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ESTIMATION OF YOUNG'S MODULUS OF ULTRATHIN POLYMERIC FILMS FOR NANOIMPRINT LITHOGRAPHY BY USE OF ATOMIC FORCE MICROSCOPE

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The tests concerning the estimation of the Young`s modulus for ultrathin polymeric films, devoted for nanoimprint lithography, with the use of atomic force microscope (AFM) were carried out. Some results will be discussed in the paper.

1. Introduction

As the nanoimprint lithography started to emerge as an alternative patterning method it became an important thing to find a suitable polymer for this application. As of that time for the NIL process a number of various polymers showing different nanomechanical properties was manufactured. The problem that emerged was how to choose the right process conditions for different/modified polymer resists as well as how to detect the change of polymer's nanomechanical properties at the stage of laboratory research without engaging imprinting tool. As long as the elastic modulus characteristic for some bulk polymers were known (e.g. for PMMA [1]) it was demanded to obtain such a temperature dependency of elastic properties for these ultrathin polymeric resists. From this the desired process conditions could be chosen, as it was with PMMA (with its bulk elastic modulus characteristic). For that it was important to develop a cheap and fast method to determine the nanomechanical properties of these films. In this study an AFM based method with stiff cantilever will be presented to evaluate the nanomechanical properties of these ultrathin polymeric resist films.

2. Experimental details

In this experiment one set of ultrathin polymeric resist samples were used to investigate their nanomechanical properties. The set consisted of two silicon wafers with thermoplastic polymer. The samples were denoted as sample 1 and sample 2. The glass transition temperature determined with DSC (differential scanning calorimetry) was 60°C. Prepared by micro resist technology, these films were spin-coated (3000 rpm for 30 sec) on silicon 4" wafers that were treated previously with an oxygen plasma for 10 minutes. After spin coating the films were soft-baked on a hot plate for 2 minutes in 140°C to evaporate solvent and form a solid layer. The thickness of this film was measured and it was 208 nm and 202 nm for sample 1 and 2, respectively.

The testing equipment, used in this study was an AFM (Microtestmachines Co., Belarus) with optical cantilever's deflection detection system (photodiode). For temperature experiments the microscope was equipped with heating unit that enabled con-

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trol of the sample temperature from room temperature up to 140°C. All experiments were performed in an air atmosphere (21°C, RH=50%) in a clean-room conditions.

The AFM probe (Fig. 1.) was a custom made high stiffness cantilever. Etched from highly polished beryllium bronze (thickness of 0.07 mm) it was coated with 300 nm thick gold layer evaporated on its top to improve the reflective properties. As a tip a steel bearing ball with diameter of 0.691 mm was used. The length and width of the cantilever was 1.68 mm and 0.43 mm respectively. The tip roughness parameters R_a and R_q were 12.2 nm and 16.5 nm respectively. The topography of the tip with its roughness parameters is shown in Fig.2.

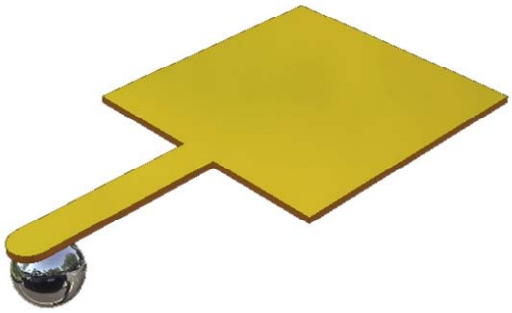

Fig. 1. The beryllium bronze cantilever, coated with gold, with a steel ball tip. The dimensions were 0.07/1.68/0.43/0.346 thickness/length/width/tip radius mm (the bigger square part is only support for the cantilever). The stiffness (calibrated) was 220 N/m

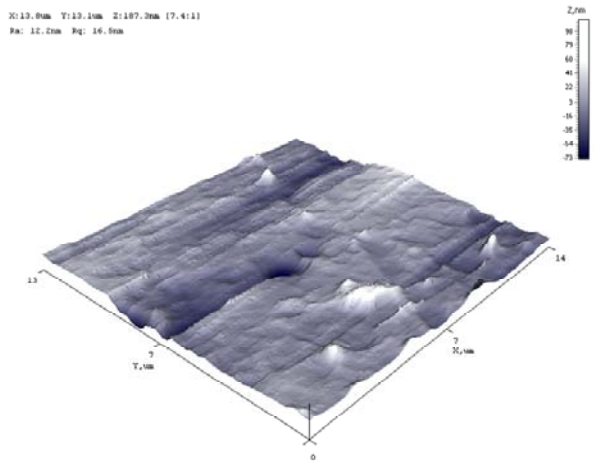

Fig. 2. The cantilever's steel ball tip topography. The R_a and R_q parameters were 12.2 nm and 16.5 nm respectively

The stiffness of the probe was calibrated, as it will be described later, and it was 220 Nm^{-1}.

2.1. Principles of AFM force distance curves (FDC)

Typical FDC is shown in Fig. 3. The piezo-stage position axis (z_{pos}) indicates the vertical position (in nm) of the sample that was mounted directly on the piezo-stage. The deflection axis indicates the deflection of the cantilever (z_{def}) (also in nm). The point denoted as '1' is the starting point of the FDC – rest position of the cantilever, when the piezo-stage (sample) started its movement toward the probe. In point '2' the cantilever jumped to contact as an effect of attraction the tip by surface forces. From this an interaction between sample and probe is observed (the deflection of the cantilever versus piezo-stage displacement). The point denoted as '3' indicates the last point in a range of the optical detection system.

The FDC piezo-stage position axis scale was corrected in a way that the zero value was placed in 'jump to contact' point (an inflexion point of the FDC – point 2) for further data analysis.

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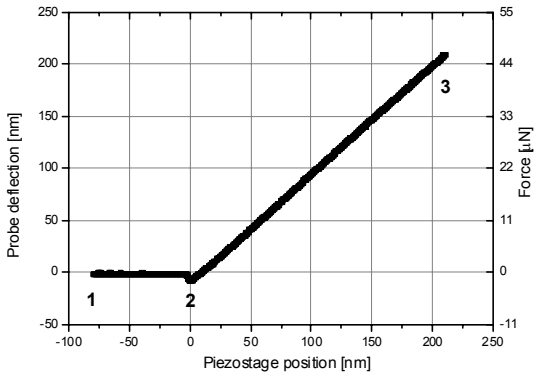

Fig. 3. Exemplary approaching Force Distance Curve on silicon sample after calibration. 1–2 – rest position of the cantilever; 2 – jump to contact point; 2–3 – contact between the sample and the cantilever. The slope of the 2–3 part was equal to 1 (the cantilever's deflection was equal to piezo-stage displacement)

2.2. Mathematical model

To evaluate the nanomechanical properties a series of FDCs on silicon and polymer were made. As shown in Fig. 4 a difference between elastic behaviour of the silicon sample and the polymeric one could be observed. The difference between these two curves represents the deformation of the polymeric film under the normal load that was applied.

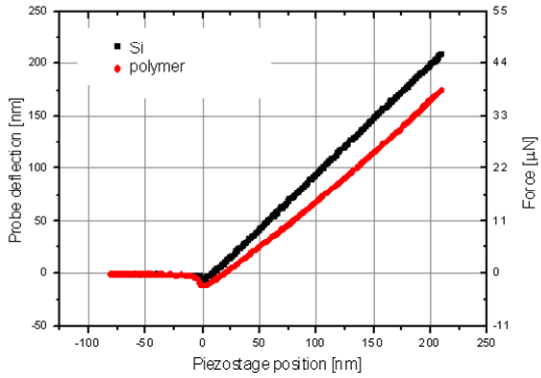

Fig. 4. Force distance curve (FDC) for silicon (upper curve) and for polymer (lower curve). Zero point of the piezo-stage position is set in 'jump to contact' point for both silicon and polymer (inflexion points of both FDCs). The difference between these two curves represented the deformation of the polymer under the normal load

To evaluate the elastic properties of these ultrathin films from these data a mathematical model given by an equation (1) was used:

$$E = \frac{3}{4} \cdot \left(1 - \nu^2\right) \cdot R^{-\frac{1}{2}} \cdot \left(z_{pos} - z_{def}\right)^{\frac{3}{2}} \cdot k \cdot z_{def} , \qquad (1)$$

where ν – Poisson's ratio of the tested material; k – stiffness of the cantilever; z_{pos} – position of the piezo-stage, equal to sample's position (zero position was set in 'jump

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to contact' point (horizontal axis); z_{def} – deflection of the cantilever (vertical axis); R – radius of the steel ball tip (attached to the cantilever).

The equation (1) was derived in [2] as an equality between forces applied by the cantilever and surface elastic deformation forces calculated from a sphere – plane contact in Hertz model. As long as the Hertz model was used it was possible to investigate a brittle state of the material rather than a viscoelastic state because of a high adhesion forces that occured while the state of the material was changing to viscoelastic. When the adhesion force came to take an important role the JKR model seemed to be much more appropriate [3].

In this study only the Hertz based model will be used and the range of investigated temperatures will be from brittle state region.

The expression $z_{pos} - z_{def}$ from equation (1) was the indentation depth value.

The force that was applied by the cantilever during the experiments was calculated from Hooke's law from equation (2).

$$F_{def} = k \cdot z_{def} \tag{2}$$

2.3. Plan of the experiment

The nanomechanical properties were investigated for room temperature. For each experiment as a reference, a number of 6 FDCs on silicon were made (3 before and 3 after nanoindentation on polymer). On polymer sample a number of 6 up to 12 FDCs were made. To ensure if the values obtained with this method were repeatable all indentations were made in different points.

The final FDC that was used to calculate the elastic modulus was an FDC that was an average of all FDCs made for this sample (as the maximum standard deviation was not higher than 5% and usually much smaller).

3. Results

3.1. System calibration

3.1.1. Calibration of the heating unit

The heating unit was equipped with a thermocouple sensor that was placed under the hot plate on which the samples' were placed. The temperature that was detected with the sensor might not be the precise temperature of the tested sample so in order to avoid that a calibration of the real temperature was made. The calibration was performed with an external thermometer. The values from the thermometer and indicated by the control unit were compared. The difference from 1 to 2°C occurred for whole range of investigated temperatures. All temperatures that will occur in this study are corrected to the real values.

3.1.2. Calibration of the detection system

In the AFM that was used in this experiment an optical system (photodiode) was used to detect the deflection of the probe. As long as the values from photodiode were in *a.u.* (arbitrary units) it was impossible to calculate the force applied by the cantile-

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ver. In order to calibrate this optical system from *a.u.* to nm a calibration procedure was engaged.

The procedure was to make a series of FDC on silicon <1 0 0> sample (cut off from a wafer). While making FDC on silicon sample it was assumed that the deflection of this sample and the tip may be neglected due to very low maximum force applied (hundreds of μN). Though the deflection of the cantilever was to be equal to the displacement of the sample (piezo-stage displacement) as it could be seen in Fig. 3. As a result the change of laser spot position on the photodiode in *a.u.* was recalculated to nm of the probe deflection.

3.1.3. Calibration of the probe stiffness

To calibrate the stiffness a microspring template with known stiffness was used. After calibration of the detection system (paragraph 3.1.2) a few series of FDCs were made on a microspring template. Comparing the deflection of the cantilever from the FDCs made on the silicon template and on the microspring template a proportion of stiffness of the template and probe was obtained. The stiffness of the cantilever used in this experiment was calibrated to be 220 Nm^{-1}.

3.2. Results

3.2.1.Influence of the indentation depth on Young's modulus

As shown in Fig.5 the elastic modulus depends on the indentation depth. In this experiment for indentation depths higher than 6 nm the value of the elastic modulus remained nearly constant.

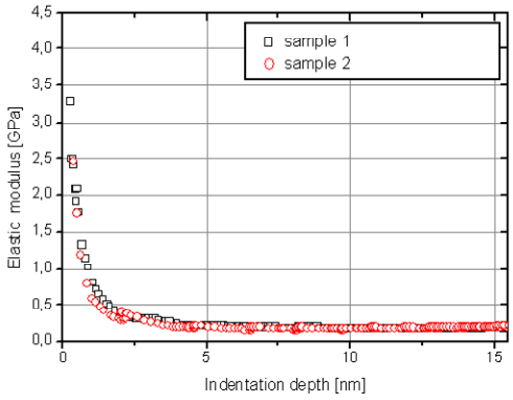

Fig. 5. Indentation depth influence on elastic modulus

For indentation depths lower than 6 nm the values tends to be higher. As it cannot be the material behaviour such a result must be an effect of the mathematical model that was applied. Finally these results for the lower depths were not taken into consideration.

4. Conclusions

The elastic modulus values of these ultrathin polymeric resist films (0.3 *GPa*) that were evaluated with this method tends to be an order of magnitude lower than the val-

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ues for bulk materials. It suggests that further calibration on known polymer have to be done for this method.

The higher values of elastic modulus for low indentation depths are due to mathematical model that was applied (shape of the function is like that) as well as the incidental errors for rather small depths are significant.

Finally, the AFM based method with stiff cantilever is a promising tool for testing the nanomechanical properties of the thin polymeric films because of an ability of the stiff cantilever to resist the high adhesion forces and to make correct (complete) FDC on polymer even for elevated tempratures.

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