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Raman and thermoelectrical study of thermally and flash lamp annealed Cu_2ZnSnS_4 nanocrystals

The increasing demand for electrical energy has led to searching for new, alternative energy sources as well as to improving existing ones. Solar energy is one of the most promising alternative energy sources. There are huge progress and developments in this field during the last decade, but one of the main issues that should be overcome to increase lifetime and efficiency of solar panels is overheating. Around 70% of the absorbed solar energy are converted to waste heat requiring additional efforts for proper cooling systems. One of the approaches to solar panel cooling and conversion of the waste heat into additional electrical energy is hybrid photovoltaic-thermoelectric devices. Accordingly, materials with both good thermoelectric and photovoltaic properties have gained popularity in recent years. One of such materials is Cu_2ZnSnS_4 (CZTS) and related compounds. It is quite promising due to the fact that all of the constituent elements are earth abundant and environmentally friendly. The CZTS-like compounds have been intensively studied for photovoltaic applications and 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 [1]. In addition, recent studies show good thermoelectric properties for CZTS-like materials [2]. This fact makes CZTS NCs very promising for hybrid photovoltaic-thermoelectric devices and can enable an improved overall energy conversion efficiency. In order to improve the properties of CZTS NCs in terms of crystallinity after their synthesis and thin film deposition, one of the most common methods is thermal annealing. However, thermal annealing can cause changes in the NC films, which are deteriorating the photovoltaic performance, namely the appearance of Cu_xS secondary phases. In addition, thermal annealing usually requires extended time durations of tens of minutes and inert atmosphere to avoid oxidation. Another technique proved to be very promising for CZTS NCs treatment is flash lamp annealing (FLA). Due to duration of about 18 ms and tuneable energy densities, it is possible to improve the crystal quality and avoid formation of oxides and secondary phases even in ambient atmosphere [3].

Here, using Raman spectroscopy we investigated and compared the effects of thermal annealing up to 350 °C and FLA treatment up to 12 J/cm^2 on spin-coated thin films of CZTS NCs obtained by "green" colloidal synthesis. In the temperature range up to 200 °C Raman spectroscopy provides clear evidence of improved crystalline quality, while atomic force microscopy additionally reveals improved surface morphology. However, the electrical conductivity of CZTS NCs films remains very low and not sufficient for proper Seebeck coefficient measurements. At annealing temperatures of 250 °C and 300 °C, Raman spectroscopy shows the appearance of a Cu_xS secondary phase and a pronounced shift of main CZTS NCs characteristic feature. A clear correlation between the Raman spectra and the thermoelectrical properties for thermally annealed samples is observed. Raman spectra for FLA treated samples, however, reveal only slight improvement of crystallinity in the whole range of studied energy densities and no significant changes in thermoelectrical properties [4]. Using higher FLA energy densities (> 15 J/cm^2) leads to the appearance of other secondary phases than Cu_xS or even full decomposition of the CZTS NCs. In such a way, Raman spectroscopy illuminates the differences between the two distinct annealing techniques applied to CZTS NCs.

[1] N. Shah, A.A. Shah, P.K. Leung, S. Khan, K. Sun, X. Zhu, Q. Liao, A *Processes*., 11(6) (2023),1852

[2] E. Isotta, N.M. Pugno, P. Scardi, Powder Diffr., 34 (2019), S42–S47.

[3] Ye.Havryliuk, O. Selyshchev, M. Valakh, A. Raevskaya, O. Stroyuk, C. Schmidt, V. Dzhagan, D.R.T. Zahn, Beilstein Journal of Nanotechnology, 10 (2019), 222–227

[4] Ye. Havryliuk, V. Dzhagan, A. Karnaukhov, O. Selyshchev, J. Hann, D.R.T. Zahn, Nanomaterials, 11 (2023), 1775