

EFFECT OF TiO₂ ANNEALING CONDITIONS ON THE PERFORMANCE OF ANTIMONY SELENIDE THIN FILM SOLAR CELL

Summary

The thesis work is focused on the post-deposition treatment (PDT) of the TiO₂ buffer layer for Sb₂Se₃ solar cells. The thesis aimed to study the impact of post-deposition thermal treatment conditions on the properties of TiO₂ thin films and TiO₂/Sb₂Se₃ solar cells and hypothesize about the effects of the TiO₂ treatment on solar cell efficiency.

The thesis is composed of three chapters. Following the Introduction, Chapter 1, "Theoretical background", provides a short review of the history of photovoltaics, a general overview of Sb₂Se₃ solar cells, and the role of the TiO₂ buffer layer in them (section 1.1). In sections 1.2-1.4 were described the involved methods of solar cell deposition, material characterization, and device characterization, respectively. The chapter ends with a summary and the formulation of the aims of the study. Chapter 2, "Experimental part", describes the methods of thin-film processing, as well as those of device fabrication. It also includes techniques used to characterize the properties of thin films and solar cells. Chapter 3 comprises three sections and includes initial experimental results and a discussion of those results. The first section describes the morphological properties of the TiO₂ film, deposited atop glass/FTO substrate by ultrasonic spray pyrolysis (USP) and consequently annealed in vacuum at the different procedures (120-450 °C). Half of the samples also experienced additional annealing in the air at 450 °C. The second section depicts the morphology of the above-deposited Sb₂Se₃ layer. The third chapter focuses on the optoelectronic characteristics of the resulting glass/FTO/TiO₂/Sb₂Se₃/Au solar cells and the dependencies of solar cell efficiency on the conditions of TiO₂ annealing. Also, the third section includes the XPS analysis of variously treated TiO₂ film.

TiO₂ thin films were prepared by ultrasonic spray pyrolysis. After it, they experienced different post-deposition treatment procedures, one-step, and two-step. The one-step procedure included only annealing in a vacuum at temperatures from 160 °C to 450 °C and labeled "Vac". In the two-step procedure, labeled "Vac+Air", samples were placed in the air furnace after the above-described vacuum annealing, where they were annealed at 450 °C. Solar cells were accomplished by the antimony selenide, deposited via close-spaced sublimation (CSS). Scanning electron microscopy, X-ray diffraction analysis, ultraviolet-visible spectroscopy, and X-ray photoelectron spectroscopy were used to study materials, whereas

current-voltage (J-V) and external quantum efficiency measurements (EQE) were used for cell characterization.

TiO₂ thin films revealed that crystallite size depended upon the temperature of vacuum annealing. The higher was the temperature, the larger the crystallites were (an increase from 20-30 to 50-60 nm), and the more homogeneous films were observed. Morphological properties of Sb₂Se₃ film, deposited atop of differently annealed glass/FTO/TiO₂, have shown a weak trend of having more oriented towards (221) and (211) directions crystallites at higher temperatures. In terms of structural properties, no significant difference between Vac and Vac+Air procedures was found. However, the device efficiencies were strongly affected by the TiO₂ annealing parameters. All electric parameters of solar cells with Vac-annealed TiO₂ buffer were overwhelmed by their counterparts with Vac+Air annealed buffers. The highest efficiency of 3.96% was achieved with the Vac160+Air TiO₂ annealing procedure.

Two significant trends were revealed: the high temperature of vacuum annealing of TiO₂ corresponds to the lower efficiency of the solar cell; air annealing, applied after vacuum annealing, increases the efficiency of the solar cell. These trends were associated with the influence of oxygen incorporation during the air annealing (could be recognized as an oxygen-rich environment) and the efficiency of this incorporation. A less crystalline film can absorb more oxygen at the step of air annealing. Low-temperature annealed TiO₂ remained less crystalline and, therefore, went through more significant recrystallization during air annealing. So, low-temperature vacuum annealing provided the most suitable conditions for consequent oxygen incorporation. XPS measurement has shown that the surface of all glass/FTO/TiO₂ samples included harmful remains of organic residuals used in USP deposition. With every following step of post-deposition treatment, the carbon content decreased, which could be a reason for the higher efficiency of Vac+Air samples.

Altogether, the research highlighted the importance of the post-deposition TiO₂ treatment. It clarified the role of different PDT steps to control the organic content and oxygen incorporation, which were both shown a significant impact on the TiO₂/Sb₂Se₃ solar cell performance.