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Abstract

Cu₂O/ZnO:Al (AZO) and Cu₂O/ZnO/AZO heterojunctions have been deposited on glass substrates by a unique three-step pulsed laser deposition process. The structural, optical, and electrical properties of the oxide films were investigated before their implementation in the final device. X-ray diffraction analysis indicated that the materials were highly crystallized along the *c*-axis. All films were highly transparent in the visible region with enhanced electrical properties. Atomic force and scanning electron microscopies showed that the insertion of a ZnO layer between the Cu₂O and AZO films in the heterojunction enhanced the average grain size and surface roughness. The heterojunctions exhibited remarkable diode behavior and good rectifying character with low leakage current under reverse bias. The presence of the ZnO interlayer film significantly reduced the parasitic and leakage currents across the barrier, improved the quality of the heterostructure, made the energy band between AZO and Cu₂O layers smoother, and eliminated the possibility of interface recombination, leading to much longer electron lifetime.

Keywords (separated by '-')

Heterojunctions - thin films - ZnO - Cu₂O - AZO - pulsed laser deposition - solar cells

Footnote Information



Improved Cu₂O/AZO Heterojunction by Inserting a Thin ZnO Interlayer Grown by Pulsed Laser Deposition

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Cu₂O/ZnO:Al (AZO) and Cu₂O/ZnO/AZO heterojunctions have been deposited on glass substrates by a unique three-step pulsed laser deposition process. The structural, optical, and electrical properties of the oxide films were investigated before their implementation in the final device. X-ray diffraction analysis indicated that the materials were highly crystallized along the *c*-axis. All films were highly transparent in the visible region with enhanced electrical properties. Atomic force and scanning electron microscopies showed that the insertion of a ZnO layer between the Cu₂O and AZO films in the heterojunction enhanced the average grain size and surface roughness. The heterojunctions exhibited remarkable diode behavior and good rectifying character with low leakage current under reverse bias. The presence of the ZnO interlayer film significantly reduced the parasitic and leakage currents across the barrier, improved the quality of the heterostructure, made the energy band between AZO and Cu₂O layers smoother, and eliminated the possibility of interface recombination, leading to much longer electron lifetime.

Key words: Heterojunctions, thin films, ZnO, Cu₂O, AZO, pulsed laser deposition, solar cells

INTRODUCTION

Over recent decades, transparent conductive oxides (TCOs) have attracted considerable scientific attention and technological interest as an indispensable element in many optoelectronic applications. Due to the coexistence of high transparency and excellent conductivity, TCO materials pervade modern technologies, being a critical component of displays, touchscreens, lighting devices, and solar cells.^{1,2}

Zinc oxide (ZnO) and its aluminum-doped variant (AZO) are among the most widely utilized TCO thin

films thanks to their abundance in Nature, nontoxicity, and low cost. It is well known that, due to oxygen vacancies and zinc interstitials, ZnO behaves like an *n*-type semiconductor with a wide bandgap (about 3.3 eV) and that Al doping is normally performed to enhance its electrical conductivity, making AZO ideal for contacts in solar cells.³ On the other hand, due to Cu vacancies in the lattice, cuprous oxide (Cu₂O) is intrinsically *p*-type, showing good optical properties and a bandgap of about 2.1 eV,⁴ which is good for use as the absorber layer in photovoltaic devices. However, the intrinsic *p*-type nature of Cu₂O makes formation of a homojunction impossible, thus hindering achievement of the maximum efficiency.⁵

Cu₂O/ZnO or Cu₂O/AZO heterojunctions, with theoretically conversion efficiency of around 20%,⁶

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are some of the most attractive candidates for use in next-generation thin-film-based solar cells,⁷ because of the comparatively favorable alignment of the conduction-band edges⁸ and use of Earth-abundant elements.^{9–17} Experimental efficiencies of 1.46%, 1.43%, and 0.3% have been reported when using Cu₂O and ZnO layers obtained by atmospheric atomic-layer deposition (AALD),⁹ electrodeposition,¹⁵ and electrodeposition and spin coating,¹⁶ respectively. Over recent years, to improve the conversion efficiency of solar cells, the Cu₂O/AZO/ZnO heterostructure has been proposed^{18–23} and efficiencies up to 4.08% reported.¹⁸ Although Cu₂O/AZO or Cu₂O/ZnO heterojunctions have already been widely studied,^{9–17} their behavior on insertion of a ZnO thin film within the Cu₂O/AZO stack has been reported in only a few works.^{18–23} Furthermore, in those studies, distinct techniques were employed to grow the different layers constituting the heterostructure. In particular, in Refs. 18–20, AZO and ZnO films were deposited by PLD, whilst Cu₂O films were obtained by thermal oxidation of a Cu sheet. In Ref. 21 instead, ZnO and AZO thin films were deposited by ALD while the Cu₂O layer was obtained by electrodeposition. In Ref. 22, all the Cu₂O/AZO/ZnO heterojunction was fabricated using a three-step electrodeposition process, and finally in Ref. 23, magnetron sputtering was used for the deposition of AZO and ZnO thin films, whilst the Cu₂O layer was grown by metalorganic chemical vapor deposition (MOCVD).

In the work presented herein, we obtained the full Cu₂O/AZO/ZnO stack structure after a unique three-step pulsed laser deposition (PLD) process,^{24–29} making the fabrication process simpler and decreasing the damage compared with other literature reports^{18–23} and further improving the quality of the heterojunction in terms of the interface, surface roughness, passivation, and leakage currents. Study of the morphological, structural, optical, and electrical properties of the deposited Cu₂O/AZO and Cu₂O/ZnO/AZO heterojunctions revealed that the *p*-Cu₂O/*n*-ZnO/*n*-AZO heterojunctions exhibited well-defined rectifying behavior and could thus be useful for future high-performance heterostructure photovoltaic devices.

EXPERIMENTAL PROCEDURES

Sample Preparation

Corning glass substrates with dimensions of 1 cm × 2 cm were ultrasonically cleaned with acetone and ethanol for 10 min. Afterwards, Ti/Au bottom contacts were deposited by thermal evaporation. Cu₂O/AZO and Cu₂O/ZnO/AZO heterojunctions were then deposited by PLD using a Q-switched tripled Nd:YAG laser (Quantel mod.-YG78C20, $\lambda = 355$ nm).^{24–29} The laser beam, with energy density of 4 J/cm² and repetition rate of 20 Hz, was focused at an angle of incidence of 25° onto the target, which was in turn placed on an *x*-*y*

translation system to enable uniform ablation of its surface. The ZnO target (99.999% pure) and AZO target (99.9% pure) were 2-inch-diameter, 0.25-inch-thick, sintered zinc oxide ceramic disks supplied by CERAC Inc. (USA) and PI-KEM Ltd., respectively, while the Cu₂O target was obtained by cold pressing Cu₂O powder (purity 99.99%, Sigma Aldrich). All films were deposited with oxygen pressure of 10⁻² mbar. Cu₂O films were deposited at room temperature, whilst ZnO and AZO films were deposited at 150°C to avoid degradation of the electrical properties of the underlying Cu₂O film.³⁰ Glass substrate was employed as a reference sample during each film deposition and for further analysis.

Characterization Techniques

X-ray diffraction (XRD) measurements were performed using a PANalytical Empyrean powder x-ray diffractometer with copper anode (Cu K _{α} radiation, $\lambda = 0.15405$ nm, with Ni filter) equipped with a PIXCel^{1D} detector, at 40 kV and 40 mA. XRD patterns were recorded over the 2 θ angle range from 25° to 80° at step size of 0.026° and speed of 4°/min. Raman spectra of all films were recorded using a Renishaw InVia Raman microscope, equipped with a 532-nm diode pulsed solid-state laser, focused on the sample by means of a Leica MS-DS microscope through a 50× magnification long-working-distance lens, capable of 4 μ m lateral resolution, edge filter cutting Rayleigh reflection at 125 cm⁻¹, and 2400-line/mm grating leading to spectral resolution of 0.5 cm⁻¹. The surface morphology of the films was analyzed by field-emission scanning electron microscopy (SEM) using a Zeiss Supra 25 microscope and atomic force microscopy (AFM) using a Bruker ICON equipped with PeakForce mode at scan rate of 0.6 Hz and tapping mode at scan rate of 0.8 Hz.

Optical transmission measurements were performed using a Cary 500 ultraviolet–visible–near infrared (UV–Vis–NIR) spectrophotometer in the range from 250 nm to 2500 nm with resolution of 0.3 nm in the UV–Vis wavelength region and 1 nm in the NIR. The film thickness was determined using a SEMILAB GES-5E spectroscopic ellipsometer and is summarized in Table I together with the resistivity, carrier concentration, and mobility values identified by the van der Pauw method, employing a commercial Hall measurement system (ECOPIA HMS-3000).

I-*V* characterization of the heterojunctions was performed at room temperature using a custom-developed electronic circuit which allowed the voltage to be swept in the range from -10 V to 10 V.²⁸

RESULTS AND DISCUSSION

Oxide Films

Figure 1 shows the XRD patterns of the films deposited on glass substrates, recorded in θ -2 θ configuration. Both the AZO and ZnO samples



Table I. Film thickness (extracted by ellipsometry), electrical properties (by Hall measurements), and optical bandgap energy (by Tauc plot) of AZO, ZnO, and Cu₂O films grown on glass substrates

Film	Thickness (nm)	Carrier Concentration (cm ⁻³)	Resistivity (Ω cm)	Mobility (cm ² V ⁻¹ s ⁻¹)	Bandgap (eV)
Cu ₂ O	210	+ 3.6 × 10 ¹⁴	2.4 × 10 ²	71.38	2.20
AZO	220	- 6.7 × 10 ²⁰	2.6 × 10 ⁻⁴	35.23	3.43
ZnO	150	- 2.2 × 10 ¹⁹	7.3 × 10 ⁻³	38.21	3.20

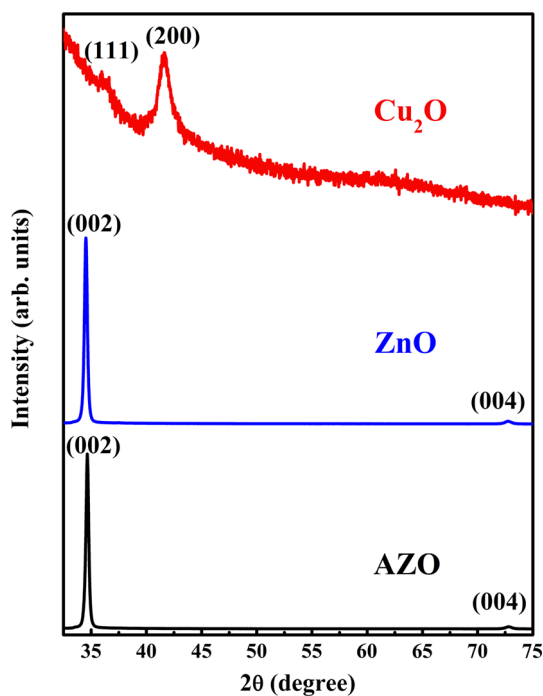


Fig. 1. XRD patterns of Cu₂O, ZnO, and AZO thin films grown on glass substrates.

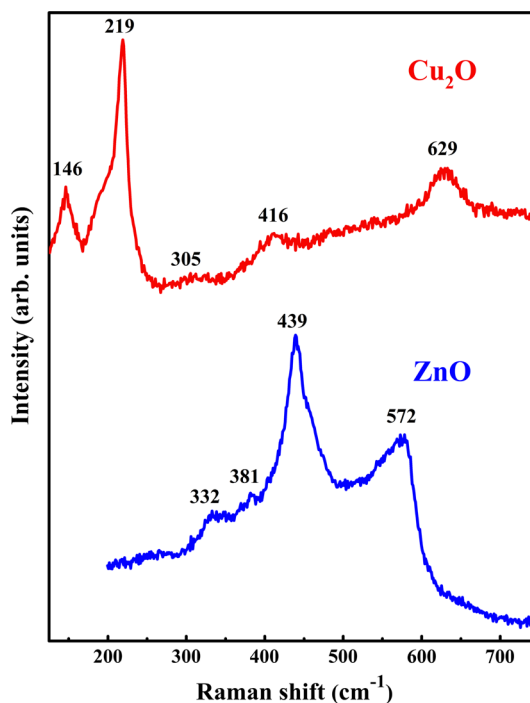


Fig. 2. Raman spectra of Cu₂O and ZnO thin films grown on glass substrates.

178 presented a ZnO phase, highly textured along the *c*-
 179 axis perpendicular to the substrate surface, with a
 180 significant (002) peak located at about 34.60°
 181 according to Joint Committee on Powder Diffraction
 182 Standards (JCPDS) card no. 036-1451³¹ with high
 183 intensity for all deposited samples, confirming the
 184 hexagonal wurtzite structure of the films. This
 185 result can be explained by the fact that the (002)
 186 plane requires a lower energy of formation.³² The
 187 Cu₂O films were also highly crystallized along the *c*-
 188 axis but with a significant (200) peak located at
 189 about 41.61° and a small peak located at about
 190 36.61° corresponding to the (111) crystal planes of
 191 Cu₂O cubic phase (JCPDS card no. 05-0667).³³ The
 192 average crystallite size of the films was estimated
 193 using the Scherrer formula,³⁴

$$D = 0.9 \frac{\lambda}{W \cos(\theta)}, \quad (1)$$

195 where *D*, *λ*, *θ*, and *W* are the mean grain size, x-ray
 196 wavelength (0.154 nm), Bragg diffraction angle, and
 197

198 full-width at half-maximum (FWHM) of the diffrac-
 199 tion peak, respectively. The average crystallite size
 200 of single-crystalline domains was obtained as
 201 33 nm, 31 nm, and 9.5 nm for AZO, ZnO, and
 202 Cu₂O, respectively.

203 These XRD results are in good agreement with
 204 Raman spectroscopy. Phonon modes with charac-
 205 teristic frequencies of crystalline Cu₂O and ZnO are
 206 evident in Fig. 2. Five peaks are observed in the
 207 Raman spectrum of the Cu₂O film. The highest
 208 peak, located at 219 cm⁻¹, is attributed to the
 209 second-order Raman-allowed mode 2E_u of Cu₂O
 210 phase, while that with low intensity at around
 211 305 cm⁻¹ is attributed to the second-order overtone
 212 mode A_{2u} while the peak located at 416 cm⁻¹
 213 corresponds to the four-phonon mode 3E_u + T_{2u}.^{35,36}
 214 The peaks located at 146.33 cm⁻¹ and 629 cm⁻¹
 215 correspond instead to two infrared-allowed modes.³⁷
 216 The Raman spectrum of the ZnO film shows four
 217 peaks. The first, located at 573 cm⁻¹, corresponds to
 218 the A₁ longitudinal optical (LO) mode, which can be
 219 attributed to lattice distortion.^{38,39} The highest

220 peak, centered at 439 cm^{-1} , may be assigned to the
 221 ZnO $E_2(\text{high})$ mode, which indicates the high crys-
 222 talline quality of the film, being a characteristic
 223 band of hexagonal wurtzite phase.^{39–41} The peak at
 224 382 cm^{-1} corresponds to the A1 (TO) mode of
 225 wurtzite ZnO crystal.^{38,42–44} The final peak, at
 226 332 cm^{-1} , can be attributed to the $E_2(\text{high}) -$
 227 $E_2(\text{low})$ mode due to multiphonon process, indicat-
 228 ing that the films were single crystals.³⁹ These data
 229 provide evidence that PLD allows deposition of
 230 good-quality ZnO and Cu_2O thin films.

231 Figure 3a shows the transmission spectra of AZO,
 232 ZnO, and Cu_2O films deposited on glass in the
 233 wavelength range from 250 nm to 2500 nm. The
 234 undoped zinc oxide film was highly transparent
 235 with optical transmittance as high as 80% to 90% in
 236 the Vis–NIR and an absorption edge at about
 237 375 nm. The most significant difference from the
 238 AZO curve can be observed in the NIR spectral
 239 region, where a pronounced drop, caused by free-
 240 carrier absorption, is visible for the AZO film. Also,
 241 the Cu_2O film showed high transmittance of up to
 242 85% in the range from 650 nm to 2500 nm. A few
 243 interference fringes can be observed in the trans-
 244 mittance spectra, indicating weak surface

roughness.⁴⁵ The optical bandgap energy, E_g , of
 the materials was evaluated using the Tauc
 relation,^{22,46}

$$(\alpha h\nu)^2 = B(h\nu - E_g), \quad (2)$$

where α is the absorption coefficient, $h\nu$ is the
 photon energy, and B is the Tauc coefficient, related
 to the light absorption efficiency. From the intercept
 of the straight-line portion of the curves at $\alpha = 0$ in
 the Tauc plot⁴⁷ in Fig. 3b, energy gaps of 3.20 eV,
 3.43 eV, and 2.20 eV were estimated for ZnO, AZO,
 and Cu_2O (Table I), respectively, in good agreement
 with literature. Also, the electrical properties of the
 films (Table I) are very close to literature values.⁴⁸
 As expected, n -type zinc oxide films have carrier
 concentration much higher and resistivity much
 lower than p -type Cu_2O samples.⁴⁹

Heterojunctions

A typical cross-sectional view of the $\text{Cu}_2\text{O}/\text{AZO}$
 heterojunction is shown in Fig. 4a. The bilayer
 $\text{Cu}_2\text{O}/\text{AZO}$ structure is clear, and both films are
 uniform with thickness in agreement with the
 ellipsometric measurements. However, while the
 presence of the ZnO interlayer, due to its similar
 lattice structure and mismatch (Fig. 1) with AZO,
 cannot be evidenced from the images in cross-
 section, it changes the surface morphology of the
 AZO on top. The plan-view images reveal that the
 top surface of the $\text{Cu}_2\text{O}/\text{ZnO}/\text{AZO}$ structure (Fig.
 4b) was rougher than that of the $\text{Cu}_2\text{O}/\text{AZO}$ struc-
 ture (Fig. 4c). This change in the morphology is due
 to the formation of nucleation sites and the change
 in the nucleation type from homogeneous to hetero-
 geneous when the AZO film is deposited on ZnO and
 Cu_2O , respectively. The presence of surface texture
 will play a significant role in the performance of the
 solar cell, since it will reduce the reflection loss at its
 front surface, enhance the light absorption, and
 increase the photocurrent.

Since the morphology (porosity and roughness) of
 the heterojunction surface is very important for
 photovoltaic applications, AFM characterization in
 tapping mode was carried out and the surface
 roughness and grain size of the films calculated
 using the NanoScope analysis program. Figure 5
 shows three-dimensional (3D) and two-dimensional
 (2D) AFM images of $\text{Cu}_2\text{O}/\text{ZnO}/\text{AZO}$ and $\text{Cu}_2\text{O}/\text{AZO}$
 heterojunctions, confirming that insertion of the
 ZnO layer between the Cu_2O and AZO films led to
 an increase in both the average grain size (from
 62 nm to 96 nm, Fig. 5a and b) and the surface
 roughness (defined by the root-mean-square rough-
 ness, from 16.5 nm to 19.5 nm). An increase of the
 porosity is also evident in Fig. 5c and d. It is worth
 mentioning that larger grains imply fewer grain
 boundaries and thus enhanced device performance.
 This is due to the fact that grain boundaries, acting

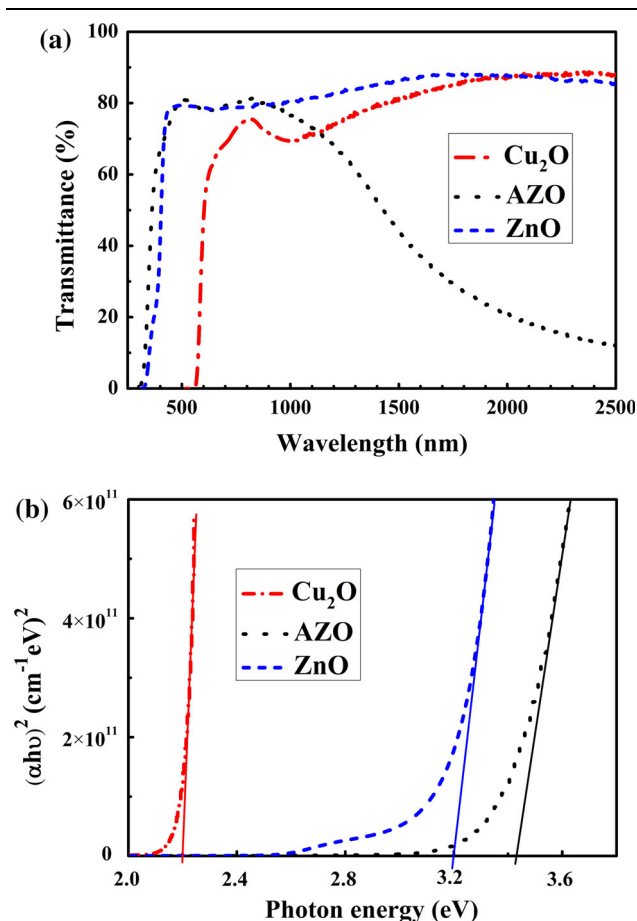


Fig. 3. (a) Optical transmittance spectra of ZnO, AZO, and Cu_2O thin films grown on glass substrates and (b) corresponding Tauc plots for determination of the optical bandgap.

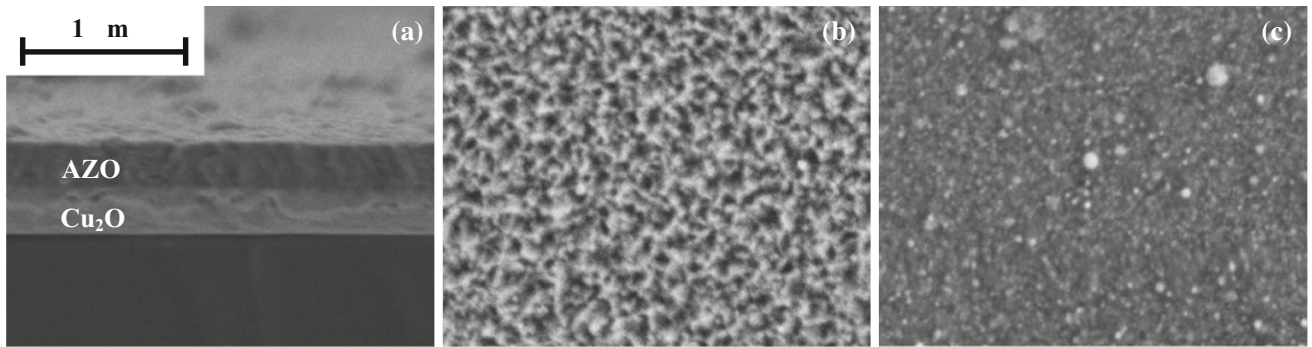


Fig. 4. Typical SEM images of: (a) $\text{Cu}_2\text{O}/\text{AZO}$ heterojunction in cross-section, (b) $\text{Cu}_2\text{O}/\text{ZnO}/\text{AZO}$ and (c) $\text{Cu}_2\text{O}/\text{AZO}$ in plan view. The scale marker in (a) applies to all three images.

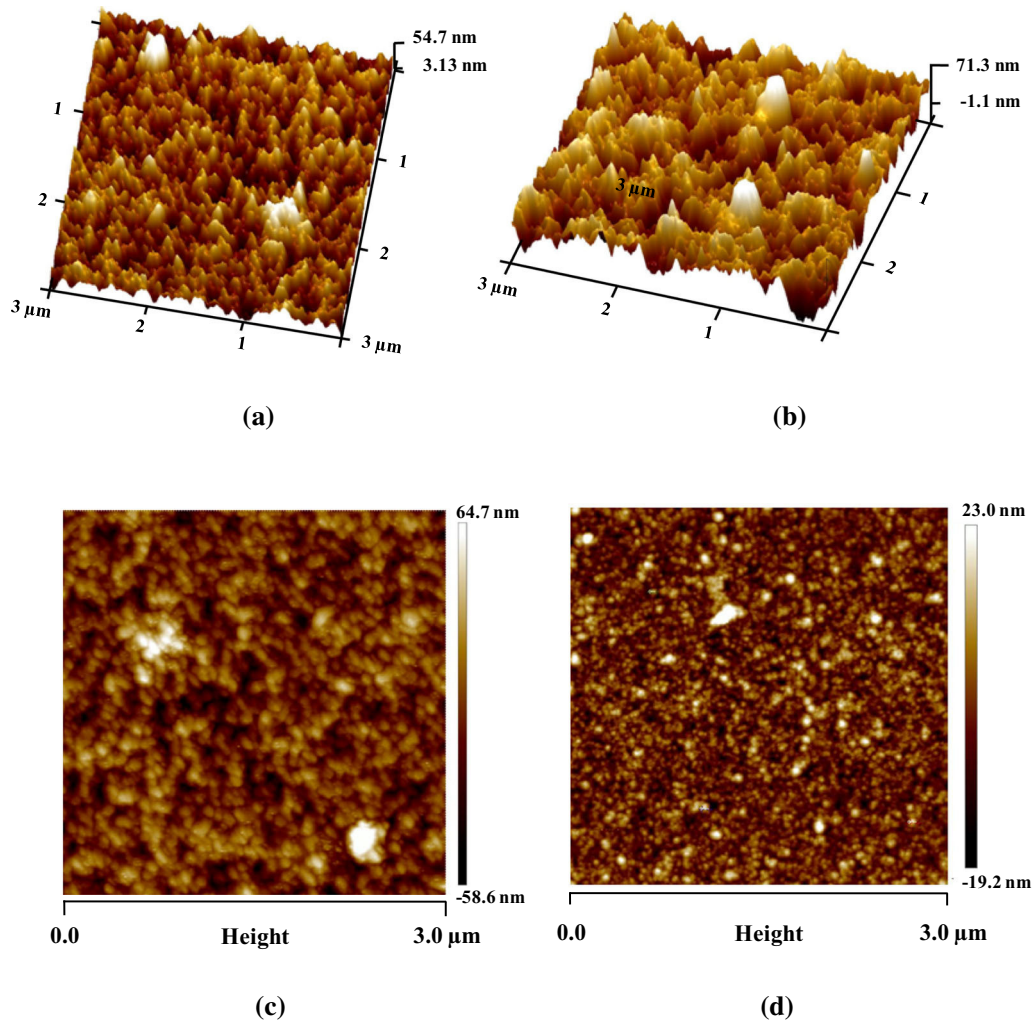


Fig. 5. Tapping-mode 3D and 2D AFM images ($3 \mu\text{m} \times 3 \mu\text{m}$) of $\text{Cu}_2\text{O}/\text{AZO}$ (a, c) and $\text{Cu}_2\text{O}/\text{ZnO}/\text{AZO}$ (b, d) heterojunctions.

302 as recombination sites for photocarriers, lead to
303 efficiency losses.

304 To investigate the electrical properties of the
305 heterojunctions, 1-mm-diameter aluminum (Al)
306 contact layers were deposited on top of the AZO
307 layers of the $\text{Au}/\text{Cu}_2\text{O}/\text{AZO}$ and $\text{Au}/\text{Cu}_2\text{O}/\text{ZnO}/\text{AZO}$
308 sandwich structures. The AZO/Al and $\text{Au}/\text{Cu}_2\text{O}$ contacts

were perfectly ohmic. Figure 6 shows the current-
voltage ($I-V$) curves for the $\text{Au}/\text{Cu}_2\text{O}/\text{AZO}/\text{Al}$ and
 $\text{Au}/\text{Cu}_2\text{O}/\text{ZnO}/\text{AZO}/\text{Al}$ structures. A defined diode-
like rectifying nature with lower reverse saturation
current (I_0), due to the reduced interface recombi-
nation, is clearly observed in the sample with the
ZnO buffer layer, implying that this device would

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316 exhibit improved photovoltaic properties under illu- 333
 317 mination. Indeed, a reduction of I_0 is known to 334
 318 enhance the open-circuit voltage (V_{OC}) and fill factor 335
 319 (FF) of a solar cell.⁵⁰ I_0 is reduced in the presence of 336
 320 the buffer layer thanks to the passivation of inter- 337
 321 face defects where recombination occurs. 338

322 Based on the measured bandgap values and 339
 323 considering the electron affinity (χ) of Cu_2O , ZnO, 340
 324 and AZO (3.2 eV, 4.2 eV, and 4.6 eV, respec- 341
 325 tively),^{22,51,52} an energy band diagram for the 342
 326 $\text{Cu}_2\text{O}/\text{AZO}$ and $\text{Cu}_2\text{O}/\text{ZnO}/\text{AZO}$ heterojunctions 343
 327 can be constructed (Fig. 7). The calculated conduc- 344
 328 tion (ΔE_c) and valence (ΔE_v) band offset of the $\text{Cu}_2\text{O}/$ 345
 329 AZO heterojunction are 1.4 eV and 2.63 eV, respec- 346
 330 tively, whilst for the $\text{Cu}_2\text{O}/\text{ZnO}$ heterojunction they 347
 331 are 1.0 eV and 2 eV, respectively. The effective 348
 332 energy gap (E_{eff}) of the $\text{Cu}_2\text{O}/\text{AZO}$ structure, defined 349

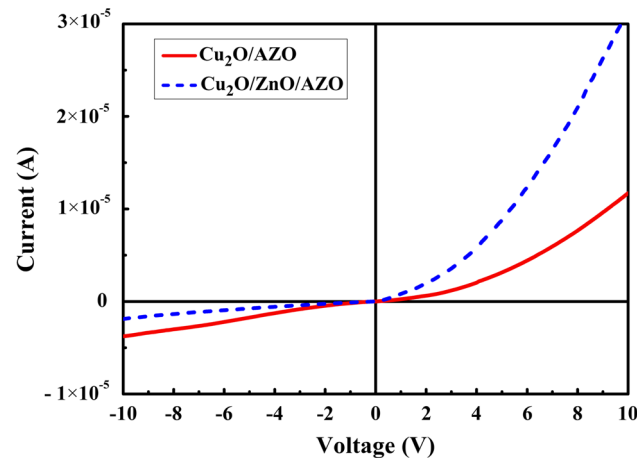


Fig. 6. I - V characteristics of $\text{Au}/\text{Cu}_2\text{O}/\text{AZO}/\text{Al}$ and $\text{Au}/\text{Cu}_2\text{O}/\text{ZnO}/\text{AZO}/\text{Al}$ heterojunctions.

333 as the energy difference between the E_c of AZO and 334
 335 the E_v of Cu_2O , is about 0.8 eV. This very low value 336
 337 may cause interface recombination between holes 338
 339 coming from the Cu_2O layer and electrons coming 340
 341 from the AZO layer. However, the E_{eff} of the $\text{Cu}_2\text{O}/$ 342
 343 ZnO/AZO structure, viz. the energy difference 344
 345 between the E_c of the ZnO and the E_v of Cu_2O , is 346
 347 about 1.2 eV. Such a larger value could be useful to 348
 349 eliminate the possibility of interface recombination 350
 351 between holes from the Cu_2O film and electrons 352
 353 from the ZnO film.^{21,53,54} The presence of the ZnO 354
 355 interfacial layer leads to a cascaded energy level in 356
 356 the sandwiched structure, having $E_c(\text{AZO}) <$ 357
 357 $E_c(\text{ZnO}) < E_c(\text{Cu}_2\text{O})$ and $E_v(\text{AZO}) < E_v(\text{ZnO}) <$ 358
 358 $E_v(\text{Cu}_2\text{O})$. This results in a driving force through 359
 359 the different layers of the device, being advanta- 360
 360 geous for carrier transport towards the electrodes.⁵⁵ 361
 362

CONCLUSIONS

351 We used a unique three-step PLD process to 352
 353 deposit thin-film $\text{Cu}_2\text{O}/\text{AZO}$ and $\text{Cu}_2\text{O}/\text{ZnO}/\text{AZO}$ 354
 355 heterojunctions on Corning glass, at temperature 356
 356 of 150°C for AZO and ZnO films and room tempera- 357
 357 ture for Cu_2O films. The Cu_2O layers were p -type 358
 358 semiconductors with concentration of 359
 359 $3.6 \times 10^{14} \text{ cm}^{-3}$ and resistivity of $2.4 \times 10^2 \Omega \text{ cm}$. 360
 360 The AZO and ZnO layers were n -type semiconduc- 361
 361 tors with carrier concentration of $6.7 \times 10^{20} \text{ cm}^{-3}$ 362
 362 and $2.2 \times 10^{19} \text{ cm}^{-3}$, and resistivity of 363
 363 $2.6 \times 10^{-4} \Omega \text{ cm}$ and $7.3 \times 10^{-3} \Omega \text{ cm}$, respectively. 364
 364 All the layers were transparent in the visible 365
 365 wavelength range with transmissivity above 80%. 366
 366

367 I - V measurements revealed remarkable diode 368
 368 behavior and good rectifying character with low 369
 369 leakage current under reverse bias. Insertion of a 370
 370 ZnO film within the $\text{Cu}_2\text{O}/\text{AZO}$ structure enhanced 371
 371

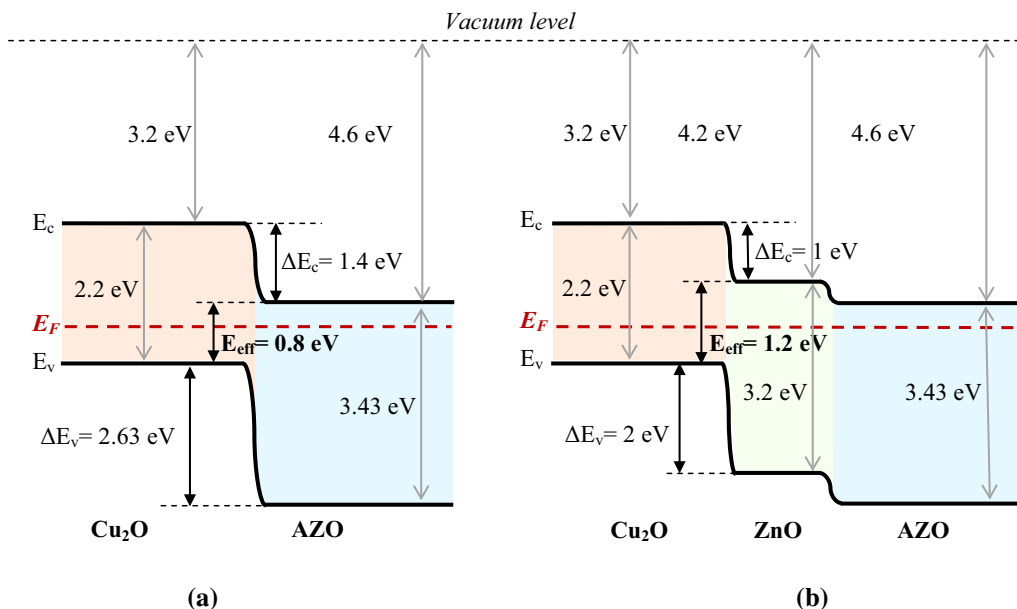


Fig. 7. Schematic band diagram of $\text{Cu}_2\text{O}/\text{AZO}$ and $\text{Cu}_2\text{O}/\text{ZnO}/\text{AZO}$ heterojunctions under equilibrium condition.



368 the average grain size and surface roughness,
 369 significantly limited the parasitic and leakage cur-
 370 rents across the barrier, and improved the quality of
 371 the heterostructure. The ZnO interlayer increased
 372 the effective energy gap from 0.8 eV to 1.2 eV with a
 373 reduction in interfacial recombination between
 374 holes from the Cu₂O film and electrons from the
 375 ZnO film. Finally, the presence of the ZnO film led
 376 to a cascaded energy level in the sandwiched
 377 structure, enabling an increase of the electron
 378 lifetime. Passivation of interface defects between
 379 the Cu₂O and AZO films by insertion of a ZnO layer
 380 could thus improve the performance of solar cells
 381 that make use of this kind of heterojunction.

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