Influence of thermal annealing and Cu_xS secondary phase on the electrical and thermoelectrical properties of Cu_2ZnSnS_4 nanocrystals

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Among the alternative energy sources, which attract attention of the researchers, one of the most promising is solar energy. But despite the great achievements in this field, one of the main issues is reduction of solar panel efficiency due to overheating. One of the approaches of solar panel cooling and using the usually waste heat to create additional electrical energy is hybrid photovoltaic-thermoelectric devices. This is why materials with thermoelectric and photovoltaic properties gain popularity in recent years. Research especially focuses on materials that are cheap, easy to produce, and environmentally friendly. One of such materials is the Cu_2ZnSnS_4 (CZTS) and related compounds. Owing to its good absorption properties and a bandgap around 1.3 eV, this material is promising for photovoltaic applications. The ability to produce CZTS nanocrystals (NCs) by „green" synthesis in colloidal solutions makes it even more attractive for use in so-called third generation photovoltaics. In addition, recent studies show good thermoelectric properties for CZTS-like materials. This fact makes CZTS NCs very promising for hybrid photovoltaic-thermoelectric devices and can enable an improved overall conversion efficiency.

One of the most common methods to tune the properties of CZTS materials is thermal annealing, which allows not only the crystallinity to be improved but also transitions between disordered and ordered kesterite structures to be induced. However, thermal annealing can cause changes in the NC films, which are deteriorating the photovoltaic performance, namely the appearing of Cu_xS secondary phases.

Here, we investigate the effect of thermal annealing up to 350 °C on spin-coated thin films of CZTS NCs obtained by "green" colloidal synthesis. In the temperature range up to 200 °C, despite improved surface morphology, as confirmed by atomic force microscopy, and crystalline quality, as confirmed by Raman spectroscopy, the electrical conductivity of CZTS NCs films is very low and does not allow us to determine the Seebeck coefficient. At the same time, the appearance of the Cu_xS secondary phase at annealing temperatures of 250 °C and 300 °C provides a significant improvement in the conductivity, making these films suitable for thermoelectric measurements. The change of Seebeck coefficient and conductivity with the content of Cu_xS phase is revealed. This lets us conclude that thermoelectrical properties of the films obtained are predominantly determined by the Cu_xS phase. Therefore, being deteriorative for photovoltaic effect, the Cu_xS phase can be beneficial for good thermoelectrical performance of thin films based on CZTS NCs.