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To cite this article: Junbo Gong et al 2017 Mater. Res. Express 4 085005

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Temperature dependent optical constants for SiO$_2$ film on Si substrate by ellipsometry

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Keywords: SiO$_2$, optical constants, temperature, refractive index, ellipsometry

Abstract

In situ ellipsometry measurements in the spectra range from 246 to 1000 nm were performed on a SiO$_2$/Si system at temperatures varying from 25 to 600 °C. By using Cauchy dispersion model to describe SiO$_2$ layer and B-spline to parameterize Si substrate, the temperature dependent optical constants of SiO$_2$ film and Si substrate were precisely determined and analyzed which is helpful to understand the temperature effect of substrate for ellipsometry measurement. The temperature coefficient of refractive index of SiO$_2$ at elevated temperature was obtained by ellipsometry. The results indicate that the temperature coefficient increases with increasing wavelength and decreasing temperature.

1. Introduction

The optical constants of a material vary with not only wavelength but also temperature. Recently, with the development of variable-temperature ellipsometry technology, temperature dependence of optical constants has attracted considerable attention [1–3] due to its wide application on studies of electronic band structures [4, 5] and phase transitions [6–8].

Ellipsometer measures the change of amplitude and phase of polarized light reflected from the sample (called as ellipsometry parameters $\Psi$ and $\Delta$). The structure information of sample can be obtained by numerical inversion of ellipsometry parameters. To conduct ellipsometry measurement on a film material, it usually requires the film material to be studied deposited on a substrate such as Si, SiO$_2$ or SiO$_2$/Si system. To obtain accurate optical constants and thickness information of the film material, it is a must to ensure a sufficient understanding about substrate including its exact optical constants. However, the optical constants of substrate are also varied with temperature.

If the optical constants of film material to be studied and substrate are fitted simultaneously, it is hard to get the correct results by numerical inversion due to the increasing unknown parameters. So temperature dependent optical properties of many film materials cannot be investigated by ellipsometry in spite of their significance. For example, if we want to conduct variable-temperature ellipsometry study on graphene while the graphene was usually deposited on SiO$_2$/Si composite substrate, then the varied optical constants with temperature of SiO$_2$/Si substrate will be the key to obtain optical constants of graphene. Some research groups [9, 10] conducted this experiment neglecting the temperature effect of substrate. However, their simulation is based on the assumption that the optical constants of substrate are temperature independent constants which is obviously not the case. This assumption is considered approximately correct when the film is relatively thick and quite correct on bulk material [11]. Consider that, a better understanding of the variable temperature optical properties of commonly used substrates would have considerable influence on most film materials’ variable temperature ellipsometry measurement.

SiO$_2$/Si composite substrate (SiO$_2$ layer with about 300 nm thickness), whose interference effect can make the film on it easy to be observed by naked-eye and also enhance Raman spectrum so as to caused the film on it easy to be detected [12], has been the most commonly used composite substrate in the semiconductor industry. This
advantage becomes more prominent especially in the study of ultra-thin film such as graphene. The temperature dependent change of ellipsometric signals of ultra-thin film is too weak to distinguish the signal of film sample from the temperature effect of the substrate. Moreover, variable temperature ellipsometry aimed at any ultra-thin film was hardly reported up to now. So it is important to clarify the temperature effect of SiO$_2$/Si system by ellipsometry. Many researchers have done a lot of work to explore the optical properties of the SiO$_2$/Si system [13–17]. However, the complexity of ellipsometric modeling [18] caused that even for room temperature measurement on SiO$_2$/Si system, there exist some different opinions. Herzinger et al systematically study the optical constants for silicon and thermally grown silicon dioxide via a multi-sample, multi-wavelength, multi-angle investigation and found that the thermal silicon dioxide refractive index was independent of the substrate model used and higher than published values for bulk SiO$_2$ [17]. In the case of variable temperature, the problems become more complicated considering that the change in SiO$_2$ refractive index with temperature is very small, about $10^{-3}$ order, which can be compared with the effect of thickness and deposition process. Considering the above, there are two points should be noted. Firstly, how to prove the validity of the model and the correctness of the results? Secondly, it will be more important to determine the tendency of the refractive index with temperature rather than the value itself. In this work, we will try to find an appropriate method to describe the optical properties variation with temperature of SiO$_2$/Si system.

2. Experimental

SiO$_2$ with ~300 nm thickness on Si was purchased from University Wafer and cleaned with acetone, alcohol and deionized water. In order to carry out the high temperature measurement, the sample was placed in a heat cell which was maintained at a vacuum of ~$10^{-3}$ Pa. To eliminate water desorption effect which may arise, we conducted a 600 °C annealing treatment on the sample before measurement under the vacuum condition. The in situ ellipsometric spectra from 246 nm to 1000 nm at different temperature were recorded at 70° incidence angle by a Spectroscopic Ellipsometer (JA Woollam M-2000U). Ellipsometry measurements were made at increment of ~25 °C from 25 °C to 600 °C.

To verify the structure of SiO$_2$/Si system we used, scanning electron microscopy (SEM) analyses were carried out on a SEISS SIGMA field emission SEM instrument. The cross section of the sample was showed in figure 1. It was clearly showed that a layer of SiO$_2$ with a thickness of about 300 nm was uniformly covered on Si surface. However, due to the limitations of the resolution and that the interface is not clear enough, it was difficult to determine the exact thickness of the SiO$_2$ layer by this way.

3. Methods

Ellipsometry need a numerical analysis of the experimental data based on some mathematical model. MSE (mean-squared error) is adopted to evaluate the quality of the match between the experimental and calculated data. The MSE is defined as:

$$\text{MSE} = \sqrt{\frac{1}{2N - M} \sum_{i=1}^{N} \left( \frac{\psi_i^{\text{mod}} - \psi_i^{\exp}}{\sigma_{\psi,i}^{\exp}} \right)^2 + \left( \frac{\Delta_{\psi,i}^{\text{mod}} - \Delta_{\psi,i}^{\exp}}{\sigma_{\psi,i}^{\exp}} \right)^2}$$

Figure 1. Cross-section image of the SiO$_2$/Si system.
where $N$ is the number of data points, $M$ is the number of variable parameters in the model, and $\sigma$ is the standard deviation which can be calculated directly by completeEASE software (Developed by J A Woollam Co., Ltd). Firstly, the effect of different parameters on fitting results is assessed by changing simulating model. A lower value of MSE usually corresponds to a more effective simulating model.

Figure 2 shows the MSE obtained by different simulating method. When the optical constants of SiO$_2$ and Si substrate is fixed according to Palik’s data and the thickness of SiO$_2$ is the only fitted parameter, the MSE values maintain at a high level (>12) and increase dramatically with increasing temperature as the black block showed. When SiO$_2$ is replaced by a Cauchy layer, the MSE value reduced but still kept larger than 8 and also increasing with increase temperature as red circles showed. If the thickness of SiO$_2$ was added to fit value, the influence on MSE is not obviously. These results show that the optical constants of silicon substrate are significantly affected by temperature and must be set as variable in the model. However, the thickness of SiO$_2$ layer set as a variable value has little influence on the results. This can also be understood by the fact that the thermal expansion coefficient of SiO$_2$ is as low as $5 \times 10^{-7}$ K$^{-1}$ level [19] and the thickness variation of an about 300 nm SiO$_2$ layer is below 0.1 nm when the temperature changed from room temperature to 600 °C.

Consider that, we use a Cauchy layer to replace the SiO$_2$ and the optical constants of silicon substrate are parameterized by B-splines. B-spline is an interpolation method which has been successfully used to obtain optical constants of some materials [20]. The exact thickness of Cauchy layer is fixed at 302 nm which is determined by the optical constants of Si and SiO$_2$ at room temperature. The MSE of this method maintain at a low level (<6) throughout and do not increase with increasing temperature as the blue del in figure 2. By this means we successfully obtained the optical data of SiO$_2$ and Si at different temperature.

In fact, due to the interfacial effects, it is likely that the optical constants of the top and bottom region of a material are different from those of main part. In this work, it may be not entirely accurate by using Cauchy model to parametrize SiO$_2$ layer and B-spline to parameterize Si. However, one of the principles of choosing appropriate model during ellipsometry fitting process is to choose the simple model as far as possible if MSE is small enough (For films with a thickness of hundreds of nanometers, MSE < 10 means that the simulation results are in good agreement with the experimental results.). When the model is more complex than required, some problems will arise such as the cross-correlation fitting parameters. In our case, the MSE of this method maintain at a low level (<6) throughout. So we can believe that this model can describe our sample structure well. If a more complicated model was used, excessive fitting parameters will make the results impracticable. Besides, in our fitting process, the optical constants of Si are forced Kramer Kroning consistent. In a word, although we used B-spline to parameterize Si optical properties which was a mathematical method, the results we obtained are physically reasonable.

In the fitting process of ellipsometry, a low enough MSE and physically reasonable are key factors to evaluate the acceptability of the results. In this work, these two factors both have a satisfactory solution.

4. Results and discussion

The detailed optical constants of SiO$_2$ and Si from 246 nm to 1000 nm wavelength at different temperature were showed in supplementary information (stacks.iop.org/MRX/4/085005/mmedia). The temperature dependent optical constants of SiO$_2$ layer at four typical wavelengths are showed in figure 3. We can see that
refractive indexes at all wavelengths decrease at first and then increase with increasing temperature. According to Prod’homme’s theory [21], refractive index of quartz glass is a function of temperature. When temperature increased, the refractive index is influenced by two competitive factors. On the one hand, the density decreases with the increasing temperature due to thermal expansion effect and then results in the lower refractive index. On the other hand, Si–O bond becomes weaker at high temperature which means a higher polarizability and this will lead to a higher refractive index. On the whole, the temperature coefficient of refractive index \( \frac{\partial n}{\partial T} \) can be described by

\[
\frac{\partial n}{\partial T} = R \frac{\partial A}{\partial T} + d \frac{\partial R}{\partial T}
\]

where \( d \) stands for coefficient of thermal expansion and \( R \) represents molecular refraction of SiO\(_2\) [21–23]. At high temperature, coefficient of thermal expansion changes little with temperature. \( \frac{\partial n}{\partial T} \) strongly depends on \( \frac{\partial R}{\partial T} \) and refractive index increases with increasing temperature. At relative low temperature, \( \frac{\partial R}{\partial T} \) plays second fiddle while \( \frac{\partial A}{\partial T} \) plays a leading role and thereby caused refractive index decreasing.

Figure 3 also showed that the critical temperature which is the turning point of the refractive index rising or falling is various with wavelength. The temperature coefficients of refractive indexes varied with temperature of seven different wavelengths are showed in figure 4. From figure 4 following significant conclusion can be obtained: (1) The temperature coefficient of refractive indexes at room temperature of 633 nm is about \( 1.0 \times 10^{-6} \) which agree well with previous results [24]. This is the first time to obtain this value by ellipsometry as far as we know. (2) At the same temperature, the longer the wavelength, the lower the corresponding temperature coefficient of refractive index just as the arrow indicates. That is to say, the shorter the wavelength, the greater the refractive index is affected by temperature. This can be understood by the fact that the refractive index at shorter wavelength is larger according to Cauchy model. (3) In general, \( \frac{\partial n}{\partial T} \) increases with increasing temperature due to the higher polarizability and thermal expansion. (4) Gray background region corresponding a negative value of \( \frac{\partial n}{\partial T} \). So we can see that \( \frac{\partial n}{\partial T} \) at different wavelengths all increase from negative value to positive with increased temperature while the difference is that \( \frac{\partial n}{\partial T} \) at a longer wavelength need a higher temperature to enter the positive value zone. In another word, the refractive index at a certain wavelength must decrease with temperature at low-temperature environment and increase with temperature at high-temperature environment, but the critical point between low-temperature and high-temperature is increasing with the increased wavelength.

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**Figure 3.** Temperature dependent optical constants of SiO\(_2\) layer at four typical wavelengths: (a) 250 nm; (b) 400 nm; (c) 633 nm; (d) 999 nm.
Wavelength dependent optical constants of Si substrate were showed in figure 5. Figure 5 showed that the change in optical constants of Si at different temperature is rather small in most spectrums of the wave bands. There are some distinguishable changes mainly located at around 400 nm wavelength. Arrows indicate the temperature increasing direction. Optical constants $n$ and $k$ exhibit similar variation characteristics which both decrease with increasing temperature at about 400 nm wavelength and increase at ultraviolet and infrared wavelengths.

5. Conclusions

In conclusion, this work confirms that it is indispensible and also feasible to consider the temperature effect of SiO$_2$/Si system when variable temperature ellipsometry experiment is conducted. The optical constants of SiO$_2$ layer and Si substrate are precisely determined by using Cauchy model to parameterize SiO$_2$ layer and B-spline to parameterize Si. The variation of optical constants at different temperatures is wavelength dependent and temperature coefficients of refractive index at different temperature of SiO$_2$ are obtained by ellipsometry for the first time which agrees well with Prod’homme’s theory. The temperature coefficient of refractive index of SiO$_2$ increases with increasing wavelength and decreasing temperature. This result is beneficial to understand glass thermal properties and the determination of temperature effect of SiO$_2$ and Si substrate also lays a solid foundation for variable temperature ellipsometry measurement on thin films with higher accuracy and reliability.
Acknowledgment

This work was supported by the National Natural Science Foundation of China (Grant Nos. 11304300 and 11404320) and 909 project of China Academy of Engineering Physics (Grant No: 991912).

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