Research Article

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Structure and optical properties of TiO$_2$ thin films deposited by ALD method

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Abstract: This paper presents the results of study on titanium dioxide thin films prepared by atomic layer deposition method on a silicon substrate. The changes of surface morphology have been observed in topographic images performed with the atomic force microscope (AFM) and scanning electron microscope (SEM). Obtained roughness parameters have been calculated with XEI Park Systems software. Qualitative studies of chemical composition were also performed using the energy dispersive spectrometer (EDS). The structure of titanium dioxide was investigated by X-ray crystallography. A variety of crystalline TiO$_2$ was also confirmed by using the Raman spectrometer. The optical reflection spectra have been measured with UV-Vis spectrophotometry.

Keywords: photovoltaic; silicon solar cell; atomic layer deposition; antireflection coating

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1 Introduction

The possibility of the development of photovoltaics is strongly dependent on the efficiency of silicon solar cells, which determines the price of electricity produced from them. One of the factors affecting the efficiency of the silicon solar cell is the reduction of light reflection from its front surface. The effect of minimizing the reflectance of light is achieved, among others, by depositing an antireflection coating. The most popular antireflection coating used in photovoltaics are: SiO$_2$, a-SiNx:H, TiO$_2$, a-Si:C:H, ZnS, Ta$_2$O$_5$, Sn$_x$O$_y$, SiN$_x$, MgF$_2$ [1–12]. Titanium dioxide is an inorganic compound, occurs naturally in three polymorphic forms: as the rutile and anatase minerals with a tetragonal structure and brookite with an orthorhombic structure. The last two forms pass in the rutile (most durable) above the 800-900°C temperature. Photoelectrochemical properties of TiO$_2$ are associated with the absorption of solar radiation. Titanium dioxide is characterized by high absorption in the UV range and up to a few percent absorption of visible VIS radiation. In order to increase the range of visible light absorption, which is essential in solar cells and in photodegradation of water, research on the modification of its properties is in progress [2–4, 13]. Methods of deposition have a significant impact on the development of antireflection coatings. Among many techniques that increase the usefulness of the surface of photovoltaic materials, chemical and physical deposition methods play an important role in industrial practice. One of the depositing methods characterized by dynamic development is the atomic layer deposition (ALD) technique. By using highly reactive precursors, which react immediately with the substrate to form a monolayer and prevent further reactions, each cycle results in an increase in the thickness of the layer with a strictly defined value. The most commonly used precursors for the preparation of TiO$_2$ are TiCl$_4$, Ti(OCH$_2$CH$_3$)$_2$ and Ti(OCH(CH$_3$)$_2$)$_2$, which react with H$_2$O. In the process of growth of metal oxides, in which H$_2$O is used as an oxygen precursor, hydroxyl groups can be formed on the surface of substrate during the oxygen precursor pulse. Thus, the adsorbed metal precursor may react with surface hydroxyl groups and release some ligands in this reaction [14, 15].

2 Materials and methodology

The TiO$_2$ thin films have been deposited by an atomic layer deposition using an R-200 system from Picosun company. As a precursor of TiO$_2$, titanium tetrachloride (TiCl$_4$) has been used, which reacted with water enabling the deposition of the thin films. The 2D and 3D topographic 2×2µm images were performed with XE-100 Park Systems.
Figure 1: AFM 2D and 3D images of the surface topography of TiO$_2$ thin films deposited on glass substrate at 300°C after 630 (a-b), 830 (c-d) and 1030 cycles (e-f)
Structure and optical properties of TiO$_2$ thin films

Figures 1-3 illustrate the surface topography and composition of TiO$_2$ thin films deposited on a silicon substrate at 300°C. The films were characterized using various techniques, including atomic force microscopy (AFM) and scanning electron microscopy (SEM), to determine the RMS and Ra coefficient values. X-ray crystallography, energy dispersive X-ray spectroscopy (EDS), and Raman spectroscopy were used to investigate the crystalline structure of the TiO$_2$ films. UV-Vis spectrometry was employed to examine the optical properties of the films.

3 Results and discussion

The films deposited at 300°C by ALD on a silicon substrate have been analyzed, based on the number of deposition cycles. It has been found that repetitive aggregations of atoms have a similar structure in the films, as observed in the images and spectra.
The morphology of TiO$_2$ layers deposited by ALD is homogeneous and uniform (Figures 2a-c). The surface doesn’t show any discontinuities, cracks, pores and defects. The SEM research confirmed the AFM results that the TiO$_2$ thin films have a granular structure and with increasing number of cycles of deposition the aggregations of atoms take milder forms. The microanalysis of the as-prepared thin films has been carried out by the energy dispersive X-ray spectroscopy. In Figure 2d is shown the EDS spectra of thin film of ALD TiO$_2$. There are observed peaks at about 0.5 and 4.5 keV in these EDS spectra’s, which are assigned to oxygen and titanium respectively. Such an analysis can be confirmed by the presence of titanium dioxide.

The structural studies were implemented by using X-ray method (Figure 3). Registered diffraction pattern of titanium dioxide thin film shows the reflection characteristic for the titanium dioxide - a variety of anatase (coming from the sample). Further structural testing of deposited thin films is made by using a Via Reflex Raman spectrometer equipped with an Ar ion laser with a 514.5 nm length. Spectral range is 150 – 3200 cm$^{-1}$ (Figure 4). Using confocal microscope images, the data point on the sample was presented. The results, processed by the WiRE 3.1 program, determining the structure of the deposited thin films as an anatase, confirmed earlier research done by the X-ray crystallography.

The reflection of bare silicon compared with different cycles of TiO$_2$ is shown in Figure 5. The best results were
obtained for silicon with 830 and 1030 cycles of TiO$_2$. The light reflection was minimized below 10% in the range of 200 nm to 600 nm.

4 Conclusions

The results and their analysis show that the atomic layer deposition method allows the deposition of homogenous thin films of TiO$_2$ with the desired geometric characteristics and good optical properties. The irregularities on the surface of the deposited layers do not exceed 4 nm and the light reflection in a wide range does not exceed 10% without texturing the silicon surface.

Considering the optimization of the antireflection coating production, it is preferable to deposit 830 of ALD cycles. Further deposition does not significantly affect the reduction of light reflection. Increasing the thickness of the coating may lead to increased absorption of light in the layer and this can lead to a decrease of solar cells efficiency. However, the technology of atomic layer deposition makes titanium dioxide thin films a good potential material for optics, optoelectronics and photovoltaics.

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References


