Thin NIL films characterization (viscosity, adhesion) with rheological nano–probe

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ABSTRACT

The approach based on the nano-indenter developed for viscosity characterization allows temperature measurement of thermoplastic, thermo- and photo-curable polymers (materials used in NILand UV-NIL) with sub-micron resolution. It could be used in design, tailoring and optimisation of soft matter for different application. In particular:

- Recommended imprint temperature can be deduced from nano-probe experiments.
- Optimal curing time as function of temperature can be established.
- Prediction on mechanical properties at imprint temperature easily can made.
- Surface adhesivity as function of *temperature* can be measured

Keywords: viscosity of thin films, surface adhesivity, AFM

1 INTRODUCTION

Polymers of different kinds are widely used in NanoImprint Lithography (NIL). First of all it is a usage of thermoplasts in thermal NIL. In step and flash imprint lithography (UV-NIL) photo-cured polymers are used. Thermocurable polymers could be used in step and flash approach when photo-exposure is changed with short heating.

Demands of high throughput in nanoimprint lithography (NIL) dictate to make glass transition temperature of polymer matter used in NIL rather low therefore an approach for measurement of viscous properties of tailored polymers should be developed. The method should allow measuring the properties at the state (films of 100-500nm) in which the polymer is intended to be used. On the other hand it would be highly desirable the method would allow characterizing polymer curing and mechanical properties of the *cured* polymer, which planned to use as cost-effective stamps. One more additional usage of the method could be characterization on adhesion properties of polymer surfaces before and after special treatment predicting release properties of stamps as function of temperature.

2 SETUP AND EXPERIMENTAL METHOD

To meet the requirements a special tool called *rheological nano-probe* was designed and fabricated consisting of several components:

a) generic AFM device (see Figure 1),
b) original stage (made of *invar* to decrease thermal expansion) with heater for *local* heating of a sample at place of indentation,
c) original control software to provide complex tip trajectory and flexibility in data acquisition and treatment.

Small heater placed under a wafer provides heating of the wafer and temperature is controlled with a thermocouple. Resist film is on the opposite side of the wafer and special measurement showed the difference of temperature of wafer both sides does not exceed 2^0C. Rate of heating could be changed with current of the heater. Maximal rate of cooling is defined with heat scattering in environment and normally it is relatively high so the cooling rate could be controlled with weak heating current. Heating-cooling cycle is controllable and normally belongs to range 100-500 seconds. Usual temperature range is RT-200^0C.

Temperature rate is sufficiently small to perform indentation because indentation cycle takes less than 0.1 second. During a heating cycle up to ten thousands probing could be made.

Main measurement action is measuring so-called "loading curve" shown in Figure2 for two temperatures (see also Figure9 and Figure10).

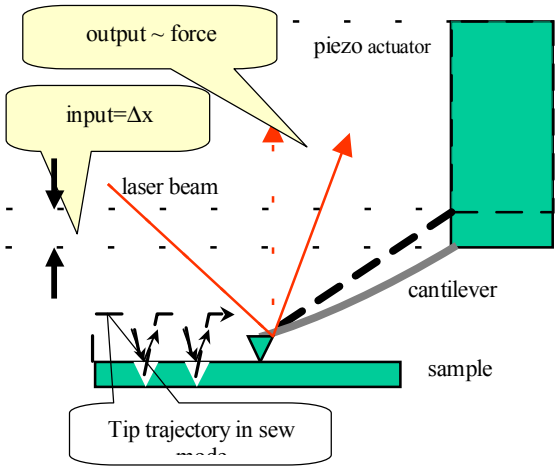

Figure 1: Principal schema of generic AFM and sew-mode of the prob. Elongation (displacement Δx) of an actuator is an input signal, force measured as cantilever bending is output signal resulting to "loading curve".

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Principal parameters acquired from "loading curves" are slopes of loading curve (compliance, DZ/DF), residual deformation and viscosity as function of temperature. Specially developed control software realises rather complicated measuring procedures. For example Figure 2 shows a mode when the tip is moving with low velocity then velocity can be increased in controllable manner so resistance to penetration (compliance, viscosity) could be measured at different velocities of indentation.

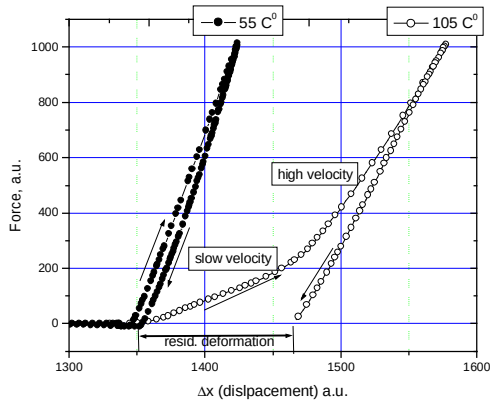

Figure 2 Examples of loading curves as function of temperature. At low temperature (55^0C) the curve shows elastic behaviour (compliance is very small and does not depend on velocity of the tip), at higher temperature compliance becomes higher demonstrating inelastic behaviour (depending on tip velocity).

Concerning compliance and residual thickness acquisition it should be noted that control software not only control tip trajectory but it contains also some postprocessing part which transfers original data considering creep and hysteresys of piezo actuators. This allows measuring real slopes of the loading curves.

3 MODEL AND MEASUREMNT APPROACH

For direct viscosity measurements a special approach was developed based on theoretical analysis.

Considering Navier-Stokes equation penetration of a paraboloid tip (with curvature R) in viscous thin film (of thickness h_0) was considered. Main approximations follow Reynolds approach [1,2] from them it follows that

$$h_0 / R >> 1 \qquad (1)$$

Details of the theoretical consideration published in [2] and main formula relating viscosity η to measurable quantities is

$$\frac{1}{h} \approx \frac{8p\,R^2 (z/h_0)^3}{\int_0^t F(t')dt'} \qquad (2)$$

z is a residual deformation (or penetration depth). The integral over time $\int F(t')dt'$ is simply an area under the loading curve (see Figure2) at its uploading part. The controlling software was modified to allow automatic acquisition of accumulated force value during loading to use formula (2)

To fulfill condition (1) tip with large radius (like 1um) should be used. Therefore a special technological approach was developed. It consists of growing a desirable tip with controllable contamination, in other words decomposition of vacuum oil residuals under intensive e-beam exposure up to pure carbon was used. The exposure was performed with e-beam lithograph under control of NanoMaker [3]. SEM image of the carbon tip is shown in Figure3.

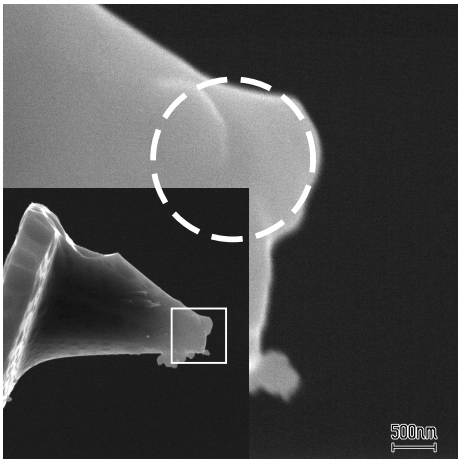

Figure3. Carbon tip of R=700nm grown with controllable contamination

4 EXPERIMENTAL RESULTS

4.1 Thermoplast polymers

Temperature dependence the *compliance* for positive resist (950K PMMA) exposed at different doses is shown as an example in Figure 4. Common feature is constant value of the compliance at low temperatures what corresponds to high viscosity (and here the compliance is equal to inverse stiffness of a cantilever) then the compliance increases what corresponds to viscosity decreasing and to plastic deformation of polymer matter. It is expected that higher exposure results to decrease of molecular weight lower molecular weight what is known results to lower viscosity. It is clearly seen the viscous behavior (and plastic deformation) in accordance to expectations starts at lower temperatures corresponding to lower molecular weight.

These measurements demonstrate that due local character of measurement with setup presented electron

exposure dose could be measured and characterized with sub-micron (and even nanometer with finer tip) spatial resolution without any real development.

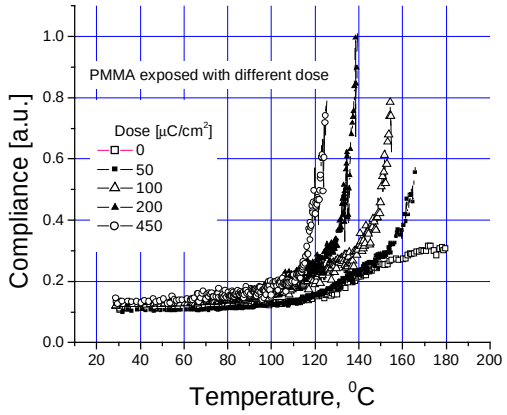

Figure 4 Compliance of 950K PMMA film subjected to different exposures as function of temperature, higher exposures result to more plastic behaviour. In principal distribution of exposure could be measured with nanometer accuracy.

4.2 Thermocurable polymers

The next example illustrates investigation of curing kinetics (Figure 5), thermo-curable polymer (submitted by *micro resist technology GmbH* [4]) was backed at 170^{0}C for different times.

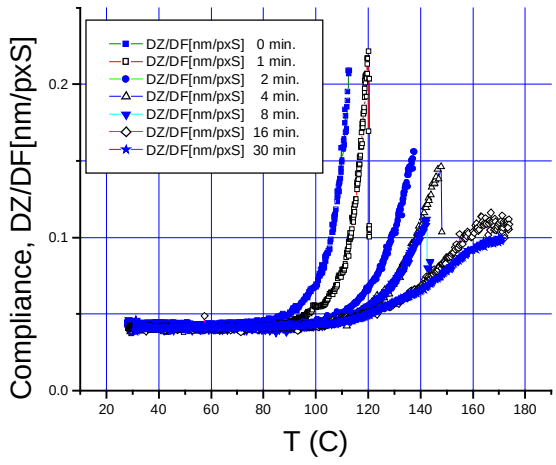

Figure 5 Compliance of a thermocurable resist (from mrt [4]) baked for different times at 170^{0}C.

Figure 6 shows residual deformation (penetration depth) for backing kinetics. And finally Figure 7 demonstrates viscosity measurements.

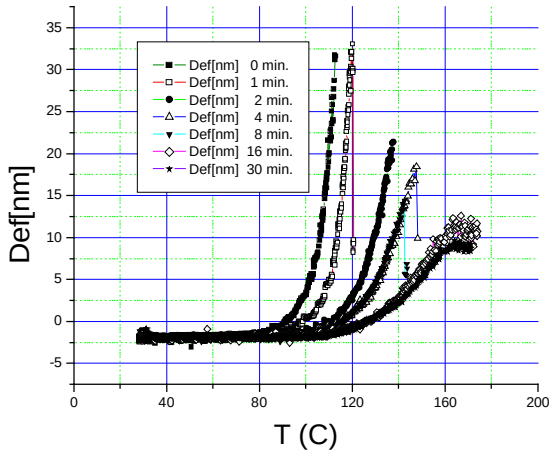

Figure 6 Residual deformation (penetration depth) of a thermocurable resist (from mrt [4]) baked for different times at 170^{0}C.

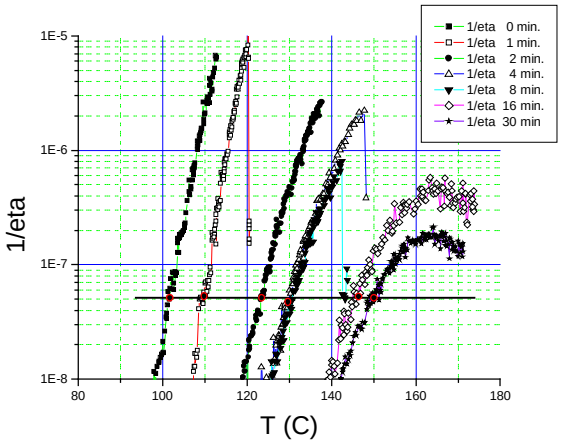

Figure 7 Viscosity of a thermo-curable resist (from mrt [4]) baked for different times at 170^{0}C..

4.3 Photocurable polymers

As example the developed approach was applied to photo-curable resist (mrJ9030M, N43). The samples were exposed with Hg lamp for different times (0min, 1min, 10min, 30min, 60min). Power of the lamp is 20.6Wt irradiated at range 240-320nm, length of lighting body is 6cm with 19mm of diameter and distance to samples from the lighting body center is 30cm at inclination angle 45^o.

Viscosity and residual deformation as function of temperature are shown in Figure8. In spite of long exposure time (1hour) it is seen that curing kinetics is still not accomplished.

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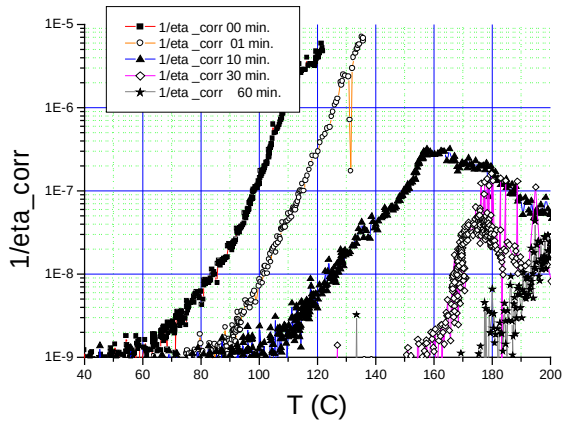

Figure 8 Viscosity of a photocurable resist (from mrt [4]) exposed for different times.

4.4 Comparison of thermo-curable and photo-curable polymers

Comparing curing processes of thermo-curable and photo-curable polymers one can see that they result to quit different results. Accomplished curing can be characterized with temperature shift equal to about 30C. As to photo-curable resist the temperature shit is more than 100C.

This could be explained as if cross-linking of photo-curable polymer results to more dense net with significantly smaller distances between cross-links.

One more conclusion can be done activation energy of viscosity is approximately two times larger for thermo-curable than for photo-curable resists.

4.5 Surface adhesivity

Up to now for investigation some averaged parameters acquired from loading curves were exploited. Example of usefulness of loading curves themselves is illustrated below. One of mrt thermoplastic resist was plasma treated to investigate whether plasma treatment (by Dr. Isabel Obieta Vilallonga from INASMET, Spain) can change and improve surface adhesivity to be used for easier detachment in thermal NIL. Figure 9 and Figure 10 shows loading curves for non-treated and treated samples. Quantitative characterization should include calculation of work done during detaching. But for quantitative judging it is sufficient to pay attention to maximal detaching force. After plasma treatment the maximal force becomes three times less than before. Very important to outline that the approach presented allows measuring surface properties as function of temperature what is not so easy with conventional technique based on measurement of wetting angle. Additionally the approach is very local in comparison to the conventional methods.

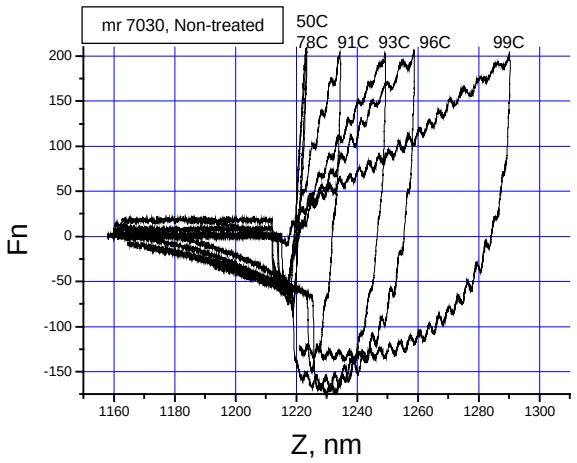

Figure 9 Loading curves as function of temperature before plasma treatment.

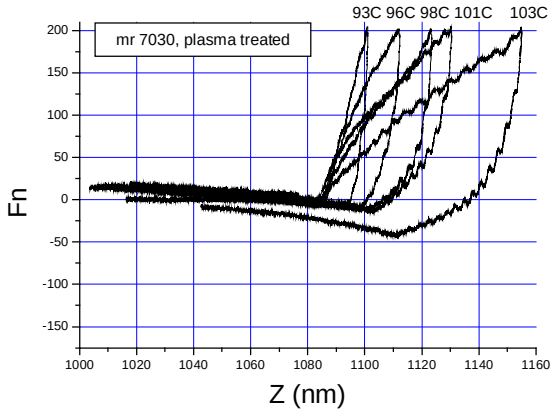

Figure 10 Loading curves as function of temperature after plasma treatment. Surface adhesivity could be easily investigated as function a temperature

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