Research of influence of laser annealing parameters on structural and morphological properties of TiO$_2$ thin films

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Abstract. The TiO$_2$ thin films are widely used as a transparent layer of n-type conductivity in the perovskite solar cells. Nanocrystalline TiO$_2$ films were deposited on fluorine-doped tin oxide (FTO) coated glass substrates by centrifugation and subsequent laser annealing with a wavelength of 1064 nm. The influence of laser annealing on the grain size in the TiO$_2$ film and spinning rate on the thickness of TiO$_2$ film was investigated. It was found that the grain size in the TiO$_2$ film ranges from 17 nm to 64 nm by using the laser annealing power of 30-70 W. The thickness of TiO$_2$ film changes in range from 72 nm to 124 nm depending on the spinning rate. The optimum parameters of TiO$_2$ thin film formed by laser annealing can increase the perovskite solar cell efficiency.

1. Introduction
Recently, nanocrystalline titanium dioxide thin films (TiO$_2$) have been intensively investigated, due to the perspective use of this material in the field of solar energy, photocatalysis, etc. The compact (non-porous) TiO$_2$ films are widely used as a transparent material of n-type conductivity and hole blocking layer in the perovskite solar cells. These cells are the most researched and promising because their energy conversion efficiency has rapidly increased from 3.8% to 19.3% within the last 5 years. The TiO$_2$ films’ formation with a low number of pores (or cracks) of the nanometer size is important for perovskite solar cells. It allows to decrease the recombination losses and increase the energy conversion efficiency of solar cells. In general, the thickness of a compact TiO$_2$ film formed by spin-coating is within 50 to 150 nm [1, 2].

The method of compact TiO$_2$ thin film formation for application in the perovskite solar cells is described in this work. It includes spin-coating of a TiO$_2$ precursor and subsequent laser annealing with a wavelength of 1064 nm. The research of laser annealing power and the influence of spinning rate on structural and morphological properties of TiO$_2$ thin films (grain size in the TiO$_2$ film and its thickness) were conducted.

Laser annealing is a promising technology that finds more and more applications in micro- and nanoelectronics. Laser annealing can improve the degree of crystallinity, lower surface roughness, enlarge grain size, increase uniformity, reduce recombination centers, and also increase compactness (continuity) [3]. Thus, effectively selected parameters of laser radiation can improve solar cell performance.
2. Experiment
The uniform compact TiO₂ films were deposited on fluorine-doped tin oxide (FTO, Sigma-Aldrich) coated glass substrates by spin-coating (SpinNXG-P1, Apex) of 0.15 M titanium diisopropoxide bis (acetylacetonate) (Sigma-Aldrich) solution in ethanol at 3000 rpm for 30 s. After this, the films were heated in oven at 120°C for 5 min and then annealed by laser for crystallization [4-7].

Laser annealing was carried out with the LIMO 100-532/1064 system. It consists of a high-power infrared laser with a wavelength of 1064 nm (Nd:YAG laser, 110 W), a two-coordinate scanner, a heating element and a control computer. In this process, the laser beam was moved along the TiO₂ film surface with the help of the scanner (XY galvanometers). The film was annealed by laser radiation at the power of 30, 50 and 70 W for a period of 60-90 s. It corresponds to the surface temperature of 400-540°C [6, 7]. The crystalline phase of TiO₂ anatase is more preferable than the rutile one. The electron transport is faster in the anatase phase. However, the anatase phase irreversibly transforms into the rutile phase at temperatures above 500 °C [2, 8]. It is necessary to note that a glass substrate with TiO₂ film was preheated to 250-300°C in order to prevent thermal shock during the laser annealing.

For the research of the influence of spinning rate (2000-5000 rpm for 30 seconds) on the thickness of nanocrystalline TiO₂ films, a laser annealing process was carried out at radiation power of 50 W, which corresponds to the surface temperature of the TiO₂ film of about 470°C [6, 7].

The surface morphology and thickness of the TiO₂ film was studied by scanning electron microscopy (SEM) using a Nova Nanolab 600 (FEI Company) microscope. The optical transmission spectra of the TiO₂ film were determined by a SF-26 spectrophotometer in the wavelength range of 200-1100 nm.

3. Results and discussion
Figure 1 shows the surface morphology of TiO₂ films at varying laser annealing power (30, 50 and 70 W).

![SEM images of the surface morphology of TiO₂ films.](image)
It can be seen that increasing laser annealing power leads to an enlargement of TiO$_2$ grain size. At the laser power of 30 W, the average grain size was 17 nm. At 50 W, the grain size was 23 nm. At 70 W, it was about 64 nm. We can observe the significant growth of grain size and increase of the relief (due to coalescence [2, 9]) at the laser power of 70 W.

Figure 2 shows SEM images of cross-sectional TiO$_2$ films at varying spinning rates (2000, 3000 and 5000 rpm) and the laser annealing power of 50 W. It was found that the thickness of TiO$_2$ compact film ranges from 72 nm to 124 nm, depending on the spinning rate.

![Figure 2. SEM images of cross-sectional TiO$_2$ films on FTO/glass substrates.](image)

The thickness of compact TiO$_2$ film has a significant effect on the solar cell performance, in particular, on its energy conversion efficiency [1, 10]. The thicker the TiO$_2$ film (more than 100 nm), the higher the resistance to charge transport, because electrons must pass a larger distance from the perovskite film to FTO. Also, a thicker compact TiO$_2$ film reduces the light absorption by the perovskite film. In turn, a decrease of the TiO$_2$ film thickness (less than 50 nm) can lead to the incomplete coating of FTO, which can result in the undesired contact of the perovskite film with FTO and also a significant increase of charge carrier recombination. Therefore, the compact (non-porous) TiO$_2$ film with optimized thickness allows to achieve a higher energy conversion efficiency.

The studies of SEM images (Figure 2) showed that some pores can be formed in the TiO$_2$ thin films (thickness less than 80 nm), whereas cracks on the surface can be formed in thicker films (thickness greater than 120 nm). Thus, the optimum thickness of compact TiO$_2$ film is near 100 nm, at which conditions the film surface is the most uniform.

Figure 3 shows the transmission spectra of the TiO$_2$ film deposited on FTO-coating glass substrate by spin-coating at 3000 rpm and laser annealing power of 50 W. The average transmittance of about 83% in the visible and near-infrared region with a sharp absorption edge at 350 nm was observed. The excellent steepness of the optical absorption edge gives clear evidence of the high quality of compact
TiO$_2$ film. Moreover, the relatively high transmission of TiO$_2$ film indicates a low surface roughness and good homogeneity.

![Graph](image)

**Figure 3.** Transmission spectra of the TiO$_2$ film on FTO/glass substrate.

### 4. Conclusion

The method of compact TiO$_2$ thin film formation with the use of spin-coating and infrared laser annealing for application in the perovskite solar cells is presented. Laser annealing leads to a significant reduction of time (up to several minutes) and to a lower substrate temperature (250-300 °C) for crystallization of TiO$_2$ in anatase phase, in comparison with annealing in a muffle furnace (which requires up to 3 hours at temperatures of 400-500°C [2, 7]).

The influence of laser annealing and spin-coating parameters on the structural and morphological properties of TiO$_2$ thin films was researched. It was found that the grain size in the TiO$_2$ film ranges from 17 nm to 64 nm at the laser annealing power of 30-70 W. The thickness of TiO$_2$ film changes in the range from 72 nm to 124 nm, depending on the spinning rate, which varies from 2000 to 5000 rpm. The analysis of SEM images shows that the optimum thickness of compact TiO$_2$ film is about 100 nm. Thus, the optimum structural and morphological properties of TiO$_2$ thin film using laser annealing can increase the perovskite solar cell energy conversion efficiency.

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