Effect of substrate temperature on the properties of plasma deposited silicon oxide thin films

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Abstract. Silicon oxide (SiO\textsubscript{x}) films were obtained from SiH\textsubscript{4}/NO\textsubscript{2}/Ar by plasma-enhanced chemical vapors deposition (PECVD) technique. Effect of substrate temperature on the properties of the deposited films have been presented. The substrate temperature of the deposition process varied from 150 to 450°C at fixed working pressure of 1000 mTorr and RF power of 10 W. The films were investigated by atomic force and scanning electron microscopies as well as laser ellipsometry. The grain size, root-mean-square roughness and refractive index of the films were in the range of 20-250 nm, 0.2-2.4 nm and 1.5-2.0, respectively. The refractive indices and stoichiometry of SiO\textsubscript{x} films are discussed using the Lorentz-Lorenz formula.

1. Introduction
The decrease Fresnel reflection and increase a fraction of a transmitted solar radiation is an actual scientific and technical problem for optics and solar power engineering [1,2]. It is solved by texturing surface and forming antireflective coatings [1-7]. They contribute to increasing efficiency and reducing costs of solar cells and improve light transmission and contrast in optics [5,6]. However, the refractive index and the film thickness must correspond to the theoretical values calculated to achieve the maximum effect.

The antireflective coatings on basic of silicon oxide films are the preferable for amorphous hydrogenated and polycrystalline silicon solar cells. Silicon oxide is relatively inexpensive and possessing both antireflection and passivating properties that reducing recombination losses [5,8].

Plasma enhanced chemical vapor deposition method (PECVD) allows to obtain uniform oxide films in a single technological cycle with Si:H, that it possible to effectively minimize the influence of negative factors and does not lead to degradation of the electrophysical and optical properties of the materials solar cells [5]. Any more, it allows to form layers at a temperature below 300°C, which is especially important in the manufacture of solar cells on glass and flexible substrates.

The purpose of the study is to determine the effect of deposition temperature on optical properties silicon oxide thin films obtained by PECVD.

2. Experimental details
The silicon oxide (SiO\textsubscript{x}) thin films were prepared from Ar:SiH\textsubscript{4}:N\textsubscript{2}O gas mixture by plasma enhanced chemical vapor deposition technique (PlasmaLab 100) [9,10]. Silicon oxide thin films were deposited on peeled a n-type silicon wafers (100). Total gas flow, gas ratio, RF power and total pressure were constant to 980 sccm and 161.5:8.5:710 sccm (Ar:SiH\textsubscript{4}:N\textsubscript{2}O), 10 W, 1000 mTorr, respectively.
Temperature was varied in the range of 150-450°C. Film thickness were controlled by profilometry (AlphaStep D-100) of the steps formed by photolithography (MJB4). Root mean squared (RMS) roughness was determined by atomic force microscopy (NTEGRA Probe Nanolaboratory) and scanning electron microscopy (Nova NanoLab600) with increase by a factor of 250 000 [11,12]. The refractive index was determined by laser ellipsometry (LEF-3M) on $\lambda=632.8$ nm and then film stoichiometry was calculated in accordance to [13].

3. Results and discussion
A series of samples with thin (less than 50 nm) SiO$_x$ films was fabricated. Surface morphology of the samples was studied (Fig.1). The grain size and RMS roughness decreased from 200-250 nm to 20-40 nm and from 2.4 to 0.2 nm, respectively (Fig.2,a), the film became denser. The deposition rate increased from 38 to 44 nm/min.

![AFM and SEM images of SiO$_x$ films deposited at various temperatures: (a) 150°C, (b) 250°C, (c) 350°C](image)

Figure 1(a-c). AFM and SEM images of SiO$_x$ films deposited at various temperatures: (a) 150°C, (b) 250°C, (c) 350°C

Then, ellipsometric measurements of the films were carried out. The obtained dependence of the refractive index on temperature (Fig.2,b) has specifics.

With a decrease in the grain size and roughness with increasing temperature, we should expect changes in the properties of the film material towards a transition to the properties of a bulk material, i.e. tendency of the refractive index to the value of 1.45-1.48 (stoichiometric silicon dioxide) [14]. However, the obtained the index values exceed the level and their difference increases with temperature. It can be assumed that despite the constancy of gas mixture composition and flow, pressure and power, the temperature affects the structure and composition of SiO$_x$ films [15,16].

The change in stoichiometry of SiO$_x$ film can be expressed as

$$
\text{Si}_{(1-1/2,x)} + \text{SiO}_2 \xrightarrow{1/2} \text{SiO}_x,
$$

and, thus, as the temperature increases, the transition from films with a large value of $x$ to smaller occurs through the SiO phase ($n = 1.85$ [17]), and it shifted toward the silicon [18], nanocrystalline silicon precipitation. The dependence of the refractive index on the composition was constructed on the basis of the Lorentz-Lorenz formula [13]:

Figure 2(a,b). Roughness (a), refractive index and $x$ (b) of SiO$_x$ films vs. deposition temperature

$$n^2 = \left(\frac{n_{Si}^2 X_{Si}}{n_{Si}^2 + 2} + \frac{n_{SiO_2}^2 X_{SiO_2}}{n_{SiO_2}^2 + 2}\right) \left(\frac{X_{Si}}{n_{Si}^2 + 2} + \frac{X_{SiO_2}}{n_{SiO_2}^2 + 2}\right),$$

where $n$ is the refractive index of the film, $X_{Si}$, $X_{SiO_2}$ and $n_{Si}$, $n_{SiO_2}$ are the volume fractions and refractive indices of components Si and SiO$_2$, respectively.

Figure 3. Value of $x$ in SiO$_x$ vs. refractive index

According to the assumption, using the Lorentz-Lorenz formula, the values of $x$ in SiO$_x$ (Fig.3) were calculated and the effect of temperature was determined (Fig. 2,b, blue colour). However, for the adequacy of a stoichiometric calculation and subsequent analysis of the obtained results, verification of the assumption is required. Investigations of the elemental composition and structure of films should be carried out.

4. Conclusion
Thin silicon oxide films of less than 50 nm thick were fabricated. The influence of deposition temperature on morphology (grain size and roughness) and refractive index in the range of 150–450°C has been studied. Atomic force microscopy, scanning electron microscopy and laser ellipsometry were
used for measuring. The grain size and roughness decreased from 200-250 nm to 20-40 nm and from 2.4 to 0.2 nm with a rise of temperature. At the same time, the refractive index (1.52-1.96) exceeded the characteristic value for stoichiometric oxide and increased with temperature. It was assumed that temperature affects the structure and composition of SiO$_x$ films and tends to saturate with silicon at high temperatures. The values of x in SiO$_x$ have been found to decrease with temperature from 1.9 to 1.2.

The obtained non-stoichiometric films of silicon oxide can be considered for use in silicon solar cells as passivation and antireflection layers. Future directions of research are mentioned.

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