

Fabrication and Characterization of Opto-electronic Devices Based on P-type Thin-film Semiconductors

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Abstract

Novel p-type thin-film semiconductors with excellent performance, that can be widely used in electronic devices, represent a necessary complement to conventional Si, Ge or III-V group semiconductors. Inspired from p-type absorber materials in photovoltaic applications, Cu(In,Ga)Se₂ (CIGS) and CuO are studied as potential candidates targeting opto-electronic devices. CIGS has been rarely studied up to now as a promising photodetection material. In this thesis, CdS/CIGS and In₂S₃/CIGS photodiodes are both investigated, realizing broadband dual-mode photodetection capabilities. As a suitable replacement of CIGS, more sustainable CuO thin films are studied by material and opto-electronic characterizations, finally realizing CuO thin-film transistors (TFTs) with the best-performing CuO thin film.

An ultra-thin CdS/CIGS heterojunction photodiode fabricated on steel firstly exhibits dual-mode broadband photodetection from ultraviolet to near infrared spectrum. In the photovoltaic mode, the CIGS photodiode, working as a self-driven photodetector, shows an outstanding photodetection capability (under a light power density of 20 $\mu\text{W cm}^{-2}$ at 680 nm), reaching a record detectivity of $\sim 4.4 \times 10^{12}$ Jones, a low noise equivalent power (*NEP*) of 0.16 pW Hz^{-1/2} and a high $I_{\text{light}}/I_{\text{dark}}$ ratio of $\sim 10^3$, but a relatively low responsivity of $\sim 0.39 \text{ A W}^{-1}$ and an external quantum efficiency (*EQE*) of $\sim 71\%$. Working under the same illumination but in the photoconductive mode (1 V reverse bias), the responsivity and *EQE* are significantly enhanced to 1.24 A W^{-1} and 226%, respectively, but with a relatively low detectivity of 7×10^{10} Jones and a higher *NEP* of 10.1 pW Hz^{-1/2}. To explain these results, a corrected photoconductive gain (*G*) model indicates that minority electrons could be localized in the defects, surface states and depletion region of the

CIGS photodiode, causing excess hole accumulation in the ultra-thin CIGS photodiode and thus high *EQE* over 100% (*G* over 1).

An In₂S₃/CIGS heterojunction photodiode fabricated on steel is shown highly photo-sensitive from ultraviolet to near infrared spectrum, with a responsivity over 0.8 A W⁻¹, an *EQE* over 100% and a detectivity over 8×10¹⁰ Jones from 505 to 910 nm under a reverse bias of 1 V. Moreover, the CIGS photodiode exhibits an outstanding weak light detection ability (i.e. at light power density of 20 μW cm⁻²), reaching a record responsivity of 2.06 A W⁻¹, an impressive *EQE* of 293%, a good detectivity of 2.3×10¹¹ Jones and a *NEP* of 3.7 pW Hz^{-1/2} at 870 nm under 1 V reverse bias. Importantly, the In₂S₃/CIGS photodiode, working as a self-powered photodetector, under 0 V, shows a record detectivity of ~3.4×10¹² Jones and a low *NEP* of 0.25 pW Hz^{-1/2} with a high responsivity of ~0.44 A W⁻¹ and a high *EQE* of ~63% at 870 nm.

However, CIGS is commercially more expensive and less sustainable due to the usage of indium and gallium. Therefore, P-type CuO thin films have been deposited and optimized by DC sputtering. By tuning oxygen concentration, the best oxygen to argon gas ratio can be chosen for CuO sputtering. To further optimize the CuO thin films, sputtering pressure, high-temperature sputtering and post-annealing are considered at the edge between transition and poisoned regime. By setting the optimal sputtering pressure of 10 mTorr (O₂/Ar=8/22 sccm) at the edge of oxidization and transition regimes, CuO with 1.64 eV bandgap reaches a stable hole mobility of 34.2 cm² V⁻¹ s⁻¹ and a hole concentration of 3.92×10¹⁴ cm⁻³ after 250 °C post-annealing. Considering heating at 150 °C during the deposition, CuO with 1.63 eV bandgap also reaches a stable record hole mobility of 113.7 cm² V⁻¹ s⁻¹ and a hole concentration of 1.39×10¹⁴ cm⁻³.

To study the interface properties of CuO with metal contacts, Au/CuO transmission line model (TLM) structures have been fabricated and measured, showing a relatively low contact resistance of $\sim 26 \text{ k}\Omega$ in N_2 . Therefore, Au has a good ohmic contact with CuO, showing the possibility of Au to be used as a contact metal in CuO devices. Additionally, the degradations of CuO thin films are discovered in vacuum, showing an obvious degradation at room temperature and a significantly accelerated degradation at 100°C .

Finally, CuO grown by room-temperature direct current (DC) reactive magnetron sputtering is introduced to realize p-type thin-film transistors (TFTs), with a high-k HfO_2 gate dielectric fabricated by atomic layer deposition (ALD). The devices work in an accumulation mode (AM) with two apparent threshold voltages corresponding to the formation of a buried channel and an accumulation layer, respectively. A CuO AM TFT with a channel length of $25 \text{ }\mu\text{m}$ exhibits a competitive on-off ratio (I_{on}/I_{off}) of 1.3×10^2 , a subthreshold swing (SS) of 1.04 V dec^{-1} , and a field-effect mobility (μ_{FE}) of $1.1 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at room temperature. By measuring a CuO metal oxide semiconductor (MOS) capacitor, a high acceptor doping density (N_A) of $\sim 5 \times 10^{17} \text{ cm}^{-3}$, a very high positive effective fixed surface charge density (Q_f) of $\sim 9 \times 10^{12} \text{ cm}^{-2}$ and a low interfacial trap charge density (D_{it}) of $\sim 6 \times 10^{10} \text{ eV}^{-1} \text{ cm}^{-2}$ at the HfO_2/CuO interface are estimated. The μ_{FE} extracted in accumulation regime appears lower than the Hall mobility measured for a similarly processed CuO layer on glass due to the increased hole concentration in CuO TFTs, compared to a Hall concentration of $\sim 10^{14} \text{ cm}^{-3}$, following the MOS process. SS appears limited by the decreased channel to gate capacitance (C_{cg}) related to the buried channel in AM TFTs, parasitic capacitance to ground and potentially very high interfacial traps at the non-passivated CuO/air interface.

Publications

Journal articles:

- [P1] Zeng Xi*, Zhukova Maria, Faniel Sébastien, Li Guoli, Flandre Denis. *Room-temperature DC-sputtered P-type CuO Accumulation-mode Thin-film Transistors Gated by HfO₂*. In: *Applied Physics Letters*, Vol. 121, no. 13, 133503 (2022). doi:10.1063/5.0098757.
- [P2] Zeng Xi*, Lontchi Jackson, Zhukova Maria, Bolt Pieter, Smor Marcel, Fourdrinier Lionel, Li Guoli, Flandre Denis. *A High-performance Dual-mode Ultra-thin Broadband CdS/CIGS Heterojunction Photodetector on Steel*. In: *Optics Express*, Vol. 30, no.8, p. 13875-13889 (2022). doi:10.1364/OE.456352.
- [P3] Zeng Xi*, Lontchi Jackson, Zhukova Maria, Fourdrinier Lionel, Qadir Israr, Ren Yi, Niemi Esko, Li Guoli, Flandre Denis. *High-responsivity broadband photodetection of an ultra-thin In₂S₃/CIGS heterojunction on steel*. In: *Optics Letters*, Vol. 46, no.10, p. 2288-2291 (2021). doi:10.1364/OL.423999.
- [P4] Wei Peng*, Sabri Alirezaei Iman, André Nicolas, Zeng Xi, Bouterfa Mohamed, Wang Bin, Zeng Yun, Flandre Denis. *The Shift of Breakdown Voltage for Silicon Membrane Strip Detectors Resulting from Surface Avalanche*. In: *Journal of Applied Physics*, Vol. 129, no.21, p. 214501-1/7 (2021). doi:10.1063/5.0049490.
- [P5] Zeng Xi*, Zhukova Maria, Faniel Sébastien, Proost Joris, Flandre Denis. *Structural and Opto-electronic characterization of CuO thin films prepared by DC reactive magnetron sputtering*. In: *Journal of Materials Science: Materials in Electronics*, Vol. 31, p. 4563-4573 (2020). doi:10.1007/s10854-020-03007-4.

Conference papers/posters:

- [P6] Zeng Xi*, Zhukova Maria, Faniel Sébastien, Proost Joris, Flandre

Denis. *Material, optical and electrical characterization of DC sputtered CuO by tuning oxygen concentration*. EMRS-Spring meeting 2021 (Virtual meeting, from 31/05/2021 to 04/06/2021). In: *Proceedings of the EMRS-Spring meeting 2021*, 2021.

[P7] Wei Peng*, André Nicolas, **Zeng Xi**, Sabri Alirezaei Iman, Li Guoli, Bouterfa Mohamed, Francis Laurent, Flandre Denis. *Micrometer-thin SOI Sensors for E-Skin Applications*. 2020 IEEE SENSORS (Rotterdam (the Netherlands), from 25/10/2020 to 28/10/2020). In: *IEEE Sensors. Proceedings*. doi:10.1109/SENSORS47125.2020.9278716.

List of Acronyms

Acronym	Description
1D	One dimensional
2D	Two dimensional
AC	Active Current
Ag	Silver
Al	Aluminum
Al ₂ O ₃	Aluminum Oxide
ALD	Atomic Layer Deposition
AM	Accumulation Mode
Ar	Argon
Au	Gold
AZO	Aluminum-doped Zinc Oxide
CBD	Chemical Bath Deposition
CBM	Conduction Band Minimum
CBO	Conduction Band Offset
CdS	Cadmium Sulfide
CIGS	Copper Indium Gallium Selenide
CMOS	Complementary Metal Oxide Semiconductor
Cr	Chromium
Cu ₂ O	Cuprous Oxide
CuO	Copper Oxide

CVD	Chemical Vapor Deposition
CZTS	Copper Zinc Tin Sulfide
D	Diode
DC	Direct-Current
DI	De-ionized
Fe	Ion
FIB	Focused Ion Beam
G/R	Generation/Recombination
GaN	Gallium Nitride
Ge	Germanium
H ₂ O	Water
HfO ₂	Hafnium Oxide
In ₂ S ₃	Indium Sulfide
InGaAs	Indium Gallium Arsenide
ITO	Indium Tin Oxide
IZO	Indium-doped Zinc Oxide
K	Potassium
LED	Light Emitting Diode
LFHC	Oxygen-Free High Conductivity
LPC	Lateral Photocurrent
LPV	Lateral Photovoltage
MgZnO	Magnesium-doped Zinc Oxide
Mo	Molybdenum

MoNa	Sodium-containing Molybdenum
N ₂	Nitrogen
NaF	Sodium Fluoride
Ni	Nickel
O ₂	Oxygen
PC	Photoconductive Mode
PCB	Printed Circuit Board
PDS	Position Sensitive Detector
PE-ALD	Plasma-Enhanced ALD
PI	Polyimide
PLD	Pulsed Laser Deposition
PV	Photovoltaic Mode
PVD	Physical Vapor Deposition
QNR	Quasi-Neutral Region
RF	Radio Frequency
SCR	Space Charge Region
SEM	Scanning Electron Microscope
Si	Silicon
SiO ₂	Silicon Dioxide
SLG	Soda Lime Glass
SOI	Silicon-On-Insulator
TCO	Transparent Conductive Oxide
TE-ALD	Thermal-Enhanced ALD

TFT	Thin-Film Transistors
Ti	Titanium
TLM	Transmission Line Model
TMDAH	$[(\text{CH}_3)_2\text{N}]_4\text{Hf}$
UV	Ultraviolet
VBM	Valence Band Maximum
VBO	Valence Band Offset
VIS	Visible
XRD	X-ray Diffraction
ZnO	Zinc Oxide

List of Symbols

Acronym	Description	Unit
α	Absorption coefficient	cm^{-1}
ε	Dielectric constant	/
ε_0	Vacuum permittivity	F m^{-1}
Θ_r	Angel of refraction	degrees
λ	Light wavelength	nm
τ_{life}	Minority carrier lifetime	s
$\tau_{n,eff}$	Effective minority carrier lifetime	s
τ_m	Electron transit time	s
τ_{tp}	Hole transit time	s
φ	Potential	V
φ_s	Semiconductor work function	eV
χ	Electron affinity	eV
ρ	Resistivity	$\Omega \text{ cm}$
ρ_{c-eff}	Effective contact resistivity	$\Omega \text{ cm}^2$
μ_{FE}	Field-effect mobility	$\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}$
μ_n	Electron mobility	$\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}$
μ_p	Hole mobility	$\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}$
A	Absorbance	/
A_{eff}	Effective area	cm^2
B	Bandwidth	Hz

B	Magnetic field	T
c	Light velocity	m s ⁻¹
C	Capacitance per area	F cm ⁻²
C_{cg}	Channel to gate capacitance per area	F cm ⁻²
C_{hi}	Low-frequency capacitance per area	F cm ⁻²
C_{it}	Interfacial trap capacitance per area	F cm ⁻²
C_{lo}	High-frequency capacitance per area	F cm ⁻²
C_{ox}	Oxide capacitance per area	F cm ⁻²
C_{stot}	Total substrate capacitance per area	F cm ⁻²
C_{sub}	Channel to ground capacitance per area	F cm ⁻²
d	Light penetration depth	m
D	Detectivity	Jones
D_{it}	Interfacial trap charge density	eV ⁻¹ cm ⁻²
D_n	Electron diffusion coefficient	cm ² s ⁻¹
D_p	Hole diffusion coefficient	cm ² s ⁻¹
E	Electric field	V cm ⁻¹
E_F	Fermi level	eV
E_{FN}	Quasi-electron Fermi level	eV
E_{FP}	Quasi-hole Fermi level	eV
E_g	Optical bandgap	eV
EQE	External quantum efficiency	/
E_U	Urbach energy	eV
f	Frequency	Hz

$F_{Lorentz}$	Lorentz force	N
g	Average photogeneration rate	$\text{cm}^{-3} \text{ s}^{-1}$
G	Conductance	S
G	Photogain	/
g_m	Transconductance	S
h	Plank constant	J s
I	Current	A
I_D	Drain current	A
I_{dark}	Dark current	A
I_{light}	Current under illumination	A
I_n	Total noise current	A
I_{ns}	Shot noise current	A
I_{photo}	Photocurrent	A
J	Current density	A cm^{-2}
J_0	Reverse saturation current	A cm^{-2}
J_{dark}	Dark current density	A cm^{-2}
k	Boltzmann constant	J K^{-1}
L_{drift}	Hole drift length	nm
L_T	Transfer length	nm
n	Non-ideality factor	/
N_A	Net acceptor concentration	cm^{-3}
N_{CV}	Net free carrier concentration	cm^{-3}
$\overline{\Delta n}$	Average excess electron concentration	cm^{-3}

Δn	Excess electron concentration	cm^{-3}
NEP	Noise equivalent power	$\text{W Hz}^{-1/2}$
N_p	Hole concentration	cm^{-3}
n_r	Refractive index	/
N_V	Effective density of states in valence band	cm^{-3}
P	Light density	W cm^{-2}
Δp	Excess hole concentration	cm^{-3}
q	Electron charge	C
Q_f	Surface charge density	cm^{-2}
R	Reflectance	/
R	Resistance	Ω
R_C	Contact resistance	Ω
$R_{diffuse}$	Diffuse reflectance	/
R_{metal}	Metal resistance	Ω
R_{ph}	Photoresponsivity	A W^{-1}
R_s	Series resistance	Ω
R_{semi}	Semiconductor resistance	Ω
R_{sh}	Sheet resistance	$\Omega \text{ sq}^{-1}$
R_{shunt}	Shunt resistance	Ω
$R_{specular}$	Specular reflectance	/
R_T	Total resistance	Ω
R_{total}	Total reflectance	/
SNR	Signal-to-noise ratio	/

SS	Subthreshold swing	$V \text{ dec}^{-1}$
t	Thickness	nm
T	Transmittance	/
$Temp$	Temperature	K
ν	Light frequency	Hz
V	Voltage	V
v_c	Drift velocity of charges	m s^{-1}
V_D	Drain voltage	V
V_{FB}	Flat-band voltage	V
V_G	Gate voltage	V
V_H	Hall voltage	V
V_r	Reverse bias	V
V_{th}	Threshold voltage	V
W_d	Depletion region width	nm
$W_{diffusion}$	Diffusion length	nm

Introduction

Photodetectors, which can convert optical signals to electrical signals, are highly demanded in various applications, including large-area imaging, optical communication, defense technology, and monitoring systems in environmental and biomedical applications [1-3]. Most of the photodetectors up to date are based on the traditional Si, Ge or III-V group semiconductors for instrumentation or communication applications, toward high performance but limited device size (maximum a few mm²). These semiconductors are already mature and currently meet a great challenge to further enhance their performances. The best reported thin-film silicon-on-insulator (SOI) photodiodes on membrane made in Université Catholique de Louvain reached the responsivity of 0.09-0.11 A W⁻¹ within the wavelength of 450-520 nm [4]. To exceed the photodetection capabilities of standard Si technologies, investigating new materials targeting photodetection applications is of great interest. In this thesis, several scientific questions are addressed.

Question 1: What are the motivations to investigate CIGS and CuO towards large-area opto-electronic devices?

In order to achieve large-area photodetection over a few cm² with higher sensitivity, higher opto-electronic transfer efficiency and lower cost, significant progress has been achieved for the studies related to n-type thin-film semiconductors, while equally well-performing p-type thin-film semiconductors still remain challenging to date, notably because of their limited material options, low mobility caused by a high valence band maximum (VBM) and strict fabrication conditions. Among limited p-type semiconductors, materials inspired from solar cell structures including CIGS [5], CuO [6], CZTS [7], etc. possess the

potential as large-area broadband photodetection materials thanks to their all-adapted bandgap and high absorption coefficient. In this thesis, two p-type thin-film semiconductors, CIGS and CuO, are investigated based on novel fabrication processes, device designs, characterizations, and simulations, to realize different high-performance large-area optoelectronic devices.

Question 2: How and by how much could the photodetection capabilities of CIGS devices be improved?

Inspired from photovoltaic cells, CIGS heterojunction photodiodes have been rarely studied up to date. Their optimization and full understanding are of great challenge. Aiming at large-area broadband photodetection with better performance and sustainability, CIGS photodiodes are optimized here by reducing the CIGS thickness below 1 μm , introducing industry-compatible flexible steel substrates, alkali doping and multiple buffer layers (CdS and Cd-free In_2S_3).

Question 3: How to understand and explain the high photogain in the CIGS photodiodes?

CIGS photodiodes could exhibit dual-mode photodetection capabilities, i.e. the photovoltaic and photoconductive modes. The photogain of CIGS photodiodes could be enhanced by external bias. High photogain over 1 observed in CIGS photodiodes remains questionable due to the lack of accurate explanation about the gain mechanism. A corrected photoconductive gain mechanism is needed to accurately explain the operation mechanisms of CIGS photodiodes.

Question 4: How to fabricate and characterize reliable large-area CuO devices?

CuO, as a more sustainable semiconductor material than CIGS, could be used in manifold applications including photodetectors, solar

cells and thin-film transistors (TFTs). However, full fabrication and characterization of large-area CuO thin films and related devices with excellent performances require further investigation. A large-area fabrication method should be considered for CuO fabrication. To further investigate the interfacial properties of CuO with metal and dielectric, transmission line model (TLM) structures and a CuO metal-oxide-semiconductor (MOS) capacitor could be studied. Finally, CuO TFTs could be fabricated, characterized, and analyzed on soda lime glass.

With these concerns, the main contributions of the thesis are as follows:

Chapter 1 presents a brief introduction of the state of the art concerning CIGS photodiodes and CuO TFTs, respectively. Characterization methodologies of CIGS photodiodes are discussed including the classical structure, the single- and double-diode models for dark characterization, and the photoresponse metrics for optical characterization. Fabrication methodologies including sputtering, atomic layer deposition and lithography are discussed. Meanwhile, core characterization methodologies for CuO TFTs are discussed towards evaluating the thin film performance.

Chapter 2 studies an ultra-thin CdS/CIGS heterojunction photodiode fabricated on steel, exhibiting dual-mode broadband photodetection from the ultraviolet to near infrared spectrum [P2]. SCAPS-1D and SILVACO ATLAS-2D simulations are investigated to understand and analyze the dark I - V and C - V behaviors, and the band offsets of the CdS/CIGS heterojunction. The optical characterizations of photodiode are discovered in the broadband spectrum, and at a constant incident wavelength of 680 and 870 nm with varying incident light power, showing high external quantum efficiency (EQE) over 100%

and photogain over 1. A corrected photoconductive gain model is firstly introduced to explain such high photoconductive gain in CIGS photodetectors.

Chapter 3 studies an ultra-thin $\text{In}_2\text{S}_3/\text{CIGS}$ heterojunction photodiode fabricated on steel, firstly considering In_2S_3 as a Cd-free buffer layer for CIGS photodetectors [P3]. The dark behaviors of the $\text{In}_2\text{S}_3/\text{CIGS}$ photodiode are described by the single-diode model. The optical characterizations of $\text{In}_2\text{S}_3/\text{CIGS}$ photodiode are investigated in a broadband spectrum from the ultraviolet to near infrared spectrum, and at a constant incident wavelength of 680 and 870 nm with varying incident light power, showing its optimized band offset, excellent broadband photoresponse, and possibility to operate both in the photoconductive and photovoltaic modes. SILVACO ATLAS-2D simulations are discovered to study the operation mechanisms and the band offsets of the $\text{In}_2\text{S}_3/\text{CIGS}$ photodiode compared to the CdS/CIGS photodiode.

Chapter 4 studies CuO , a p-type metal oxide semiconductor. Targeting the best-performing p-type CuO with a bandgap around 1.5 to 1.7 eV, a carrier concentration around 10^{15} cm^{-3} , an absorption coefficient over 10^5 cm^{-1} , and a maximum carrier mobility, direct-current (DC) reactive magnetron sputtering is introduced as a reliable technique in the large-area fabrication [P5, P6]. By tuning oxygen concentration during sputtering, the best sputtering regime is confirmed considering the structural and opto-electronic characterizations. In order to optimize CuO thin films, more sputtering parameters are considered including sputtering pressure and oxygen to argon gas ratio. Meanwhile, high-temperature processes including substrate heating during sputtering and post annealing are both considered. Related

optical and electrical characterizations are introduced to select the best-performing CuO thin films for future applications.

Chapter 5 studies the Au/CuO transmission line model (TLM) structures to find a suitable metal with an ohmic contact with CuO. By fabricating and measuring Au/CuO TLM down structures, contact characteristics at the Au/CuO interface are investigated. TLM structures are characterized both in N₂ ambient and vacuum considering different structure configurations like strip widths and CuO widths. Furthermore, the degradation of sputtered CuO is discovered and analyzed in vacuum at room temperature and 100 °C, respectively.

Chapter 6 studies room-temperature DC-sputtered p-type CuO thin-film transistors (TFTs) gated by HfO₂ [P1]. Selected CuO thin film by previous research is introduced in the fabrication of CuO TFTs. Material characterizations are investigated to determine the properties of DC sputtered CuO thin film on glass. A CuO MOS capacitor is fabricated and characterized to investigate the electrical properties of CuO/HfO₂ interface. Finally, CuO TFTs are fabricated and characterized, showing competitive performances in an accumulation mode.

Chapter I

State of the Art and Methodologies

1.1 State of the art

1.1.1 CIGS photodiodes

Large-area broadband photodetectors from ultraviolet to infrared regime with higher sensitivity, responsivity and detectivity, are more and more sought in recent studies. However, most of the commercial photodetectors optimally operate only at a specifically narrow spectral range, such as GaN-, Si-, or InGaAs-based photodetectors for ultraviolet, visible or near infrared spectrum photodetection, respectively [1, 8]. To realize photodetection from ultraviolet to infrared light, with sufficient performance, broadband photodetectors with wide spectral sensitivity and high opto-electronic transfer efficiency are required in the optical communication, wide spectral switches, or memory storage by using a single detector [9].

Photodetectors normally work either in a photovoltaic mode without an external bias or in a photoconductive mode with an external bias. In the photovoltaic mode, a self-driven photodetector usually demonstrates high detectivity for weak signal detection [10]. However, its external quantum efficiency (EQE) is theoretically below 100%, which also limits the responsivity. Conversely, in the photoconductive mode, the responsivity is significantly enhanced thanks to an external bias and an improved charge collection efficiency [11, 12]. However, the illumination to dark current ratio and the detectivity are sacrificed in this mode due to a rising dark current. Besides, conventional photodetectors working in the photoconductive mode consumes external energy, while self-driven photodetectors working in the photovoltaic mode can sustainably operate as individual sensors in the harsh environments without external energy consumption [10, 13]. Therefore, dual-mode photodetectors, which can dynamically switch

operation modes, show their potential to realize high detectivity and responsivity simultaneously in a single device [14].

Heterojunctions used in photovoltaic devices usually have excellent designs for broadband photodetection thanks to their wide light detection in solar spectrum. As a high-efficient p-type semiconductor used in photovoltaic applications, Cu(In,Ga)Se₂ (CIGS) is one of the candidates to be used as a light absorbing material in broadband ultra-thin photodetectors covering the whole visible spectrum thanks to its tunable direct bandgap between 1.04 and 1.67 eV [15]. Additionally, relatively high absorption coefficient over 10⁵ cm⁻¹ makes it possible to limit the thickness of CIGS below 1 μm [16], which reveals the ability to fabricate high-quality ultra-thin commercial CIGS in a low-cost way. Due to its photovoltaic property, CIGS photodetectors can also work in a self-powered way for low or no energy consumption and thus possess the potential to be used as dual-mode photodetectors [5].

While being a promising photosensitive semiconductor material for photodetection, few CIGS photodetectors have been reported. CIGS was proved as a mature material to form heterojunctions by introducing CdS as a buffer layer in solar cell designs, achieving ultra-high power conversion efficiency both on glass [17] and flexible polyimide (PI) [18]. Among various structures for CIGS photodetectors, CdS/CIGS heterojunctions were proved to be mature structures for photodetection [5, 16, 19]. Working in the photoconductive mode, CdS/CIGS heterojunction photodiodes on polyimide were firstly studied, demonstrating broadband photodetection between 350 and 1200 nm, a responsivity of 1.18 A W⁻¹ at 808 nm illumination and an enhanced responsivity of 2.07 A W⁻¹ under a compressive strain [5]. By potassium (K) incorporation into CIGS, CdS/CIGS heterojunction photodiode was

improved specifically for the near infrared photodetection, reaching a responsivity of 1.87 A W^{-1} and an EQE of 237% at 980 nm [19]. Working in the photoconductive mode as a self-driven photodetector, Al_2O_3 passivation layer was introduced in CdS/CIGS self-driven heterojunction to decrease the leakage current and improve the photodetection performance, obtaining a high detectivity of 1.84×10^{12} Jones [16]. In this mode, CdS/CIGS heterojunctions were also used to fabricate self-driven lateral photovoltage (LPV) and photocurrent (LPC) -based optical position sensitive detectors (PSD) thanks to a lateral photovoltaic effect [20, 21]. Additionally, p-CIGS nanoparticles/n-Si nanowire array core-shell structure realized self-driven broadband photodetection [22].

Expect for CdS/CIGS heterojunctions, heterojunctions considering other n-type materials were studied because traditional CdS is not a perfect buffer layer due to an optical absorption loss at shorter wavelength and the toxicity of the element Cd to the environment [23, 24]. Among various options for the buffer layer, In_2S_3 is regarded as an ideal replacement of CdS because of its non-toxicity, long-term stability, and an upshift of conduction band minimum (CBM) level, which is helpful to reduce the carrier recombination at interface [25, 26]. However, In_2S_3 has not been studied as a buffer layer for CIGS photodetectors.

All previously-reported CIGS photodetectors with CdS or Cd-free buffer layers had relatively high CIGS thicknesses over $1 \mu\text{m}$, focused either on a single mode, or on a specifically narrow band photodetection. For several CIGS photodiodes working in the photoconductive mode under high bias, EQEs have reached over 100%, which was explained by a classical photoconductive gain mechanism caused by photogenerated carrier recirculation and hole injection [5, 19]. However,

this hypothesis is problematic because hole injection appears both in the dark and under illumination if this injection is caused by the band bending from external bias. Both light and dark currents would thus increase, but it's questioned whether the injection gets stronger when the device is illuminated. Therefore, it is vital to investigate an accurate photoconductive gain mechanism for CIGS photodiodes.

Fabricating photodetectors on flexible substrates is of great interest because roll-to-roll deposition methods can be implemented to lower the manufacturing cost compared to traditional batch-to-batch or in-line methods on rigid glass substrates [27]. As a well-known promising flexible substrate, a low-cost stainless-steel foil is used in this work because of its commercial availability, mechanical stability, and resistance to high temperature [28, 29]. However, flexible substrates cannot provide alkaline doping due to the lack of alkaline elements compared to standard rigid substrates like soda lime glass substrates. Soda lime glass substrates are indeed considered as mature substrates to provide the diffusion of alkaline elements like Na and K through the Mo back electrode into CIGS during the CIGS growth [30]. The doping from alkaline elements can passivate the defects at the CIGS surface, increase the hole concentration in the CIGS absorber and thus contribute to a higher free carrier density used for photoresponse [31-33]. To provide alkaline elements on flexible substrates, an additional layer like NaF precursor, MoNa, etc. can be introduced in prior to the CIGS deposition.

1.1.2 CuO thin-film transistors

Considering that CIGS is commercially more expensive and less sustainable because of indium and gallium, earth-abundant materials, that can be fabricated in a lower-cost way, are highly demanded like CZTS and CuO. Copper oxide appears a good candidate as one of the

most promising p-type metal oxide semiconductors because of its abundance in the earth crust, low cost, nontoxicity, easy recyclability, stability in the air as well as high optical absorption and good charge transport properties [34, 35]. Copper oxide with three different phases (CuO , Cu_4O_3 and Cu_2O) can be obtained by varying the fabrication parameters. Compared to Cu_4O_3 and Cu_2O , p-type monoclinic CuO with lower tunable bandgap from 1.2 to 1.9 eV, higher optical absorption and more stable chemical performance, is more suitable to be used as the photo-absorption material in photodetector applications [35-37].

Several techniques have been considered in the synthesis of CuO , including thermal oxidation [38,39], atomic layer deposition [40], ionic layer deposition [41], chemical bath deposition [42], sol-gel process [43], solution process [44], vapor-liquid-solid method [45], pulsed laser deposition [46], spin-coating [47], microwave-activated sputtering [48], magnetron sputtering [49, 50] etc. Among these techniques, DC reactive magnetron sputtering is an easy-controlled, low-cost and reliable technique in large-area industrial fabrication. The structural, physical, optical or electrical properties of CuO prepared by direct current (DC) reactive magnetron sputtering have been recently studied considering variations in oxygen partial pressure [51-57]. Radio frequency (RF) reactive magnetron sputtering is also considered in CuO deposition [58]. However, few research focus on the overall fabrication, characterization and analysis of sputtered CuO thin films. Therefore, sputtering and optimization of CuO thin films by tuning the sputtering parameters are necessary before the fabrication of high-performance CuO -based semiconductor devices.

Metal oxide semiconductors, as the most abundant materials in the earth's crust, are widely used in thin-film transistors (TFTs) because of

their good carrier mobilities, low off-current, large-area uniformity and processibility, mechanical stress tolerance, good stability, and low cost [59-61]. Particularly for n-type metal oxides, significant progress has been achieved to fabricate n-type TFTs with excellent electrical performances [62]. However, realization of equally well-performing p-type metal oxides and TFTs still remains challenging because of limited options for p-type oxides, low mobility caused by a high valence band maximum (VBM), and their strict fabrication conditions [63, 64]. Few p-type metal oxides like tin oxide [65], nickel oxide [66], and copper oxide [67] have exhibited good performances in TFTs. Therefore, it is of great interest to study p-type metal oxides, realizing either sensing or memory applications with a single p-type TFT, or p-n junctions and complementary metal oxide semiconductor (CMOS) logic circuits along with n-type counterparts [64, 68].

Among different techniques used to fabricate copper oxide TFTs, one of the earliest Cu₂O TFTs was fabricated by pulsed laser deposition (PLD) at high temperatures from 400 to 700 °C [67]. Room-temperature RF magnetron sputtering was used to fabricate Cu₂O TFTs, showing the possibility to further oxidize Cu₂O to CuO with air annealing [69, 70]. More recently, sol-gel processed CuO TFT with a field-effect mobility (μ_{FE}) of $4 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and an on-off ratio of $\sim 10^2$ exhibits good photodetection capabilities [43]. Hypochlorous acid oxidation was used to tune the oxygen concentration in copper oxide, reaching an improved on-off ratio of 4.86×10^4 , with a μ_{FE} of $2.83 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ [61]. Atomic layer deposition (ALD) was used to fabricate Cu₂O TFT with an Al₂O₃ surface passivation, showing a μ_{FE} of $1.3 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ [71]. Ni doping can improve the crystalline quality of CuO fabricated by solution-processed method and thus enhance the μ_{FE} to $0.01 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ [72]. Relatively low μ_{FE} from 10^{-4} to $10^{-1} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ have been obtained for most of the copper oxide TFTs related to high contact resistance and

interfacial trap states [73]. However, most reported works focused on SiO₂ gate dielectrics based on standard silicon techniques. Another suitable high-k dielectric, HfO₂, deposited either by anodic formation from Hf [74] or PLD [75], has been rarely studied in CuO TFTs. ALD, as one of the best fabrication methods to produce an ultrathin high-quality dielectric, has been rarely studied yet to realize CuO TFTs with HfO₂ gate dielectrics.

1.2 Methodologies for CIGS photodiodes

1.2.1 Structure of CIGS heterojunctions

To make the most use of incident illumination and improve the device performance, several layers are required in CIGS heterojunctions except for the CIGS absorber. Figure 1.1 shows the classical design of solar cells or photodetectors with CIGS heterojunctions. The substrates used for CIGS devices can be either rigid substrates like glass or flexible substrates like polyimide and steel. In this thesis, steel substrates are firstly used for CIGS photodetectors but an additional isolation layer on top is required because steel is conductive and could cause leakage current on the bottom. Meanwhile, the isolation layer prevents the diffusion of Fe and Cr from the steel substrate toward the device.

On top of the substrate, a stack of layers is deposited to make a complete design of CIGS heterojunctions. Mo layer is considered as the rear contact of the device, while MoSe₂ is formed on top of Mo in some designs to make a good ohmic contact with CIGS. CIGS as the absorber layer is the key material in the whole structure and makes up the majority thickness of the whole stack. The standard thickness for CIGS absorber is 1-2.5 μm , while the thickness of CIGS is reduced below 1 μm in this thesis to fabricate photodetectors in an easier and lower-cost

way. On top of the CIGS, a buffer layer is deposited, which can be either CdS or other Cd-free materials like In_2S_3 , MgZnO , etc. Above the buffer layer, a high-resistive window layer like intrinsic ZnO is deposited to avoid any possible shunting paths in the device. Finally, a conductive layer and metal grids are deposited on top to form a front contact of the device. The conductive layer with high carrier mobility and low resistivity is normally a n-type transparent conductive oxide (TCO) like ITO, AZO, etc. to make an ohmic contact with top metal electrodes.

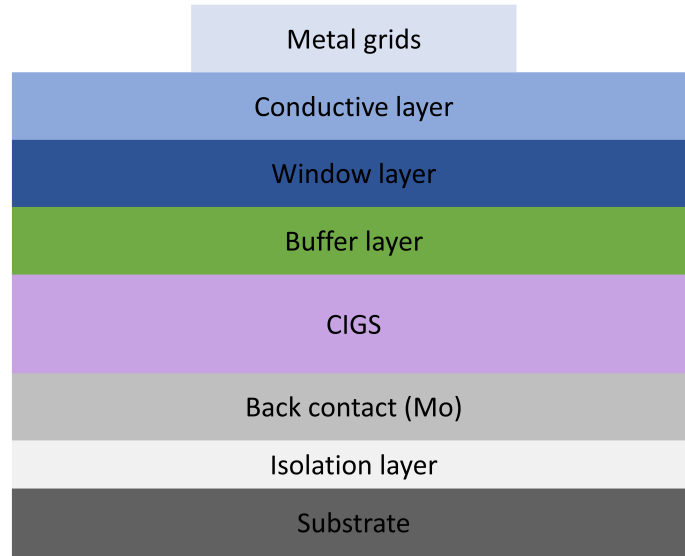


Figure 1.1. Schematics of conventional CIGS heterojunctions.

1.2.2 Single- and double-diode models

In order to investigate the dark characteristics of photodiodes, single-diode and double-diode models are normally discovered to fit the dark current-voltage ($I_{\text{dark}}-V$) and dark current density-voltage ($J_{\text{dark}}-V$) experimental curves and extract the electrical parameters of dark experimental curves.

Single-diode model, which includes a diode (D), a shunt resistance (R_{shunt}) and a series resistance (R_s), is widely used in most situations

thanks to its simplicity and accuracy. The equivalent circuit of this model is presented in **Figure 1.2(a)**. In this model, each component is extracted from corresponding bias region to distinguish the different contributions to J_{dark} , which is modelled by:

$$J_{dark} = J_0 \left\{ \exp \left[\frac{q(V - J_{dark}R_s)}{n_0 k Temp} \right] - 1 \right\} + \frac{V - J_{dark}R_s}{R_{shunt}} \quad (1.1)$$

where J_0 is the reverse saturation current density, V is the applied voltage, q is the electron charge, n_0 is the non-ideality factor, k is the Boltzmann constant, and $Temp$ is the temperature. Under forward bias, the reverse saturation current density (J_0) and non-ideality factor (n) of D, as well as R_s , jointly contribute to J_{dark} . However, R_{shunt} , here contributes mainly to J_{dark} under reverse bias, and is hence a more important parameter for photodiodes, because light absorption is studied under such conditions.

A constant n dominated by R_s especially in large area devices is assumed in the single -diode model, but the ideality factor is normally a function of voltage across the device. In such case, the carrier recombination in the junction at low bias is not considered. Introducing a second diode in parallel with the first one, **Figure 1.2(b)** represents the equivalent circuit of the double-diode model, which consists of Diode 1 (D1), Diode 2 (D2), series resistance (R_s) and shunt resistance (R_{shunt}). The total dark current density J_{dark} is presented by:

$$J_{dark} = J_{01} \left\{ \exp \left[\frac{q(V - J_{dark}R_s)}{n_1 k Temp} \right] - 1 \right\} + J_{02} \left\{ \exp \left[\frac{q(V - J_{dark}R_s)}{n_2 k Temp} \right] - 1 \right\} + \frac{V - J_{dark}R_s}{R_{shunt}} \quad (1.2)$$

In this model, the photodiode is analyzed at each corresponding bias region to extract every current contribution from the total dark current. At high forward voltage, diffusion current in the PN junction is dominated in D₁, which can be characterized by its current density J_{01} and non-ideality factor n_1 . While at low forward voltage,

generation/recombination (G/R) current is dominated in D_2 , which can be characterized by its current density J_{02} and non-ideality factor n_2 . Ideally for silicon diodes, n_1 and n_2 are equal to 1 and 2, corresponding to diffusion current and recombination current, respectively. In practice, the recombination mechanism is complex and varied with different external bias. In such case, the single-diode model is better suited for photodiodes operating in the reverse bias while the double-diode model is usually used for photovoltaic cells in the forward bias.

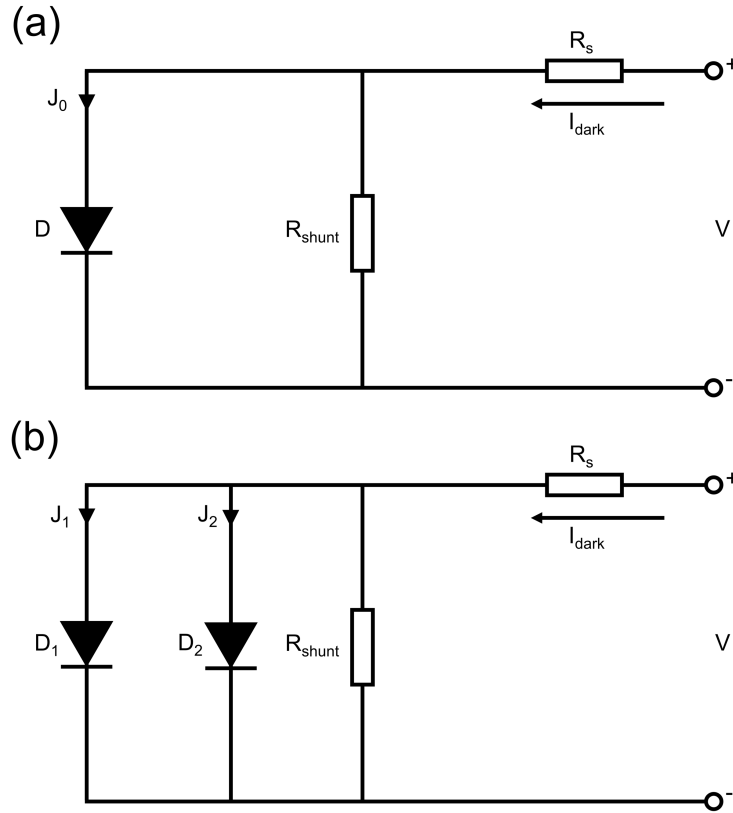


Figure 1.2. Equivalent electrical circuit of (a) single- and (b) double-diode models.

1.2.3 Photoresponse metrics

Photodetectors are semiconductor devices which can detect and convert the optical signals through electronic processes and extract photoexcited carriers as the terminal current to provide output electrical

signals [76]. In this process, the photodetection performances of a photodetector can be evaluated by several parameters, including photoresponsivity (R_{ph}), detectivity (D), noise equivalent power (NEP), external quantum efficiency (EQE), and photogain (G). These figures of merits are widely studied in this thesis to investigate the optical performances of photodetectors.

Photoresponsivity (R_{ph}), a critical parameter defined as the ratio of photo-generated current to the illumination light power on the effective device surface, evaluates the photodetector sensitivity to the incident light and is calculated by [77]:

$$R_{ph} = \frac{I_{photo}}{PA_{eff}} = \frac{I_{light} - I_{dark}}{PA_{eff}} \quad (1.3)$$

where I_{photo} is the excited photocurrent, I_{light} is the current under illumination, I_{dark} is the current in the dark, P is the incident light density, and A_{eff} is the effective illuminated area of the photodetector.

Detectivity (D), a normalized parameter to evaluate the ability to detect weak optical signal, assuming that the total noise is dominated by shot noise, is given by:

$$D = \frac{R_{ph}A_{eff}^{0.5}}{(2qI_{dark})^{0.5}} \quad (1.4)$$

Apart from photodetection signals, noise is another key figure of merit to determine the minimum detectable signal strength. Many factors contributing to the noise would degrade the device performance, including leakage current, background radiation, thermal noise, shot noise, flicker noise, generation-recombination noise, generation noise etc [76]. But it's not necessary to analyze every detailed noise source, the total noise is normally considered in a related figure of merit called noise equivalent power (NEP). NEP is defined as the minimum incident optical power to produce a signal-to-noise ratio (SNR) of 1 in a 1 Hz

bandwidth, is obtained by [78, 79]:

$$NEP = \frac{I_n}{R_{ph}} \approx \frac{I_{ns}}{R_{ph}} = \frac{(2qI_{dark}B)^{0.5}}{R_{ph}} = \frac{(A_{eff}B)^{0.5}}{D} \quad (1.5)$$

where I_n is the total noise current, and B is the bandwidth (B is normalized as 1 Hz). In photodetectors, shot noise current (I_{ns}) from the dark current is dominant [80]. Defining B as 1 Hz, NEP of the photodetectors can be simply calculated from D [78, 80].

External quantum efficiency (EQE), which can also be described as photogain (G), is defined as the ratio of photogenerated carriers to incident photons, and obtained by [79]:

$$G = EQE = \frac{hcR_{ph}}{q\lambda} \quad (1.6)$$

where h is the Plank constant, c is the light velocity, and λ is the incident light wavelength. EQE is highly dependent on the incidence light wavelength and device geometry.

1.3 Methodologies for CuO TFTs

CIGS photodetectors were mainly fabricated by our partners, but CuO thin films and related CuO structures were fabricated in the clean room of UCLouvain. Various fabrication methods are utilized in this thesis including e-beam evaporation, magnetron sputtering, atomic layer deposition, optical lithography, etc. Meanwhile, various characterization methods are used to obtain the best-performing CuO thin films for the fabrications of CuO devices. In this section, general principles of some important fabrication and characterization methods used in this thesis are introduced and analyzed. More fabrication details of materials and devices will be illustrated in the later chapters.

1.3.1 Magnetron sputtering

Magnetron sputtering is a physical vapor deposition (PVD) technique, targeting on obtaining homogenous thin films with well-controlled thickness and material composition. Magnetron sputtering is widely used in industrial fabrication especially for large-area applications as an easy-controlled, low-cost and reliable technique. **Figure 1.3** shows the deposition principles of magnetron sputtering and the configuration of ATC Orion 5 Sputter System from AJA International used in this thesis. In this system, the target is placed above several permanent magnets and electrically connected to the oxygen-free high conductivity (OFHC) copper to apply a bias and evacuate the heat. Inside the OFHC copper, water channels under the target are also introduced to maintain a constant sputtering temperature. The substrate fixed in the sample holder is rotated at a rate of 45 rpm and positioned 122 mm away from the target.

In order to create a gaseous plasma during sputtering, atoms of an inert gas like Ar are introduced into the high vacuum sputtering chamber. Such plasma, described as the fourth state of matter, is a dynamic condition when neutral atoms, ions, electrons and photons exist simultaneously. To ignite the plasma, a DC or RF energy source is required to apply a negative bias on the target while the chamber is grounded. DC energy source is typically used for the conductive targets while RF is used for the insulating targets. Upon applying a negative bias, free electrons near the target are immediately accelerated by the electrical field and move away from the negatively charged target. These electrons would collision the Ar atoms and result in the ionization of neutral Ar atoms, leaving positively charged Ar ions. Accelerated by the negatively biased electrode, Ar ions would hit the surface of the target and transfer the energy to the atoms of the target. Once the energy

is larger than the bonding energy, the atoms on the target surface would be released and more free electrons would be created. The additional free electrons would feed back the formation of ions and the continuation of plasma state. In this process, free electrons always tend to be captured by the outer electron shells of the ions, forming neutral Ar atoms, releasing photons and creating glow.

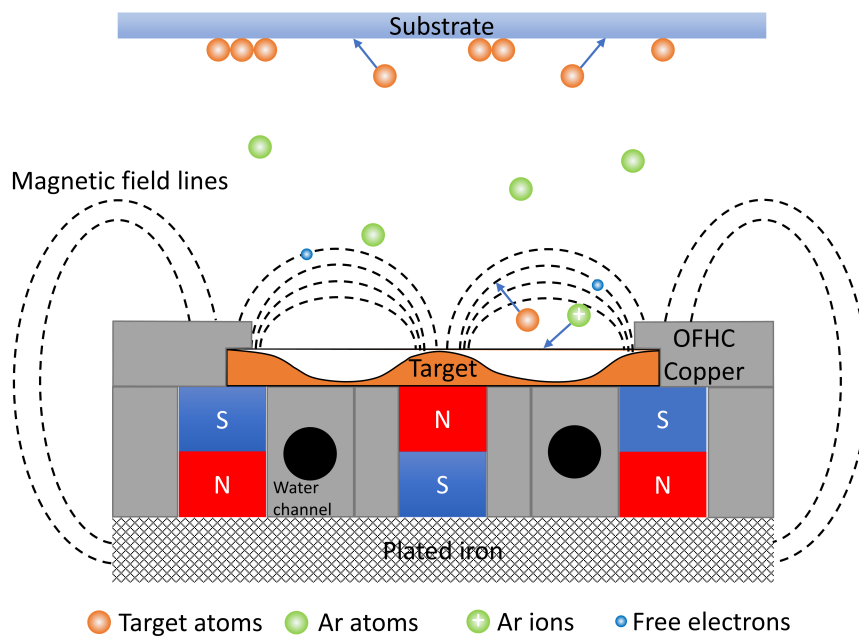


Figure 1.3. Configuration and deposition principles of AJA sputtering system.

However, such sputtering has some disadvantages including slow deposition rate and structure damage of sputtered layer caused by the electron bombardment on the substrate. Therefore, permanent magnets are placed under the target, creating closed magnetic lines to trap free electrons in a magnetic field above the target surface and prevent the electrons from bombarding the substrate. Meanwhile, the probability of Ar ionization can be significantly enhanced and therefore increases the sputtering rate. The configuration of magnets shown in **Figure 1.3** is

responsible for the circular racetrack erosion pattern of target like the Cu target in **Figure 1.4**. The erosion pattern would finally penetrate the target and needs to be replaced before the penetration. However, such configuration is only suitable for the sputtering nonmagnetic elements because closed magnetic field lines would also strongly confine the sputtered atoms like Ni, leading to a low deposition rate.

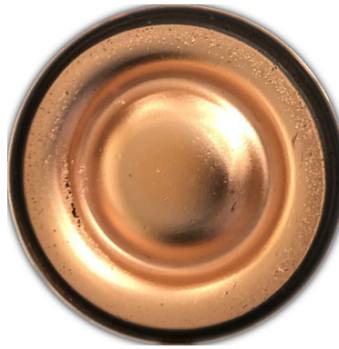


Figure 1.4. Circular racetrack erosion pattern of Cu target.

Non-reactive sputtering is relatively simple because the target is directly released after being hit by the Ar plasma without a chemical reaction. Reactive sputtering is also widely used to sputter a film with more complicated compositions on a certain substrate. In addition to Ar, another reactive gas needs to be introduced in the chamber to form the plasma. O_2 and N_2 are two commonly used reactive gas in sputtering to obtain oxide or nitride thin films, respectively. The reactive gas would chemically combine with the sputtered atoms from the target to form a desired compound. The properties of reactive gas like pressure, relative flow rate of inert and reactive gases, etc. have huge influences on the quality of sputtered thin film. Therefore, by varying different sputtering properties, it is possible to deposit metal, semiconductor, or insulator with tunable properties, making it possible to optimize the sputtered

thin films for specific applications.

1.3.2 Atomic layer deposition

As a key process in nanofabrication, atomic layer deposition (ALD) is a chemical vapor deposition (CVD) method for thin-film deposition. In most of the ALD reactions, there are two half-reactions using two precursors. In every single cycle of ALD process, these precursors successively react with the surface of the substrate in a sequential and self-limiting manner, forming an atomic layer of the desired material. By repeated reaction cycle layer by layer, the film growth and thickness of the deposited material can be well controlled. Two kinds of ALD are normally used in nanofabrication, including thermal-enhanced ALD (TE-ALD) with water precursor and plasma-enhanced ALD with oxygen plasma (PE-ALD). TE-ALD requires a relatively high temperature while low temperature process is possible for PE-ALD thanks to the assistance of plasma without sacrificing the quality of deposited film.

Taking TE-ALD as an example, the fabrication principles of HfO_2 by ALD are illustrated in [Figure 1.5](#):

(a). The substrate is exposed to the first precursor TMDAH ($[(\text{CH}_3)_2\text{N}]_4\text{Hf}$), forming a chemisorbed sub monolayer. $(\text{CH}_3)_2\text{N}$ group reacts with the hydroxyl group on the substrate, forming a layer of Hf atoms. Meanwhile, $(\text{CH}_3)_2\text{NH}$ by-product is produced.

(b). After adsorption, to purge the gas phase of unreacted TMDAH and by-product, argon gas is introduced over the substrate surface.

(c). Successively the substrate is exposed to the second precursor H_2O , reacting with the monolayer created by TMDAH and forming a layer of HfO_2 .

(d). To purge the unreacted H_2O and by-product, argon gas is again

introduced.

After finishing one cycle of growth, the whole process can be repeated to obtain a uniform thin layer of HfO_2 until the desired thickness is obtained. Taking TE-ALD (Cambridge Fiji F200) of HfO_2 at 200 °C as an example, the thickness of each cycle is 1 Å, making it possible to control the thickness of the targeting layer easily.

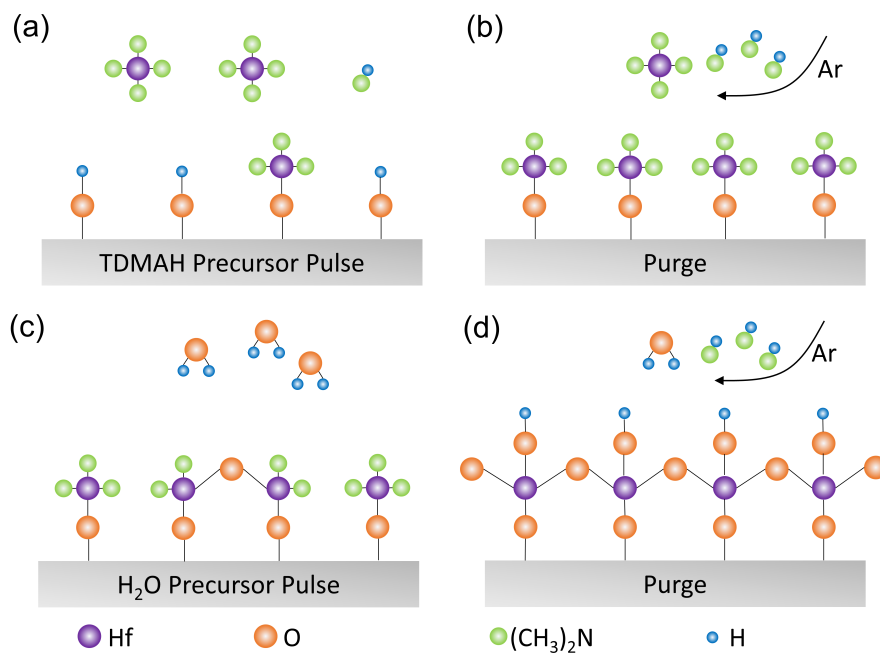


Figure 1.5. Schematics of HfO_2 growth by ALD.

1.3.3 Optical lithography

Optical lithography is an important fabrication process in the nanofabrication to transfer patterns from a lithography mask to a substrate by using a radiation source. In this process, a photosensitive material called photoresist is firstly coated on the substrate and exposed by the UV light with a photomask placed in between the substrate and the UV light. After development, either the exposed part or the unexposed part of the photoresist is removed by the developer solution,

corresponding to the positive and negative optical lithography, respectively. After the lithography, thin film deposition is normally carried out to obtain the desired patterns on the substrate. In this work, UV reverse optical lithography in **Figure 1.6** is considered based on a light-field mask, which means that the transparent part of the mask would result in a resist pattern on the substrate.

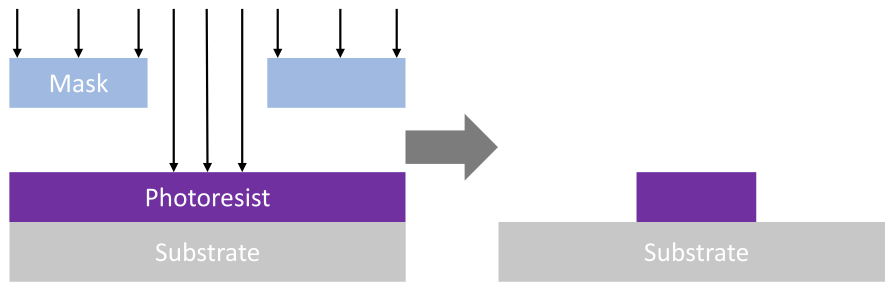


Figure 1.6. Principles of UV reverse optical lithography.

Based on the principles of typical lift-off reverse optical lithography, light-field lithography masks are designed. In **Figure 1.7**, the final patterns that would be obtained after the whole process is shown. The design in the center is used in this work while the rest part at the edge of the mask is for other partners. Two specific masks for CuO and metal patterns are designed in **Figure 1.8** with four alignment modules at the edges of the design. In this design, several structures are included for the future fabrication of TLM up structure, TLM down structure, lateral resistor with rectangle electrodes or integrated fingers, thin film transistor, etc. More design information of each part will be detailed in the later chapters when necessary.

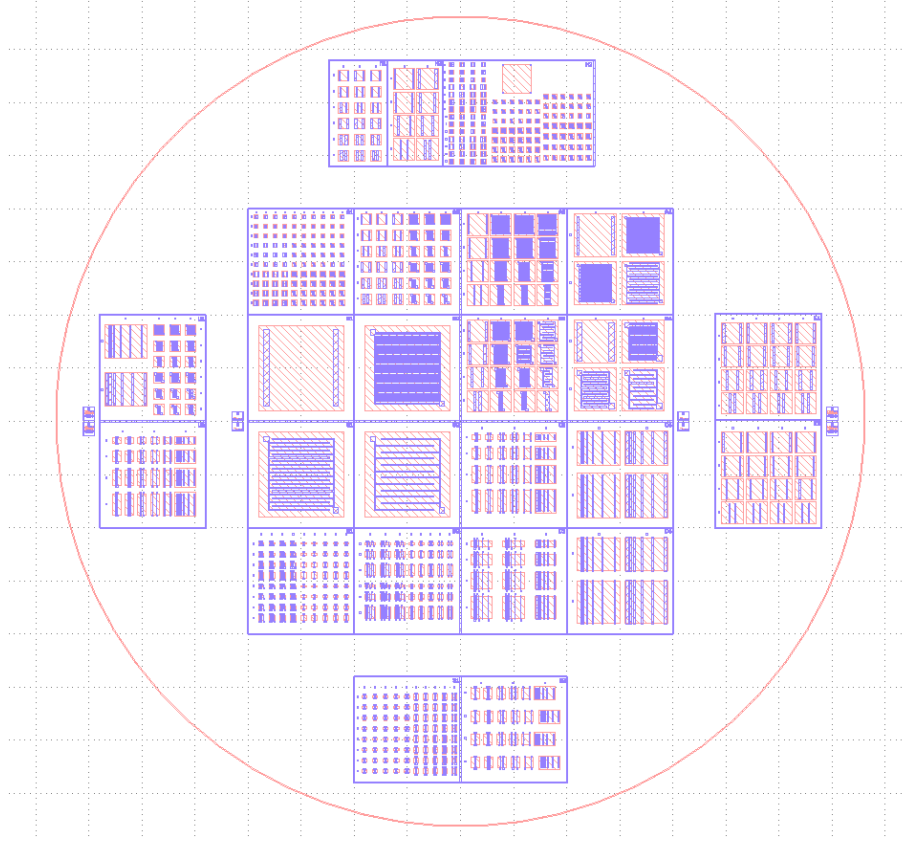


Figure 1.7. Design of lithography masks for CuO devices (center patterns).

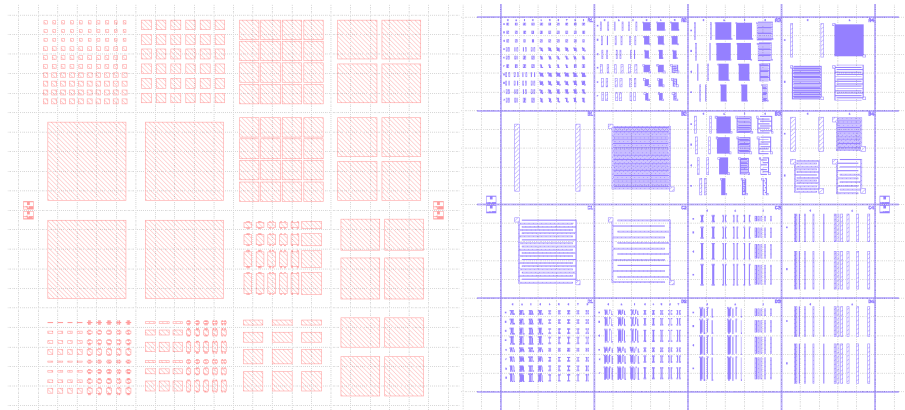


Figure 1.8. Lithography masks for (a) CuO and (b) metal.

1.3.4 UV-VIS-IR spectrophotometer

Optical characterizations are of great interest to determine the optical properties of thin films. While illuminated by the incident light, optical processes occurring at the thin films deposited on glass are illustrated in **Figure 1.9**. A glass substrate is always preferred in such measurement to detect the transmission light from the back side of the sample. Considering the air, thin film and glass substrate with different refractive index (n_0 , n_1 , n_2), the incident light is partially reflected, absorbed or transmitted with different angles of refraction (θ_0 , θ_1 , θ_2). According to these theories, the optical parameters can be measured by a proper equipment, which is known as the UV-VIS-IR spectrophotometer.

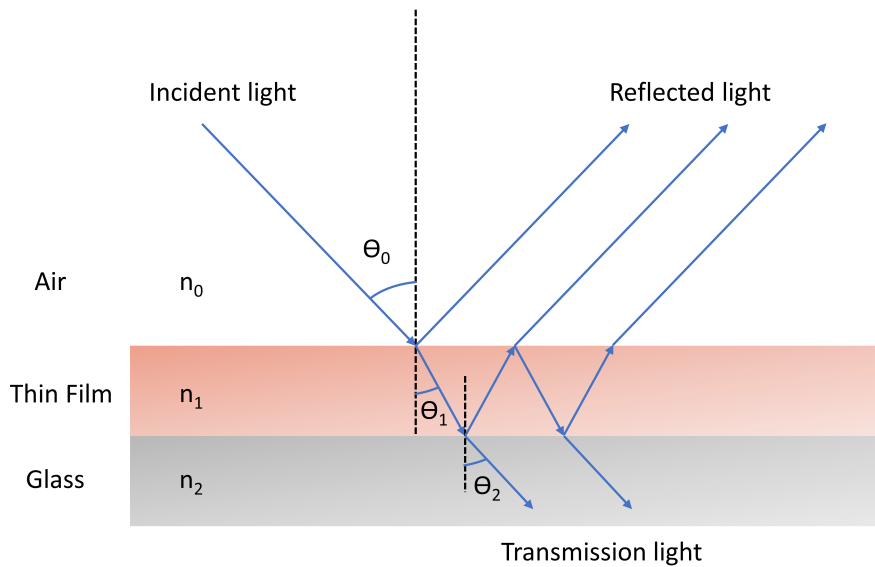


Figure 1.9. Optical processes of thin films on the glass substrate under illumination by spectrophotometer.

In this thesis, Specord 200 from Analytik Jena, a double-beam UV-VIS-IR spectrophotometer with two large-area photodiodes, is used to measure the optical characteristics of thin films. The measurement

wavelengths range from 190 to 1100 nm, with a deuterium lamp for ultraviolet illumination (190-320nm) and a halogen lamp for visible and infrared illumination (320-1100nm). By different configurations integrated in the measurement system, reflectance (R) and transmittance (T) can be measured by two separate photodiodes of spectrophotometer. By measuring R and T , various optical parameters, including absorbance (A), absorption coefficient (α), light penetration depth (d), optical bandgap (E_g) and Urbach energy (E_U), can be easily calculated by different models.

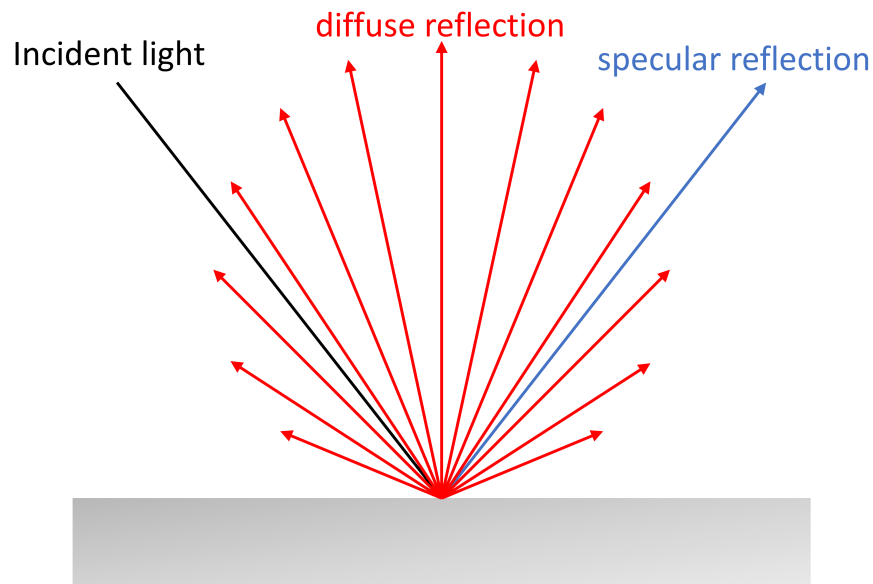


Figure 1.10. Specular and diffuse reflection on thin films.

Considering different reflection mechanisms in **Figure 1.10**, specular reflection or diffuse reflection can possibly happen on different materials. The specular reflection, where incident light and reflected light emerge at the opposite sides of the surface normal with the same angles, is a mirror-like reflection of light from the material surface. In contrast, the diffuse reflection appears when the incident light on the surface is scattered at many angles instead of a single angle like the

specular reflection. The diffuse reflection can be caused by the rough surface but most of the diffuse reflection is contributed by the scattering centers in the bulk material. Therefore, the specular reflection is more dominant when the material is thin, while the diffuse reflection is more pronounced when the material is thick, highly absorbing and intensely scattering.

Table 1.1. Two models for calculations of α and related parameters

Methods	Tauc plot	Kubelka-Munk Theory (With integrating sphere)
Measured parameters	R_{specular}, T	$R_{\text{total}} = R_{\text{specular}} + R_{\text{diffuse}}, T$
Formulas	$\alpha = \frac{1}{d} \ln \left(\frac{(1 - R_{\text{specular}})^2}{T} \right)$ $(\alpha h\nu)^n = A(h\nu - E_g)$	$K = \frac{(1 - R_{\text{total}})^2}{2R_{\text{total}}}$ $(Kh\nu)^n = A(h\nu - E_g)$
Notes	Standard method for thin films	Case of highly absorbing, intensely scattering, and thick material ^[1]

According to different reflection mechanisms, two well-known models are generally considered to determine the optical properties of thin films, namely Tauc plot and Kubelka-Munk theory as demonstrated in **Table 1.1**. In Tauc plot, only the specular reflectance (R_{specular}) is considered, while the total reflectance (R_{total}) is considered as a sum of specular and diffuse reflectances (R_{diffuse}) in Kubelka-Munk theory. To capture R_{diffuse} , an additional accessory of integrating sphere, which can capture both specular and diffuse reflectances, is required in the measurement. However, such integrating sphere is not implemented in Specord 200. To compare two models, reference samples were measured by a spectrophotometer with an integrating sphere in the

University of Mons, showing similar results with Specord 200. Therefore, the specular reflectance is dominant in our samples and Tauc plots are more correlated for thin films deposited in this thesis with a thin thickness of around 100 nm.

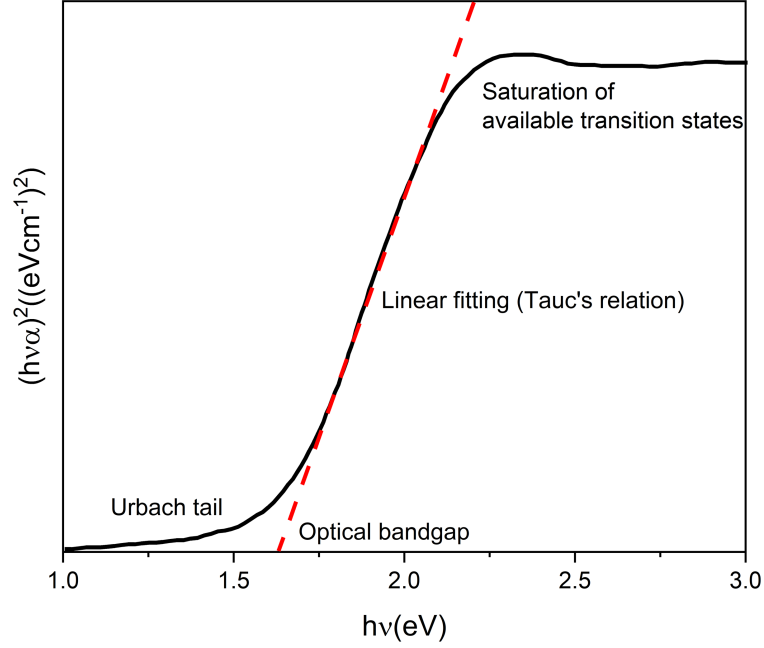


Figure1.11. Principles of parameter extractions by Tauc plot.

After determining α , E_g and E_U can be defined and obtained by Tauc plot as demonstrated in **Figure 1.11**. By plotting the absorbance data as a function of photon energy, the Tauc plot can be divided into three regions. In the saturation region where photon energy is much larger than E_g , available transition states in material are almost filled. In the linear region where photon energy is close to E_g , E_g can be determined by extracting the x-intercept of the linear part from Tauc relation:

$$(\alpha hv)^n = A(hv - E_g) \quad (1.7)$$

where α is the absorption coefficient, h is the Plank constant, ν is the incident light frequency, n is the transition probability of material, and

A is a constant value related to the material corresponding to the slope of Tauc plot in the linear region [54]. The magnitudes of n depending on the nature of electronic transition in the material equals 2, 3, 0.5 and 1.5 for direct allowed, direct forbidden, indirect allowed and indirect forbidden transitions, respectively. The main absorption edge of materials determines E_g at the bandgap, while the region well below E_g shows lower energy defect absorption states of materials. This region is known as the Urbach tail, which is a key parameter related to the defect conditions in semiconductors.

1.3.5 Hall effect measurement system

The electrical characterizations of materials are important especially for semiconductors. Simple parameters like resistance and conductance can be easily measure by I - V measurement. To further study the electrical transport in semiconductors, Hall effect was discovered to determine accurately carrier type, carrier density, electrical resistivity, and carrier mobility. Based on the theories of Hall effect, the Hall effect measurement system provides a simple, low-cost, and fast way to determine the electrical parameters of materials in industry and laboratories.

Hall effect is characterized by the Hall voltage (V_H) that appears transverse to an electric current under an applied magnet field perpendicular to the current. Taking electron transport as an example, **Figure 1.12** gives the schematics and principles of the Hall effect happening inside a bulk material. The basic physical principle of Hall effect is the Lorentz force, which is a combination of electrical force and magnetic force induced by an electromagnetic field. The Lorentz force ($F_{Lorentz}$) is given by:

$$F_{Lorentz} = q(E + v_c \times B) \quad (1.8)$$

where q is the electron charge, v is the drift velocity of charges, E is the electric field and B is the magnetic field. Considering a p-type material, holes as majority carriers are subject to the Lorentz force toward the same direction as electrons due to their opposite velocity and positive charge.

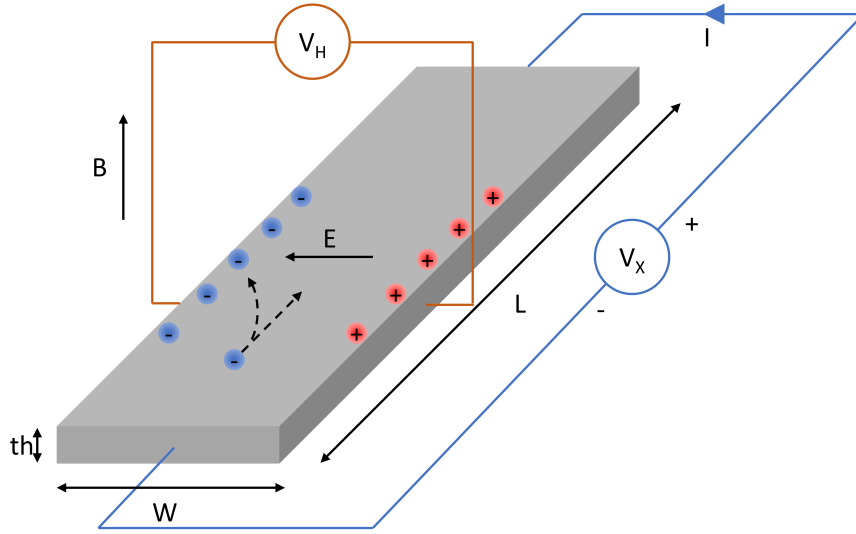


Figure 1.12. Schematic of the Hall effect in a bulk material.

When an external bias is applied to a material without a magnetic field, electrons move straight toward the opposite direction of the bias. Once an external magnetic field B perpendicular to the electron paths is applied, electrons are subject to a magnetic force and move following the curved arrow towards the left side of the material according to the right-hand rule. Finally, electrons accumulate on the left side of the material, leaving holes on the right side of the material. Such phenomenon creates an electrical field $E = -V_H/W$ and leads to a potential difference of V_H between two sides of the material. To reach a steady state, charges would finally stay still in the transverse direction and thus the magnetic force is canceled by the electrical force. Considering the opposite direction of magnetic and electrical force,

$F_{Lorentz}=0$ in steady state, so $E = v \times B$. Considering electron transport in the material, $V_H = vBW$, where v can be obtained by $I = nq \cdot Wt \cdot v$. Therefore, Hall voltage V_H can be obtained by:

$$V_H = \frac{IB}{qnt} \quad (1.9)$$

where I is the input current, n is the number of charges, and t is the thickness of the material. According to its sign, V_H gives the charge carrier density and the type of charge carrier.

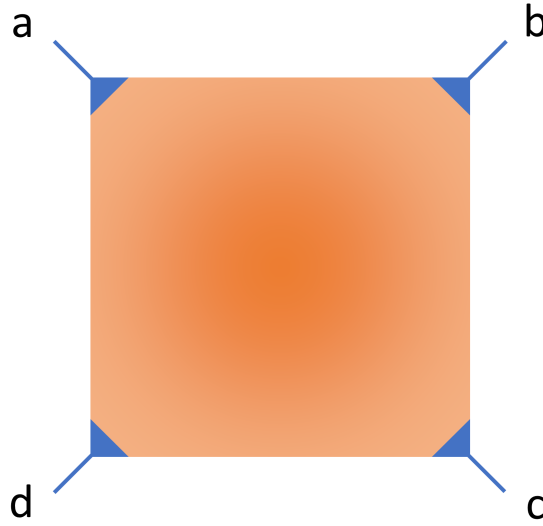


Figure 1.13. Van der Pauw Configuration.

In order to measure the mobility and the sheet resistance simultaneously, a van der Pauw technique is usually carried out in the Hall effect measurement. Based on HMS-3000 from Microworld, Hall measurements are done in the Van der Pauw configuration as shown in **Figure 1.13**. A square sample is mounted in the PCB sample board which can fit a maximum sample size of 2×2 cm. The PCB sample board with four gold-plated probes can make a good electrical contact between the sample and the measurement system. If the contact is not ideal, indium compound like 95/5% In/Sn soldering or additional

electrode deposition are suggested on the four corners of the sample. For samples that are not exactly square in shape, accurate measurements can be hardly obtained especially for the material resistivity. In the Van der Pauw geometry, the current is applied between two contacts at the same side while the voltage is measured at the opposite side of the sample. Therefore, the sheet resistance can be calculated by the van der Pauw equation:

$$\exp\left(-\frac{\pi R_{vertical}}{R_{sh}}\right) + \exp\left(-\frac{\pi R_{horizontal}}{R_{sh}}\right) = 1 \quad (1.10)$$

where $R_{vertical}$ and $R_{horizontal}$ are average resistances measured in the vertical and horizontal directions of the sample. In an ideal situation, $R_{vertical}$ equals $R_{horizontal}$ since the contacts are placed at the corners, meaning a constant distance between every two adjacent probes. Therefore, R_{sh} can be calculated by:

$$R_{sh} = \frac{\pi}{\ln 2} R \quad (1.11)$$

where $\pi/\ln 2$ is the Van der Pauw constant and R is the average resistance. Corresponding resistivity (ρ) can also be determined by:

$$\rho = \frac{R_{sh}}{t} \quad (1.12)$$

Meanwhile, Hall measurement can also be done in the van der Pauw configuration, introducing a permanent magnet of 0.55 T perpendicular to the square sample. The overall Hall voltage induced in the sample can be measured and calculated after introducing the positive and negative magnetic field. The polarity of V_H indicates the p or n type of semiconductor when V_H is positive or negative. Another important parameter, Hall coefficient (R_H) can be calculated after measuring the Hall voltage:

$$R_H = \frac{tV_H}{BI} \quad (1.13)$$

Finally, the mobility (μ) and carrier concentration (N) of measured sample can be calculated by:

$$\mu = \frac{R_H}{\rho} \quad (1.14)$$

$$N = \frac{1}{qR_H} \quad (1.15)$$

1.3.6 Four-point probe resistivity measurement system

Electrical resistivity determined by the availability of free electrons is a basic figure of merit to evaluate the properties of semiconductors. The resistivity is strongly related to the doping level, mobility, and other parameters of semiconductors. In addition to the Hall measurement system, another important technique to measure the resistivity of materials is known as the four-point resistivity measurement. The setup for four-point resistivity measurement system (Luca Labs) and measurement principles are shown in [Figure 1.14](#). The external input current is provided by a Keithley 2400 source meter. Upon applying a lateral current passing through the sample, the resistance of a 3-dimensional thin film can be written by:

$$R = \frac{\rho L}{wt} \quad (1.15)$$

where L , W and t are the length, width and thickness of thin film, and ρ is the resistivity of thin film in $\Omega \cdot \text{cm}$. Sheet resistance (R_{sh}), defined as the resistance for one square of the thin film in $\Omega \text{ sq}^{-1}$, can be defined according to [Equation \(1.12\)](#).

In order to measure R_{sh} , a four-point resistivity measurement is usually performed as shown in [Figure 1.14](#). Compared to the two-point measurement where current and voltage are measured by the same

probe, the four-point measurement consists of 4 probes equally spaced with a constant probe spacing (S) in a line when the current is sent by two outer probes and the voltage is measured by two inner probes. Such measurement is more accurate because the separation of current and voltage measurement makes it possible to neglect the contact and wire resistance especially for the low-resistivity measurement. For a thin film with t much smaller than either L or W , R_{sh} can be obtained by:

$$R_{sh} = \frac{V}{I} \frac{\pi}{\ln 2} \quad (1.17)$$

where V and I are measured voltage and applied current, respectively. This equation is the same like [Equation \(1.11\)](#) because of similar configurations and principles for the resistivity measurements.

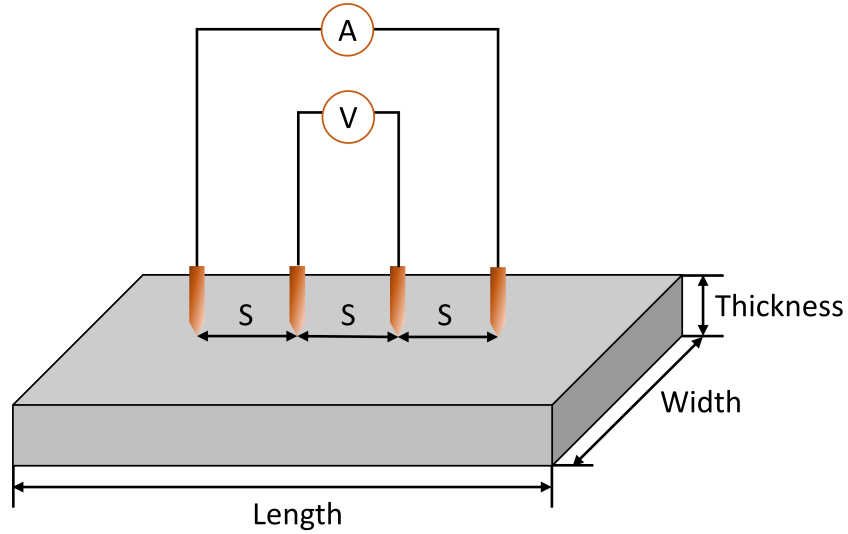


Figure 1.14. Setup and measurement principles of four-point probe measurement system.

Chapter II

A CdS/CIGS Heterojunction Photodiode on Steel

In this chapter, dual-mode operation of an ultra-thin AZO/ZnO/CdS//CIGS/Mo heterojunction photodiode on low-carbon steel substrate is firstly realized in broadband photodetection from UV to near-infrared spectrum (375-910 nm). This photodiode can work either in the photovoltaic mode as a self-driven photodetector without external energy consumption or in the photoconductive mode as a conventional photodetector to reach higher responsivity by consuming more external energy. The CIGS thickness is firstly reduced to 750 nm for CdS/CIGS heterojunction photodetectors, which allows to fabricate commercial CIGS photodetectors in a low-cost way.

To understand the dark characteristics and band offsets of the CdS/CIGS photodiode, SCAPS-1D and SILVACO ATLAS-2D simulations are investigated. To fully understand the photodetection mechanism, a corrected photoconductive gain model is investigated for the CdS/CIGS photodiode, in comparison with the misleading classical model. These characterizations demonstrate excellent broadband photodetection abilities of the CdS/CIGS heterojunction photodiode by switching the operation modes.

2.1 Experimental methods

2.1.1 Device structure and fabrication

The schematic structure of the CdS/CIGS photodiode is shown in **Figure 2.1 (a)**. A cross-section scanning electron microscope (SEM) image of the CdS/CIGS photodiode shows well prepared distinct interfaces for each layer in **Figure 2.1 (b)**. Mo back-contact layer, CIGS absorber, CdS buffer layer, ZnO window layer and AZO contact layer can be seen clearly in the SEM image from bottom to top on the low-carbon steel foil substrate.

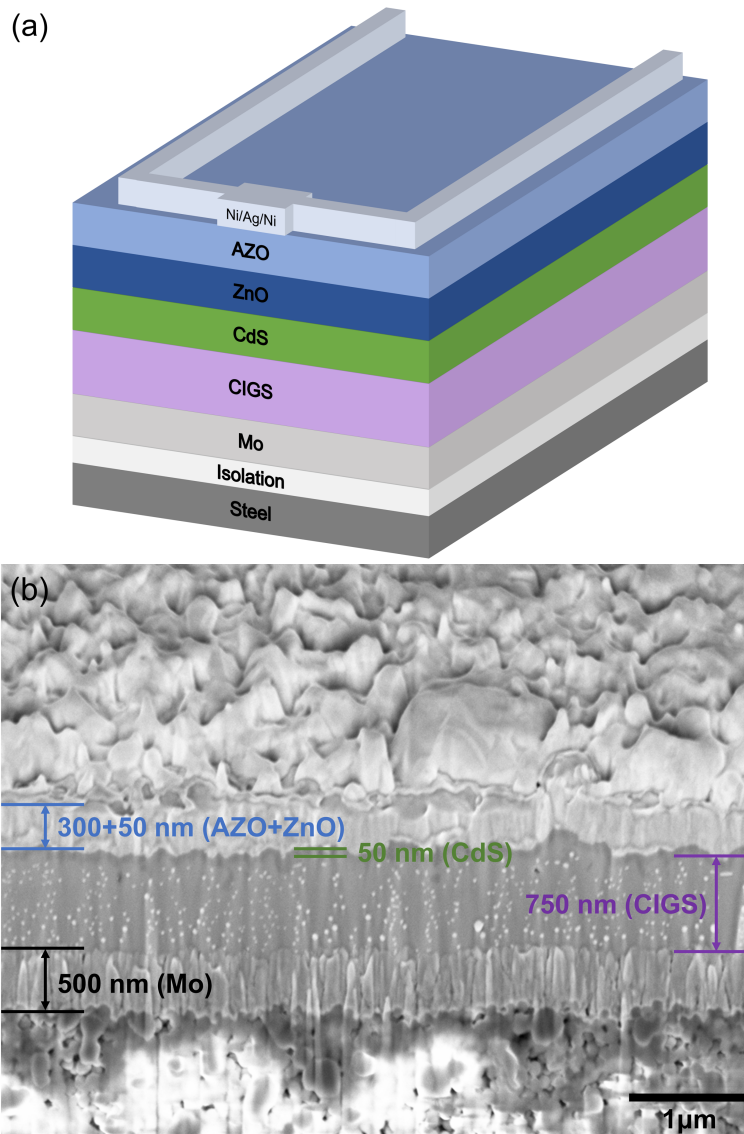


Figure 2.1. (a) Schematic structure and (b) cross-section SEM image of the CdS/CIGS photodiode.

The CdS/CIGS photodiode was fabricated by several groups within European H2020 ARCIGS-M project. The top layers of the CdS/CIGS photodiode were fabricated by TNO (Netherlands) on a commercial low-carbon steel foil substrate with a top isolation layer from AC&CS in CRM group (Belgium). Mo (500 nm) was DC sputtered on the steel

substrate as a back ohmic contact with CIGS. After introducing an Alkali element (Na) doping from a thin NaF precursor (8 nm), CIGS (750 nm) with less defects and higher hole concentration was evaporated by a three-stage co-evaporation process. Chemical portions of Cu, In and Ga in CIGS are 22.95%, 17.72% and 9.6% respectively. CdS (50 nm) buffer layer was deposited by the chemical bath deposition (CBD). Intrinsic ZnO (50 nm) and aluminum-doped ZnO (AZO) (300 nm) were sputtered as a highly resistive window layer and a low resistive contact layer, respectively. The photodetector was completed by the evaporation of Ni/Ag/Ni top contacts. The whole stack of devices was finally divided into individually contacted photodiodes (50×100 mm) by mechanical scribes.

2.1.2 Device characterization

The structure and morphology of the CdS/CIGS photodiode were characterized by Zeiss Auriga focused ion beam–scanning electron microscopy (FIB-SEM). The dark current-voltage (I - V) curve and capacitance-voltage (C - V) curve at 5000 Hz frequency were measured by four-point probe measurements on a low signal probe station (PM8PS) connected to Agilent B1500A Semiconductor Device Analyzer. The current-voltage, and time-dependent transient current were measured by the same technique under the illumination of light emitting diodes (Thorlabs, LED375L-LED1050L) specifically at 375, 395, 430, 450, 490, 505, 555, 590, 630, 680, 760, 810, 870, 910 nm. For the I - V measurements, the LEDs were powered by Keithley 2400 source meter. For the transient response measurements, the LEDs were powered by Tektronix AFG2021 Arbitrary Function Generator. The incident light densities of LEDs were measured by a power meter (Ophir Optronics, Ophir Nova 1Z01500), integrating a standard silicon photodetector PD300 with detection range from 200 to 1100 nm. A

shadow mask was used to fix the effective photodetection area of the CdS/CIGS photodiode ($A_{eff}=0.5 \text{ cm}^2$) and eliminate the influence of neighbor devices. All the measurements were performed at a constant chuck temperature of 25 °C.

2.2 Dark characterization

In this section, dark characteristics of the CdS/CIGS photodiode are investigated, considering both I - V and C - V measurements. In the I - V measurements, single- and double-diode models are introduced and analyzed to fit the experimental results. Better fitting between the single-diode model and SCAPS simulation proves the accuracy of the model. In the C - V measurements, the net free carrier concentration and the depletion region width are calculated by the capacitance at corresponding bias, providing necessary parameters for the further analysis of the device operation mechanism.

2.2.1 Experimental fitting

In order to better analyze the dark characteristics of the CdS/CIGS photodiode, single-diode model and double-diode models are both used to fit the experiment results. Experimental dark I - V curve is obtained in **Figure 2.2**, showing standard diode characteristics. The CdS/CIGS heterojunction is cut off in the reverse bias region while it is turned on in the forward bias region. According to the theories in Section 1.2.2, Single- and double-diode models are introduced in **Figure 2.3**. Different terms from **Equation (1.1)** and **(1.2)** are calculated, corresponding to the current density flowing through the diode $D_{i,1,2}$ ($= J_{0,1,2} \left\{ \exp \left[\frac{q(V - J_{dark} R_s)}{n_{0,1,2} k T_{emp}} \right] - 1 \right\}$) and the last term ($= \frac{V - J_{dark} R_s}{R_{shunt}}$) dominated by R_s and R_{shunt} .

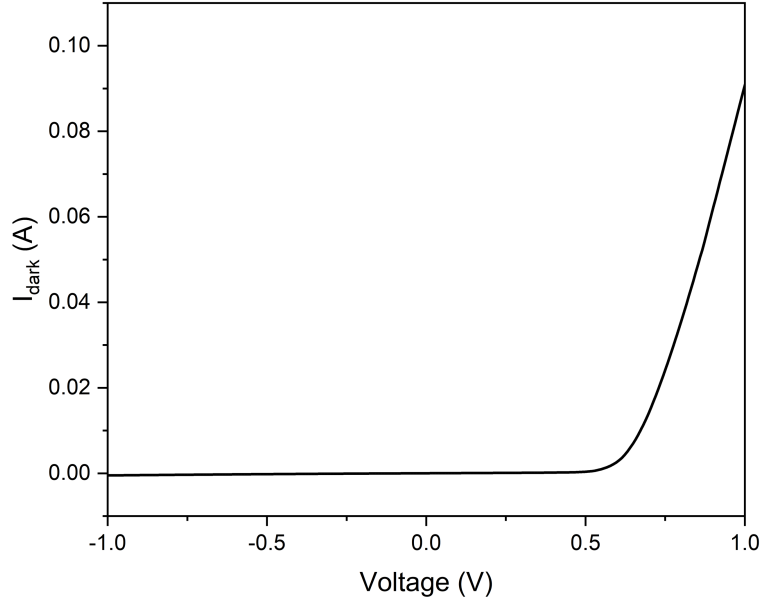


Figure 2.2. (a) Dark I - V curve of CdS/CIGS photodiode.

In **Figure 2.3(a)**, the single-diode model provides good fitting in the forward bias between the measurement curve (dark dashed line) and **Equation (1.1)** (red line). D , the first term of **Equation (1.1)**, extracting diffusion current parameters and R_s from high forward bias, with J_0 of $7.33 \times 10^{-8} \text{ A cm}^{-2}$, n of 1.86 and R_s of $0.5 \text{ } \Omega \cdot \text{cm}^2$. Considering that the shunt leakage current is dominant under low reverse bias and low forward bias, R_{shunt} is obtained from the minimum of dJ/dV [81]. The CdS/CIGS photodiode on steel shows a lower R_{shunt} of $5.33 \times 10^2 \text{ } \Omega \cdot \text{cm}^2$, than the reported R_{shunt} from 10^3 to $10^4 \text{ } \Omega \cdot \text{cm}^2$ for a CdS/CIGS heterojunction on glass and thus a higher dark shunt leakage current [82].

In **Figure 2.3(b)**, the double-diode model is used between the measurement curve (dark dashed line) and **Equation (1.2)** (red line). Expect for the same extracted parameters like in the single-diode model, G/R current in D2 is considered, with J_{02} of $1.64 \times 10^{-4} \text{ A cm}^{-2}$ and n_2 of 9.18. Obviously, n_2 is much higher than a standard value close to 2 and

a clear upshift of dark current calculated by the model can be seen, demonstrating worse fitting under low voltage bias. Under reverse bias, dominant R_{sh} causes a linear tendency of the fitted curve, and the usual double-diode model only adds a constant effect, while the measured

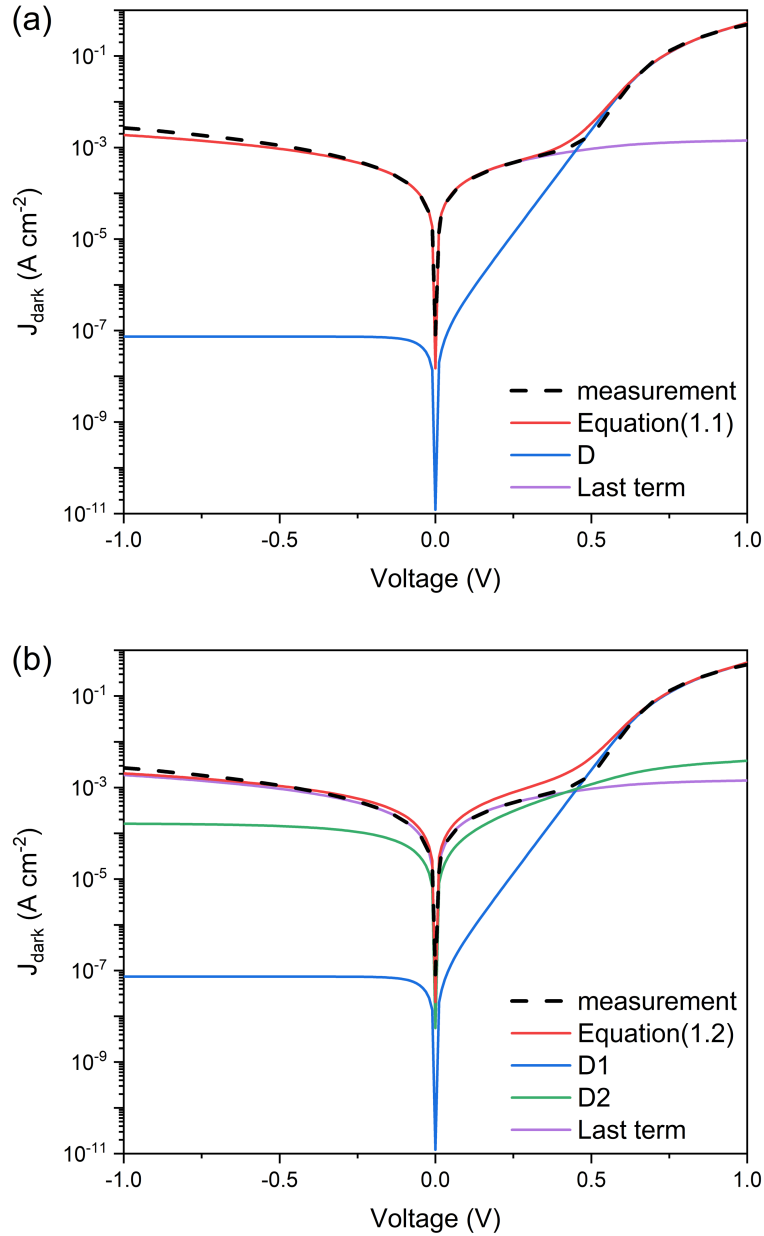


Figure 2.3. (a) Single-diode and (b) double-diode models of CdS/CIGS photodiode.

current exhibits an exponential tendency. Such difference between the fitted and measured current is caused jointly by an ignored current component that could be induced by either Poole-Frenkel mechanism, Fowler-Nordheim mechanism or space charge limited current [83-85]. By increasing R_{shunt} , the upshift can be lowered, but the reverse current would be lowered simultaneously, which is not preferred due to the target of photodetection in the reverse bias. Therefore, the single-diode model suits better CdS/CIGS photodiode. To verify the accuracy of the model, by setting the calculated R_{shunt} and R_s in SCAPS simulation [86], the dark characteristics in Figure 2.4 reveal excellent fitting between measurement and simulation, that justifies the use of the single-diode model. The simulation parameters of CdS/CIGS photodiode in SCAPS are presented in Table A2.

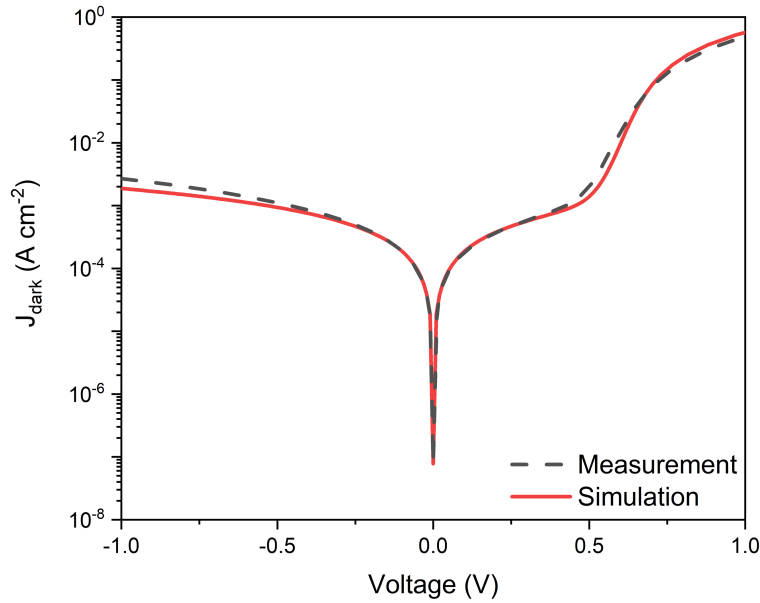


Figure 2.4. Measured dark J - V curve fitting with SCAPS simulation.

2.2.2 C-V measurement

To better understand the device operation mechanism, the low-frequency capacitance-voltage (C - V) curve at 5 kHz of the CdS/CIGS

photodiode is performed in the dark (**Figure 2.5**). The capacitance increases sub-linearly from reverse to low forward bias region with the decrease of depletion region depth, but exponentially when the diode current dominates. Such variation is related to the varying depletion width of space-charge region with the external bias. At high forward bias, the series resistance increases dramatically and soon reaches the measurement compliance. Such high series resistance coming from the substrate and other layers can strongly impacts the capacitance measurement.

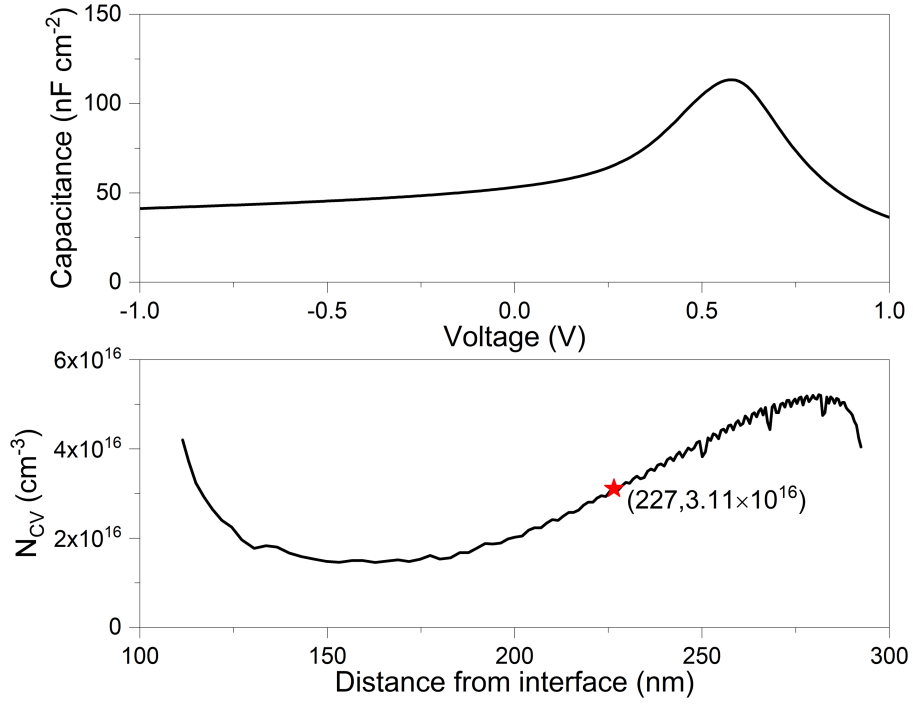


Figure 2.5. Dark C - V and N_{CV} - W curves of the CdS/CIGS photodiode.

From C - V curve, the net free carrier concentration (N_{CV}) and the depletion region width (W_d) can both be calculated by [87]:

$$N_{CV} = \frac{-2}{q\epsilon_0\epsilon A^2[d(1/c^2)/dV]} \quad (2.1)$$

$$W_d = \frac{\epsilon_0\epsilon A}{c} \quad (2.2)$$

where ϵ_0 is the vacuum permittivity ($=8.854 \times 10^{-14} \text{ F cm}^{-1}$), ϵ is the CIGS dielectric constant ($=13.6$), and A is the device area ($=0.5 \text{ cm}^2$). In **Figure 2.5**, N_{CV} is plotted against W_d , extracting N_{CV} of $3.11 \times 10^{16} \text{ cm}^{-3}$ and W_d of 227 nm at 0 V. Such high N_{CV} , which is close to other CIGS/CdS heterojunctions on glass, is attributed to an enhanced Na concentration from the NaF precursor [19, 88]. More defects within the bandgap for CIGS fabricated on steel substrates causes a narrower W_d compared to CIGS/CdS heterojunctions on glass [87, 88], which is consistent with high capacitance measured for the device on steel.

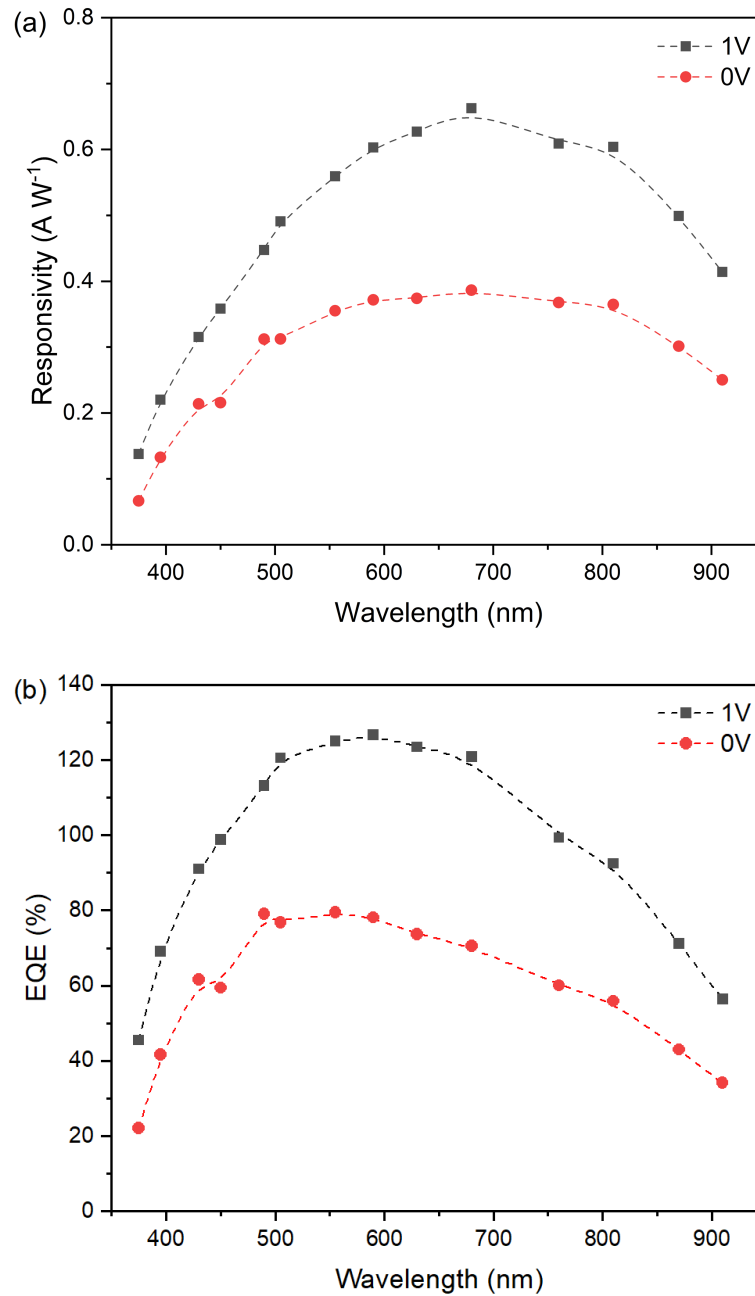
2.3 Optical characterization

2.3.1 Spectral photoresponse

Broadband photodetection is important for photodetectors to extend their applications to a wider spectral range. To analyze the dual-mode broadband photodetection capabilities of the CdS/CIGS photodiode, LEDs with different wavelengths from UV to near-infrared spectrum are considered to measure the photoresponse. By using **Equations (1.3-1.6)**, corresponding spectral responsivity, EQE and detectivity of the CdS/CIGS photodiode from 375 to 910 nm illuminations of $100 \mu\text{W cm}^{-2}$ are calculated in **Figure 2.6(a-c)** both in the photovoltaic mode (0 V bias) and photoconductive mode (1 V reverse bias). In both modes, the CdS/CIGS photodiode exhibits good photoresponse in a broadband spectrum but higher photoresponsivity and EQE are obtained in the visible spectrum.

In the photovoltaic mode, high detectivities over 2×10^{12} Jones ($\text{Jones} = \text{cm Hz}^{1/2} \text{ W}^{-1}$) are obtained from 395 to 910 nm thanks to their negligible dark current with the absence of external bias. The maximum detectivity and minimum NEP reach 4.4×10^{12} Jones and $0.16 \text{ pWHz}^{-1/2}$ at 680 nm, respectively. However, the responsivities and $EQEs$ are

below 0.4 A W^{-1} and 100%, respectively, because of low photocurrent without external bias. In contrast, in the photoconductive mode, enhanced responsivities over 0.4 A W^{-1} are obtained from 490 to



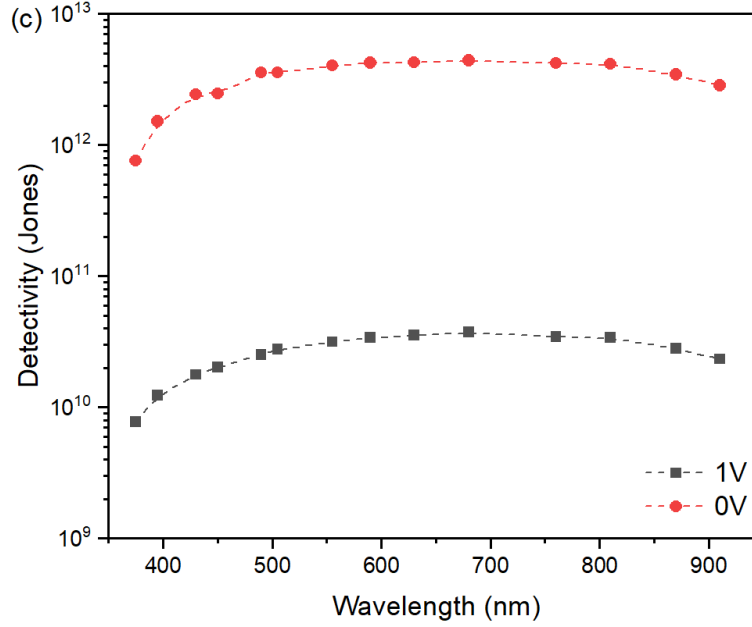


Figure 2.6. (a) Responsivity, (b) *EQE* and (c) Detectivity of the CdS/CIGS photodiode under $100 \mu\text{W cm}^{-2}$ illuminations from 375 to 910 nm with 0 V and 1 V reverse biases.

910 nm. Meanwhile, impressive *EQEs* over 100% are observed from 490 to 680 nm due to the photoconductive gain mechanism. The maximum responsivity is extracted to be 0.66 A W^{-1} at 680 nm, corresponding to a high *EQE* of 121%. However, the detectivities and *NEPs* are below 4×10^{10} Jones and over $17.68 \text{ pW Hz}^{-1/2}$ due to the enhanced dark current.

In summary, the CdS/CIGS photodiode is broadband photosensitive both in the photovoltaic and photoconductive modes, demonstrating either excellent detectivity or responsivity. To reach higher responsivity or photogain, higher external bias is always expected but its detectivity has to be sacrificed due to an enhanced dark leakage current.

2.3.2 Photoresponse at 680 nm

To better clarify the photoelectrical performances of the CdS/CIGS photodiode, the J - V characteristics are characterized in **Figure 2.7(a)** under 680 nm illumination in the visible spectrum with incident light power densities varying from 20 to 500 $\mu\text{W cm}^{-2}$. Under light illumination, the photocurrent of the photodiode increases obviously especially at higher voltage bias. At the same voltage, the light current increases gradually with the increasing incident light intensities due to the increased photon intensity from the incident light. In **Figure 2.7(b)**, the dependence of photocurrent on the light power density under 0, 0.5 and 1 V reverse bias can be fitted by a power law:

$$I_{photo} \sim CP^\beta \quad (2.3)$$

where P is the light power density, C is a scaling constant, β is the exponent factor, which reflects the efficiency of photoexcited carriers and is ideally equal to 1 [14]. Such behavior is caused by increased photogenerated carriers with increasing incident photons from the LED illumination. In the photovoltaic mode (0 V bias), the exponent factor $\beta \approx 1$ verifies very few trap states in the band gap and a good quality of the CdS/CIGS heterojunction [16]. However, β decreases with the increasing voltage bias to ~ 0.8 in the photoconductive mode (here 1 V reverse bias). Such sublinear behavior indicates that the photocurrent is dominated by the photoconductive mechanism [89, 90]. With increasing photon flux in the photodiode, the reduced available traps result in the saturation of photocurrent, while the charge carrier photogeneration efficiency is proportional to the absorbed photon flux at a lower light density [91, 92]. From the time-dependent transient photoresponse under 1 V reverse bias in **Figure 2.8(a)**, low rise and decay times of the CdS/CIGS photodiode are both estimated below 5 ms in **Figure 2.8(b)**, suggesting a stable, fast, and repeatable photoresponse of the CdS/CIGS photodiode. However, in such mode,

the ratio of I_{light}/I_{dark} (~ 1.07) is quite low under $100 \mu\text{W cm}^{-2}$ illumination, which can be significantly enhanced to over $\sim 10^3$ in the photovoltaic mode.

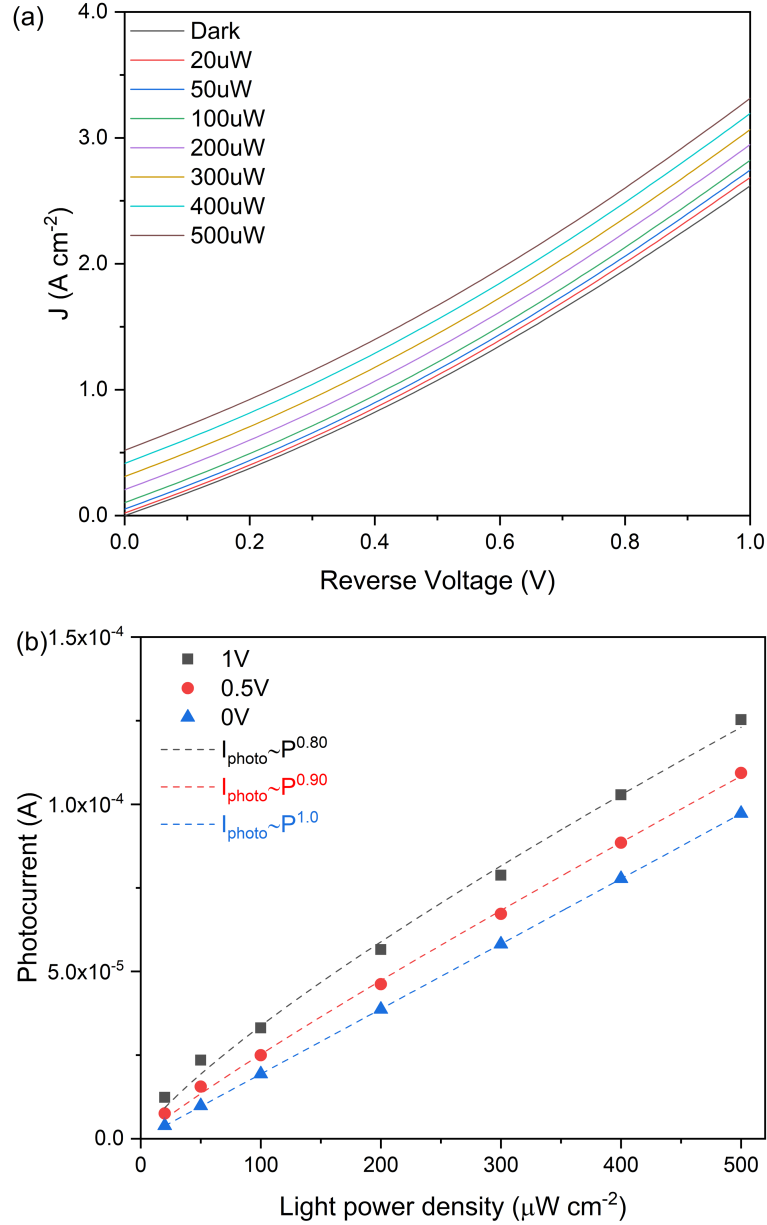


Figure 2.7. (a) J - V curves in the dark and under 680 nm illumination at different incident light power densities. (b) Power density-dependent photocurrent fitted by power law.

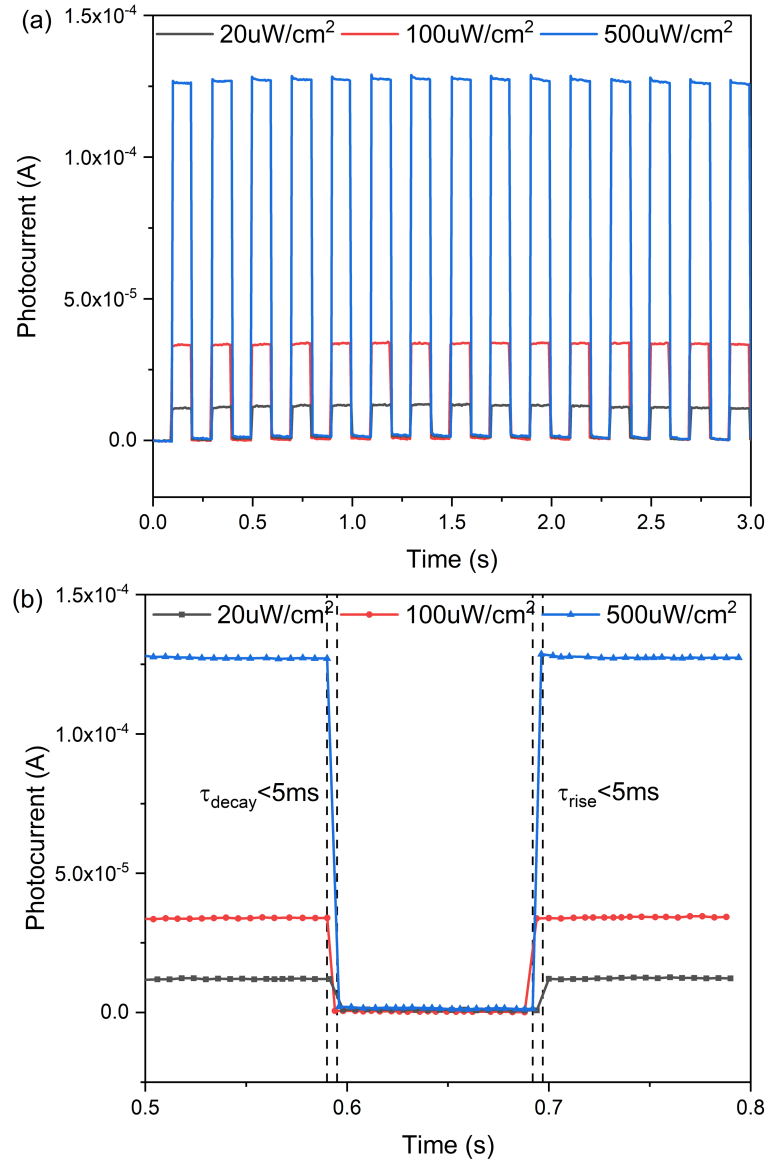
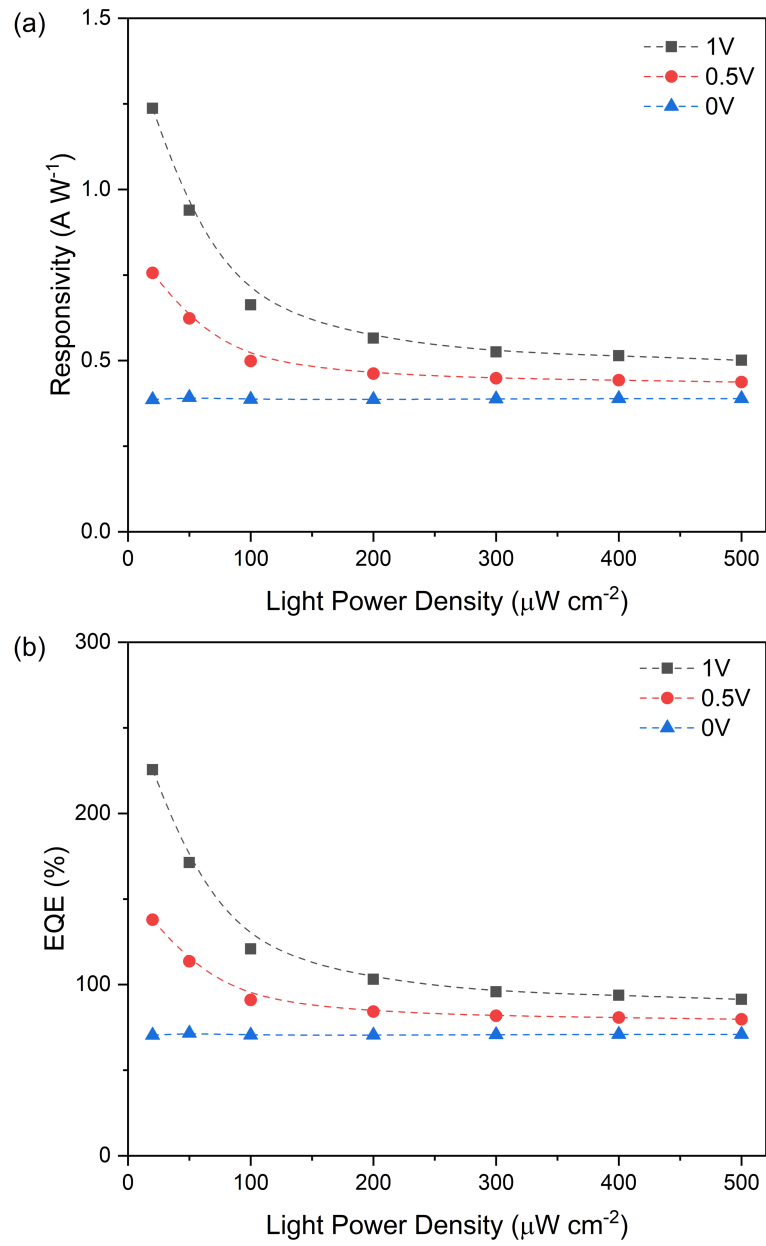


Figure 2.8. (a) Time-dependent transient photoresponse and (d) the rise and decay times of the photodiode under 680 nm illumination of 20, 100 and 500 $\mu\text{W cm}^{-2}$ with 1 V reverse bias.



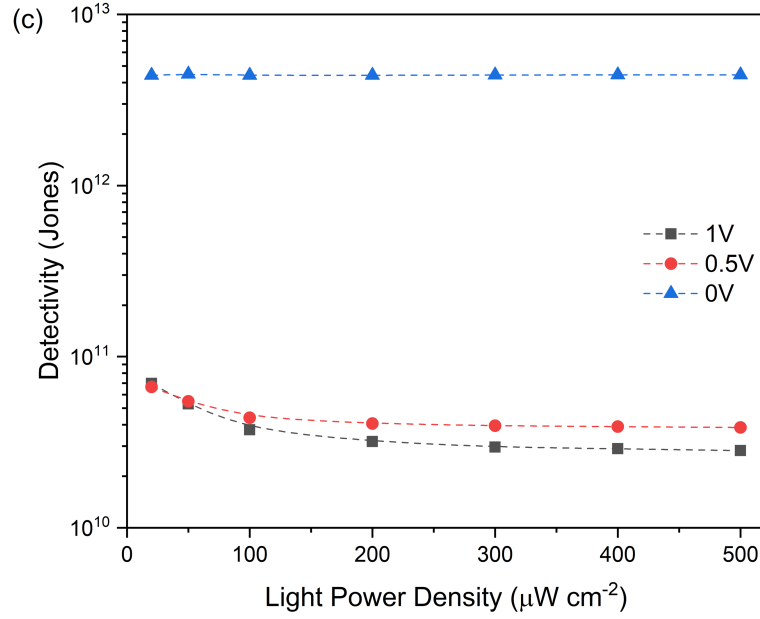


Figure 2.9. (a) Responsivity, (b) *EQE*, and (c) Detectivity of the CdS/CIGS photodiode under 680 nm illumination with 0, 0.5 and 1 V reverse biases.

Additionally, the responsivity, *EQE* and detectivity of the CdS/CIGS photodiode with varying light power densities from 20 to 500 $\mu\text{W cm}^{-2}$ under 0, 0.5 and 1 V reverse biases are calculated in **Figure 2.9(a-c)**. In the photovoltaic mode (0 V bias), the CdS/CIGS photodiode works as a self-driven photodiode at a light density of 20 $\mu\text{W cm}^{-2}$ under 680 nm illumination and reaches a record detectivity of $\sim 4.4 \times 10^{12}$ Jones and a low *NEP* of 0.16 $\text{pW Hz}^{-1/2}$, but a relatively low responsivity of $\sim 0.39 \text{ A W}^{-1}$ and an *EQE* of $\sim 71\%$. In the photoconductive mode (1 V reverse bias), the CdS/CIGS photodiode demonstrates an excellent responsivity of 1.24 A W^{-1} and an ultra-high *EQE* of 226%, but a relatively low detectivity of 7×10^{10} Jones and a higher *NEP* of 10.1 $\text{pW Hz}^{-1/2}$ due to the photoconductive gain mechanism. This mechanism will be discussed in detail below.

2.3.3 Photoresponse at 870 nm

Broadband photodetection is important to extend the spectral range

of application for photodetectors. To further study the capability of broadband photodetection for the CdS/CIGS photodiode, the photoresponse characteristics are extended to the wavelength of 870 nm, which corresponds to the near-infrared light. The J - V characteristics are characterized in **Figure 2.10(a)** under 870nm illumination with incident light power densities varying from 20 to 500 $\mu\text{W cm}^{-2}$. In **Figure 2.10(b)**, the dependence of photocurrent on the light power density under 0, 0.5 and 1 V reverse bias can be fitted by the power law. In the photovoltaic mode (0 V bias), $I_{\text{photo}} \sim P^{0.98}$, approaching the ideal exponent factor of 1, implies very few trap state excitations. In the photoconductive mode (1 V reverse bias), $I_{\text{photo}} \sim P^{0.78}$, obtaining a decreased exponent factor, is attributed to the photoconductive mechanism [89, 90]. From the time-dependent transient photoresponse under 1 V reverse bias in **Figure 2.11(a)**, low rise and decay times of the CdS/CIGS photodiode are both estimated below 5 ms again in **Figure 2.11(b)**.

Additionally, the responsivity, EQE and detectivity of the CdS/CIGS photodiode with varying light power densities from 20 to 500 $\mu\text{W cm}^{-2}$ under 0, 0.5 and 1 V reverse biases are calculated in **Figure 2.12(a-c)** under 870 nm illumination. The CdS/CIGS photodiode exhibits excellent light detection abilities under an incident light power density of 20 $\mu\text{W cm}^{-2}$ in both modes. In the photovoltaic mode (0 V bias), the CdS/CIGS photodiode, working as a self-driven photodiode, reaches a high detectivity of $\sim 3.3 \times 10^{12}$ Jones and a low NEP of 0.21 $\text{pW Hz}^{-1/2}$, but a relatively low responsivity of $\sim 0.29 \text{ A W}^{-1}$ and an EQE of $\sim 41\%$. In the photoconductive mode (1 V reverse bias), the CdS/CIGS photodiode demonstrates an excellent responsivity of 1.11 A W^{-1} and a high EQE of 158%, but a relatively low detectivity of 6.2×10^{10} Jones and a NEP of 11.4 $\text{pW Hz}^{-1/2}$ thanks to the photoconductive gain mechanism.

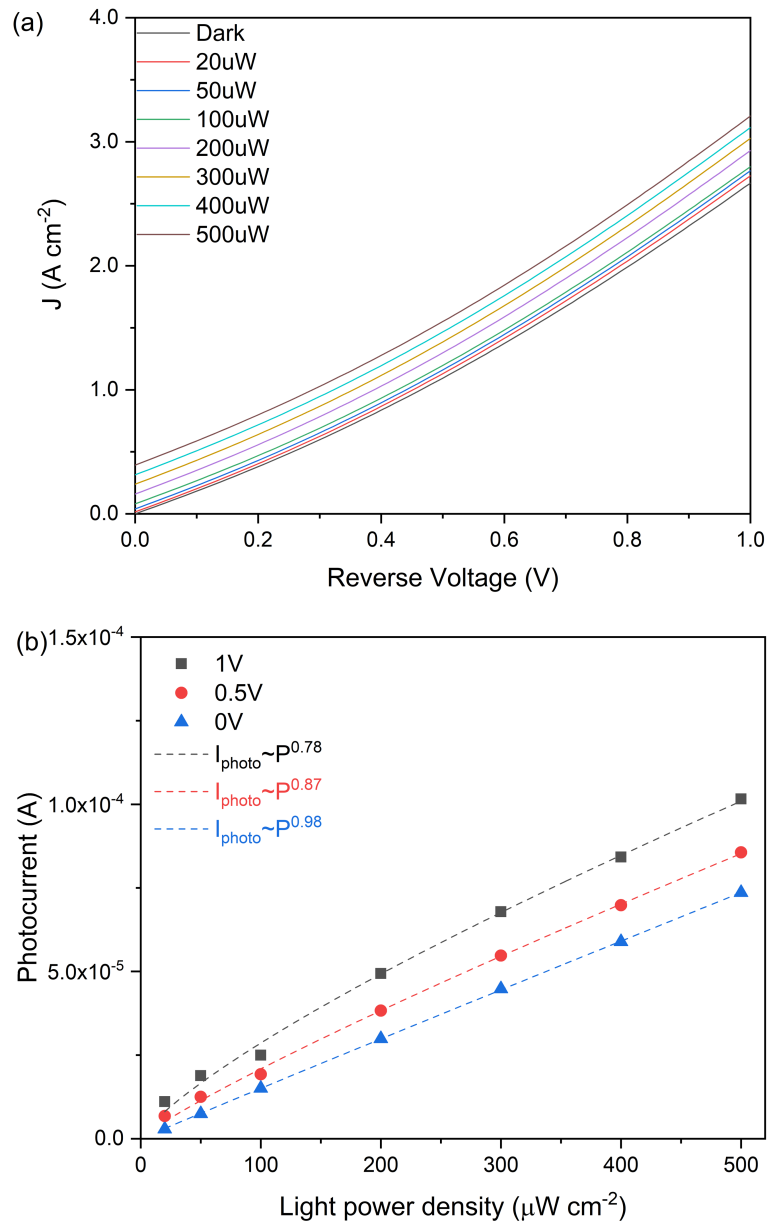


Figure 2.10. (a) J - V curves in the dark and under 870 nm illumination at different incident light power densities. (b) Power density-dependent photocurrent fitted by power law.

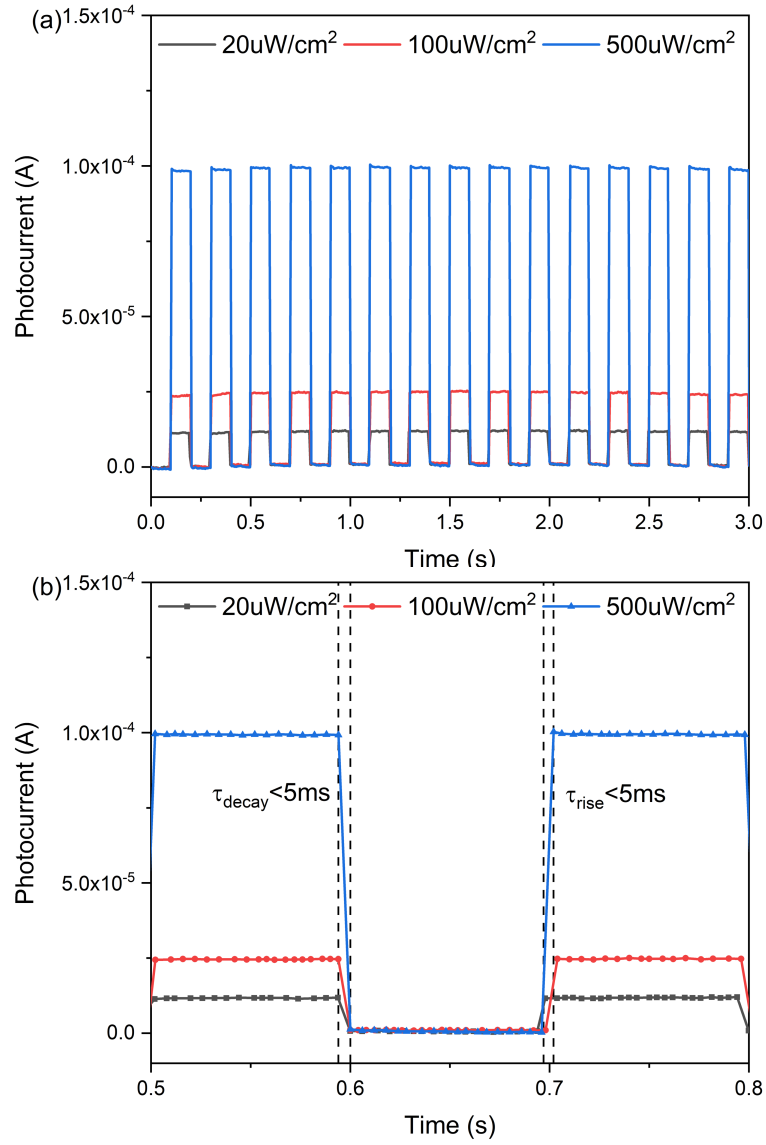
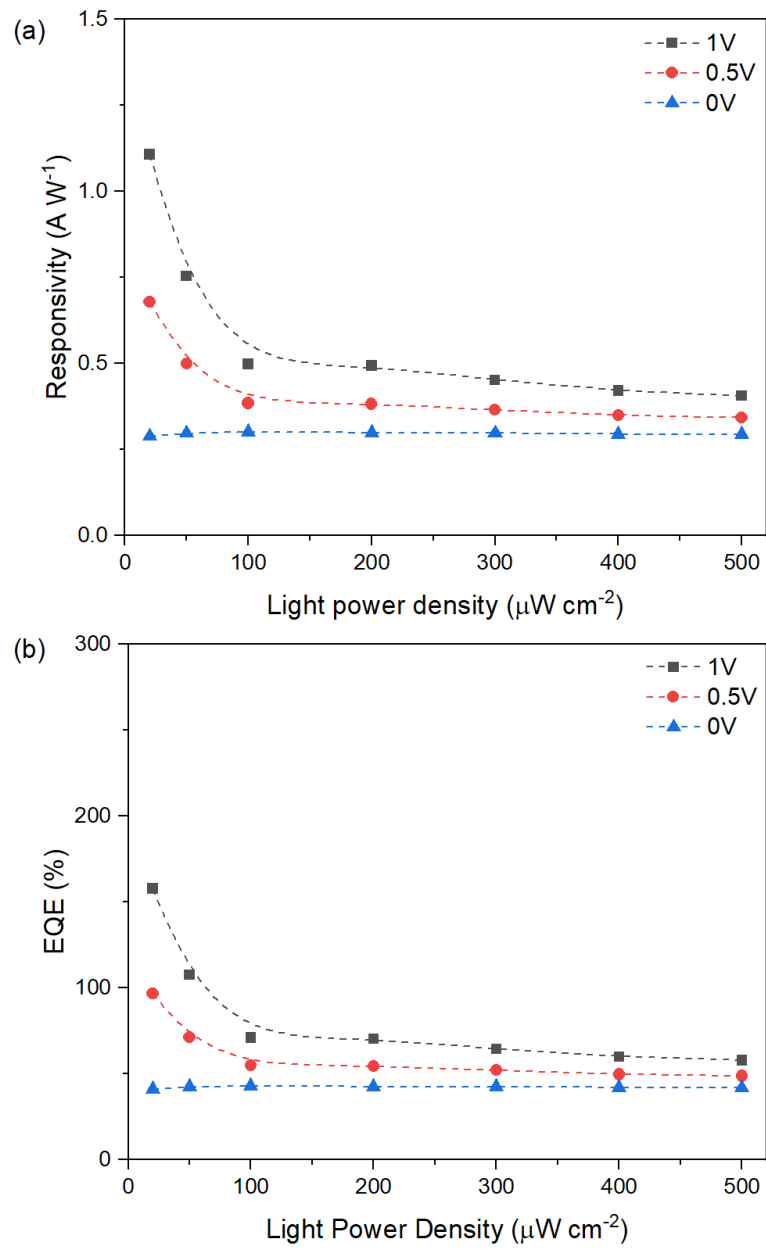


Figure 2.11. (a) Time-dependent transient photoresponse and (b) the rise and decay times of the photodiode under 870 nm illumination of 20, 100 and 500 $\mu\text{W cm}^{-2}$ with 1 V reverse bias.



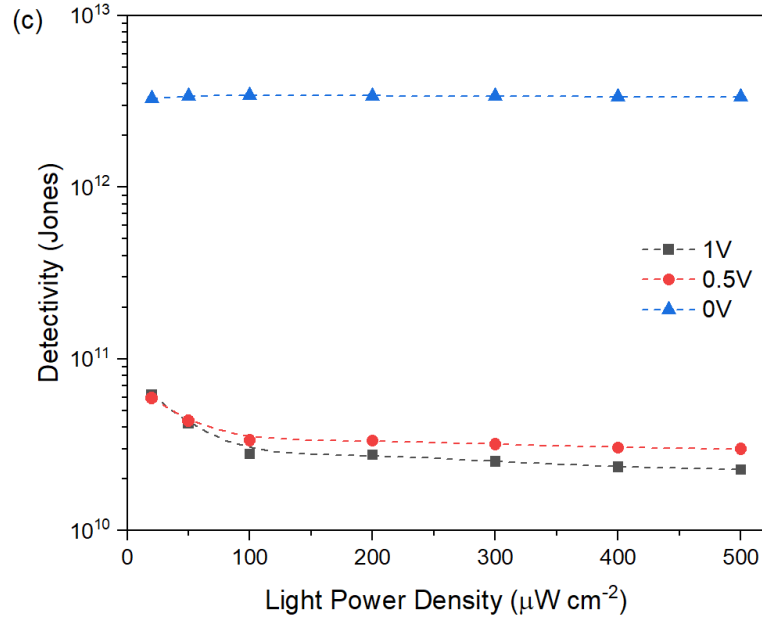


Figure 2.12. (a) Responsivity, (b) EQE , and (c) Detectivity of the CdS/CIGS photodiode under 870 nm illumination with 0, 0.5 and 1 V reverse biases.

2.4 Photoconductive gain mechanism

2.4.1 Band alignment of CdS/CIGS photodiode

To better clarify the photodetection mechanism of the CdS/CIGS photodiode, the dependence of the ratio between the current under illumination (680 nm, $100 \mu\text{W cm}^{-2}$) and the dark current on the reverse bias is shown in **Figure 2.13**, which illustrates two distinct regions with different slopes. SILVACO ATLAS numerical device simulations [93] are performed to obtain the schematic energy band diagrams in both photovoltaic mode in **Figure 2.14(a)** and photoconductive mode in **Figure 2.14(b)**, and the electric field distribution at 0 V and 1 V reverse bias in **Figure 2.15**, respectively. The simulation parameters of CdS/CIGS photodiode in SILVACO are presented in **Table A2**. A n-p CdS/CIGS heterojunction and a n-n CdS/ZnO interface are observed. At the CdS/CIGS heterojunction, a moderate spike-like conduction

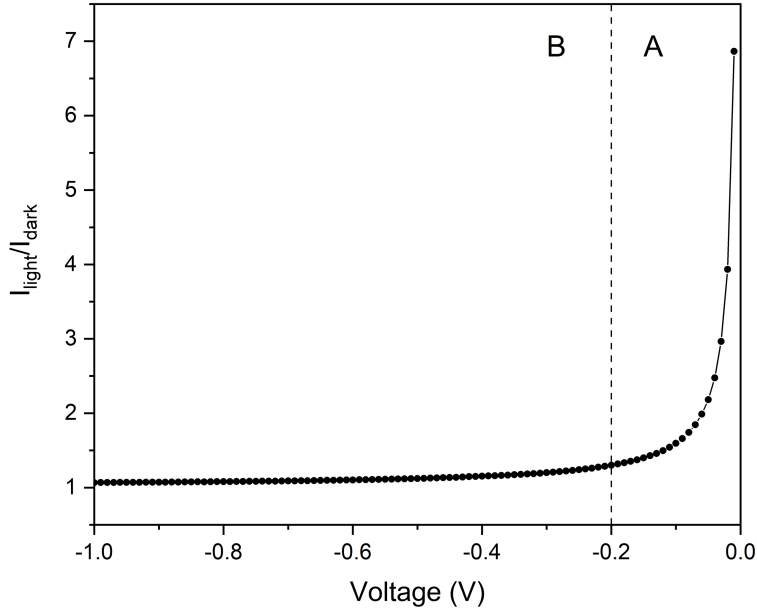


Figure 2.13. The ratio between the current under 680 nm illumination at $100\mu\text{Wcm}^{-2}$ and the dark current versus reverse bias.

band offset (CBO) where the conduction band minimum (CBM) of CdS is higher than that of CIGS, is helpful to reduce the interfacial carrier recombination by increasing the interface recombination barrier without prohibiting the transport of photogenerated electrons from CIGS towards CdS [94, 95]. In the meantime, a large valence band offset (VBO) at the CdS/CIGS interface can reflect the photogenerated holes and reduce the interfacial carrier recombination [95]. Under low bias in Region A, the increasing dark current due to higher probability of trap-assisted tunneling and less photogenerated carriers blocked by the spike CBO with increasing bias jointly contribute to the decrease of $I_{\text{light}}/I_{\text{dark}}$. Next, when increasing the external bias in Region B, all the photogenerated carriers can cross the spike CBO, which causes saturation and almost constant slope of $I_{\text{light}}/I_{\text{dark}}$. This means that the heterojunction acts like a photoconductor rather than a photodiode in Region B [96]. Therefore, the performances of the CdS/CIGS photodiode operating in Region B can be analyzed as

a pure photoconductor, taking the photoconductive gain mechanism into account.

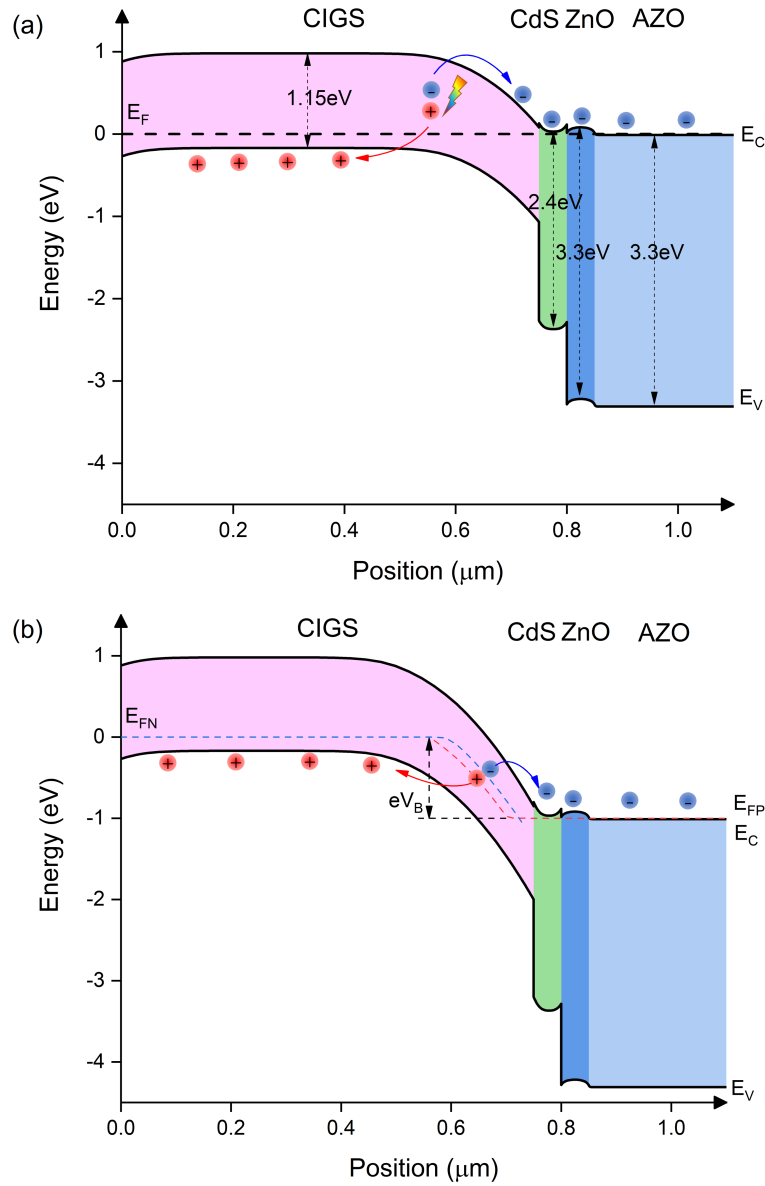


Figure 2.14. Schematic energy band diagrams of the CdS/CIGS photodiode under an illumination of 680 nm in (a) photovoltaic (0 V bias) and (b) photoconductive mode (1 V reverse bias).

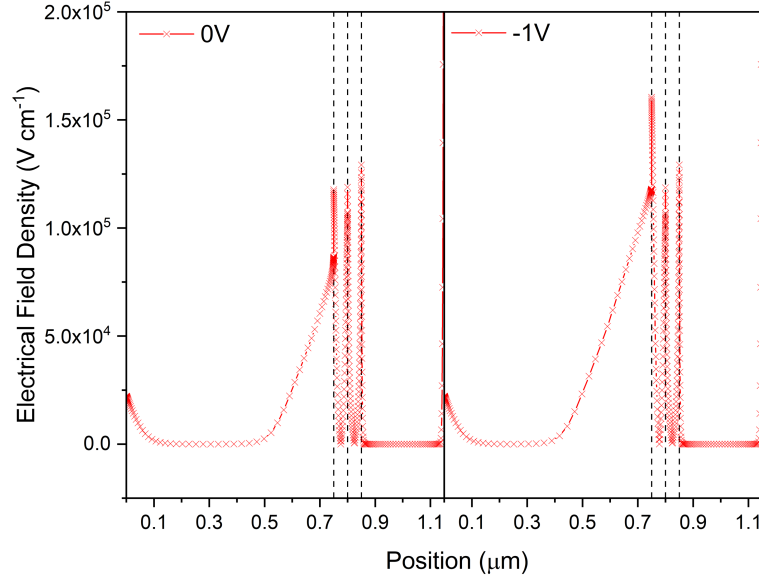


Figure 2.15. Electric field density distribution of the CdS/CIGS photodiode at 0 V and 1 V reverse bias.

In the photovoltaic mode illustrated in **Figure 2.14(a)**, which corresponds to Region A of **Figure 2.13**, a self-driven photogeneration process is supported by effective photon absorption in CIGS absorber, photogenerated carrier separation by the built-in electrical field in space charge region (SCR), diffusion of photogenerated carriers towards quasi-neutral region (QNR), and collection of photogenerated electron-hole pairs at the contacts. In **Figure 2.14(b)**, which corresponds to Region B of **Figure 2.13**, 1 V reverse bias applied to the photodiode, splits the Fermi-level (E_F) into quasi-electron Fermi level (E_{FN}) and quasi-hole Fermi level (E_{FP}) due to the thermodynamic equilibrium. Applied reverse voltage (V_r) increases the p-n junction barrier by eV_r , seems to narrow the effective bandgap and enhances the electrical field density in pn junction, which is also observed from **Figure 2.15**. Applying a reverse V_r of 1 V, SCR width is extended from 227.3 to 292.4 nm, as extracted from **Figure 2.5** and consistent with the simulation results in **Figure 2.15**.

2.4.2 Classical photoconductive gain model

CIGS photodiodes show higher responsivity and impressive *EQE* over 100% ($G > 1$) in the photoconductive mode. According to the standard theory, such high gain can originate from either a multiple electron-hole pair generation process from a single photon or extra charges injected from the external circuit [97]. The second hypothesis is consistent with the classical photoconductive gain mechanism especially when the incident photon energy is low. By preventing carrier recombination, this mechanism producing multiple charge carriers by one single photon, is realized by carrier recirculation after one single photon absorption. However, this classical theory remains controversial and problematic [98, 99]. Therefore, in this paper, a corrected model is introduced to explain the origin of the high gain observed in our experiments.

The classical photoconductive gain model predicts the photoconductive gain (G) by [76, 99]:

$$G = \tau_{life} \left(\frac{1}{\tau_{tn}} + \frac{1}{\tau_{tp}} \right) = \frac{\tau_{life}}{\tau_{tn}} \left(1 + \frac{\mu_p}{\mu_n} \right) \quad (2.4)$$

where τ_{life} is the minority carrier lifetime, τ_{tn} and τ_{tp} are the free-flowing electron and hole transit times between electrodes, μ_n and μ_p are the electron and hole mobilities. Equation (2.4) suits both n-type and p-type semiconductors, but it is normally simplified as [79, 100]:

$$G = \frac{\tau_{life}}{\tau_{transit}} \quad (2.5)$$

where $\tau_{transit}$ is simplified as the device transit time. Such approximation is correct only for n-type semiconductors, when μ_n is much larger than μ_p , or when τ_{tn} is much smaller than τ_{tp} . For p-type semiconductors, G is underestimated by Equation (2.5) and can be correctly estimated by Equation (2.4). More specifically, photogenerated carriers could travel

several times through the circuit, once the carrier transit time decreased by external electrical field gets smaller than the carrier recombination time [12, 101]. In the photoconductive mode, increasing reverse bias enhances drift and diffusion velocities for free-flowing carriers and thus reduces τ_m and τ_{tp} , which can be predicted by simulations in Figure 2.15 and calculated by [76]:

$$\tau_{tn,p} = \tau_{drift} + \tau_{diffusion} = \frac{L_{drift}}{E\mu_{n,p}} + \frac{4W_{diffusion}^2}{\pi^2 D_{n,p}} \quad (2.6)$$

where L_{drift} is the hole drift length, E is the average electrical field density in SCR, $W_{diffusion}$ is the diffusion length, $\mu_{n,p}$ is the electron or hole mobility, and $D_{n,p}$ is the electron or hole diffusion coefficient according to Einstein relation ($D_{n,p} = \frac{kT}{q} \mu_{n,p}$). For our device working at 1 V reverse bias, with $L_{drift} = 292$ nm, $W_{diffusion} = 458$ nm, $E = 6 \times 10^4$ V cm⁻¹, and $\mu_p = 12.5$ cm² V⁻¹ s⁻¹ in CIGS [82], τ_{tp} is estimated to be ~ 2.67 ns ($\tau_{drift} = 0.039$ ns, $\tau_{diffusion} = 2.63$ ns). Neglecting τ_{drift} due to the short drift length and the high electrical field in CdS and ZnO, with $W_{diffusion} = 300$ nm, and $\mu_n = 100$ cm² V⁻¹ s⁻¹ in AZO, τ_{tn} is estimated to be ~ 0.14 ns. According to Equation (2.4), $G > 1$ ($EQE > 100\%$) can be obtained once τ_{life} is larger than $\frac{\tau_n \tau_p}{\tau_n + \tau_p} = 0.133$ ns, the measured electron

lifetime in CIGS, being normally about tens of nanoseconds [102, 103]. In this model, photogenerated electrons (minority carriers) can be trapped for a duration of τ_{life} due to the built-in-field in SCR and the electron traps in CIGS [97, 104]. To maintain charge conservation, a hole is replenished from ZnO once a hole reaches Mo, enabling multiple holes to circulate through the circuit after one single electron-hole photogeneration [104]. Such hole injection is possibly caused by the thermionic emission or field emission when majority carriers tunnel through the junction at an ultra-high applied voltage [105]. However, in

this work, the photogain exceeds 1 at a low reverse bias of 0.5 or 1 V, which can hardly cause hole tunneling. The thick CdS/CIGS heterojunction (i.e., 292.4 nm at 0 V, 227.3 nm at -1 V) blocks the hole tunneling and no clear tunneling point was observed in the I-V curves. Here, the classical model mistakenly assumes a uniform distribution of photogenerated excess carriers and equal concentrations of photogenerated excess holes and electrons in the semiconductor [99]. Obviously, the concentration of excess carriers in CIGS is nonuniform and voltage-dependent due to the metal-semiconductor boundary and the external bias. At the CIGS/Mo interface, the photogenerated carriers become zero since the metal doesn't generate any photocarrier. To keep continuity, the photogenerated carrier concentration has to decrease sharply near the interface. The external bias helps the photogenerated holes to drift towards the QNR in CIGS, which causes an excess hole accumulation in the QNR.

2.4.3 Corrected photoconductive gain model

Considering the metal-semiconductor boundary and the extrinsic trapping effect from defects, surface states and depletion region, a new corrected model is given by [99]:

$$G = \frac{\tau_{n,eff}}{\tau_{transit}} \left(1 + G' \frac{\mu_p}{\mu_n} \right) \quad (2.7)$$

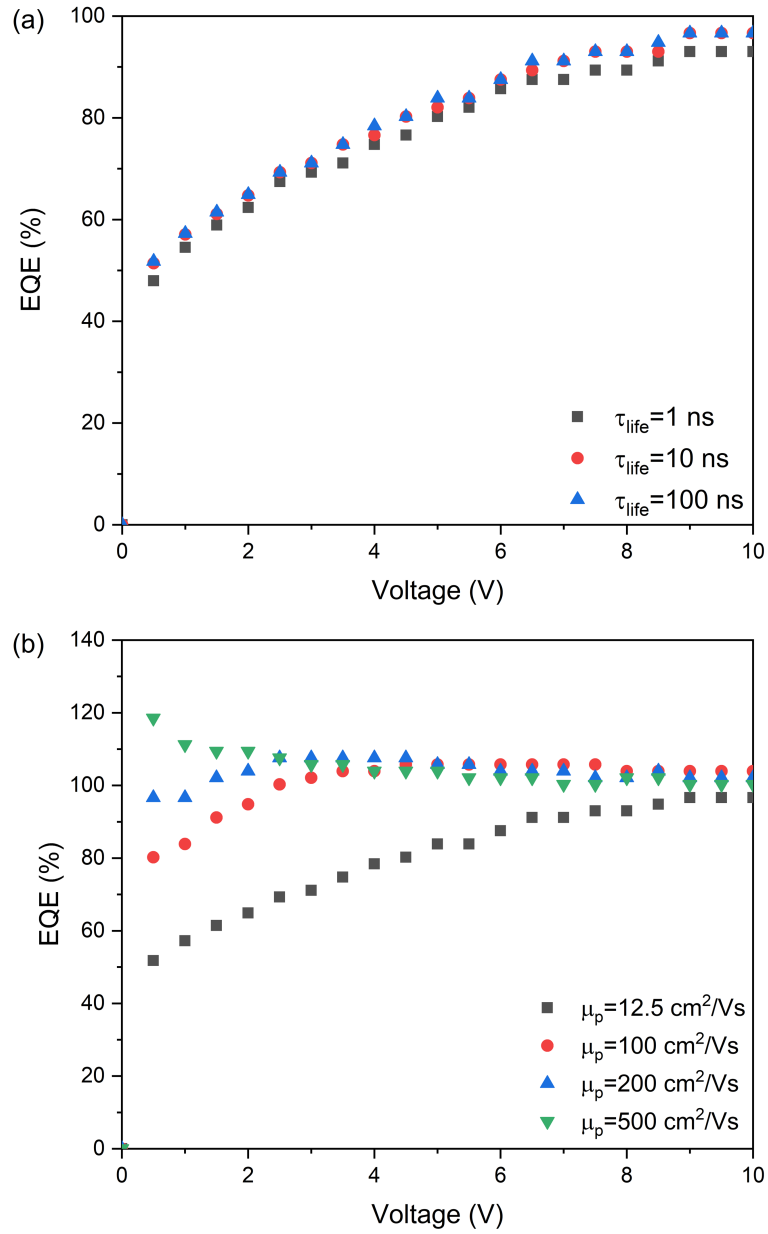
where $\tau_{n,eff}$ is the effective minority carrier lifetime, G' is defined as the gain calculated from excess carrier concentration, and μ_n is the CIGS electron mobility. In this corrected model, $\tau_{n,eff} = \overline{\Delta n} / g$, where g is the average photogeneration rate, introduces $\overline{\Delta n}$ as the average excess electron concentration to avoid the wrong assumption of uniform distribution of excess carriers. $G' = \frac{\Delta p}{\Delta n}$ considers Δp and Δn as the excess hole and electron concentrations, respectively.

According to the corrected model, there are two main ways to improve the photogain of a photodetector. Firstly, if μ_p is larger than μ_n , the photogain can be improved but always stays lower than the ratio of the majority to minority mobilities [99]. However, experimentally, it's hard to reach a higher μ_p than μ_n for a p-type semiconductor such as CIGS. Secondly, G' can be enhanced to over 1, once $\Delta n < \Delta p$. If the semiconductor is perfect without any defects and surface states, G' is equal to 1. However, with defects and surface states and depletion region, excess minority electrons might be trapped, while the same number of holes are left in the CdS/CIGS photodiode [98]. In such case, the number of excess holes becomes higher than that of electrons, which causes $G' > 1$ and thus $G > 1$ ($EQE > 100\%$). However, with increasing light density, available trap states would be gradually saturated, which makes the extra electron-hole pairs recombine immediately and prevent the photoconductive gain process [106]. Therefore, photoconductive gain mechanism is more pronounced at a lower incident light density under higher bias voltage.

2.4.4 SILVACO Atlas simulation

Considering that CdS/CIGS heterojunction acts like a photoconductor in the photoconductive mode [96], SILVACO Atlas simulations [93] are carried out to verify qualitatively the corrected photoconductive mechanism for a CIGS photoconductor with a dimension of 1 μm at all directions. The left and right surfaces are considered as electrodes with default ohmic contact. The material parameters in SILVACO used for CIGS photoconductor are the same as the CIGS parameters in Table A2. Constant default values of electron mobility and hole lifetime are set at $100 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and 100 ns. To validate the influence of different parameters on the photoconductor, various simulations are done in Figure 2.16(b-c). All simulations are

done at applied biases from 0 to 10 V reverse bias under an illumination of 680 nm with an illumination power density of 100 uWcm^{-2} .



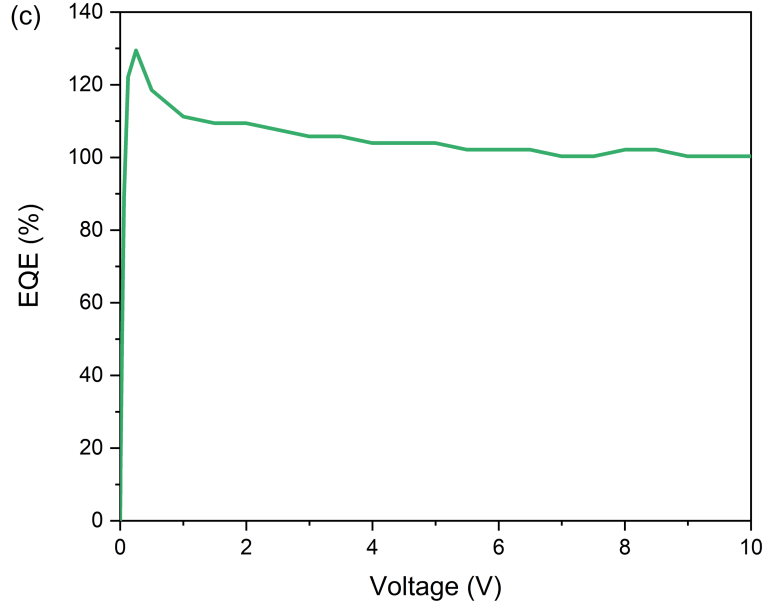


Figure 2.16. *EQE* of CIGS photoconductor from 0 to 10 V reverse bias under an illumination of 680 nm (100 uWcm^{-2}) at (a) varying electron lifetime from 1 to 100 ns, (b) varying hole mobility from 12.5 to $500 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ with a constant electron lifetime of 100 ns, and (c) hole mobility of $500 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ with an electron lifetime of 100 ns.

According to the corrected model in [Equation \(2.7\)](#), τ_{life} , μ_n and μ_p mainly influence the photogain. Varying τ_{life} from 1 to 100 ns is first investigated in [Figure 2.16\(a\)](#) with a constant electron lifetime of 100 ns, showing a slightly enhanced *EQE* with increasing τ_{life} , which indicates limited influence of minority carrier lifetime. At high bias, *EQE* always tends to saturate because the slower excess holes would accumulate in the semiconductor while the hole mobility is smaller than electron mobility. Therefore, varying μ_p from 12.5 to $500 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ is investigated in [Figure 2.16\(b\)](#) with a constant μ_n of $100 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, showing enhanced *EQE* with increasing μ_p . Such behavior can be clearly seen in [Figure 2.16\(c\)](#) with μ_p of $500 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, showing a sharp increase of *EQE* from photovoltaic mode to photoconductive mode and a saturation at ultra-high bias. Such phenomenon appears

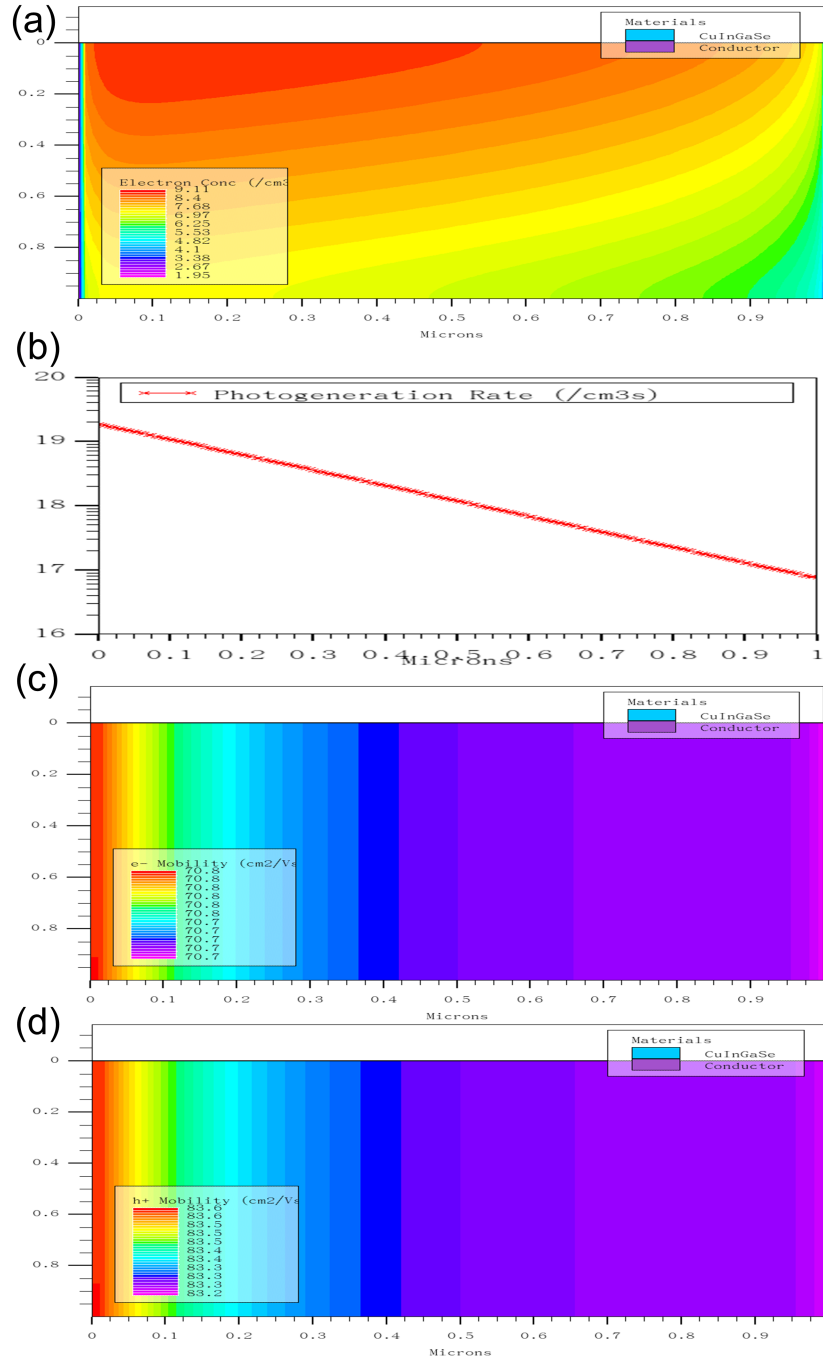


Figure 2.17. (a) Distribution of electron concentration, (b) photogeneration rate, (c) electron mobility and (d) hole mobility in CIGS photoconductor under an illumination of 680 nm ($100 \mu\text{Wcm}^{-2}$) at 1V reverse bias in SILVACO Atlas simulations.

when μ_p is larger than μ_n , showing a significantly enhanced EQE over 100% or G over 1.

In order to validate the corrected photoconductive model, a reference point ($\mu_n=100 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, $\mu_p=100 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, $\tau_{life}=100 \text{ ns}$) is extracted from **Figure 2.16(b)**, showing EQE of 84% under 1 V reverse bias. According to **Equation (2.7)**, various parameters are extracted from the simulations in **Figure 2.17** to make a comparison between the simulation and the corrected model, concerning the same parameters in the simulation with the reference point. According to the simulation results in **Figure 2.17**, g , $\overline{\Delta n}$, μ_n and μ_p are extracted to be $1.26 \times 10^{18} \text{ cm}^{-3} \text{ s}^{-1}$, $6.9 \times 10^7 \text{ cm}^{-3}$, $70.8 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and $83.5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, respectively. Therefore, $\tau_{n,eff}$ and τ_t can be determined to be 0.0548 ns and 0.141 ns, respectively. Considering a perfect semiconductor with few defects, EQE can be finally calculated to be 84.7% according to **Equation (2.7)**. The EQE value calculated by the corrected photoconductive model is therefore close to the simulation result of 84% by SILVACO Atlas simulations [93], validating the accuracy of the corrected model to be used in the future discussion of CIGS photodiodes.

2.5 Summary

The optoelectrical performances of the as-fabricated CdS/CIGS photodiode in this work are summarized and compared to other recently reported CIGS- or CdS-based heterojunction photodiodes in **Table 2.1**. The K-doped CIGS shows the highest responsivity but is designed specifically for the near-infrared photodetection [19]. Compared to other broadband CdS/CIGS photodiodes, our ultra-thin photodiode with the thinnest reported CIGS film of 750 nm for photodetectors, exhibits outstanding performances while working at both photovoltaic and

photoconductive mode. Under 0 V bias, the as-fabricated photodiode indicates a record detectivity, which is 139% higher than the best reported detectivity for CdS/CIGS photodetectors [16]. Under 1 V reverse bias, excellent responsivity and *EQE* are 4% and 25% higher, respectively, than the reported highest values for broadband CdS/CIGS photodetectors [5]. Meanwhile, relatively low predicted rise and decay times, lower than 5 ms, are obtained. Compared to other CdS-based heterojunction photodiodes, CdS/CIGS photodiode in this work shows obviously higher responsivity and *EQE*, as well as competitive detectivity and response times [107-109].

In this work, a high-performance ultra-thin CdS/CIGS heterojunction photodiode, fabricated on steel, firstly exhibits dual-mode broadband photodetection from UV to near-infrared spectrum, reaching both high responsivity and detectivity by switching the detection modes of the device. From 395 to 910 nm, excellent responsivities over 0.4 A W^{-1} and impressive *EQEs* over 100% are observed in the photoconductive mode (1 V reverse bias), while high detectivities over 2×10^{12} Jones are obtained in the photovoltaic mode (0V). Importantly, the CdS/CIGS photodiode shows its best performances under an incident light power of $20 \text{ } \mu\text{W cm}^{-2}$. Operating in the photovoltaic mode as a self-driven photodetector without external energy consumption, the photodiode reaches a record detectivity of $\sim 4.4 \times 10^{12}$ Jones, a low *NEP* of $0.16 \text{ pW Hz}^{-1/2}$, and a high $I_{\text{light}}/I_{\text{dark}}$ ratio of over $\sim 10^3$ at 680 nm illumination. Working in the photoconductive mode, the photodiode reaches a significantly enhanced responsivity of 1.24 A W^{-1} and an impressive *EQE* of 226%.

By SILVACO ATLAS simulation and theoretical analysis, a moderate spike-like CBO and a large VBO help to reduce the interfacial carrier recombination. In the photovoltaic mode, the responsivity and

EQE of the photodiode are both limited due to the lack of an effective photoconductive gain mechanism. According to the corrected gain mechanism, EQE over 100% can originate from the difference between photogenerated excess hole and electron concentrations in the device, caused by the trapped minority electrons in the defects, surface states and depletion region. These superior results indicate that the CdS/CIGS heterojunction photodiode is a promising photodetector to balance the responsivity and detectivity in a single device. Finally, the steel substrate offers the possibility to further study its flexible performances for potential portable applications.

Table 2.1. Comparison with previously reported CIGS- or CdS-based heterojunction photodiodes

Structure	CdS/Al ₂ O ₃ /CIGS	Flexible CdS/CIGS	CdS/K-doped CIGS	CdS/Se	Flexible CdS/Si	CdS/SnS	CdS/CIGS
Measured Conditions^a	PV (0 V, $\lambda=800$ nm)	PC (-2 V, $\lambda=808$ nm)	PC(-0.4V, $\lambda=980$ nm) PV (0 V, $\lambda=980$ nm)	PV (0V, $\lambda=500$ nm)	PV (0V, $\lambda=325$ nm)	PV (0V, $\lambda=650$ nm)	PC (-1V, $\lambda=680$ nm) PV (0V, $\lambda=680$ nm)
<i>R</i> (A W⁻¹)	0.54	1.18	1.87 ~0.35	0.04	0.0046	0.0104	1.24 ~0.39
<i>EQE</i>	~90%	181% ^b	237% ~45%	9.9% ^b	1.8% ^b	2%	226% ~71 %
<i>D</i> (Jones)	1.84×10^{12}	6.65×10^{10}	6.45×10^{10} $\sim 1 \times 10^{10}$	1.3×10^{13}	1×10^{12}	3.56×10^{11}	7×10^{10} $\sim 4.4 \times 10^{12}$
Rise/Decay Times (ms)	0.003/0.006	70/88	20/20 /	0.002/22	245/277	<30	<5/<5 /
Refs.	[16]	[5]	[19]	[107]	[108]	[109]	Chapter 2

^a The photovoltaic and photoconductive modes are abbreviated as PV and PC, respectively.^b This value is not obtained from the literature but calculated from Equation (1.6).

Chapter III

An In₂S₃/CIGS Heterojunction Photodiode on Steel

In this chapter, a Cd-free buffer layer (In_2S_3) is firstly introduced to fabricate and characterize a high-performance broadband ultra-thin ITO/IZO/ $\text{ZnMgO}/\text{In}_2\text{S}_3/\text{CIGS}/\text{MoNa}/\text{Mo}$ heterojunction photodiode on a commercial low-carbon steel substrate, demonstrating an optimized band offset, a significantly improved broadband photoresponse in the whole spectrum from UV to near-infrared spectrum (375-1050 nm), as well as the potential to be used as a self-powered photodetector. SILVACO ATLAS-2D simulations are done to better understand the operation mechanisms of the photodiode [93].

CIGS thickness is reduced to 800 nm and integration on steel paves the way towards flexible, low weight, photodetectors for portable applications in the future. The CIGS/ In_2S_3 heterojunction photodiode fabricated on steel with high responsivity, high detectivity and broadband photoresponse creates new possibilities for large-area commercial photodetector fabrication in a lower-cost, lighter-weight, and more environment-friendly way.

3.1 Experimental methods

3.1.1 Device structure and fabrication

The schematic structure of the $\text{In}_2\text{S}_3/\text{CIGS}$ photodiode is shown in [Figure 3.1](#). The effective photodetection area is determined, by a shadow mask excluding the edges, to be $0.85 \times 0.85 \text{ cm}^2$ (without subtracting the electrode shading area of about 0.015 cm^2). A commercial DC01 low-carbon steel foil with a dielectric coating was used as the substrate because of its mechanical stability, resistance to high temperature, specific light weight, and eco-friendlier life-cycle analysis at low prices, compared to glass. The potential flexibility properties of interest for future flexible portable applications are not studied in this work. Mo (500 nm) was deposited as the back contact

for its ohmic contact to CIGS, perfect adhesion, low resistivity, and good stability. MoNa layer (500 nm) provides enough Alkali element (Na) doping to CIGS, to passivate the defects at CIGS surface, increase the hole concentration in CIGS absorber and thus contribute to a higher free carrier density used for photoresponse. The thickness of CIGS was limited to 800 nm, enabling large-area commercial fabrication at a lower cost and more environment-friendly way. In_2S_3 (30 nm) was firstly introduced in CIGS photodetector applications as an n-type semiconductor to form pn junction with p-type CIGS, and meanwhile as the buffer layer between CIGS and MgZnO. MgZnO (50 nm) was deposited on In_2S_3 as an intrinsic, non-doped, highly-resistive window layer, which mitigates the impact of any localized shunting paths. As contact layers, IZO (50 nm) with higher carrier mobility and lower resistivity has good optical transmission and electrical performance, but a contact layer of ITO (150 nm) is required on top to make a better contact with Ag (2 μm), which was deposited as top electrode to collect the photogenerated carriers in CIGS.

The In_2S_3 /CIGS heterojunction photodiode was fabricated by different research groups involved in European H2020 ARCIGS-M project. The thin low-carbon steel substrate with a dielectric coating on top was fabricated by AC&CS in CRM group. The top layers of In_2S_3 /CIGS photodiode were fabricated in Midsummer by the DUO sputtering tool, which consists of three groups of sputtering chambers [110, 111]. Na-doped Mo and Mo were deposited in the first group of chambers by DC sputtering as a stack of back contact. The sample was then transferred to an intermediate chamber for heating and the second group of chambers to deposit CIGS composed of different layers by pulsed DC sputtering. To extend the Ga-grading, a thin layer of CuGaSe_2 (CGS) was firstly deposited from CGS target and followed by the sputtering of a thin CIGS from CIGS targets with different

Ga/(In+Ga)-ratios. The bulk part of CIGS was sputtered by quaternary targets containing Cu, In, Ga and Se. The sample was then rapidly cooled down by He in the intermediate chamber and sent to the third group of chambers for In_2S_3 sputtering from a compound target. Finally, IZO/ITO were sputtered as transparent conductive oxide (TCO) bilayers in the third group of sputtering chambers and Ag grids were screen-printed on top of the sample.

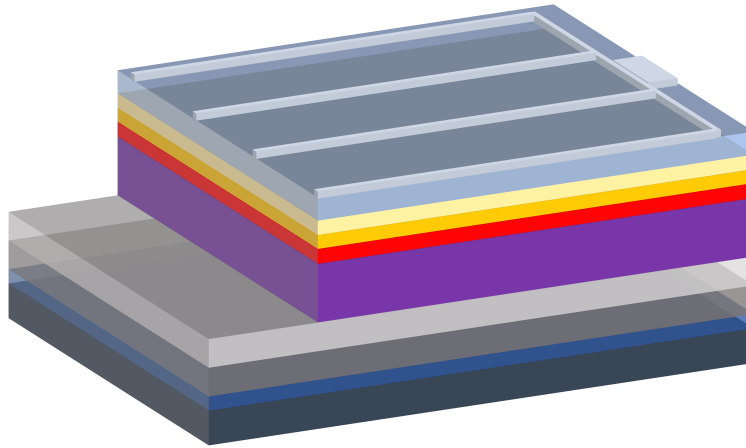


Figure 3.1. Schematic structure of the In_2S_3 /CIGS photodiode.

3.1.2 Device characterization

Four-point probe measurements were performed to extract the current-voltage (I - V) curves of In_2S_3 /CIGS heterojunction photodiode on a low signal probe station (PM8PS) combined with Agilent B1500A Semiconductor Device Analyzer at dark and under the illumination of light emitting diodes (Thorlabs, LED375L-LED1050L) specifically at 375, 395, 430, 450, 490, 505, 525, 555, 590, 630, 680, 760, 810, 870, 910, 970, 1050 nm. The LED light densities were measured by a power

meter (Ophir Optronics, Ophir Nova 1Z01500), integrating a standard silicon photodetector PD300 with detection range from 200 to 1100 nm. A shadow mask was used to fix the effective photodetection area of the In₂S₃/CIGS photodiode. All the measurements were performed at a constant chuck temperature of 25 °C.

3.2 Dark characterization

The $I_{\text{dark}}-V$ curve of In₂S₃/CIGS photodiode at dark are characterized by 4-probe measurement in [Figure 3.2](#). The compliance of the measurement output current is set at 0.1 A to avoid the breakdown of pn junction caused by large diode current. The $I_{\text{dark}}-V$ curve shows clear diode performance of the device. The pn junction is turned on at the forward bias while turned off at the reverse bias. The photodiode reaches the compliance at a high bias.

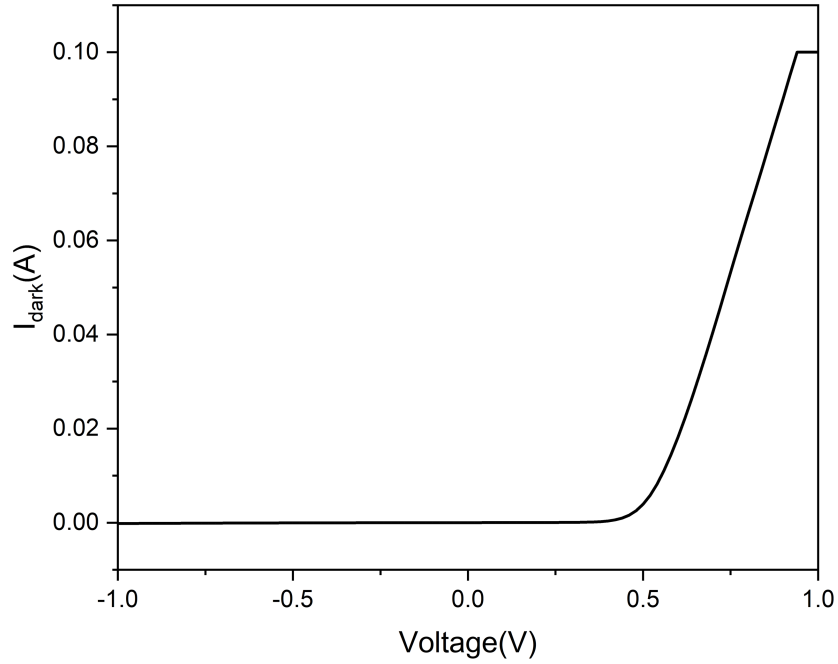


Figure 3.2 Dark I - V curve of the In₂S₃/CIGS photodiode.

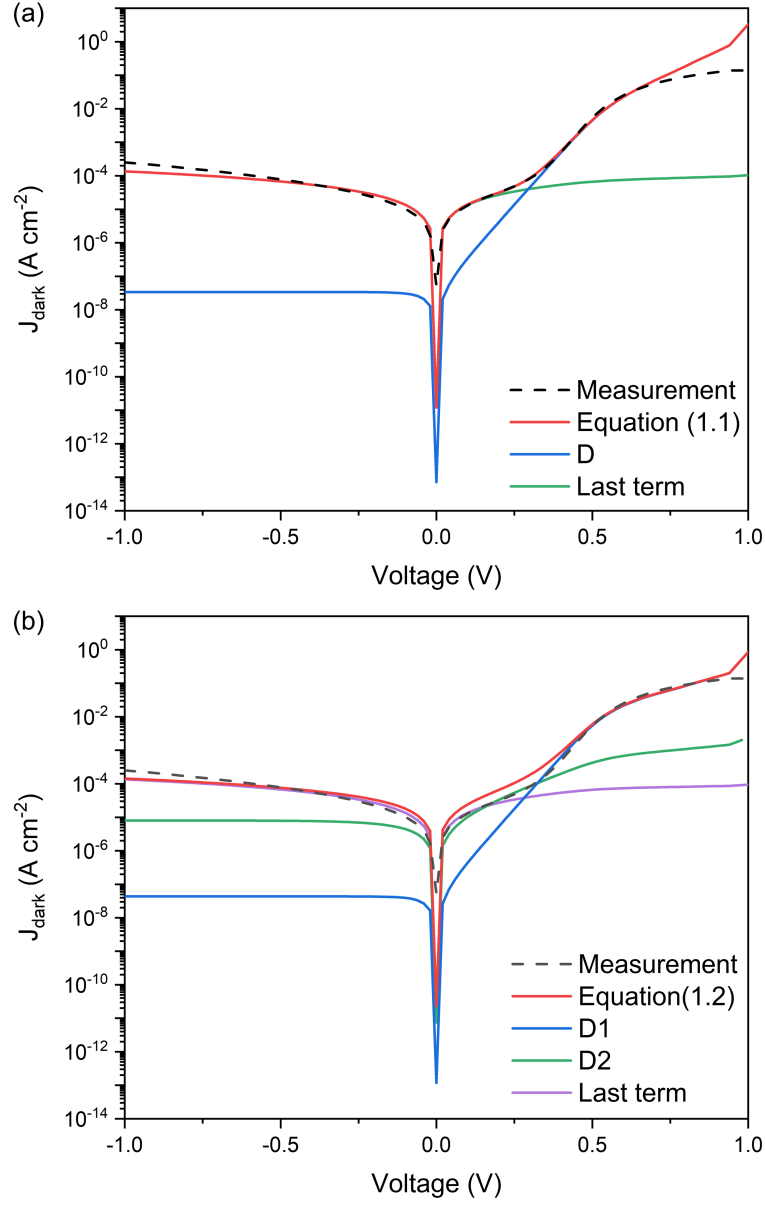


Figure 3.3 (a) Single-diode and (b) double-diode models of $\text{In}_2\text{S}_3/\text{CIGS}$ photodiode.

Single- and double- diode models are both investigated to analyze the dark characteristics of the $\text{In}_2\text{S}_3/\text{CIGS}$ photodiode in **Figure 3.3**. Different terms from **Equation (1.1)** and **(1.2)** are calculated, corresponding to the current density flowing through the diode $D_{/1,2}$ (=

$J_{0,1,2} \left\{ \exp \left[\frac{q(V - J_{dark} R_s)}{n_{0,1,2} k T_{emp}} \right] - 1 \right\}$) and the last term $(= \frac{V - J_{dark} R_s}{R_{shunt}})$ dominated by R_s and R_{shunt} .

In **Figure 3.3(a)**, analyzing the forward bias region of the J_{dark} - V curve with the single-diode model, J_0 of 3.37×10^{-8} A/cm² and n of 1.61 are obtained. By the linear fitting at high forward bias, R_s of $1.7 \Omega \cdot \text{cm}^2$ is extracted. Conversely, R_{shunt} is extracted under the reverse bias from the minimum of dJ/dV [81]. For the In₂S₃/CIGS photodiode, the dark current under the reverse bias is relatively large due to a R_{shunt} of $7.38 \times 10^3 \Omega \cdot \text{cm}^2$, which is close to the generally observed R_{shunt} in the range of 10^3 to $10^4 \Omega \cdot \text{cm}^2$ reported for a CdS/CIGS heterojunction [82].

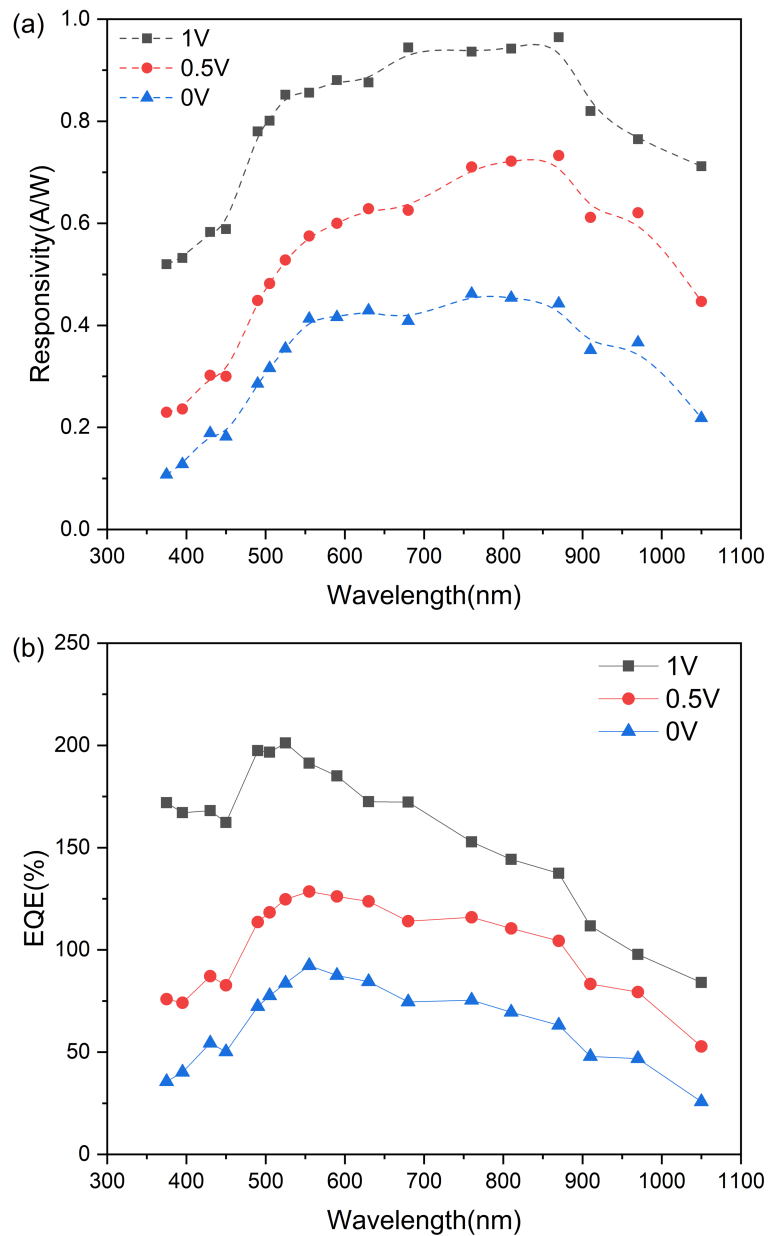
Considering the double-diode model in **Figure 3.3(b)**, G/R current in D₂ is considered, with J_{02} of 7.99×10^{-6} A cm⁻² and n_2 of 4.73. Obviously, n_2 is too high compared to a standard value close to 2 and a clear upshift of dark current calculated by the model is caused by an extra high current flow in D₂ under low forward bias. As discussed for the CdS/CIGS photodiode in Section 2.2.1, a smaller difference between the fitted and measured current is obtained for the In₂S₃/CIGS photodiode under high reverse bias. Such phenomenon could be caused by less carrier recombination in the In₂S₃/CIGS heterojunction thanks to an improved band offset. Similar to the CdS/CIGS photodiode, the single-diode model reveals a better fitting compared to the double-diode model, neglecting the compliance influence on the fitting at high bias.

3.3 Optical characterization

3.3.1 Spectral photoresponse

The spectral responsivity, EQE and detectivity of In₂S₃/CIGS photodiode from 375 to 1050 nm illuminations of $100 \mu\text{W cm}^{-2}$ are

calculated in [Figure 3.4\(a-c\)](#) with 0, 0.5 and 1 V reverse biases. The $\text{In}_2\text{S}_3/\text{CIGS}$ photodiode demonstrates excellent photoresponse in the broadband spectrum from the ultraviolet to near infrared light, showing responsivity over 0.8 A W^{-1} and impressive EQE over 100% from 505 to 910 nm under 1 V reverse bias. Similar responsivity trends with



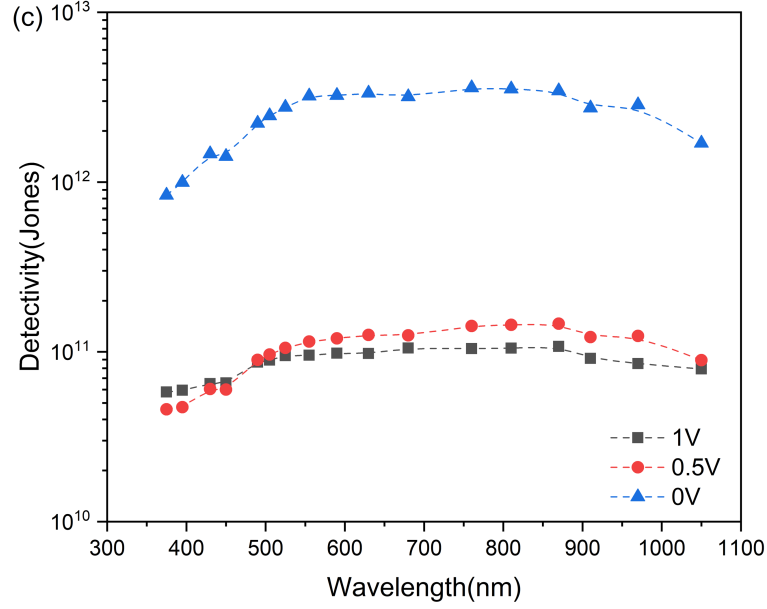


Figure 3.4. (a) Responsivity, (b) EQE , and (c) Detectivity of $\text{In}_2\text{S}_3/\text{CIGS}$ photodiode at $100 \mu\text{W cm}^{-2}$ illuminations from 375 to 1050 nm with 0, 0.5 and 1 V reverse biases.

CdS/CIGS photodiode can be observed in Figure 3.4(a), showing three different regimes. Responsivity loss at shorter wavelength is due to the photon absorption in the layers on the top of CIGS. The loss at higher wavelength is from CIGS absorption limited by the bandgap and very long penetration length towards the CIGS/Mo interface enhancing the carrier recombination with interfacial traps.

The highest responsivities are extracted to be 0.94 and 0.96 A W^{-1} at 680 and 870 nm with a reverse bias of 1 V, corresponding to EQE of 172% and 137%. The maximum detectivity and minimum NEP are extracted to be around 1.1×10^{11} Jones and $7.7 \text{ pW Hz}^{-1/2}$ under 1 V reverse bias. Under 0 V bias, the maximum detectivity and minimum NEP are extracted to be 3.6×10^{12} Jones and $0.24 \text{ pW Hz}^{-1/2}$, which reveals a good ability to detect signals and possibility to work without external power. Without effective photoconductive gain mechanism under 0V, an absorbed photon can excite maximum one electron-hole

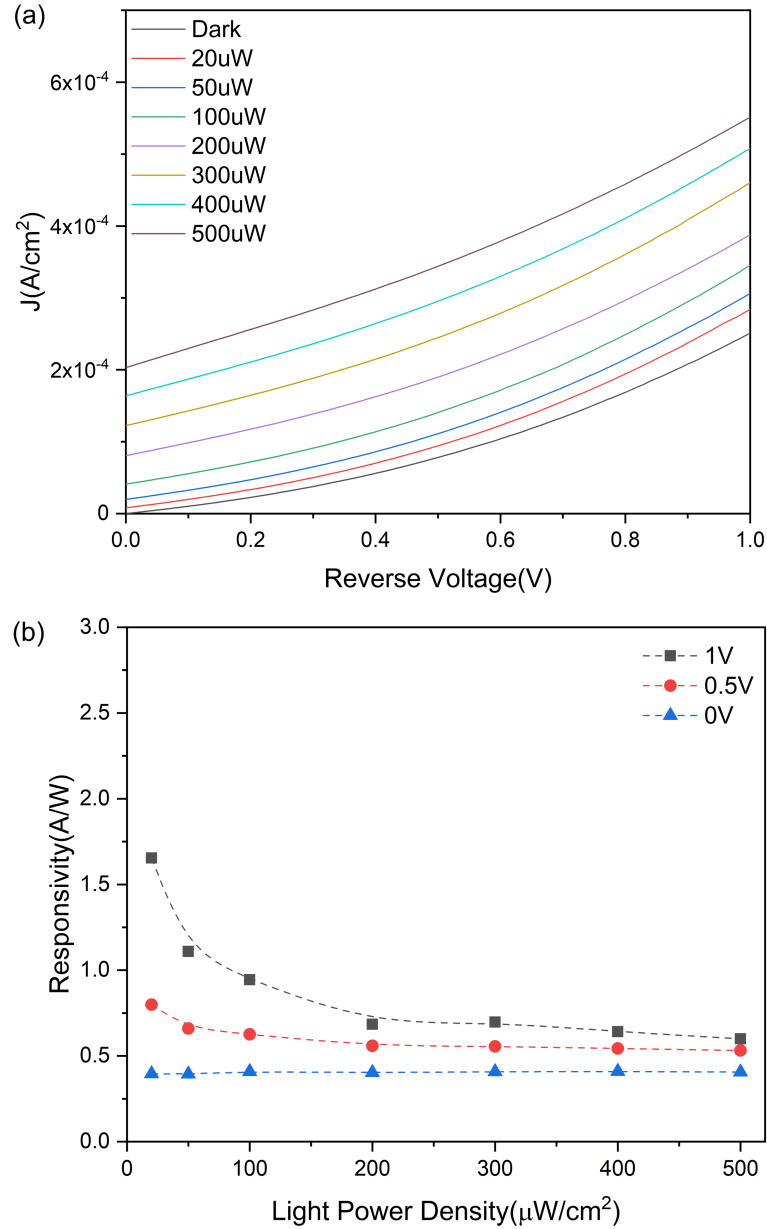
pair and thus EQE is theoretically limited below 100%. However, under external bias, EQE and photogain are significantly enhanced by a photoconductive gain mechanism as illustrated in Section 2.4.

3.3.2 Photoresponse at 680 nm

To further characterize the photoelectrical performances of In₂S₃/CIGS photodiode, 680 nm in the visible spectrum and 870 nm in the near infrared spectrum are chosen to explore the photosensitivity dependence on incident light power density. The current density-voltage (J - V) characteristics of In₂S₃/CIGS heterojunction photodiode have been measured in **Figure 3.5(a)** under 680 nm LED light at varied incident light densities from 20 to 500 $\mu\text{W cm}^{-2}$, indicating a linearly proportional increase of light current density with increasing incident light density. Such behavior is attributed to increased photo-generated carriers in photodiode excited by an increase of incident photon density from the illumination, corresponding to a power law (**Equation (2.3)**). The exponent factor relates to the balance of generation, separation, and recombination of photogenerated carriers in CIGS heterojunction. In this section, the factor β is extracted to be ~ 0.75 by fitting photocurrent as a function of light density at 680 nm under 1 V reverse bias.

Additionally, the responsivity, EQE and detectivity of the In₂S₃/CIGS heterojunction photodiode at 680nm are calculated in **Figure 3.5(b-d)** with light density variation from 20 to 500 $\mu\text{W cm}^{-2}$ under 0, 0.5 and 1 V reverse biases. The In₂S₃/CIGS heterojunction photodiode exhibits an excellent optical sensitivity, while working under 1 V reverse voltage with a low light density of 20 $\mu\text{W cm}^{-2}$ at 680 nm, reaching an ultimate high responsivity of 1.65 A W^{-1} , an EQE of 302%, a detectivity of 1.8×10^{11} Jones and a NEP of 4.7 $\text{pW Hz}^{-1/2}$. Considering that such structure is normally utilized in solar cells, photovoltaic effect is expected to exist, which makes In₂S₃/CIGS

heterojunction photodiode heterojunction photodiode possibly working as a self-powered photodiode. The detectivity and NEP reaches a stable value of $\sim 3.1 \times 10^{12}$ Jones and $0.27 \text{ pW Hz}^{-1/2}$ under 0 V bias at different light densities, while keeping a good responsivity of $\sim 0.4 \text{ A W}^{-1}$ and an



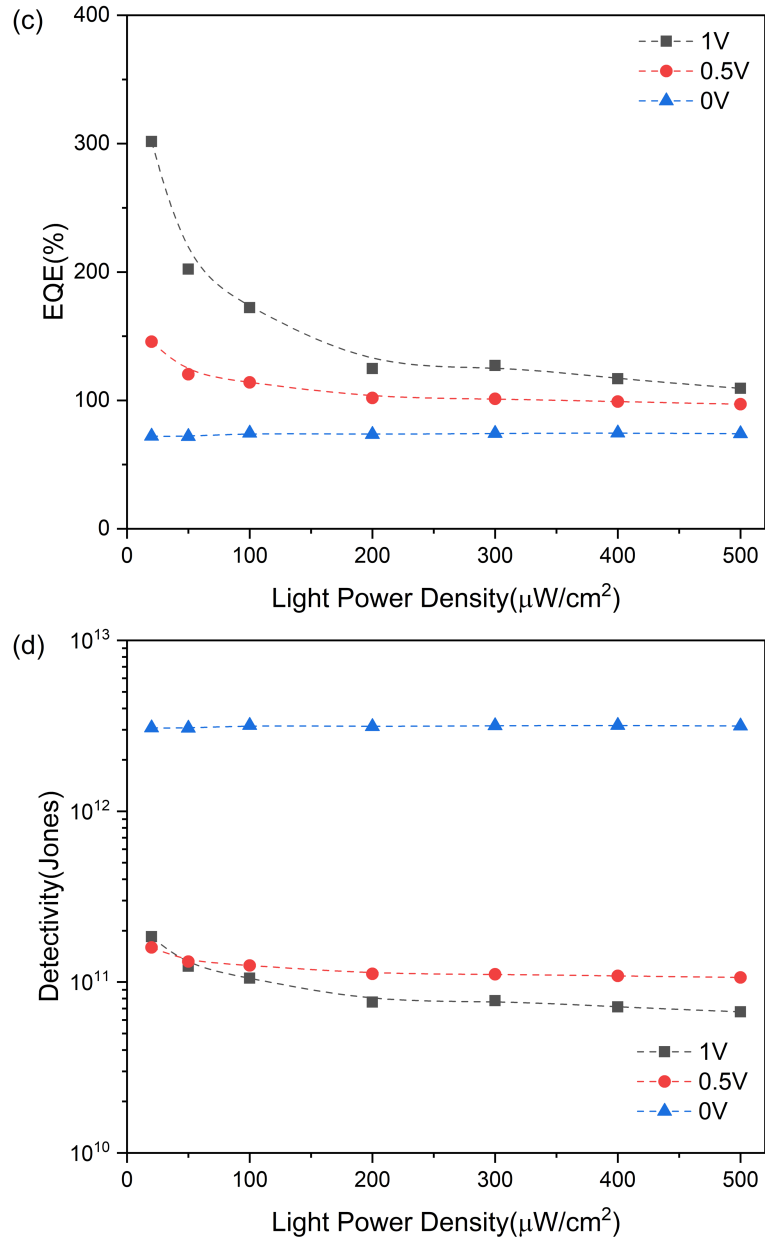


Figure 3.5. (a) J - V curves in the dark and under 680 nm illumination at different incident light power densities; (b) Responsivity, (c) EQE , and (d) Detectivity as a function of incident light densities under 680 nm illumination with 0, 0.5 and 1 V reverse biases.

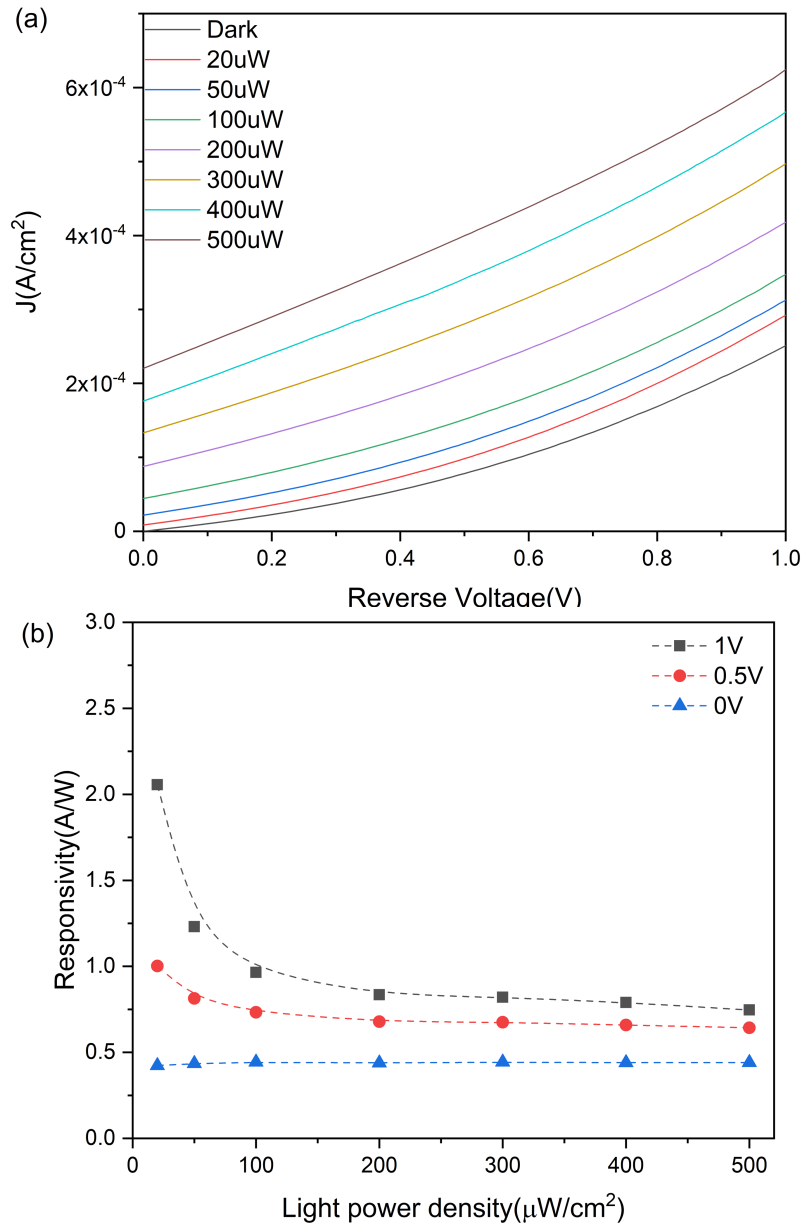
EQE of $\sim 74\%$, which shows a great potential of CIGS-based

photodiodes to be used as photoelectrical sensors without external energy consumption.

3.3.3 Photoresponse at 870 nm

Figure 3.6(a) gives the J - V characteristics of In₂S₃/CIGS photodiode under 870 nm LED light at increasing incident light densities from 20 to 500 $\mu\text{W cm}^{-2}$. The light intensity dependence of the photocurrent under 1 V reverse bias can be fitted by the power law, $I_{photo} \sim P^{0.82}$. The exponent factor $\beta = 0.82$ is much higher than previously reported β of 0.34 for CdS/CIGS photodiode at 808 nm [5], which indicates better quality of CIGS with very few defects and traps [112], as well as less interfacial traps in the spike-like band structure of In₂S₃/CIGS heterojunction. The exponent β is close to β of CdS/CIGS photodiode studied in Chapter 2. The exponent $\beta = 0.82$ at 808 nm is slightly higher than $\beta = 0.75$ at 680 nm, indicating similar recombination kinetics but lower trap states active in the near-infrared spectrum than that in visible spectrum [113]. At longer wavelength, incident light penetrates deeper in CIGS, where less recombination centres from charge impurities and defects exist than CIGS closer to In₂S₃/CIGS defective interface.

Moreover, the responsivity, EQE and detectivity of In₂S₃/CIGS photodiode at 870nm are calculated in **Figure 3.6(b-d)** with light density from 20 to 500 $\mu\text{W cm}^{-2}$ under 0, 0.5 and 1 V reverse biases. Illuminated by low 870 nm LED light (20 $\mu\text{W cm}^{-2}$) under 1 V reverse bias, the In₂S₃/CIGS photodiode reaches a record responsivity of 2.06 A W^{-1} , an impressive EQE of 293%, an excellent detectivity of 2.3×10^{11} Jones, and a NEP of 3.7 pW $\text{Hz}^{-1/2}$. Under 0V bias, In₂S₃/CIGS photodiode, working as a self-powered photodiode, exhibits a good responsivity of $\sim 0.44 \text{ A W}^{-1}$, EQE of $\sim 63\%$, a record detectivity of $\sim 3.4 \times 10^{12}$ Jones, and a low NEP of 0.25 pW $\text{Hz}^{-1/2}$.



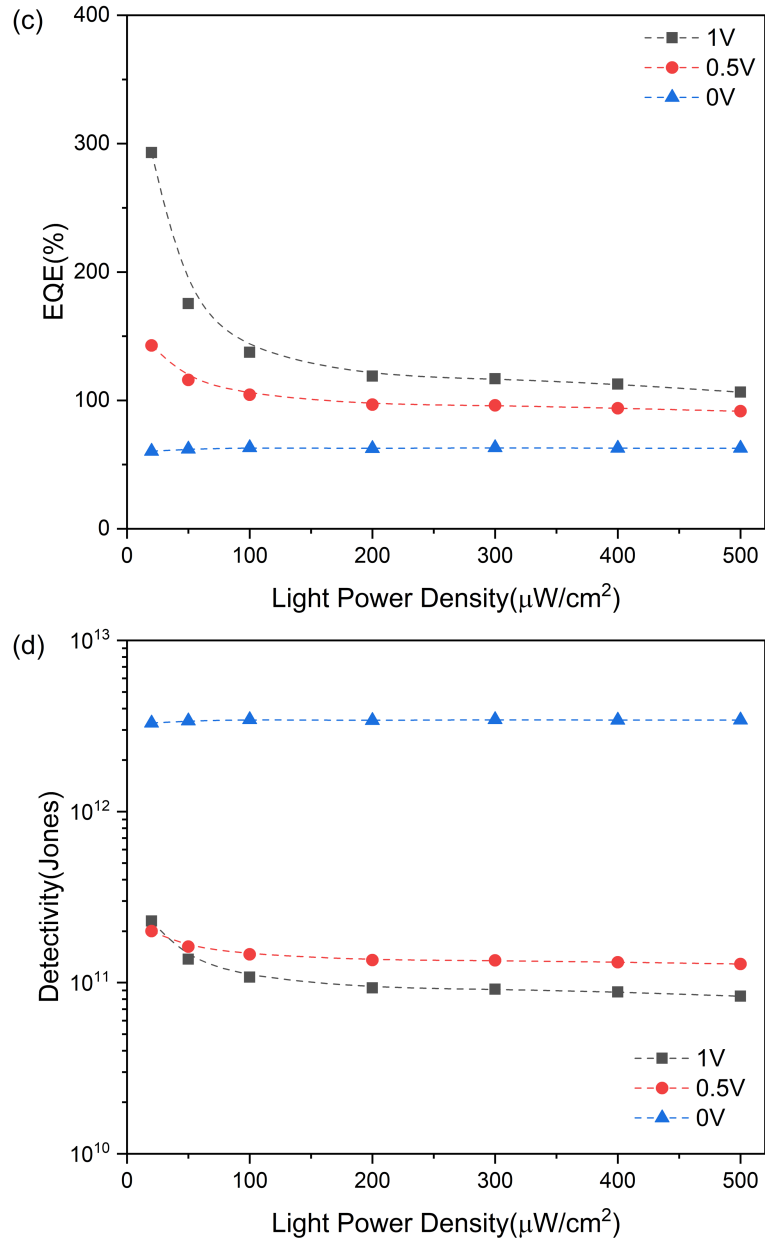


Figure 3.6. (a) J - V curves in the dark and under 870 nm illumination at different incident light power densities; (b) Responsivity, (c) EQE , and (d) Detectivity as a function of incident light densities under 870 nm illumination with 0, 0.5 and 1 V reverse biases.

3.4 Operation mechanism

3.4.1 Spike- and cliff- like CBO

The band alignment at the interface between n-type buffer and p-type absorber layer is crucial for CIGS heterojunctions. The band alignment at the p-n junction is decided by the difference between electron affinities of buffer and CIGS absorber layer, resulting in the discontinuity of conduction band at the interface. Such discontinuity is defined as conduction band offset (CBO), which includes spike-like and cliff-like CBO [114].

For the spike-like CBO in **Figure 3.7(a)**, the electron affinity of buffer layer is larger than that of CIGS absorber, which causes a higher conduction band edge of the buffer layer compared to the CIGS absorber. Such positive CBO acts as a barrier in the reverse bias for photogenerated electrons in CIGS flowing towards the buffer layer if the energy of CBO is too high. Therefore, controlling this CBO at a relatively lower value is critical for photo-generated electrons to cross over this barrier or otherwise the photo-generated current would decrease abruptly [114]. A moderate spike-like CBO is helpful to reduce the interfacial carrier recombination by increasing the interface recombination barrier without prohibiting the transport of photogenerated electrons.

In contrast, for the cliff-like CBO in **Figure 3.7(b)**, the electron affinity of buffer layer is smaller than that of CIGS absorber, which causes a lower conduction band edge of the buffer layer compared to the CIGS absorber. Such negative CBO does not stop the photogenerated electrons flowing toward the buffer layer in the reverse bias, but the interfacial recombination would be significantly enhanced. Such phenomenon is caused by the reduced activation energy for carrier

recombination (E_a). Considering the spike-like positive CBO, E_a is equal to the bandgap of CIGS (E_g). Conversely, E_a is lowered for a cliff-like CBO and equals to $E_g - E_{|CBO|}$, where $E_{|CBO|}$ is the energy of CBO. The reduction of E_a would obviously increase the interfacial recombination and degrade the device performance [115].

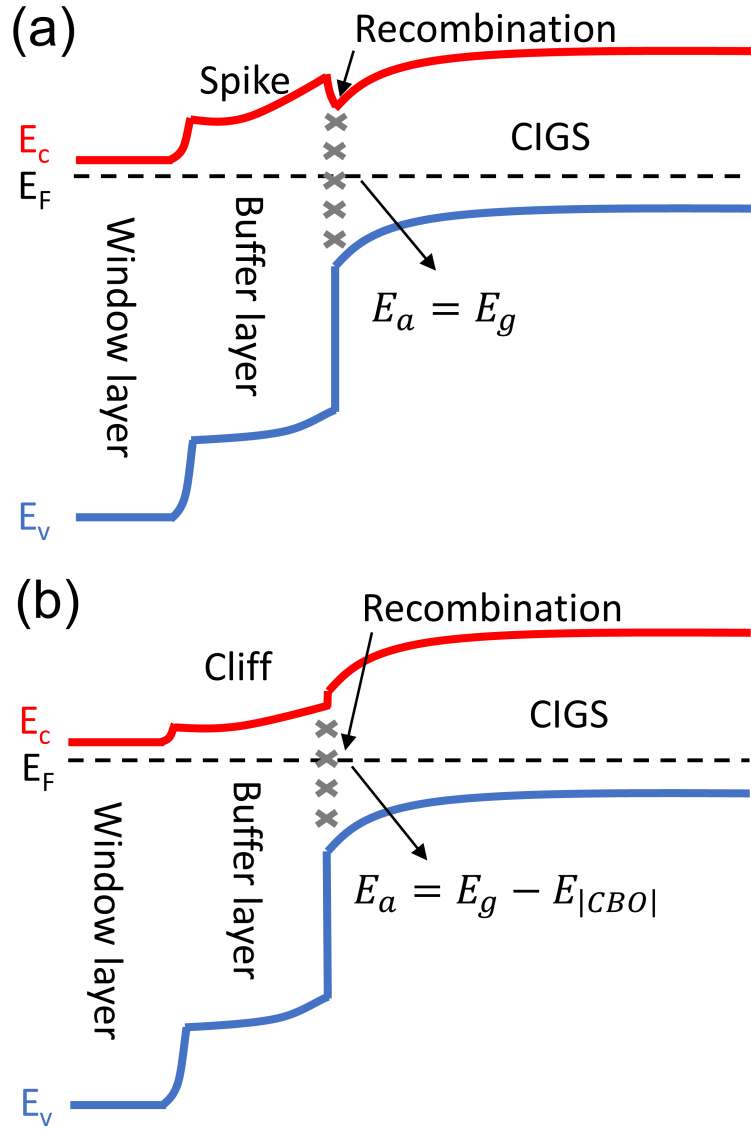


Figure 3.7. Spike- and cliff- like CBO for CIGS heterojunctions (Crosses are traps in the bandgap).

In summary, a positive CBO corresponding to a spike-like CBO is preferred when choosing an ideal buffer layer for CIGS. The optimum $E_{|CBO|}$ should range from 0 to 0.3 eV to reduce the interfacial carrier recombination and protect the transport of photogenerated electrons simultaneously [114].

3.4.2 SILVACO simulation

By Atlas simulation in SILVACO software [93], the energy band diagram of In₂S₃/CIGS heterojunction is obtained at the thermal equilibrium state in Figure 3.8(a). The simulation parameters of In₂S₃/CIGS photodiode in SILVACO are presented in Table A3. As a comparison, the band diagram of the traditional CdS/CIGS heterojunction studied in Chapter 2 is also simulated at the thermal equilibrium state in Figure 3.8(b). At 860 nm illumination with 1 V bias, the energy band diagram of In₂S₃/CIGS heterojunction is shown in Figure 3.9. In Figure 3.8(a), an n-n heterojunction at the interface of ZnMgO/In₂S₃ junction and a p-n heterojunction at the interface of In₂S₃/CIGS junction are observed. At the In₂S₃/CIGS junction, a spike-like conduction band offset (CBO) of ~0.14 eV, where the conduction band minimum of In₂S₃ is higher than that of CIGS, is favorable in CIGS heterojunctions, because this spike structure can reduce the interfacial traps and carrier recombination and make the charge flow easier at the interface [116]. In contrast, traditional CdS/CIGS heterojunction in Figure 3.8(b) has a lower CBO of ~0.05 eV, where interface recombination becomes significant due to the reduced activation energy of carrier recombination [115]. Therefore, enhanced photodetection capabilities of In₂S₃/CIGS photodiode were observed compared to CdS/CIGS photodiode because fewer recombination is expected in the improved band offsets.

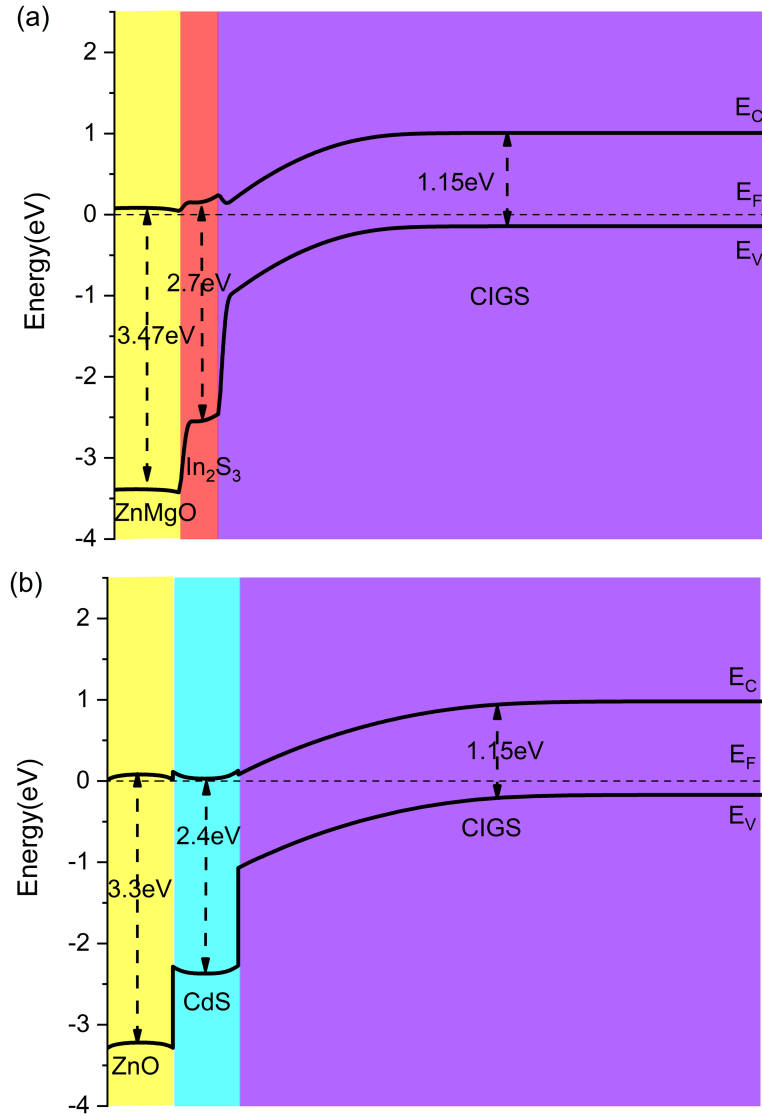


Figure 3.8. Energy band diagrams of (a) $\text{In}_2\text{S}_3/\text{CIGS}$ and (b) CdS/CIGS heterojunctions in Chapter 2 at the thermal equilibrium state.

While working as a self-powered photodiode at 0 V, photons mainly absorbed by the CIGS layer excite photo-generated carriers, which diffuse to the depletion region and are separated by the built-in electrical field to form photo-generated current. To enhance the photoresponse, a reverse bias of 1 V in [Figure 3.9](#), can significantly

increase the built-in potential and leads to a deeper depletion in CIGS. According to the corrected photoconductive gain model, the effective minority carrier lifetime is increased due to an increased spike CBO in the $\text{In}_2\text{S}_3/\text{CIGS}$ photodiode. Same as the CdS/CIGS photodiode, excess minority electrons would be trapped by defects and surface states and depletion region. Therefore, $G > 1$ is also observed for $\text{In}_2\text{S}_3/\text{CIGS}$ photodiode thanks to the photoconductive gain mechanism.

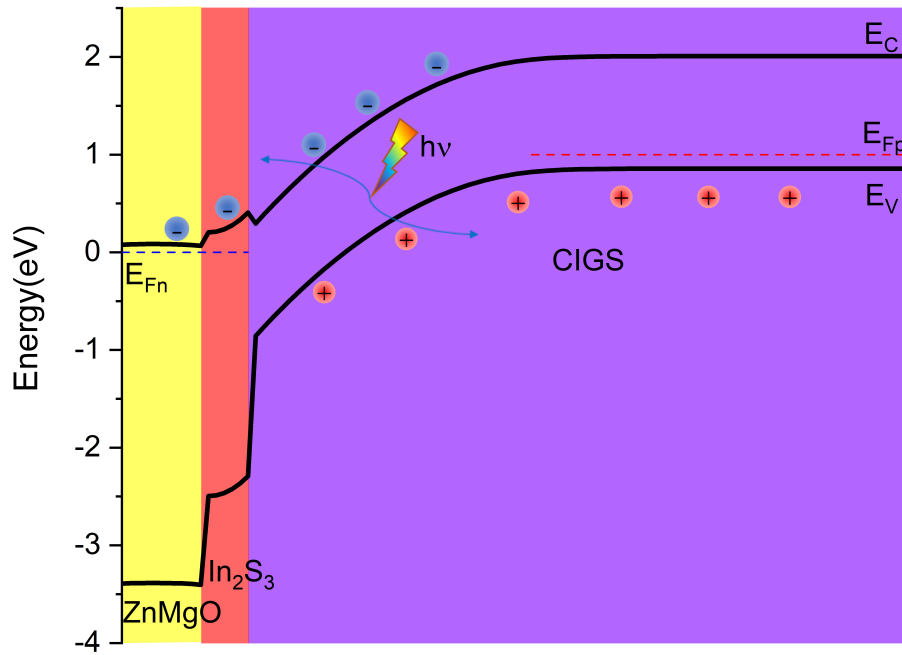


Figure 3.9. Energy band diagrams of $\text{In}_2\text{S}_3/\text{CIGS}$ heterojunction at 870 nm illumination with 1 V reverse bias.

3.5 Summary

The as-fabricated $\text{In}_2\text{S}_3/\text{CIGS}$ photodiode with record optoelectrical performances is compared with other reported CIGS photodetectors in [Table 3.1](#). Our photodiode with 800 nm CIGS, which is the thinnest reported CIGS film for CIGS photodetectors, exhibits outstanding performance while working under both 0V and 1 V reverse bias. Under 0 V bias, the $\text{In}_2\text{S}_3/\text{CIGS}$ photodiode indicates a record

Table 3.1. Comparison of optoelectrical performances for CIGS-based Photodetectors with previously reported literatures

Structure	Measured Conditions*	R (A W ⁻¹)	EQE	D (Jones)	Refs.
CdS/Al ₂ O ₃ /CIGS	$\lambda=800$ nm ($V_r=0$ V)	0.54	~90%	1.84×10^{12}	[16]
Flexible CdS/CIGS	$\lambda=808$ nm ($V_r=2$ V)	1.18	/	6.65×10^{10}	[5]
CdS/K-doped CIGS	$\lambda=980$ nm ($V_r=0.4$ V)	1.87	237%	6.45×10^{10}	[19]
CdS/CIGS	$\lambda=680$ nm ($V_r=-1$ V)	1.24	226%	7×10^{10}	Chapter 2
	$\lambda=680$ nm ($V_r=0$ V)	~0.39	~71%	$\sim 4.4 \times 10^{12}$	
	$\lambda=870$ nm ($V_r=-1$ V)	1.11	158%	6.2×10^{10}	
	$\lambda=870$ nm ($V_r=0$ V)	~0.29	~41%	$\sim 3.3 \times 10^{12}$	
In ₂ S ₃ /CIGS	$\lambda=680$ nm ($V_r=1$ V)	1.65	302%	1.8×10^{11}	Chapter 3
	$\lambda=680$ nm ($V_r=0$ V)	~0.4	~74%	$\sim 3.1 \times 10^{12}$	
	$\lambda=870$ nm ($V_r=1$ V)	2.06	293%	2.3×10^{11}	
	$\lambda=870$ nm ($V_r=0$ V)	~0.44	~63%	$\sim 3.4 \times 10^{12}$	

*The working reverse bias voltage is abbreviated as V_r .

detectivity, which is 85% higher than the best reported detectivity for CIGS photodetectors based on CIGS solar cell structures [16]. Under 1 V reverse bias, the record responsivity, EQE and detectivity of In₂S₃/CIGS photodiode are 10%, 24% and 256% higher than the reported highest CdS/K-doped CIGS heterojunction [19]. Compared to the CdS/CIGS photodiode studied in chapter 2, the In₂S₃/CIGS photodiode also shows significantly enhanced responsivity, EQE and

detectivity under the same illumination situations of 680 or 870 nm thanks to the improved band offsets and effective photoconductive gain mechanism.

In conclusion, by introducing In_2S_3 as a Cd-free buffer layer, high-performance broadband ultra-thin $\text{In}_2\text{S}_3/\text{CIGS}$ heterojunction photodiode was firstly fabricated on low-carbon steel and characterized in this chapter. By SILVACO Atlas simulation and optoelectrical measurements, the $\text{In}_2\text{S}_3/\text{CIGS}$ photodiode exhibits optimized band offset, excellent photoresponse and broadband photosensitivity from UV to near-infrared spectrum. These results superior to other reported CIGS photodiodes indicate that $\text{In}_2\text{S}_3/\text{CIGS}$ heterojunction photodiode is an excellent candidate for broadband photodetection applications, and more importantly, in the weak light photodetection area as a self-powered photodetector. Finally, integration on steel paves the way towards flexible, low weight, photodetectors for portable applications.

Chapter IV

CuO Thin Films Prepared by Sputtering

In this chapter, DC reactive magnetron sputtering is utilized to fabricate copper oxide thin films under different sputtering parameters including sputtering pressure, oxygen to argon gas ratio and substrate temperature during sputtering. Furthermore, post-annealing is considered to boost the carrier mobility of CuO thin films.

Full material, optical and electrical characterizations of the obtained CuO films have been carried out with the aim to obtain the best-performing CuO with bandgap around 1.5 to 1.7 eV, carrier concentration around 10^{15} cm^{-3} and maximum carrier mobility. With characterization results, CuO thin films show a great potential to be utilized as semiconductor materials in optoelectrical devices targeting on the photodetection in the UV and near visible spectral range.

4.1 Experimental methods

4.1.1 Experimental details

Soda lime glass (SLG) substrates with a size of $2.4 \times 2.4 \text{ cm}^2$ were cleaned by acetone, methanol, iso-propanol and de-ionized water, and dried by nitrogen before the deposition of CuO thin films by direct current (DC) reactive magnetron sputtering (ATC Orion 5 Sputter System from AJA International). The substrates fixed in the sample holder were positioned 122 mm away from the Cu target (99.999% purity) and rotated at 45 rpm under a vacuum base pressure of around 10^{-7} Torr. The total gas flow rate of Ar and O_2 was set to a constant value of 30 sccm under a sputtering pressure varied from 5 to 15 mTorr. All the samples were sputtered with a constant sputtering power of 50 W for 30 minutes, after a target cleaning of 5 minutes with Ar plasma and 3 minutes with Ar/ O_2 plasma. Post annealing was carried out in N_2 for 30 minutes at 250 and 450 °C. High-temperature sputtering at 150, 250 and 350 °C were also investigated.

After deposition, the material properties were analyzed by X-ray diffraction (XRD) with $\text{CuK}\alpha$ radiation ($\lambda=1.5418 \text{ \AA}$), field-emission gun scan electron microscope (FEGSEM, Zeiss Ultra 55 field-emission gun), Raman Spectroscopy (LabRAM HR from Horiba Scientific) and Film Thickness Measurement System (Veeco Dektak 150). The optical properties were characterized by UV-VIS-IR spectrophotometer (Specord 200 PLUS from Analytic Jena) with illumination between 200 and 1100 nm with a resolution of 1 nm to extract the transmittance and reflectance of CuO thin films. The electrical properties were measured by Hall Effect Measurement System (HMS3000) in the van der Pauw geometry with gold probes as contacts under a permanent magnet field of 0.55 T and by 4 Point Probe Resistivity Measurement (Lucas-Signaton with SUM-Keithley 2400) at room temperature.

4.1.2 DC reactive sputtering

In the reactive magnetron sputtering, several parameters, including sputtering pressure, sputtering power, oxygen to argon gas ratio, sputtering temperature, etc. can be varied, significantly affecting the crystal structure, grain growth and material performance of CuO. When varying the oxygen concentration in the sputtering chamber, three regimes can be possibly observed: oxidization regime, transition regime and poisoned regime. The variation of other sputtering parameters can also cause the shift of these regimes. Therefore, it's necessary to discover the corresponding oxygen concentrations to the three regimes under different sputtering circumstances to determine the possible sputtering parameters for CuO deposition.

In order to determine the best copper oxide thin film for future device fabrication, discharge voltage (i.e., voltage between the chamber and the target, with the substrate floating) obtained on the SLG substrate is measured as a function of oxygen concentration varied from

3.33% ($O_2/Ar=1/29$ sccm) to 66.67% ($O_2/Ar=20/10$ sccm) in **Figure 4.1**. In addition, different sputtering pressures of 5, 10 and 15 mTorr are investigated because the pressure can significantly influence the microstructures of thin films. When increasing oxygen concentration in the sputtering chamber, the copper target is gradually oxidized and three regimes can be observed in **Figure 4.1**, corresponding to the oxidation regime, transition regime and poisoned regime of copper oxide successively. Three phases of copper oxides including CuO, Cu_4O_3 and Cu_2O can be deposited in the oxidation regime. After fully oxidizing CuO, the discharge voltage gradually decreases in the transition regime until reaching the second plateau (poisoned regime), where the film is over-oxidized to form poor-quality copper oxides. The transition regime can be used to tune different qualities of CuO with various bandgaps, while the poisoned regime is not recommended [117].

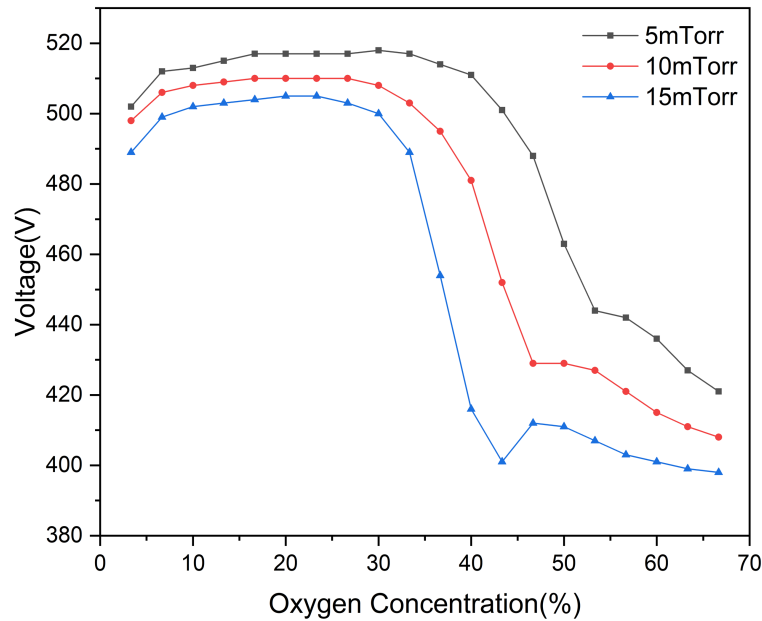


Figure 4.1. Discharge voltage as a function of oxygen concentration in the sputtering chamber, with a constant sputtering power of 50 W and a constant total gas flow rate (O_2+Ar) of 30 sccm at room temperature.

In order to determine the phase and quality of copper oxides in different regimes, 5 mTorr is firstly selected, investigating three different oxygen concentrations in three regimes. After determining the best sputtering regime for copper oxide, reactive sputtering under pressures of 5, 10 and 15 mTorr are investigated, considering varied annealing or sputtering temperatures. Finally, the best CuO thin films are investigated for further analysis.

4.2 Tuning oxygen concentration

Copper oxide has three different phases with different stoichiometric compositions (CuO , Cu_4O_3 and Cu_2O), which could be tuned by the oxygen concentration inside the deposition chamber. Under low oxygen concentration, Cu_2O phase containing only Cu^+ is formed, while Cu^+ is further oxidized into Cu^{2+} with increasing oxygen concentration, forming the phase of CuO . In between phases of CuO and Cu_2O , Cu_4O_3 is a metastable state, meaning that the deposition of Cu_4O_3 requires strict sputtering conditions. Therefore, most research focus on CuO and Cu_2O thanks to their better stability compared to Cu_4O_3 . On the other hand, the physical properties of copper oxides, including bandgap, mobility, carrier concentration and sheet resistance can be easily tuned by varying the oxygen concentration. In this part, the variation of oxygen concentration in the sputtering chamber is discovered to obtain the best oxygen concentration for the sputtering of targeting thin films.

In order to obtain a compact crystal structure of as-deposited thin films, a low sputtering pressure of 5 mTorr at room temperature is set as the reference pressure to check the film quality in different regimes: $\text{O}_2/\text{Ar}=10/20$ sccm in oxidization regime (O10 sample, 160 nm thickness), $\text{O}_2/\text{Ar}=15/15$ sccm in transition regime (O15 sample, 65

nm), and $O_2/Ar=20/10$ sccm in poisoned regime (O20 sample, 66 nm). The sputtering parameters for three samples are illustrated in [Table 4.1](#). Expect for the oxygen to argon ratio, other sputtering parameters keep the same for these samples.

Table 4.1. Sputtering Parameters of O10, O15 and O20 samples at 5 mTorr sputtering pressure.

Sample	O10	O15	O20
Target	Cu	Cu	Cu
O ₂ (SCCM)	10	15	20
Ar (SCCM)	20	15	10
Power (W)	50	50	50
I (mA)	95	105	115
V (V)	515	470	427
Deposition Time (min)	30	30	45
Temperature (°C)	Room	Room	Room
Base pressure (Torr)	1.4×10^{-7}	2×10^{-7}	2×10^{-7}
Sputtering pressure (mTorr)	5	5	5
Thickness (nm)	160	65	66

4.2.1 Structural characterization

In [Figure 4.2](#), the XRD patterns of O10, O15 and O20 samples are obtained, showing the phase of CuO (JCPDS-45-0937) from the edge of oxidization regime and transition regime to the poisoned regime. Several key figures of merits can be extracted from XRD patterns. All as-deposited CuO feature the phase of tenorite CuO, and monoclinic crystal structure in the C2/c(15) space group. Moreover, the main peaks at $2\theta = 32.5^\circ, 35.5^\circ, 38.7^\circ$ are corresponding to the reflection planes of (-110), (002) and (111) axes. The (002) peak at 35.5° is the dominant

peak for sputtered CuO because the spontaneous growth orientation is with the c-axis perpendicular to the glass substrate. Some small noise peaks can also be seen and originate from the substrate. (002) as a dominant peak indicates the crystalline fraction in CuO.

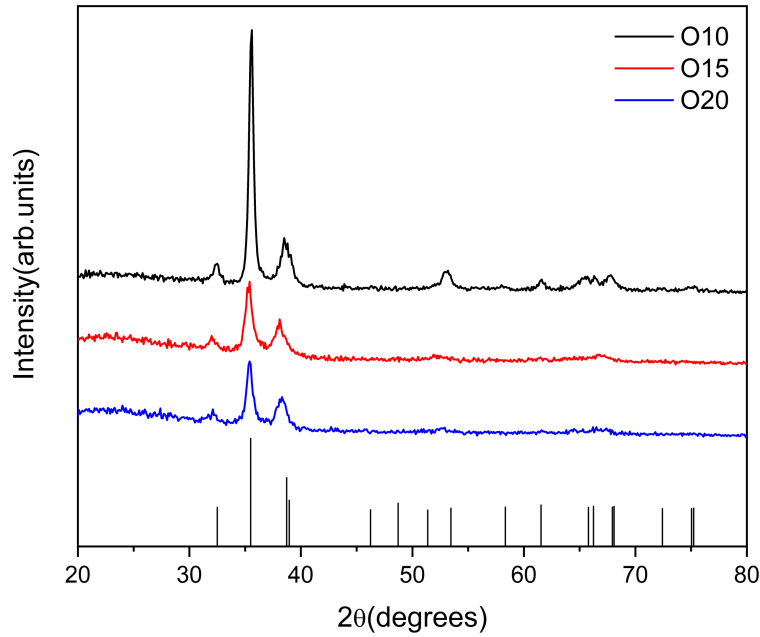


Figure 4.2. XRD pattern (JCPDS-45-0937) of O10 sample ($O_2/Ar=10/20$ sccm), O15 sample ($O_2/Ar=15/15$ sccm), O20 sample ($O_2/Ar=20/10$ sccm) at 5 mTorr sputtering pressure.

FWHM (full width of the half maximum) is an important parameter related to the crystallite size and defects. Larger FWHM indicates smaller crystallite size and thus more grain boundaries. In grain boundaries, there are defects locally strain the crystal, broadening the main peak in XRD patterns. Therefore, smaller FWHM and sharper peak are expected for perfect grain structures, indicating less defects in thin films. Such relation can be expressed by Debye-Scherer relation,

$$D = 0.94\lambda / \beta \cos \theta \quad (4.1)$$

where λ is the X-ray wavelength, and β is the FWHM [49]. The calculated crystallite sizes for O10, O15 and O20 samples are 19.34 nm, 18.02 nm and 17.55 nm, respectively. O10 sample demonstrates larger grain size, less grain boundaries and less defects. Such behavior can also be seen by SEM images in the following content, where sharper and more homogeneous grains can be observed for O10 sample.

Raman measurement is another effective method to determine the material characteristics of thin films. Raman spectra of O10, O15 and O20 samples under a laser radiation of 514 nm are illustrated in Figure 4.3. The main peaks of Raman spectra are obtained in Table 4.2 compared to typical Raman peaks for copper oxides with different phases [118-120]. For CuO thin films, the Raman peaks lie around 288 cm^{-1} for the first A_g mode, 330 cm^{-1} for the second much weaker B_g mode and 621 cm^{-1} for the third broader B_g mode [118]. The crystallite size change would cause a slight change of CuO peaks.

Raman peaks of O10 sample in Figure 4.3 are 291, 343 and 623 cm^{-1} , which are consistent with the results in literature [118]. With the increase of oxygen concentration, the Raman peaks become weaker and blunter, which corresponds to the decreasing grain size as observed in the XRD results. For all Raman spectra, an abnormal peak at 310 cm^{-1} is observed. Raman measurement is thus done for SLG substrate from the back side of the sample, indicating that this peak corresponds to the peak of SLG substrate and can be neglected in further analysis. While increasing oxygen concentration, intensity increases in the Raman shift from $400\text{-}600\text{ cm}^{-1}$ could be observed due to the increase of CuO structural defects and the increase of amorphous phase fraction [121]. The crystal qualities for O15 and O20 samples become worse with increasing oxygen concentration, which shifts the third peak towards shorter wavelength. If this increase was removed, the third peak of O15

and O20 samples would still lie at a close position with O10 sample, showing standard Raman peak for CuO phase.

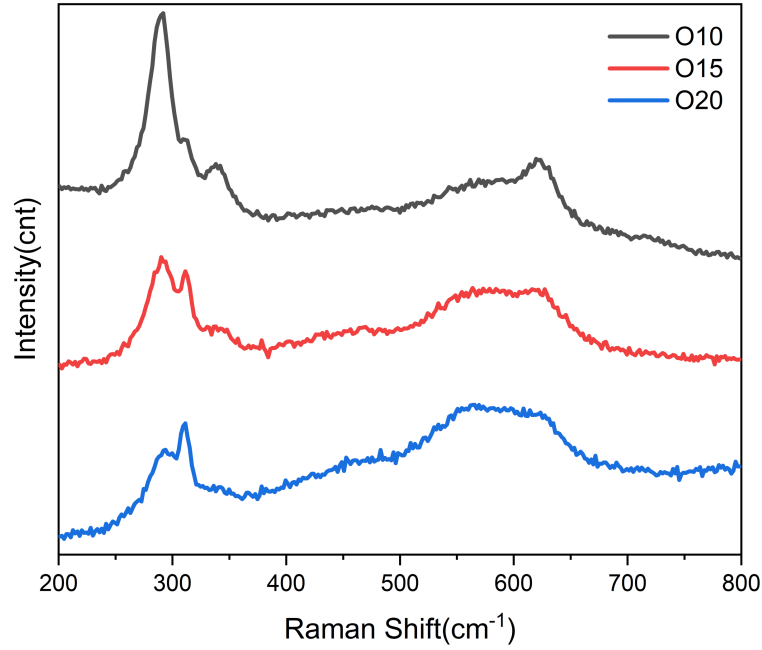


Figure 4.3. Raman spectra of O10, O15, O20 samples at 5 mTorr at room temperature and SLG substrate, by 514 nm radiation.

Table 4.2. Raman Peaks of O10, O15 and O20 samples compared to literatures

Samples	Peak positions (cm ⁻¹)
O10	291,313,343,623
O15	289,311,343,589
O20	293,311,340,587
CuO in [118]	295,343,629
Cu ₄ O ₃ in [119]	318,541,651
Cu ₂ O in [120]	220,525,625

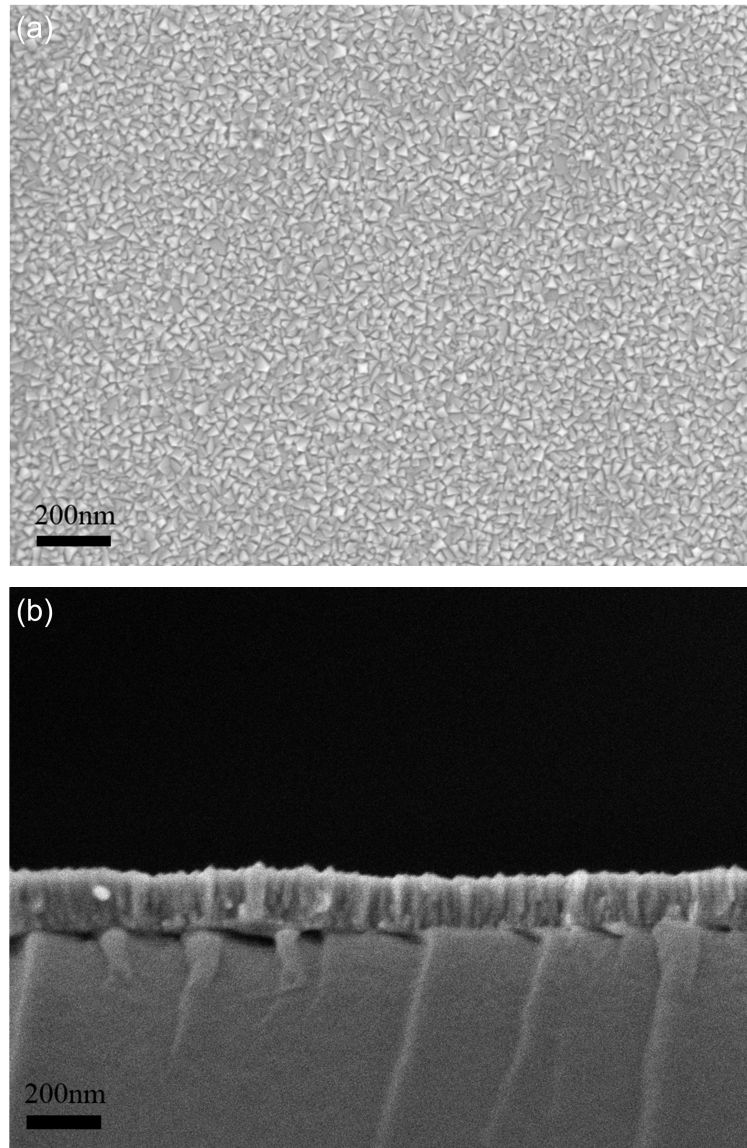


Figure 4.4. (a) SEM plane section view and (b) SEM cross section view of CuO deposited on SLG at 5 mTorr with 33% oxygen ($O_2/Ar=10/20$ sccm).

The SEM plain-view micrograph of O10 sample in **Figure 4.4(a)** reveals a sharp and clear triangular grain structure of CuO and an estimated grain size of about 20 nm, which is consistent with the XRD result and similar to the CuO grain size of 22 nm in literature [49]. The SEM cross-sectional view of O10 sample in **Figure 4.4(b)** shows a

columnar growth of poly crystallized CuO from the glass surface to the top of CuO thin film. Meanwhile, no clear SEM graphs of the O15 and O20 samples could be obtained because of poor-quality CuO crystal structures and too much charge effect from the glass substrate.

According to the structural characterizations, the best copper oxide thin film is the O10 sample with a phase of CuO, sputtered at the edge of oxidation and transition regimes, showing better grain growth, excellent morphological performance, larger grain size and less defects. Next, the opto-electronic properties of these samples would be discovered to further characterize the CuO thin films.

4.2.2 Opto-electronic characterization

UV-VIS-IR spectrophotometer is used to measure the optical properties of sputtered thin films. In order to estimate the bandgap and Urbach energy, reflectance and transmittance are measured to calculate the absorption coefficient of sputtered CuO thin films.

The reflectance spectra of CuO samples sputtered under different argon to oxygen gas ratios (oxygen concentration) are shown in [Figure 4.5\(a\)](#). The reflectance stays between 5% and 25% for O10 sample, while the reflectance keeps below 5% for O15 and O20 samples. Such behavior is caused by the thickness differences among three samples. O10 sample is around 100 nm thicker than O15 and O20 samples. It can also be clearly seen by the color of the samples that O10 samples is dark brown while the other samples are light brown.

The transmittance spectra of CuO samples sputtered under different argon to oxygen gas ratios (oxygen concentration) are shown in [Figure 4.5\(b\)](#). The average optical transmittance in the visible and near infrared region (400-1000 nm) increases with oxygen concentration from 44.3% for O10 sample to 44.6% for O15 sample and 47.2% for

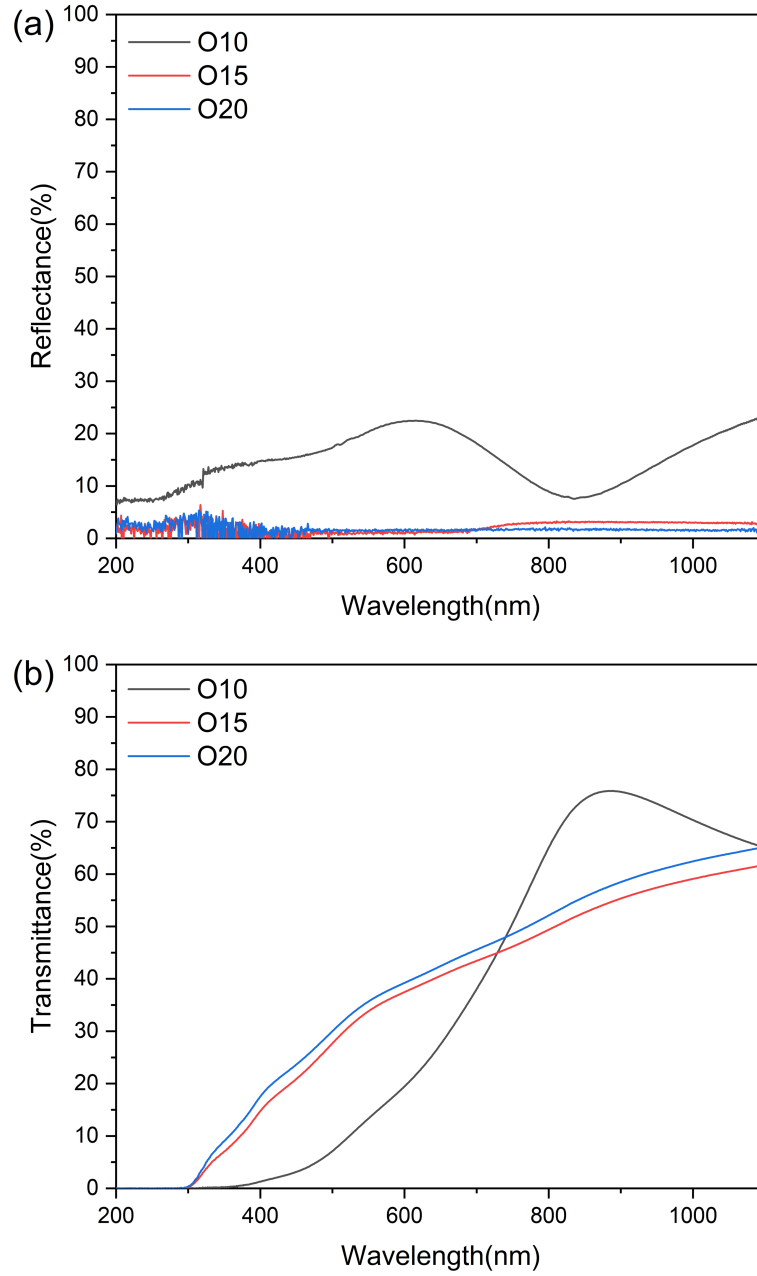


Figure 4.5 (a) Reflectance and (b) Transmittance spectra of O10, O15, O20 samples.

O20 sample and 47.2% for O20 sample. For O10 sample, transmittance increases with increasing wavelength, reaches the maximum value at

around 800 nm near the limiting absorption wavelength of O10 sample, and decreases at infrared region. For O15 and O20 samples, transmittance increases in the whole spectrum, which is related to the increasing limiting absorption wavelength at higher oxygen concentration.

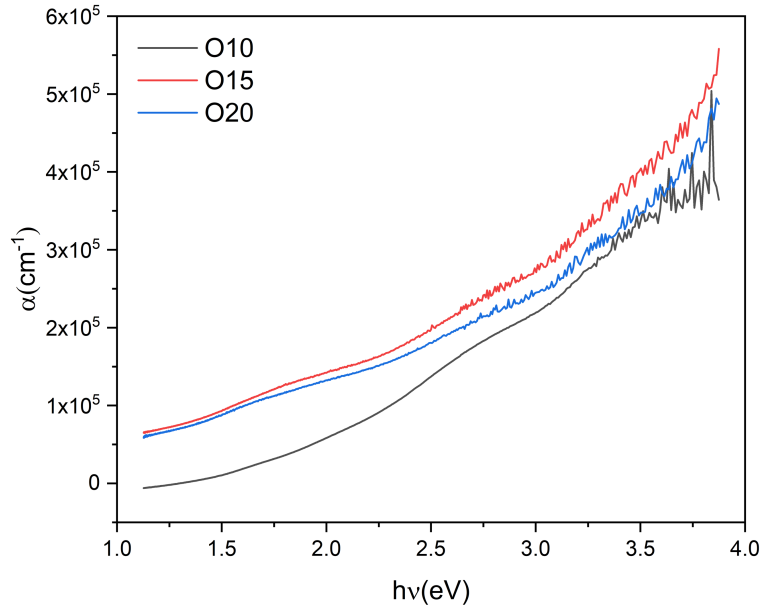


Figure 4.6. Absorption coefficient spectra of O10, O15, O20 samples.

By measuring reflectance and transmittance, the absorption coefficients of copper oxide thin films in the spectral range from 320 to 1100 nm ($h\nu=3.875-1.127$ eV) are calculated in **Figure 4.6** by utilizing the standard equation:

$$\alpha = \frac{1}{t} \ln \left(\frac{(1-R)^2}{T} \right) \quad (4.2)$$

where t is the film thickness, R and T are the reflectance and transmittance obtained in **Figure 4.5(a)** and **Figure 4.5(b)**. The absorption coefficient α , which decreases with the increase of incident wavelength and with the decrease of incident light energy, can reach over 10^5 cm^{-1} . When α is over 10^5 cm^{-1} , the maximum wavelength for

O10, O15 and O20 samples are 540, 800 and 770 nm, respectively. For samples sputtered at higher oxygen concentrations, higher α is obtained. According to the relation: $d = 1/\alpha$, where d is the light penetration depth, the incident light is absorbed by copper oxide near the surface, within less than 100 nm in the UV and near visible spectral region. In the far visible and infrared region, the films reveal very low absorption coefficient, which shows that copper oxide is almost transparent to the long-wavelength incident light and the incident light penetrates through the copper oxide with few photoexcitation. Low penetration depth of copper oxide in the UV and near visible spectral region allows the limitation of the copper oxide thickness in the photodetector applications to less than 100 nm.

The optical bandgaps of copper oxide thin films are calculated in **Figure 4.7** by using the Tauc relation in **Equation (1.7)**. The magnitude of n is equal to 2 or 1/2 for direct allowed or indirect allowed transitions respectively. The general type of CuO bandgap stays controversial, but CuO with lower bandgap (1-1.5 eV) utilizes indirect transition in long-wavelength photodetection [44]. Conversely, copper oxide with higher bandgap is considered as direct transition semiconductor, which corresponds to the n magnitude of 2 [41,49]. In this thesis, the magnitude of 2 is used to extract the linear portion of plot, in which the x-intercept value of the linear portion is equal to the bandgap value. The Tauc plots of O10 sample, O15 and O20 samples are demonstrated in **Figure 4.7 (a)** and **Figure 4.7 (b)**, respectively. With increasing oxygen concentration, the bandgap of CuO decreases from 1.39 eV to around 1 eV. However, the bandgaps of O15 and O20 samples cannot be exactly extracted because of the equipment limitation. To precisely predict the bandgaps of these samples, the wavelength of incident light from UV-VIS-IR spectrophotometer has to exceed 1100 nm.

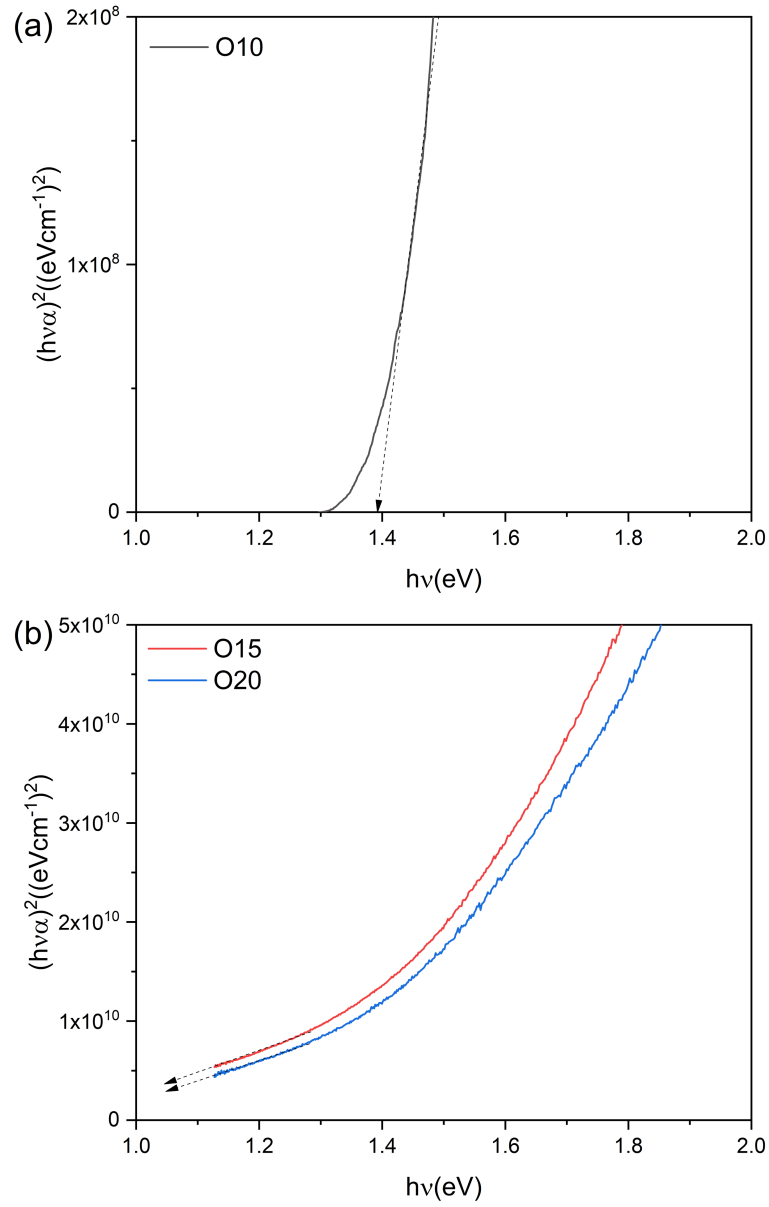


Figure 4.7. Tauc plots of O10, O15, O20 samples.

In semiconductors and insulators, the absorption edge below the optical bandgap is considered as Urbach tail, which is a key parameter related to the defect condition in semiconductors. The Urbach tails of

copper oxide thin films are calculated in **Figure 4.8** by the Urbach's rule:

$$\alpha(h\nu, T) = \alpha_0 e^{\left[\frac{h\nu - E_0}{E_U(T)} \right]} \quad (4.3)$$

where α_0 and E_0 are the characteristic parameters of materials, and $E_U(T)$ is the Urbach energy, which is reverse to the absorption edge slope $E_U^{-1} = \frac{\Delta(\ln\alpha)}{\Delta(h\nu)}$ [122]. Urbach energy is highly related to the measurement temperature, so in this chapter all the measurements are done at room temperature. The Urbach energy for O10 sample is extracted to be 4.1 meV, which is quite low for semiconductors. However, the Urbach energies for O15 and O20 samples are not predictable due to the maximum detection wavelength of 1100 nm for UV-VIS-IR spectrophotometer.

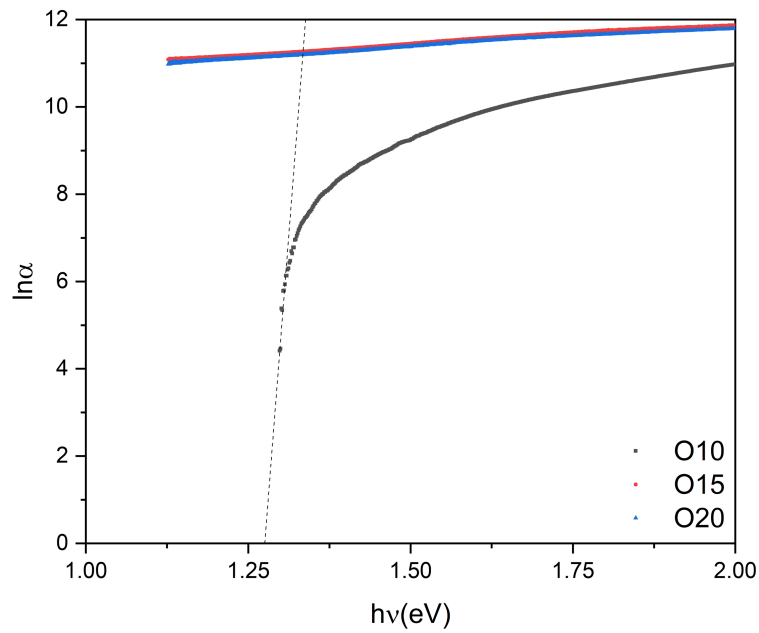


Figure 4.8. Urbach tails plots of O10, O15, O20 samples.

In order to better evaluate the electrical properties of as-deposited CuO samples, Hall measurements are also carried out to measure the carrier type, carrier mobility, carrier concentration and sheet resistance. Opto-electronic properties of as-deposited CuO samples are summarized in **Table 4.3**. Oxygen concentration has a significant influence on the electrical properties of CuO thin films. The Hall measurements reveal p-type conductivity for all CuO samples. With increasing oxygen concentration, hole concentration increases from 1.75×10^{15} to $2.10 \times 10^{18} \text{ cm}^{-3}$, while hole mobility decreases from 11.1 to $0.44 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. The sheet resistance shows a decrease from 1.9×10^7 to $\sim 1.10 \times 10^6 \text{ } \Omega \cdot \text{sq}^{-1}$ with increasing oxygen concentration, which is attributed to the higher intrinsic hole density of CuO sputtered under higher oxygen concentration.

Table 4.3. Opto-electronic properties of O10, O15 and O20 samples

Sample	O10	O15	O20
Bandgap (eV)	1.39	<1	<1
Absorption Coefficient (cm^{-1})	$>10^5$ (320-540 nm)	$>10^5$ (320-800 nm)	$>10^5$ (320-770 nm)
Urbach Energy (meV)	4.1	/	/
Hole Concentration (cm^{-3})	1.75×10^{15}	3.30×10^{17}	2.10×10^{18}
Hole Mobility ($\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}$)	11.1	2.43	0.44
Sheet resistance ($\Omega \cdot \text{sq}^{-1}$)	1.90×10^7	1.10×10^6	1.13×10^6

In summary, oxygen concentration during sputtering has an obvious impact on the structural and opto-electronic properties of deposited copper oxides. By varying the oxygen to argon ratio, p-type CuO with high absorption coefficient of over 10^5 cm^{-1} in UV and near visible spectral range shows a decreasing bandgap from 1.39 to around 1 eV with the increase of oxygen ratio from 33.3% to 66.7%. The best-

performing O10 sample ($O_2/Ar=10/20$ SCCM) exhibits a low Urbach energy of 4.1 meV, a good carrier concentration of $1.75 \times 10^{15} \text{ cm}^{-3}$, an excellent hole mobility of $11.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, and a sheet resistance of $1.90 \times 10^7 \Omega \cdot \text{sq}^{-1}$.

P-type CuO thin films exhibit obviously improved optical and electrical performances, which can be used as p-type semiconductor materials in the future applications. Therefore, oxygen concentration at the edge between the transition and poisoned regimes is the best regime where p-type CuO thin films exhibit excellent morphological performance, larger grain size and less defects, excellent optical and electrical performances.

4.3 Optimization by high-temperature processes

In order to obtain the best-performing copper oxide, copper oxide should be sputtered under the oxidation regime to avoid poor-quality CuO in transition and poisoned regimes. After determining the best oxygen concentration for CuO sputtering, DC reactive magnetron sputtering is utilized to fabricate copper oxide thin films under different sputtering parameters including sputtering pressure, oxygen to argon gas ratio and substrate temperature during sputtering. Furthermore, post-annealing is considered to boost the carrier mobility of CuO.

Therefore, in this part, oxygen to argon ratios are next set to 10/20, 8/22 and 7/23 sccm for 5, 10 and 15 mTorr sputtering pressure respectively, which corresponds to 5mTorr (O10), 10mTorr (O8) and 15mTorr (O7) samples at the edge of oxidation and transition regimes. In order to improve the quality of copper oxide thin films, we consider post-annealing at 250 and 450 °C for 30 min in N_2 as well as substrate heating at 150, 250, and 450 °C for 30 min during the sputtering. The sputtering parameters and thickness for samples on SLG substrates

considering different post-annealing temperatures and different sputtering temperatures are demonstrated in [Table 4.4](#) and [4.5](#), respectively. Considering the constant sputtering time for all samples, the thicknesses of copper oxide thin films decrease gradually with the increase of annealing temperature and sputtering temperature. Meanwhile, the XRD and Raman measurements keep similar for all samples, which reveals the phase of CuO and a good grain growth of CuO for all samples. Next, optical and electrical characterizations of sputtered CuO thin films are carried out to optimize the performances of CuO thin films considering sputtering pressure and high-temperature processes.

Table 4.4. Sputtering Parameters of CuO samples considering varied annealing temperatures

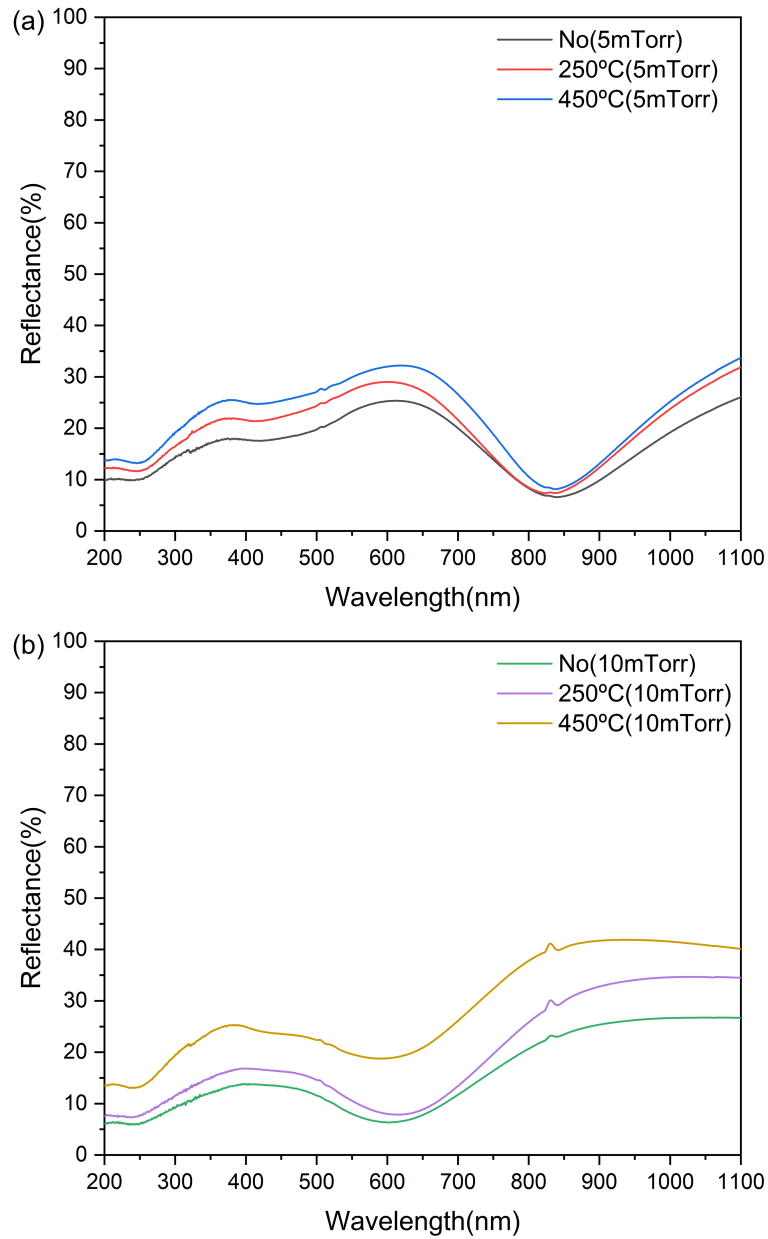
Sample	Sputtering pressure (mTorr)	Ar(SCCM)	O ₂ (SCCM)	Power (W)	I(mA)	V(V)	Sputtering Temperature (°C)	Thickness (nm)	Annealing Condition
No(5mTorr)	5	20	10	50	100	497	Room	160	/
250°C(5mTorr)	5	20	10	50	98	506	Room	148	250°C, N ₂
450°C(5mTorr)	5	20	10	50	98	504	Room	140	450°C, N ₂
No(10mTorr)	10	22	8	50	100	493	Room	120	/
250°C(10mTorr)	10	22	8	50	99	499	Room	114	250°C, N ₂
450°C(10mTorr)	10	22	8	50	101	489	Room	96	450°C, N ₂
No(15mTorr)	15	23	7	50	101	485	Room	90	/
250°C(15mTorr)	15	23	7	50	101	492	Room	80	250°C, N ₂
450°C(15mTorr)	15	23	7	50	102	478	Room	60	450°C, N ₂

Table 4.5. Sputtering Parameters of CuO samples considering varied sputtering temperatures

Sample	Sputtering pressure (mTorr)	O ₂ (SCCM)	Ar(SCCM)	Power(W)	I(mA)	V(V)	Sputtering temperature (°C)	Thickness (nm)	Annealing Condition
10mTorr(Room)	10	8	22	50	101	488	Room	120	/
10mTorr(150°C)	10	8	22	50	101	486	150	110	/
10mTorr(250°C)	10	8	22	50	101	485	250	100	/
10mTorr(350°C)	10	8	22	50	102	483	350	100	/

4.3.1 Optical characterization

The reflectance spectra of copper oxide thin films sputtered under different pressures and different gas ratios with varied annealing and sputtering temperatures are shown in [Figure 4.9](#). With the increase of



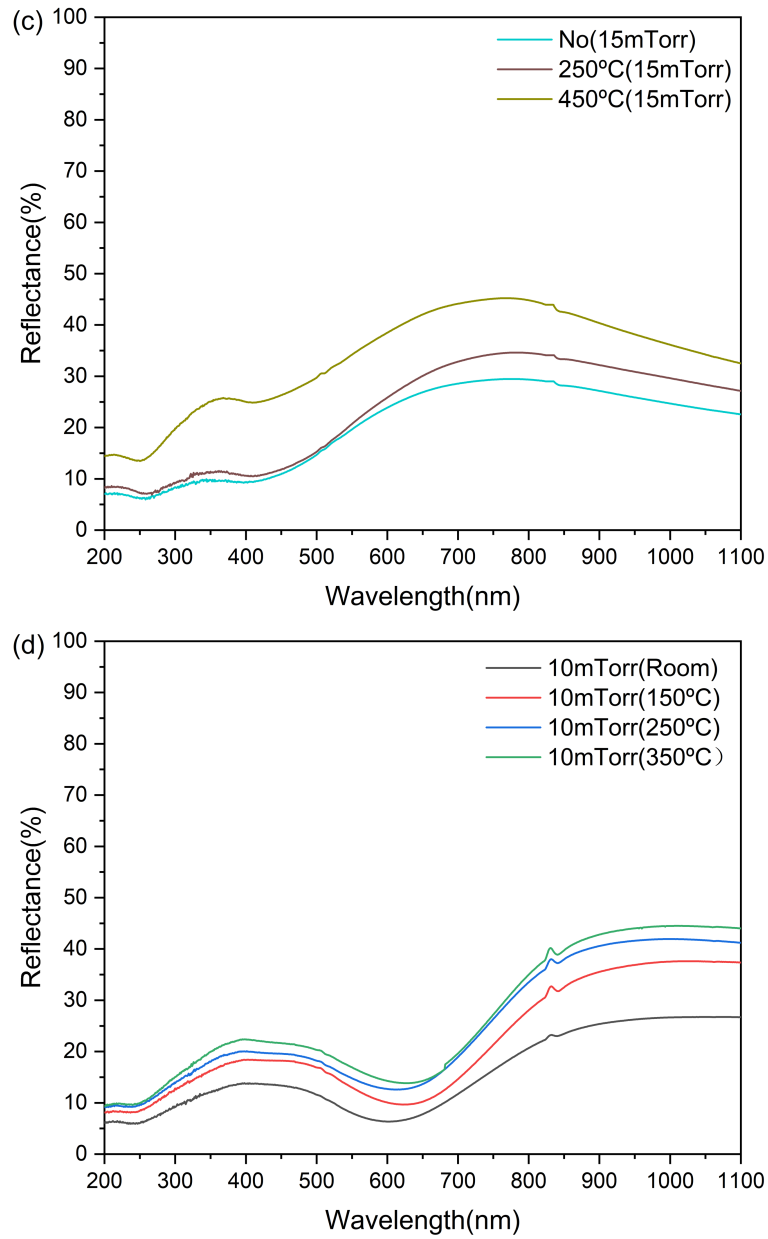


Figure 4.9. Reflectance spectra of CuO thin films deposited under different post-annealing temperatures (250 and 450°C) at (a) 5mTorr (O10), (b) 10mTorr (O8), (c) 15mTorr (O7), and (d) 10mTorr (O8) under different sputtering temperatures from 150 to 350°C.

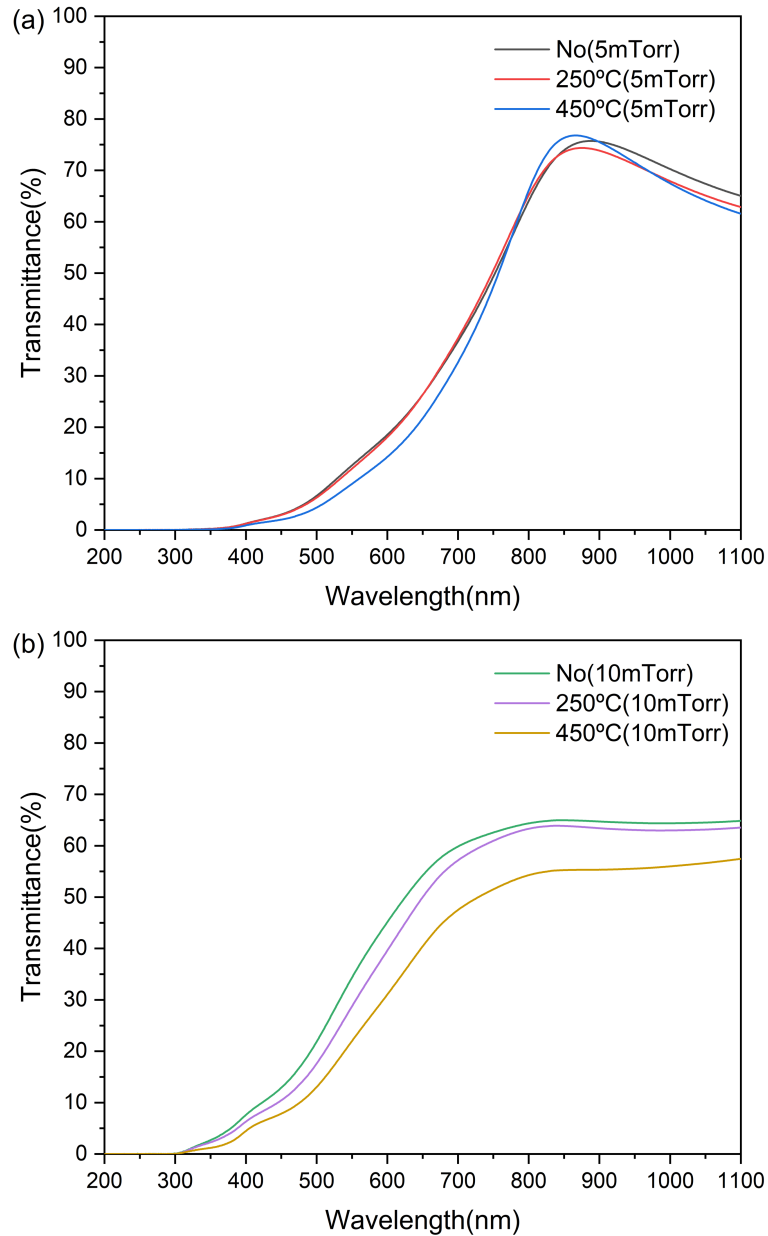
incident wavelength, a hump could be observed near 400 nm for all

samples because of the interferences related to the small thicknesses of the films. Besides, the valleys near the bandgaps are caused by the limiting absorption wavelength of copper oxides. The high reflectance in infrared regime is mainly caused by the back reflectance of the glass substrate. For the sputtering at room temperature, the reflectance of as-deposited samples keeps low at 6%-26% for 5mTorr (O10), 5-27% for 10mTorr (O8), and 6%-30% for 15mTorr (O7). With the increase of post-annealing or sputtering temperature, the reflectance of copper oxide film increases in the whole wavelength, which corresponds to the decrease of copper oxide thickness.

Next, the transmittance spectra of copper oxide thin films are given in **Figure 4.10**. The average optical transmittance in the visible and near infrared region increases with increasing annealing temperature from 43.71% to 41.75% for 5mTorr (O10), 51.12% to 41.31% for 5mTorr (O10), and 54.96% to 45.76% for 5mTorr (O10), respectively. With the increase of sputtering temperature, the average transmittance of copper oxide films also decreases from 51.17% for 10mTorr (Room) to 41% for 10mTorr (350 °C).

With the increase of incident wavelength, more incident photons are transmitted through the film, which corresponds to less excited charge carriers across the optical bandgap [123]. A hump near the limiting absorption wavelength of CuO is also found in transmittance spectra, which demonstrates the optical tuning properties of sputtering technique [49]. High transmittance in infrared regime exhibits high transparency of CuO for infrared light, which corresponds to no carrier excitation behavior for incident photon energy less than the bandgap. The transmittances of all samples reach stable values of around 60% in near infrared regime, while the transmittance humps observed around 850 nm in the samples of **Figure 4.10(a)** are due to much lower

reflectance caused in this range by a larger thickness of the CuO films compared to other samples. For the samples in [Figure 4.10\(a\)](#), transmittances decrease beyond 850 nm, towards 60%, that other samples also show around 1100 nm.



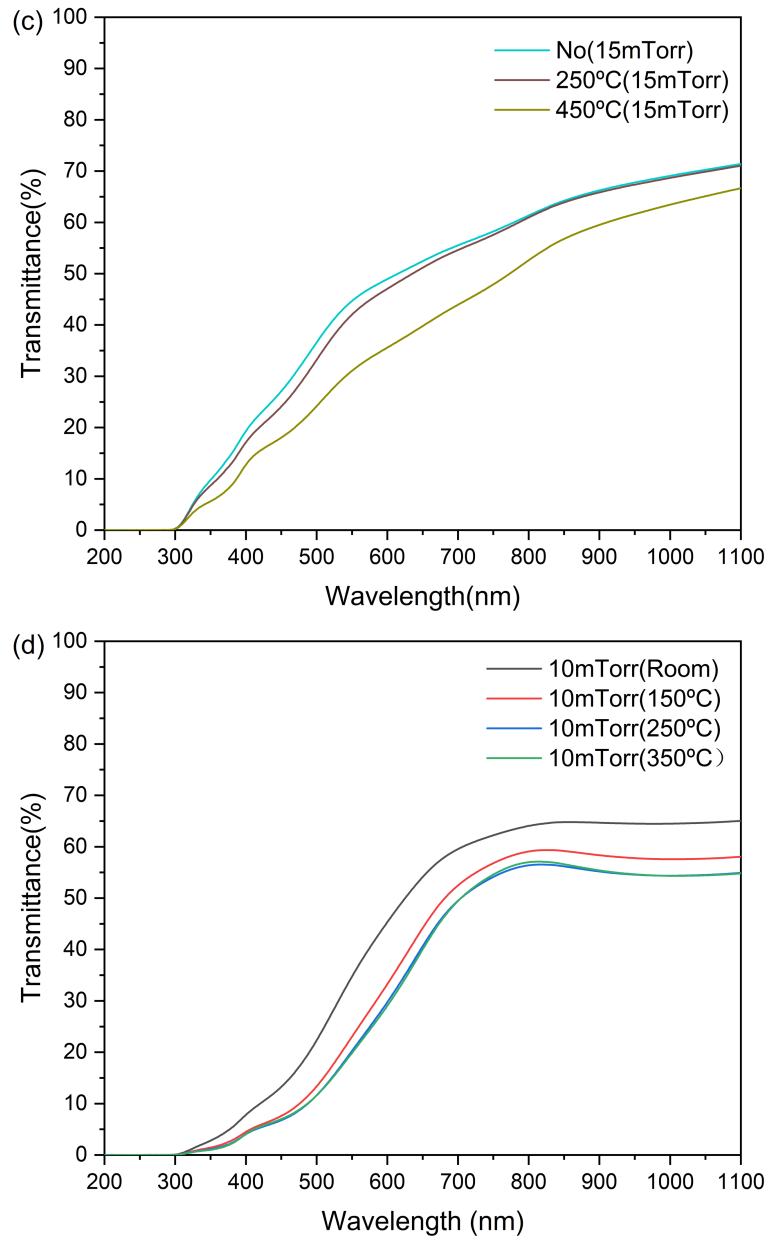
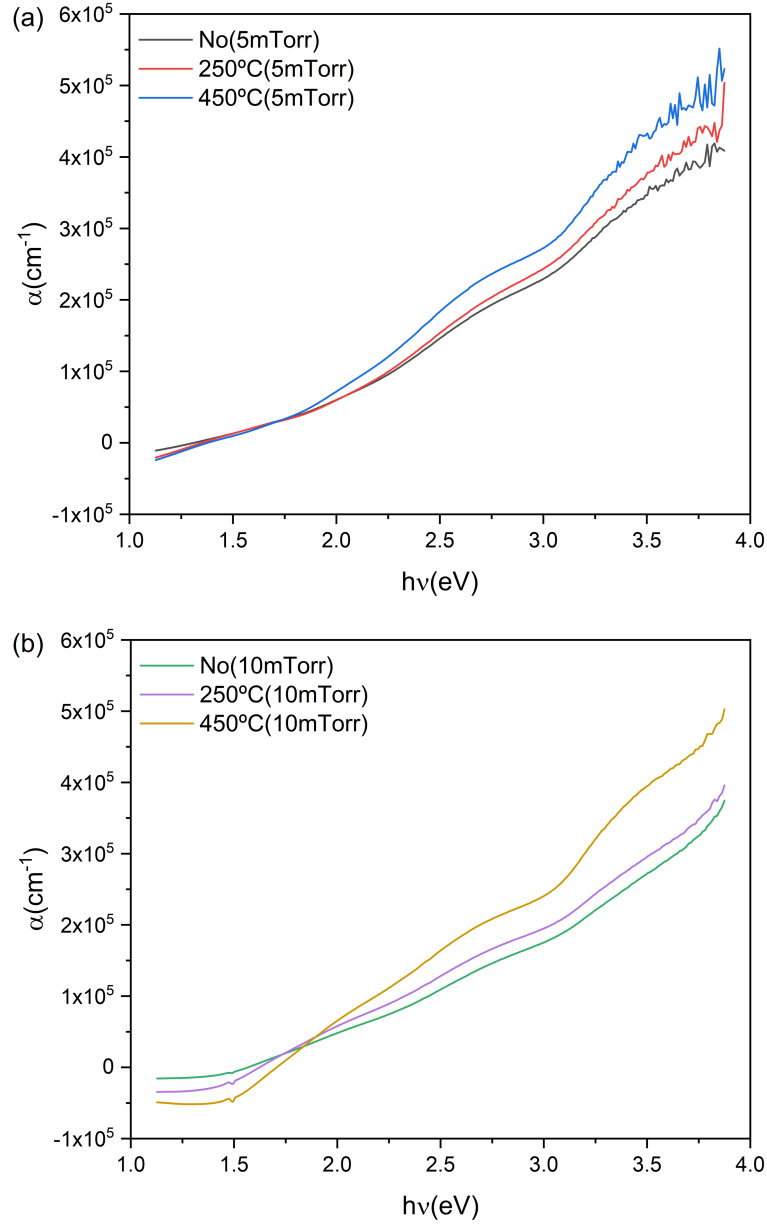


Figure 4.10. Transmittance spectra of CuO thin films deposited under different post-annealing temperatures (250 and 450 °C) at (a) 5mTorr (O10), (b) 10mTorr (O8), (c) 15mTorr (O7), and (d) 10mTorr (O8) under different sputtering temperatures from 150 to 350 °C.

In **Figure 4.11**, the absorption coefficients (α) of copper oxide thin

films in the spectral range from 320 to 1100 nm ($h\nu=3.875\text{-}1.127$ eV) are calculated by utilizing [Equation \(4.2\)](#). The tendencies of α curves are consistent with the samples studied in Section 4.2. α decreases with the increase of incident wavelength and with the



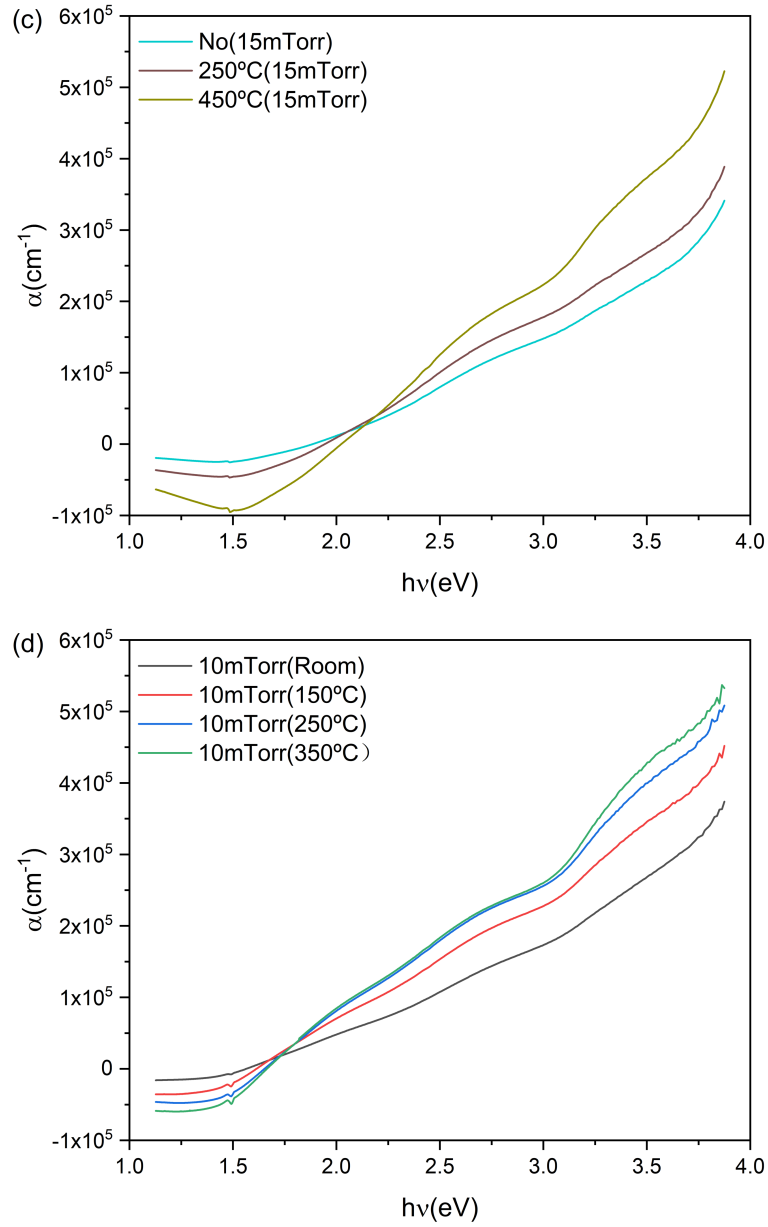


Figure 4.11. Absorption coefficient spectra of CuO thin films deposited under different post-annealing temperatures (250 and 450 °C) at (a) 5mTorr (O10), (b) 10mTorr (O8), (c) 15mTorr (O7), and (d) 10mTorr (O8) under different sputtering temperatures from 150 to 350°C.

decrease of incident light energy, reaching over 10^5 cm^{-1} . Therefore, penetration depth inside the copper oxides can be easily limited below 100 nm in specific spectral region for different samples, making it possible to reduce the thickness of copper oxides to less than 100 nm in specific applications.

The optical bandgaps of copper oxide thin films are calculated in **Figure 4.12**. By using the Tauc relation in **Equation (1.7)**, considering relatively high bandgaps of sputtered copper oxides, a magnitude of 2 is considered to extract the linear portion of Tauc plot. Considering the increase of sputtering pressure and the decrease of oxygen concentration for the sputtering at room temperature, the bandgap of CuO increases from 1.39 to 2.04 eV with the decrease of film thickness from 160 to 90 nm. With the increase of annealing temperature or sputtering temperature, the bandgap of CuO increases gradually while the CuO film thickness decreases gradually. The most suitable bandgaps could be obtained under the sputtering pressure of 10 mTorr ($\text{O}_2/\text{Ar}=8/22 \text{ sccm}$). In this sputtering condition, the CuO bandgap increases from 1.6 to 1.72 eV with increasing annealing temperature, while the thickness decreases from 120 to 96 nm. Meanwhile, the CuO bandgap increases from 1.6 to 1.68 eV with increasing sputtering temperature, while the thickness decreases from 120 to 95 nm.

In order to understand and analyze the absorption edge below the optical bandgap, Urbach tails of as-sputtered samples are calculated by the Urbach's rule as illustrated in **Equation (4.3)**. Considering the sensitivity of Urbach energy to the measurement temperature, all the samples are measured at room temperature in **Figure 4.13**. For all the samples, the Urbach energies are less than 8 meV, which reveals a very low defect density for all the CuO samples. The bandgaps and Urbach energies for all deposited samples are listed in **Table 4.6**.

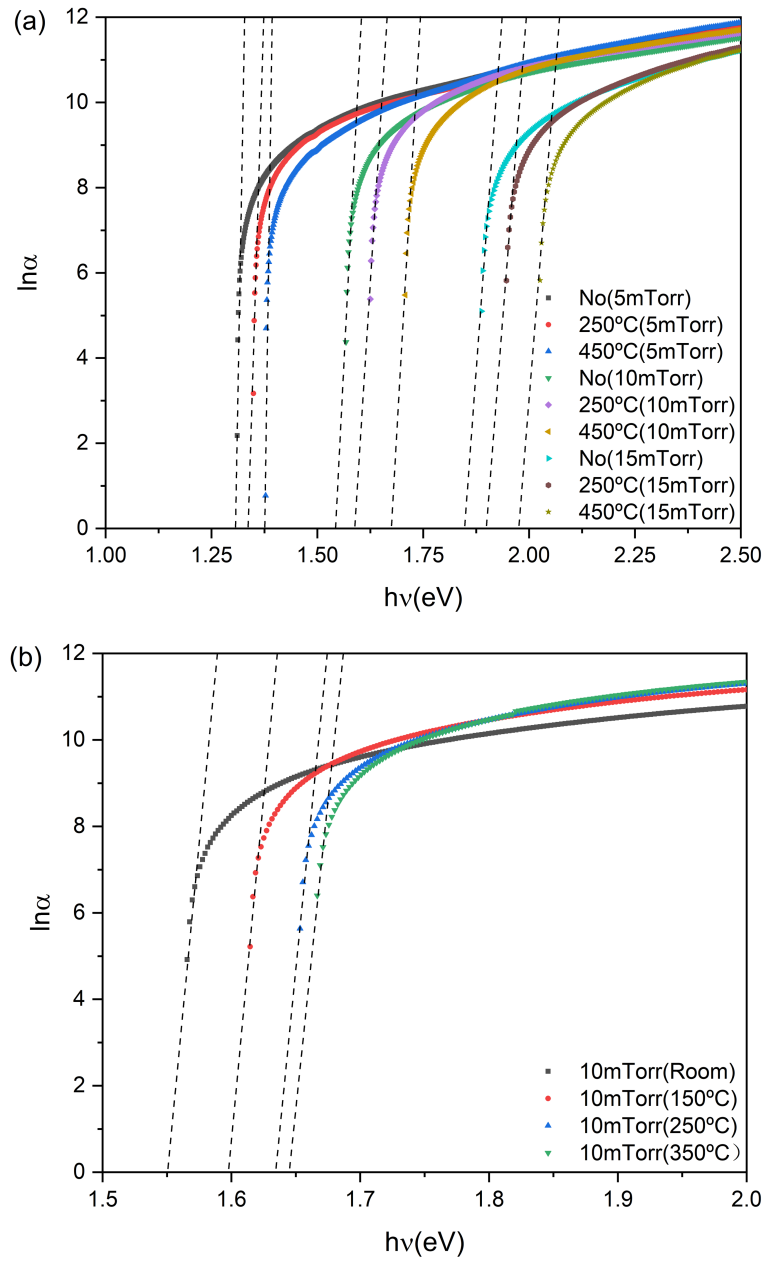


Figure 4.12. Tauc plots of CuO thin films deposited at (a) 5mTorr(O10), 10mTorr(O8) and 15mTorr(O7) with varied post-annealing temperatures; (b) 10mTorr(O8) with varied sputtering temperatures.

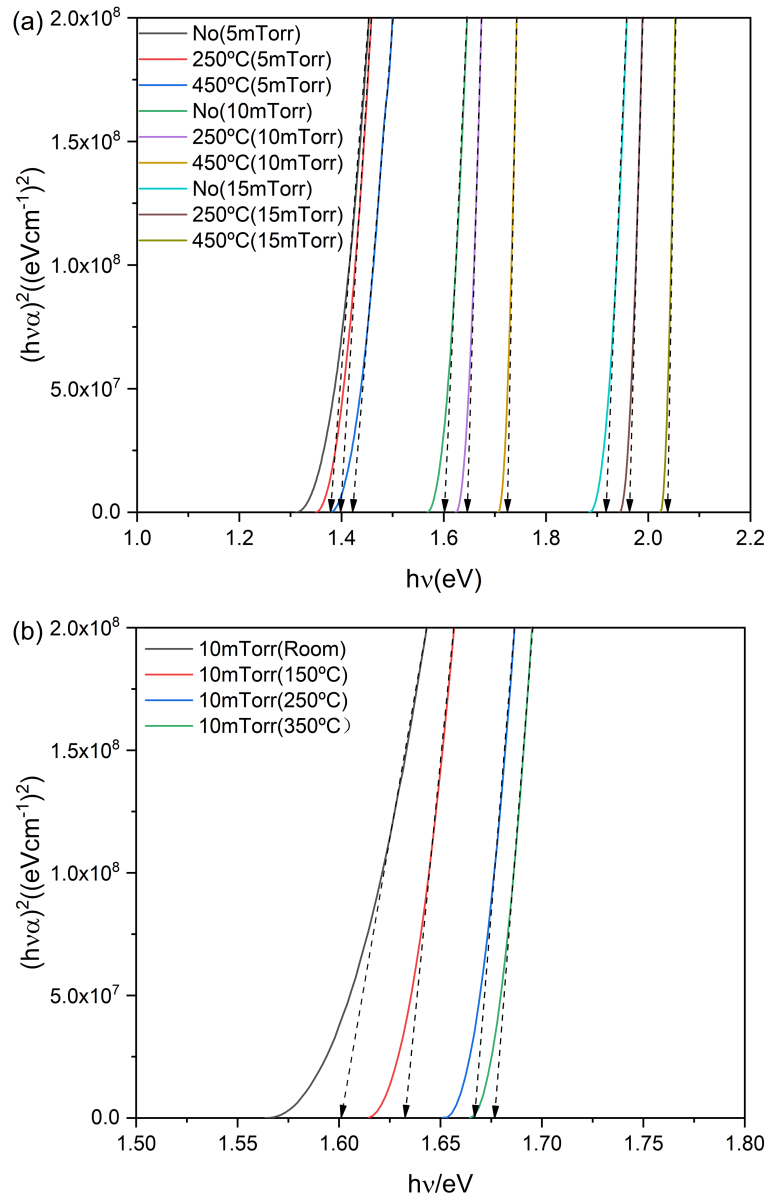


Figure 4.13. Urbach tails plots of copper oxide thin films deposited at (a) 5mTorr (O10), 10mTorr (O8) and 15mTorr (O7) with varied post-annealing temperatures; (b) 10mTorr (O8) with varied sputtering temperatures.

Table 4.6. Bandgaps and Urbach energies (in parenthesis) of samples deposited on SLG substrates under varied sputtering pressures and oxygen concentrations, annealing temperatures and sputtering temperatures.

Varied annealing temperatures	Room	250 °C	450 °C	
5mTorr(O10)	1.39 eV (2.1 meV)	1.4 eV (2.3 meV)	1.42 eV (1.4 meV)	
10mTorr(O8)	1.60 eV (4.3 meV)	1.64 eV (5.1 meV)	1.72 eV (5.4 meV)	
15mTorr(O7)	1.92 eV (6.7 meV)	1.96 eV (7.1 meV)	2.04 eV (7.1 meV)	
Varied Sputtering temperatures	Room	150 °C	250 °C	350 °C
10mTorr(O8)	1.60 eV (2.9 meV)	1.63 eV (2.5 meV)	1.67 eV (2.8 meV)	1.68 eV (4.0 meV)

4.3.2 Electrical characterization

Hall measurements using van der Pauw method have been carried out (**Figure 4.14**) to obtain Hall mobility and carrier concentration of deposited copper oxide thin films compared to the reference CuO considering the gas ratio, sputtering pressure, sputtering temperature and annealing temperature variations. Sheet resistances characterized by both Hall Effect measurement and four-point probe measurement (**Figure 4.15**) are also important parameters to check the accuracy of Hall measurement and quality of copper oxide. Considering that no doping was done in the fabrication process, the measured Hall mobility (μ), carrier concentration (N_p) and sheet resistance (R_s) come from the intrinsic doping of copper oxide.

For the measurements of 15mTorr as-deposited and 250 °C-annealed samples, the sheet resistances are too high according to 4-probe measurements, that show a big difference compared to the results of Hall measurements. Therefore, these two samples are highly

insulating, which causes a very low measured voltage and thus an unreliable Hall mobility. For all other samples, the sheet resistances for both Hall and four-point probe measurements keep close, which enables their correct Hall characterization. The reliable Hall measurements reveal the p-type conductivity of all copper oxide samples. When setting both x and y-axis in logarithmic scale, the hole mobility reveals an increasing linear tendency with decreasing hole concentration, which fits the formula of $\log \mu + 0.495 \log N_p = 8.988$. To realize stable high-performance copper oxide thin films for photodetector applications, several points could be extracted from the Hall measurements. For room-temperature sputtering at 10mTorr, from one sample to another, Hall mobility could vary from $143.3 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ (with hole concentration $N_p = 9.64 \times 10^{13} \text{ cm}^{-3}$) to $36.33 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ ($N_p = 6.76 \times 10^{14} \text{ cm}^{-3}$), corresponding to the varying sheet resistance R_s from 3.6×10^7 to $2.12 \times 10^7 \Omega \cdot \text{sq}^{-1}$. Hence, these samples are hardly

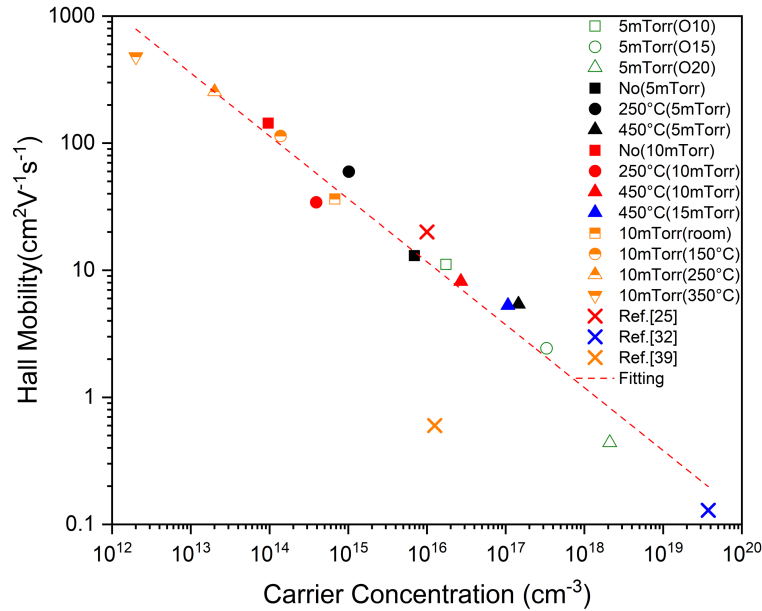


Figure 4.14. Reliably-extracted Hall mobility of deposited and reference p-type CuO thin films versus carrier concentration.

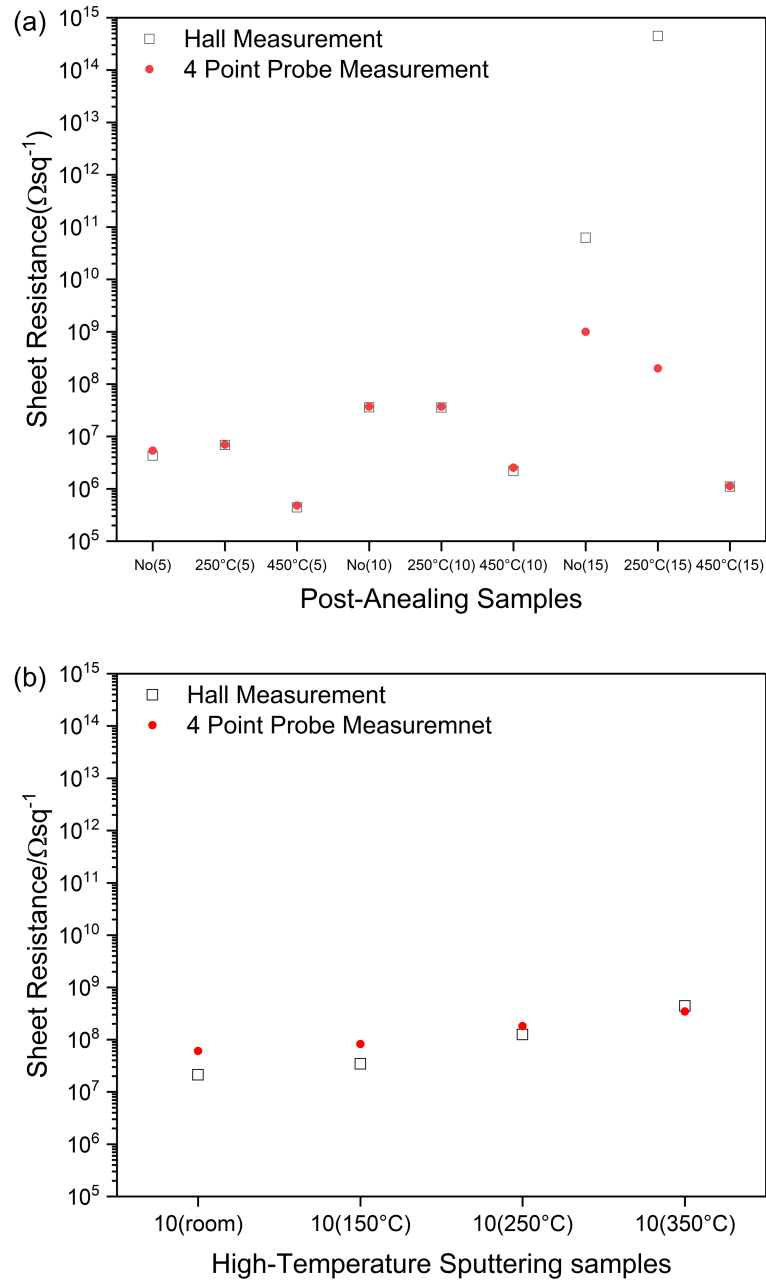


Figure 4.15. Sheet resistance of CuO thin films deposited at (a) 5mTorr (O10), 10mTorr (O8) and 15mTorr (O7) with varied post-annealing temperatures; (b) 10mTorr (O8) with varied sputtering temperatures.

reproducible and furthermore reveal lower mobility values several days after the deposition. Post-annealing at 250 °C has shown the ability to stabilize the Hall measurements and to improve the film quality, yielding reproducible hole mobility of $34.2 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ ($N_p=3.92 \times 10^{14} \text{ cm}^{-3}$) for sample sputtered at 10mTorr ($R_s=3.58 \times 10^7 \Omega \cdot \text{sq}^{-1}$). Heating at 150 °C during deposition can also stabilize the hole mobility to $113.7 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ ($N_p=1.39 \times 10^{14} \text{ cm}^{-3}$) for sample sputtered at 10mTorr ($R_s=3.43 \times 10^7 \Omega \cdot \text{sq}^{-1}$). High-temperature sputtering and post-annealing obviously improve the adatom mobility of the atoms on the substrate and thus improve the quality of the final CuO films, which results in the boost and stabilization of hole carrier mobility [124, 125]. These enhanced hole mobilities lead to improved conductivities of CuO films and thus a higher output current, with dark carrier concentrations adequate for future device designs [126].

4.4 Summary

By tuning the sputtering parameters, considering high-temperature sputtering or post-annealing, the optical and electrical properties of CuO thin films in Table 4.7 are obviously improved compared to the previously reported best DC room-temperature sputtered CuO (with 100nm thickness) for photodetector fabrications [49]. CuO thin films obtained in the present work feature twice the absorption coefficient than in previous works, which results in a shallower optical absorption depth in CuO surface and thus promises faster photo-response in future applications. Few studies have reported the calculation of Urbach energy for DC sputtered CuO. For RF-sputtered CuO with a bandgap of 1.7 eV, the calculated Urbach energy is 167 meV in [127], which is much higher than in this work. For most of the previously reported DC sputtered CuO films, the hole mobility stays lower than $1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ [56, 128]. The best reported CuO film to date reaches a hole mobility

of $20 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ [49], which is still much lower than the values in our work. Meanwhile, the hole concentration and sheet resistance keep in adequate value regions for photodetectors. In this work, CuO thin films with a bandgap of about 1.6 eV, high absorption coefficient and very low Urbach energy reach record hole mobilities of $34.2 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ after 250°C post-annealing and $113.7 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ when sputtered at 150°C , which are both the highest stable mobilities reported till now.

Table 4.7. Opto-Electronic properties of improved CuO thin films (Sample A sputtered at 10 mTorr and post-annealed at 250°C , Sample B sputtered at 10 mTorr and 150°C) compared to best results in literature

Samples	A	B	Reference [49]
Bandgap (eV)	1.64	1.63	1.43
Absorption coefficient (cm^{-1}, 320-500nm)	$(1.25-4) \times 10^5$	$(1.5-4.5) \times 10^5$	$(1-2) \times 10^5$
Urbach Energy (meV)	5.1	2.5	/
Hole Mobility ($\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}$)	34.2	113.7	20
Hole concentration (cm^{-3})	3.92×10^{14}	1.39×10^{14}	10^{16}
Sheet resistance ($\Omega \cdot \text{sq}^{-1}$)	3.58×10^7	3.43×10^7	/

Detailed structural, optical and electrical characterizations have been performed to obtain the best p-type CuO thin films, as deposited and improved by tuning the DC reactive magnetron sputtering conditions on soda lime glass substrate for large-area photodetection applications in UV and near visible spectral range. The curves of sputtering discharge voltage to oxygen concentration show three different sputtering regimes of copper oxide, from which the best CuO quality is obtained at the edge of oxidization and transition regimes, as demonstrated by XRD, SEM and Raman analyses.

After extracting the best oxygen concentration at different sputtering pressures of 5, 10 and 15mTorr, high-temperature sputtering from 150 °C to 350 °C and post-annealing at 250 °C and 450 °C are both considered to improve the opto-electronic quality of CuO. By measuring the reflectance and transmittance with the UV-VIS-IR spectrophotometer, the calculated absorption coefficient can reach over 10^5 cm^{-1} in UV and near visible light spectral range, which reveals the possibility to reduce the CuO thickness to less than 100 nm. These copper oxide films achieve tunable bandgap from 1.30 to 2.04 eV and Urbach energies lower than 8 meV, which reveals a low defect density of sputtered copper oxides. Reliable Hall measurements reveal the inverse double logarithmic variation of Hall mobility with carrier concentration, which can be used to choose proper copper oxide film for specific applications.

In conclusion, our best room-temperature sputtered CuO (10mTorr, $\text{O}_2/\text{Ar}=8/22 \text{ sccm}$) thin films have achieved suitable $E_g=1.6 \text{ eV}$, and $\mu_p=143.3 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ or $36.33 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, but not repeatable several days after deposition. Post-annealing at 250 °C can stabilize the hole mobility to $34.2 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ (with $E_g=1.64 \text{ eV}$, $N_p=3.92 \times 10^{14} \text{ cm}^{-3}$, $R_s=3.58 \times 10^7 \Omega \cdot \text{sq}^{-1}$). Heating at 150 °C during the deposition can also stabilize the hole mobility to $113.7 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ (with $E_g=1.63 \text{ eV}$, $N_p=1.39 \times 10^{14} \text{ cm}^{-3}$, $R_s=3.43 \times 10^7 \Omega \cdot \text{sq}^{-1}$). These two mobilities are both the highest reported values till now. These p-type CuO films with suitable bandgaps, very low Urbach energies, high hole mobilities, proper hole concentrations and sheet resistances are highly suitable to be utilized as p-type semiconductor in the future opto-electronic applications.

Chapter V

Au/CuO Transmission Line Model

After determining the best-performing CuO thin film, it is necessary to find a suitable metal to realize ohmic contact with the semiconductor for future device fabrication. For example, to make an ohmic contact between p-type CIGS and n-type Mo, MoSe₂ is normally introduced between at the CIGS/Mo interface, revealing a contact resistivity of less than 0.08 $\Omega \text{ cm}^2$ [129, 130]. Therefore, measuring the contact resistance between the semiconductor and metal is of great interest. The contact resistance can be localized from a contact pad, a probe or the metallization process on the semiconductor. Among different measurement techniques, Transmission line model (TLM) structure, which consists of various metal grids with unequal spacing between contacts, is one of the commonly used methods to determine the contact characteristics. In this chapter, TLM down structures with different dimensions are fabricated and characterized to investigate the contact characteristics between CuO and Au. CuO usually has a high work function, Au is thus selected thanks to its high work function and potential to form an ohmic contact with CuO.

5.1 Experimental methods

5.1.1 Devices structures and fabrication details

Soda lime glass (SLG) substrates with a size of 4×4 cm² were cleaned by acetone, methanol, iso-propanol and de-ionized water, and dried by nitrogen. UV reverse lithography was firstly done to pattern the metal contacts. Ti/Au contacts of 10/100 nm were e-beam evaporated by E-gun Vacotec and the sample was later placed in acetone for lift-off. 10 nm of Ti was deposited between SLG and Au to enhance the adhesion of Au on the SLG substrate. Reverse lithography and lift-off were also used on top of Ti/Au contacts to pattern CuO. CuO films were deposited by DC reactive magnetron sputtering in AJA sputtering

system. A constant sputtering power of 50 W was set in the chamber at a sputtering pressure of 10 mTorr with an O_2/Ar ratio of 8/22 sccm. Post annealing was carried out in N_2 for 30min at 250 °C. To have a smaller total resistance for TLM structures, samples were sputtered at a longer time of 5 hours. Sputtering was considered as the last step to avoid the influence from multiple process on CuO especially for the high-temperature processes. TLM samples were measured on a LakeShore CPX probe station connected to Keithley 4200-SCS semiconductor characterization system under dark. TLM samples were measured either in N_2 flow ambient or in vacuum after a pumping of 2 hours.

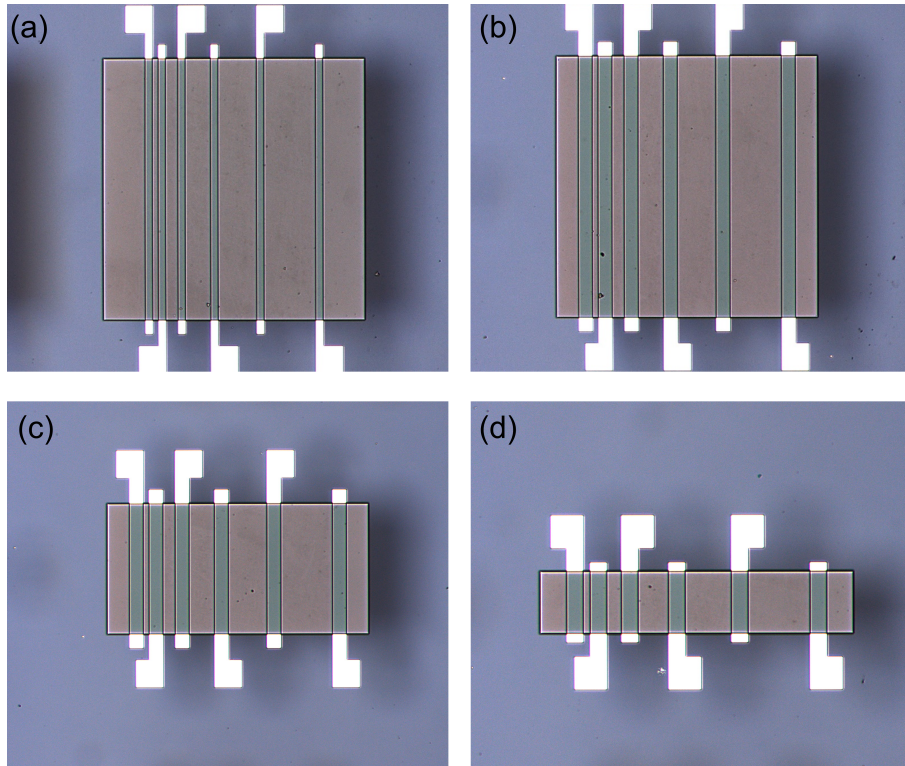


Figure 5.1. Top-viewed photographs of CuO/Au TLM samples (the brown and white parts are CuO and Au) by optical microscope: (a) Sample A, (b) Sample B, (c) Sample C, (d) Sample D.

In order to validate the contact resistance, TLM structures with different dimensions are studied. In **Figure 5.1**, the top-viewed photographs of CuO TLM structures are obtained by optical microscope. The dimension parameters of these samples are shown in **Table 5.1**. These samples share the same strip distance (d) of 25, 50, 100, 150, and 200 μm and the same CuO length of 1000 μm . Sample A and B have the same CuO width (W) of 1000 μm but different electrode widths of 25 and 50 μm . Sample B, C, and D have the same electrode widths of 50 μm but varying W of 200, 500 and 1000 μm .

Table 5.1. Dimension parameters of CuO/Au TLM samples.

	CuO Size (μm)	Electrode Width (μm)	Strip Distance (μm)
A	1000*1000	25	25,50,100,150,200
B	1000*1000	50	25,50,100,150,200
C	500*1000	50	25,50,100,150,200
D	200*1000	50	25,50,100,150,200

5.1.2 Electrical characterization of TLM structures

By introducing TLM structures, contact resistance between the active layer and the metal electrode can be extracted by measuring the resistance between two adjacent electrodes. **Figure 5.2(a)** shows the top and cross section views of typical TLM structure with strip contacts (S) from S_1 to S_6 and increasing strip distance (d) from d_1 to d_5 . Upon flowing from one electrode to another, current passes through Au electrode, CuO/Au contact, CuO layer and again CuO/Au contact, successively. Therefore, several resistors can be measured by varying the strip distance and the total resistance (R_T) of each resistor obtained from I - V curves can be divided into several portions like in the equation:

$$R_T = 2R_C + R_{metal} + R_{semi} \approx 2R_C + R_{sh} \frac{d}{W}. \quad (5.1)$$

where metal resistance (R_{metal}) is much smaller than semiconductor resistance (R_{semi}), thus R_{metal} can be neglected.

In this chapter, electrical characterizations of TLM structures are carried out on each adjacent contacts with varying strip distance by 4-probe measurement on a LakeShore CPX probe station connected to Keithley 4200-SCS semiconductor characterization system at room temperature under dark. In 2-probe measurement, probes are used to provide voltage and record current as source and sense connections at the same time and thus the internal resistance of the measurement system and probes are included. Conversely, 4-probe measurement separates the source and sense connections, so the current does not flow through the source. In such case, the internal resistance from the probes and measurement system can be minimized or eliminated

In **Figure 5.2(b)**, by plotting the measured total resistance (R_T) as a function of strip distance (d), several parameters can be deduced from the slope $\times$ intercept ($x_{intercept}$) or y intercept ($y_{intercept}$) of the linear fitting. From R_T - d curve, the sheet resistance (R_{sh}) of CuO, transfer length (L_T) and contact resistance (R_C) of CuO/Au, can be easily estimated by:

$$R_{sh} = slope \times W \quad (5.2)$$

$$R_{sh} = 0.5 \times x_{intercept} \quad (5.3)$$

$$R_C = 0.5 \times y_{intercept} \quad (5.4)$$

When studying TLM structures with different dimensions or contact technologies, effective contact resistivity (ρ_{c-eff}) is an important figure of merit showing the specific contact resistance in $\Omega \text{ cm}^2$. Considering that $L \geq 1.5L_T$ for all the CuO TLM samples, ρ_{c-eff} can be obtained by **[131]**:

$$\rho_{c-eff} = R_{sh} \times L_T^2 = R_C A_{eff} = R_C W L_T \quad (5.5)$$

where effective contact area (A_{eff}) is defined as WL_T .

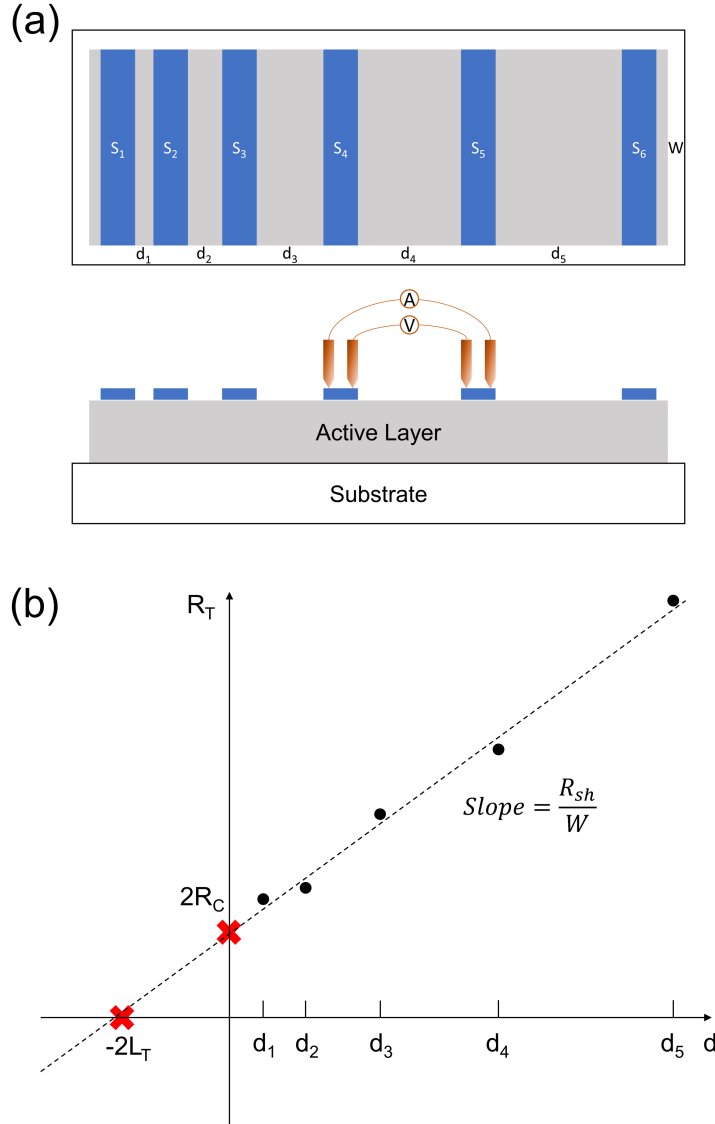


Figure 5.2. (a) Top and cross section views, and (b) R_T - d plot of typical TLM structures.

Generally, contact resistivity should be calculated directly by contact resistance divided by the contact area. However, the contact area is very hard to be defined due to ununiform current flow in the

contact. Therefore, the contact area cannot be determined by the physical size of the contact. Transfer length (L_T), indicating the average length along electrode width of current transferring between CuO and Au, is introduced to determine A_{eff} by [131]:

$$L_T = \sqrt{\frac{\rho_{c-eff}}{R_{sh}}} \quad (5.6)$$

5.2 TLM characterization in N₂

5.2.1 TLM structures with different strip widths

To validate the contact resistance by TLM structures, samples with thicker CuO of 830 nm are fabricated and characterized in N₂ flow considering different strip widths. I - V curves of sample A and B passing by the origin are obtained in Figure 5.3(a) and 5.4(a), respectively. The corresponding resistances at each applied biases are extracted by 3-point derivatives in Figure 5.3(b) and 5.4(b) for sample A and B, respectively. With increasing strip distance, the current between adjacent pairs decreases while the resistance increases. The resistances are almost constant at different applied bias and the resistances at -0.5 V are extracted for further analysis.

Table 5.2. Extracted parameters of Sample A and B measured in N₂ Flow

Sample (Strip Width)	A (25um)	B (50um)
Linear Fitting	Y=11971x+51655	Y=12938x+53198
$R_{sh} (\Omega \text{ sq}^{-1})$	1.20×10^7	1.29×10^7
$R_c (\Omega)$	25828	26599
$L_T (\mu\text{m})$	2.16	2.06
$\rho_{c-eff} (\Omega \text{ cm}^2)$	0.56	0.55

The total resistances between two adjacent pairs dependence on the strip distance (R_T-d) of CuO TLM structures are shown in [Figure 5.5](#). By linear fitting on R_T-d curves, key parameters are extracted in [Table 5.2](#). The sheet resistance of CuO is $\sim 1.2 \times 10^7 \Omega \text{ sq}^{-1}$, while the contact

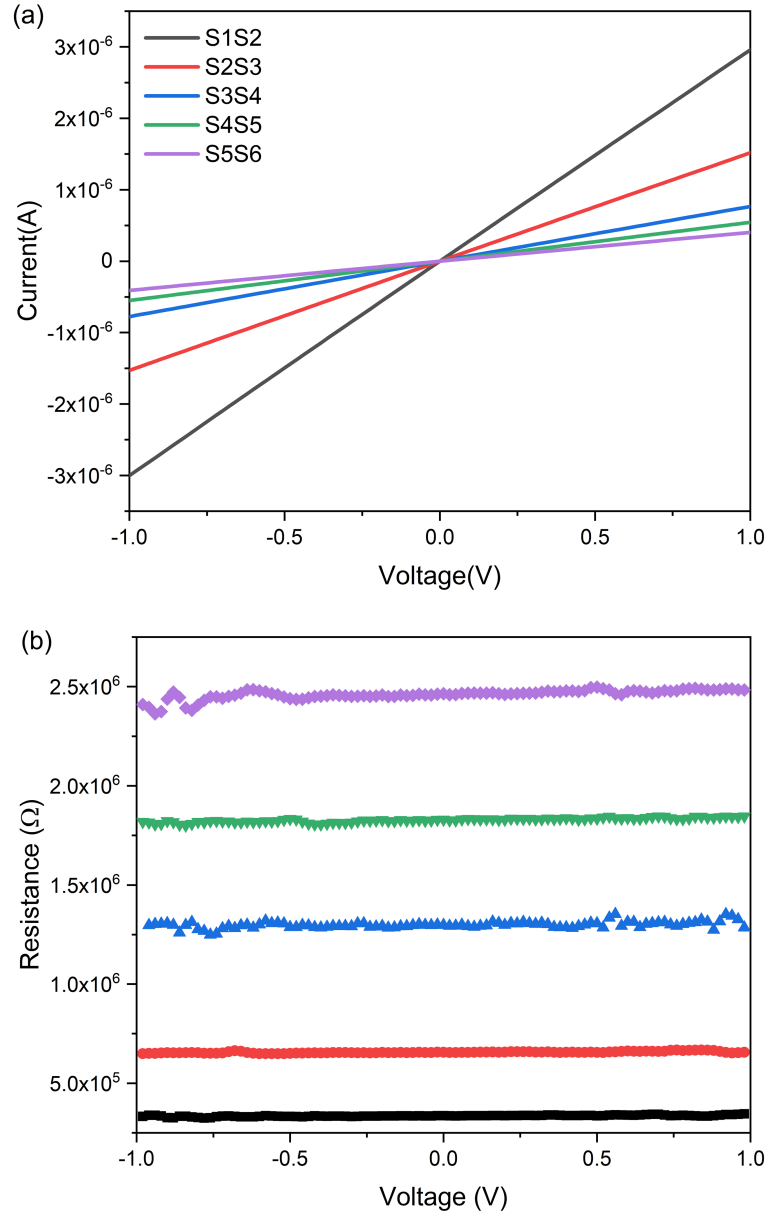


Figure 5.3. (a) I - V curves and (b) R - V curves of sample A.

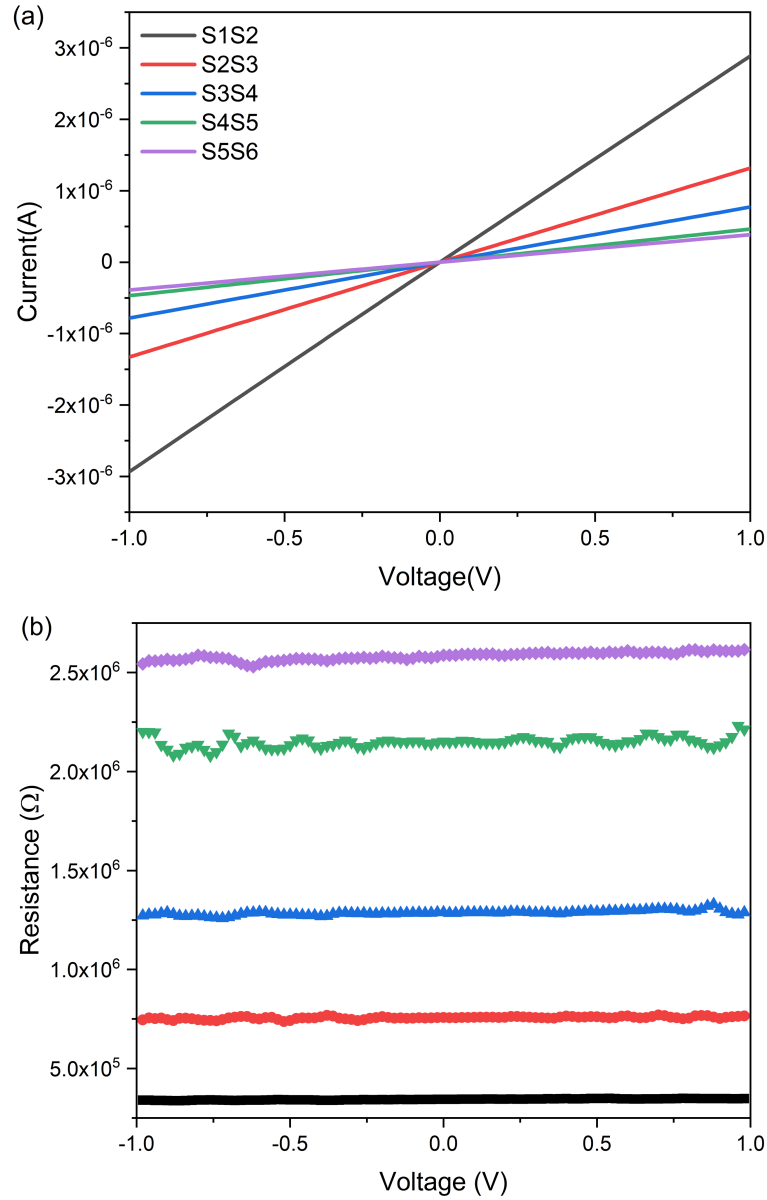


Figure 5.4. (a) I - V curves and (b) R - V curves of sample B.

resistances between CuO and Au for both samples are about 26 k Ω . The contact resistance is relatively low compared to the total resistance of CuO, which indicates a good ohmic contact between CuO and Au and can also be seen by the linear I - V curves in [Figure 5.3\(a\)](#) and [5.4\(a\)](#).

Considering different strip widths of 25 and 50 μm for Sample A and B, the transfer lengths keep almost the same to be $\sim 2.1 \mu\text{m}$. Such short L_T is much lower than the strip width, meaning that relatively wide electrodes have no influence on R_c and R_c is determined by the effective contact area instead of the physical contact size.

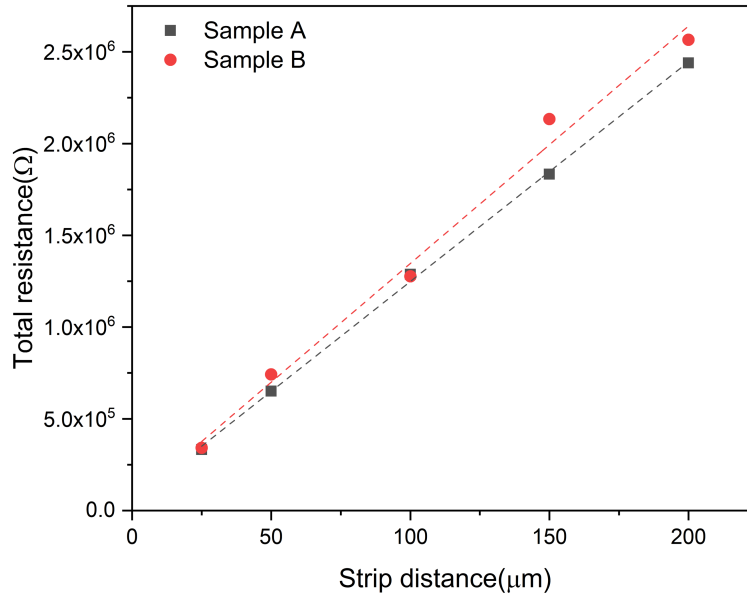


Figure 5.5. Total resistance verses distance of TLM structure.

To eliminate the influence from the contact size and have a standard quantity for comparison, ρ_{c-eff} is also calculated. Similar ρ_{c-eff} of around $0.55 \Omega \text{ cm}^2$ are calculated for both samples by Equation (5.5). In comparison, n-type or p-type Si show typical ohmic contact with W (Tungsten) with ρ_c ranging from 10^{-8} to $10^{-3} \Omega \text{ cm}^2$ [132]. Other contact metals with copper oxides, including Au/CuO, Au/Cu₂O and Ni/Cu₂O, have been attempted, showing high contact resistivities over $10^3 \Omega \text{ cm}^2$ [73, 133]. In contrast, our samples show obviously improved contact resistivities compared to other reported results. However, ρ_{c-eff} obtained in this work is still relatively higher than standard ρ_c of $< 0.08 \Omega \text{ cm}^2$ for

CIGS/MoSe₂, which can be caused by a thin oxidized film on CuO surface in fabrication process or degradation in measurement [130].

5.2.2 TLM structures with different CuO widths

In addition to the contact geometry, the dimension of CuO also influences the total resistance between adjacent contacts and contact resistance. Therefore, TLM samples with varying CuO widths are further investigated in this part. In **Figure 5.6(a)** and **5.7(a)**, I - V curves of sample C and D with W of 500 and 200 μm are measured in N_2 . The corresponding resistances at each applied biases are extracted in **Figure 5.6 (b)** and **5.7(b)** for sample C and D, respectively. The R_T - d curves of sample C and D are compared with that of sample B in **Figure 5.8**. By linear fitting, key parameters of sample B, C and D are extracted from R_T - d curves in **Table 5.3**.

Table 5.3. Extracted parameters of Sample B, C, D measured in N_2 flow

Sample (CuO Width)	B (1000 μm)	C (500 μm)	D (200 μm)
Linear Fitting	$Y=12938x+53198$	$Y=37935x+130620$	$Y=97114x+319052$
$R_{sh} (\Omega \text{ sq}^{-1})$	1.29×10^7	1.9×10^7	1.94×10^7
$R_c (\Omega)$	26599	65310	159526
$L_T (\mu\text{m})$	2.06	1.72	1.64
$\rho_{c\text{-eff}} (\Omega\text{cm}^2)$	0.55	0.56	0.52

According to TLM methods, sample C and D show an increased R_{sh} of $\sim 1.9 \times 10^7 \Omega \text{ sq}^{-1}$ because they were measured several hours later than the measurement of sample B. Such phenomenon indicates a degradation of CuO thin film in air and it would be further studied in the following part. With decreasing W from 1000 to 200 μm , the contact

resistance increases from 26599 to 159526 Ω due to the decreased electrode length and CuO width, which is consistent with [Equation \(5.5\)](#). Caused by the increase of R_{sh} , L_T decreases from 2.06 to 1.64 μm . Considering the contact resistivity, ρ_{c-eff} for all samples are around 0.55 $\Omega\text{ cm}^2$ regardless of the sample geometries.

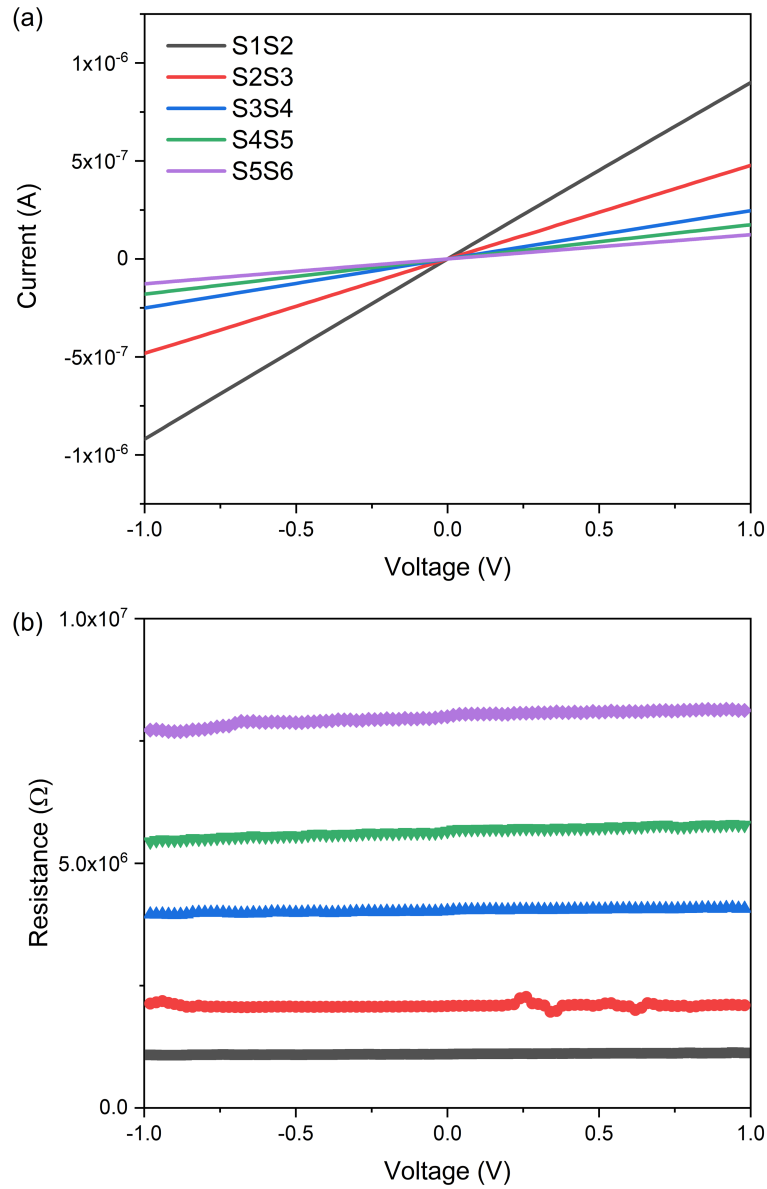


Figure 5.6. (a) I - V curves and (b) R - V curves of sample C.

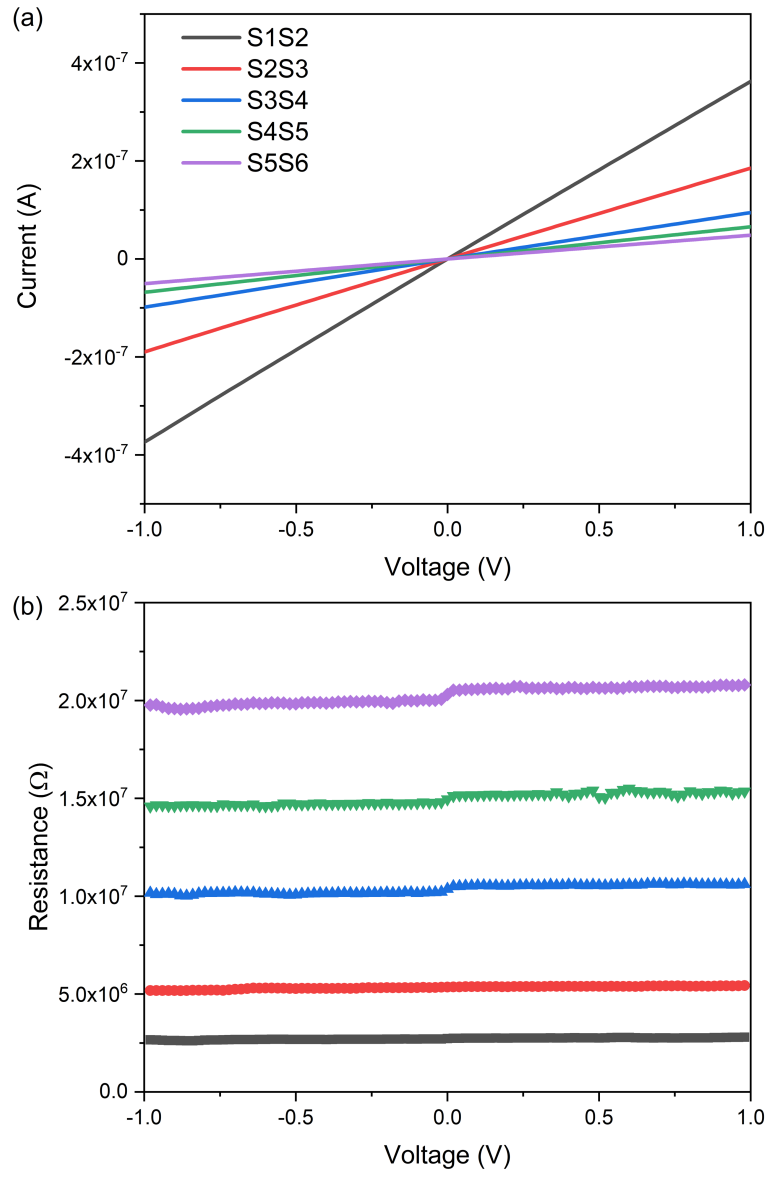


Figure 5.7. (a) I - V curves and (b) R - V curves of sample D.

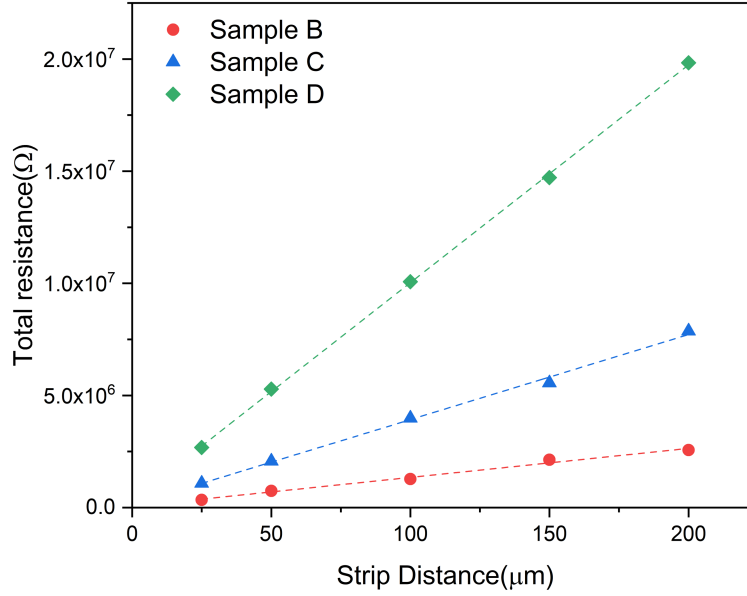


Figure 5.8. Total resistance verses distance of TLM structure measured in N₂.

5.3 TLM characterization in vacuum

5.3.1 TLM structures with different strip widths

To figure out whether the increase of R_{sh} with time is caused by the degradation of CuO or the ambient environment, TLM structures with the same dimensions as illustrated in Section 5.2.1 are fabricated and characterized in vacuum. After a sputtering of 5 h, CuO of 750 nm was deposited, which is thinner than the previously sputtered CuO of 830 nm due to the consumption of Cu target and decrease of discharge voltage. In **Figure 5.9(a)** and **5.10(a)**, I - V curves of sample A' and B' with strip widths of 25 and 50 μm are measured in vacuum. In **Figure 5.9(b)** and **5.10(b)**, the corresponding resistances at each applied biases are extracted for sample A' and B', respectively. The R_T - d curves of sample A' and B' are shown in **Figure 5.11**. By linear fitting, key parameters of sample A' and B' measured in vacuum are extracted from R_T - d curves in **Table 5.4**.

Table 5.4. Extracted parameters of Sample A' and B' measured in vacuum

Sample (Strip Width)	A' (25um)	B' (50um)
Linear Fitting	Y=69068x+39268	Y=71464x+35120
$R_{sh} (\Omega \text{ sq}^{-1})$	6.9×10^7	7.14×10^7
$R_c (\Omega)$	19634	17560
$L_T (\mu\text{m})$	0.28	0.25
$\rho_{c-eff} (\Omega \text{ cm}^2)$	0.054	0.045

In vacuum, samples A' and B' show a higher R_{sh} of $\sim 7 \times 10^7 \Omega \text{ sq}^{-1}$ compared to sample A and B due to a thinner CuO film, which can be explained by $R_{sh} = \frac{\rho}{t}$, where ρ is the CuO resistivity and t is the CuO thickness. R_c for sample A' and B' is $\sim 18 \text{ k}\Omega$, which is relatively low compared to the total resistance and at the same magnitude with R_c of sample A and B. Due to an increased R_{sh} , L_T decreases from ~ 2.1 to $\sim 0.25 \mu\text{m}$ and thus ρ_{c-eff} decreases from ~ 0.55 to $\sim 0.05 \Omega \text{ cm}^2$. Lower L_T compared to the physical contact size again proves that the wide electrodes have no influence on R_c . These results again confirm a good contact between CuO and Au no matter in N_2 flow or vacuum. However, sample B' measured later than sample A' still shows a slight increase of R_{sh} , which is similar to the results in N_2 flow. Therefore, the degradation of CuO needs to be further discovered.

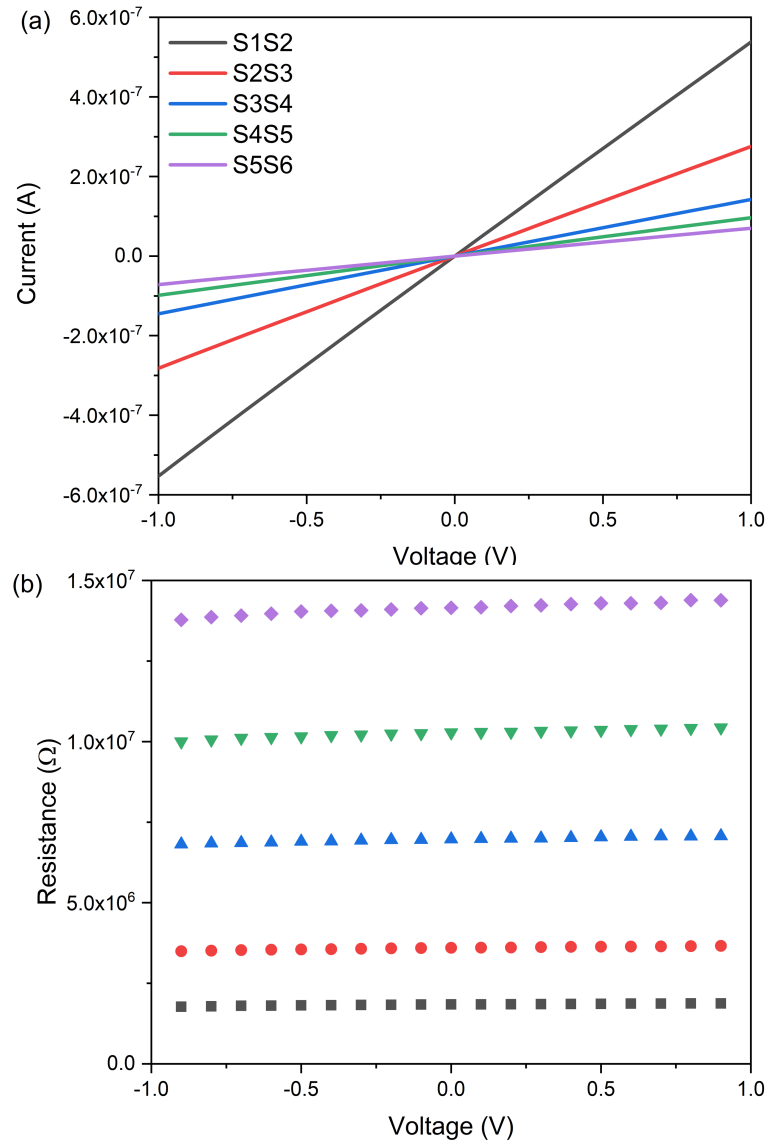


Figure 5.9. (a) I - V curves and (b) R - V curves of sample A'.

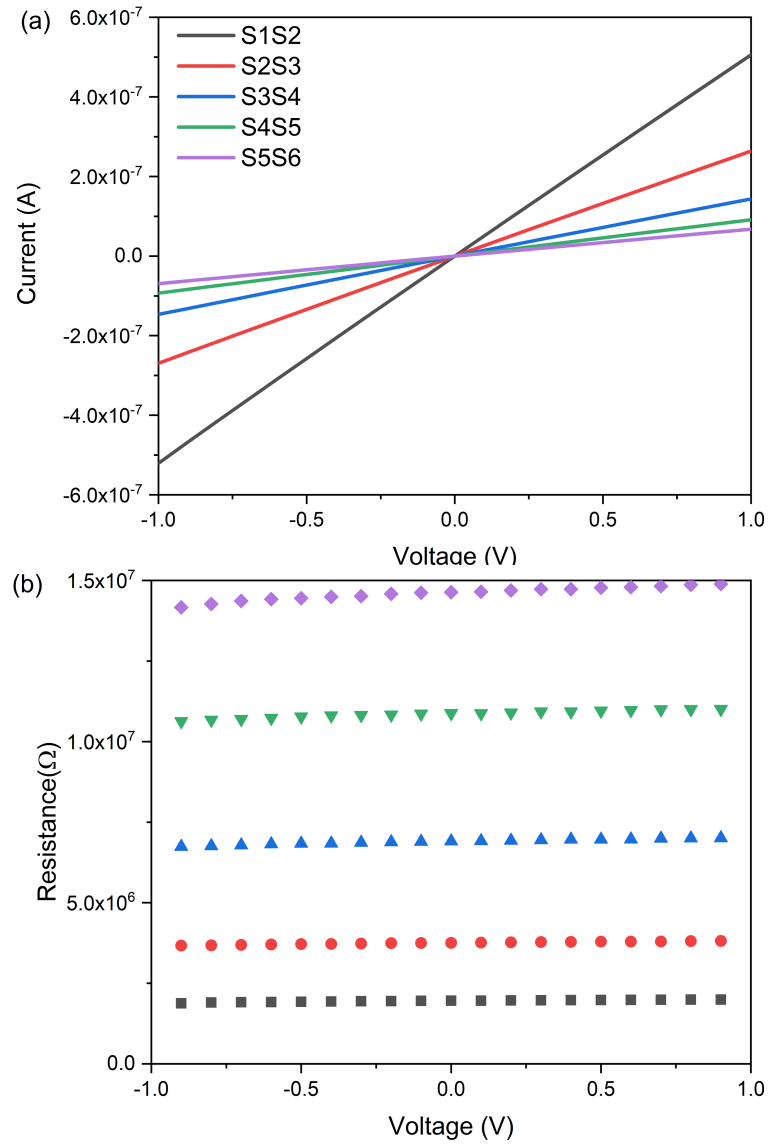


Figure 5.10. (a) I - V curves and (b) R - V curves of sample B'.

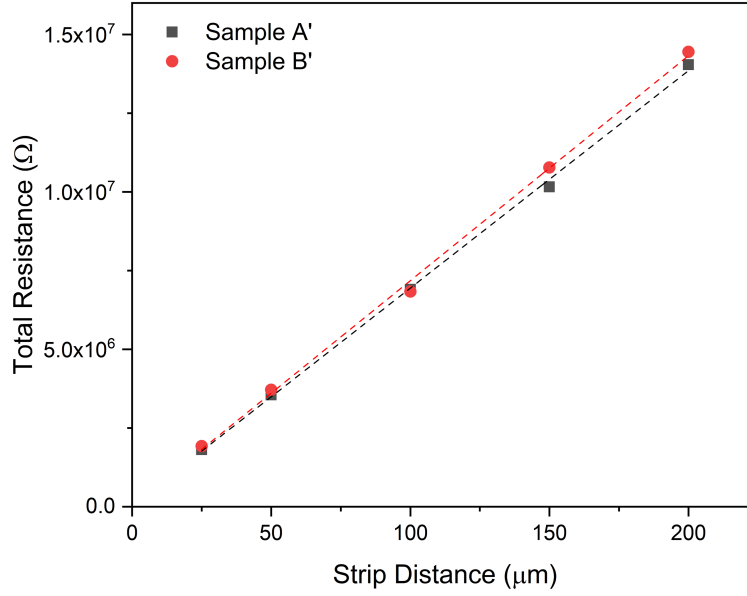


Figure 5.11. Total resistance versus distance of TLM structure measured in vacuum.

5.3.2 Degradation at room temperature in vacuum

Degradation of thin semiconductor layer is often influenced by the environmental impacts including temperature, moisture, and other mechanical, physical, or chemical influence from the fabrication and measurement environment. Among various elements, temperature is very important since most degradation mechanisms are thermally activated. The temperature variation can come from the external heating or the self-heating of the device.

To avoid the environmental influences, sample B' was measured every 30 minutes in vacuum at room temperature under dark. **Figure 5.12(a)** shows the resistance variation between S1 and S2 in 3 hours and R_T - d curves in 3 hours are shown in **Figure 5.12(b)**. The resistance between S1 and S2 increases from 1.92×10^6 to $3.82 \times 10^6 \Omega$ after 3 hours in vacuum. The sheet resistance of CuO also increases obviously from 7.1×10^7 to $1.1 \times 10^8 \Omega \text{ sq}^{-1}$ after 3 hours in vacuum. Since the sample

was measured in vacuum, such degradation is probably caused by the self-heating when applying an electrical field.

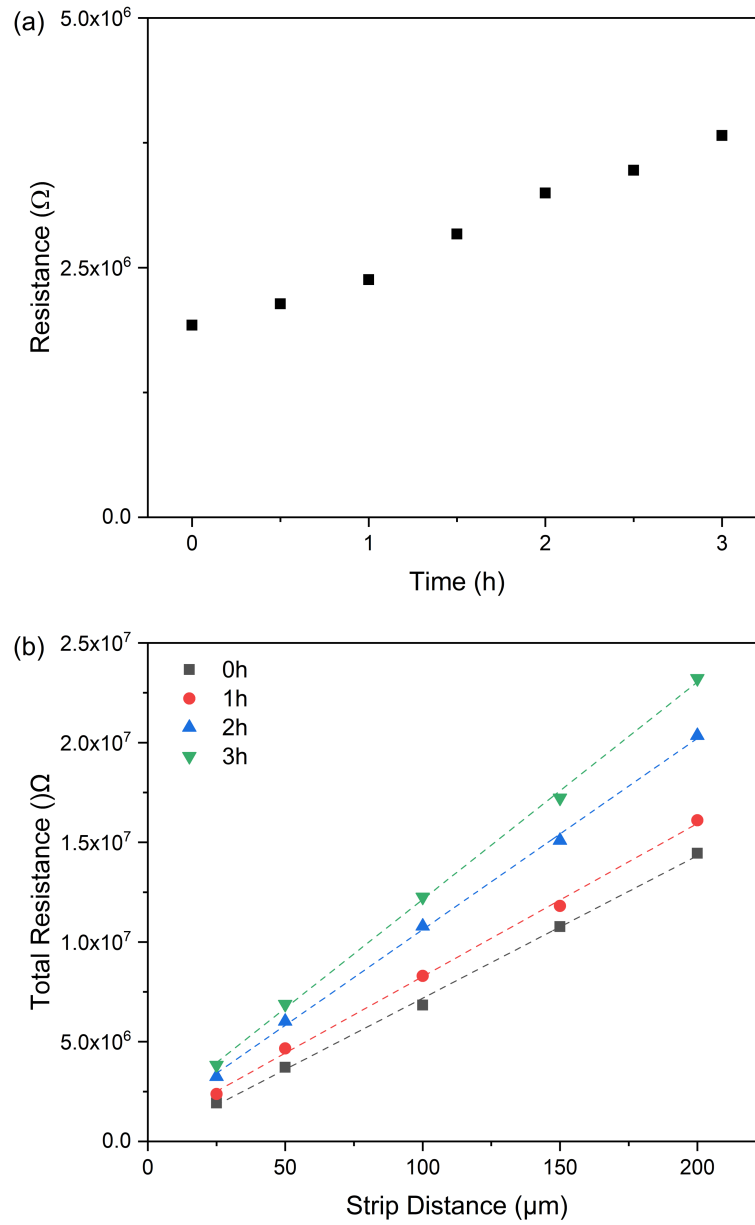


Figure 5.12. (a) S1S2 resistance variation with time at room temperature; (b) Total resistance verses distance of TLM structure after 0 to 3 hours.

5.3.3 Degradation at 100 °C in vacuum

In order to further investigate the degradation of CuO TLM structures, sample B' was measured at a high temperature of 100 °C in vacuum. Such method called dry heating measurement helps to accelerate the device degradation in a relatively short time. After heating up from 25 to 100 °C and stabilization of temperature in vacuum, the electrical characteristics between S1 and S2 were measured every 30 minutes and the resistance between S1 and S2 were demonstrated as a function of time in **Figure 5.13**. After placing the sample at 100 °C for 5 hours, the resistance increases gradually from 9.24×10^5 to $3.19 \times 10^6 \Omega$, showing a significant accelerated degradation of the CuO TLM structure.

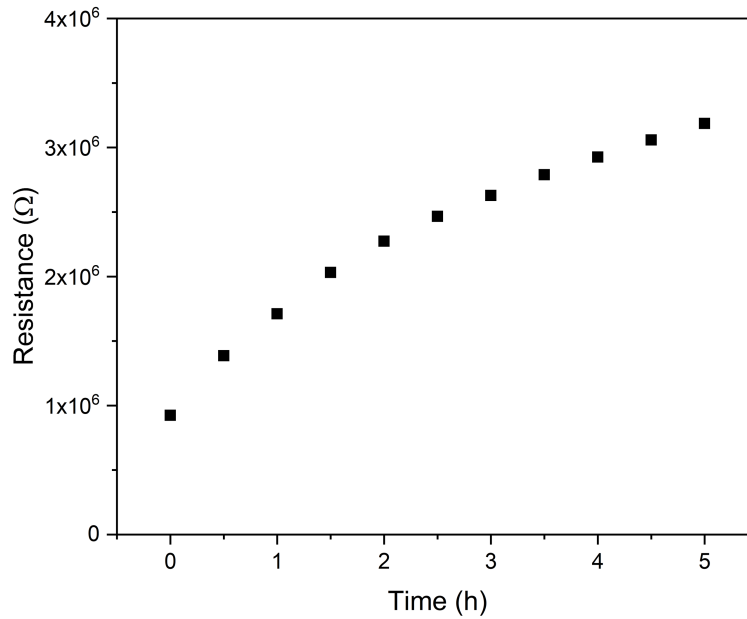


Figure 5.13. S1S2 resistance variation in 5 hours at 100 °C.

5.4 Summary

To study the interface properties of CuO with metal contacts, Au/CuO TLM structures were fabricated and measured both in N₂ and vacuum considering Au evaporation in prior to CuO sputtering. Considering different strip widths, Au/CuO TLM structures measured in N₂ show close R_c of $\sim 26 \text{ k}\Omega$, which is relatively low compared to the total resistance of CuO and reveals an ohmic contact between Au and CuO. Au/CuO TLM structures with different CuO widths are also studied, showing increased sheet resistance with time but close ρ_{c-eff} of $\sim 0.55 \text{ }\Omega \text{ cm}^2$ regardless of increased R_c with increasing CuO widths.

The intrinsic ohmic contact between Au and thick CuO on SLG observed in this chapter can be influenced by other factors, including the reduction of CuO thickness, temperature and structure differences of fabricated CuO devices. Especially when a thick CuO film was deposited in this chapter, the diffusion of Au atoms into CuO can be ignored considering an increased current. Once the thickness of CuO film is reduced targeting specific device applications, a Schottky contact can be induced at the Au/CuO interface due to the Au diffusion.

In order to investigate the degradation of CuO thin films, Au/CuO TLM structures measured in vacuum show lower R_c of $\sim 18 \text{ k}\Omega$ and lower ρ_{c-eff} of $\sim 0.05 \text{ }\Omega \text{ cm}^2$ for TLM structures with different strip widths compared to samples measured in N₂. Au/CuO TLM structures show degradation in vacuum at room temperature and significantly accelerated degradation in vacuum at 100 °C. Therefore, it is important in the future work to limit the degradation of CuO e.g. by a passivation layer.

Chapter VI

CuO Thin Film Transistors

Copper Oxide (CuO) is considered as one of the promising p-type metal oxides to realize thin-film transistors and logic circuits with n-type counterparts. In this chapter, CuO is grown by room-temperature DC reactive magnetron sputtering to fabricate thin film P-type transistors (TFTs), with a high- k HfO₂ gate dielectric fabricated by ALD. Unlike most of the previous reported CuO TFTs with SiO₂ dielectric based on silicon techniques, CuO TFTs in this chapter were fabricated on glass and HfO₂ fabricated by ALD is firstly reported as gate dielectric in CuO TFTs. Full characterizations and analysis have been performed, including material measurement of CuO thin film, C - V measurement of CuO MOS capacitor, I - V measurement of CuO TFTs. By characterizing a CuO MOS capacitor, related parameters were extracted to fully explain the performances of CuO TFTs. Overall, the results demonstrate that the transistor operation corresponds to the accumulation-mode type whose theoretical understanding supports the analysis.

6.1 Experimental methods

6.1.1 Device structure and fabrication

The schematic for the fabrication process of the CuO TFTs is shown in [Figure 6.1](#) and all fabrication process details are listed in [Table 6.1](#). Soda lime glass (SLG) substrate was first rinsed by acetone, methanol, isopropanol, and de-ionized water, and dried by N₂. Ti/Au (10/100 nm) was deposited by e-beam evaporation on a SLG substrate to form a bottom gate. A thin layer of Ti helps to enhance the adhesion between Au and SLG. HfO₂ (25 nm) was deposited by thermal atomic layer deposition (TE-ALD, Cambridge Fiji F200) at 200 °C. The deposition rate of HfO₂ by TE-ALD was 1 Å per cycle, so 250 cycles of ALD deposition were done to form HfO₂ with desired thickness. P-

type CuO (115 nm) was deposited at room temperature for 30 minutes by direct current (DC) reactive magnetron sputtering (ATC Orion 5 Sputter System for AJA International) as detailed in Chap. A constant sputtering power of 50 W was set in the chamber at a sputtering pressure of 10 mTorr with an O₂/Ar ratio of 8/22 sccm. The Au/Ti/Al (100/10/500 nm) source and drain electrodes were deposited by e-beam evaporation. UV reverse lithography and lift-off were used to pattern both the CuO active layer and the top electrode contacts with a channel width (Z) of 270 μm and channel lengths (L) of 25 and 10 μm.

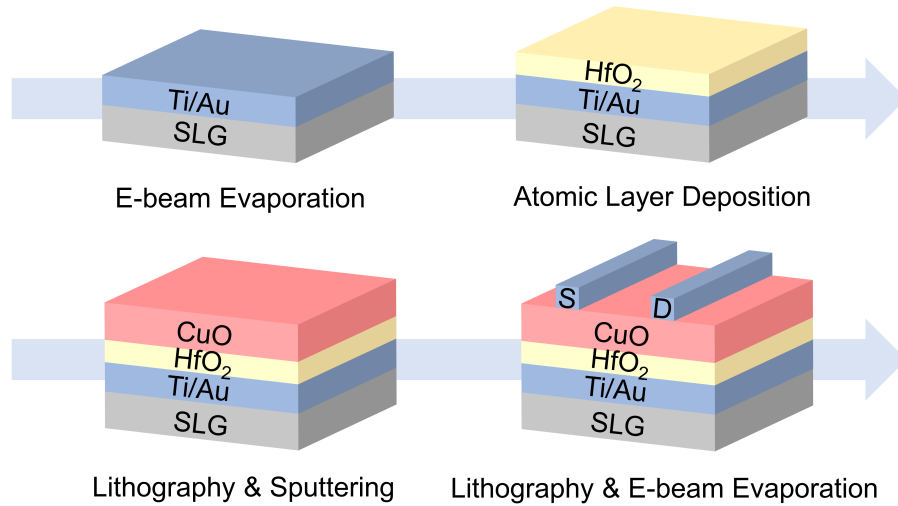


Figure 6.1. Schematics for the fabrication process and structure of CuO TFTs.

Table 6.1. Fabrication process sheet of CuO TFTs.

Step No.	Illustration	Fabrication step description
1		SLG cleaning: Clean room soup and DI water rinse. Aceton, methanol, iso-propenal and DI water rinse, N ₂ dry.
2		Bottom gate metal deposition: E-beam evaporation, 10/100 nm Ti/Au, 1 Å/s.
3		Gate dielectric deposition: TE-ALD, 25 nm HfO ₂ , 200 °C, 1 Å per cycle, 250 cycles.
4		Lithography and CuO sputtering: Photoresist coating AZ 2020 (reverse resist) 60 s at 3000 rpm and bake 135 s at 90 °C Lithography with CuO light-field mask Exposure (90 mJ cm ⁻²) in the hard contact mode Post-bake 135 s at 105 °C Development 60 s MIF + DI water rinse +N ₂ dry CuO Sputtering 3×10 ⁻⁷ Torr base pressure, room temperature, 50W, 10mTorr, O ₂ /Ar=8/22 SCCM, 30min Lift-off in acetone 30 min (45 °C) + acetone, methanal, DI water rinse + N ₂ dry
5		Lithography and Drian/Source Deposition: Photoresist coating AZ 2020 (reverse resist) 60 s at 3000 rpm and bake 135 s at 90 °C Lithography with CuO light-field mask Exposure (90 mJ cm ⁻²) in the hard contact mode Post-bake 135 s at 105 °C Development 60 s MIF + DI water rinse +N ₂ dry E-beam evaporation Au/Ti/Al (100/10/500 nm) Lift-off in acetone 30 min (45 °C) + acetone, methanal, DI water rinse + N ₂ dry

6.1.2 Device characterization

The material properties were analyzed by focused ion beam-scanning electron microscopy (FIB-SEM, Zeiss Auriga), X-ray diffraction (XRD, Bruker-D8 Advance diffractometer) with CuK α radiation ($\lambda=1.5418$ Å), and Raman spectroscopy (LabRAM HR, Horiba Scientific). The thicknesses of layers were confirmed by a Sentech SE850 ellipsometer, Veeco Dektak 150 and FIB-SEM. The electrical characteristics were measured on a LakeShore CPX probe station connected to a Keithley 4200-SCS semiconductor characterization system at room temperature in the air under dark.

6.2 Material characterization of CuO thin film

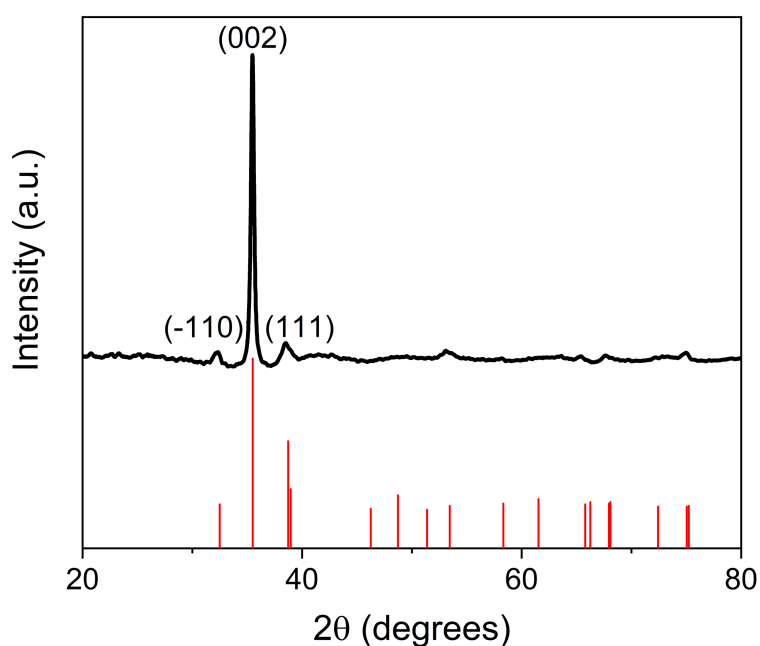


Figure 6.2. XRD pattern (JCPDS-45-0937) of deposited CuO thin film.

In order to determine the material properties, the XRD pattern and Raman spectra of the DC-sputtered CuO thin film are both characterized. In [Figure 6.2](#), CuO features a phase of tenorite CuO

(JCPDS-45-0937), with monoclinic structure in the C2/c(15) space group. The peaks at 2θ values of 32.3° , 35.5° , and 38.5° are identical to the reflection planes of (-110), (002), and (111). According to the Debye-Scherrer relation ([Equation \(4.1\)](#)), the crystallite size of CuO can be calculated to be about 29 nm, which is larger than CuO characterized in Section 4.2.1 due to an enhanced sputtering pressure. Such larger crystallite size is preferred to form a more intense thin film with less defects.

In [Figure 6.3](#), Raman peaks of CuO lie around 295, 341 and 628 cm^{-1} , which are close to the values in [\[118\]](#). The peak at 320 cm^{-1} is related to the SLG substrate and a small hump observed from 500 to 600 cm^{-1} is due to the defects and amorphous phase fraction in CuO [\[121\]](#). A much smaller intensity increases from 400 to 600 cm^{-1} can be observed, indicating less defects and decrease of amorphous phase fraction compared to copper oxides characterized in Section 4.22.

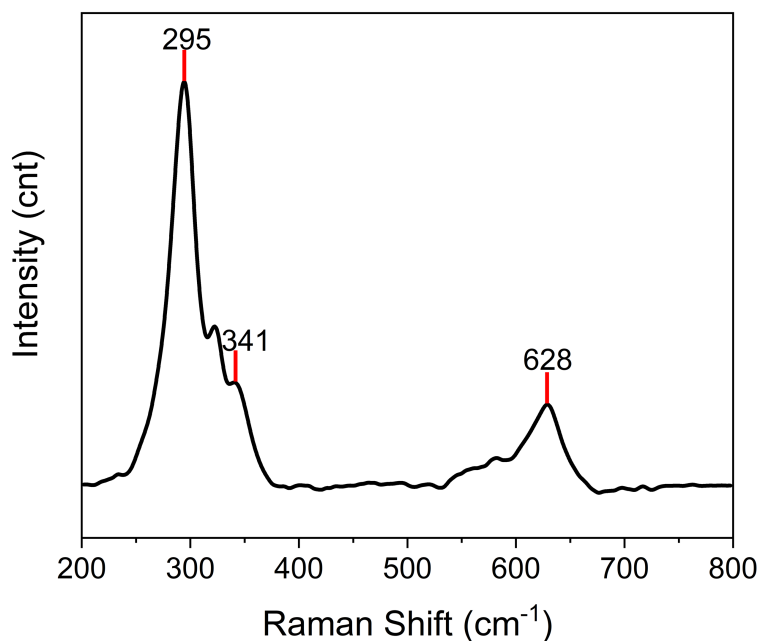


Figure 6.3. Raman spectra of the deposited CuO thin film.

Well prepared distinct interfaces can be clearly seen by the SEM cross-sectional view of the CuO TFT in **Figure 6.4**. The Ti/Au bottom gate, HfO₂ gate dielectric, CuO active layer, and Au/Ti/Al top electrodes can be observed from bottom to top on the SLG substrate. However, the crystal structures of each thin film can be hardly observed due to a strong charge effect on the highly insulating SLG substrate.

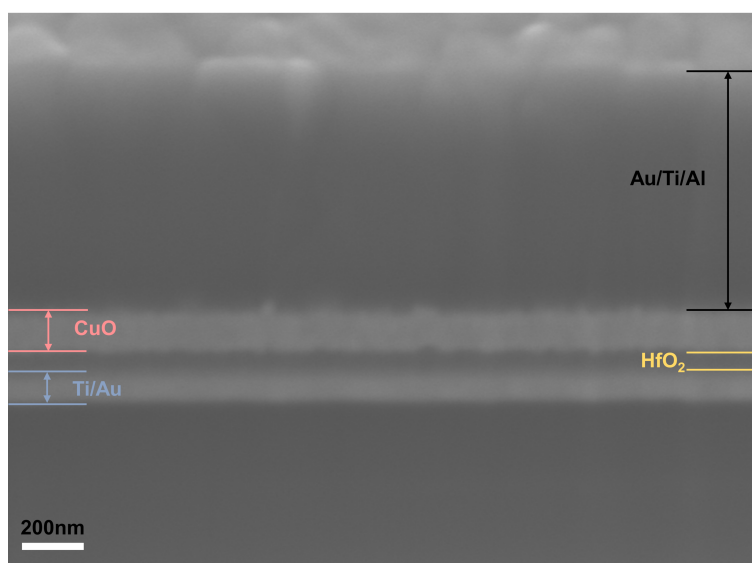


Figure 6.4. SEM cross-sectional image of CuO TFT.

To further investigate the crystal quality, the CuO thin film was sputtered on a bare SLG substrate under the same conditions as CuO TFTs. SEM plain view of the poly crystallized CuO thin film in **Figure 6.5(a)** shows a triangular grain structure and an estimated grain size of about 30 nm, which is consistent with the XRD results. The cross-sectional view of CuO in **Figure 6.5(b)** shows a columnar growth of CuO. These results reveal better crystal structures and grain growth of CuO sputtered at 10 mTorr with O₂/Ar =8/22 sccm, compared to our previous CuO thin films sputtered at 5 mTorr with O₂/Ar =10/20 sccm in Section 4.2.1.

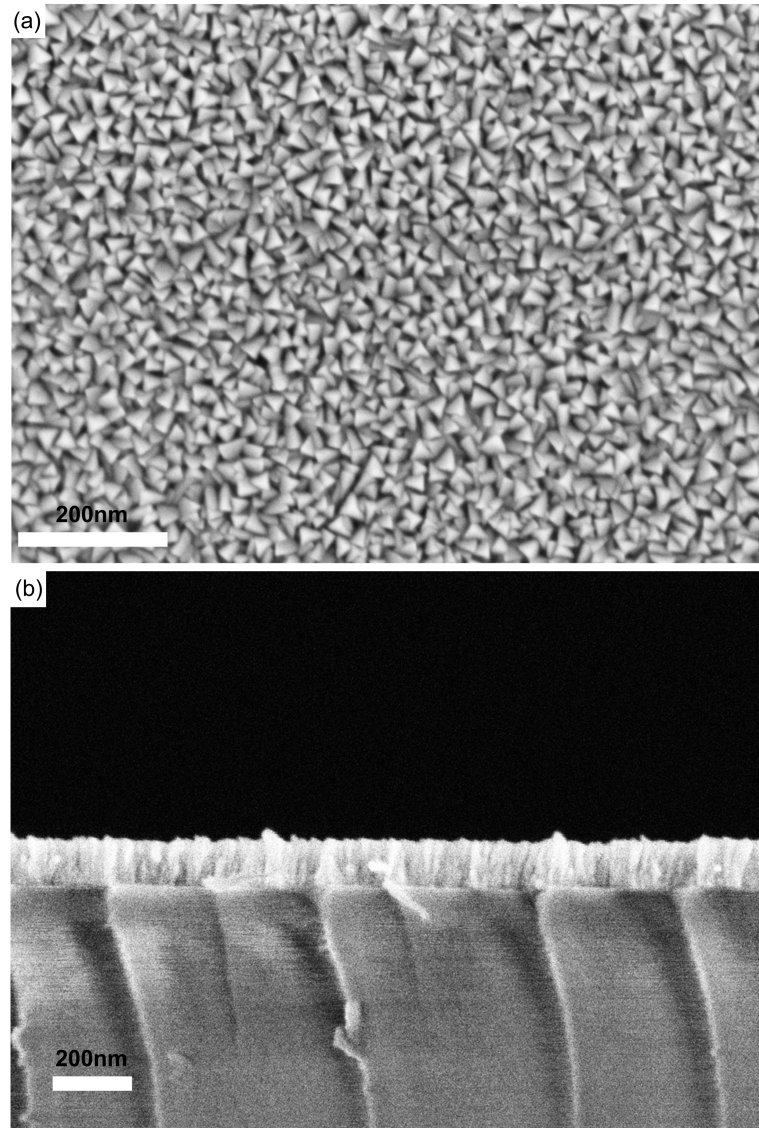


Figure 6.5. (a) SEM plain-sectional and (b) SEM cross-sectional images of the CuO thin film on the SLG substrate.

6.3 CuO MOS capacitor

To investigate the electrical properties of the CuO/HfO₂ interface, a CuO MOS capacitor (1000×1000 μm²) was fabricated by the same processes as CuO TFTs with a gate-biased bottom electrode and a

grounded top electrode. The schematic structure of the CuO MOS capacitor is shown in **Figure 6.6**, where the back gate is applied by a gate voltage (V_G) and the front electrode is grounded. A reference CIGS capacitor was measured in prior to the measurement of the CuO MOS capacitor to validate the measurements.

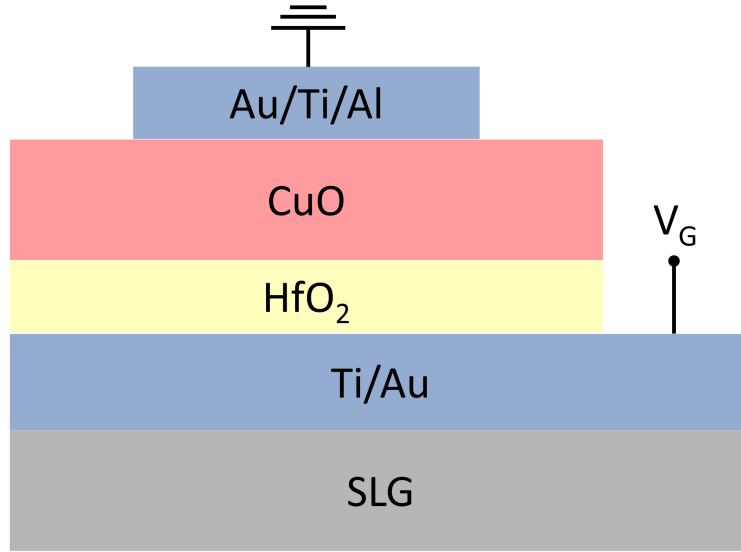


Figure 6.6. Schematic structure of CuO MOS capacitor.

In **Figure 6.7(a)**, the measured p-type capacitance vs gate voltage (C_m - V_G) curves at applied active current (AC) frequencies (f) from 5 to 500 kHz are corrected by the methods in [134, 135] to remove the influence of series resistance (R_s). Series parasitic elements originating from the substrate, measurement system and neighbor devices, can cause a large dispersion of C - V curves. An accurate model of correction is thus required for raw C - V data. A clear shift from 5 to 500 kHz caused by the interfacial traps can be seen from the absolute value of derivative C_m - V_G curves in **Figure 6.7(b)**. Interfacial traps can only follow slow quasi-static and lower frequency signals while the higher frequency signals are too fast for the minority carriers and the interfacial traps to respond [76]. Charges induced by interfacial traps are, therefore, more

pronounced at lower frequency and cause a shift of C-V curves. To avoid the influence of interfacial traps when extracting the effective CuO parameters, high-frequency curves are preferred.

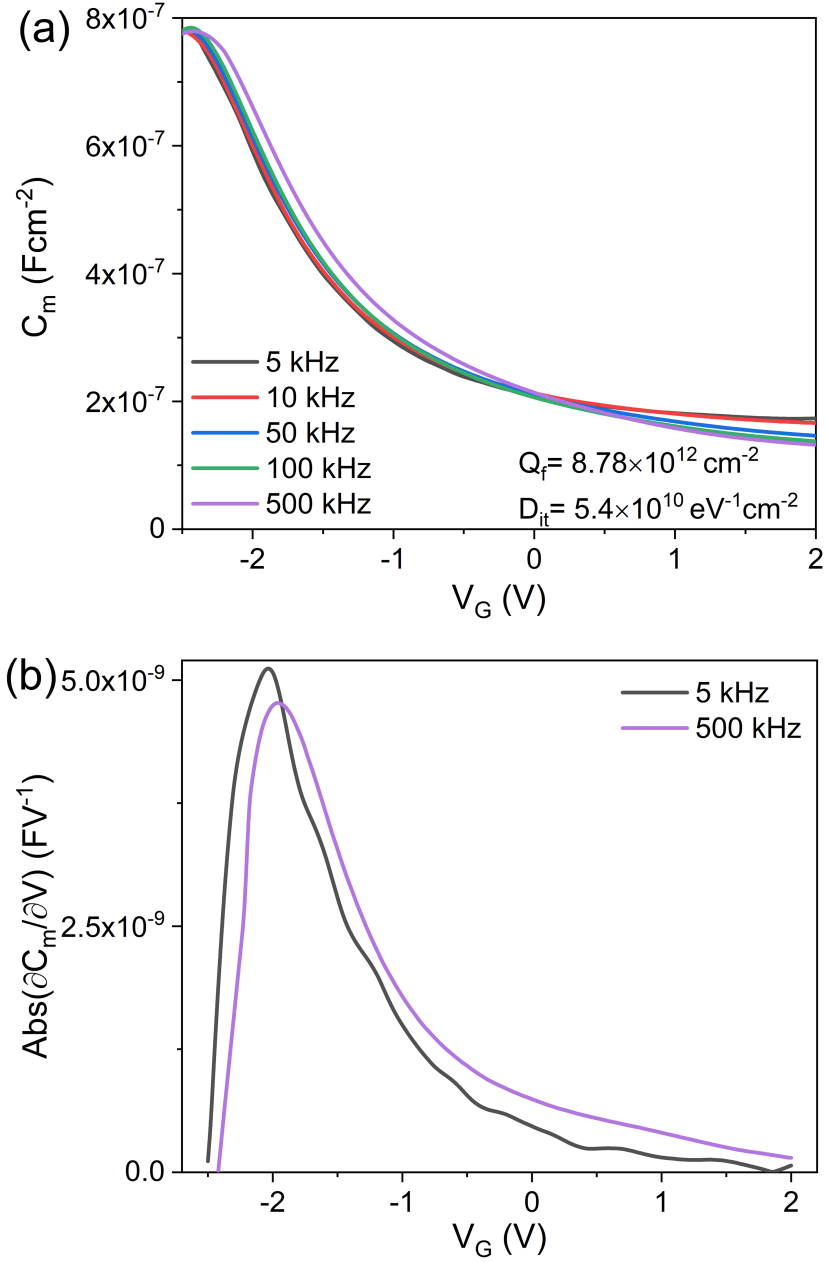


Figure 6.7. (a) Corrected C_m - V_G curves from 5 to 500 kHz, (b) $\text{abs}(\partial C_m / \partial V)$ - V_G curves at 5 and 500 kHz.

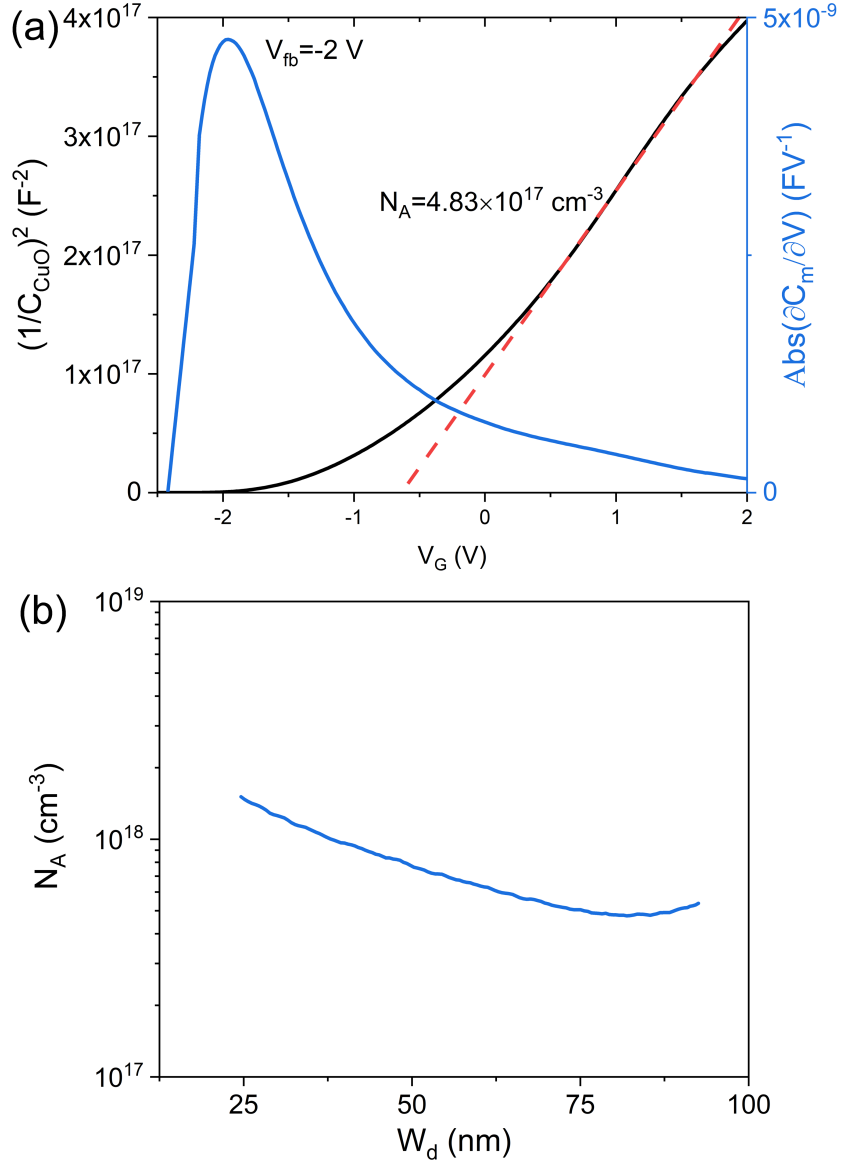


Figure 6.8. (a) Calculated $(1/C_{CuO})^2 - V_G$, $abs(\partial C_m/\partial V_G) - V_G$ and (b) $N_A - W_d$ curve at 500 kHz.

Therefore, the $C_m - V_G$ curve at 500 kHz is used in the analysis of **Figure 6.8(a)** and **Figure 6.8(b)**. To analyze it separately, the CuO depletion capacitance (C_{CuO}) is obtained from $C_{CuO} = (C_{ox} \times C_m) / (C_{ox} - C_m)$ where C_{ox} is the theoretical oxide capacitance (7.8×10^{-7}

F cm⁻² for HfO₂ of 25 nm) equal to the maximum capacitance in accumulation regime in **Figure 6.7(a)**. The flat-band voltage (V_{FB}) is extracted to be about -2 V from the absolute value of the derivative C_m - V_G curve (blue line in **Figure 6.8(a)**). The apparent acceptor doping density (N_A) is extracted from the slope of the linear part in the $(1/C_{CuO})^2 - V_G$ curve to be 4.83×10^{17} cm⁻³ (red and black lines in **Figure 6.8(a)**). Next, the fixed surface charge density (Q_f) at the HfO₂/CuO interface is estimated by **[136]**:

$$Q_f = C_{ox} \left(\frac{V_{ms} - V_{FB}}{q} \right) \quad (6.1)$$

where $V_{ms} = (\varphi_m - \varphi_s)/q$ with φ_m as the work function of Au (5.47 eV) and q is the electron charge. The work function of CuO (φ_s) can be estimated by **[76]**:

$$\varphi_s = \chi_{CuO} + E_g - \left| \frac{kTemp}{q} \ln \left(\frac{N_A}{N_V} \right) \right| \quad (6.2)$$

where χ_{CuO} is the electron affinity of CuO (4.07 eV), E_g is the bandgap of CuO (1.6 eV from our previous measurement in Section 4.32), k is the Boltzmann constant, $Temp$ is the temperature and N_V is the valence band effective density of states of CuO ($=5.5 \times 10^{20}$ cm⁻³) **[137]**. φ_s is estimated to be 5.49 eV and a calculated positive Q_f of 8.78×10^{12} cm⁻² is obtained for the capacitor. Even considering deviation in the estimation of φ_s due to slight difference of χ_{CuO} and N_V for specific CuO films, a high positive Q_f of $\sim 10^{13}$ cm⁻² remains expected. Such high Q_f repels the hole carriers inside CuO leading to a thick depletion layer at zero gate voltage **[138]**.

At 500 kHz, the depletion width (W_d) and the net acceptor concentration (N_A) are obtained in **Figure 6.8(b)** using:

$$N_A = \frac{-2}{q\epsilon_0\epsilon A^2 [d(1/C_{CuO}^2)/d\varphi_{CuO}]} \quad (6.3)$$

$$W_d = \frac{\varepsilon_0 \varepsilon A}{C_{CuO}} \quad (6.4)$$

where ε_0 is the vacuum permittivity, A is the device area ($=0.01 \text{ cm}^2$), φ_{CuO} is the potential at the HfO_2/CuO interface (in inversion regime, $\varphi_{CuO} = V_G + Q_{ox}/C_{ox}$) and ε , the CuO permittivity, is assumed to be 18.1 [137]. Consistently with the slope in the $(I/C_{CuO})^2 - V_G$ curve, the minimum N_A is $\sim 5 \times 10^{17} \text{ cm}^{-3}$, and increases toward HfO_2 , to a much higher value than in previous Hall measurements on SLG in Section 4.32 due to high acceptor activation energy and high compensation ratio [139]. Such behavior could be caused by the oxygen diffusion from HfO_2 . Closer to the interface of HfO_2/CuO interface, a higher oxygen concentration and hole concentration is expected in CuO according to Table 4.3.

Another important figure of merit is the interfacial trap charge density (D_{it}) at the HfO_2/CuO interface. D_{it} is related to the material and chemical processes in fabrication and can be estimated either by the parallel capacitance or conductance, variation with V_G , or f , corresponding to the high-low frequency method [140], or the parallel conductance method, respectively. In the high-low frequency method, the interfacial traps respond to variations of input signal only at low frequency but not at high frequency. Corresponding D_{it} can be calculated by:

$$D_{it} = \left(\frac{C_{ox}C_{lo}}{C_{ox}-C_{lo}} - \frac{C_{ox}C_{hi}}{C_{ox}-C_{hi}} \right) / q \quad (6.5)$$

where C_{lo} and C_{hi} are the low and high frequency capacitances. In Figure 6.7(a), a clear shift of V_{fb} can be observed due to D_{it} . After removing this shift and extracting D_{it} at a V_G of 0 V, a D_{it} of $5.4 \times 10^{10} \text{ eV}^{-1} \text{ cm}^{-2}$ is obtained at the HfO_2/CuO interface. By the conductance

method, which is less affected by parasitic elements, D_{it} can be calculated by [136]:

$$D_{it} = \frac{2.5}{q} \left(\frac{G}{A\omega} \right)_{max} \quad (6.6)$$

where $(G/A\omega)_{max}$ is the height of the peak in the $G/A\omega$ curve, and 2.5 is a correction factor for the peak width statistical fluctuation.²⁶ The peak value is caused by the maximum energy loss from charge exchange with interface states. In Figure 6.9, G/ω is plotted against ω ($=2\pi f$) at a V_G of 0 V and a D_{it} of $6.8 \times 10^{10} \text{ eV}^{-1} \text{ cm}^{-2}$ is extracted at HfO₂/CuO interface, which is close to the calculated value by high-low frequency method. Therefore, D_{it} is estimated to be $\sim 6 \times 10^{10} \text{ eV}^{-1} \text{ cm}^{-2}$, showing lower value than a D_{it} of $3 \times 10^{13} \text{ eV}^{-1} \text{ cm}^{-2}$ at SiO₂/Cu₂O interface [73] and $6.8 \times 10^{11} \text{ eV}^{-1} \text{ cm}^{-2}$ at HfO₂/Cu₂O [75]. Lower D_{it} in this work compared to SiO₂/Cu₂O and HfO₂/Cu₂O interfaces is due to a better quality of the HfO₂/CuO interface than [73] and [75].

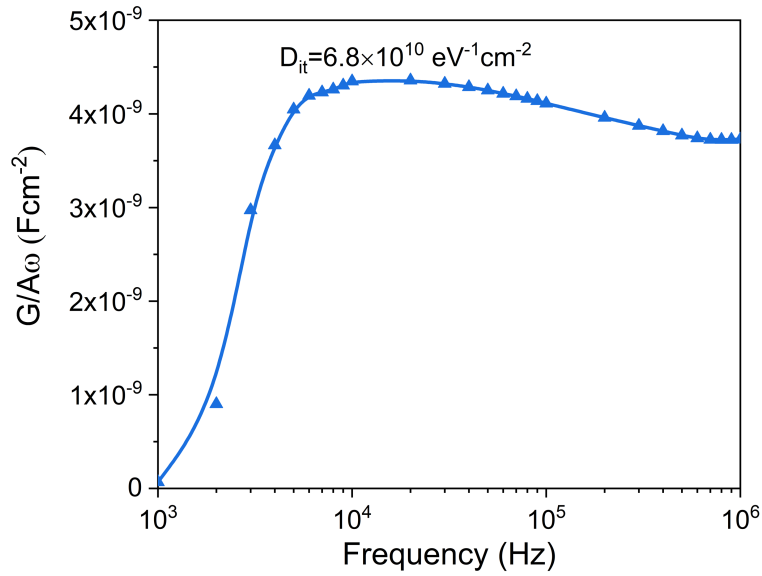


Figure 6.9. $G/A\omega$ curve from 1 kHz to 1 MHz at 0 V.

6.4 CuO thin-film transistors

Finally, CuO TFTs with the L of 25 and 10 μm are investigated in **Figure 6.10** and **Figure 6.11**, respectively. Their top-viewed photographs by optical microscope and transfer curves (i.e., drain current vs gate voltage, I_D - V_G) at a drain voltage (V_D) of -1 V are reported in **Figure 6.10(a)** and **Figure 6.11(a)**, respectively. By extracting the derivatives of transconductance g_m in **Figure 6.10(a)** and **6.11(a)**, two main peaks are observed after smoothing, showing accumulation-mode (AM) behaviors of CuO TFTs [141, 142].

Their output curves (i.e., I_D - V_D) are reported in **Figure 6.10(b)** and **Figure 6.11(b)** with a gate voltage (V_G) varying from 0 V to -2 V, showing a tendency to saturate with lowering V_D . When a buried channel is formed (V_G between V_{th1} and V_{th2}), the loss of gate control degrades the output conductance in saturation (like it does for the subthreshold slope) [141, 143]. When an accumulation layer is formed at a V_G below V_{th2} , the coupling from the V_D still greatly controls the carriers in the accumulation layer due to the quasi-neutral region between the drain electrode and the channel [141, 143]. Therefore, clear saturation regions can be harder to reach in the AM TFTs.

Several parameters are calculated from the transfer curves. The on/off current ratio (I_{on}/I_{off}) is defined as the ratio of maximum to minimum I_D . The field-effect mobility in accumulation layer is expressed by [144]:

$$\mu_{FE} = \frac{L}{ZC_{ox}V_D} g_m \quad (6.7)$$

where g_m is extracted below V_{th2} from -3 to -2 V. In **Figure 6.10(a)**, the CuO TFT ($L=25 \mu\text{m}$) shows an I_{on}/I_{off} of 1.3×10^2 and a μ_{FE} of $1.1 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. In **Figure 6.11(a)**, CuO TFT ($L=10 \mu\text{m}$), shows

similar performances, with an I_{on}/I_{off} of 1.7×10^2 and a μ_{FE} of $0.62 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. Such low μ_{FE} is typical for TFTs based on copper oxides

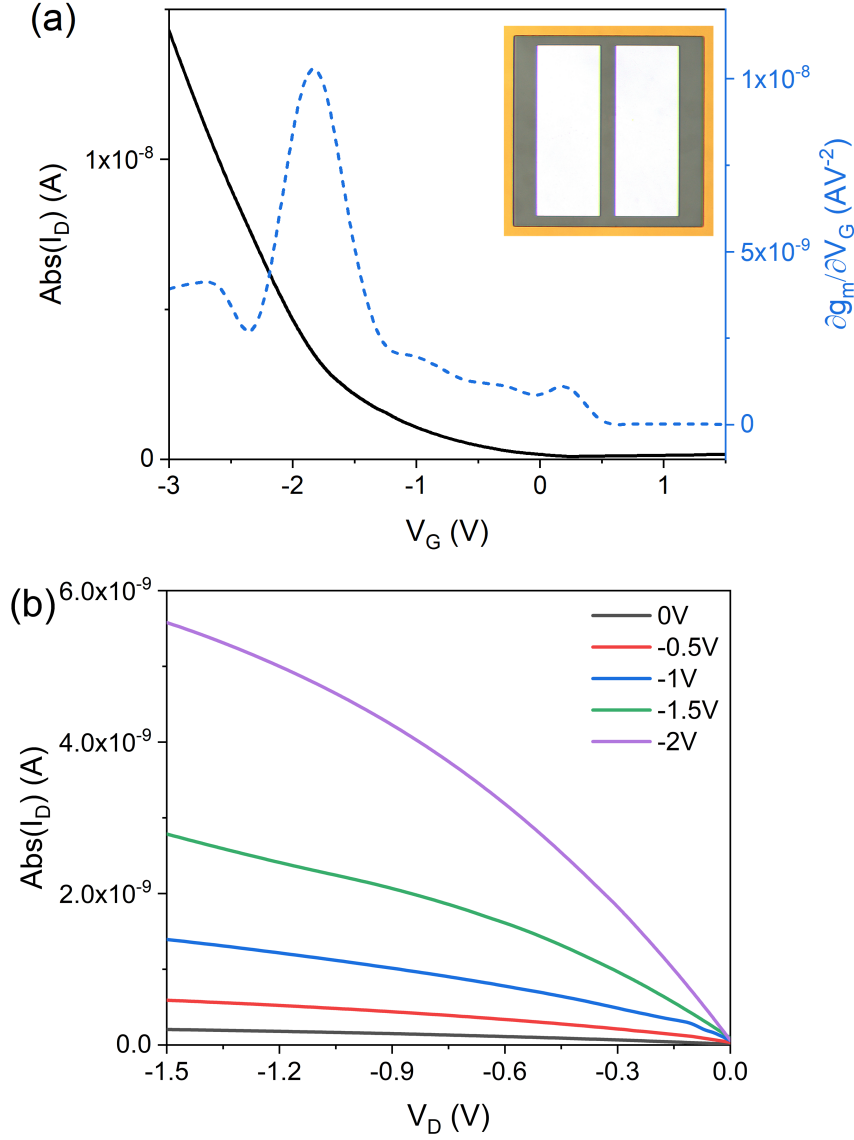


Figure 6.10. (a) Transfer I_D - V_G curves ($V_D = -1 \text{ V}$) and transconductance derivatives (blue dashed lines), the inset is the top-viewed photograph by an optical microscope (the white, brown and yellow parts are Au/Ti/Al, CuO and Au, respectively) (b) Output I_D - V_D curves ($V_G = -2 \text{ V}$ to 0 V) of CuO TFTs with channel lengths of $25 \mu\text{m}$.

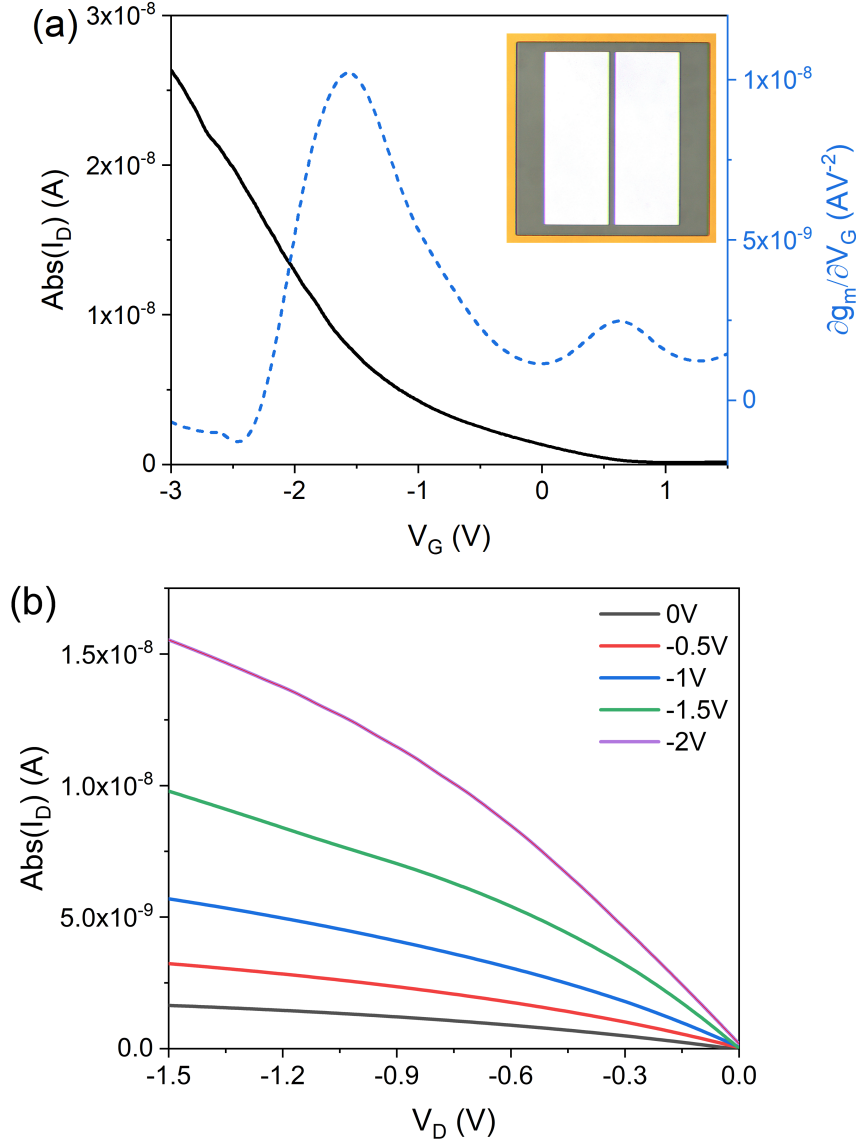


Figure 6.11. (a) Transfer I_D - V_G curves ($V_D=-1$ V) and transconductance derivatives (blue dashed lines), the inset is the top-viewed photograph by an optical microscope (the white, brown and yellow parts are Au/Ti/Al, CuO and Au, respectively) (b) Output I_D - V_D curves ($V_G=-2$ V to 0 V) of CuO TFTs with channel lengths of 10 μm .

regardless of the deposition techniques due to TFT nonidealities from the contact resistance or interfacial traps [71]. Here, compared to a measured Hall concentration of $\sim 10^{14} \text{ cm}^{-3}$ for a bare CuO thin film on

SLG in Section 4.3.2, the N_A of CuO measured in TFTs increases significantly to a minimum of $4.83 \times 10^{17} \text{ cm}^{-3}$ following the MOS process. Considering that μ_{FE} is extracted from the accumulation region of the CuO TFT, accumulation carrier density (N_{accu}) can be estimated by:

$$N_{accu} = \frac{Q_{accu}}{qt_{accu}} = \frac{C_{ox}(|V_G| - |V_{th2}|)}{qt_{accu}} \quad (6.8)$$

where Q_{accu} is the accumulation charge density and t_{accu} is the thickness of the accumulation layer. t_{accu} is simulated to be $\sim 20 \text{ nm}$ in SILVACO Atlas simulation [93], and N_{accu} of CuO TFT ($L=25 \text{ }\mu\text{m}$) is calculated to be $3 \times 10^{18} \text{ cm}^{-3}$. According to the increasing linear tendency of the hole mobility with decreasing hole concentration for CuO in Section 4.3.2, the hole mobility is limited at such high N_{accu} . In addition, traps induced in TFT fabrication process, electrical field in CuO, possible Au diffusion through grain boundaries, and degradation in air would limit the μ_{FE} .

The subthreshold swing (SS) that describes the switching quality of TFTs is given by [76, 145]:

$$SS = \left(\frac{\partial \log(I_D)}{\partial V_G} \Big|_{max} \right)^{-1} = \frac{kT}{q} \ln 10 \left(1 + \frac{C_{stot}}{C_{cg}} \right) \quad (6.9)$$

where C_{cg} is the channel to gate capacitance and C_{stot} is the total substrate capacitance, including trap capacitance at the HfO_2/CuO interface ($C_{it1}=qD_{it1}$), trap capacitance at the CuO/Air interface ($C_{it2}=qD_{it2}$) and total coupling parasitic capacitance from channel to ground (C_{sub}). Extracting SS of the buried channel around V_{th1} , 1.04 and 1.78 V dec⁻¹ are obtained for CuO TFTs with the L of 25 and 10 μm , respectively. In this voltage regime, the C_{cg} of around $2 \times 10^{-7} \text{ F cm}^{-2}$ is extracted from Figure 6.7(a). As C_{it1} is about $9.6 \times 10^{-9} \text{ F cm}^{-2}$ and C_{sub} is considered low for CuO TFTs on SLG, then the high SS should be

explained by D_{it2} , i.e. probably interfacial traps between unpassivated CuO and air, estimated using Equation (6.9) to be up to 2.04×10^{13} and $3.57 \times 10^{13} \text{ eV}^{-1} \text{ cm}^{-2}$ for CuO with the L of 25 and 10 μm , respectively. With top surface passivation, D_{it2} could be decreased and thus SS and μ_{FE} could be improved [71].

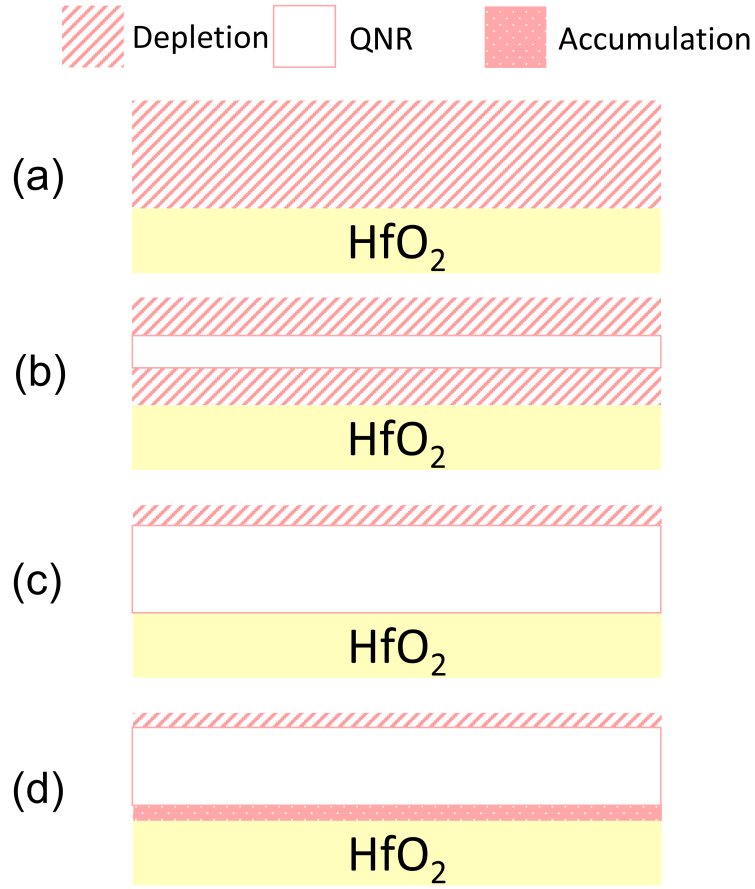


Figure 6.12. Operation mechanism of CuO TFTs (a) fully depletion (b) buried channel (c) increase of QNR (d) accumulation channel.

Figure 6.12 illustrates the operation mechanism of CuO TFTs with lowering V_G . According to the N_A - W results from C - V measurements, the CuO thin film is almost fully depleted at very positive V_G as shown in **Figure 6.12(a)**. When lowering V_G , a buried conduction channel is

first formed in the middle of the CuO layer in **Figure 6.12(b)**, corresponding to the first apparent threshold voltage (V_{th1} as the right peak of the g_m derivative curve, at about 0.2 V in **Figure 6.10(a)** and 0.6 V in **Figure 6.11(a)**). The thickness of the buried channel and hence the related current increase when further lowering V_G , forming a wider QNR region in **Figure 6.12(c)** and finally an accumulation layer in **Figure 6.12(d)** below the second threshold voltage ($V_{th2} \approx V_{fb}$, as the left peak of the g_m derivative curve, -1.8 V in **Figure 6.10(a)** and -1.6 V in **Figure 6.11(a)**). Therefore, I_D is dominated by the current in the buried channel or the current in the accumulation layer or both at different V_G .

6.5 Summary

In conclusion, the CuO thin film fabricated by room-temperature DC reactive magnetron sputtering shows an excellent crystal growth of tenorite CuO. P-type CuO TFTs fabricated on SLG with a gate dielectric of HfO₂ deposited by ALD demonstrate competitive performance in the accumulation mode compared to standard copper oxide TFTs based on silicon techniques [43, 61, 71, 146] in **Table 6.2**. By characterizing a CuO MOS capacitor, the field-effect mobility appears much lower than in Hall measurements due to a high apparent doping concentration in CuO film and a high Q_f in HfO₂. Subthreshold swing appears limited by the high interfacial traps between CuO and air, and to a lesser extent by a decreased C_{cg} caused by the buried channel dominance in subthreshold and possible parasitic coupling capacitance in a bottom-gate configuration. These results show great potential of CuO TFTs toward future applications in sensors or CMOS logic circuits.

To further optimize CuO TFTs, CuO could be annealed in a controlled ambience at a temperature compatible with the HfO₂ stability and the top CuO surface could be passivated by Al₂O₃ sputtered in the

same chamber after CuO sputtering without exposing the sample to the air [147]. Additionally, reducing the thickness of CuO can be of great interest to improve the TFT performance in a lower-cost way of fabrication. By thickness reduction, the depletion region can be minimized, and C_{cg} can be effectively lowered when a buried channel is formed. In such a case, the performance of CuO TFTs could be improved, such as the subthreshold swing, carrier mobility, carrier velocity, output drain current, short channel effects and impact of doping fluctuation as it was demonstrated in silicon [148, 149].

Table 6.2. Comparison of electrical performances for CuO TFTs (last 2 lines) with previously reported literature

Structure	Technology	L/Z (μm)	μ ($\text{cm}^2\text{V}^{-1}\text{s}^{-1}$)	I_{on}/I_{off}	SS (V/dec)	Refs.
Au/CuO/SiO₂/Si	Spin Coating, Annealing (500°C)	100/1000	0.4×10^{-3}	10^2	/	[43]
Pt/CuO_x/SiO₂/Si	Spin Coating, Annealing (500°C), HClO treatment (300°C)	150/1000	2.83×10^{-3}	4.86×10^4	0.7	[61]
Au/Cu₂O/SiO₂/Si	ALD, Annealing (300°C), Al ₂ O ₃ top passivation	50/1000	1.5×10^{-3}	5×10^3	11.5	[71]
Ni/Cu_xO/SiO₂/Si	Spin Coating, Annealing (250°C)	100/1000	0.32	5×10^4	1.1	[145]
Au/CuO/HfO₂/Au	Room-temperature Sputtering	25/270	1.1×10^{-3}	1.3×10^2	1.04	L=25 μm
Au/CuO/HfO₂/Au	Room-temperature Sputtering	10/270	0.62×10^{-3}	1.7×10^2	1.78	L=10 μm

Conclusions and Perspectives

Conclusions

Two p-type thin-film semiconductors were investigated in this thesis to fabricate and characterize opto-electronic devices based on CIGS and CuO. CdS/CIGS and In₂S₃/CIGS heterojunction photodiodes fabricated on steel were characterized, demonstrating excellent photoresponsivity. To overcome the disadvantage of higher cost for CIGS fabrication, CuO thin films were DC sputtered to obtain materials with proper bandgap, good optical and electrical performances. Transmission line model structures were fabricated and discussed, revealing a good ohmic contact between Au and CuO but CuO degraded with time. Finally, CuO thin-film transistors gated by HfO₂ were fabricated and characterized.

A high-performance ultra-thin CdS/CIGS heterojunction photodiode fabricated on steel was firstly discovered to show dual-mode broadband photodetection from UV to near-infrared spectrum. By switching the detection modes of the photodiode at 680 nm illumination ($20 \mu\text{W cm}^{-2}$), a record detectivity of $\sim 4.4 \times 10^{12}$ Jones and an enhanced responsivity of 1.24 A W^{-1} can be obtained in the photovoltaic mode and photoconductive mode, respectively. Ultra-high *EQE* over 100% in the photoconductive mode is obtained and explained thanks to a corrected photoconductive gain mechanism.

However, CdS is not an ideal buffer layer in CIGS heterojunctions, In₂S₃ is thus introduced as a Cd-free buffer layer. A high-performance broadband ultra-thin In₂S₃/CIGS heterojunction photodiode fabricated on steel was firstly simulated and characterized, showing optimized

band offset, excellent photoresponse and broadband photosensitivity from UV to near-infrared spectrum. Outstanding dual-mode broadband photodetection is realized at 870 nm illumination ($20 \mu\text{W cm}^{-2}$), reaching an excellent detectivity of $\sim 3.4 \times 10^{12}$ Jones in the photovoltaic mode and a record responsivity of 2.06 A W^{-1} in the photoconductive mode. Additionally, an enhanced responsivity of $\sim 0.44 \text{ A W}^{-1}$ under 0 V bias and an impressive EQE of 293% under 1 V reserve bias show improved photodetection ability thanks to the improved spike CBO of $\text{In}_2\text{S}_3/\text{CIGS}$ heterojunction and the corrected photoconductive gain mechanism.

CuO was studied as a potential candidate to replace CIGS in the future. Structural, optical and electrical characterizations have been performed to obtain the best p-type CuO thin films. By tuning the DC reactive magnetron sputtering conditions on soda lime glass substrate, the best room-temperature sputtered CuO (10mTorr, $\text{O}_2/\text{Ar}=8/22$ sccm) thin film has achieved suitable $E_g=1.6 \text{ eV}$, and $\mu_p=143.3 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ or $36.33 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. Post-annealing at 250°C or heating at 150°C during the deposition can stabilize and enhance the performances of CuO thin films, reaching record hole mobility of 34.2 and $113.7 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, and hole concentration of 3.92×10^{14} and $1.39 \times 10^{14} \text{ cm}^{-3}$, respectively.

To find a good contact with CuO , Au was considered to make a contact with CuO , forming Au/ CuO transmission line model. A good ohmic contact was obtained between Au and CuO , showing relatively low contact resistance of $\sim 26 \text{ k}\Omega$ compared to the total resistance and an effective contact resistivity of $\sim 0.55 \Omega \text{ cm}^2$ in N_2 . However, obvious degradations of CuO thin films are discovered in vacuum at room temperature and can be accelerated in vacuum at 100°C .

Finally, p-type CuO TFTs were fabricated on SLG with a high-k HfO_2 gate dielectric deposited by ALD, demonstrating competitive

performances in accumulation mode. CuO AM TFT with a channel length of 25 μm exhibits competitive on-off ratio (I_{on}/I_{off}) of 1.3×10^2 , subthreshold swing (SS) of 1.04 V dec^{-1} , and field-effect mobility (μ_{FE}) of $1.1 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at room temperature. These results show great potential of CuO utilized as a p-type semiconductor in sensors or CMOS logic circuits.

Perspectives

Based on the research presented in this thesis, several works can be extended in the future to help further understanding and improving CIGS and CuO as p-type semiconductors utilized in opto-electronic devices.

For CIGS Research:

- 1) **Passivation layer implantation:** Due to the complicated design of the CIGS heterojunctions, various defect states exist in several interfaces. It is important to minimize the defect density at the interface to reduce the carrier recombination and thus enhance the photoresponse. Except for the suitable choices of different layers, it is possible to reduce the defect states by absorber surface treatments (e.g. alkali doping) or by introducing a passivation layer. Several passivation processes can be considered in the future, including front passivation on CdS/CIGS heterojunction, rear passivation below CdS/CIGS heterojunction, or passivation between CdS/CIGS heterojunction. Several oxides can be used as passivation layers, like Al_2O_3 , Ga_2O_3 , and SiO_2 [82, 88, 150].
- 2) **Ga-grading:** By altering the amount of Ga and In in CIGS, the $\text{Ga}/(\text{Ga}+\text{In})$ (GGI) ratio can be varied, corresponding to the varied CIGS bandgap from 1.01 eV to 1.67 eV. If GGI is continuously varied throughout the CIGS layer, a normal bandgap grading, where

bandgap increases from the front towards the back contact of the heterojunction, would be formed. Such Ga-grading of CIGS bandgap would cause less probability of recombination. Due to the grading bandgap, higher energy photons are absorbed closer to the surface and lower energy photons penetrate deeper inside the material, enabling the cell to absorb more photons and thus generate more photocurrent.

- 3) **Flexible performances:** CdS/CIGS and $\text{In}_2\text{S}_3/\text{CIGS}$ heterojunctions studied in this thesis were both fabricated on low-carbon steel substrate. It could be possible to study the performances of these devices under deformation in the future. As reported in [5], CdS/CIGS heterojunction photodiode grown on polyimide showed variation of photodetection capabilities when applying a compressive or tensile strain. Considering the flexible steel substrates, CIGS photodiodes on steel studied in this thesis also possess the possibility to extend its application as piezophototronic sensors via the piezophototronic effect.
- 4) **Substrate or heterojunction alternations:** Both CIGS photodiodes were fabricated on steel, but it would be interesting to investigate similar designs on polyimide or glass substrates. New photodiodes on polyimide can extend their applications as flexible devices, while those on glass can benefit from the alkali doping. Another potential research direction in the future is to introduce other new n-type buffer layers like ZnMgO [151]. The photoresponse of new structures can be discovered and improved photoresponse might possibly be obtained
- 5) **Lateral photovoltaic effect:** As reported in [20, 21], CdS/CIGS heterostructures on glass substrate showed excellent lateral photovoltaic effect (LPE), indicating its potential to be used as

position sensitive detectors (PSDs). The reported devices have traditional structures and high CIGS thickness of 2 μm . Based on our current research, longitudinal photocurrent was always obtained. By introducing two top contacts on the devices, LPE characteristics can be studied for our CdS/CIGS and In_2S_3 /CIGS heterojunctions with improved designs and thinner CIGS of less than 1 μm .

For CuO Research:

- 6) **Cu_2O or Cu_4O_3 :** Except for CuO phase, copper oxides have the other two phases (Cu_2O , Cu_4O_3). Cu_4O_3 as a transition phase between CuO and Cu_2O is relatively unstable and easily oxidized to CuO. Therefore, it is difficult to obtain pure Cu_4O_3 and a mixture product with other phases is normally obtained. Cu_2O is an excellent candidate as p-type materials to be used in photodetectors [49] or TFTs [71, 133]. Cu_2O has a narrower bandgap, high hole mobility of over $100 \text{ cm}^2\text{V}^{-1}\text{S}^{-1}$ and good power conversion efficiency, which makes also it a promising material to be used as an absorber layer in solar cell or as a top window cell to form a tandem solar cell with the bottom Si or CIGS solar cell. In this thesis, we focused only on the magnetron sputtering from the edge of oxidation regime to the poisoned regime. Only CuO phase was obtained in this thesis, but it is of great interest to study the sputtering in the oxygen regime to fabricate Cu_2O , which might have better opto-electronic performances than CuO for solar cell, photodetector or TFT applications.
- 7) **Degradation mechanism:** The degradation of CuO thin films was found in Chapter 5 by characterizing Au/CuO TLM structures. But the degradation mechanism has not been studied yet in the thesis. Therefore, it would be important to further study degradation

mechanism of CuO thin films by material and opto-electronic characterizations before and after the degradation.

- 8) **CuO/HfO₂/Au TLM structure:** Au/CuO TLM structures studied in Chapter 5 were fabricated on SLG, so possible sodium diffusion from substrate could induce a thin depletion layer at the CuO/SLG interface. In the fabrication of CuO devices, CuO is deposited on top of other materials instead of SLG, which might cause different performances of CuO. Therefore, TLM structures of CuO with back gate stack like CuO/HfO₂/Au could be studied in the future to determine the contact resistance between CuO and the back gate stack.
- 9) **Noise characteristics of CuO TFTs:** Noise in electronic devices refers to the inevitable spontaneous signals originating from random fluctuations. Noise mainly includes thermal noise, flicker noise and shot noise [76]. To validate the noise in CuO TFTs and improve their performances by reducing the noise, low-frequency noise characterization can be considered in the future research. Frequency and transient noise measurements can both be done, possibly revealing flicker noise, random thermal noise and Generation/Recombination noise.
- 10) **Top passivation of CuO TFTs:** For metal oxide semiconductors, a thin layer on top of the surface in contact with air is difficult to be avoided during or after the fabrication. CuO can have a reaction with the compositions in air like O₂, H₂O, etc. to form such a thin layer. An effective method to avoid such reaction is to introduce a top passivation layer (e.g. Al₂O₃) on the CuO surface [71]. Interfacial traps simultaneously appear in the interface between passivation layer and CuO, which can be further studied in the future.

- 11) **CuO annealing in CuO TFTs:** CuO thin films showed enhanced opto-electronic properties after high-temperature process in Chapter 4. The performances of CuO thin films could be boosted if annealed at 250 °C or sputtered at 150°C. Considering that photoresist can hardly afford the high-temperature sputtering, annealing after room-temperature sputtering is recommended after the whole fabrication processes to improve and stabilize the performances of CuO TFTs.
- 12) **CuO thickness reduction in CuO TFTs:** In most of the research, the thickness of the active layer in TFT is less than 50 nm. But the CuO thickness of TFTs studied in Chapter 6 was 115 nm, which is relatively thick for TFTs, because we followed the standard CuO fabrication process in Chapter 4. Thought for photodetectors, it would be important to reduce the CuO thickness and study its influence on the performance of CuO TFTs.
- 13) **Photoresponse of CuO TFTs:** CuO thin films studied in this thesis targeted firstly on the large-area photodetection in the UV and near visible spectrum range. However, much attention was paid on the electrical performances of CuO TFTs instead of the photodetection performances in Chapter 6. CuO TFTs possess the probability to be used as thin-film phototransistors in the future due to the excellent optical performances and suitable bandgap of CuO thin films for the photodetection at short wavelengths. CuO TFTs in Chapter 6 showed limited field-effect mobility, which limits a lot the photoresponse and should be improved in the future. With enhanced carrier mobility in TFT, it should be possible to detect obvious photoresponse in the improved TFTs.
- 14) **CuO TFTs based on silicon process:** CuO TFTs can be fabricated on conventional silicon wafers based on silicon fabrication process. In this design, highly-doped p-type silicon wafers are considered as

substrates. Dry thermal oxidized SiO_2 can be introduced as high-k dielectric. Al can be deposited by e-beam evaporation on the back side of the wafers as back contact. The samples are expected to have similar characteristics with CuO TFTs fabricated on glass but worse subthreshold characteristics considering SiO_2 dielectric with smaller oxide capacitance.

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Annex

Table A1. Default SCAPS simulation parameters of CdS/CIGS photodiode

	CIGS	CdS	ZnO	AZO
t (nm)	750	50	50	300
E_g (eV)	1.15	2.4	3.3	3.3
ϵ	13.6	10	9	9
χ (eV)	4.5	4.45	4.55	4.55
N_C (cm ⁻³)	2.2×10^{18}	1.3×10^{18}	3.1×10^{18}	3.1×10^{18}
N_V (cm ⁻³)	1.5×10^{19}	9.1×10^{18}	1.8×10^{19}	1.8×10^{19}
μ_n (cm ² V ⁻¹ s ⁻¹)	100	72	100	100
μ_p (cm ² V ⁻¹ s ⁻¹)	12.5	20	31	3
V_n (cm s ⁻¹)	3.9×10^7	3.1×10^7	2.4×10^7	2.4×10^7
V_p (cm s ⁻¹)	1.4×10^7	1.6×10^7	1.3×10^7	1.3×10^7
N_A (cm ⁻³)	3×10^{16}	5×10^{17}	1×10^{17}	5×10^{18}

$$R_s = 0.5 \Omega \text{ cm}^2, R_{sh} = 5.33 \times 10^2 \Omega \text{ cm}^2$$

t : thickness, E_g : Bandgap, ϵ : permittivity, χ : affinity, N_C , N_V : effective density of states in conduction and valence bands, μ_n , μ_p : electron and hole mobility, V_n , V_p : velocity of electrons and holes, N_A : doping density, R_s : series resistance, R_{sh} : shunt resistance.

Table A2. Default SILVACO simulation parameters of CdS/CIGS photodiode

	CIGS	CdS	ZnO	AZO
t (nm)	750	50	50	300
E_g (eV)	1.15	2.4	3.3	3.3
ϵ	13.6	10	9	9
χ (eV)	4.5	4.45	4.55	4.55
N_C (cm ⁻³)	2.2×10 ¹⁸	1.3×10 ¹⁸	3.1×10 ¹⁸	3.1×10 ¹⁸
N_V (cm ⁻³)	1.5×10 ¹⁹	9.1×10 ¹⁸	1.8×10 ¹⁹	1.8×10 ¹⁹
μ_n (cm ² V ⁻¹ s ⁻¹)	100	72	100	100
μ_p (cm ² V ⁻¹ s ⁻¹)	12.5	20	31	3
τ_n (ns)	100	100	130	130
τ_p (ns)	100	100	240	240
N_A (cm ⁻³)	3×10 ¹⁶	5×10 ¹⁷	1×10 ¹⁷	5×10 ¹⁸
N_T (cm ⁻³)	1×10 ¹⁴	5×10 ¹⁶	1×10 ¹⁶	1×10 ¹⁶

t : thickness, E_g : Bandgap, ϵ : permittivity, χ : affinity, N_C , N_V : effective density of states in conduction and valence bands, μ_n , μ_p : electron and hole mobility, τ_n , τ_p : recombination lifetimes of electrons and holes, N_A : doping density, N_T : total density of defects.

Table A3. Default SILVACO simulation parameters of In₂S₃/CIGS photodiode

	CIGS	In ₂ S ₃	MgZnO	ZnO
t (nm)	800	30	50	50
E_g (eV)	1.15	2.7	3.47	3.3
ϵ	13.6	13.5	9	9
χ (eV)	4.5	4.3	4.45	4.55
N_C (cm ⁻³)	2.2×10 ¹⁸	1.8×10 ¹⁹	3×10 ¹⁸	3.1×10 ¹⁸
N_V (cm ⁻³)	1.5×10 ¹⁹	4×10 ¹³	1.7×10 ¹⁹	1.8×10 ¹⁹
μ_n (cm ² V ⁻¹ s ⁻¹)	100	400	100	100
μ_p (cm ² V ⁻¹ s ⁻¹)	12.5	200	25	25
τ_n (ns)	100	100	100	100
τ_p (ns)	100	100	9	9
N_A (cm ⁻³)	3×10 ¹⁶	5×10 ¹⁷	1×10 ¹⁷	1×10 ¹⁷
N_T (cm ⁻³)	1×10 ¹⁴	/	/	/

t : thickness, E_g : Bandgap, ϵ : permittivity, χ : affinity, N_C , N_V : effective density of states in conduction and valence bands, μ_n , μ_p : electron and hole mobility, τ_n , τ_p : recombination lifetimes of electrons and holes, N_A : doping density, N_T : total density of defects.