Revealing the incorporation sites and local structure of nickel and selenium in doped copper iodide thin films

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Copper iodide (CuI) is a promising p-type semiconductor for transparent electronic applications such as solar cells, flat panel displays, and LEDs. The electrical properties of CuI can be tailored by substituting it, for example, with nickel (Ni) or selenium (Se) [1,2], yet the specific incorporation sites and mechanisms of these elements within the CuI matrix are not fully understood. This study presents an investigation of polycrystalline CuI thin films with varying selenium and nickel concentrations, deposited by pulsed laser deposition (PLD) and reactive co-sputtering on glass substrates[3]. CuI:Ni thin films (1–30 at% Ni) and CuI:Se thin films (0.4–3.8 at% Se) were prepared and capped with 150 nm and 200 nm Al_2O_3 layers, respectively, to prevent oxidation. X-ray Absorption Spectroscopy (XAS) was performed at ~10 K at the Cu, Se, and Ni K-edges to investigate the local structure of Ni and Se in the CuI matrix.

For the CuI:Ni thin films, the near edge structure and the extended X-ray absorption fine structure (EXAFS) at the Cu K-edge indicate potential copper oxidation[4]. These effects diminish with increasing Ni concentration. Preliminary results from Ni K-edge EXAFS analysis reveal that Ni is coordinated by both I and O atoms, indicating different bonding environments. This is supported by microstructural studies, which show phase separation and the formation of secondary Ni-containing phases, such as NiI_2 and $NiI_2(H_2O)_6$, especially at high Ni content[3]. These secondary phases complicate the interpretation of the Ni local structure, and further detailed EXAFS analysis at the Ni K-edge is currently underway to clarify these findings.

For the CuI:Se thin films, EXAFS fitting at the Cu K-edge reveals only a slight increase in the Cu–I bond length with increasing Se content, suggesting that Se doping up to 3.8 at% induces only minor changes in the local Cu environment. EXAFS analysis at the Se K-edge shows that Se atoms are predominantly coordinated by Cu, with no evidence of Se–Se bonding. The Se–Cu bond lengths remain nearly constant across doping levels, and structural disorder is low. These findings indicate that at the studied low concentrations, selenium incorporates uniformly, most likely substituting copper on lattice sites without significantly disrupting the CuI structure. Overall, these results highlight the contrasting behavior of the two dopants: while selenium has minimal structural impact at low concentrations, nickel appears to oxidize at low doping levels and potentially forms secondary phases at the higher concentrations.

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