JVSTB
JOURNAL OF VACUUM SCIENCE AND TECHNOLOGY B

Development of an experimental technique for testing rheological properties of ultrathin polymer films used in nanoimprint lithography

Dariusz M. Jarzabek, Zygmunt Rymuza, Akira Horiba, and Yoshihiko Hirai

Citation: J. Vac. Sci. Technol. B **29**, 061603 (2011); doi: 10.1116/1.3656377
View online: http://dx.doi.org/10.1116/1.3656377
View Table of Contents: http://avspublications.org/resource/1/JVTBD9/v29/i6
Published by the AVS: Science & Technology of Materials, Interfaces, and Processing

Related Articles

Measurement of the elastic stress of thin films deposited on gallium arsenide
J. Vac. Sci. Technol. A 14, 2483 (1996)

Micromechanics via xray assisted processing
J. Vac. Sci. Technol. A 12, 2559 (1994)

Instrument for the measurement of adhesion forces in ultrahigh vacuum surface analysis apparatuses
J. Vac. Sci. Technol. A 12, 889 (1994)

Rolling friction in a linear microactuator
J. Vac. Sci. Technol. A 11, 803 (1993)

A simple way to build a linear motion manipulator
J. Vac. Sci. Technol. A 9, 170 (1991)

Additional information on J. Vac. Sci. Technol. B

Journal Homepage: http://avspublications.org/jvstb
Journal Information: http://avspublications.org/jvstb/about/about_the_journal
Top downloads: http://avspublications.org/jvstb/top_20_most_downloaded
Information for Authors: http://avspublications.org/jvstb/authors/information_for_contributors

ADVERTISEMENT

Development of an experimental technique for testing rheological properties of ultrathin polymer films used in nanoimprint lithography

Dariusz M. Jarzabek[a] and Zygmunt Rymuza[b]
Warsaw University of Technology, Faculty of Mechatronics, Institute of Micromechanics and Photonics, Boboli 8 Street, 02-525 Warsaw, Poland

Akira Horiba[c] and Yoshihiko Hirai[c]
Osaka Prefecture University, 1-1, Gakuencho, Nakaku, Nakaku, Sakai, Osaka 599-8531, Japan

(Received 25 February 2011; accepted 19 September 2011; published 3 November 2011)

A new method for the measurement of rheological properties (complex viscosity, viscosity and elasticity) of thin polymeric films is presented. The probe, which is placed on the end of an arm of a mini tuning fork, is caused to oscillate and then is put into poly(methyl methacrylate) films, whose thickness ranges from 30 nm to 1080 nm. All measured properties depend on temperature, thickness of the films, indentation depth and the molecular weight of PMMA. Complex viscosity, viscosity and elasticity are found to be lower at higher temperatures and higher with greater molecular weight. They are also lower for thicker films. The results gained from this experiment may be useful in the development of nanoimprint lithography and many other branches of nanotechnology. Furthermore, the method allows for the measurement of the rheological properties of many different thin films (nanoimprint polymers, oils, lubricants) at different temperatures. © *2011 American Vacuum Society*.
[DOI: 10.1116/1.3656377]

I. INTRODUCTION

Development of nanotechnology faces many problems, one of which is lack of a fast and cheap method for fabricating structures whose dimensions are less than 0.1 μm. One method to solve this problem is nanoimprint lithography (NIL). The method of fabricating nanometer scale patterns by NIL was first proposed by Chou[1,2] in 1995. Nanoimprint lithography creates patterns by the mechanical deformation of imprint resist and has many advantages, such as low cost and high resolution. Unfortunately, in spite of the simplicity of the idea and significant development of the method, there are many problems which must be overcome. Scientists and engineers are working to make the process faster and to find resist with optimal properties and to lower the adhesion and friction forces, which can destroy the pattern of the stamp.

Viscosity is a very important property of resists used in NIL and many methods to measure viscosity in thin films have been developed. There is a method to calculate effective viscosity using a friction force measurement performed on the atomic force microscope (AFM).[3] Professor Isrealachvili has developed a surface force apparatus which also can be used to measure the viscosity of thin films,[4,5] and there are many improvements of this method.[6–9] There is a wide variety of acoustic and optical methods of viscosity measurements,[10–21] and a very interesting method of viscosity measurement which uses nanoindentation.[22] This last method was particularly interesting because the samples studied were nanoimprint resists.

The method described in this study is innovative because it not only allows measurement of the viscosity but also gives information about the elastic properties of the thin films. Complex viscosity may be measured by this method and calculated to its real component, which is traditional viscosity, and imaginary component, which is connected to elasticity. In addition, it is found to be possible to measure the viscosity of thin films as a function of indentation depth. Thickness of the measured films was reduced to 30 nm whereas resolution of the indentation depth was reduced to 5 nm.

II. EXPERIMENT

The experiment was carried out in a clean room, where the temperature and humidity were held constant and the temperature was measured to be $21 \pm 1\,^{\circ}\mathrm{C}$ and the humidity was $50 \pm 5\%$.

A. Samples

During the experiment thirteen samples were investigated, all of which were thin films of PMMA that differ from each other in thickness of the film and molecular weight. The description of the samples is shown in Table I. Poly(methyl methacrylate) films powders having various molecular weights (obtained from Sigma-Aldrich, Inc.) are dissolved into a solvent (Cyclohexane). Before the sample was produced the silicon surface was cleaned by ultrasonic method in acetone and boiled in H_2O_2 and dried by an air stream. On this prepared surface one droplet of hexamethyldisilazane (HMDS) was spun. After that the PMMA was spin-coated on the Si surface at various rotation speeds. Finally samples were baked at 140 °C for 20 mins to evaporate the solvents.

B. Measurement setup

To conduct the experiment, a tuning fork produced by Microtestmachines Co. (Belarus) was used. It was mounted in a standard AFM holder and inserted into the Atomic Force

[a]On leave Institute of Fundamental Technological Research of the Polish Academy of Sciences.
[b]Electronic mail: z.rymuza@mchtr.pw.edu.pl
[c]Present address: Core Research for Evolutional Science and Technology, Japan Science and Technology Agency, Kawaguchi, Saitama 332-0012, Japan.

TABLE I. Description of the samples.

No	Thickness of the film [nm]	Molecular weight Mw [g/mol]
(1)	30	120 000
(2)	50	120 000
(3)	53	120 000
(4)	104	120 000
(5)	115	120 000
(6)	220	120 000
(7)	270	120 000
(8)	450	120 000
(9)	511	120 000
(10)	518	120 000
(11)	1080	120 000
(12)	920	350 000
(13)	1020	996 000

Microscope which is available at the Institute of Micromechanics and Photonics (Fig. 1). A schematic of the tuning fork is shown in Fig. 2. The tuning fork is caused to oscillate by the bimorph actuator, which composed of two thin layers of piezoceramics (PZT) which are polarized in two different directions. If an oscillating voltage is applied the bimorph oscillates. The arms of the tuning fork are also made of PZT so they are able to measure the response of the tuning fork and the lateral force. At the end of the working arm there is a spherical probe made of steel whose diameter is 0.7 mm. An identical probe was mounted on the free arm as a counterbalance. The dimensions of the tuning fork were measured on the optical microscope to be $L = (3{,}77 \pm 0{,}01)$ mm, $W = (1{,}94 \pm 0{,}01)$ mm and $T = (0{,}67 \pm 0{,}01)$ mm [Fig. 2(b)].

It is possible to calculate the stiffness of the working arm of the tuning fork from the equation:

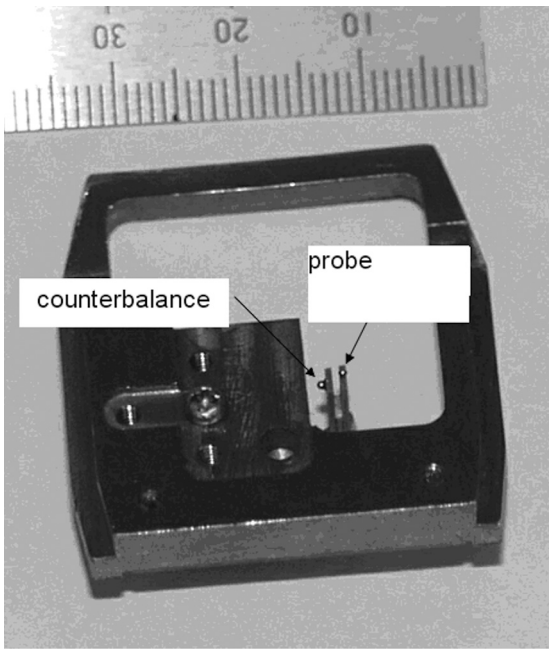

FIG. 1. Tuning fork as mounted in a standard AFM holder.

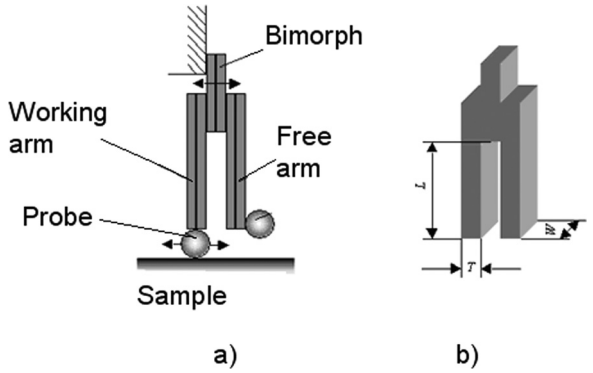

FIG. 2. Schematic of the tuning fork (a) and its dimensions (b).

$$k = \frac{E}{4} W \left(\frac{T}{L}\right)^3, \tag{1}$$

where k is the stiffness of the working arm of the tuning fork and $E = 4.9 \cdot 10^{10}$ N/m^2 is the Young's modulus of PZT. The measured resonant frequency of the tuning fork was 15 625 Hz.

During the experiment it is important to measure the amplitude and frequency of the working arm of the tuning fork. Acquiring and transforming these signals are accomplished using the electronic systems of the AFM (model NT-206, Microtestmachines Co. Belarus). Two drives are used in this system to position the sample; the coarse drive which is executed by the step motor, and a fine drive executed by a piezotube.

The tuning fork is set into oscillation by a sinusoidal voltage with a 5V amplitude. The piezovoltage, which appears on the working arm of the tuning fork, is also used in a feedback loop (Fig. 3) to assure a constant and accurate distance between the probe and the sample.

C. Calibration and measurement

Before measurement, the tuning fork must be calibrated. In this work, the load was not important so only the resonant frequency in air was measured. The plot of amplitude versus frequencies close to the resonant frequency is shown in Fig. 4.

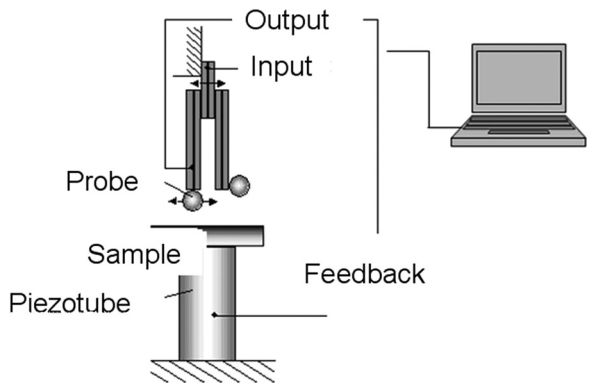

FIG. 3. Schematic of the system with feedback which was used to measure the rheological properties of thin polymer films.

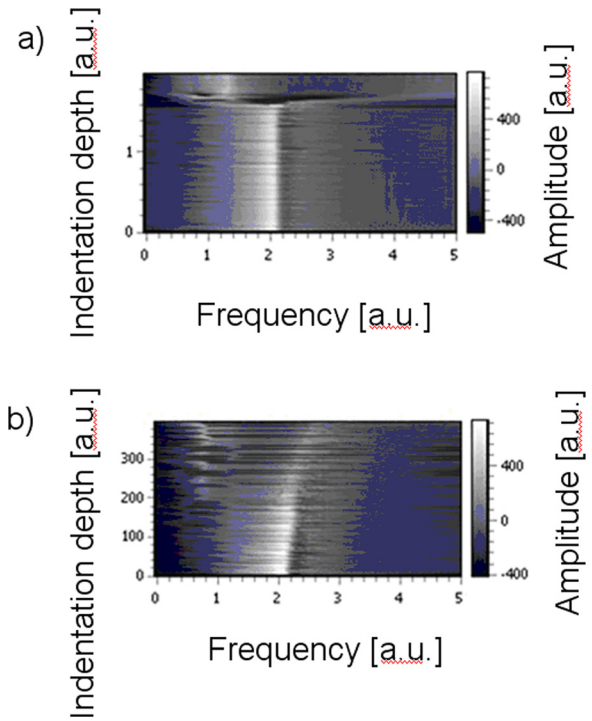

FIG. 4. (Color online) Example of a coarse approach to the sample during the measurement (a) and the proper measurement (b). The resonant frequency is shifted due to an increase of the effective mass. The units here are arbitrary units. After the measurement they are calculated to the proper values.

Ten 'amplitude versus frequency' curves were typically made to evaluate the damping coefficient of the air.

At the beginning of the measurement a coarse approach was taken to find the contact position between the probe and the sample [Fig. 4(a)]. After this a proper investigation can begin. The beginning position of the probe was set a little above the surface of the sample and the range of the movement and the resolution was set dependent upon the thickness of the film. An example of the results is shown in Fig. 4(b). For each sample, five measurements were taken for statistical purposes.

III. MODELING

A. Oscillations in air

Oscillations of the probe can be described by the Newton's second law:

$$m\frac{d^2x}{dt^2} + c_p\frac{dx}{dt} + kx = F_0\sin(\Omega t), \tag{2}$$

where m is the effective mass of the probe, x is its position, c_p is the damping coefficient of air, F_0 is the force amplitude and Ω is the angular frequency. The constant, k, may be calculated from Eq. (1). The solution for this equation in established state is:

$$x = A_p\sin(\Omega t - \varphi), \tag{3}$$

where Ap is the amplitude of the oscillation of the tuning fork and φ is a phase shift. We assumed that the damping oscillations, which are also the solution of the Eq. (2), are irrelevant.

The maximal amplitude of the oscillations may be calculated from the equation:

$$A_{p\max} = \frac{F_0}{\frac{C_p}{m}\sqrt{km - \frac{C_P^2}{4}}}. \tag{4}$$

The angular frequency for the maximal amplitude is:

$$\Omega_{rp} = \sqrt{\frac{k}{m} - \frac{c_p^2}{2m^2}}. \tag{5}$$

The experimental system does not measure angular frequency but frequency, so to calculate the angular frequency from the frequency of the tuning fork the following equation should be used:

$$\Omega_{rp} = 2\pi f_{rp}, \tag{6}$$

where f_{rp} is the resonant frequency of the air.

Finally, the damping coefficient may be calculated:

$$c_p = \frac{\sqrt{2\left(\frac{k}{m} - 4\pi^2 f_{rp}^2\right)}}{m}. \tag{7}$$

The effective mass, m, may be found from the method described in Ref. 22. This method; however, requires the density of the material from which the tuning fork is made, dimensions of tuning fork and the mass of the probe. Moreover, during the measurements we have observed that the resonant frequency grows, which is possible only if the stiffness of the arm or the effective mass increase. The stiffness cannot increase because it is defined by Eq. (1) so it must be assumed that the effective mass changes. For this reason, m should be eliminated from our equations. To do this, another characteristic point near the resonant frequency on the amplitude versus frequency curve should be taken, and we chose the frequency for which the amplitude is half of the maximal amplitude (there are two such points so we have taken the one with lower frequency). Comparison of these two points gives:

$$\frac{1}{2}\frac{F_0}{\frac{c_p}{m}\sqrt{km - \frac{c_p^2}{4}}} = \frac{F_0}{m\sqrt{\left(\frac{k}{m} - \Omega_{\frac{1}{2}}^2\right) + \left(\frac{c_p}{m}\right)^2\Omega_{\frac{1}{2}}^2}}, \tag{8}$$

where $\Omega_{[1/2]}$ is the angular frequency for which the amplitude is half of the maximal amplitude. After some algebraic transformations the damping coefficient of the air may be calculated from:

$$c_p = \frac{k\sqrt{2\sqrt{f_r^4 + \left(f_r^2 - f_{\frac{1}{2}p}^2\right)^2} - 2f_r^2}}{2\pi\left(2\sqrt{f_r^4 + \left(f_r^2 - f_{\frac{1}{2}p}^2\right)^2} - f_r^2\right)}, \tag{9}$$

where $f_{[1/2]}$ is the frequency calculated from $\Omega_{[1/2]}$.

B. Oscillations in contact with sample

During the measurement, the probe is partially inserted into the sample film so the damping coefficient of the film should be added to the damping coefficient of the air. In this case the equation, which describes the probe movement, is:

$$m\frac{d^2x}{dt^2} + (c_p + c_s)\frac{dx}{dt} + kx = F_0 \sin(\Omega t), \tag{10}$$

where c_s is the damping coefficient of the sample.

Analogous to the reasoning shown in Sec. III A, the damping coefficient of the film can be calculated from the equation:

$$c_s = \frac{k\sqrt{2\sqrt{f_{rs}^4 + \left(f_{rs}^2 - f_{\frac{1}{2}s}^2\right)^2} - 2f_{rs}^2}}{2\pi\left(2\sqrt{f_{rs}^4 + \left(f_{rs}^2 - f_{\frac{1}{2}s}^2\right)^2} - f_{rs}^2\right)} - c_p, \tag{11}$$

where f_{rs} is the resonant frequency during the measurement and $f_{[1/2]s}$ is the frequency for which the amplitude is half of f_{rs}.

C. Rheological properties of the measured film

The damping coefficient, c_s, is dependent upon the geometrical parameters of the measurement system and it may be used to calculate the complex viscosity using the equation:

$$\eta^* = \frac{c_s}{\Gamma}, \tag{12}$$

where Γ is a geometric coefficient. In this case, the spherical probe slides on a flat surface and is immersed in the film. According to Ref. 23, the Γ coefficient can be calculated from the equation:

$$\Gamma = \frac{8}{5}\pi d 1\mathrm{n}\left(\frac{d}{h}\right), \tag{13}$$

where d is the diameter of the probe and h is the depth of the indentation into the film.

The complex viscosity is described by the equation:

$$\eta^* = \eta' - i\eta'', \tag{14}$$

where η' is the traditional viscosity whereas η'' is the elasticity. For Newtonian fluids there is only a real component. However, for viscoelastic materials such as PMMA, near the glass transition temperature both components appear. To calculate them from the complex viscosity two equations are needed:

$$\eta' = \eta * \cos\delta \tag{15}$$

$$\eta'' = \eta * \sin\delta, \tag{16}$$

where δ is the phase shift of the oscillations.

D. Range of method

The method described has some limits of application. Due to the roughness of the probe and the samples, it was impossible to find the true contact point between the probe and the sample with an accuracy greater than 5 nm. Furthermore, the mathematical model treats thin films as a continuum. It is difficult to determine the point at which the molecular structure has enough influence to make this model inappropriate. In this work, the thinnest film successfully measured was 30 nm and all films thicker than this can be studied by this method. The highest resolution of depth of the probe indentation successfully measured was 1 nm. However, because such measurements were extremely time-consuming the highest resolution which was typically used was 4 nm. The resolution of the

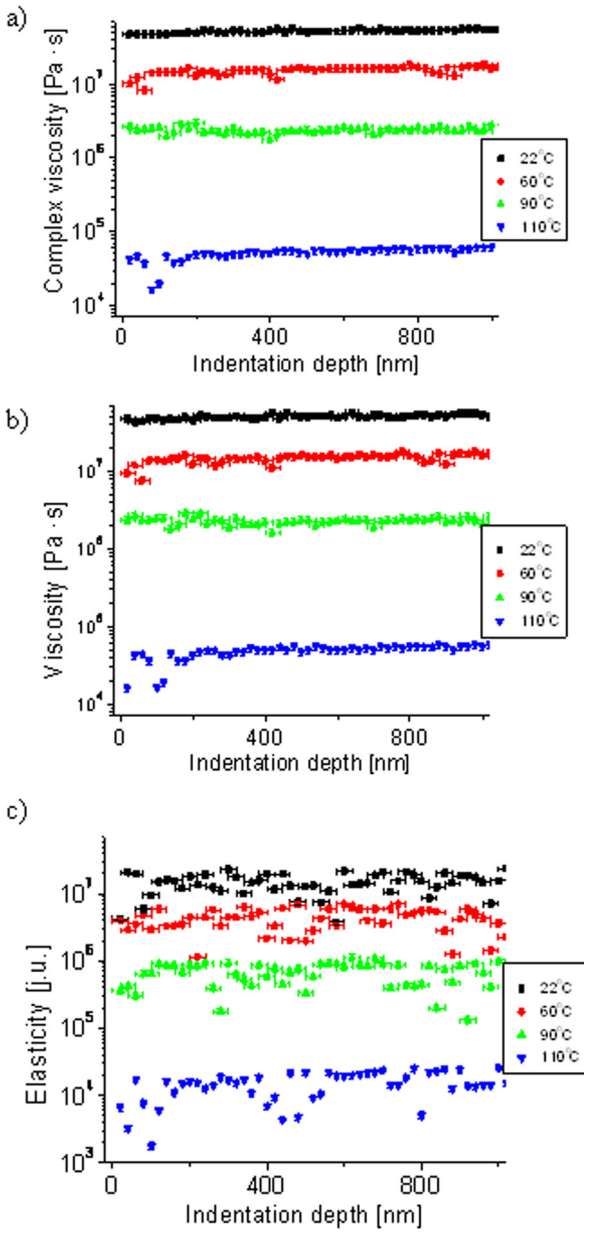

FIG. 5. (Color online) Example of the results. Three graphs show the dependence of the complex viscosity (a), viscosity (b) and elasticity (c) on the depth of the indentation for sample no. 11. Mw = 120 000 u.

frequency was 20 Hz. It was possible to use a higher resolution; however, the resonant frequency is almost one thousand times larger than the resolution so that a measurement using higher resolution would have a very small effect on the final results.

IV. RESULTS AND DISCUSSION

Examples of the results are shown in Fig. 5. Thirteen samples were examined which differ from each other by the thickness of the film and the molecular weight. The results show that the indentation depth has little influence on the measured complex viscosity, viscosity and elasticity. Both complex viscosity and viscosity increase by a small amount with the indentation depth. This is quite an interesting result because we supposed that this increase would be greater (an influence of the substrate). On the other hand, Itoh showed that for oils which are used to lubricate hard discs, the viscosity decreases with the depth of indentation.[21] It is difficult to compare these two results because PMMA is much more strongly connected with the substrate than oils with the surface. Hiroshima[24] also reported that viscosity increases for film thickness below 2 um. We have also noticed such phenomenon — the viscosity is higher for films thinner than 1 um. Elasticity also increases with indentation depth. However, it is difficult to say something more about the physics of this phenomenon because there is no method to calculate the results of elasticity acquired from our experiment (in a.u.) to pascals. Further investigation should be done in this matter.

Each sample shows a strong dependence of viscosity on temperature. Above the glass transition temperature viscosity is much less than at 90 °C. We measured the viscosity also at room temperature and it is extremely high. However, it is possible that these results may be so high because at room temperature PMMA is a solid and the damping is very high, which gives a large measurement error. The influence of temperature and the thickness of the film on viscosity is shown in Fig. 6. The molecular weight of the measured films also has a large influence on viscosity. The higher the molecular weight, the greater the complex viscosity, viscosity and elasticity are found to be. This dependence on viscosity is shown in Fig. 7. In Ref. 22, the viscosity of PMMA was also measured. The results shown in that study are within the same range as those found in ours.

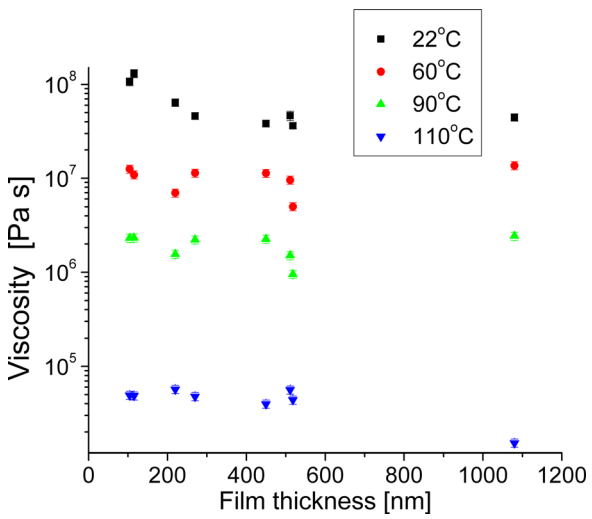

FIG. 6. (Color online) Dependence of temperature and the thickness of the film on the viscosity of thin PMMA films. The depth of indentation was 100 nm for samples 4 – 11. For sample 1 it was 25 nm, sample 2 and 3 – 50 nm. Mw = 120 000.

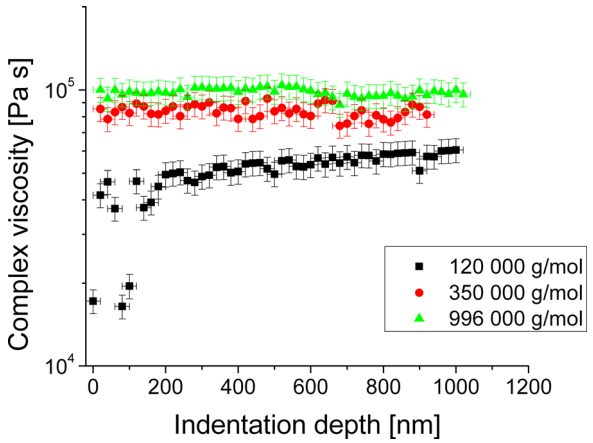

FIG. 7. (Color online) Dependence of the molecular weight on viscosity at 110 °C. Samples 11, 12 and 13.

V. CONCLUSIONS

A new and promising method of viscosity measurement is presented in this article. At the beginning it was assumed that this method would be useful to measure only thin films of NIL resists. However, it is also possible to measure other materials. The results of the measurement were compatible with our expectations and with results from other experiments.[22] This approach allows one to measure the rheological properties of thin films as a function of temperature and with nanometer resolution and can be used not only in the design of new resists to be used in nanoimprint lithography but also in many other fields.

[1]S. Y. Chou, P. R. Krauss, and P. J. Renstrom, Appl. Phys. Lett. **67**, 3114 (1995).
[2]S. Y. Chou, P. R. Krauss, and P. J. Renstrom, J. Vac. Sci. Technol. B **14**, 4129 (1996).
[3]B. Bhushan, *Nanotribology and Nanomechanics*, 2nd ed. (Springer, Berlin, 2005), pp. 417–497.
[4]J. N. Israelachvili, J. Colloid Interface Sci. **110**, 263 (1986).
[5]J. N. Israelachvili, Colloid Polym. Sci. **264**, 1060 (1986).
[6]D. Y. C Chan and R. G. Horn, J. Chem. Phys. **83**, 5311 (1985).
[7]A. Dhinojwala and S. Granick, Macromolecules **30**, 1079 (1997).
[8]J. Van Alstine and S. Granick, Phys. Rev. Lett. **61**, 327 (1988).
[9]J. P. Montfort and G. Hadziioannou, J. Chem. Phys. **88**, 7187 (1988).
[10]S. J. Martin, A. J. Ricco, and R. C. Hughes, *Proc. 4th Int. Conf. Solid-State Sensors and Actuators* (IEEE of Japan, Tokyo, 1987), pp. 478–481.
[11]B. A. Martin, S. W. Wenzel, and R. M. White, Sens. Actuators A **22**, 704 (1997).
[12]H. Muramatsu, M. Suda, T. Ataka, A. Seki, E. Tamyia, and I. Karube, Sens. Actuators A. **21**, 1404 (1990).
[13]P. I. Oden, G. Y. Chen, R. A. Steele, R. J. Warmack, and T. Thundat, Appl. Phys. Lett. **68**, 3814 (1996).
[14]B. Jakoby and M. J. Vellekoop, Sens. Actuators A **68**, 275 (1998).
[15]W. Y. Shih, X. Li, H. Gu, W.-H. Shih, and I. A. Aksay, J. Appl. Phys. **89**, 1497 (2001).

[16]M. Papi, G. Arcovito, M. De Spirito, M. Vassalli, and B. Tiribilli, Appl Phys. Lett. **88**, 194102 (2006).
[17]N. McLoughlin, S. L. Lee, and G. Hähner, Appl. Phys. Lett. **89**, 184106 (2006).
[18]M. Papi, G. Maulucci, G. Arcovito, P. Paoletti, M. Vassalli, and M. De Spirito, Appl. Phys. Lett. **93**, 124102 (2008).
[19]W.-C. Wang, M. Afromowitz, and B. Hannaford, IEEE Trans. Biomed. Eng. **40**, 298 (1994).
[20]A. I. Fedorchenko, I. Stachiv and A.-B. Wang, Sens. Actuators B **142**, 111 (2009).
[21]S. Itoh, Y. Fukuzawa, K. Hamamoto, Y. Zhang, and H. Mitsuya, Tribol. Lett. **30**, 177 (2008).
[22]A. A. Svintsov, O. V. Trofimov, and S. I. Zaitsev, J. Vac. Sci. Technol. B **25**, 2435 (2007).
[23]A. J. Goldman, R. G. Cox, and H. Brenner, Chem. Eng. Sci. **22**, 637 (1967).
[24]H. Hiroshima and H. Atobe, J. Vac. Sci. Technol. B **25**, 2346 (2007).