

Disruption of the chemical environment and electronic structure in p-type Cu₂O films by alkaline doping

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Abstract

In this work we present an experimental and theoretical study of Cu₂O films doped with alkaline ions (Li⁺, Na⁺, K⁺, and Cs⁺) prepared by Cu anodization. By X-ray photoelectron spectroscopy we determined dopant incorporation as high as 1% for Na⁺. Three oxygen species were found: O²⁻ ions in the bulk cuprite structure, adsorbed OH⁻ and oxygen in hydroxylated dopant sites. The main effects of the alkaline doping on the optical properties were a reduction in the direct band gap and an approach of the acceptor level edge to the maximum of the valence band. Electrochemical tunneling microscopy experiments confirmed that the valence band maximum energy position is almost invariant. Additional electrochemical impedance, photoelectrochemical activity, and current sensing atomic force microscopy measurements showed an increase of the carrier density and electrical conductivity and a reduction in the photocurrent response with the dopant ion size. Urbach tail parameter analysis suggested additional interaction between copper vacancy derived states and dopant states. From first-principles calculations with the B3LYP hybrid functional on models for the alkaline-doped Cu₂O systems we determined that the main effect of the alkaline substitution of copper atoms consists of polarizing the O states, which causes a reduction in the insulating gap and splitting of the density of states just below the Fermi level. The nature of the oxygen-dopant interaction was also calculated: there is a net attractive interaction for Li-O, a slightly repulsive interaction for Na-O, and a net repulsive interaction for K-O and Cs-O. The repulsive interactions between K⁺ or Cs⁺ and O cause an accumulation of the dopant at the surface of the crystallites, whereas for Na⁺ and Li⁺ the doping ions are more uniformly distributed in the film bulk. It was found that the surface accumulation of K⁺ and Cs⁺ hinders vacancy diffusion and therefore blocks film growth, leading to a reduction of roughness and thickness as the ion size increases. © 2012 American Chemical Society.

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