Physical properties of Cu$_2$SnS$_3$ thin films, prepared by the spray pyrolysis method

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Cu$_2$SnS$_3$ (CTS) thin films possess optimal properties for photovoltaics: high value of the absorption coefficient $\sim 10^4$ cm$^{-1}$ and the band gap in the range from 0.96 to 1.6 eV depending on the crystalline phase. The spray pyrolysis deposition of the CTS films is a low cost and reproducible method [1].

The CTS thin films were deposited by the spray pyrolysis method from the following aqueous solutions: 0.1 M CuCl$_2$·2H$_2$O, 0.1 M SnCl$_4$·5H$_2$O and 0.1 M (NH$_2$)$_2$CS which were mixed in the appropriative ratio. The volume ratio of the solutions was CuCl$_2$·2H$_2$O : SnCl$_4$·5H$_2$O : (NH$_2$)$_2$CS = 2 : 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.

The amount of thiourea, as a source of sulfur, which is supplied to the substrates during the spray pyrolysis was increased to 10 volume parts. The sulfur vacancies in the Cu$_2$SnS$_3$ compound provide the electron-type of conductivity which is favorable for the majority of solar cells structures. Basing on our experimental results we established that the optimal sulfur content in Cu$_2$SnS$_3$ thin films was reached at the volume ratio of the mixed solution SnCl$_4$·5H$_2$O : (NH$_2$)$_2$CS 1 : 10. The electrical properties of the thin films with the low content of sulfur are very sensitive to the thermal treatment in the range of temperatures 250°C÷500°C. The increase of the conductivity of the n-type CTS film after thermal treatment resulted from the structural improvement and the decrease of the effect of the grain boundaries. The annealing increases the density of sulfur vacancies and thus increases the electron concentration and electrical conductivity. In the case of the thin film prepared from the solution with volume ratio CuCl$_2$·2H$_2$O : SnCl$_4$·5H$_2$O : (NH$_2$)$_2$CS = 2 : 1 : 10 the thermal treatment negligibly affects their electrical properties.

The band gap of the Cu$_2$SnS$_3$ thin films, determined from the optical measurements, was equal to 1.89 eV. This value mainly results from the high concentration of charge carriers (the specific resistance of the as-deposited films was $\rho \sim 10^{-2}$ Ohm·cm). The low value of the reflection coefficient $R \sim 7\%$ in the visible range of spectrum is caused by the roughness of surface of the thin films under investigation. The average thickness of the thin films was 0.7-0.9 um. Subject to the increase of the electrical resistivity of the films after annealing it will be possible to shift the location of the self absorption edge toward the photon energy of 1.5 eV that will be optimal for their application as an absorber layer in heterojunction solar cells.