Materials Research Express

PAPER

Chemical modulation of valence band and photoelectric properties of epitaxial p-type infrared transparent conducting CuScO\textsubscript{2} thin films

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Keywords: delafossite, thin films, optical properties, electronic properties, p-CuScO\textsubscript{2}/n-In\textsubscript{2}O\textsubscript{3} heterojunctions

Abstract

Epitaxial p-type infrared transparent conducting oxide (TCO) CuScO\textsubscript{2} thin films were grown by polymer-assisted-deposition (PAD) method on a-plane sapphire substrates. Valence band of CuScO\textsubscript{2} (largely consisting of localized O-2p and Cu-3d orbitals) was chemically modified by annealing the films under O\textsubscript{2} presence with the goal to delocalize carrier holes. Films with c-axis orientation were obtained at 1\%–3\% O\textsubscript{2} pressure. The orientation relationship between CuScO\textsubscript{2} and the substrate was [3 1 0](0001)//a-Al\textsubscript{2}O\textsubscript{3}(1 2 1 0). Conduction processes followed the small-polaron hopping mechanism with the hopping activation energies in the 0.032–0.51 eV range (depending on the O\textsubscript{2} partial pressure). The films demonstrated p-type conductivity. The conductivity of CuScO\textsubscript{2} thin film annealed at 1\% O\textsubscript{2} partial pressure at room temperature was 22.1 S cm\textsuperscript{-1}. Films prepared with O\textsubscript{2} pressure equal to 1 and 3\% retained their optical transparency (>90 and >75\%, respectively) in the visible and mid-IR regions. To the best of our knowledge, these are the best performing p-type transparent conductive thin films produced by chemical methods. To demonstrate the practical usage of these films, we fabricated p-CuScO\textsubscript{2}/n-In\textsubscript{2}O\textsubscript{3} heterojunction diodes, which showed ~2.5 V threshold voltage, which agreed reasonably with CuScO\textsubscript{2} bandgap value. High optical transparency and electrical conductivity of these films make them very promising for optoelectronic applications, in which wide wavelength ranges, from visible to IR, are required.

1. Introduction

Transparent conducting oxides (TCOs) combine properties typically mutually exclusive: optical transparency and high electric conductivity. Thus, TCOs are crucial components for the optoelectronic industry as they are used for invisible security circuits, low-emissivity windows and transparent electrodes in solar cells and displays [1, 2]. Most common semiconducting TCOs (e.g. In\textsubscript{2}O\textsubscript{3}:Sn [3], ZnO:Al [4] and SnO\textsubscript{2}:F [5]) belong to n-type semiconductors. Oxygen atom contributes its O-2p orbitals to the valence band maximum (VBM) and metal 4s band provides the oxide with its conduction band minimum (CBM). Thus, TCOs typically have very large (over 3 eV) optical band gaps and possess outstanding n-type conductivity when doped [6, 7]. Lack of p-type TCOs significantly hinders their practical applications because devices like bipolar transistors and diodes need p-n junctions to function. Localization of the TCO valence band makes it difficult to introduce a significant number of holes and shallow acceptors. In general, holes in such materials are spontaneously negated by the appearance of ionic donor defects under all conditions. Thus, n-type TCOs cannot be designed from n- to p-type simply by doping them with acceptors under equilibrium conditions [8]. Because of this, the fabrication of effective p-type TCOs is challenging.

Since the first truly p-type TCO, CuAlO\textsubscript{2}, was reported in 1997 by Hosono and co-workers [9], wide-bandgap p-type cuprous delafossite oxides attracted a lot of research interest. Fully occupied Cu3d states of these materials hybridize with the O2p states at the valence band creating a more dispersed valence band maximum. This, in turn, increases valence band energy in relationship to the binary n-type TCOs, which makes hole
formation easier because Cu3d states are typically occupied, and the corresponding materials have (a) less localized holes, (b) large bandgaps and (c) poor optical transparency.

CuXO2 delafossite family (X = Al, Cr, Fe, In) is a very promising material gaining popularity among researchers because of its stability, p-type behavior, wide bandgap, and transparency, all of which can be achieved without doping [10–13]. But these oxides have much lower electrical conductivity compared to other common n-type semiconductors. Deep acceptor levels and localized p-orbitals of the O2p states of these p-type binary oxides significantly decrease hole mobility, which, in turn, substantially hinders the conductivity of these oxides [14]. To increase the electrical conductivity of CuXO2 delafossite films, doping, and various synthesis and preparation techniques were attempted [15–17]. Typically, substitution of a trivalent metal with a divalent one enhances conductivity. In fact, the conductivity of CuGaO2 increased ten times when it was doped with Mg, which confirmed successful p-type doping of this material [18]. Mg-doping also increased conductivity of bulk CuCrO2 by three orders of magnitude: highest p-type conductivity (equal to 220 S cm⁻¹) was achieved for CuCr0.95Mg0.05O2 films [19]. However, the synthesis of crystalline delafossite oxides is challenging: as a result, only a few attempts were reported in the literature. The most widely used techniques of delafossite oxide film preparation are based on physical deposition methods such as DC and RF sputtering, vacuum evaporation, pulsed laser deposition, etc [20–23]. However, these techniques are expensive and can only coat small areas. Chemical deposition can overcome these drawbacks and is indeed often commonly used for delafossite film growth. It is not only a less expensive technique but it can also coat larger areas. Solution-based methods of delafossite film preparation result in low crystallinity of the resulting films and formation of undesired by-products [17, 24]. Thus, all conventional methods have their drawbacks. Recently developed polymer-assisted deposition (PAD) technique can successfully produce advance transparent thin films, consisting of simple as well as complex metal-oxide materials with variety of useful electronic applications.

This work is a continuation of our previous work [25, 26], in which we prepared pure and doped CuScO2 thin films using PAD. However, the optical and electrical properties of the resulting films were unsatisfactory. Therefore, we further improved our method. Thus, this work demonstrates an improved PAD-based growth of single-phase epitaxial CuScO2 thin films on a-plane sapphire. Selection of initial materials, which in this work were soluble polyethyleneimine (PEI) and ethylenediamine tetra-acetic acid (EDTA), plays a very crucial role in high-quality film formation by PAD since they not only control process viscosity but also bond with the metal ions to inhibit premature precipitation of metal oxide oligomers. The resulting precursor solution possessed high quality and purity and was used for the preparation of a wide variety of high-quality films. In addition, to chemically modulate the CuScO2 valance band, we annealed as-prepared films under O2 presence to obtain more delocalized carrier holes. O atoms, acting as interstitials, chemically modulate valance band without any metal doping. To demonstrate practical applications of the PAD-fabricated films, we assembled p–CuScO2/n-In2O3 heterojunction diodes. Since PAD is more economical than other methods, it has strong potential for high volume device fabrication and large-scale production [27].

2. Experimental methods

2.1. Preparation of precursor solution and CuScO2 thin films

To prepare precursor solutions, two aqueous solutions of Sc and Cu were mixed with PEI and EDTA. 0.1 mol of copper (II) nitrate (99.9% pure) was first mixed with 40 ml of deionized (DI) water, after which 3 g of PEI was added. In a separate beaker, 0.1 mol of scandium (III) nitrate (99.9% pure) was also mixed with 40 ml of DI water, after which 4 g of EDTA and 3 g of PEI were added. Both PEI and EDTA are soluble, easily complex various cations, decompose easily and volatilize upon heating. Cu binds with PEI while EDTA complexes Sc. When mixed together, EDTA complexes can form hydrogen bonds and interact electrostatically with PEI-based complexes.

Both solutions were filtrated and concentrated (to 3000 molecular weight cut-off) using Amicon filtration setup equipped with stirring cells and flat cellulose YM3 filters. These procedures were performed under 65 psi of N2 pressure. The final concentration of each solution was 250 mM. These solutions were then mixed at various ratios. The mixtures were then used to spin-coat (at 3000 rpm) a-plane sapphire substrates (for 30 s), after which they were baked in the air for 30 min at 300 °C to eliminate organics. Spin coating and baking steps were performed six times until a film with a desired thickness was obtained. The resulting films were then annealed at 900 °C under constant N2 flow (containing 1, 3 and 5% of O2) for 1 h, after which the films were allowed to cool inside the annealing furnace under the same atmosphere.

2.2. Fabrication of heterojunction diodes

To demonstrate practical applications of CuScO2 thin films synthesized in this work, p–CuScO2/n-In2O3 heterojunction diodes were fabricated. Schematic presentation of the diode structure is shown in figure 6(b).
Radiofrequency magnetron sputtering system was utilized to deposit the In$_2$O$_3$ layer on CuScO$_2$ using 99.99% pure In$_2$O$_3$ ceramic target. Deposition conditions were 1 Pa chamber pressure, 120 W power, constant gas flow (containing 1:9 O$_2$:N$_2$ weight ratio) and 40 min sputtering duration. Prior to the sputtering, the chamber was evacuated to $6.5 \times 10^{-4}$ Pa. Prior to the film deposition, the surface of the target was pre-sputtered for 10 min to remove contamination. The contact electrode was fabricated by vacuum deposition of Au contacts on the p-CuScO$_2$/n-In$_2$O$_3$ heterojunctions using a shadow mask.

2.3. Film characterization

The crystallinity of CuScO$_2$ thin films was assessed by x-ray diffraction (XRD) performed using Bruker D8 Advance X Pert diffractometer with Cu-Ka radiation as an x-ray source. XRD scans were performed at 4° min$^{-1}$ scanning speed in the 10$^\circ$–70$^\circ$ 2θ range. Chemical analysis was conducted by x-ray photoelectron spectroscopy (XPS) performed using ESCALAB 250 instrument. Surface morphologies and microstructures were inspected by JSM-7500F field emission scanning electron microscope and Veeco DI-3100 atomic force microscopes (FF-SEM and AFM, respectively). We also performed high-resolution transmission electron microscopy (HRTEM) using 2010F TEM instrument. Optical transmission and absorption were measured using a UV–VIS–NIR spectrophotometer (Shimazu UV-3600PC) and Fourier transform infrared (FTIR) spectrometer in the 200–3000 nm and 400 to 4000 cm$^{-1}$ ranges, respectively. First, spectra of the film–coated sapphire were recorded and then corrected by the substrate transmission/absorption. Photoluminescence emission and excitation spectra were collected using Fluoromax–4 spectrometer (HORIBA JOBIN YVON) equipped with He-Cd laser operated at 250 nm excitation wavelength. Hall-effect measurements conducted by the ACCENT HL500PC system in the 150–300 K range were performed for electrical characterization of the films.

2.4. HRTEM sample preparation

To detach films from the substrate, polymethyl methacrylate (PMMA) was spin-coated on the thin films, after which the whole substrate was placed on a hot plate for 5 min. Scotch tape, large enough to cover the whole sample and having a small opening in the middle, was then applied to the substrate with the sticky part touching the sample. The edges of the tape were then cut to the sample shape and size. This assembly was then soaked in 5% HF for 1 h, after which the tape was removed. PMMA and thin films layer were then gently removed from the tape with a needle, rinsed in DI water and placed on a Cu grid, which was then baked under an IR lamp for 5 min to ensure its strong adhesion to PMMA. The whole film was then cut to the shape of the Cu grid, after which PMMA was removed with hot acetone leaving CuScO$_2$ film on the Cu grid.

3. Results and discussion

3.1. Structure

Figure 1(a) shows optical photographs of CuScO$_2$ thin films annealed at O$_2$ partial pressure equal to 1, 3 and 5%. Film transparency gradually decreased as partial oxygen pressure during annealing increased. XRD patterns of the CuScO$_2$ thin films are shown in figure 1(b). The unannealed film did not show any distinguishable XRD peaks indicating an amorphous structure. Films annealed at 1 and 3% oxygen partial pressure exhibited strong peaks corresponding to (0003), (0006), (0009) and (00012) planes of rhombohedral R$3_1$m delafossite according to JCPDF card number 79-0599. The appearance of these peaks confirmed the epitaxial orientation of CuScO$_2$ films relative to the substrate and along the CuScO$_2$ c-axis. Films annealed at 5% oxygen partial pressure contained CuO, Cu$_2$Sc$_2$O$_5$, Sc$_2$O$_3$ and CuScO$_2$, which formed very likely because Cu$^{2+}$ oxidized to Cu$^{3+}$ in O$_2$-rich atmosphere and CuScO$_2$ decomposed according to the following reaction:

$$4\text{CuScO}_2(s) + \text{O}_2(g) \rightarrow \text{Cu}_2\text{Sc}_2\text{O}_3(s) + 2\text{CuO}(s) + \text{Sc}_2\text{O}_3(s)$$

(1)

The full widths at half-maxima (FWHM) of the (0009) peaks were in the 0.17$^\circ$–0.22$^\circ$ range (see figure 1(c)). As O$_2$ content increased, diffraction peaks shifted towards larger angles because of lattice strain and deformations caused by annealing under excessive oxygen presence. We used Jade 5.0 software to calculate $a$ and $c$ lattice constants for all our films (see table 1). Increase in $a$ indicated that O atoms occupied lattice gaps, in particular, between planes parallel to the a-axis. Oxygen incorporation on the c-axis was the opposite: $c$ decreased as more oxygen was incorporated into the CuScO$_2$ films.

3.2. XPS results

XPS analysis was performed to analyze the chemical state of the thin films (see figure 2). Cu-2p spectra showed two distinct peaks with high intensity at 931.8–932.8 eV (Cu-2p$_{3/2}$) and 951.8–952.8 eV (Cu-2p$_{1/2}$) binding energies. These values agree with the literature ones for Cu$^{2+}$ in films with delafossite structure [28]. Two broad and weak satellite peaks at 941.2 and 961.5 eV were observed in the spectrum of the film annealed at 5% O$_2$.
partial pressure, which implies the existence of Cu$_2^{2+}$ [29] caused by the formation of CuO and Cu$_2$Sc$_2$O$_5$ due to excessive oxygen intercalation into the CuScO$_2$ lattice. The close-packing index of the R3(____)m space group is usually equal to 74.05%, while the packing index of delafossite CuScO$_2$ is $\sim$50%. Thus, some amount of oxygen can be easily incorporated into CuScO$_2$ lattice without changing its symmetry. Sc-2p spectra showed two strong peaks at 401.2–401.8 eV (Sc-2p$_{3/2}$) and 405.8–406.4 eV (Sc-2p$_{1/2}$) (see figure 2(b)). Thus, Sc present in the films was three-valent [26]. Oxygen XPS spectra demonstrated peaks positioned very close to each other: at 530 and 531.6 eV. These peaks correspond to oxygen in the CuScO$_2$ lattice and to interstitial oxygen, respectively [30]. XPS data confirmed that the films annealed at 1 and 3% of O$_2$ partial pressure consisted of only the CuScO$_2$ phase. However, divalent copper oxide appeared in the films annealed at 5% oxygen partial pressure.

### 3.3. Microstructure and morphology of the CuScO$_2$ thin films

SEM and AFM data are presented in figures 3(a1)–(c1) and (a2)–(c2), respectively. All films exhibited granular morphology with small grains uniformly distributed over the film surfaces. As annealing O$_2$ partial pressure increased, average grain sizes slightly decreased. Root-mean-square (RMS) values for surface roughness of the films annealed at 1, 3 and 5% of O$_2$ partial pressure were 9.35, 9.27 and 9.17 nm, respectively. The Scherrer equation was used to calculate average crystal sizes of all films:

$$\tau = k\lambda/\beta \cos \theta,$$

where $k$ is a dimensionless shape factor close to 0.9, $\beta$ is FWHM, $\lambda$ is Cu K$_\alpha$ wavelength, and $\theta$ is a diffraction angle (chosen in this work equal to the 2$\theta$ value of the peak corresponding to the (0009) plane). Average grain sizes of CuScO$_2$ films annealed at O$_2$ partial pressure equal to 1, 3 and 5% were $\sim$101, $\sim$92 and $\sim$87 nm, respectively. Surface roughness and grain size also decreased as O$_2$ partial pressure during annealing increased because of strain caused by the crystal defects induced by incorporation of excess O$_2$ into the film crystalline
structure. Thicknesses of the CuScO$_2$ films annealed at O$_2$ partial pressure equal to 1, 3 and 5% were 245, 240 and 235 nm, respectively. A slight decrease in film thickness was observed as O$_2$ partial pressure during annealing increased.

Results of HRTEM and selected area diffraction (SAD) showed that spacings between adjacent planes were 4.20 and 4.22 Å for thin films annealed at O$_2$ partial pressure equal to 1 and 3%, respectively (see figures 3(a3)–(c3)). These values were attributed to the d-spacings of (1210) planes. CuScO$_2$ thin films annealed at 1 and 3% of O$_2$ partial pressure were single-crystalline with their c-axes oriented perpendicular to a-plane sapphire.

Figure 2. XPS Cu-2p (a), Sc-2p (b) and O-1s (c) spectra of CuScO$_2$ films annealed at 1, 3 and 5% O$_2$ partial pressure.
substrates (see figures 3(a3) and (b3)). However, selected area diffraction patterns showed some scattered irregular spots, indicating that the arrangement of atoms in the film is disordered and no obvious lattice orientation was observed for the film annealed at 5% of O2 partial pressure (see figure 3(c3)), which indicated the absence of single crystallinity.

3.4. Optical measurements of the CuScO2 films

UV–vis–IR transmission spectra demonstrated excellent transparency of all films in the vis-IR region. Total optical transmission in the whole vis–NIR region of the films annealed at 1 and 3% of O2 partial pressure was over 92 and 75%, respectively (see figure 4(a)). Transmittance of the film annealed at 5% of O2 was the lowest—only 67%. This gradual decrease of transmittances in the visible range with the increase of O2 partial pressure may due to enhanced carrier scattering induced by oxygen intercalation. Knowing optical film properties is essential to successfully design optoelectronic devices. Additionally, we observed a sharp absorption edge at ∼255 nm, which corresponds to the transitions occurring inside the direct optical bandgap of the film. Correlation between photon energy ($hv$) and optical absorption coefficient ($\alpha$) is shown below [31]:

$$\alpha hv = A (hv - E_g)^m,$$

where $A$ is a constant, $E_g$ is an optical bandgap, and $m$ is a factor depending on the type of transition: it is equal to 1/2 and 2 for direct and indirect bandgaps, respectively [32]. Linear relationship between $(\alpha hv)^2$ and $hv$ plotted using our experimental data (see figure 4(a)) [33] indicates direct bandgap transitions, which were equal to ∼3.45, 3.35 and 3.25 eV for the films annealed at O2 partial pressure equal to 1, 3 and 5%, respectively. These energies agree with the range reported in the literature (3.2–3.6 eV) [34, 35]. The bandgap energy variation for the same material can be described by the following equation: $\Delta E = \Delta E (0) - kp^{1/3}$, where $p$ is a carrier concentration [36]. Oxygen incorporated into the lattice occupied interstitial sites and acted as an acceptor.
increasing hole content in the film. Therefore, optical band gap energy decreased as \( O_2 \) partial pressure during annealing increased.

The optical transmission of the films in the mid-IR is shown in figure 4(b). \( \text{CuScO}_2 \) film annealed at 1% \( O_2 \) partial pressure showed over 90% transmittance in 2.5–5 \( \mu \text{m} \) (or 4000–2000 cm\(^{-1}\)) range without any sharp absorption features. Low absorption (or high transmittance) especially in the mid-IR region is generally because of the free-carrier plasma edge position being in the far-IR region. Sudden transmittance decrease at 5 \( \mu \text{m} \) is typically caused by the collective oscillations of the conduction band electrons, known as plasma oscillations. Frequency of free-carrier plasma oscillation (\( \omega_p \)) defines the low cut-off frequency of transmission bands. \( \text{CuScO}_2 \) thin films annealed at 3 and 5% of \( O_2 \) partial pressures showed transmission at lower wavelength (below 4 \( \mu \text{m} \)). According to the Drude dispersion theory, the plasma oscillation frequency is inversely proportional to the carrier mobility, because of decreased carrier mobility (due to the interstitials being occupied by oxygen atoms), which resulted in higher \( \omega_p \). Thus, the mid-IR transmission range of the films narrowed. We also observed decreased transmittance for the films annealed at 3 and 5% \( O_2 \) partial pressures, accompanied by two distinct absorption peaks. Typically, optical transmittance is affected by the grain sizes, point, and void defects as well as surface roughness and film thickness. Grain sizes and thicknesses of our films were 90–100 and 240 ± 5 nm, respectively. Because all these values are so close to each other, it is unlikely that they are responsible for observed transmittance decrease. The surface roughness of the films decreased only slightly as \( O_2 \) partial pressure during annealing increased. Thus, surface roughness also could not significantly affect transmittance. Additionally, films deposited under a high oxygen content atmosphere might still have a significant amount of interstitial oxygen defects potentially acting as light scattering centers. Therefore, transmittance decrease in the Vis–IR region probably occurred due to the lattice distortion and defect formation caused by the insertion of oxygen. Small peaks at 2263 and 2670 cm\(^{-1}\) (see figure 4(b)) were attributed to absorption associated with Cu–O and Sc–O stretching vibrations caused by oxygen incorporation into the lattice.

![Figure 4](image.png)
Room-temperature photoluminescence (PL) spectra of our CuScO$_2$ films are shown in figure 5. As O$_2$ partial pressure during annealing increased, PL peaks shifted to higher wavelength because of changes in their optical bandgap energies. PL spectra of the films annealed at 1, 3 and 5% of O$_2$ partial pressure exhibited violet emission at 361 nm (3.43 eV), 372 nm (3.33 eV) and 384 nm (3.23 eV). Thus, PL was mainly caused by the near-band edge (NBE) radiative recombinations. Corresponding energy values obtained from PL spectra agree very well with the values obtained from the $\alpha$hv$^2$ versus $T$ plots.

3.5. Electrical properties of CuScO$_2$ films

The electrical conductivity of $p$-type delafossite thin films is typically poor because of strong localization of the holes in the valence band caused by the strong ionic nature of the metallic $d$ and oxygen $p$ orbitals, both of which constitute the valence band [37]. Therefore, we chose Cu-based delafossite because its valence band maximum is controlled by the Cu3d states and because holes occupying Cu ion positions are less localized. However, strong hole localization caused by electronegative oxygen behavior is the major obstacle in creating a well-functioning $p$-type transparent conductive oxide. To solve this problem, we simply annealed the films in the oxygen-rich environment to induce the incorporation of oxygen into the film crystal structure. This approach was adopted based on Kawazoe et al [9], who proposed chemical modulation of the valence band. Their approach involved mixing molecular orbitals of certain counter cations (e.g. Ag-4d$^{10}$ and Cu-3d$^{10}$) possessing filled energy levels comparable to the O-2p level with the goal to reduce strong columbic attraction of oxygen ions, which would lead to hole delocalization.

Temperature dependence of electrical conductivity was analyzed to gain further insights into the intrinsic characteristics of our CuScO$_2$ films. All films were thermally activated at 150–300 K, which was judged by the linearity of the corresponding $\ln \sigma \sim 1000/T$ plots (see figure 6(a)). The $\ln \sigma \sim 1000/T$ plots were linear, which indicates that the conduction mechanism was related to a small-polaron hopping [38]. Hole hopping between nearest neighboring Cu sites defines electrical transport properties. Conductivity can be expressed as

$$\sigma = A \exp \left[ \frac{-E_a}{k_B T} \right]$$

where $E_a$ is activation energy, $k_B$ is the Boltzmann constant, and $A$ is a pre-exponential constant [39]. Higher electrical conductivity at elevated temperatures confirmed semiconducting behavior of our films: their conductivity values were 13.8, 22.1 and 0.39 S cm$^{-1}$ at 300 K, while $E_a$ values were estimated to be 0.091, 0.032 and 0.51 eV for the CuScO$_2$ thin films annealed at O$_2$ partial pressure equal to 1, 3 and 5%, respectively. These activation energy values are 15% less than the optical bandgap energy of CuScO$_2$ (which is equal to $\sim$3.3–3.7 eV). Thus, hole transport in the valence band was thermally activated by acceptors [18]. $E_a$ decreased as O$_2$ partial pressure during annealing increased very likely because of different carrier densities related to the Fermi level positions.

Such disorder translates to the formation of Cu vacancies and oxygen interstitials upon film annealing. These defects play a very significant role in the $p$-type conductivity of copper oxides because each provides a hole to the valance band, which can be described by the reactions shown below.

![Figure 5. Photoluminescence (PL) spectra of CuScO$_2$ thin films annealed at O$_2$ partial pressure equal to 1, 3 and 5%. Measurements were performed at 250 nm excitation wavelength and at room temperature.](image-url)
where $h^+$ is a hole and $Cu^0$ represents a copper vacancy. Increased hole density shifts the Fermi level to the upper level of the valence band. Thus, carriers can transition to the Fermi level, which would decrease $E_a$. Formation energies of acceptors (e.g. interstitial oxygen and/or copper vacancies) are typically lower than of donors (e.g. interstitial copper and oxygen vacancies). They are responsible for the improved hole-driven p-type conductivity of our CuScO$_2$ thin films.
To demonstrate how our films can be applied for practical applications, we fabricated the p-CuScO₂/n-In₂O₃ heterojunction diode. The schematic of this diode is shown in figure 6(b). Thicknesses of as-deposited CuScO₂ film and In₂O₃ layer were ∼240 and ∼300 nm. Judging by the results obtained from the I–V curves, diodes containing CuScO₂ films annealed at 1 and 3% of O₂ partial pressure showed good rectification characteristics with 2.5 V voltage threshold (see figure 6(c)), which agrees with the CuScO₂ bandgap value. However, no diode-like properties were obtained for the device containing CuScO₂ film annealed at 5% O₂ partial pressure very likely because of poor interface and current leakage paths caused by the lattice mismatch.

4. Conclusion

In this work, we used a polymer-assisted-deposition method to obtain CuScO₂ thin films, which were then incorporated into p-CuScO₂/n-In₂O₃ heterojunction diodes. CuScO₂ thin-film valence band energies were adjusted by annealing them in the oxygen-rich environment to induce the content of nonstoichiometric oxygen in the CuScO₂ crystal structure. When annealed at 1 and 3% of O₂ partial pressure, CuScO₂ films grew along the c-axis. These films showed good optical transparency in vis-IR and demonstrated excellent p-type electrical conductivity. The p–n heterojunction diodes based on CuScO₂ films exhibited rectifying I–V properties with ∼2.5 V threshold voltage. Thus, heterojunction formed by CuScO₂ and In₂O₃ materials, both of which possess wide-bandgap values, demonstrated good carrier blocking contact. Our results proved that CuScO₂ films possess unique photoelectric properties over the wide wavelength range. Thus, CuScO₂ films are very promising candidates for novel and current applications related to window electrodes and displays.

Acknowledgments

Authors would like to express their gratitude to the Science and Technology Research Project of Jilin Education Department for its financial support through grants numbers JJKH20181097KJ, JJKH20190545KJ and JJKH20190576KJ, to the National Natural Science Foundation of China for its grants numbers 61627823, 61874091 and 51602028 and to the Jilin Province Science and Technology Development Project for the grant number 20180804009HJ.

Compliance with ethical standards

Conflict of interest

The authors declare no conflicts of interest.

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