Thin Solid Films 516 (2008) 8646–8654

Contents lists available at ScienceDirect

Thin Solid Films

journal homepage: www.elsevier.com/locate/tsf

Analysis of the composite and film hardness of electrodeposited nickel coatings on different substrates

J. Lamovec [a,*], V. Jović [a], D. Randjelović [a], R. Aleksić [b], V. Radojević [b]

[a] IChTM-MTSC, Njegoševa 12, 11000 Belgrade, Serbia
[b] Faculty of Technology and Metallurgy, University of Belgrade, Karnegijeva 4, 11000 Belgrade, Serbia

ARTICLE INFO

Article history:
Received 27 April 2007
Received in revised form 30 May 2008
Accepted 6 June 2008
Available online 17 June 2008

Keywords:
Vickers microhardness
Nickel electrodeposition
Composite hardness
Hardness models

ABSTRACT

Fine-grained nickel thin films were electrodeposited from a self-made sulphamate-based electrolyte on different substrates: polycrystalline cold-rolled copper and single crystal silicon with two different orientations, namely (100) and (111). The influence of the substrate and chosen plating conditions on mechanical properties of these composite structures were investigated by Vickers microhardness testing for different loads. 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. Four composite hardness models (Jönsson–Hogmark, Burnett–Rickerby, Chicot–Lesage and Korsunsky models) are chosen and applied to the experimental data. The applicability of mentioned models is critically tested on two types of composite systems: Ni film on Cu substrate, which is example for "hard film on soft substrate" and electrodeposited Ni on Si substrate ("soft film on hard substrate") and their reliability is given.

1. Introduction

It has been well known that materials and structures with small-scale dimensions do not behave in the same manner as their bulk counterparts. This became significantly important when we deal with thin films which are routinely employed as components in micro-electronics and microelectromechanical systems (MEMS). 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. Tribology (friction and wear) is an important factor affecting the performance and reliability of MEMS. Good mechanical properties are also critical for mechanical integrity of microsystems. There is a need for fundamental understanding of tribological phenomena and to evaluate mechanical material properties on the scale pertinent to MEMS.

Using electroplated materials possessing optimum mechanical properties for the micromechanical parts give several preferences compared to conventional technology. Many different metals or alloys can be electroplated whereby different properties can be obtained. Electroplating is compatible with integrated circuits technology as it is low-temperature and high rate deposition technology [1].

Processing parameters affect many of properties of the electroplated material. Through controlling the grain size and microstructure, metals can be strengthened and hardened with little or no loss of ductility. With electrodeposition it is possible to fabricate the movable structures consisting of layers with a very low level of internal (residual) stress.

Nickel is widely used material for electroplating. Large grained Ni is expected to deform easier whereas electrodeposited fine-grained structured nickel will resist. Electrodeposited nickel has good mechanical properties such as high yield strength and hardness that are beneficial in the high aspect ratio microstructures. For a MEMS device a high electrical and thermal conductivity of nickel is also very important for some applications.

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 by indentation methods, the influence of the substrate must be considered. The substrate starts to contribute the measured hardness at penetration depths of the order of 0.07–0.20 times the coating thickness. The measured "composite" hardness is a complex value depending on the relative indentation depth and mechanical properties of both the film and the substrate.

2. Composite hardness models

To obtain the hardness of the coating alone from the experimental measurements, several models exist. The predictive models advanced by Jönsson and Hogmark (J–H) [2], Burnett and Rickerby (B–R) [3],

* Corresponding author. IChTM-MTSC—Institute for Chemistry, Technology and Metallurgy, The Microelectronic Technologies and Single Crystals Department, Njegoševa 12, 11000 Belgrade, Serbia. Tel.: +381 011 630 757; fax: +381 011 182 995.
E-mail address: jejal@nanosys.ihtm.bg.ac.yu (J. Lamovec).

0040-6090/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.tsf.2008.06.035

Chicot and Lesage (C–L) [4,5], and descriptive model by Korsunsky et al. (K) [6,7], will be applied to different types of composite systems. These models operate on a number of different principles.

J–H model [2] used a simple geometrical approach to separate the substrate and coating contributions to the measured hardness. Coefficient a represents the ratio of the projected area of the film deformed under the indent, A_F, and the total projected area deformed, $A=A_F+A_S$, such that:

$$a = \frac{A_F}{(A_F + A_S)} = 2C\frac{t}{d} - \left(C\frac{t}{d}\right)^2 \tag{1}$$

where t represents the coating thickness, d is the indent diagonal and C is a constant that depends on the mode in which the film adjusts itself to the shape of the indenter [7]. It was emphasized by the authors that $C=1$ should be taken when the behaviour of the film was supposed to be brittle and $C=0.5$ for ductile films. The original form of the J–H model can be expressed as:

$$H_C = H_S + \left[2C\frac{t}{d} - \left(C\frac{t}{d}\right)^2\right](H_F - H_S) \tag{2}$$

The model proposed by Burnett and Rickerby [3] is based on the assumption of the existence of a hemispherical plastic zone beneath the indenter and that the composite hardness could be expressed in terms of a volume law of mixtures, as a function of the film and substrate hardness. The fraction of the film involved in the indentation test is given by:

$$a = 3\left(\frac{H_F}{E_F}\right)\frac{t}{d}\tan^{1/3}\xi \tag{3}$$

where E_F represents the Young's modulus of the film. The final expression for composite hardness according to this model is:

$$H_C = H_S + 3(H_F - H_S)\left(\frac{H_F}{E_F}\right)^{1/2}\frac{t}{d}\tan^{1/3}\xi \tag{4}$$

where ξ is the indenter semi-angle.

The model proposed by Chicot and Lesage [4,5] avoids the knowledge or choice of any other data than that obtained easily from standard measurements (thickness and apparent hardness). They have constructed a model based on the analogy between the variation of the Young's modulus of reinforced composites in function of the volume fraction of particles [8], and the variation of the composite hardness between the hardness of the substrate and that of the film.

Hardness value deduced from an indentation test is not constant because hardness is load-dependent. Meyer's law expresses 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:

$$P = a^* d^{n^*} \tag{5}$$

The variational part of the hardness number with load is represented by the factor n^*. Then they adopted the following expression:

$$f\left(\frac{t}{d}\right) = \left(\frac{t}{d}\right)^m = f \quad \text{where} \quad m = \frac{1}{n^*} \tag{6}$$

Now the composite hardness can be expressed by the following relation:

$$H_C = (1-f)/\left(1/H_S + f\cdot\left(\frac{1}{H_F} - \frac{1}{H_S}\right)\right) + f\cdot(H_S + f\cdot(H_F - H_S)) \tag{7}$$

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

$$A\cdot H_F^2 + B\cdot H_F + C = 0 \tag{8}$$

with

$$A = f^2\cdot(f-1)$$
$$B = \left(-2f^3 + 2f^2 - 1\right)\cdot H_S + (1-f)\cdot H_C$$
$$C = f\cdot H_C\cdot H_S + f^2\cdot(f-1)\cdot H_S^2$$

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

$$\ln d = m\cdot\ln P + b \tag{9}$$

With the known value of m, only the hardness of the films remains to calculate.

Korsunsky and co-workers [6,7] have advanced a different approach to analyze hardness data for coated materials, employing dimensionless parameters. Model is applicable to either plasticity- or fracture-dominated behaviour, with all scales measured relative to the coating thickness. The approach is based on the assumption that the total work-of-indentation during a hardness test is composed of two parts: the plastic work of deformation in the substrate, W_S, and the deformation and/or fracture energy in the coating, W_F. In the case of plasticity-dominated coating response, the expenditure of energy may be assumed to be proportional to the plastically deforming volume, and may be written as:

$$W_F = \frac{\lambda H_F t^2 \delta}{3\kappa} \tag{10}$$

where κ represents a parameter that describes the indenter geometry. According to this model, the constant a, that represents the fraction of the film involved in the hardness test and whose expression depends on the model employed, is given by:

$$a = \frac{1}{1 + k\beta^2} \tag{11}$$

where k represents a dimensionless materials parameter related to the composite response mode to indentation and, β the relative indentation depth ($\beta = d/7t$). The composite hardness, according to this model, is given by:

$$H_C = H_S + \left[\frac{1}{1 + k'(d^2/t)}\right](H_F - H_S); \quad k' = \frac{k}{49t} \tag{12}$$

From Eq. (12) it is not possible to compute the film hardness at each indentation diagonal value since the magnitude of k should also be determined simultaneously from the experimental measurements of the composite hardness. This model does not allow computing the change in the film hardness with the indentation diagonal from the individual measurements of this property.

3. Experimental details

For these experiments three different substrates were prepared: cold-rolled copper rectangle pieces chemically polished, single crystal Si wafers with (100) or (111) orientations. The plating base for the silicon wafers were sputtered layers of 100 Å Cr as the adhesion film and 800 Å Ni as nucleation film. Electroplating was carried out using direct current galvanostate mode, from a sulphamate bath consisting of 300 g l^{-1} Ni $(NH_2SO_3)_2\cdot 4H_2O$, 30 g l^{-1} $NiCl_2\cdot 6H_2O$, 30 g l^{-1} H_3BO_3 and 1 g l^{-1} saccharine. The pH-value and the temperature of the process were maintained at 4.00 and 50 °C, respectively. The current density values were maintained at 10 mA cm^{-2} and 50 mA cm^{-2}, which resulted in