Nanoplasmonics and surface enhanced spectroscopy

Raman spectroscopy of nanocrystalline Cu$_2$ZnSnS$_4$ thin films obtained by pulsed spray pyrolysis

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The quaternary semiconductor compound Cu$_2$ZnSnS$_4$ (CZTS) is an excellent alternative material to the traditional chalcopyrite CuIn$_{1-x}$Ga$_x$Se$_2$ (CIGS) and CdTe ones for applications in the thin-film solar cells due to its relatively low toxicity and the earth abundance of its constituent elements. Moreover, CZTS possesses the band-gap around 1.5 eV and optical absorption coefficient around $10^5$ cm$^{-1}$, which make this compound particularly suited for the design of solar cells absorber layers. Among the different techniques, the pulsed spray pyrolysis is an especially simple, low-cost, vacuum-free and highly scalable method to obtain CZTS layers.

The sprayed CZTS thin films were deposited using an aqueous solution containing CuCl$_2$·2H$_2$O (0.02 M), ZnCl$_2$ (0.01 M), SnCl$_2$·2H$_2$O (0.015 M) and SC(NH$_2$)$_2$ (0.1 M) at the temperature substrate of 400 °C with the different values of starting solution volume per sample (2 ml, 3 ml, 4 ml, 5 ml).

Because of CZTS is a quaternary compound, it is difficult to avoid the presence secondary phases during the growth process, in particular, using the chemical techniques. For this reason, herein, it was carried out the detailed phase analysis of CZTS thin films using Raman spectroscopy with three different lasers (green, Ar+, 514.5 nm; red, He-Ne, 632.8 nm; UV, He-Cd, 325 nm) as excitation sources to obtain more information about undesirable phases.

The spectra of all samples are characterized by the presence of the peaks at about 287 cm$^{-1}$, 337 cm$^{-1}$, 670 cm$^{-1}$. These peaks were attributed to the second, main and third A symmetry mode of the kesterite-CZTS phase, respectively. In order to determine secondary phases, such as ZnS and Cu$_2$SnS$_3$ (CTS), we carried out Raman experiments with various excitation sources. Using the UV laser we found the peak of ZnO mode, which could be caused by the conditions of layer depositions. No secondary phases were observed.

From the results of Raman spectroscopy using the different lasers as excitation sources for the scrupulous studying of the secondary phases in the CZTS, it is concluded that kesterite CZTS films with a partly appearing of ZnO are obtained using the pulsed spray pyrolysis method.