Spray pyrolysis deposition and optical properties of Cu$_2$ZnSnS$_4$ thin films

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Cu$_2$ZnSnS$_4$ (CZTS) thin films with near to optimal values of the band gap ~ 1.5 eV and the absorption coefficient ($>10^4$ cm$^{-1}$) in the visible range for the fabrication of high efficient solar cells are of great interest for research and application. CZTS solar cells are a low-cost alternative of the expensive CuInS$_2$ (CIS) solar cells. The chemical elements of the CZTS thin films are not toxic and widely available. The fabrication process of the CZTS-based solar cells is usually carried out by the sulfurization of the Cu-Zn-Sn thin films [1]. However, the application of low-cost and simple, from the technological point of view, spray pyrolysis method can considerably decrease the final cost of the solar cells.

For the deposition of the Cu$_2$ZnSnS$_4$ thin film the 0.1 M aqueous solution of copper chloride CuCl$_2$·2H$_2$O, zinc chloride, ZnCl$_2$, tin tetrachloride SnCl$_4$·5H$_2$O and thiourea (NH$_2$)$_2$CS were used. The solutions were mixed before the spray pyrolysis process in the appropriate volume ratios and consistency. As usually, CZTS thin films with the p-type of conductivity and specific resistance of $\rho = 1\div10$ Ohm·cm are used in solar cells. Therefore, the elevated sulfur composition in comparison to the stoichiometric composition of the CZTS thin films should be reached (CuCl$_2$·2H$_2$O : ZnCl$_2$ : SnCl$_4$·5H$_2$O : (NH$_2$)$_2$CS = 2.1 : 1 : 1 : 10). The spraying of the solutions was carried out with the velocity of 3 ml/min onto heated glass substrates. The best structural perfection and adhesion was obtained at the substrate temperature $T \approx 290$ °C. Depending on the deposition time, the CZTS films were 0.2-1 um thick.

The fig. 1 shows the spectral distribution of the transmittance $T$ and absorption ($\alpha h \nu$)$^2 = f(h \nu)$ coefficients of the Cu$_2$ZnSnS$_4$ thin films. The value of the band gap $E_g = 1.54$ eV of the thin films was determined.