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X-ray reflectivity investigation of polystyrene thin films

Summer Student Report

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Abstract

The X-ray reflectivity is a good method to investigate thickness, roughness and electron density of materials. Thin polystyrene films with different thickness were prepared using spin-coating technique. The thickness and roughness of polystyrene films at various temperatures were observed after fitting experimental curves.

Introduction

The investigation of surfaces and interfaces with x-ray scattering methods is a field that has grown enormously last years. Increasing surface quality, technological developments concerning surface diffractometers and synchrotron radiation facilities, and a development of surface scattering theory have made this progress possible. Nowadays detailed and precise results from various liquids, glassy, and solid surfaces are available, and even complex layer structures can be characterized [1].

In our daily life polymer films are playing a more and more important role: they are used as coating in many technological applications e.g. use thin films as protection of surfaces against corrosion, organic multilayers are promising materials for biosensors. The thin polymer films show very different properties from those in bulk, for instance it is very interesting to observe the temperature dependence of thickness and roughness. The X-ray reflectivity method is powerful tool to investigate the basic physical properties such as film thickness and roughness, surface tension and conformality [1], [2].

Our project includes thin films with different thickness preparation, X-ray reflectivity measurements at different temperature and data analysis.

Theory of X-ray reflectivity

The electromagnetic radiation interacts principally with the electrons, and very weakly with atomic nuclei (the ratio of the amplitudes is an inverse of masses). A photon which meets an atom can undergo one of the three following events:

- *elastic scattering*, with no change in energy;
- *inelastic scattering*, with change in energy
- *absorption*, all the energy is transferred to the atom and photon vanishes. Another photon can be subsequently re-emitted, with a lower energy.

For description of X-ray reflectivity theory we neglect inelastic scattering and absorption.

1. Scattering at single electron

The incident electromagnetic wave is a plane wave with wavelength λ and wave number, $k=2\pi/\lambda$:

$$A(\mathbf{k}) \propto \exp(i\mathbf{k}\mathbf{r}) \quad (1.1)$$

The incident electromagnetic wave excites the electron which radiates a spherical wave with the same length as the incident beam (elastic scattering). In the Born approximation, the scattering of a group of electrons is just a sum of corresponding spherical waves. In the case of far field approximation (the distance of the observer from the sample is much larger than the sample size), the curvature of the spherical waves is negligible and they can be approximated by a plane waves. In the fig. 1 [3] it is shown the incoming wave \mathbf{k}_i and outgoing wave \mathbf{k}_f . The different paths which the waves have to travel leads to the phase difference between them

$$\mathbf{k}_f \cdot \mathbf{r}_0 - \mathbf{k}_i \cdot \mathbf{r}_0 = (\mathbf{k}_f - \mathbf{k}_i) \cdot \mathbf{r}_0 = \mathbf{q} \mathbf{r}_0 \quad (1.2), \text{ where}$$

$\mathbf{q} = \mathbf{k}_f - \mathbf{k}_i$ is vector transfer, which is equal $q = 2k \cdot \sin \frac{2\theta}{2} = \frac{4\pi}{\lambda} \sin \theta_{\text{Bragg}}$, and θ_{Bragg} is so-called Bragg-angle.

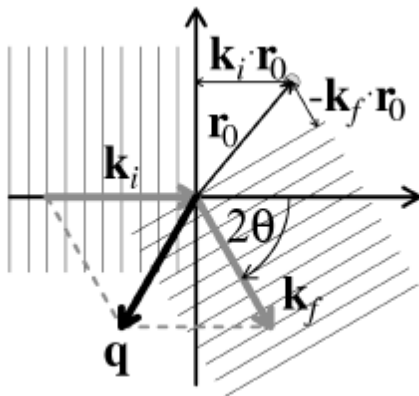


Figure 1. Scheme of wave scattering. The scattering object is located at r_0 , scattering angle is 2θ .

The scattered amplitude of a single electron is given by

$$A(\mathbf{q}) \propto \exp(i\mathbf{q}\mathbf{r}) = \int_{-\infty}^{\infty} \delta(\mathbf{r} - \mathbf{r}_0) \exp(i\mathbf{q}\mathbf{r}) d^3r \quad (1.3)$$

The 1.3 form is a complex Fourier transformation of a delta-function. Thereby, the scattered amplitude of a single charged particle is a Fourier transformation of delta-function in the position r_0 .

2. Scattering at bulk material

Bulk matter consists of many electrons. In Born approximation, the scattered amplitude of a group of electrons can be calculated by summing up the scattered amplitudes of each electron. In the case of system with N electrons, the scattered amplitude $A(\mathbf{q})$ is

$$A(\mathbf{q}) \propto \sum_{j=1}^N A_j(\mathbf{q}) \propto \sum_j \exp[i(\mathbf{k}_f - \mathbf{k}_i) \cdot \mathbf{r}_j] = \sum_j \exp(i\mathbf{q}\mathbf{r}_j) \quad (2.1)$$

This equation can be rewritten in the terms of Fourier transformation by

$$A(\mathbf{q}) \propto \sum_{j=1}^N A_j(\mathbf{q}) \propto \int (\sum_j \delta(\mathbf{r} - \mathbf{r}_j)) \exp(i\mathbf{q}\mathbf{r}) d^3r = \int \rho(\mathbf{r}) \exp(i\mathbf{q}\mathbf{r}) d^3r \quad (2.2)$$

Here $\rho(\mathbf{r})$ is an electron density distribution of the illuminated matter. Thus, for scattering at bulk matter the scattered amplitude is proportional to the Fourier transformation of the electron density distribution. It should be mentioned that the measured signal is intensity which is an absolute square of the amplitude $I(\mathbf{q}) = |A(\mathbf{q})|^2$. Thus, we lose information about phase, what makes data analysis process more difficult and that's why we need additional information about sample or independent measurements.

3. Surface scattering

Every sample which we measure has a surface, so in every measurement additional scattering contributions from the surface are present. This contribution is extremely important if the object of investigations is surface itself or in the case of very thin layer.

As it is shown at (2.2), the scattered amplitude $A(\mathbf{q})$ is given by the complex Fourier transformation of the electron density. To transform equation (2.2) from infinite bulk material to surface we need to determine $\rho(\mathbf{r})$ outside the sample. Introducing function $B(\mathbf{r})$:

$$\begin{cases} B(\mathbf{r}) = 1, r \text{ inside the sample} \\ B(\mathbf{r}) = 0, r \text{ outside the sample} \end{cases}$$

$$\rho(\mathbf{r}) = \rho_{\infty}(\mathbf{r}) \cdot B(\mathbf{r}) \quad (3.1)$$

According to this, the equation for scattered amplitude is given by

$$A(\mathbf{q}) \propto \int \rho(\mathbf{r}) \exp(i\mathbf{q}\mathbf{r}) d^3r = \int \rho_{\infty}(\mathbf{r}) \cdot B(\mathbf{r}) \exp(i\mathbf{q}\mathbf{r}) d^3r \quad (3.2)$$

After several transformations using the convolution theorem for $A(\mathbf{q})$ and $B(\mathbf{r})$, the scattering process for surface with density profile such as shown at fig. 2 is described by

$$A(\mathbf{q}) \propto \frac{1}{q_z^2} \cdot \int \frac{d\rho(z)}{dz} \exp(iq_z z) dz \quad (3.3)$$

The reflected intensity is the absolute square of amplitude and depends on the derivative of the electron density profile and thus in the film thickness, the roughness and the density contrast between the layers and the substrate:

$$I(q_z) \propto \frac{1}{q_z^4} \left| \int \frac{d\rho(z)}{dz} \exp(iq_z z) dz \right|^2 \quad (3.3)$$

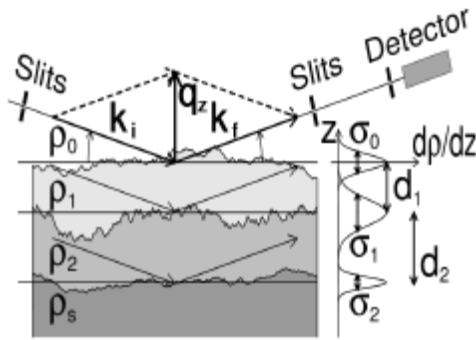


Figure 2. Schematic view of a substrate and two layer sample on it.

The roughness of the interface reduces to one parameter σ_j , which is referred as Gaussian width of the interface. The typical reflectivity curve is shown in fig. 3. [4]

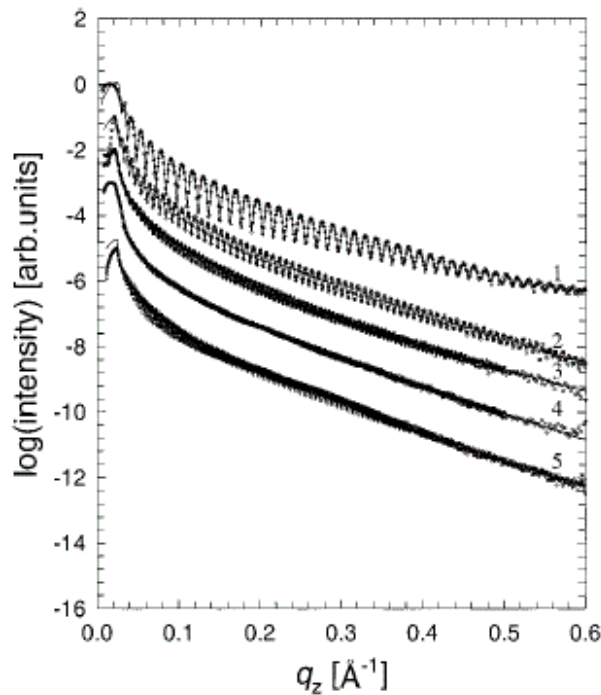


Figure 3. The typical reflectivity curves for samples with different thickness and roughness.

As it was already mention that from the reflectivity curve we can observe thickness of layer d and roughness σ . The equation for thickness easily follows from fig. 1 and Bragg law:

$$2d\sin\theta = n\lambda,$$

$$q = 2k\sin\theta$$

$$d = \frac{2\pi}{\Delta q}$$

On the figure 3 it is seen that oscillations becomes narrow from curve 1 to 5, so the thickness increase with the number of sample there. The roughness σ can be calculated after fitting experimental curves via special software.

Experimental part

Sample preparation

Polystyrene thin films were chosen as objects of our research. Polystyrene is an aromatic polymer made from the monomer styrene. Polystyrene is one of the most widely used plastics. Polystyrene is in a solid state at room temperature, but flows if heated above its glass transition temperature of about 100 °C (for molding or extrusion), and becomes solid again when cooled. Pure solid polystyrene is a colorless, hard plastic with limited flexibility. Solid polystyrene is used, for example, in disposable cutlery, plastic models, and smoke detector housings, high gloss transparent packaging, lights in all sorts for interior lighting, displays in electronics, simple toys, model kits [5]

During the work three samples with different concentrations of polystyrene were obtained.

Table 1. List of polystyrene thin films with different concentrations of PS.

<i>SAMPLE</i>	<i>PS CONCENTRATION, [G/L]</i>
<i>1</i>	<i>3.41</i>
<i>2</i>	<i>2.60</i>
<i>3</i>	<i>7.05</i>
<i>4</i>	<i>4.14</i>
<i>5</i>	<i>10.20</i>
<i>6</i>	<i>19.80</i>

For preparation of our samples the polymer with molecular weight is equal to 100000 mol/g was taken. The toluene was used as the solvent of PS. Single-crystal silicon was taken as a substrate. It should be noted that the purification of substrates is the very important task. The purity of the substrate affects the quality structure of the samples. Surface of single-crystal Si (100) substrate was purified in several stages. At the first step, the cleaning of the surface from the organic phase was carried out. Substrate was wiped with acetone and placed in the ultrasonic bath with acetone for 5 min. Then silicon was washed in distilled water. Further we repeated this procedure with ethanol. Substrates were put in hot water in the last stage. They were dried with a stream of nitrogen and put on the hot surface.

The polystyrene thin films were obtained by spin coating technique. Spin coating is a procedure used to apply uniform thin films to flat substrates. An excess amount of a solution is placed on the substrate, which is then rotated at high speed in order to spread the fluid by centrifugal force. A machine used for spin coating is called a spin coater, or simply spinner. Rotation is continued while the fluid is distributed to the edges of the substrate, until the desired thickness of the film is achieved. The applied solvent is evaporated. So, the higher the angular speed of spinning, the thinner the film. The thickness of the film also depends on the concentration of the solution and the solvent. In our case the speed of spinning is equal to 2500 rps (cycles per second). The possible structure of our samples is shown on the fig. 4.

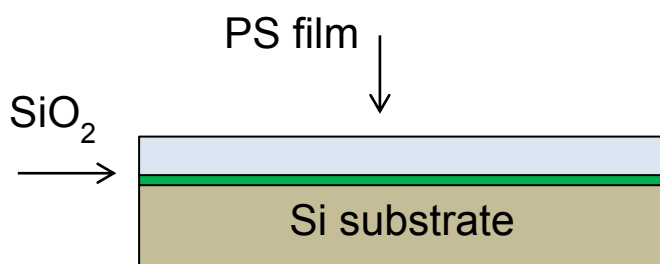


Figure 4. The possible structure of samples.

Experimental setup

1. General information about the beamline

All reflectivity measurements were carried out on source of synchrotron radiation DORIS III, beamline W1.

Beamline W1 is dedicated to X-ray diffraction and scattering experiments at energies between 6 and 11keV. The endstation is equipped with a 6+2-circle diffractometer and a high-resolution fluorescence spectrometer. The energy range of the beamline overlaps with many absorption edges of 3d-transition metals and 4f rare earth elements, which makes it perfectly suited for resonant scattering experiments.

Present applications are:

- > X-ray reflectivity
- > grazing incidence reflection
- > anomalous X-ray scattering
- > resonant and non-resonant inelastic X-ray scattering

All these techniques utilize the intense and focused beam of the wiggler, and require in some cases to tune the photon energy across an absorption edge. Beamline W1 layout is shown on the figure 5. Sketch of the beamline: The white x-ray beam from the 32-pole wiggler is made monochromatic by a double-crystal Si (111) monochromator. The toroidal mirror focuses the divergent beam into a spot of approximately $1.6 \times 4 \text{ mm}^2$ at the position of the sample. This sketch is not drawn to scale, and the distances are rather approximate values.

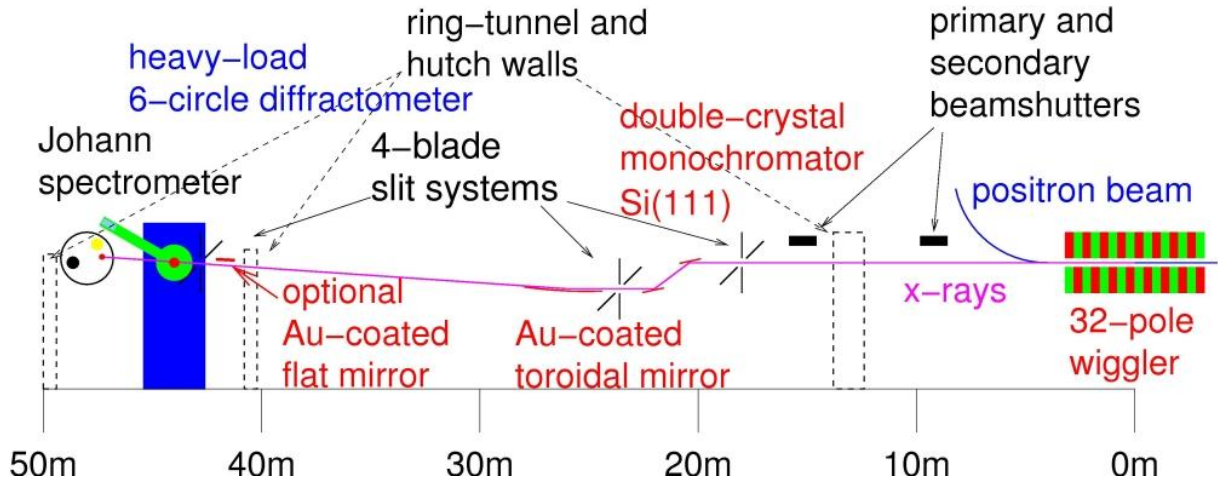


Figure 5. Beamline layout.

2. Experimental setup

The scheme of experimental setup which was used during our experiment is shown at fig. 6. The primary beam goes through the monitor, system of slits and absorber called attenuator. Then it is reflected on a sample located here and the intensity of the exit beam is measured by the detector.

Both sample and detector can be moved independently with angles: omega (related to sample movement) and theta-theta (related to the detector arm movement). The sample is clamped to the sample stage and is covered by the beryllium dome to maintain the vacuum. What is more, we also installed some additional equipment such as temperature sensor and controller to change and measure the temperature of the sample. Before every measurement it is necessary to calibrate the position of the beam and the sample. The calibration procedures are the following: firstly, theta-theta motor should be set at the center of the beam; secondly, the sample should be set at the position of the half-intensity of the primary beam and lastly, the reflection conditions should be checked by an omega scan.

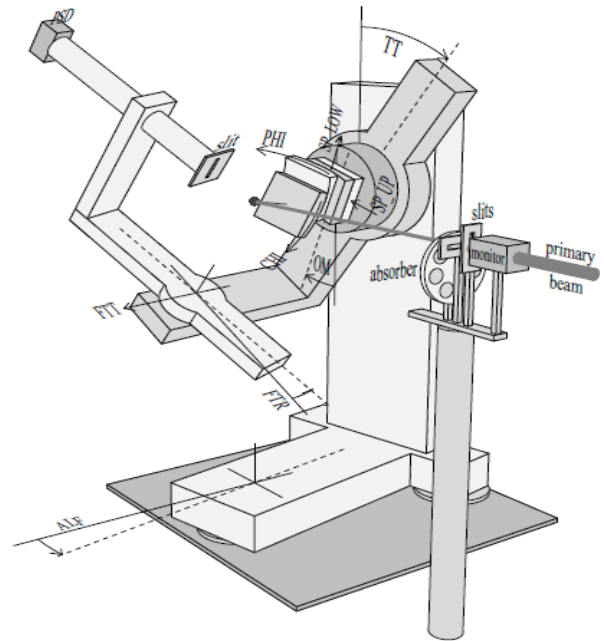


Figure 6. Experimental setup.

Results and discussion

We measured reflectivity curves for all samples at the room temperature and at the 70, 130, 160 and 200 °C for samples 01, 04 and 06. The results of our measurements are reflectivity curves similar to the curve which you can see at the figure 7. In order to observe thickness and roughness we need to fit our curves using special software e.g. LSFIT.

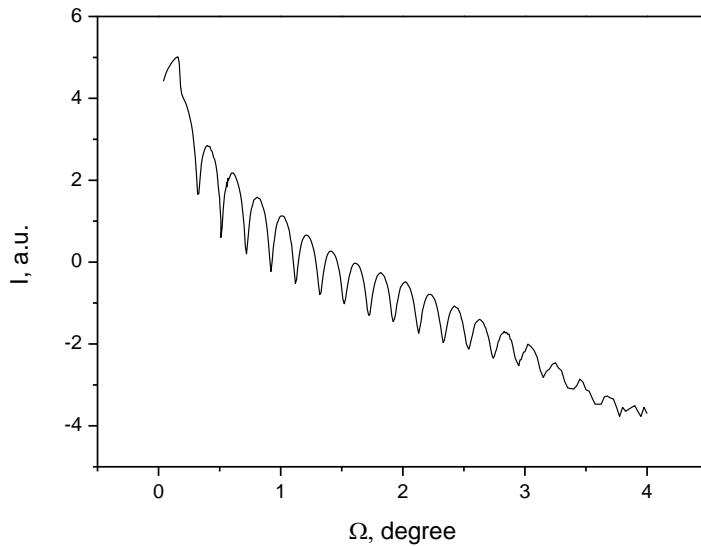


Figure 7. Reflectivity curve for sample 04.

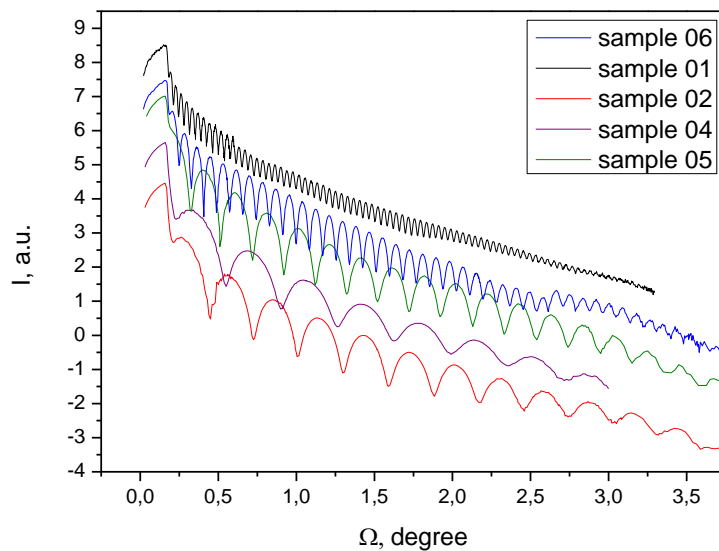


Figure 8. Reflectivity curves from all samples at the room temperature. The curves are shifted for clarity in the intensity scale.

It was observed from reflectivity curves that with decrease of polystyrene concentration the thickness of sample decrease as well, that is clearly seen from the figure 8.

The thickness of all the samples at the room temperature is shown at the table 2.

Sample number	Thickness, A
01	117.58
02	93.97
04	167
05	393.13
06	869.24

Table 2. Thickness of the samples at the room temperature.

The temperature dependence of thickness was observed for three samples – 02, 04 and 06 (thinnest, middle and thickest ones). The results can be seen at the figure 9, 10, 11.

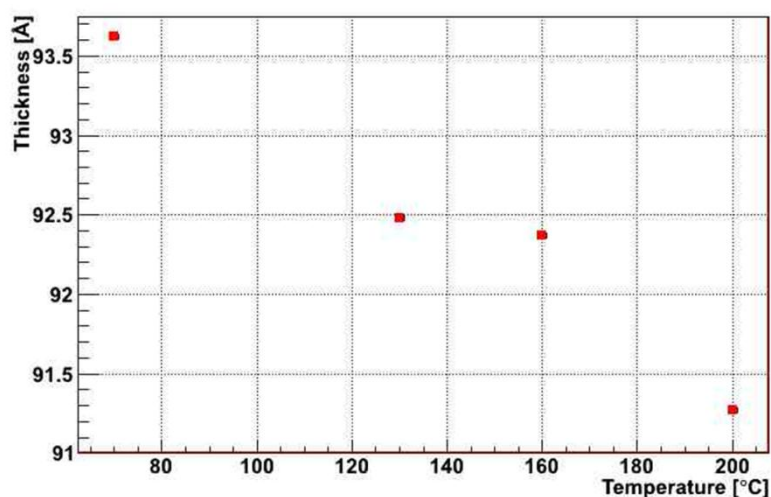


Figure 9. Temperature dependence of thickness for the thinnest sample for the sample 02.

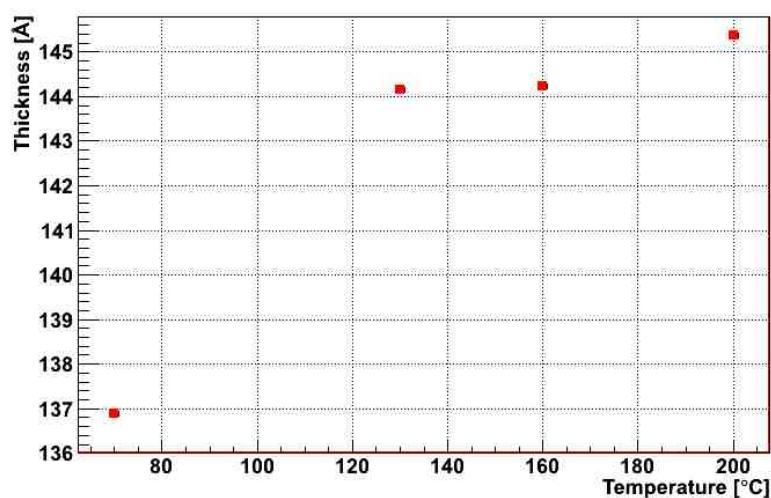


Figure 10. Temperature dependence of thickness for the thinnest sample for the sample 04.

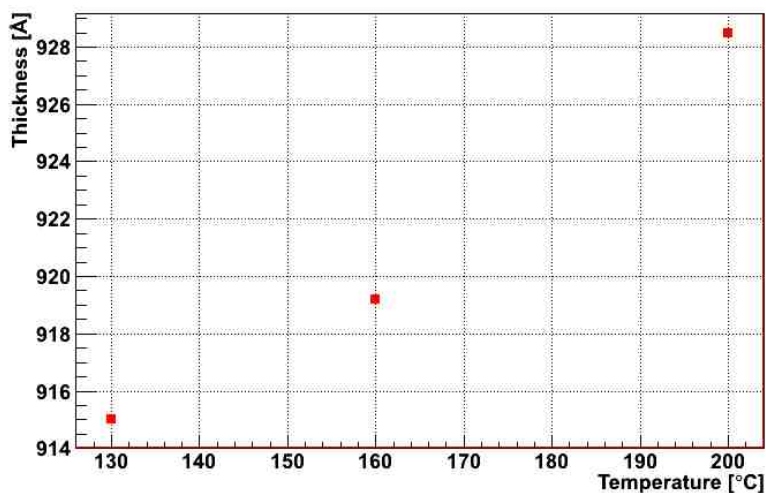


Figure 11. Temperature dependence of thickness for the thinnest sample for the sample 05.

From the figures you can see that the thinnest sample become thinner and thinner with the temperature increase, but for the middle and thick samples temperature dependence is completely different – the thickness increase with temperature. The difference in behavior of very thin and middle and very thick samples could be explained in the next way: it is known that materials are expected to have temperature expansion, but in the case of very thin film the interaction between substrate and polymer layer is dominate and molecules are located chaotically with a lot of holes between them. During the heating molecules start fluctuate around their positions, so they can occupy a position closer to substrate, like they are felt down due to the fluctuations which are increased with temperature. We suppose film thickness to go down with temperature until temperature expansion is enough to cover this accumulation decrease.

The temperature dependence of roughness is shown at the figures 12, 13, 14.

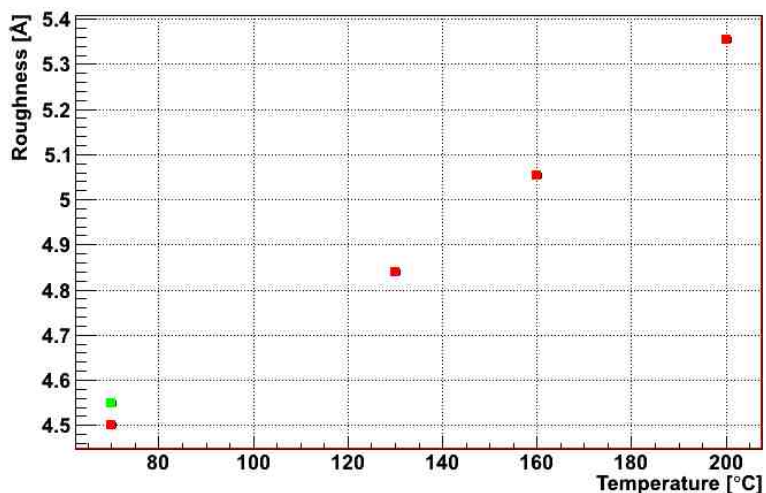


Figure 12. Temperature dependence of roughness for the sample 02.

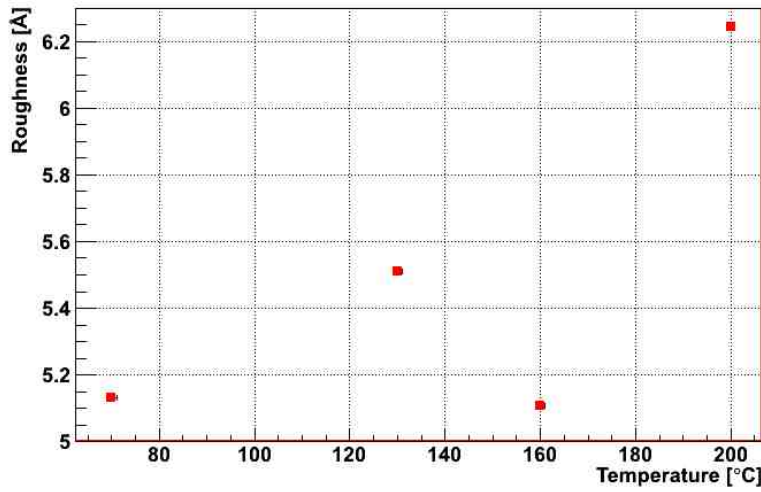


Figure 13. Temperature dependence of roughness for the sample 04.

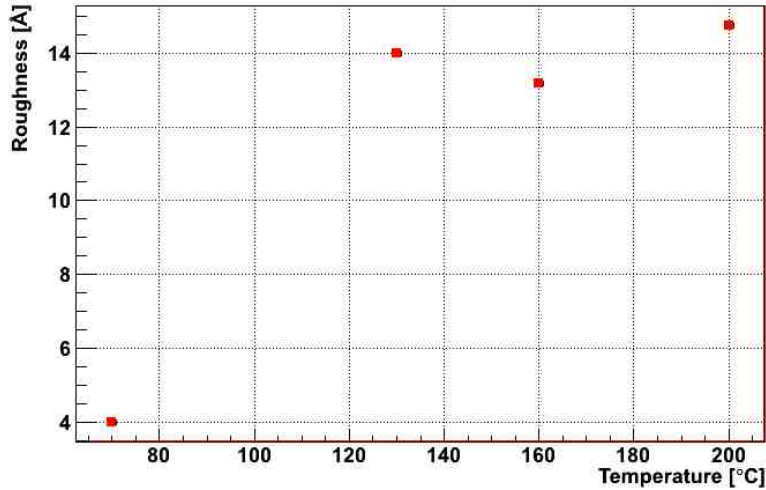


Figure 14. Temperature dependence of roughness for the sample 06.

The roughness increases with temperature for all samples and the increase in roughness is bigger for the thick sample. As it was already mentioned, the interaction between film and substrate is high in case of thin film, so as substrate is ordered material (crystalline silicon) the roughness increases slowly at thin film and faster at thick film. As it was already mentioned, the interaction between film and substrate is dominate in case of thin film, so as substrate is ordered material (crystalline silicon) the roughness increases slowly at thin film and faster at the thick film.

All reflectivity curves were similar except for the thickest sample at the temperature 70°C. This curve is shown at the figure 15. Besides the narrow oscillations from the thick polymer layer it is also present the wide oscillations which can be related to the third layer with thickness near 16 Å. This third layer might be the result of difference in the interaction near the substrate and the top of the surface, but we need additional measurements in order to explain such behavior.

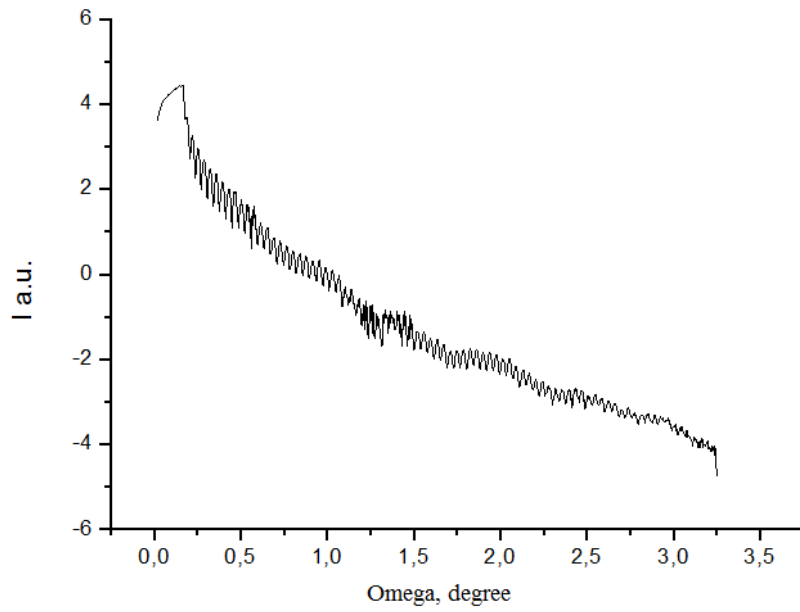


Figure 15. The reflectivity curve for the thickest sample at the 70 °C.

To additional confirmation of reflectivity results the AFM measurements were done. The 3D AFM images are shown on figures 16, 17, 18.

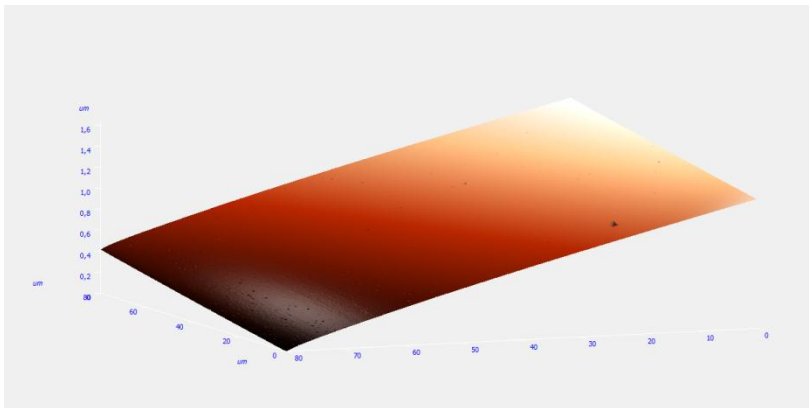


Figure 16. The AFM image of sample 02.

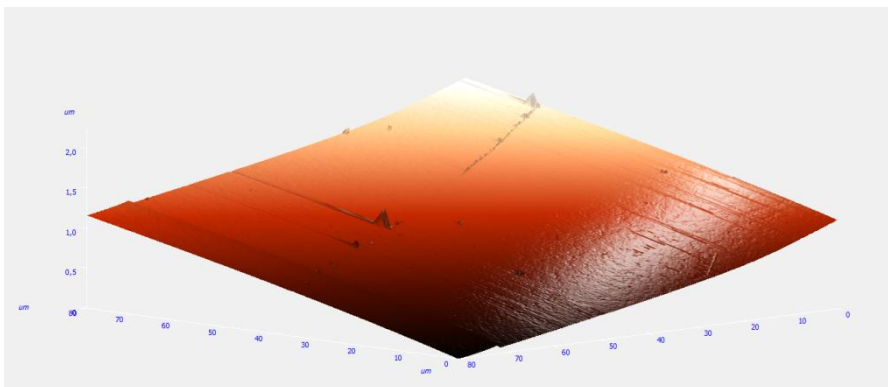


Figure 17. The AFM image of sample 04.

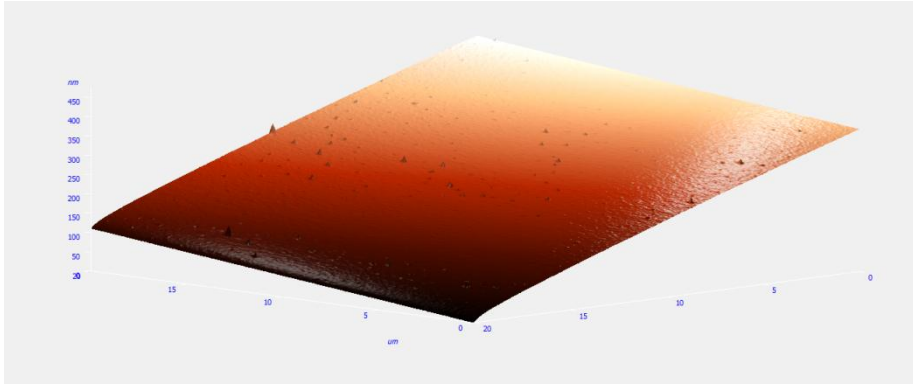


Figure 17. The AFM image of sample 06.

It is seen from the AFM images that the surface of the samples become rougher with the increase of thickness, that confirms our reflectivity results.

Conclusions

During the work thin polystyrene films with different thickness were prepared and the thickness and roughness of polystyrene films at various temperatures were observed. It is vital to note that roughness with temperature for all samples is increasing rapidly. It appeared that highest increase of roughness is noticed for the thickest sample. In regard to middle and thick samples, there is an increase of thickness with temperature. Concerning the thinnest sample, decrease of thickness with temperature is observed.

References

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