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Microhardness of Thin Solid Films

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Dedicated to Professor Dr. PAVEL LUKÁČ on the occasion of his 60th birthday

The microhardness of various thin solid films was measured by using a method based on the calculation of the relative contribution of substrate and coating to the "composite" microhardness value measured for hard coatings on softer substrate. The results obtained confirm the application of the method used and allow to give some conclusions concerning the influence of the technological process on the mechanical properties of thin films.

Es wurde die Mikrohärte verschiedener dünner Schichten unter Verwendung einer Methode gemessen, die auf der Berechnung des Beitrags der Unterlage und der Schicht zur „zusammengesetzten" Mikrohärte beruht, die für den Fall einer harten Schicht auf einer weicheren Unterlage gemessen wird. Die gewonnenen Ergebnisse bestätigen die Berechtigung der Anwendung der genannten Methode und ermöglichen es, zu einigen Schlußfolgerungen zu kommen, die den Einfluß des technologischen Produktionsprozesses einer dünnen Schicht auf deren mechanische Eigenschaften betreffen.

1. Introduction

The use of surface coatings to improve corrosion resistance, mechanical, electrical, and optical properties of solids is rapidly increasing. Better knowledge of microstructure and other properties of thin solid films is conditioned by developing new testing methods. One of the mechanical test methods, applied to coatings is indentation microhardness measurement. One way to measure the microhardness of thin films is an ultramicrohardness test [1, 2]. However, according to the results deduced from ultramicrohardness tests, there are problems to compare them with those of microhardness tests [3].

A quite different approach to measure the microhardness of thin films is based on the calculation of the relative contributions of substrate and coating to the "composite" hardness values measured for hard coatings on soft substrates [4, 5]. In this paper, such a model proposed by Jönsson and Hogmark [6] is verified for various types of systems hard film (brittle or ductile)–softer substrate.

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2. Experimental Details

2.1 Materials

Thin copper (99.9%) films were prepared by the vacuum thermal evaporation technique at a pressure of 4×10^{-3} Pa. The films were deposited on pure aluminium (99.9%). The thicknesses of the films studied were 100, 200, 300, 500, 700, and 1000 nm.

Compact nonporous aluminium oxide films (thicknesses 225, 325, and 360 nm) were prepared by anodic oxidation in 5% vine acid.

Diamond-like films were prepared in rf plasma by the hybrid method connecting bias sputtering of carbon and plasma decomposition of hydrocarbon gases (CH_4 and C_6H_6). These films were deposited on Si(100) and on glass [7]. In the course of our investigations the parameters varied were the pressure (5 to 15 Pa), the upper electrode bias voltage, and the substrate bias voltage (0 to 1000 V).

The a-Si:H films, 2 to 6 μm thick were prepared by glow discharge decomposition of pure silane and silane–helium mixtures under different plasma conditions and at different substrate temperatures (from 100 to 350 °C) with decomposition rates ranging from 0.05 to 1.5 nm s^{-1} [10].

2.2 Hardness measurements

Vickers microhardness indentation testing was used to explore the hardness indentation deformation. Vickers microhardness number H is obtained as the ratio of the applied load to the area of the resulting indentation. With the given pyramid geometry the microhardness is expressed by

$$H = 2 \cos 22° \frac{L}{d^2}, \qquad (\text{kp mm}^{-2} = \text{HV}), \tag{1}$$

where L is the applied load and d the indentation diagonal (the indentation depth D is close to one-seventh of the diagonal). As the geometry of the indentation is independent of its size, in principle, the microhardness is independent of the applied load. In practice there is a load dependence particularly for small loads (indentation-size effect) [8]. According to Jönsson and Hogmark [6] the coating hardness can be separated from that of the composite by means of the formula

$$H_f = H_s + \frac{H_c - H_s}{2C_1 \frac{t}{D} - C_1^2 \left(\frac{t}{D}\right)^2}, \tag{2}$$

where $C_1 = \sin 22°$, for hard ductile film on softer substrate (model A), and

$$H_f = H_s + \frac{H_c - H_s}{2C_2 \frac{t}{D} - C_2^2 \left(\frac{t}{D}\right)^2}, \tag{3}$$

$C_2 = 2 \sin^2 11°$ for hard brittle film on softer substrate (model B). In both formulas H_f is the film hardness, H_s the substrate hardness, H_c the composite hardness, t is the film thickness, and D the indentation depth.

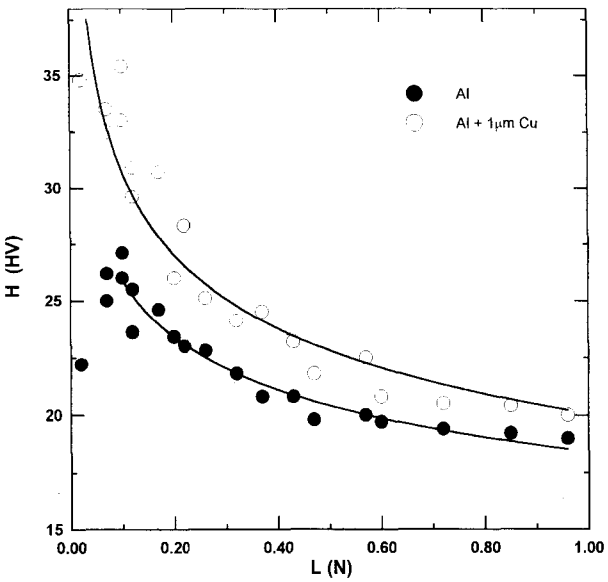

Fig. 1. The dependence $H = H(L)$ for pure Al and the system pure aluminium + 1 μm thick copper film (● Al, ○ Al + 1 μm Cu)

From (1) and (2) the relation for the easier calculation of the film hardness H_f was derived,

$$H_f = H_s + \frac{2 \cos 22° L}{ctd - c^2 t^2} \frac{d_s^2 - d_c^2}{d_s^2} . \tag{4}$$

L is the load, d_s and d_c are the diagonals of substrate and the composite diagonal with film, respectively, at load L, and c is a constant (for hard ductile film on soft substrate $c = 2 \sin 44°$ and for the hard brittle film on soft substrate $c = 8 \operatorname{tg} 11° \cos 22°$). But the derived relation does not consider the dependence of the hardness by the Vickers method on the load L. Therefore, the following empirical relation of the hardness to the load was used:

$$H = H_0 \, e^{K/L} , \tag{5}$$

where H_0 is the macrohardness (it means hardness at higher load, where the hardness is already a material constant) and K is a constant.

The microhardness measurements were made with a Hanneman (Vickers) microhardness tester in connection with Zeiss-Neophot microscope. On each specimen indentations were made with five loads ranging from 2 to 1000 mN and five impressions were made at each load. Both diagonals were measured to estimate the influence of the substrates as well as the asymmetry of the diamond pyramid.

3. Results and Discussion

3.1 Model A (hard ductile film deposited on softer substrate)

The "composite" hardness of all systems Al substrate + Cu films was measured. In Fig. 1 we can see as a representative the dependence $H = H(L)$ (H is the microhardness of the system, L the load) for the system pure aluminium +1 μm thick copper film (with the

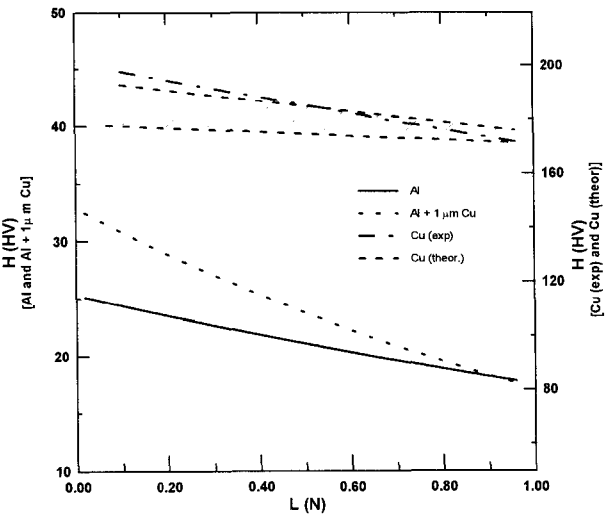

Fig. 2. The dependence $H = H(L)$ for Al and for the system pure aluminium + copper film together with calculated and experimentally measured microhardness of pure copper

typical indentation-size effect). The same dependence supplied by the results of the microhardness measurements of pure copper and microhardness H_f, calculated from (4) is shown in Fig. 2. We can see that both results of hardness dependence $H = H(L)$ (calculated and experimentally measured) are in relatively good agreement. (The values Cu(theor) calculated from the curves $H = H(L)$ for all systems Al + Cu occur in the band between the two dashed curves in Fig. 2.)

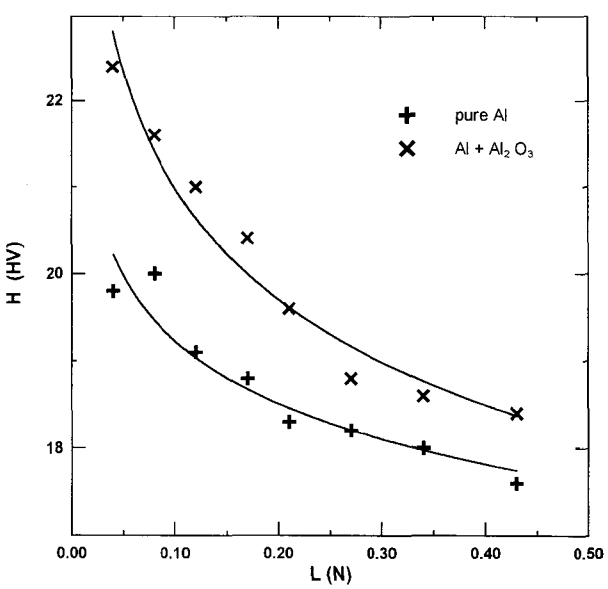

Fig. 3. The dependence $H = H(L)$ for pure Al and for the system Al + Al_2O_3 (thickness of the Al_2O_3 film is 360 nm)

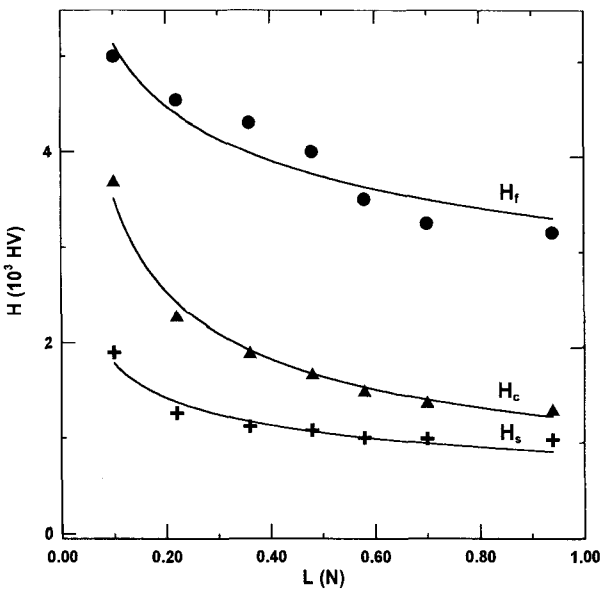

Fig. 4. The dependence $H = H(L)$ for a diamond-like film deposited on Si(100) (thickness of the film is 500 nm)

3.2 Model B (hard brittle films deposited on softer substrate)

As the representative of that structure three systems were elected:

3.2.1 System aluminium substrate + aluminium oxide (Al_2O_3)

The thicknesses of Al_2O_3 films were 225, 325, and 360 nm. The dependence $H = H(L)$ for the system Al $+Al_2O_3$ (360 nm) is shown in Fig. 3. The microhardness H_0 calculated for the Al_2O_3 layer according to (5) is (750 ± 50) HV which is in qualitatively agreement with measurements of other authors [9].

3.2.2 Diamond-like films deposited on Si(100) and glass

The microhardness of approximately 50 samples of diamond-like films on Si or glass was measured. The microhardness and other physical properties of these samples were much different because of a very wide spectrum of input parameters. For example, the microhardness H_0 varies from 500 to 4000 HV. Also adhesion was widely different. Therefore, our results can be only qualitative: the microhardness of diamond-like films is proportional to the concentration of hydrogen in the gas mixture. Brittleness and internal stress are inversely proportional to the film thickness. The adhesion seems to be a complicated function of plasma parameters. A typical dependence $H = H(L)$ of a diamond-like film is shown in Fig. 4 ($H_0 = (3100 \pm 100)$ HV).

3.2.3 Amorphous semiconductor a-Si:H films deposited on glass

The microhardness of approximately 20 samples of amorphous semiconductor glass + a-Si:H systems was investigated. The input parameters were: temperature of substrate, various rates of film growth, and various types of n- and p-doping [10]. Also in this case

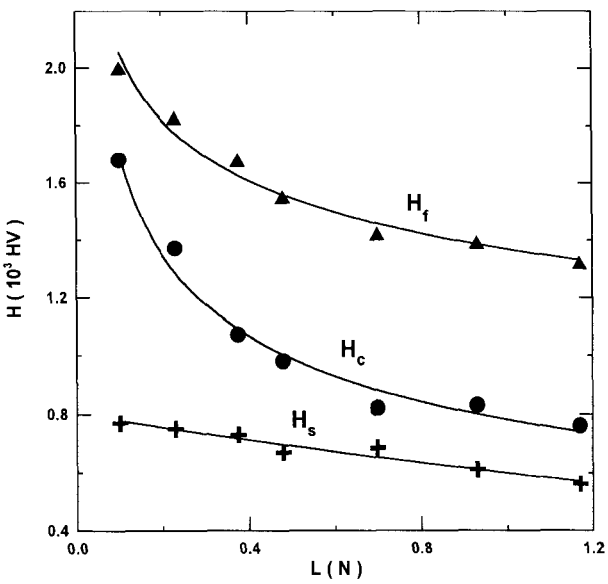

Fig. 5. The dependence $H = H(L)$ for the system amorphous a-Si:H film deposited on glass (thickness 2 μm, decomposition rate 0.1 nm s^{-1}, temperature of the substrate 200 °C)

our results can only be qualitative: the intrinsic a-Si:H samples are softer than the doped ones. The increases in the flow rate in the plasma during decomposition of silane lead to an increase in their microhardness. The value of the adhesivity was much larger for p-type than for n-type doped films (roughly estimated from the load at which removing of the film is observed). The typical dependence $H = H(L)$ of a-Si:H film on glass is shown in Fig. 5 ($H_0 = (1200 \pm 100)$ HV).

4. Conclusions

On the basis of our measurements it can be concluded that microhardness measurements are one of the very valuable diagnostic methods of thin film investigation. The results of these measurements can be used as a supplementary method together with others. Jönsson and Hogmarks's model is suitable for the calculation of the film hardness.

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