

CONSIDERATIONS ON NANOHARDNESS MEASUREMENT

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Abstract: Measurement of hardness on nano-scale is discussed. Methods and instruments used are described and energy definition of hardness is introduced. Results of nanohardness measurements of materials, in particular ultrathin films, used in Micro Electro Mechanical Systems (MEMS) technology are presented.

Keywords: hardness, nanohardness measurement, MEMS materials

1 INTRODUCTION

Hardness is not a fundamental property of a solid. It is a combination of elastic and plastic properties and can be understood as some measure of resistance to penetration or measure of resistance to surface contact deformation. Since the surface and bulk properties of material may differ hardness depends on the depth of penetration of an indenter. The measure of hardness can be expressed as a mean contact pressure required to force an indenter of a specific geometry into the surface of a solid.

Measurement of hardness by indentation technique is simple. On macro/micro-scales hardness is measured by pressing an indenter into the surface under constant load, holding for a fixed period, removing load and measurement are of residual impression (assuming that any elastic recovery can be neglected) and calculating mean contact pressure. In the case of nanohardness nanoindentation techniques must be used where the following steps of measurement procedure are applied: press the indenter into surface (constant loading rate or constant strain rate), record indenter displacement as function of load during loading and unloading, calculate elastic modulus (E) from unloading curve and calculate hardness (H) from geometry of tip and load-displacement curve [1,2].

2 TESTING NANOHARDNESS OF MEMS MATERIALS

Very little is understood on the micromechanical behaviour of bulk silicon and polysilicon films used in the construction of MEMS microdevices [2]. Mechanical properties of polysilicon and other films are not well characterized. Monolayers of lubricants and other materials need to be developed for ultralow friction and near zero wear. Such films need to be known as relates to their mechanical behaviour (hardness, modulus of elasticity).

The nanohardness was measured by nanoindentation of the tested material (Fig. 1). Even though during loading a sample undergoes elastic-plastic deformation, the initial loading is an elastic event. Therefore, the Young's modulus of elasticity or, simply, the elastic modulus of the specimen can be inferred from the initial slope of the unloading curve (dW/dh) called stiffness ($1/\text{compliance}$) (at the maximum load) (Fig. 1).

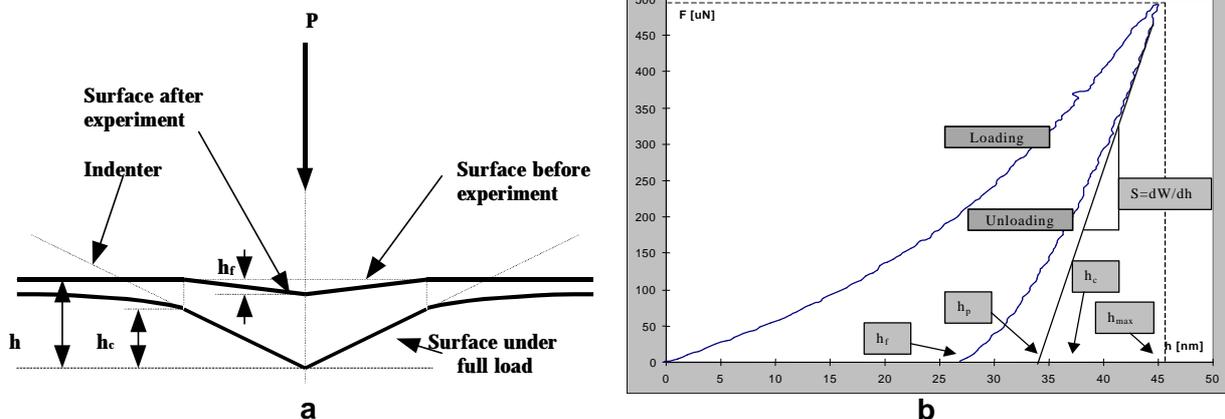


Figure 1. Schematic representation of the indenting process (a) and load-displacement curve (b).

The relationship for the stiffness S for an (Vickers, Knoop, Berkovich, Cube-corner) indenter is given as [3]:

$$S = \frac{dP}{dh} = \frac{2}{\sqrt{p}} E_r \sqrt{A} \quad (1)$$

where: A - area of the indent, E_r - reduced Young modulus of sample and the indenter.

$$\frac{1}{E_r} = \frac{(1-\nu^2)}{E} + \frac{(1-\nu_i^2)}{E_i} \quad (2)$$

where: E - Young modulus of sample, ν - Poisson's ratio of the sample, E_i - Young modulus of the indenter, ν_i - Poisson's ratio of the indenter.

Stiffness is calculated as derivative of the relation:

$$F = a(h-b)^c \quad (3)$$

where: F - force, h - depth of penetration, a , b , c - arbitrary constants, obtained by fitting it to unloading curve (Fig. 1b), for the maximum applied force. Depth at which the derivative equals zero is called contact depth (h_c).

For deep indents it can be assumed, that geometry of the indenter is perfect, then:

$$A = ch_c^2 \quad (4)$$

where: h_c - contact depth, c - indenter's shape dependant constant.

For ultra thin films imperfections of the indenter, which relates in general to wear of the indenter, have to be taken into account. For this purpose proceeding function is in wide use:

$$A = C_0 h_c^2 + C_1 h_c + C_2 h_c^{1/2} + C_3 h_c^{1/4} + C_4 h_c^{1/8} + C_5 h_c^{1/16} \quad (5)$$

Where C_0 describes ideal geometry of the indent and C_n describes it's imperfections. C_n are being found as the result of calculation based on series of indents made in known material, which usually is fused silica. In calculations equation (1) is used. In the experiments only indenters with known relation between A and h_c can be used.

The hardness is obtained by dividing the maximum indentation load by the projected contact area.

The described procedure was used by us to measure nanohardness of various MEMS materials in particular silicon (undoped, doped, various crystallographic orientations), polysilicon and ultrathin films (below 100 nm thick) of silicon dioxide and silicon nitride manufactured on single-crystal silicon using glow discharge at atmospheric pressure technique [4,5]. The loading-unloading curves were found using Hysitron TriboScope transducer mounted on an Atomic Force Microscope which allows visualization of the area of interest before and after experiments. TriboScope possesses electrostatic actuation hardware, which applies normal load force to the indenter, and a capacitive sensor, which measures normal displacement of the indenter [6]. The load range employed in the tests was 0.001 to 10 mN and the load resolution was 100 nN. The displacement resolution of the device is 0.2 nm. A three-sided Cube-corner indenter was used in the experiments.

Hardness implies the resistance to local deformation. The classic, above mentioned definition of hardness which we can call „force related hardness“ does not describe precisely the resistance of the material to local deformation. We think that since the deformation is volume process and it takes energy to induce it, the energy related definition of the hardness is more descriptive in particular in the case of nanohardness measurement where the volume of the deformed material is very small.

Energy approach relates energy dissipated in the sample to the volume of the indent after withdrawal of the indenter. Dissipated energy is derived out of whole load-displacement data (L-D curves) obtained during the experiment by discrete integration of force being function of displacement. Volume of the indent is derived as an integral of the area of the indenter being function of penetration depth and then corrected by factor of final depth divided by maximum depth of penetration.

$$V_{final} = \frac{V_{load} \times h_r}{h_c} \tag{6}$$

where: V_{final} - volume of the indent after withdrawal of the indenter, V_{load} - volume of the indent under full load (volume of the indenter being in contact with the sample), h_r - depth of the indent after withdrawal of the indenter, h_c - contact depth (under full load).

Finally energy related hardness marked as H_e is

$$H_e = \frac{E}{V_{final}} \tag{7}$$

where: E - energy dissipated in the sample.

Using Hysitron Inc.'s, Minneapolis, USA, TriboScope testing instrument, series of experiments were conducted on two groups of samples: silicon obtained with different methods, identical as for IC purposes, and thin layers obtained with new method invented in Department of Chemistry of Warsaw University of Technology, Poland. Loading cycle consisted of 10s loading period, 5s hold period and 10s unloading period. Holding of the load was provided in order to reveal time dependant properties of tested samples for purpose of further experiments. Data obtained during the experiments were processed according to force related hardness definition and then according to energy related definition of hardness.

3 RESULTS AND DISCUSSION

Presented graphs show hardness calculated according to force related definition by software provided by Hysitron along with TriboScope (H) and custom developed software for energy analysis (H_a), hardness according to energy related definition as described before, calculated by the developed software (H_e), and relationship between force and energy related hardnesses (H_e / H_a). Custom software used force related definition only for the purposes of comparison to results obtained with commercial software. Differences of values between force related hardnesses are related to different method of fitting equation (3) to experimental data utilized by our software and the fact that equation (3) in our software included additive constant in order to get better fit.

$$F = a(h - b)^c + d \tag{3'}$$

Lines on the graphs are provided only for easier localization of the points and their affiliation, and have no interpolation meaning.

Following graphs are results of experiments conducted on following materials:

Table 1. Description of samples

1	N <100>	Bulk Czochralski Si wafer 0.008 - 0.02 Ω cm, i.e. 1.3 - 6.5 e18 at/cm ⁻³ P in Si
2	N <100>	Bulk Cz Si wafer 1 - 2 Ω cm, i.e. 3 - 8 e16 at/cm ⁻³ P in Si

Because of high homogeneity of tested material load-displacement curves exhibit high repeatability of loading part of the curve and parallelity of unloading part of curves.

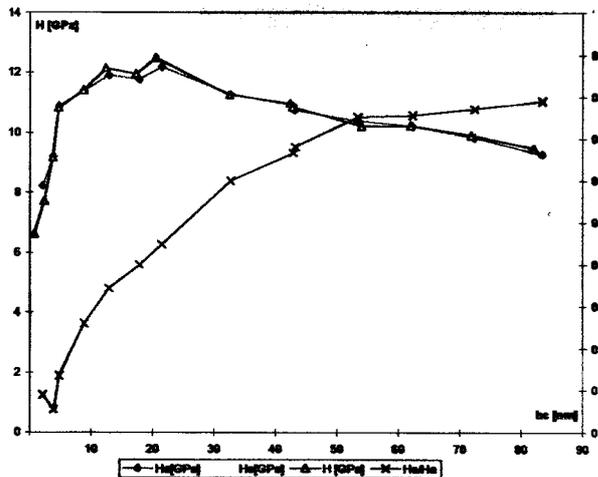


Figure 3. Hardness curves for sample 1

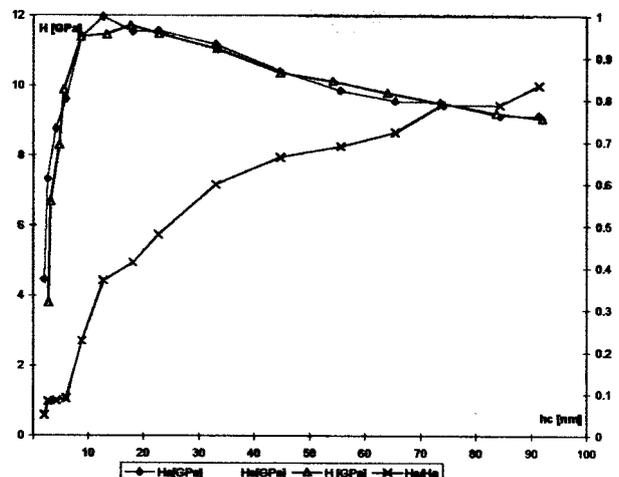


Figure 4. Hardness curves for sample 2

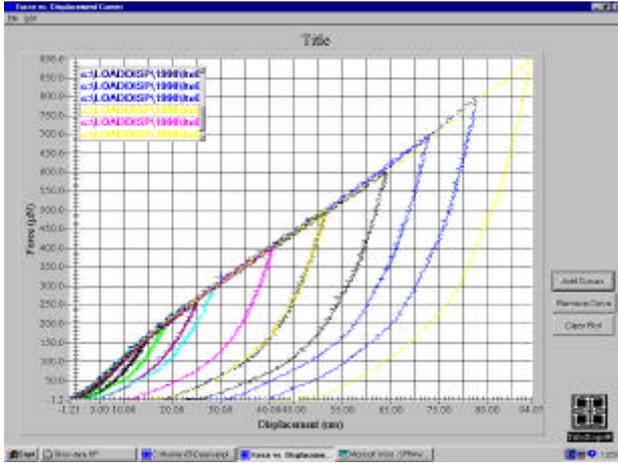


Figure 5. L-D curves for sample 1

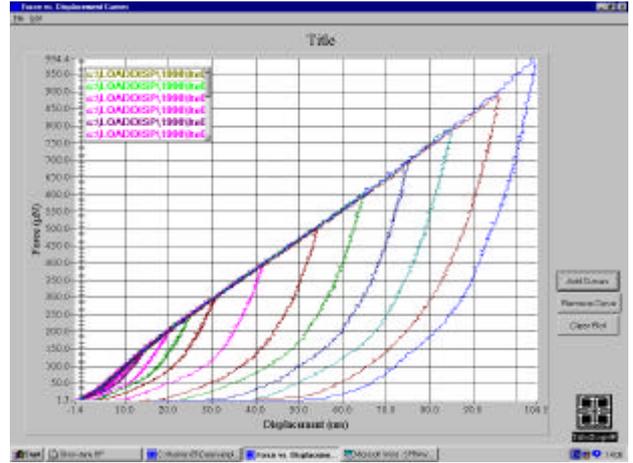


Figure 6. L-D curves for sample 2

Next set of graphs are results of experiments conducted on samples of thin films obtained by electric discharge in mixture of gases under atmospheric pressure. Method of deposition is described elsewhere [5].

Non-homogeneity and roughness of tested samples resulted in visible spread of hardness values and diversity of L-D curves.

Table 2. Description of deposition conditions

No.	Carrier Gas	$V_{Ar/N2}$ [l/hr]	V_{O2} [l/hr]	V_{NH3} [l/hr]	Deposition temp. [°C]	Time of deposition [min]	Thickness Of film [nm]	Remarks
13.	TEOS	9/Ar	0.005	-	300	60	86.3	Exposed to UV, 18hr, 110°C
14.	As previous	a.p.	a.p.	-	370	a.p.	a.p.	a.p.

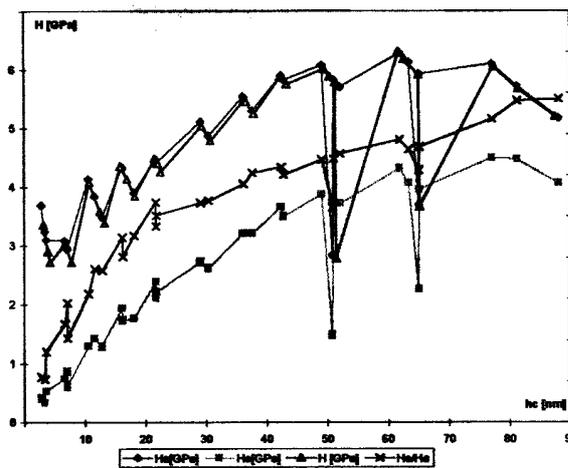


Figure 7. Hardness curves for sample 13

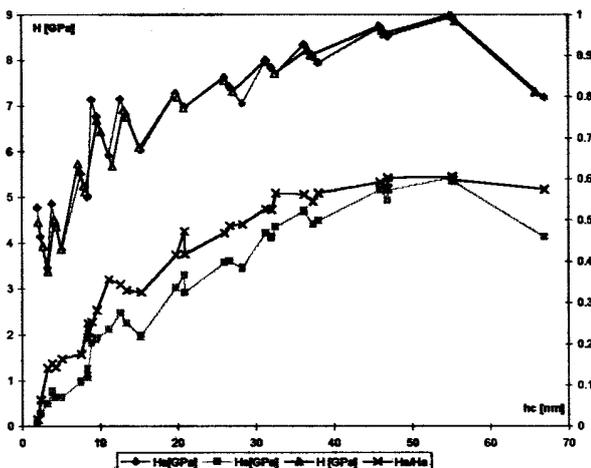


Figure 8. Hardness curves for sample 14

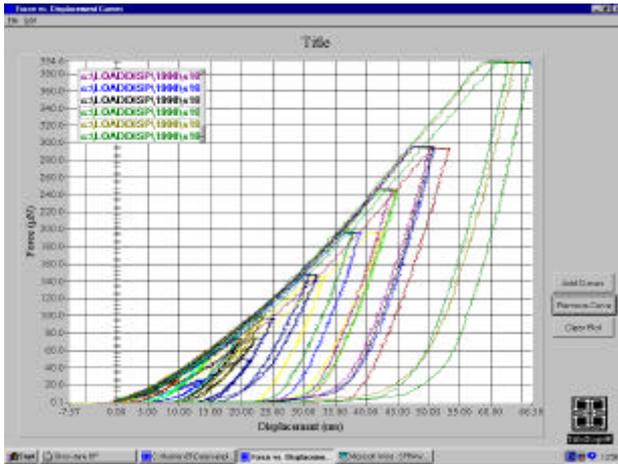


Figure 9. L-D curves for sample 13

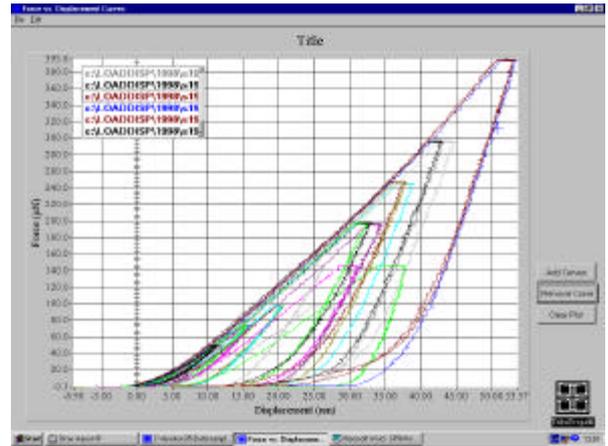


Figure 10. L-D curves for sample 14

Last set of graphs is a result of tests conducted on layers of Si_3N_4 obtained with the same method in different conditions.

Table 3. Description of samples

10	N <111>	coated with Si_3N_4 230 nm; DCS/ NH_3 reactant ratio = 1:8
11	N <111>	coated with Si_3N_4 210 nm; DCS/ NH_3 reactant ratio = 8:1

Visible scatter of L-D curves and higher roughness of hardness curves for sample 11 suggest scatter of values of mechanical properties of tested material on it's surface

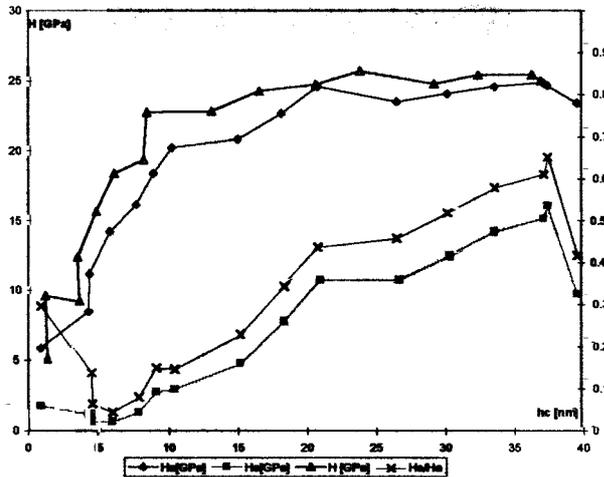


Figure 11. Hardness curves for sample 10

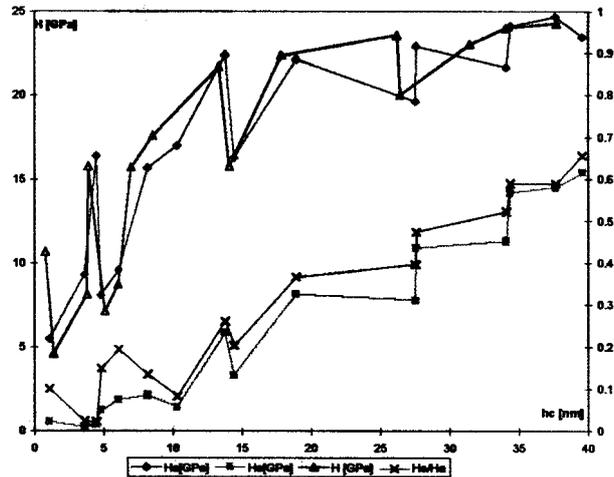


Figure 12. Hardness curves for sample 11

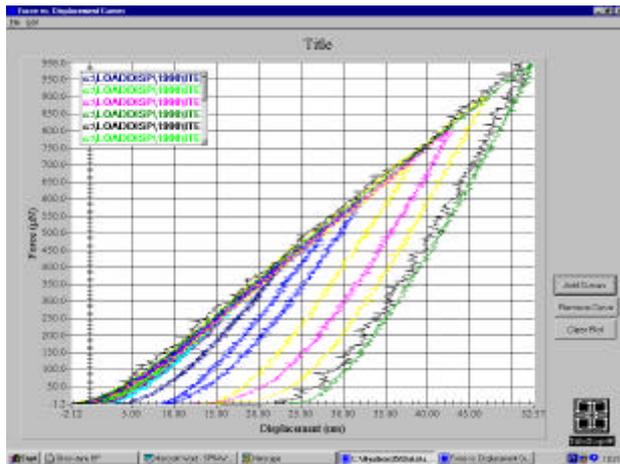


Figure 13. L-D curves for sample 10

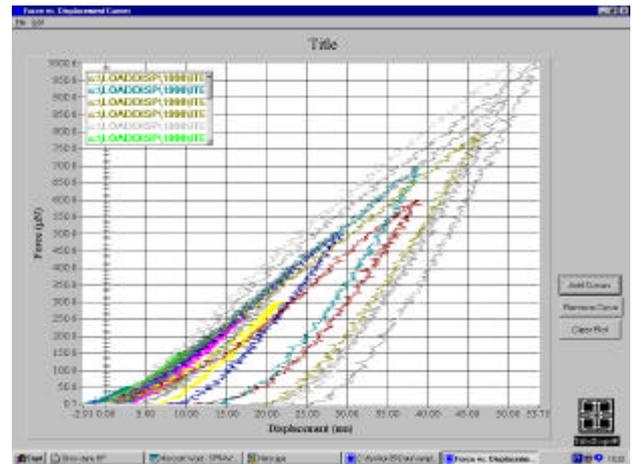


Figure 14. L-D curves for sample 11

4 CONCLUSIONS

The new method of processing the data allows evaluation of the amount of energy required to alter the structure of the unit of tested material. Obtained results are in general different from results obtained with force related definition of hardness. Moreover no simple relationship between results obtained with energetic and force based method was found.

Presented results show that damage of layers of material close to the surface is easier than damage of deeper layers. It is worth to note, that according to force related definition of hardness silicon exhibits higher resistance to deformation of near surface layers, while according to energy related definition of hardness resistance to deformation of the same layers of silicon is lower.

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