t/d)^m$ change than the system of ED Ni/Cu on Si(111) substrate especially in the substrate-dominant region. Different deformation response of the substrates, which is for the brittle Si substrate probably crack formation and for polycrystalline ED Ni substrate work hardening is responsible for such composite hardness response.

5. CONCLUSION

Analysis of the composite hardness of different composite systems of the same type (”soft film on hard substrate”) was performed. Metallic multilayer films of Ni and Cu were electrodeposited on different substrates: brittle Si(111) wafers and thick film of polycrystalline electrodeposited Ni. Vickers microhardness testing was done with different applied load and composite hardness values were obtained.

The tendency of the composite hardness H_c, depends on the type of the composite system, i.e. the differences in the mechanical properties of the film and of the substrate: microstructure and hardness of the substrate, structure/microstructure and hardness of the film, and their relative differences.

Composite hardness model of Chicot-Lesage (C-L) was chosen and applied to experimental data in order to get the film hardness values. Layer thickness, layer thickness ratio but also the microstructure of the substrate (single crystal or polycrystalline substrate material) are important parameters for “tailoring” the mechanical properties of the composite systems.

The composite Meyer index, *m*, and parameter $(t/d)^m$ deserves more attention in analysis of the composite system hardness, because with increasing the load, the influence of the substrate become dominant and this parameter depends mostly on the type of the substrate.

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