Determining thickness and optical properties of a-SiO$_x$ thin films by PUMA and envelope method

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Abstract. The gas-jet electron beam plasma chemical vapor deposition method was used for silicon suboxide (a-SiO$_x$) thin films synthesis. According to the EDS data, stoichiometric coefficient of the films varied from 0.5 to 1.63 with changes in the flow rate of 5%SiH$_4$+95%Ar gas mixture (R) from 89 to 18 sccm. Spectral transmittance, containing interference maxima and minima, was obtained in the range from 300 to 1000 nm. The refractive index and the thickness of a-SiO$_x$ thin films obtained from transmission spectra by the envelope method and PUMA were in good agreement with each other. The refractive index of the thin films at 650 nm increased from 1.6 to 3.1 and the film thickness changed from 500 to 1200 nm with an increase of R. The thickness values discrepancy for sample synthesized with R=18 sccm may be explained as the difficulty of using PUMA for systems with close refractive index of the film and the substrate.

1. Introduction

Amorphous silicon suboxide thin films (a-SiO$_x$, 0 < x < 2) are widely used in science and technology. These films are most commonly applied in microelectronics [1] and photovoltaics [2]. In addition, silicon suboxide may be used as a basic element for obtaining material with silicon nanoclusters [3] and continuous polycrystalline silicon layers [4]. The reason is the possibility of variation of optical parameters (refractive index and extinction coefficient) by changing of film stoichiometry. Thus, estimation of optical parameters and film thickness is actual task.

Now, researchers can use different well-established optical methods for determining the optical parameters and thickness of films. These are ellipsometry, interferometry, transmission and reflection spectra and etc. In paper [5] parameters of thin films were obtained using prism coupling into waveguides to measure m-line coupling angles. It is worth mentioning that this method allows making calculations for films with refractive index smaller than the substrate. The author of the work [6] uses multiple-beam interferometry to measure simultaneously both the thickness (d) and refractive index (n) of thin films. The most common method to obtain the refractive index and absorption coefficient of a-SiO$_x$ thin film is ellipsometry [7] and this method is not suitable for thin films with strong absorbance and high surface roughness. To obtain optical parameters and thicknesses of SiO$_x$ films in the work [8] spectrophotometric analysis was used. It is cheaper than ellipsometry one as the authors explain. To determine complex refractive index and thickness from spectrophotometric measurements with quasi-normal light incidence, the curve fitting method in the UV/Vis/NIR and Clustering Global Optimization algorithm were used.

In this study, the envelope method and Pointwise Unconstrained Minimization Approach (PUMA) were chosen for calculation of refractive index and thickness values of a-SiO$_x$ thin films. The a-SiO$_x$ thin films with different stoichiometry were synthesized by gas-jet electron beam plasma CVD method.
2. Methods for measuring optical parameters
In this work for evaluation of optical parameters from transmission spectra the envelope method, (express-method, which is described in [9]), was applied. The transmission spectra obtained in the area of weak and medium absorption (600-800 nm) were used for thickness and refractive index calculation. The experimental spectra have revealed several interference extremes. The envelopes were obtained by polynomial approximation over the three neighboring extremes. The thickness and the refractive index for the corresponding wavelengths were calculated by using the transmittance values on the envelope curves. Although this method is widely used to determine thickness and optical constants of thin films, it has restrictions on samples properties [10], such as low absorbance, high optical thickness \((n\cdot d)\) and significant difference between refractive index values of film and substrate.

Besides, the problem of calculation of optical parameters of thin films can be solved by using the PUMA [11]. PUMA analysis is a more universal method, since it allows calculating optical parameters of thin films even in the region of strong absorption. The use of PUMA allows obtaining thickness of a thin film with high accuracy. In addition, it is possible to get values of refractive index and absorption coefficient for the whole interval of wavelength. The calculation of \(n\) and \(d\) of a thin film by PUMA is based on comparing the theoretical transmission spectrum with experimental one, obtained with normal light incidence for samples with thick substrate with known refractive index. This method of calculation is suitable even in cases, where the calculation of the parameters by the envelope method is difficult or even impossible.

3. Experimental details
The a-SiO\(_x\) thin films with different stoichiometry were obtained by gas-jet electron beam plasma chemical vapor deposition (GJ EBP CVD) [12]. The films were synthesized on borosilicate glass substrates at a temperature of 260°C. The gas mixture of hydrogen (H\(_2\)) and 5%SiH\(_4\)+95%Ar was used in the film synthesis process. Oxygen (O\(_2\)) is supplied to the vacuum chamber separately from the H\(_2\) and 5%SiH\(_4\)+95%Ar gas mixture and enters the activation zone by diffusion from a background gas. The stoichiometry of the films was varied by changing the flow rates of 5%SiH\(_4\)+95%Ar gas mixture (R) at the constant hydrogen flow rate of 386 sccm. The flow rates R were 18, 36, 53, 71 and 89 sccm. O\(_2\) flow rate was maintained constant and equal to 3 sccm. The pressure in the vacuum chamber during the synthesis was 20 Pa. The supersonic gas jet was activated by an electron gun with an accelerating voltage of 1000 eV and an emission current of 75 mA.

In order to estimate the elemental composition of the thin films on quartz substrates JEOL JSM-6700 F microscope, equipped with an X-ray energy dispersive spectroscopy (EDS) was used. The optical transmittance spectra of the samples were measured in the range of 300-1000 nm by SF-2000 spectrometer equipped with a photodiode array and a tungsten lamp as a source of radiation.

4. Results and discussion
The EDS method was used to obtain the silicon and oxygen atomic concentrations in the synthesized samples. Figure 1 shows the dependence of the stoichiometric coefficient \(x\) on R. The value of \(x\) decreases from 1.63 to 0.5 with an increase in R. The effect of argon flow rate during synthesis on the stoichiometry of silicon suboxide films is described in detail [13].
Figure 1. The stoichiometric coefficient of the a-SiO$_x$ films as a function of $R$.

The optical measurements were carried out at normal light incidence. The transmission spectra measured for samples synthesized with different $R$ are shown in figure 2. The spectra are a sequence of alternating maxima and minima of interference. The transmittance varies from 0.4 to 1 in the range from 700 to 1000 nm. It can be seen that the absorption edge moves towards higher wavelengths with increase of $R$.

Figure 2. Spectral transmission coefficient of a-SiO$_x$ films measured in the interval of 300-1000 nm for samples with different $R$.

The spectral transmittance of the films was used to obtain $d$ and $n$ of a-SiO$_x$ thin films by PUMA and envelope method. Figure 3 shows the experimental spectrum of the sample synthesized with $R = 71$ sccm and the envelope curves. The envelopes curves are second-order functions of wavelength, obtained by polynomial approximation over three adjacent points of maxima or minima. Using the values of transmittance on envelopes at wavelengths, corresponding to interference extremes, values of $d$ and $n$ were found from the spectra in the region of weak and medium absorption.

Figure 4 presents a comparison of a-SiO$_x$ film transmission spectrum for the sample synthesized with $R=71$ sccm and the spectrum calculated by PUMA. To evaluate the film parameters by PUMA a four-
layer model “air\-film\-substrate\-air” was chosen. The substrate was borosilicate glass. The thickness of thin film in calculations was ranged from 400 to 1500 nm.

The dependence of the refractive index on R, obtained by envelope method and PUMA at a wavelength of 650 nm, is shown in figure 5. We assume that the increase of the refractive index with R growth is mainly due to a decrease in the oxygen concentration in the film. It was stated in [14] that for silicon-containing films the value of the refractive index at a fixed wavelength is inversely proportional to the value, which is a measure of the covalent bond strength. It means that substitution of strong Si – O bonds with weaker Si – Si bonds leads to an increase of the refractive index of the film.

The dependence of the film thicknesses on R, obtained by the envelope method and PUMA, is shown in figure 6. It can be seen, that the d values obtained by two methods demonstrate good agreement with each other. The discrepancy in the values for sample synthesized with R = 18 sccm arises due to the error in calculating PUMA and it can be explained by the fact that n value of the film is close to n of the substrate.
Conclusion
The a-SiO$_x$ thin films with different stoichiometry were synthesized by GJ EBP CVD. The EDS analysis has shown that the stoichiometry of films is from 0.5 to 1.63 with a change of R from 89 to 18 sccm. The envelope method and PUMA were used to calculate the thicknesses and refractive index of the a-SiO$_x$ thin films from optical transmission spectra, obtained in the range from 300 to 1100 nm.

The values of the refractive index and thickness of a-SiO$_x$ thin films obtained by the envelope method and PUMA show good agreement with each other. An increase of R leads to an increase of the refractive index of the thin films from 1.6 to 3.1 for a wavelength of 650 nm. The film thickness varies from 500 to 1200 nm with an increase of R.

It should be noted, that for sample synthesized with R = 18 sccm there is the discrepancy in the thickness values, which can be explained by the peculiarity of the PUMA method for systems with close film and substrate refractive indices.

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