Measure Thickness and Glass-transition Temperature of PMMA sample using Spectroscopic Ellipsometry

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Abstract

Spectroscopic Ellipsometry, an optical technology, is often used for measuring properties of materials, such as electrical property, thermal property and optical property. In order to measure the thickness and glass-transition temperature of PMMA sample, spectroscopic ellipsometer and one heater are used in this experiment. The thickness of PMMA sample under room temperature(22℃) measured in this experiment is 121.17±0.032 nm and the glass transition temperature of PMMA sample without solvent is 113.19℃ which is a good and trustable result. Generally, spectroscopic ellipsometry is such a useful technique which enable us to do so many precise and accurate measurements.

1. Introduction

The purposes of this experiment are to measure the thickness and glass transition temperature of sample. And the method of determining glass transition temperature of sample is through ratio of changes on thickness of sample as temperature goes higher. Therefore, it is important to measure the thickness of sample accurately. A few of previous methods of measuring the thickness of material are using ruler, vernier caliper or spiral micrometer. However, these type of methods are not available for measuring the thickness and the change of thickness of nanosized sample in this experiment. For this reason, some other technology is needed.

Ellipsometry, a method to generate and analyse light's polarization property and using polarized light to characterise the properties of material, has been successful in the past few decades [1]. Ellipsometry is a quite useful method to analyse materials at the nanoscale [2]. One of the instruments used in this experiment is spectroscopic ellipsometer, which is an important application of Ellipsometry. Since spectroscopic ellipsometry could measure two unrelated values at a particular wavelength, this allows spectroscopic ellipsometry to measure the properties of thin film accurately [1]. That is also why spectroscopic ellipsometry is selected for this experiment. As spectroscopic ellipsometer is potential for highly precise and accurate measurements [3], many excellent works had been done in this area, such as relationship between thickness and glass transition temperature in thin polymer films completed by Jae Hyun Kim et al. [4]. Furthermore, spectroscopic ellipsometry can also be used for measuring thermal property of material and electrical property and so on, which makes researches on properties of nanosized objects easier than before.

2. Theory

The key formula of this experiment is relation between two main ellipsometric parameters, amplitude ratio ψ and the phase difference Δ:

$$\frac{r_p}{r_s} = tan(\psi)e^{i\Delta} \tag{1}$$

where r_p is parallel (p) component of the amplitude coefficients of incident light and r_s is that of perpendicular (s) component. Basically, many mathematical models of sample are available for us to adjust and these models can produce a series of ψ and Δ to match with amplitude ratio and phase difference measured in experiment. The better they match, the more appropriate model is. If the model chosen is good enough, the thickness of sample that outputted by software will be excellent too. The method of judging whether the fit of data is good or not is through Chi-square test. The formula used for calculating the value of chi-square of linear fit is given:

$$\chi^2 = \sum_{i}^{N} \frac{(y_i - y_i(x_i))^2}{\sigma^2} \tag{2}$$

where i and N are the starting point and the final point. y_i is the value measured and $y_i(x_i)$ is the fitted value. σ is the uncertainty in y component. And if the fit is an ideal fit, $\chi^2 = N$ will be satisfied.

3.Method

Firstly, α-SE™, a type of spectroscopic ellipsometer which is connected to Complete EASE software on computer, was used for examining the polarization properties of light in this experiment. Secondly, the model selected for PMMA sample need fixing through a standard sample of 25nm SiO_2 on Silicon which is shown in Figure 1. Then, a sample of clean silicon was needed for adjusting the offset angle of model. The samples needed in experiment are shown in Figure 2.

Figure 1: Standard sample of 25nm SiO_2 on Silicon.

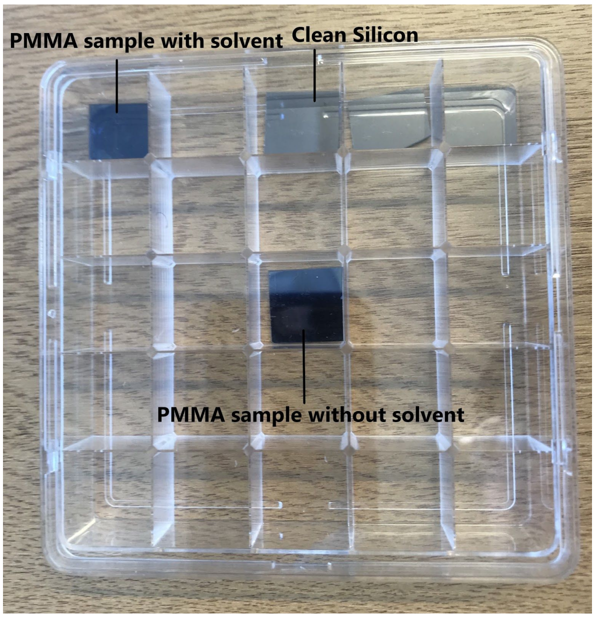

Figure 2: Samples needed in experiment.

Next, the PMMA sample was put on the heater. The heater was connected to TMS 94, which is a type of machine used for controlling the temperature and heating rate. In this experiment, two PMMA samples were used, they are PMMA sample with and without solvent. The apparatuses used in experiment are shown in Figure 3. Finally, the thickness of PMMA sample was measured and recorded under temperature range between 70℃ and 170℃ with interval 5℃. And the thickness of PMMA sample under room temperature was measured as well. There is one aspect that needs specific attention, the measurement at a certain temperature should be followed by that waiting for the temperature of sample become stable in order to prevent the influence of unstable temperature.

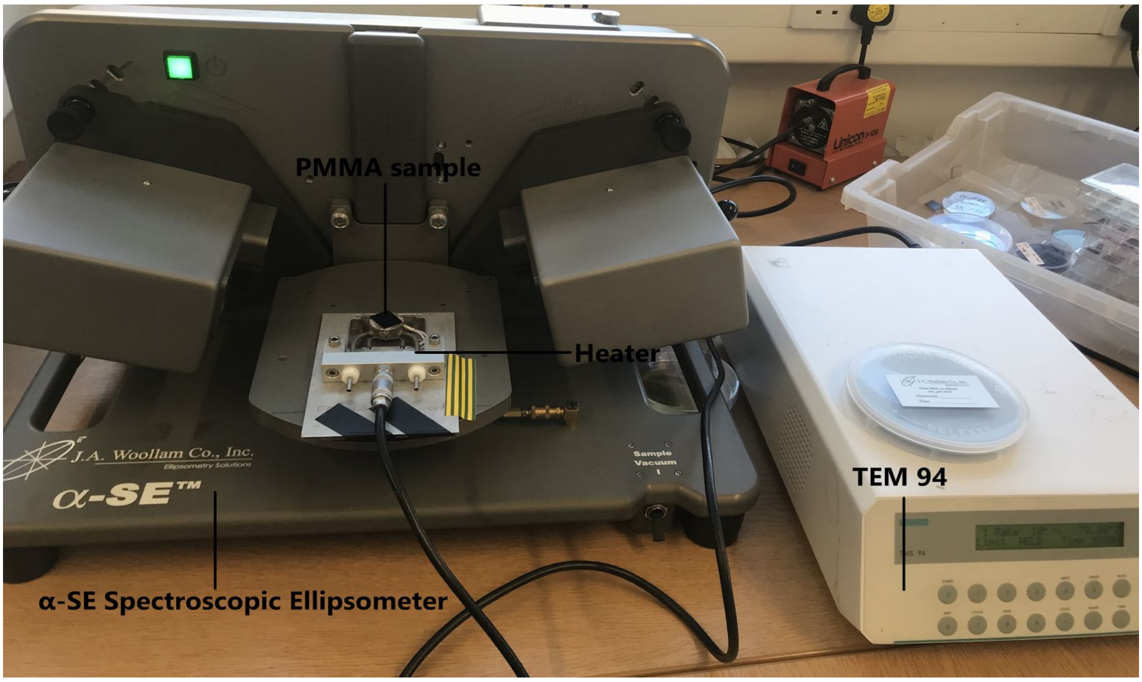

Figure 3: Apparatuses used in experiment.

4.Analysis

There are two PMMA samples provided in all. The first one is PMMA sample without solvent. The thickness of sample was recorded as the temperature changes from 70℃ to 170℃. Then linear fit was done on the scatter plot and the graph is shown in Figure 4. Apparently, the graph is divided at the eighth data point and the gradient of two linear fit lines changes a lot. This vividly indicates that the sample underwent a special process, glass transition.

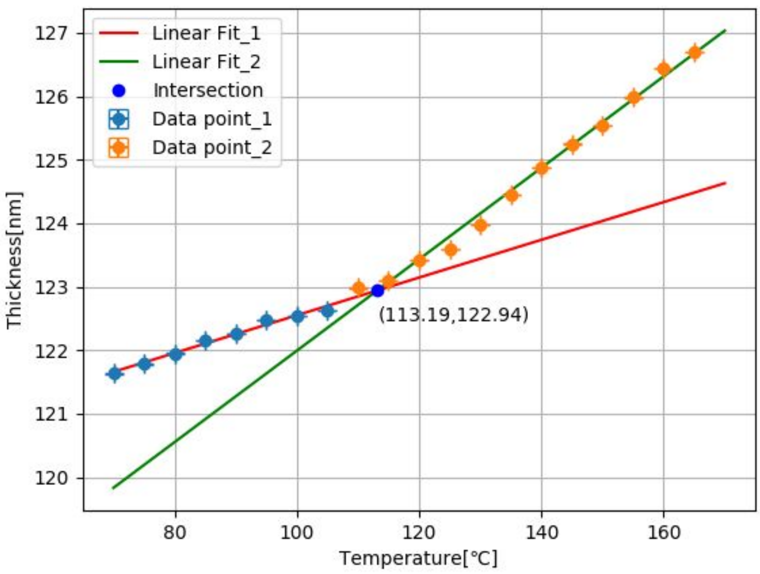

Figure 4: Linear fit of thickness of PMMA sample without solvent which divided at the eighth point.

Therefore, the glass transition temperature of PMMA sample without solvent is 113.19℃. The second experiment sample is PMMA sample with solvent. The graph of this sample is shown in Figure 5. And the intersection of Figure 5 doesn't represent the glass transition temperature because the solvent affect sample's glass transition temperature a lot. The intersection in this case is meaningless. The important point in this case is that the trend of two linear fit lines which will be explained later.

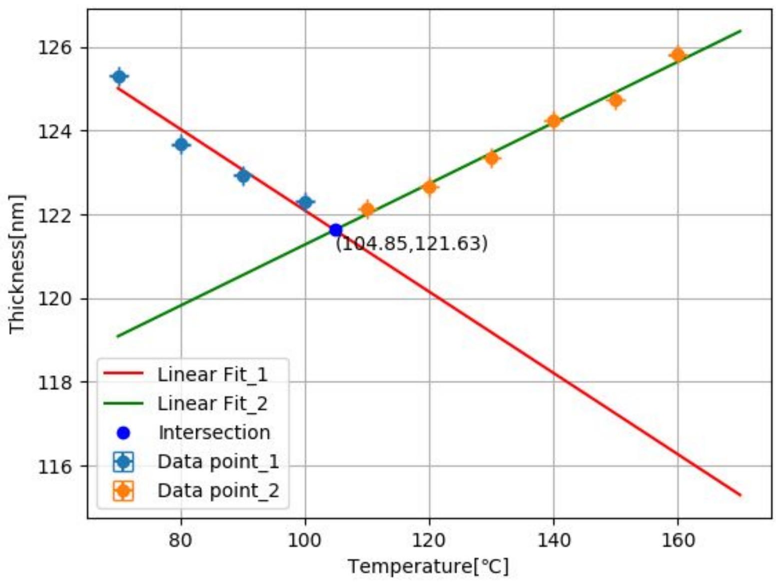

Figure 5: PMMA sample with solvent.

The thickness of PMMA sample without solvent under room temperature (22℃) are also measured and shown in Table 1. By comparing the initial thickness of PMMA sample without solvent to thicknesses in Figure 4, the glass transition process could be explained more detailed.

Name	Thickness[nm]
PMMA sample without solvent	121.17 ± 0.032 nm

Table 1: Relevant parameter of PMMA sample without solvent under room temperature.

5. Discussion of results

The glass transition of PMMA sample in this experiment is 113.19℃. However, it is also vital to figure out what process does the sample undergoes. The thickness of PMMA sample without solvent is keep increasing as temperature goes higher. The sample has thermal expansion all the way. However, the gradient of its changes is different before glass transition point and after. The reason for this phenomenon is that the sample is glass before glass transition point and the sample becomes rubber after glass transition point. And the chi-squared value for linear fit lines in Figure 4

are 6.0 and 10.0 respectively while N is 8 and 12 respectively. The close values of chi-squared and N indicates that both two fit lines are good fit.
In Figure 5, the thickness of PMMA sample with solvent decrease before intersection. The reason for this weird phenomenon is because of the evaporation of solvent as the temperature goes higher. After that, the PMMA sample undergoes glass transition at some point and the thickness gets higher again. The chi-squared value for linear fit lines in Figure 5 are 2.0 and 4.0 respectively when N is 4 and 6 respectively. The chi-squared values and its corresponding N are also quite close, which indicates two excellent fit too. In all, spectroscopic ellipsometry is really a good tool for measuring such properties.

6. Conclusion

In this experiment, the thickness of PMMA sample were recorded exhaustively. The measured glass transition temperature of PMMA sample without solvent is 113.19℃, through the intersection of two linear fit between thickness and temperature. This report also explains the glass transition process undertook by PMMA sample without solvent and interprets the reason why the same method doesn’t work on PMMA sample with solvent. The success of this experiment indicates that spectroscopic ellipsometry is a powerful optical technique for people to measure these similar properties and people already have such technique to examine the specific thin film. However, there is still no general model for scientists to estimate the glass transition temperature of thin polymer film [4]. Therefore, further study of some general model or equation would be useful in the future.

Acknowledgments

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