# Effect of Sn doping in $CuGaS_2$ thin films deposited by chemical spray pyrolysis

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**[Introduction]** Engineering of sub-bandgap using intermediate states in a wide bandgap semiconductor is promising for high-efficiency photovoltaic technology. The direct bandgap of 2.46 eV in the green part of the visible spectrum attracts the chalcopyrite $CuGaS_2$ (CGS) as a host for Intermediate Band solar cell applications. Pristine and tin (Sn) doped CGS ($CuGa_{1-x}Sn_xS_2$) crystalline thin films were deposited using chemical spray pyrolysis method, and their structural and optical properties are characterized.

**[Experimental]** $CuGa_{1-x}Sn_xS_2$ were subjected to XRD, DRS absorption spectroscopy, and X-ray photoelectron spectroscopy (XPS) measurements.

**[Results and discussion]** The measured XRD diffraction peaks of the thin films revealed chalcopyrite tetragonal structure without any presence of secondary phases ($Cu_2S$, CuO, $SnO_2$, and $Ga_2S_3$). The substitutional doping of Sn is evidenced by a lower 2θ angle shift of XRD peaks due to the larger atomic radius of Sn (0.69 Å) than that of Ga (0.62 Å). The Sn doping has affected the sub-bandgap absorption spectra and bandgaps of CGS films. Apart from primary strong absorbance edges at 490 nm (Fig.1), strong shoulder absorbance edges are also observed in the NIR region between 1000 to 1600 nm for the Sn doped films, and Tauc-plot analyses revealed below-bandgap responses at around 1.25 eV while the host bandgaps were estimated at 2.49 eV.

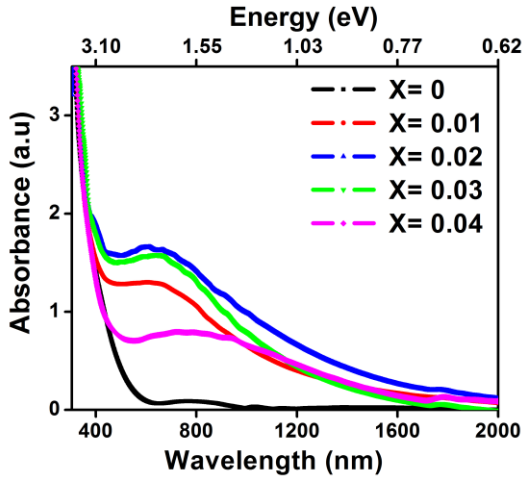


*Fig.1Absorbance spectra of $CuGa_{1-x}Sn_xS_2$ films*

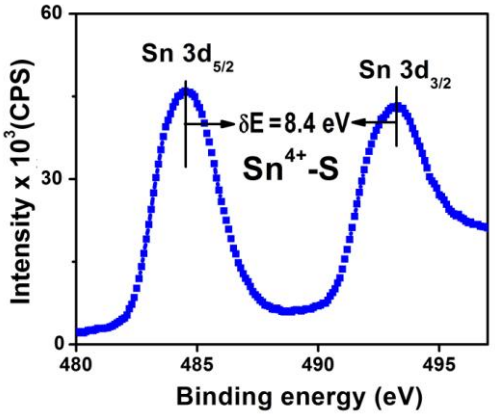


*Fig.2 Sn 3d XPS spectra of $CuGa_{0.97}Sn_{0.03}S_2$*

This could be due to the formation of sub-bandgap, in between the conduction band (CB) and valence band (VB) at 1.25 eV. The valence state of Sn was analyzed by XPS has shown in Fig.2, and our analyses revealed that tetravalent Sn atom ($Sn^{4+}$) is replacing the trivalent Ga atom in the host. The origin of the sub-bandgap at 1.25 eV could be connected to the extra electron state generating from the $Sn^{4+}$ state substituting the $Ga^{3+}$ sites.

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