

n-ZnO/Out-of-Stoichiometry p-CuCrO₂ Diodes for Efficient and Low-Cost Transparent Electronic Applications

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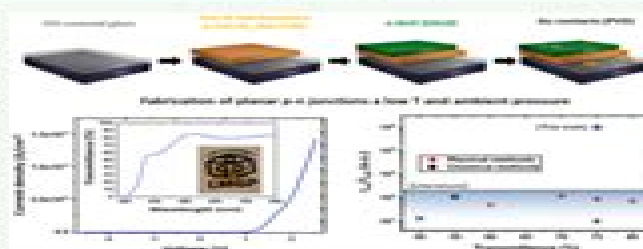
ABSTRACT: In this work, we present the synthesis of high-performance transparent diodes based on p-type out-of-stoichiometry CuCrO₂ and n-type ZnO thin films. The oxides were fabricated by scalable chemical deposition methods at low temperature and ambient pressure, without any further postdeposition annealing treatment. We report the optimization of the devices through the fine-tuning of the deposition parameters of the two layers, namely, the composition of the p-type semiconductor and the deposition temperature of the n-type counterpart, and their thorough characterization. UV–vis spectroscopy measurements highlighted the antireflection function of the ZnO layer, resulting in an optical transmittance of the junction above 75% in the visible range. In-depth XPS profile studies confirmed the absence of atomic diffusion between the different layers. The optimized junction between a nanocomposite Cu₂O + CuCrO₂ coupled with polycrystalline ZnO presents the highest rectification ratio reported in the literature for similar devices, with values greater than 10⁵ between −2.5 and +2.5 V. These extremely high performances are attributed to the formation of intraband levels, due to the stoichiometry variation of the CuCrO₂ phase and the low crystallinity of n-type ZnO. These results open many prospects for optoelectronics and are particularly promising for the transparent oxide electronics industry.

KEYWORDS: chemical deposition methods; transparent electronics; transparent p–n junctions; MOCVD; spatial ALD; thin films

1. INTRODUCTION

The production of transparent and performant all-oxide p–n junctions fabricated through low-cost processes represents one of the greatest challenges for the transparent electronics industry. The versatility of such devices, which can be applied as diodes, photodetectors,^{1,2} transparent solar cells,^{3–5} and light-emitting diodes,⁶ justifies the growing interest in this field. Diodes are especially important because can be considered the fundamental brick of more complex structures such as transistors. The electrical performances of a p–n junction are generally evaluated in terms of rectification ratio (I_{on}/I_{off}), defined as the ratio between the current measured at a positive voltage, and the one measured at the same negative bias.

Various metal oxides have been integrated as active and passive components in the previously mentioned devices. In this framework, one of the limiting factors is the lack of highly conductive p-type transparent conductive oxides (TCOs) and issues related to the low energy of the valence bands.⁷ Among promising p-type oxide semiconductor materials, Cu₂O⁸ and NiO⁹ were successfully applied in optoelectronic devices.^{10–12} Cu₂O is considered an important p-type TCO and its suitability in diodes has been already demonstrated.^{13–16} Previous works by our group¹⁰ highlighted the rectifying



behavior of the Cu₂O/ZnO structure, around $I_{on}/I_{off}(\pm 0.5 \text{ V}) \sim 3 \times 10^5$. However, the optical properties in the visible range are still far from optimal, with low values of average total transmittance, around 40%, over the visible range. Moreover, NiO-based devices were also reported,¹⁷ showing a rectifying characteristic in the order of 10⁵. However, this material is characterized by small carrier mobility.^{18,19} Therefore, more research efforts are required to obtain novel more efficient p-type TCOs.

CuCrO₂ is considered a promising p-type TCO for efficient p–n junctions due to its relatively high conductivity, around 1 Ω·cm for the stoichiometric compound,²⁰ and good transparency, around 70% in the visible range.²⁰ Various deposition methods have been used for its syntheses, such as pulsed laser deposition (PLD),²¹ RF magnetron sputtering,²² metal–organic chemical vapor deposition (MOCVD),^{23–25} spray

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