Fabrication and characterization of CuO based heterojunction solar cells

Saeid Masudy-Panah

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SAEID MASUDY-PANAH

**DEPARTMENT OF ELECTRICAL AND
ELECTRONIC ENGINEERING**

2015

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BASED HETEROJUNCTION SOLAR CELLS**

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FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

**DEPARTMENT OF ELECTRICAL AND ELECTRONIC
ENGINEERING**

NANYANG TECHNOLOGICAL UNIVERSITY

2015

DECLARATION

I hereby declare that the thesis is my original work and it has been written by me in its entirety.

I have duly acknowledged all the sources of information which have been used in the thesis.

The thesis has also not been submitted for any degree in any university previously.

A handwritten signature in blue ink, appearing to read 'Saeid Masudy-Panah', with a stylized flourish at the end.

SAEID MASUDY-PANAH

23th Aug 2015

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Summary

Cupric oxide (CuO) is one of the potential candidates for photovoltaic (PV) industry because of its exceptional electronic and optical properties. Despite attempts by several researchers improve the performance of the CuO-based solar cells, both V_{oc} and J_{sc} remain low for practical applications. The quality of CuO and the interface quality at the p/n junction are crucial. Lower carrier concentration, higher series resistance of absorber layer and poor carrier collection efficiency are the possible reasons for lower conversion efficiency these solar cells

In this thesis, the influence of CuO absorber quality and heterojunction interface properties on the efficiency of CuO based heterojunction solar cell are investigated in detail. Novel layer designs have been used to enhance the carrier collection efficiency of p -CuO/ n -Si heterojunction solar cells by studying a series of layer structures prepared by sputtering method. The optical, electrical, microstructural, material quality, chemical composition, surface morphology and photovoltaic properties have been systematically investigated. It is shown that the material quality of the deposited films and interface properties at p-n heterojunction can be significantly improved by tuning the sputtering power and working pressure during the film deposition.

A two-step sputter deposition method was adopted to reduce the effect of poor interface quality due to Cu-rich interlayer at the heterojunction. In addition, the effect of Ti doping to improve the conductivity of the CuO films has been studied to obtain lower

sheet resistance in CuO films, while retaining the optical properties and crystal quality. Photovoltaic properties with a V_{OC} of 421 mV, J_{SC} of 4.5 mA/cm² and a photocurrent of 8.3 mA/cm² have been achieved for p -CuO/ n -Si heterojunction solar cells. The efficiency of the device is about 1.21%, which is the highest reported value. Further, a novel method has been demonstrated to obtain significantly higher short-circuit current and fill-factor with front surface field (FSF) design, using Al followed by N doping of the CuO layer. The improvement in J_{sc} and FF is attributed to the enhancement of charge carrier collection and increase in the carrier concentration.

Finally, a new compact model has been proposed for easily predicting the physical parameters of solar cells focusing the improvement of predicted series resistance. It has been shown that the proposed compact model could predict the physical parameters with high accuracy, using several examples.

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List of Symbols

I_{sc}	short-circuit current
I_{ph}	photo current
I_o	saturation current
J_{sc}	short-circuit current density
J_o	saturation current density
J_{ph}	photo current density
I_m	maximum power current
V_m	maximum power voltage
V_{oc}	open-circuit voltage
V_{th}	thermal voltage
R_s	series resistance
R_{sh}	shunt resistance

Nomenclature

AFM	atomic force microscopy
BSF	back surface field
c-Si	crystalline silicon
DP	derivation percentage
FSF	front surface field
HF	hydrofluoric acid
HRTEM	high-resolution transmission electron microscopy
J-V	current density-voltage
RTA	rapid thermal annealing
RTP	rapid thermal processing
SEM	single exponential model
SIMS	secondary ion mass spectroscopy
TEM	transmission electron microscopy
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction

Chapter 1

Chapter 1- Introduction

- 1.1. Need for sustainable energy
- 1.2. Solar cells: an effective solution
- 1.3. Overview of solar cells technologies
- 1.4. Copper oxide based heterojunction solar cell
- 1.5. Overview of thesis

1.1 Need for sustainable energy

Fossil fuels are the main resources of the current global energy needs and supply more than 80 percent of world energy use. The growing consumption of energy and finite resource of fossil fuels have raised the alarm and concern regarding the capability of fossil fuels to support the energy demands of our daily life. In addition, due to rapid growth of world population, the energy prices are set to rise with limited sources of fossil fuels. Furthermore, fossil fuels not only produce the toxic by-products but also contribute greatly to climate change through emission of greenhouse gases. Therefore, finding alternative energy resources is of great interest.

1.2 Solar cells - an effective solution

Solar energy, bioenergy, ocean energy, geothermal energy, hydropower and wind energy are the main promising sustainable and renewable energy technologies for energy generation. All renewable energies are powered either directly or indirectly by the sun. The amount of solar energy reaching to the surface of the earth is almost 10,000 times of the world energy consumption.

Photovoltaics (PV), generation of electrical power at the atomic level by direct conversion of sunlight using certain types of semiconductor materials, is considered as one of the most promising methods to generate clean energy from the sun. However, the cumulative generated power by global PV installations is only ~0.1 % of the total generated global power today. The cumulative PV installed capacity is estimated to

increase nearly a 100 times and produce around 11% of the total electricity generated by 2050, according to the report released by International Energy Agency (IEA) [1]. To achieve that goal, more research is required to reduce the cost of PV technologies for gigawatts scale solar industry. Consequently, PV technologies with higher device power conversion efficiency and earth abundant materials are sought to develop low cost PV devices.

1.3 Overview of solar cells technologies

Crystalline silicon is widely used as the light absorber for most types of solar cells and constitutes around 90% of the PV market [2,3]. However, the current silicon solar cell technology requires crystalline Si wafers with a thickness of around 200 μm , which makes it an expensive process and extremely material and energy-intensive. In order to reduce the production cost of PV systems, the PV industry is searching for thin film solar cell technologies and alternative low cost material.

Therefore, it is critical to develop strong light absorber, earth abundant and environmental friendly materials for energy harvesting [4]. In recent years, there are enormous research efforts on photovoltaic devices using earth abundant materials such as copper zinc tin sulfide (CZTS) [5,6], beta-phase FeSi_2 [7,8], metal oxides [9-14], etc. Among them, metal oxide (MO) based materials are potential candidates since the range of electronic and optical properties they support is truly exceptional.

Many of the MOs are nontoxic, chemically stable, abundant, and satisfy the

requirements for low-cost industrial fabrication. Therefore, solar cells made of MO can be environmental friendly, cost effective, and stable, which are, apart from the efficiency of the devices, the essential necessities for solar cells. MOs are mainly used as transparent conducting oxides (TCOs) in solar cells. Aluminium-doped zinc oxide (AZO), indium tin oxide (ITO) and fluorine-doped tin oxide (FTO) are the most commercially used TCO in thin film solar cells based on amorphous or microcrystalline Si, $\text{CuIn}_x\text{Ga}_{1-x}\text{Se}_2$ (CIGS) and CdTe. Promising future-generation of solar cells such as quantum-dot-sensitized solar cells, dye-sensitized solar cells or ultrathin absorber cells are also prepared using a TCO substrate. However, fewer MOs have been used as the absorber for solar cell application. One of the most widely investigated MO absorber for solar cell application is copper oxide.

Copper oxide is one of the promising candidates for large scale deployment of future generation of solar cells due to its low cost, abundance of the source materials in earth crust, high absorption coefficient in the visible region, high minority carrier diffusion length, and the possibility of straightforward processing [15-18]. Furthermore the optical absorption of copper oxide is better than the crystalline silicon in the range of 550 nm to near ultraviolet [19] and it was also shown that copper oxide has the capability to reduce costs of solar cells as compared with crystalline silicon and meet worldwide electricity demand [4]. These promising characteristics of copper oxide have renewed its interest for copper oxide based low cost solar cells.

However, the highest reported efficiency is far from the predicted efficiency by Shockley–Queisser limit and there is a lot of room for improvement. The low efficiency

of prepared devices is mainly ascribed to the difficulty of doping this material to make it low resistivity n- type semiconductor and prepare the p - n homojunction. Therefore, a common solar cell structure for this material is heterojunction. Other important parameters, which are responsible for the low efficiency of copper oxide based solar cells are high series resistance, recombination through interface defect states and bulk non-radiative recombination, low built-in potential caused by non-ideal band alignment between the absorber and metal electrode or transparent conducting oxide (TCO).

Copper oxide is p -type in the nature. The p -type conductivity of copper oxide is mainly originated from excess oxygen exhibited as oxygen interstitial, O_i , or copper vacancies, V_{cu} [20]. Vacant copper ion lattice sites are the main impurity centres, acceptors in copper oxides. The amount of cation deficiency also significantly influences the carrier concentration and introduces hole states lying above the top of valance band [21].

It was also shown that in Cu-poor and Cu-rich conditions the vacancy in the so-called split configuration and copper vacancy have the lowest formation energies compared to the oxygen interstitials [22]. The dominant contributions that affect to the mobility are ionized impurity scattering at low temperatures (below 200 K) and phonon scattering at high temperatures [23].

Copper oxide has two principle oxides: cupric oxide (or copper (II) oxide, CuO) and cuprous oxide (or copper (I) oxide, Cu₂O). Cu₂O crystallizes in a cubic Bravais lattice [24]. The unit cell of Cu₂O contains six atoms, the two oxygen atoms forming a

body-centred cubic sublattice and four copper atoms positioning in a face-centred cubic lattice. CuO is in the form of tenorite with monoclinic symmetry where copper atom is coordinated by four oxygen atoms in an approximately square planar configuration. [25].

Schematic diagrams of the crystal structure of Cu_2O and CuO are shown in Fig. 1.1, and the corresponding crystallographic properties are listed in Table 1.1 and 1.2, respectively.

Figure 1.1. Crystal structures of Cu_2O and CuO [26].

Table 1.1. Crystallographic properties of Cu₂O [25]

lattice constant	$4.2696 \pm 0.0010 \text{ \AA}$
space group	$Pn\bar{3}m$ (224)
bond length Cu–O	$1.849 \text{ \AA}$
separation O–O	$3.68 \text{ \AA}$
separation Cu–Cu	$3.012 \text{ \AA}$
cell volume	$(77.833 \pm 0.055) \times 10^{-24} \text{ cm}^3$
formula weight	143.14
density	$5.749\text{--}6.140 \text{ g/cm}^3$
melting point	$1235 \text{ }^\circ\text{C}$

Table 1.2. Crystallographic properties of CuO [25]

space group	C2/c (No. 15)
unit cell	$a = 4.6837 \text{ \AA}$ $b = 3.4226 \text{ \AA}$ $c = 5.1288 \text{ \AA}$ $\beta = 99.54^\circ$ $\alpha, \gamma = 90^\circ$
cell volume	$81.08 \text{ \AA}^3$
cell content	4 [CuO]
formula weight	79.57
density	6.515 g cm^{-3}
distances	
Cu–O	$1.96 \text{ \AA}$
O–O	$2.62 \text{ \AA}$
Cu–Cu	$2.90 \text{ \AA}$
melting point	$1201 \text{ }^\circ\text{C}$

Cu_2O has a direct bandgap of 2.0 eV and the theoretically predicted power conversion efficiency of 20% for homojunction solar cells due to the Shockley–Queisser limit (SQL). On the other hand, CuO is an indirect band gap material with an ideal band gap energy of 1.2~1.6 eV, which is suitable for solar cell applications [27]. Optical transitions between the conduction and valence band of direct band gap Cu_2O are stronger than indirect band gap CuO. This is because absorption and emission of a photon have to occur simultaneously with the absorption or emission of a phonon for conserving momentum. Although CuO is an indirect band gap material, it has the ideal band gap for solar light absorption (~1.4 eV), high optical absorption coefficient and recombination lifetime, as well as long diffusion length, which makes it a suitable candidate for solar cells application. Figure 1.2 shows comparison between optical absorption of CuO and Cu_2O . As shown in this figure, CuO exhibits higher optical absorption than Cu_2O in the whole visible spectral region [25].

Figure 1.2. Comparison between the optical absorption of CuO and Cu₂O [25].

Higher optical absorption coefficient of CuO than Cu₂O significantly influences the theoretically predicted photocurrent. While the theoretically predicted photocurrent, under standard AM1.5 irradiation, of Cu₂O is 14.7 mA.cm⁻² [28], CuO is able to generate higher photocurrent of 35 mAcm⁻² [29]. Furthermore, the theoretical conversion efficiency of homojunction CuO based solar cell under air mass (AM) solar illumination is approximately 31% better than that of a single crystalline Si solar cell [19]. Compared with Cu₂O, CuO is more stable, easy to prepare and it requires low thermal treatment [30-32]. The bandgap of CuO is in the range of 1.2 eV to 1.6 eV, closely matching the spectrum of sunlight for absorbing more sunlight [33]. Even though it is one of the popular materials for solar cell applications, there are only a few reports available in the development of CuO based solar cells.

1.4 Copper oxide based heterojunction solar cell

In 2009, a hybrid heterostructure of inorganic *p*-type CuO nanowire core and an organic n-type C60 shell was demonstrated by Qiaoliang Bao et al [34]. They have found that devices with contacts on core-shell shows photovoltaic effects under illumination. In 2011, Oku et al prepared the CuO thin films by using the electrodeposition and spin-coating techniques [26]. Thin film solar cells of CuO/C60 heterojunction were then prepared on F-doped or In-doped SnO₂ with the highest power conversion efficiency of 0.0023%. In 2012, Lim et al have used the facile alcohothermal route to synthesise CuO nanocrystals [35]. They have found that nanocrystals can be dispersible in a solvent mixture of chloroform and methanol, which is required for processing of CuO by solution. They produced the bilayer solar cell comprising of phenyl-C61-butyric acid methyl ester (PCBM) and CuO nanocrystals with a conversion efficiency of 0.04%.

Wang et al prepared the nanowire based heterojunction solar cell of p-CuO/n-ZnO [36]. They used the thermal oxidation technique and solution processing method to prepare the CuO nanowire and ZnO layer, respectively. Photovoltaic and optoelectronic properties of the prepared solar cells were then investigated in detail. The efficiency of their best devices was around 0.1%.

Dimopoulos et al prepared the sputter deposited heterojunction solar cell of p -CuO/ n -ZnO and investigated the impact of CuO-absorber thickness on the power conversion efficiency of the prepared solar cells [37]. By optimizing the thickness of the CuO absorber layer, a conversion efficiency of 0.08% was achieved for the cell with 500 nm thick absorber layer. It was also found that the restricted carrier collection efficiency, caused by the small carrier lifetime, is one of the main limiting factors of CuO based solar cells. In 2012, Gao et al sputter deposited thin film of CuO at different O₂ and Ar flow rates. It was shown that flow rate ratio of O₂ to Ar significantly influences the electrical and structural properties of the deposited CuO thin films [38]. They have also shown that by increasing the flow rate ratio, the resistivity and mobility of the CuO thin film can be increased due to the reduction of hole concentration. They also reported a p -CuO/ n -Si heterojunction solar cell with the record efficiency of 0.41% by adjusting the Ar and O₂ gas flow rates.

Most recently, Visalakshi et al prepared p -CuO/ n -Si heterojunction solar cell by using the SILAR-deposited technique and investigated the influence of salt concentration on the material and photovoltaic properties of prepared devices [39]. It was shown that crystal quality and efficiency of the prepared samples are significantly influenced by copper sulphate concentration. It was also found that the bandgap of the samples can be tuned by controlling the content of copper salt.

However, the highest reported efficiency is far from the predicted efficiency of 31% as limited by SQL, and there is still a lot of room for improvement. The low efficiency of prepared devices is partly ascribed to the difficulty of doping this material to make it low resistivity n- type semiconductor and prepare the p-n homojunction. Therefore, heterojunction architectures are investigated for all CuO based solar cells. Other important parameters which are responsible for the low efficiency of CuO based solar cells are high series resistance, recombination through interface defect states and bulk non-radiative recombination, and the low built-in potential caused by non-ideal band alignment between the absorber and metal electrode or TCO.

1.5 Overview of thesis

The CuO film can be obtained by various methods such as thermal evaporation [30], electrochemical deposition [40] and other physical deposition methods [39, 41]. Compared to the other physical deposition techniques, RF magnetron sputtering could provide more durable coating. Also, the thickness of the sputtered films can be precisely controlled by adjusting the sputtering power and time. By optimising the deposition parameters, uniform film with improved optoelectronic properties can be obtained.

Crystalline-silicon (c-Si) is the most dominant technology for PV applications. However, this technology is material intensive owing to its low absorption, which acts as a bottleneck for further reduction in cost. By combining thin-film Si with high

absorption materials, it is possible to fabricate cost-effective solar cells.

Fabrication of CuO based solar cells is cheap and it requires low thermal budget, which makes CuO as the most preferred metal oxide based semiconductor for PV applications. It was also demonstrated that the CuO nanoleaves on the pyramid-textured crystalline Si to improve the efficiency of crystalline-Si solar cells [42]. Furthermore, the electron affinity of CuO is similar to that of Si, which makes CuO a suitable candidate for developing p -CuO/ n -Si-based heterojunction solar cells. Higher power conversion efficiency can be realised by (i) improving the quality of the metal oxide, (ii) enhancing the interface quality at the p - n junction, (iii) increasing the carrier concentration, (iv) reducing the series resistance of the absorber layer and (V) enhancing the charge collection efficiency of the absorber layer.

In this thesis, CuO based heterojunction solar cells have been fabricated and characterized. The impact of material quality of the thin film CuO absorber layer and interface properties of p -CuO/ n -Si heterojunction solar cell are investigated in detail. A systematic investigation is carried out to find a suitable doping technique and potential dopants to increase the carrier concentration of CuO for solar cell application. In addition, it is aimed to present the approach to reduce the resistive power loss and enhance the carrier collection efficiency without influencing the material and interface quality.

Chapter 2

Chapter 2- Fabrication and Characterization of CuO based heterojunction Solar Cells

2.1. Fabrication process of CuO based heterojunction solar cells

2.2. Characterization methods

2.1 Fabrication process of CuO based heterojunction solar cells

The fabrication process of p -CuO/ n -Si heterojunction solar cells is described in this section. The flow chart of the fabrication process is presented in Figure 2.1.1.

Figure 2.1.1: Fabrication process of p -CuO/ n -Si heterojunction solar cells.

2.1.1 Pre-cleaning

Si and glass substrates were cleaned by IPA using standard RCA processing. Then, the Si substrates were dipped into diluted hydrofluoric acid (DHF) solution for 4 min to remove the native oxide. All the glass and Si substrates were dried with blowing nitrogen gas before loading into the sputtering chamber.

2.1.2 Sputter deposition

This section briefly introduces the sputtering system, which was employed for thin film deposition, and explains the mechanism of sputter deposition method.

(a) Overview of the sputtering machine

A magnetron sputtering system (Denton Sputtering Discovery-18 System) was

used in this work to deposit thin film of copper oxide on Si and glass substrates. This system is capable of depositing thin films of various metals and oxide materials using direct current (DC) and radio frequency (RF) sputtering techniques. It consists of two DC cathodes (mainly for metal deposition) and one RF cathode (mainly for oxide deposition). The rotating substrate rests between three cathodes. The distance between the each cathode and substrate is around 25 cm. The equipment is able to purge argon (Ar) and nitrogen (N) with different flow rates ranging from 0 to 120 sccm.

(b) Mechanism of magnetron sputter deposition

Magnetron sputtering is an easy controllable low cost method to deposit thin films of a material on a wide range of substrates. RF magnetron sputtering is mainly used to deposit electrically insulating oxide films and is one of the best candidates for large scale thin film deposition. But, it requires impedance matching networks and RF power supplies. In this method, strong magnetic and electric fields are used to create plasma around the surface of the sputtering target. Energetic ions generated in a glow discharge plasma and situated in front of the target bombards the target plate. Due to the interaction between the target material and the Ar-ions, introduced into the vacuum chamber as inert Ar-gas, the source material is eroded in the form of neutral particles. These neutral particles reach the surface of the substrate and get deposited as thin film. Ion bombardment of the surface of the target also causes emitting of secondary electrons, which play an essential role in maintaining the plasma. To further increase the ionization rate by emitted secondary electrons, a magnetic ring is placed under the target

of magnetron sputtering system. One pole of the magnet is created by a ring of magnets around the outer edge of the target and the second pole is situated at the central axis of the target. This magnetic ring traps and circulates the electrons in its field over the target and increases the ionization probability by enhancing the dwell time in the gas. The enhancement of ionization rate provides denser plasma in the vicinity of the target, which results in increased ion bombardment of the target, higher sputtering rate and hence the higher deposition rates at the substrate.

The properties of sputter deposited thin film can be controlled by:

1. Sputtering power: The sputtering power determines maximum energy with which sputtered particles can escape from the target, and the deposition rate as well as sputtering yield
2. Working pressure: Working pressure controls the mean free path of the sputtered material and determines how many collisions happen for the particles on their way from the target to the substrate
3. Substrate temperature: The substrate temperature significantly influences the density and crystallinity of the samples. Depending on the system, it can be adjusted from room temperature up to 800 °C.

Figure 2.1.2 illustrates a) the schematic representation of the sputter deposition mechanism and b and c) images of the real system that was used to conduct the experiment.

(a)

(b)

(c)

Figure 2.1.2: a) A schematic representation of sputter deposition mechanism [43] and b and c) images of the real system which was used to conduct the experiments of this thesis.

2.1.3 Rapid thermal processing (RTP) of copper oxide thin films

After the sputter deposition, the copper oxide coated samples were annealed in nitrogen ambient using the rapid thermal processing (RTP) system, Jet First 150

(Jipelec). The RTP step is required to densify the deposited films, activate the dopant and improve the crystallinity of thin films. In this annealing method, the thermal treatment is performed by heating the samples using an IR-lamp. Once the samples reached the indicated temperature, it is annealed for a short time and then immediately quenched.

An example of thermal treatment recipe, and an image of the RTP machine used for annealing the samples are shown in Fig. 2.1.3.

Figure 2.1.3: (a) Thermal treatment recipe and (b) an image of RTP system used for annealing CuO thin films.

2.1.4 Metallisation of p -CuO/ n -Si heterojunction solar cell

After sample-annealing, Ti/Al metal contacts were sputtered on the front side of p -CuO and back surface of n -Si substrates using metal mask. The typical thickness of Ti/Al used is about 100/100nm. The thickness of Al and Ti was measured by using the

profile meter.

2.2 Characterisation Techniques

This section introduces and briefly explains the characterization methods that were used in this thesis to investigate the properties of CuO based heterojunction solar cells.

2.2.1 Transmission electron microscopy (TEM)

The transmission electron microscope is a useful tool to analyze and evaluate the crystal structure and phases, grain boundaries, line and planar defects and interfaces with atomic scale resolution by using the combination of small probe capabilities, electron diffraction and optical-electron imaging [44]. TEM operates by generating a high energy electron beam and focusing the electrons with electromagnetic lenses onto the very thin sample to provide highly magnified image on a fluorescent screen or record by light sensitive sensor such as a charge-coupled device for displaying on a monitor. It should be mentioned that the TEM sample thickness should be less than 100 μm to let the electrons penetrate the sample. Thus, the sample preparation involves mechanical polishing followed by ion milling to mill a small hole at the samples interface. A schematics representation of the TEM setups was illustrated in Fig. 2.2.1.

Figure 2.2.1. A schematics representation of the TEM setups

In this thesis, high resolution Philips CM300 transmission electron microscopy (HR-TEM) was employed to investigate the microstructure-properties, crystal quality and interface properties as well as the thickness of sputter deposited thin films. Figure

2.2.2 (a) and (b) illustrate the typical cross-sectional image of p -CuO/ n -Si structure and HR-TEM image of the CuO thin film, respectively.

Figure 2.2.2: (a) Cross-sectional and (b) high resolution TEM images of p -CuO/ n -Si heterojunction solar cell

2.2.2 X-ray diffraction (XRD)

X-ray diffraction (XRD) is a non-destructive analytical technique to understand the arrangement of atoms in the crystal structure of materials [45]. It was extensively used in this work to differentiate between amorphous and crystalline materials, provide information about unit cell dimensions, identify the crystalline phases, determine the structure of crystalline materials, etc. The main effect that happens when a monochromatic X-ray beam falls on the target material is the production of scattered radiation by the atoms in the target material. These scattered waves undergo destructive and constructive interference, which in turn results in exhibiting minima and maxima in

the intensity of the scattered radiation. The intensities of the diffracted waves and directions of possible diffractions are influenced by atomic arrangements of materials, and shape and size of the unit cell of the target material, respectively [46]. A schematic representation of the XRD setups was illustrated in Fig. 2.2.3.

Figure 2.2.3. A schematic representation of the XRD setups

In this study, thin film samples were characterized by Bruker AXS General Area Detector Diffraction System (GADDS) in θ - 2θ scan using CuK α ($\lambda = 0.15418$ nm) radiation. A typical XRD spectra of CuO thin film deposited on Si substrate obtained with Cu-K α radiation and wavelength of $1.5456 \text{ \AA}$ is presented in Fig. 2.2.4

Figure 2.2.4: XRD spectra of sputter deposited CuO on Si substrate.

2.2.3 X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) is a spectroscopic method, which is mainly used to investigate the binding energy and density of electronic states as well as chemistry and elemental composition of materials at the surface level [47]. It is also known as ESCA (Electron Spectroscopy for Chemical Analysis) to highlight the importance of chemical information that can be obtained using this technique [48]. XPS spectra are obtained by irradiating the surface of a target material by X-ray beam under ultra-high vacuum conditions and measuring the number of escaped electrons and their corresponding kinetic energy from the top 1 to 12 nm of the sample surface. A schematic representation of the XPS setups was illustrated in Fig. 2.2.5.

Figure 2.2.5. A schematic representation of the XPS setups

A typical Cu2p XPS spectrum of CuO thin film obtained using VG ESCALAB 220i-XL XPS system with monochromatic Al-K α source (1486.6 eV) is presented in Figure. 2.2.6.

Figure 2.2.6: Cu2p XPS spectra of sputter deposited CuO on Si substrate.

2.2.4 Secondary ion mass spectroscopy (SIMS)

In this work, SIMS was used to investigate the elemental distribution of doped and undoped copper oxide thin films, and also the atomic distribution at the *p-n* junction of CuO based heterojunction solar cells. In SIMS, the surface of the specimen is sputtered by focused negative (e.g., O) or positive (e.g., Cs) ion beams (primary ion beams). The ejected secondary ions are then collected and analyzed to determine the elemental composition and distribution-versus-depth profile of the deposited thin films [49]. Ion extraction lenses and mass spectrometer are used to collect the ions and measure the mass to charge ratio of the secondary ions, respectively. A schematic representation of the SIMS setups was illustrated in Fig. 2.2.7.

Figure 2.2.7. A schematic representation of the SIMS setup.

2.2.5 Transient photovoltage (TPV)

Charge transport rate at open-circuit potential (V_{oc}) is an efficient characterization technique to evaluate the performance of solar cells. At V_{oc} , charge density is measurable and flat, which can help to quantitatively compare the charge

density and transport. It allows further investigation on the influence of deposition conditions and different treatments on the charge transport rates. Therefore, the study of charge transport at $\sim V_{oc}$ is of great interest that can provide valuable information in the development of solar cells.

Transient photovoltage (TPV) measurement is a powerful technique that can be used to obtain the information about the charge carrier recombination and extract the carrier lifetimes [50]. Also, it can be used to measure the total carrier concentration in devices. In this work, the small perturbation TPV measurements were carried out to determine lifetime of the photogenerated carrier by exciting p -CuO/ n -Si heterojunction solar cell with a pulsed Nd :YAG laser (pulse width < 5 ns) of wavelength 532 nm. At the same time, the V_{oc} of the p -CuO/ n -Si heterojunction solar cell was controlled by illuminating the device with a strong white light as background.

The laser intensity was reduced by using suitable neutral density filters in order to keep small perturbation compared to the dc-level due to white light illumination. The TPV signals were recorded using a digital oscilloscope (Agilent, 1GHz) for different white light conditions. The transient signals were fitted with a single exponential function in order to estimate the charge carrier lifetime. The current–voltage characteristics were measured using an Agilent B1500A semiconductor device analyzer in dark and under sunlight of air mass 1.5 and 100 mW/cm^2 illumination. A schematic representation of the transient photovoltage measurement setup is illustrated in Fig. 2.2.8.

Figure. 2.2.8. A schematic representation of the transient photovoltage measurement setup.

2.2.6 Atomic force microscopy (AFM)

Atomic force microscopy (AFM) is a type of high resolution scanning probe microscopy, which is commonly used to probe the object surface in nanoscale size. In this method, a mechanical probe is used to gather the information by feeling the surface [51]. Based on the nature of tip motion, AFM is mainly operates in three different modes:

- static mode, also called contact mode
- intermittent contact, also called, tapping mode
- non-contact mode

In this study, Bruker Dimension Icon AFM system was used. The scanned area for all

the samples was $1\ \mu\text{m} \times 1\ \mu\text{m}$, and the images were then processed using the image processing data analyses software. A schematic representation of the AFM setups was illustrated in Fig. 2.2.9.

Figure. 2.2.9. A schematic representation of the AFM setup.

2.2.7 Optical spectroscopy

Optical characterisation of sputtered thin film on glass substrate using the optical spectroscopy is an efficient method to measure transmittance, reflectance, and absorbance [52]. The bandgap of the deposited sample can also be determined based on the measured absorbance data. The transmittance, absorbance and reflectance spectra of

the prepared samples for this study were measured at normal incidence (0°) using double-beam Shimadzu UV-3101 UV-VIS-NIR Scanning Spectrophotometer. A schematic representation of the UV-visible spectrophotometer setups was illustrated in Fig. 2.2.10.

Figure. 2.2.10. A schematic representation of the UV-visible spectrophotometer setup.

2.2.8 Raman spectroscopy

The working principle of the Raman spectroscopy is based on Raman scattering of monochromatic light. Due to the interaction between monochromatic light and molecular vibrations, the energy of the monochromatic light is changed, which provides information about the molecular vibrations in the material. This method can be used for

sample identification and quantification [53]. In this study Raman spectroscopy was used to investigate the microstructure-properties of sputter deposited copper oxide thin films on glass and Si substrates. The films were analyzed using Witec Alpha 300R confocal Raman microscope equipped with a 532-nm Nd:YAG laser. The samples were always measured from the air side to investigate the crystallinity of the samples, defects in the host lattice and structural disorder. A schematic representation of the Raman spectroscopy setup was illustrated in Fig. 2.2.11.

Figure. 2.2.11. A schematic representation of the Raman spectroscopy setup.

2.2.9 I-V Measurements

The I-V measurement is a useful technique to evaluate the performance of the fabricated solar cells and determine the important parameters such as open circuit voltage (V_{oc}), short circuit current (I_{sc}), fill factor (FF) and efficiency (η). In this study, the current density-bias voltage (J-V) characteristics were measured using XES-151S solar simulator that was calibrated earlier with a standard reference Si cell to produce light with AM 1.5G spectrum with a power intensity of 100 mW/cm^2 . The dark current-voltage (J-V) characteristics were performed using Hewlett-Packard 4140B semiconductor parameter analyzer. A schematic representation of the J-V measurement setup was illustrated in Fig. 2.2.12.

Figure. 2.2.12. A schematic representation of the J-V measurement setup.

Chapter 3

Controlling phase transformation and interfacial properties of p -CuO/ n -Si heterojunction solar cells

- 3.1. Introduction
- 3.2. Experimental
- 3.3. Results and discussion
- 3.4. Summary

3.1 Introduction

The growth of high quality single-phase CuO is the primary step to fabricate CuO-based low-cost solar cells. The CuO film can be obtained by various methods such as thermal evaporation [40], electrochemical deposition [27], and other physical deposition methods [23]. However, it has not been easy to control the elemental distribution of copper and oxygen, defect states in copper oxides, and interface quality at the p-n junction, which has held back the development of CuO based devices for several years. Development of high-quality interface at the *p-n* junction is among the most challenging problems for oxide-based heterojunction solar cells. However, it is important to study in order to realise cost effective solar cells.

Recently, Gao et al. reported a *p*-CuO/*n*-Si heterojunction solar cell with a V_{oc} of 330 mV, where CuO was deposited by a sputtering technique [38]. A possible reason for low V_{oc} could be the formation of a thin interfacial oxide at the interface of *p*-CuO/*n*-Si during the sputtering process and the subsequent thermal treatment. Recently, our group has also identified the presence of thin amorphous oxide layer of Si_xO_y at the interface of *p*- β -FeSi₂/*n*-Si for the observed reduction of V_{oc} [7,8,54]. Despite the attempts by several research groups to improve the performance of the CuO-based solar cells, both V_{oc} and J_{sc} remained low to be considered for practical applications.

In this Chapter, *p*-CuO/*n*-Si heterojunction solar cells have been studied using a conventional sputter deposition technique and rapid thermal annealing treatment. The interface at the *p*-CuO/*n*-Si heterojunction was naturally engineered by increasing the working pressure during sputter to demonstrate a high performance heterojunction thin-

film solar cell. Furthermore, the impact of working pressure during sputtering and thermal treatment on the composition, material quality, microstructure, electrical performance, and interfacial properties of CuO-based solar cells have been investigated in detail.

3.2 Experimental

Polycrystalline CuO thin films were deposited on *n*-type Si substrates by radio frequency (RF) magnetron sputtering at room temperature. After cleaning, as described in Chapter 2, the Si-substrates were immediately loaded into the sputtering chamber. The sputter deposition was performed using 3-inch diameter CuO target at room temperature in argon (Ar) ambient with a base pressure of $\sim 10^{-7}$ Torr. The RF power was maintained at 150 W for all the samples. CuO-deposition was conducted at four different working pressures of 3.3, 8.3, 30, and 35 mTorr corresponding to the argon gas flow of 25, 55, 100, and 125 sccm, respectively. All the samples were then annealed at 300 °C in nitrogen ambient using rapid thermal annealing technique for the duration of 1– 60 min. Structural quality and chemical composition of the sputter-deposited CuO film were studied by X-ray diffraction (XRD) in θ – 2θ scan using a Cu K α ($\lambda = 0.15418$ nm) radiation, Raman spectroscopy, and X-ray photoelectron spectroscopy analysis. The microstructural analysis and the interface quality between *p*-CuO and *n*-Si substrate were studied using high-resolution transmission electron microscopy (HRTEM) analysis and energy-dispersive X-ray spectroscopy (EDX) analysis.

Metal contact of the solar cells significantly influences the efficiency of the prepared devices. It has been found that at the interface of copper oxide, most of the metals formed copper enriched region due to straight reduction or subsequent interdiffusion phenomena at the copper oxide/metal interface. Siah et al have shown that employing Pd is an effective method to minimize the formation of copper enriched layer [55]. However, Pd is costly, and hence we have considered inexpensive Ti metal. But, Ti can be easily oxidized. Therefore, an environmentally stable metal is required to avoid the oxidation of Ti. Al is one of the environmentally stable and inexpensive metal that can be used for this propose. Ti/Al is also widely used as the metal contacts for solar cell with Si substrate [8, 54]. Moreover, the efficiency of *p*-CuO/*n*-Si heterojunction solar cell with Pd metal contact is similar to the efficiency of the same solar cell with Ti/Al metal contact. Therefore, Ti/Al metal contacts were sputtered on the front side of *p*-CuO and back surface of *n*-Si substrates. Figure 3.1 shows the schematic diagram of the *p*-CuO/*n*-Si heterojunction solar cell.

The small perturbation TPV measurements were carried out to determine the photogenerated carrier lifetime by exciting *p*-CuO/*n*-Si heterojunction solar cell with a pulsed Nd :YAG laser (pulse width <5 ns) of wavelength 532 nm and illuminating the device with a strong white light as background. The laser intensity was reduced by using suitable neutral density filters in order to keep small perturbation compared to the dc level due to white light illumination. The TPV signals were recorded using a digital oscilloscope (Agilent, 1GHz) for different white light conditions. The transient signals were fitted with a single exponential function in order to estimate the charge carrier lifetime. The current–voltage characteristics were measured using an Agilent B1500A

semiconductor device analyzer in dark and under sunlight of air mass 1.5 and 100 mW/cm² illumination.

The size of the samples investigated was around 5 mm by 5mm and were illuminated by a solar simulator from the top. The size of the shadow mask used is 1 mm by 1 mm in all the cases. All the JV characteristics were measured at least 5 times. It may be noted that all the experiments were also repeated at least 3 times to ensure reliable data.

Figure 3.1: Schematic diagram of *p*-CuO/*n*-Si(100) heterojunction solar cell.

3.3 Results and discussion

Figure 3.2 (a) shows the XRD spectra of CuO thin films deposited at a working pressure of 3.3 mTorr and annealed at 300°C for the duration of 1, 25, 50, and 60 min.

Figure 3.2. X-ray diffraction analysis of sputter-deposited CuO on *n*-Si(100) substrate. Impact of (a) thermal treatment and (b) working pressure on the structural property of CuO films.

The two peaks observed in the spectra located at 38.9° and 36.7° are associated with CuO (111) and Cu_2O (111) planes, respectively [18]. The evolution of Cu_2O phase can be seen as the annealing time is increased from 1 to 60 min. Moreover, the intensity of the peaks appears to increase with the annealing duration indicating improvement in the crystal quality of sputter-deposited film through thermal treatment. A series of samples were investigated to study the effect of working pressure during sputter deposition on the crystal quality of CuO thin film. Figure 3.2 (b) shows the XRD spectra of CuO layers that were deposited at different working pressures of 3.3, 8.3, 30, and 35 mTorr and annealed at 300°C for 1 min. There are two peaks at 35.6° and 38.9° , which correspond to CuO (002) and CuO (111) planes, respectively [56]. With the increase of working pressure from 3.3 to 35 mTorr during sputter deposition, the peak intensity of CuO (002) increases, suggesting the improvement in the crystal quality of CuO thin film

without significant phase transition, unlike in the case of thermal treatment as seen in Figure 3.2 (a).

At low working pressures, the energetic O^2 and Cu^{2+} particles arrive separately onto the substrate resulting in the formation of CuO in (111) plane. By increasing the Ar flow rate to 100 sscm (corresponding to a working pressure of 30 mTorr), most of the highly energetic particles lose part of their energy, and it is more likely that O^{2-} and Cu^{2+} particles arrive at the same time onto the Si surface and form CuO in (002) plane. The transition of the preferred orientation of CuO thin film from (111) to (002) may be due to the change in the arrangement of O^{2-} , which is affected by the surface energy, the energy of the arriving particle to the substrate, and the strain energy of the growing film; all are dependent on the working pressure during the deposition [56–58].

The crystal quality improvement and phase transformation have been investigated by Raman spectroscopy. The peaks at 119, 585, and 970 cm^{-1} correspond to the formation of CuO [59, 60], while the peak at 520 cm^{-1} is from the Si [7]. The peaks associated with Cu_2O are observed at 161, 218, 305, and 439 cm^{-1} [61]. The intensity of the Cu_2O peak at 305 cm^{-1} is observed to be significantly influenced by annealing time and is more pronounced for the sample annealed for 50 min. It is also worth to note that the peak intensity at 1110 cm^{-1} increases with annealing duration, which suggests the presence of elemental copper (Cu) in the oxide [62], as shown in Figure 3.3 (a). Figure 3.3 (b) shows the comparison of Raman characteristics of $p\text{-CuO}/n\text{-Si}$ structure with the CuO film deposited at 3.3, 8.3, and 30 mTorr. The intensity of the broad copper peak is significantly affected by the working pressure and is more pronounced for the sample deposited at low working pressure. From XRD and Raman study, it is clear that the

crystal quality can be improved and the presence of Cu can be suppressed naturally by the increasing working pressure during sputtering.

Figure 3.3. Raman spectra of sputter-deposited CuO on *n*-Si(100) substrate (a) annealed at 300 °C for 1, 25, and 50 min and (b) deposited at the working pressure of 3.3, 8.3, and 30 mTorr.

Figure 3.4 (a) shows Cu2p XPS spectra obtained from CuO samples deposited at 3.3 mTorr and annealed at 300°C for different durations of 1, 25, and 50 min. The Cu 2p peaks have been located at binding energies of 934.0 and 932.4 eV together with the satellites located between 940.0 and 970.0 eV [63,64].

Figure 3.4. Cu2p spectra of CuO deposited on *n*-Si(100) substrate. (a) The CuO phase changes to Cu₂O after thermal treatment of CuO for 50 min at 300°C. (b) Impact of working pressure on the formation of CuO films. At a higher working pressure, high crystal quality CuO can be obtained.

The samples that have been annealed for 1 min show a peak at 934.0 eV, suggesting the formation of dominating CuO phase. By increasing the annealing time from 1 to 25min, full-width at half maximum (FWHM) increased from 2.6 to 2.9 eV. The increase in FWHM and reduction of relative intensity of Cu2p peak indicate the presence of surface oxygen [65]. The samples that have been annealed for 25min show mixed phase of CuO and Cu₂O. By increasing the annealing time up to 50min, the core level binding energy and the corresponding FWHM value become 932.4 and 1.0 eV, respectively. These observations indicate the phase transformation from CuO to Cu₂O, which is in good agreement with the XRD and Raman analysis. The observation of satellite characteristics at higher binding energies further confirms that the sample annealed for longer duration is Cu₂O phase [63,64]. Figure 3.4 (b) shows Cu2p XPS spectra of the films deposited at various working pressures of 3.3, 8.3, and 30mTorr and

annealed at 300°C for 1min. The peaks obtained are associated with CuO phase, and no phase transition is observed.

To understand the impact of working pressure and thermal treatment on the structural and interface quality of p -CuO/ n -Si, HRTEM analysis has been performed. Figure 3.5 shows the cross-sectional image of p -CuO/ n -Si structure.

Figure 3.5. Cross-sectional transmission electron microscopy image of 150-nm-thick CuO films deposited on n -type Si(100) substrates at a working pressure of 3.3 mTorr: (a) as-deposited, (b) annealed at 300°C for 1 min, and (c) annealed at 300°C for 50 min. The same thickness CuO film deposited at a working pressure of 30 mTorr and annealed for 1 min at 300°C is shown in (d).

The thickness of CuO thin film deposited on Si at the working pressure of 3.3 mTorr is 150 nm. There is a presence of thin amorphous interfacial layer of ~2.8 nm between p -CuO and n -Si substrate for the as-deposited CuO, as shown in Figure 3.5 (a). The interfacial layer formation may be attributed to the presence of residual oxygen in the chamber. The interfacial layer thickness was found to increase to ~3.8 and 4.3nm,

when annealed for 1 and 50 min, respectively, as shown in Figure 3.5 (b) and (c). However, it was found that the interfacial layer thickness decreased to 2.5 nm when the CuO film was deposited at a higher working pressure of 30 mTorr and annealed at 300°C for 1 min, as shown in Figure 3.5 (d). In addition, the presence of a thick copper-rich oxide (Cu_xO_y) layer (thickness ~30 nm) was also observed between the interfacial layer and CuO active layer, for the as-deposited CuO (Figure 3.5 (a)). The thickness of this Cu_xO_y layer increased to ~35 nm when the CuO was annealed at 300°C for 1 min, as shown in Figure 3.5 (b). However, it reduced to ~27 nm for the film deposited at 30 mTorr for the same annealing condition, as shown in Figure 3.5 (d). The EDX line scanning across *p*-CuO/*n*-Si interface showed the presence of Si, oxygen (O), and Cu in the amorphous interfacial layer, indicating that this is a complex oxide of $\text{Si}_a\text{Cu}_b\text{O}_c$. At the interface, the atomic percentage of elemental Si, Cu, and O are 38.2, 13.6, and 48.2, respectively. The EDX analysis has also been carried out at different regions of CuO film on Si substrate to further investigate the elemental distribution of Cu and O. The results of EDX analysis and the corresponding TEM images are presented in Table 3.1. According to the EDX analysis, for all the samples, there is a Cu-rich oxide layer between the thin interface amorphous layer and CuO layer. The samples deposited at the high working pressure shows uniform distribution of elemental Cu and O in the bulk CuO layer, and the percentage of elemental Cu is less in the Cu-rich layer compared with samples deposited at lower working pressure. The reduction of the Cu_xO_y thickness and elemental Cu may be due to the reduction of residual oxygen in the chamber as the working pressure is increased during deposition. A similar observation was also made from Raman characteristics. The presence of thin amorphous oxide, Cu-rich oxide layer,

and elemental Cu at the p–n junction degrade the interfacial quality and device performance. Therefore, sputter deposition conditions can be optimized to engineer the interfacial layer formation without inserting any passivation layer.

Table 3.1. The results of energy-dispersive X-ray spectroscopy analysis of the samples prepared at different working pressure and annealing conditions

Working pressure and annealing condition	AsD, 3.3 mTorr				RTA, 1min, 3.3 mTorr				RTA, 50 min, 3.3 mTorr				RTA, 1min, 30 mTorr

Region	I	II	III	IV	I	II	III	IV	I	II	III	IV	I	II	III	IV
O K (Atomic%)	58	55	54	44	62	46	37	28	41	41	40	37	51	51	52	45
Cu K (Atomic%)	42	45	46	56	38	54	64	72	59	59	60	63	49	49	48	55

To further investigate the impact of working pressure during deposition on the interface quality as well as the performance of *p*-CuO/*n*-Si heterojunction solar cells, TPV spectroscopy and carrier lifetime analysis have been carried out. Figure 3.6 (a) shows the TPV characteristics of the solar cells. Comparison of photogenerated carrier lifetime with V_{oc} is shown in Figure 3.6 (b). The change of carrier lifetime with V_{oc} is very drastic for the device fabricated at a working pressure of 3.3 mTorr compared to the device fabricated at the higher working pressure of 30 mTorr. This change can be attributed to the increased recombination rate with the increase of carrier concentration. The presence of high degree of traps and the poor charge transport at the interface enhances the recombination rate. Consequently, the carrier lifetime is reduced drastically.

Figure 3.6. Transient photovoltage and carrier life time characteristics of the samples that are deposited under different working pressures during CuO deposition.

In order to understand the performance of the p -CuO/ n -Si heterojunction solar cells with CuO layer deposited at different working pressures, PV characteristics have been studied. The dark current and photocurrent characteristics of solar cells with CuO deposited at 3.3 mTorr and annealed at 300°C for 1, 25, and 50 min are shown in Figure 3.7. The dark current characteristics demonstrate p - n junction behaviour as illustrated in Figure 3.7 (a) and show rectifying behaviour with the forward current to reverse current ratio of 104. The inset of Figure 3.7 (a) shows the dark current characteristics in log scale. Three apparently different regions are observed and are labelled as (I), (II), and (III). In region (I), which corresponds to low applied bias, the dark current increases linearly with the bias voltage and the electrical behaviour is like Ohmic characteristics. This is due to the presence of the thin interfacial layer of SiO_x [66]. In this region, the number of injected electrons is very small, and all the electrons are generated thermally [66]. Consequently, the electrical resistance of this region is very high. In region (II), the

conduction mechanism can be explained by tunneling-recombination theory, and in region (III), the dominant mechanism of conduction is the space charge limited current [66,67]. By increasing the annealing duration from 1 to 25min, the voltage range of regions (I) and (II) is significantly changed. It is worth to note that the increase of region (I) enhances the overall resistance, which degrades the performance of the device [66,67]. On the other hand, the reduction of voltage range of region (II) reduces the recombination and enhances the performance of the devices [34,66,67].

Figure 3.7. Impact of thermal treatment on *p*-CuO/*n*-Si heterojunction solar cells (a) dark current and (b) photo current.

Figure 3.7 (b) shows photocurrent characteristics of *p*-CuO/*n*-Si solar cells with the V_{oc} of 380mV and J_{sc} of 1.2mA/cm² for the CuO films annealed at 300°C for 1min. The CuO film annealed for 25 and 50 min shows higher photocurrents compared with

the films annealed for 1min because of improvement in the crystal quality as discussed. However, V_{oc} degrades for the device structure annealed for 25 min. As already shown by HR-TEM image (Fig. 3.5), increasing the annealing time influences the interface properties between sputter deposited CuO and Si substrate. The thickness of amorphous like isolation layer of Si_xO_y of the samples annealed for longer time is found to become thicker, which enhances the interfacial recombination. As a result, despite the improvement of the crystal quality of the samples annealed for 25min, the V_{oc} degrades. In the case of samples annealed for 50 min at 300°C, V_{oc} actually increased even though the interfacial layer thickness is higher compared with the samples annealed for 1 and 25min. This may be the result of the partial phase transformation from CuO to Cu_2O . The bandgap energy of Cu_2O is around 2eV which is higher compared to CuO with bandgap of around 1.4eV, and hence, the higher value of V_{oc} observed. XRD, Raman characteristics, and XPS analysis also confirm the partial phase transformation occurring in the films annealed for 50 min at 300°C.

The presence of thicker interfacial layer and Cu-rich oxide layer between p -CuO and n -Si may induce Fermi level pinning, which may result in low effective built-in potential in p -CuO/ n -Si heterojunction. Consequently, a small V_{oc} is obtained for the p -CuO/ n -Si heterojunction solar cells. Figure 3.8 (a) shows the current density–voltage characteristics of p -CuO/ n -Si heterojunction solar cells with identical thickness of CuO deposited at two different working pressures of 3.3 and 30 mTorr followed by annealing at 300°C for 1 min. A high open-circuit voltage of 509mV with a short-circuit current of 4 mA/cm² for the device structure fabricated at a higher working pressure. A

photocurrent of 12 mA/cm^2 was observed at an applied bias of 3V for the same device. To the best of our knowledge, the V_{oc} of 509mV is the highest reported value for $p\text{-CuO}/n\text{-Si}$ heterojunction solar cells. The improvement of the device performance is due to the better interface quality and bulk CuO quality as observed by XRD, XPS, Raman characteristics, HRTEM, and TPV measurements. The partial enhancement of V_{oc} is due to the improvement of crystal quality. Increasing the grain size of samples reduces the losses at the grain boundaries and influences the V_{oc} . As also shown at Fig 3.7 (b) and 3.8, there are clear kinks for the all of the prepared samples. The main origin for the kink is due to the existence of amorphous like isolation layer of Si_xO_y and formation of copper rich interfacial layer. As already demonstrated, by increasing the working pressure during the sputtering of copper oxide, the thickness of isolation layer of Si_xO_y is reduced, which has influenced the S shape of J-V characteristics, as shown in Fig. 3.8 (b). The efficiency of the best device is $\sim 0.36\%$. This is primarily due to the poor fill factor (FF) and the presence of interfacial layer at the $p\text{-}n$ junction. Even though the efficiency of the device is low, the present work shows the feasibility of CuO-based solar cells on Si substrate with high open-circuit voltage and photocurrent. By eliminating the interfacial layer and improving the FF , the performance of the devices can be improved. As a preliminary study to improve the FF of the device, nitrogen (N) dopant was introduced at the top layer of CuO by sputter deposition of CuO in nitrogen and argon ambient.

Figure 3.8. (a) Comparison of dark current and photocurrent densities of p -CuO/ n -Si heterojunction solar cells with CuO deposited at 3.3 and 30 mTorr working pressures. The V_{oc} and photocurrent increased significantly for the sample deposited under high working pressure. Inset of the figure shows schematic diagram of nitrogen-doped CuO device. (b) Variation of open-circuit voltage and short-circuit current of the solar cells.

The schematic diagram of the nitrogen-doped device is shown in the inset of Figure 3.8(a). The N-doped CuO was deposited at 30 mTorr with the argon and nitrogen gas flow rate of 70 and 10 sccm, respectively. Figure 3.8(b) shows the variation of short-circuit current and open circuit voltage of the solar cells fabricated with and without nitrogen-doped CuO. Results indicate that FF and efficiency of the solar cells have improved significantly, and N-doping of CuO seems to be a promising technique. Table 3.2 summarizes the solar cell parameters of photocurrent density (J_{ph}), short-circuit current density (J_{sc}), V_{oc} , FF , and efficiency (η) of all the samples studied.

Table 3.2. J_{ph} , J_{sc} , V_{oc} , FF , and η of the heterojunction solar cells.

Solar cell parameter	300°C for 1min	300°C for 25min	300°C for 50min	300°C for 1min (HP)	300°C for 1min (HP+ N)
J_{ph} @ -3 V (mA.cm ⁻²)	2.9	4.4	5.1	12.1	13.5
J_{sc} (mA.cm ⁻²)	1.2	1.3	1.3	4.0	6.4
V_{oc} (mV)	380	190	404	509	494
FF (%)	28	30	19	20	32
η (%)	0.14	0.08	0.11	0.36	1.0

3.4 Summary

The cupric oxide thin-film solar cells were prepared by RF magnetron sputtering. It has been shown that the crystalline quality and phase transformation of sputtered copper oxide thin films substantially depend on the working pressure during sputter deposition and annealing time during thermal treatment. XPS, XRD, and Raman spectral analysis show formation of dominating CuO phase for the as-deposited films and annealed at 300°C for 1 min in nitrogen ambient. A gradual phase transformation from CuO to Cu₂O was observed with the increase of annealing time. It was found that the crystalline quality and interface quality can be improved by increasing working pressure during deposition. The impact of interface traps on the performance of CuO based solar cells was studied, and it was shown that charge carrier recombination rate can be reduced by increasing the working pressure. PV properties with the high open-circuit voltage of 509mV and short-circuit current of 4mA/cm² can be obtained for the *p*-CuO/*n*-Si heterojunction solar cells. Further improvement in FF and efficiency has been achieved by introducing N-doped CuO of the solar cell structure.

Chapter 4

Improvement of thin film CuO property and interfacial quality *p*-CuO/*n*-Si heterojunction solar cell

- 4.1. Introduction
- 4.2. Experimental
- 4.3. Results and discussion
- 4.4. Summary

4.1 Introduction

The highest obtained power conversion efficiency of CuO based solar cell is far from the theoretical conversion efficiency which is about 31%. The quality of the metal oxide and the interface quality at the p-n junction are crucial for oxide-based heterojunction solar cells. Thus, the low efficiency exhibited by CuO based heterostructure solar cells can be attributed to poor material quality of CuO and its interface with the *n*-type semiconductor. In the previous chapter, we have demonstrated sputter deposited *p*-CuO/*n*-Si heterojunction solar cells with the efficiency of 1%. It was hypothesized that the formation of interface native oxide and Cu-rich IL at the p-n junction are responsible for the poor performance of the device. The impact of interface native oxide on the performance of *p*-CuO/*n*-Si heterojunction solar cells was studied in detail. It was shown that the performance of *p*-CuO/*n*-Si solar cell can be improved significantly through the reduction of native oxide thickness by increasing the working pressure during sputter deposition. However, the working pressure had only marginal impact on the formation of Cu-rich IL. Towards this, in this chapter of thesis, we have introduced two-step sputter deposition to improve the interface quality at the p-n junction and thin film CuO property. The formation of Cu rich IL and its impact on the performance of *p*-CuO/*n*-Si heterojunction solar cells have been studied in detail in this work.

A series of CuO thin film samples were deposited using conventional RF sputtering technique with different sputtering power varying from 50W to 150 W. For the two-step sputtering, CuO thin film was first deposited at 50W and subsequent thick

CuO film was deposited at 150 W. The interface properties between *p*-CuO and *n*-Si, bulk CuO properties, microstructure analysis, and surface morphology of CuO thin film were investigated using the X-ray Diffraction (XRD), secondary ion mass spectroscopy (SIMS), high resolution transmission electron microscopy (HR-TEM), UV-VIS Spectrophotometer, and atomic force microscopy (AFM).

4.2 Experimental

CuO thin film was deposited on n-type Si wafers and glass substrates by radio frequency (RF) magnetron sputtering at room temperature. Si wafers and glass substrates were cleaned by IPA using standard RCA processing. Then, Si substrates were dipped into diluted hydrofluoric acid (DHF) solution for 4 min to remove the native oxide. All the glass and Si substrates were dried with blowing nitrogen gas before loading into the sputtering chamber. Sputter deposition was carried out using a stoichiometric CuO target with pure Ar gas as the sputtering gas with a base pressure of 10^{-7} Torr.

CuO thin film was deposited with different RF power of 50 W, 100 W, and 150W at a working pressure of 3.3 mTorr. For the two-step sputtering method, CuO thin film was first deposited with an RF power of 50W and subsequently thick CuO was deposited with an RF power of 150 W. All the samples were annealed at 300°C for 1min in nitrogen ambient using rapid thermal annealing technique to improve the interface quality and bulk oxide properties. Structural quality of the sputter-deposited CuO films was studied by X-Ray Diffraction (XRD) using a Bruker AXS General Area Detector Diffraction System (GADDS) in θ - 2θ scan using a CuK α ($\lambda=0.15418$ nm) radiation. Furthermore, material quality of sputter deposited CuO films evaluated using Raman

spectroscopy measurements (Witec Alpha 300R confocal Raman microscope equipped with a 532-nm Nd:YAG laser). The microstructural analysis, crystal quality, and the interface properties between *p*-CuO and *n*-Si substrate were studied using high-resolution Philips CM300 transmission electron microscopy (TEM). Grain height distribution and surface morphology of the sputter deposited CuO films have been investigated by using Bruker Dimension Icon atomic force microscopy (AFM). Current density-voltage (*J-V*) characteristics of the p-n junction solar cells were performed using a Hewlett-Packard 4140B semiconductor parameter analyzer.

Photovoltaic (PV) characteristics of the *p*-CuO/*n*-Si heterojunction solar cells prepared using sputtering power of 50 W, 100 W, 150W, and 50W followed by 150W were measured with a XES-151S solar simulator that has been calibrated with a standard reference Si cell to produce light with AM 1.5G spectrum of power intensity 100 mW/cm².

4.3 Results and discussion

Chemical composition of the sputter-deposited CuO film was studied by X-ray photoelectron spectroscopy using a VG ESCALAB 220i-XL XPS system with monochromatic AlK α source (1486.6 eV). The XPS spectra of thin film copper oxide sputter deposited at various RF power levels of 50 W, 100 W, and 150W are compared in Fig. 4.1. The observed peaks at 956 eV and 933 eV correspond to the binding energies of Cu 2p_{1/2} and Cu 2p_{3/2}, respectively, due to spin-orbit splitting of Cu2p [63]. The other peaks observed between 940 eV and 970 eV are related to the satellites, indicating the formation of CuO film on the surface of the samples. Also, as illustrated in this figure,

there is no shift in the binding energy of O1s spectra (Figure 4.1: (b)) and Cu2p spectra of the samples prepared at different RF sputtering power, further confirming that there is no phase change in the CuO film on the sample surface.

Figure 4.1: (a) Cu2p and (b) O1s XPS spectra of sputtered CuO on Si substrate. The CuO was deposited using different RF power and annealed at 300°C for 1 min in nitrogen ambient.

Effects of sputtering power on the grain height distribution and surface morphology of CuO samples are illustrated in Fig. 4.2. As shown in Fig. 4.2, smoother surface morphology with smaller grain height is obtained for the CuO samples prepared at the low sputtering power of 50W compared to samples prepared at higher power levels. The grain height distribution and surface morphology can be influenced by many parameters such as island forming, nucleation, and adatom adsorption.

Figure 4.2: (a) Grain size distribution and (b) AFM images of the CuO samples prepared at sputtering power of 50, 100, and 150W.

It was shown in the model proposed by Bartelt et al. [68] that the island size depends on the deposition rate (r), which is controlled by the sputtering power and the diffusion rate (h_0) that depends on the growth temperature. Then, the island size distribution can be determined by the ratio $D=h_0/r$. In Bartelt et al. model [68] as the ratio D increases, the deposited adatom can travel farther. In our case, the deposition rate of samples prepared at the RF power of 150W is almost 3 times faster than that for the samples prepared at 50W. However, since the deposition was done at room temperature, the diffusion rate is almost same for all the samples. This may decrease the island

density and may lead to bigger grain size for the samples prepared at the higher sputtering power [69]. Enhancement of surface roughness has impact on the light scattering and consequently changes the transmittance and absorbance.

Figure 4.3: (a) Transmittance and (b) reflectance spectra of CuO samples prepared at sputtering power of 50W, 100 W, and 150 W.

Transmittance and reflectance spectra of CuO films have been measured with Shimadzu UV-3101PC scanning spectrophotometer. Figure 4.3 shows the transmission and reflectance spectroscopy of CuO film deposited at different RF power. With the increase of RF power, there is a significant reduction of transmission near IR region. However, the effect of sputtering power on the reflectance is negligible. The high surface roughness of the samples prepared at the RF sputtering power of 150W leads to more light scattering and thus reduces the transmittance and increases absorption.

The optical bandgap of the prepared samples at different sputtering power were determined. It was found that by increasing the sputtering power from 50 W to 150 W the optical bandgap slightly increased from 1.35 eV to 1.4 eV. The increase in the optical band gap with sputtering power is mainly ascribed to the increase in the grain size of the samples. Deposition at high sputtering power causes higher energy of adatoms and increases the diffusion of sputtered species towards the previously formed grains, which results in larger grain size. The increase in the grain size leads to the decrease in grain boundary scattering (the larger the grain size, the higher hole mobility) and decrease in density of defect states, which affects tailing of bands.

Elemental distribution of copper (Cu) and oxygen (O) was investigated using time of flight secondary ion mass spectrometry (ToF-SIMS). Figure 4.4 shows the elemental distribution of Cu and O of CuO deposited using RF power of 50W, 100W, and 150W.

Figure 4.4: SIMS depth profiles of elemental (a) oxygen and (b) copper from p -CuO/ n -Si heterostructure grown at different RF power and annealed at 300°C for 1 min in nitrogen ambient. The Cu-rich IL is marked with the circle.

The O elements were distributed uniformly irrespective of RF power used. However, the distribution of Cu is significantly influenced by the RF sputtering power. At a low sputtering power, Cu was distributed uniformly across CuO film. With the increase of RF power, the intensity of elemental Cu shows an increasing trend between CuO and silicon substrate, as observed in Fig. 4.4 (b). The highest peak intensity was obtained for the film deposited at 150W. This region is the Cu-rich interfacial layer and its thickness is also found to change with RF power. The elemental Cu may degrade the electrical performance of the devices. Although CuO films deposited at high RF power show better crystal quality, optical property and surface morphology, the interface quality at the p - n junction becomes degraded. Therefore, it is essential to control and improve the interface quality as well as bulk properties of CuO. By employing two step

sputtering method, it is possible to deposit high crystal quality CuO film with thinner Cu-rich interfacial layer. In the following sections, we will discuss the improvement of both the crystal quality and interface properties of samples prepared by two-step sputtering technique through Raman analysis, XRD, and photovoltaic characteristics.

Figure 4.5: Raman spectra of the CuO samples prepared at sputtering power of 50, 100, and 150W.

Figure 4.5 shows the Raman spectra of CuO thin film deposited at different sputtering power. The peak at 522 cm⁻¹ is associated with the Si substrate. The peak observed at 1121 cm⁻¹ corresponds to elemental Cu. The peaks at 119, 305, 595 cm⁻¹ are associated with CuO and Cu₂O [59, 61]. It can be seen that the peak intensity of elemental Cu increases with the increase of RF power, which is in good agreement with the observation made from SIMS analysis. The film deposited using two-step sputtering

shows similar crystal quality of CuO that was deposited at 150W, with lower peak intensity for elemental Cu. In the two-step sputtering method, since CuO film was deposited at 50W first followed by a thick CuO deposited at 150W, it maintained the higher crystal quality and lower elemental Cu at the interface compared to single-step sputter deposited sample.

The formation of Cu-rich IL and interface properties of *p*-CuO/*n*-Si heterojunction solar cell were also investigated by high-resolution transmission electron microscopy (HRTEM) analysis. Fig. 4.6 illustrates the cross sectional HRTEM images of as-deposited (AsD) and annealed CuO films. The CuO was deposited with sputtering power of 50W, 100W, 150W, and 50W+150W. The HRTEM image shows the presence of a thin interfacial native oxide layer on Si surface and Cu-rich IL between sputter deposited CuO and Si substrate. The thickness of the Cu-rich IL layer is found to be the same even after annealing the CuO film at 300°C for 1min. The thickness of Cu-rich IL was found to vary with RF power. It suggests that the Cu-rich IL was most likely formed during the sputter deposition. The thicknesses of Cu-rich IL layer are 14nm, 25 nm, and 45 nm for the films grown at 50 W, 100W, and 150W, respectively.

Figure 4.6: HRTEM of *p*-CuO/*n*-Si heterojunction. *P*-CuO was deposited on *n*-Si using different RF power of 50W, 100W, 150W, and by using two step sputter. There is significant impact of RF power on the material quality and interface properties.

On the other hand, the crystal quality of CuO film improved with the increase of RF power. The results are in good agreement with Raman analysis, where we observed that the crystal quality of CuO and intensity of elemental Cu peak increased with RF power. It is worth to note that the CuO film grown by using 50W followed by 150W shows crystal quality similar to CuO film grown at 150W with the thinnest Cu-rich IL.

The thickness of the interfacial native oxide layer has also slightly reduced when two-step sputter deposition was employed.

The XRD spectra of copper oxide thin films with the sputtering power of 50, 100, and 150W are shown in Fig. 4.7. The sputter deposited samples show two major preferred orientations. The diffraction peak observed at $2\theta=35.482$ and 38.956 have been identified as the (111) and (002) diffraction lines of CuO, respectively [7].

Figure 4.7: XRD pattern of the CuO films prepared at sputtering RF power of 50, 100, and 150W. The XRD pattern of the CuO sample prepared with two-step sputtering method was also illustrated.

The corresponding full width half maximum (FWHM) of the samples are presented in Table 4.1. The CuO film deposited at higher RF power shows sharp diffraction peak and narrow FWHM. This result suggests that by increasing the RF

power during deposition, it is possible to improve the crystalline quality of CuO thin film. By increasing the sputtering RF power, the positive ions in the glow discharge plasma may gain higher energy, and consequently the mobility of the particles in the surface of the films may increase. Therefore, the particles can reach the favoured crystallographic sites more readily and enhance the nucleation, which can improve the crystal quality.

Table 4.1. XRD FWHM of CuO samples on Si substrate.

Crystal orientation	(002)	(002)	(002)	(002)	(111)	(111)	(111)	(111)
Sputtering power (W)	50	100	150	50 + 150	50	100	150	50 + 150
FWHM (degree)	0.5	0.5	0.4	0.4	0.6	0.5	0.4	0.4

Titanium/Aluminium bi-layer electrodes were sputter deposited on both the front side of *p*-CuO and back side of *n*-Si, as shown in Fig. 4.8.

Figure 4.8: Schematic diagram of *p*-CuO/*n*-Si heterojunction solar cells.

The current density-voltage (J - V) characteristics of the solar cells prepared using a single-step and two-step sputter deposition method at a constant working pressure of 3.3mTorr are illustrated in Fig. 4.9.

Figure 4.9: (a) Current-voltage characteristics of p -CuO/ n -Si heterojunction solar cells. (b) Elaboration of Fig. (a) to show the variation of short-circuit current and open circuit voltage of p -CuO/ n -Si solar cells. The solar cells were fabricated with various RF power and two-step sputter at a working pressure of 3.3mTorr.

Figure 4.9 (a) shows the variation of the dark-current and photocurrent of the heterojunction solar cells. Figure 4.9 (b) is enlargement of Fig. 4.9 (a) to illustrate the noticeable variation of open-circuit voltage and short-circuit current of the solar cells. The PV parameters V_{oc} , J_{sc} , FF and η determined for the various solar cells are presented in Table II. Among the three types of p -CuO/ n -Si solar cells prepared with single step sputter deposition of CuO, the samples deposited at the low sputtering power of 50W showed the best PV properties with a V_{oc} of 438 mV, J_{sc} of 3.3 mA/cm^2 , FF of 26.3%, and η of 0.38%.

It is worth noting that the PV properties degraded with the increase of sputtering power even though the crystal quality and optical properties of the CuO film improved with RF sputtering power. The significant enhancement of J_{sc} of p -CuO/ n -Si heterojunction solar cell prepared at the sputtering RF power of 50W is due to the thinner Cu-rich IL, as shown by SIMS and Raman analysis. The HRTEM analysis (Fig. 4.6) also showed that there is a presence of Cu-rich IL and the thickness of Cu-rich IL increased as the RF power was increased, keeping all other deposition parameters constant.

This suggests that the presence and the thickness of Cu-rich IL play a critical role in the performance of p -CuO/ n -Si heterojunction solar cells. In fact, the thin Cu-rich IL can reduce the distribution of interface states and recombination loss at the p - n junction, thus improving the open-circuit voltage and short-circuit current. However, the FF of the solar cell obtained is lower compared to the cells prepared at higher RF power levels. Enhancement of the FF for solar cells prepared at higher RF power levels is due to the improvement of bulk crystal quality of the sputtered films, as shown by XRD, Raman analysis, and HRTEM analysis. Therefore, to improve the both CuO material quality and interface quality at p -CuO and n -Si junction, two-step sputtering method was introduced. In this method, firstly a thin layer of CuO was sputtered on n -Si substrate at a low sputtering power of 50W to reduce the thickness of Cu-rich IL.

Subsequently, thick layer of CuO was deposited at a high sputtering power of 150W to improve the material quality of the sputtered CuO film. The PV properties of the solar cells fabricated by using two-step sputtering method improved significantly compared to the cells fabricated using a single step deposition, as shown in Fig. 4.9. The

J_{sc} , FF , and g significantly increased from $3.3\text{mA}/\text{cm}^2$, 26.3%, and 0.38% to $4.5\text{mA}/\text{cm}^2$, 42.9%, 0.82%, respectively.

HRTEM image and energy-dispersive X-ray spectroscopy (EDX) analysis showed that there exists a 2.5 nm thin interfacial native oxide of $\text{Si}_x\text{Cu}_y\text{O}_z$ layer at $p\text{-CuO}/n\text{-Si}$ interface. The presence of thin amorphous oxide layer at the $p\text{-}n$ junction was found to reduce the V_{oc} [7,8, 54]. In chapter 3, we have shown that the performance of the $p\text{-CuO}/n\text{-Si}$ based heterojunction solar cells can be improved by increasing the working pressure during deposition. Indeed, by increasing the sputtering pressure, the thickness of the interfacial insulating layer can be decreased significantly. Thus, samples were prepared by employing two-step sputter deposition at a higher working pressure and the performance of the $p\text{-CuO}/n\text{-Si}$ heterojunction solar cells was investigated.

Fig. 4.10 (a) demonstrates the current density-voltage characteristics of the solar cells fabricated by two-step sputtering method at the higher working pressure of 30 mTorr. Clear variation of open-circuit voltage and short circuit current of the solar cells is shown in Fig. 4.10 (b), which is elaboration of Fig. 4.10 (a). By employing two-step sputtering method at high working pressure, performance of the solar cells improved further. This is due to the reduction of both; interfacial native oxide and Cu-rich IL. Existence of thin interfacial native oxide layer may induce the Fermi level pinning [8]. Moreover, formation of Cu-rich IL between $p\text{-CuO}/n\text{-Si}$ enhanced Fermi level pinning effect, thus, $p\text{-CuO}/n\text{-Si}$ exhibits low V_{oc} and large leakage current. Therefore, employing two-step sputtering method at high working pressure can alleviate the Fermi level pinning effect through the reduction of Cu-rich IL and interfacial native oxide. Electric field in the absorber layer can be boosted through the increase of doping

concentration of hole transport layer [71]. The FF of the device has been improved further by doping nitrogen in the top layer of CuO. Thin layer of nitrogen doped (N) CuO was introduced between CuO absorber layer and top electrode to enhance the collection efficiency of photogenerated carriers. The N-doped CuO was deposited at 30 mTorr with the argon and nitrogen gas flow rate of 70 sccm and 10 sccm, respectively.

Figure 4.10: (a) Current-voltage characteristics of *p*-CuO/*n*-Si heterojunction solar cells fabricated with various RF power and two-step sputter at a working pressure of 30 mTorr. (b) Variation of short-circuit current and open circuit voltage of *p*-CuO/*n*-Si solar cells (elaboration of Fig. (a)). Nitrogen was introduced at the top layer of CuO to improve the FF of the device.

Table 4.2 summarizes the solar cell parameters. The efficiency of the best device in this study is 1.21%, which is the highest reported value for *p*-CuO/*n*-Si heterojunction based solar cells. Even though the efficiency of the device is still very low compared to the theoretical efficiency, the present work provides the route to improve the CuO

crystal quality and interface defects. The results are promising towards realizing CuO based heterojunction PV devices.

Table 4.2. V_{oc} , I_{sc} , FF and η of the heterojunction solar cells. HP: thin film deposition at 30mTorr. HP:N: thin film deposition at 30mTorr with nitrogen doping in the top CuO layer.

Solar cell parameters	150 W	100 W	50 W	50 W + 150 W	50 W + 150 W HP	50 W + 150 W HP + N
V_{oc} (mV)	360.9	407	438	421	494	498
I_{sc} (mA/cm ²)	1.4	1.7	3.3	4.5	4.8	6.1
FF (%)	41.2	33.0	26.3	42.9	35.2	39.9
η (%)	0.22	0.23	0.38	0.82	0.84	1.21

4.4 Summary

In summary, a series of p -CuO/ n -Si heterojunction solar cells were fabricated and their interface, material and photovoltaic properties were studied in detail. Cu-rich IL formed during sputter deposition at the p - n junction was found to degrade the quality of interface and reduce the efficiency of p -CuO/ n -Si solar cells. While the crystal quality of CuO film and optical properties improved with the increasing of the RF power, the thickness of the Cu-rich IL increased decreasing the interface quality. By employing two-step sputtering method, high crystal quality CuO film with thinner Cu-rich interfacial layer was obtained with better quality interface. Photovoltaic properties with an open-circuit voltage (V_{oc}) of 421 mV, short circuit current (J_{sc}) of 4.5 mA/cm² and a photocurrent of 8.3 mA/cm² have been achieved. The efficiency of the best device in this study is approximately 1.21%.

Chapter 5

Effects of titanium and nitrogen doping on the characteristics of CuO thin films

- 5.1. Introduction
- 5.2. Experimental
- 5.3. Results and discussion
- 5.4. Summary

5.1 Introduction

The predicated theoretical conversion efficiency of CuO based solar cells is around 31%. However, the highest efficiency value obtained thus far is far from the theoretical results. Low carrier concentration and high series resistance of absorber layer are the possible reasons for poor conversion efficiency of copper oxide based solar cells [70]. Therefore, to improve the efficiency of CuO based solar cells, a systematic investigation is needed to develop CuO material with lower resistivity. Doping of CuO can increase the carrier concentration and hence the conductivity, which will reduce the resistive power loss and also improve the efficiency of CuO based solar cells. Thus, finding a suitable dopant to reduce the resistivity of CuO, while retaining the optical properties and crystal quality of CuO, is of considerable interest.

Suda et al [71] investigated the influence of Lanthanum (La) incorporation on the electrical conductivity of CuO. It was shown that the conductivity of La doped CuO was not only significantly influenced by La concentration but also considerably affected by the annealing temperature. They concluded that the sensitivity of La doped CuO to the annealing temperature is mainly attributed to the change of chemisorbed oxygen species from O_2 to O^{2-} . The effects of Li incorporation on the electrochemical properties of CuO electrode were investigated by Chiang et al [72]. They used the flame spray pyrolysis followed by spin coating to deposit their samples. It was found that incorporation of Li can improve the photoelectrochemical properties of CuO electrode. They have also shown that the improvement in the photoelectrochemical properties is mainly ascribed to the enhancement of charge carrier density.

Fermi energy level in CuO varies between valence band maxima ($E_F = 0$ eV) and conduction band minima ($E_F = 1.32$ eV). It was theoretically shown that at Fermi energy level around or less than 1 eV, the Ti dopant has the maximum solubility in CuO and lower formation energy than copper vacancies [19]. Therefore, incorporation of Ti may enhance *p*-type conductivity and increase the carrier concentration of CuO. However, despite the potential of Ti to enhance the carrier concentration and decrease the resistive power loss of CuO, no research was reported in this regard. On the other hand, nitrogen (N) is found to be an effective *p*-type dopant that can be easily incorporated into the crystal lattice of Cu₂O at high concentration to substitute oxygen atoms and reduce its electrical resistivity [73]. However, the structural and optical properties of N-doped CuO have not yet been thoroughly investigated.

Toward this, in this part of the thesis, the potential of Ti doping for improving the conductivity and photovoltaic properties of CuO devices have been investigated. The effects of Ti concentration on the crystal quality and electrical properties as well as optical properties and surface morphology have also been studied. Heterojunction solar cells of Ti doped *p*-type CuO on *n*-type Si substrate have been prepared and compared with a control solar cell without doping. In addition, structural and optical properties of N-doped CuO thin films annealed at different temperatures have been investigated and compared with Ti-doped CuO.

5.2 Experimental

Si and glass substrates were used for the thin film deposition of CuO(Ti) and CuO(N). The substrates were ultrasonicated in IPA for 10 min. In the case of Si

substrates, the native oxide was removed by dipping into 2% HF solution for 5 min before loading into the sputtering chamber. Stoichiometric CuO and pure Ti targets were used for sputtering. The sputtering power was held constant at 50 W for CuO deposition but was varied from 1 to 10 W for Ti cosputtering to obtain CuO films with different Ti concentration. For the control CuO sample without doping, Ar gas flow rate was set to the 25 sccm. For the deposition of CuO(N), Ar and N gas flow rates were set to 20 sccm and 5 sccm, respectively. A rapid thermal annealing (RTA) system was used for thermal treatment of samples in the nitrogen ambient at 300 °C and 600 °C for 1 min. Ti followed by Al was deposited on the front side of copper oxide film and back side of Si substrate to make the contact for solar cells.

5.3 Results and discussion

Ti concentration in the 60 nm thick CuO thin films was determined using secondary ion mass spectrometry (SIMS) and the values are tabulated in Table 5.1. As shown in the table, the Ti concentration varied approximately in a linear manner from 0.049 to 0.598% by increasing the cosputtering power of Ti target from 1 to 10 W.

Table 5.1. Sheet resistance of CuO(N), and CuO (Ti) as a function of Ti concentration

	Undoped CuO	B1	B2	B3	B4	CuO(N)
Ti Sputtering power (W)	0	1	2	4	10	0
Ti concentration (%)	0	0.049	0.099	0.19	0.598	0
Sheet resistance (Ω /square)	$\sim 6 \times 10^8$	$\sim 8 \times 10^6$	$\sim 5 \times 10^6$	$\sim 2 \times 10^6$	$\sim 5 \times 10^5$	$\sim 2 \times 10^6$

The effect of Ti concentration on the electrical conductivity of CuO(Ti) thin films was investigated using a four point probe system. As included in Table 5.1, the undoped CuO exhibits a higher resistivity than the Ti doped thin films. Higher incorporation of Ti decreased the resistivity of CuO(Ti) thin films continuously, and the value was found to decrease by two orders of magnitude when the Ti concentration was 0.598%. The resistivity of CuO(N) films is also listed in Table 5.1, which shows lower resistivity with N incorporation in CuO. Thus, the significant reduction of resistivity of CuO(Ti) and CuO(N) is mainly attributed to the incorporation of Ti and N dopant, respectively, into the O lattice sites. The radius of Ti^+ (0.095 nm) is very close to Cu^+ (0.096 nm). Therefore, it is very difficult for Ti atom to incorporate at the substitution sites of CuO lattice to act as an acceptor. It is also well known that oxygen vacancy self-compensates copper vacancy in undoped CuO. The mechanism of the resistivity reduction for titanium doped CuO is possibly due to the charge compensation effects, which occur because of the incorporation of Ti atom at an interstitial site of CuO lattice and acts as a donor. Since the ionic radius of N is much smaller than Cu^+ , it can incorporate at the substitution sites of CuO lattice and act as an acceptor. The crystalline quality of CuO samples was investigated by XRD in θ - 2θ scan using a $\text{CuK}\alpha$ ($\lambda = 0.15418$ nm) radiation. Figure 5.1 shows the XRD spectra of as-deposited CuO(Ti) samples with various Ti concentration denoted as (AsD) together with the results of annealed samples at different temperatures. The XRD spectra of sputter deposited control CuO and CuO(N) thin films are also presented in this figure. The FWHM (full width at half maximum) of XRD peaks are listed in Table 5.2.

Table 5.2: XRD FWHM of CuO, CuO(Ti) and CuO(N) samples on Si substrate

	FWHM of CuO(002)					FWHM of CuO(111)				
	CuO	B1	B2	B3	B4	CuO	B1	B2	B3	B4
AsD	0.56	0.6	0.6	0.72	0.8	0.72	0.76	0.76	0.92	1.04
RTA @300°C	0.48	0.52	0.52	0.64	0.72	0.44	0.48	0.52	0.88	1
RTA @600°C	0.4	0.4	0.4	0.44	0.48	0.4	0.4	0.44	0.52	0.56

The XRD spectra clearly show the presence of CuO (002) at 35.482 and CuO (111) at 38.764 for all the undoped and Ti doped samples. As shown in Figure 5.1(a) the CuO(Ti) thin film samples exhibited no significant change in the peak intensity and FWHM value as the Ti concentration was increased from 0 to 0.099% (sample B2), maintaining good crystalline quality. However, further increase of Ti concentration resulted in the reduction of the peak intensity as well as widening of FWHM, highlighting the dependence of crystal quality on Ti concentration. As also shown here there are no extra peaks related to the metallic Cu and Ti or other phases of Cu and Ti in the doped CuO films. Indeed, in the lightly doped samples, due to proper substitution of Ti in CuO lattice, no secondary defect phases are observed.

However, in the highly Ti-doped CuO samples, the presence of more Ti-induced crystalline disordering resulted in lattice imperfection degrading the crystal quality of thin films. As shown in the Figure 5.1(c), the formation of additional CuO(110) peak at 32.548 can be clearly observed in the samples annealed at higher temperatures. However, the crystal structure of copper oxide was retained in all the samples and no other phases such as Cu₂O and/or CuTi appeared.

Figure 5.1. X-ray diffraction analysis of sputter-deposited CuO on *n*-Si(100) substrate. Impact of Ti concentration on the structural property of CuO films (a) AsD sample, (b) annealed samples at 300 °C for 1 min and (c) annealed samples at 600 °C for 1min. XRD spectra of control CuO and N-doped CuO are also illustrated for comparison.

As shown in Fig. 5.1, there is a broad peak at around 36° for the AsD and annealed CuO(N) sample at 300 °C, which is due to the formation of mixed CuO-Cu₂O thin film. When the annealing temperature was increased to 600 °C, two sharp XRD spectra peaks appeared at 36.45° and 42.334° corresponding to Cu₂O(111) and Cu₂O(200), respectively. These results indicate that incorporation of N in sputter deposited CuO thin film significantly influences the structural properties of CuO and cause the formation of Cu₂O dominated thin films at high annealing temperature of 600 °C.

The sputter deposited CuO, CuO(Ti) and CuO(N) thin films on glass substrates were analyzed by Raman spectroscopy using a confocal Raman microscope equipped with a 532-nm Nd:YAG laser. The samples were measured from the air side to

understand and evaluate the effects of Ti concentration on the structural disorder, defects in the host lattice and crystallinity of the samples. Figure 5.2 presents the Raman spectra of CuO, CuO(N) and CuO(Ti) thin films with various Ti concentration annealed at 300 °C for 1 min. The distinct peaks, observed at ~ 125 , 288, 599 and 1106 cm^{-1} indicate the formation of CuO. The intensity of all the Raman peaks does not significantly change with increasing Ti concentration from 0 to 0.099 %, further confirming that good crystallinity is retained in the case of lightly doped samples. However, the Raman peaks become broad and the intensity shows a gradual decrease as the Ti concentration is increased further, which could be related to the decrease in crystalline ordering with higher Ti incorporation. Furthermore, a detailed analysis of the Raman spectra shows an additional small feature at $\sim 343\text{ cm}^{-1}$ for CuO(Ti) thin films. This feature can be ascribed to the disorder-induced Raman scattering due to the presence of lattice imperfection when Ti is added into CuO.

The Raman spectra obtained for CuO(N) samples are also shown in Fig. 5.2. The peaks observed at ~ 157 , 215 and 525 cm^{-1} are due to presence of Cu_2O , indicating the formation of mixed CuO- Cu_2O . This finding clearly demonstrates that incorporation N induces phase transition in sputter deposited CuO thin films.

Figure 5.2. Raman spectra of sputter-deposited control sample of CuO, N-doped CuO and CuO samples with different Ti concentration on glass substrate followed by annealing at 300°C for 1 min.

In order to investigate the effects of Ti concentration on the microstructural properties and crystal quality of CuO(Ti) thin films as well as the interface properties of *p*-CuO(Ti)/*n*-Si heterojunction solar cells, HR-TEM was employed. Figure 3 shows the cross sectional HR-TEM images of CuO(Ti) thin films with various Ti concentration deposited on Si substrate and annealed at 300 °C for 1 min. It can be seen that the thickness of CuO(Ti) thin films are ~60 nm. The presence of ~ 2.5 nm thin amorphous-like isolation layer is also observed. The formation of this isolation layer may be due to the thermal treatment, presence of residual oxygen in the chamber and sputtering of the oxide target. The cross-sectional TEM images of the *p*-CuO(Ti)/*n*-Si devices show the formation of a thin Cu rich interfacial layer (IL) at CuO(Ti)/Si interface. This Cu rich IL layer depends on the sputtering conditions used during deposition as described in Chapter 4.

Figure 5.3. Cross-sectional TEM image of 60-nm-thick CuO films with different Ti concentration deposited on *n*-type Si(100) substrates followed by annealing at 300 °C for 1 min.

The cross-hatched regions, indicated by dashed circles, are also observed in the HR-TEM images of CuO(Ti) thin films as shown in Fig 5.3. The size of the cross-hatched areas and roughness of crosshatch lines seem to be directly related to the concentration of Ti. As the Ti concentration increases, the crosshatched region grows bigger in size, and the crosshatched lines become rougher. This may possibly be due to different bonding lengths and atomic diameters of Ti and Cu. As a result, Ti and Cu might exchange their lattice sites to relieve the stress, causing interference pattern and phase shift in the TEM images, as observed in Figure 5.3.

Figure 5.4. XPS spectra of (a) Cu2p, (b) Ti2p and (c) N1s core levels of the control CuO, N-doped CuO and CuO samples with different Ti concentration. All the samples were annealed at 300 °C for 1 min.

The chemical composition of the CuO(Ti) and CuO(N) thin film samples were examined by XPS with monochromatic AlK α source (1486.6 eV). Figure 5.4 shows the

XPS spectra of Cu, Ti and N core levels of the films annealed at 300 °C for 1 min. Cu2p spectra of CuO, CuO(Ti) and CuO(N) are compared in Fig. 5.4 (a). Satellite peaks around 940-950 eV and Cu 2p peaks at 932.2 and 934.2 eV are observed for CuO and CuO(Ti) films, which confirm the formation of CuO phase. Moreover, there is no shift in the core level binding energy of CuO(Ti) thin films with different Ti concentration, further confirming that there was no formation of CuTi or other phases. On the other hand, for the nitrogen doped CuO, the core level binding energy shifts to the 932.4 eV and the relative intensity of satellite peaks are reduced. These observations indicate the formation of mixed CuO to Cu₂O phase, which is consistent with the Raman and XRD analysis.

The Ti2p and N1s core level XPS spectra of CuO(Ti) thin films are presented in Fig. 5.4 (b) and 5.4 (c), respectively. As shown in Fig. 5.4 (b), a peak at 458 eV is observed when Ti is introduced by cosputtering. When the sputtering power is increased from 1 to 10 W, the intensity of the core level peak at 458 eV is also increased, indicating that Ti incorporation is proportional to the applied sputtering power. The peak position of N1s spectra indicates partial substitution of oxygen with nitrogen and formation of CuO:N at the surface level as shown in Fig. 5.4 (c).

To gain deeper insight into the suitability of Ti and N as the potential dopants for CuO thin films, the electrical conductivity, optical properties and surface morphology of CuO(Ti) and CuO(N) thin films were analyzed. The effects of Ti and N doping on the optical absorbance, bandgap, transmittance and reflectance of CuO thin films were studied using a scanning spectrophotometer and the results are shown in Figure 5.5.

Figure 5.5 presents optical transmittance and reflectance of the CuO film with and without doping. Figure 5.5 (a) shows the transmittance spectra of Ti-doped and N-doped CuO. Figure 5.5 (b) is the enlarged version of Fig 5.5 (a) to observe clearly the impact of Ti on the transmittance spectra. The reflectance spectra are presented in Fig. 5.5 (c). The transmittance and reflectance spectra for Ti-doped CuO are also independent of titanium doping concentration. However, for N-doped CuO, transmittance and reflectance increased significantly compared with CuO and Ti-doped CuO films. The optical properties of N-doped CuO is found to be significantly influenced compared to that of CuO and CuO(Ti). CuO(N) thin film has lower absorbance and higher transmittance and reflectance in the visible region compared to CuO. The main reason is likely the bandgap widening of CuO thin film and formation of Cu₂O.

Figure 5.5. (a) Transmittance (b) local enlarged transmittance spectra of doped CuO. (C) Reflectance spectra of CuO, N-doped CuO and CuO samples with different Ti concentration. All the samples annealed at 300°C for 1 min.

To determine the optical bandgap, absorbance spectra and Tauc curves of $(\alpha h\nu)^{0.5}$ versus photon energy ($h\nu$) are plotted in Fig. 5.6 (a) and (b), respectively, where α is the absorption coefficient. The optical bandgap, E_g is estimated from the intercept of $h\nu$ axis with the extrapolated linear segments of the Tauc curve. The estimated optical bandgap of CuO is around 1.35 eV, which is in agreement with the reported results of Dimopoulos et al [37]. However, by incorporation of N, the optical bandgap of the films shifted from 1.35 to 1.95 eV, which may be attributed to mixed CuO-Cu₂O phase.

The direct bandgap energy of copper oxide can be estimated from Tauc curves of $(\alpha h\nu)^2$ versus $h\nu$. The direct optical bandgap of doped CuO(N) is about 2.92 eV, which is even much higher than the undoped Cu₂O that is about 2.1eV [14]. These results

highlight that the enhancement of transmittance, reflectance and optical bandgap of CuO(N) thin films is not only due to the phase transformation from CuO to Cu₂O but also due to the bandgap widening of CuO(N) samples. The energy band diagram of *p*-CuO(N)/*n*-Si is shown in Fig 5.6 (c) and compared with that of *p*-CuO/*n*-Si. It is worth noting that Ti doping has marginal influence on the optical absorbance, bandgap, transmittance and reflectance properties.

Figure 5.6. Absorbance spectra of Ti-doped and N-doped CuO. (b) plot of $(\alpha h\nu)^{0.5}$ versus photon energy ($h\nu$) of control CuO, N-doped CuO and CuO samples with different Ti concentration. All the samples were annealed at 300 °C for 1 min. (c) The energy band diagrams of p -CuO(N)/ n -Si and p -CuO/ n -Si.

The effects of Ti and N doping on the surface morphology of CuO thin films were studied by AFM. The scanned area was $1 \mu\text{m} \times 1 \mu\text{m}$. Figure 5.7 (a) and (b) illustrate the AFM images and the grain height distribution of CuO, CuO(Ti) and

CuO(N) thin films. It can be realized that the surface roughness of CuO(Ti) thin films is almost independent of Ti concentration. The AFM results are also consistent with the optical reflectance data, further confirming the suitability of Ti doping for retaining the optical properties. From Figure 5.7 (b), it can also be seen that the grain height of CuO(Ti) thin films is only slightly increased by increasing the Ti concentration up to 0.099%. The grain height increase may be a consequence of island growth due to the sputtering Ti and CuO simultaneously. The island formation produces a path to relax the strain induced by energy built up due to intricate balance between chemical bonding and surface energy [74].

However, as observed from Figure 5.7, further increase of Ti concentration slightly reduces the grain height. This reduction for highly doped samples may be due to the reduction of surface mobility due to the lateral expansion of the grains when more Ti is incorporated into CuO film. The reduced surface mobility makes the coalescence phenomena less effective and aids increased micro-porosity between the adjacent grains, which, in turn, results in the formation of smaller grains [75]. The AFM images and grain height distribution also showed slight broadening of the grains and reduction of grain heights with N incorporation. The lower surface roughness of the N-doped CuO film gives higher reflectance compared with CuO and CuO(Ti).

Figure 5.7. (a) Grain size distribution and (b) AFM images of the CuO, CuO(N) and CuO(Ti) samples with different Ti concentration and annealed at 300°C for 1 min.

So far, the impact of Ti and N incorporation on the material and optical properties of sputter deposited CuO thin film have been investigated. It has been shown that addition of Ti can help to maintain the crystal quality, optical properties, and surface morphology of CuO while improving its electrical properties. The impact of Ti and N doping on the performance of *p*-CuO/*n*-Si solar cells have been studied. Employing a 60 nm thick CuO(Ti) and CuO(N) as an absorber layer, the heterojunction solar cells of *p*-CuO on *n*-Si substrate were fabricated. In order to study the PV properties of these cells, current density-bias voltage (J-V) characteristics were measured using a solar simulator that was calibrated earlier with a standard reference Si cell to produce light with AM 1.5G spectrum with a power intensity of 100 mW/cm². The dark J-V characteristics were performed using the semiconductor parameter analyzer.

Figure 5.8 (a) presents the dark current density of *p*-CuO(N)/*n*-Si and *p*-CuO(Ti)/*n*-Si heterojunction solar cells as a function of Ti concentration. Three different regions, labelled as (I), (II) and (III) are identified in Figure 5.8 (b). In region (I), the electrical behaviour is found to be ohmic and the electrical resistance is high due to less injected electrons. In region (II) and (III), the main conduction mechanism is attributed to the recombination-tunneling and space-charge limited current, respectively [36]. As already discussed in this Chapter, by incorporation of Ti, the resistance of CuO(Ti) thin films is significantly reduced. As a result, the voltage range of region (I), which corresponds to the overall resistance of the samples is significantly reduced in CuO(Ti) and CuO(N) thin films. From Figure 5.8 (b), it can also be seen that in the highly doped CuO(Ti), the corresponding voltage range of region (II) is wider than the other samples,

which is possibly due to high recombination rate because of the incorporation of more Ti.

Figure 5.8. The impact of Ti and N incorporation on p -CuO/ n -Si heterojunction solar cells (a) dark current and (b) conduction mechanism.

Figure 5.9 (a) shows the J-V characteristics of p -CuO(N)/ n -Si and p -CuO(Ti)/ n -Si heterojunction solar cells with various Ti concentration in comparison to a control solar cell using the same structure. The enlarged version of Fig. 5.9 (a) is illustrated at Fig. 5.9 (b) to show the clear variation of short-circuit current and open-circuit voltage. The corresponding solar cell parameters are listed in Table III.

Figure 5.9: (a) Photo and dark current of Ti and N doped p -CuO/ n -Si hetero-junction solar cells prepared at a working pressure of 3.3 mTorr (b) enlargement of figure (a) to show the clear variation of short-circuit current and open-circuit voltage.

Table 5.3. V_{oc} , I_{sc} , FF and η of the heterojunction solar cells

Solar cell parameters	CuO	B1	B2	B3	B4	CuO(N)	B2 @ HP
V_{oc} (mV)	370	367	403	390	362	183	510
J_{sc} (mA/cm²)	1.42	1.93	2.78	2.3	1.16	1.23	6.41
FF (%)	34.6	32.1	34.7	33.4	13.3	24.2	36.6
η (%)	0.18	0.22	0.39	0.30	0.06	0.054	1.2

HP: thin film deposition at 30 mTorr

CuO(Ti) with a Ti concentration of 0.099 at% shows the best performance compared to other CuO(Ti), CuO and CuO(N) devices. The J-V characteristic of the control solar cell is limited by the higher series resistance of undoped CuO absorber layer. Addition of Ti clearly improves the conductivity of the CuO absorber layer,

reducing the series resistance and enhancing the charge collection efficiency. As a result, the open circuit voltage (V_{oc}) and short circuit current density (J_{sc}) of CuO(Ti) based solar cell were improved. However, as shown in this figure, the performance of the highly doped CuO(Ti) is significantly degraded because of the high recombination rate in the CuO layer. Also, it is clear from Fig 5.9 that V_{oc} and efficiency of CuO(N) solar cell are lower compared to the control device. The efficiency degradation of CuO(N) solar cell is probably due to nitridation of Cu-rich interfacial layer at the copper oxide-Si interface and formation of poor quality copper oxide nitride interface.

As discussed in Chapters 3 and 4, the formation of Cu rich IL and amorphous like isolation layer between CuO absorber layer and Si substrate degrades the interface properties at p -CuO/ n -Si heterojunction and may intensify the Fermi level pinning effect, which results in large leakage current and low V_{oc} . The formation of interfacial insulation layer may be due to the residual oxygen in the sputter chamber. Similar observation has been reported for sputter deposited beta-phase iron silicide based solar cells [7,8, 54].

The issues related to the formation of interfacial insulation layer and Cu-rich interfacial layer were addressed by a two-step sputtering technique at high working pressure in Chapter 4. Using this method, the crystal quality of the deposited thin film was improved, while simultaneously improving the interface properties at p -CuO/ n -Si heterojunction. The Fermi level pinning effect was also alleviated by reducing the thickness of both Cu rich IL and amorphous like isolation layer, which resulted in improving the efficiency of p -CuO(Ti)/ n -Si heterojunction solar cells. Similar approach was adopted in this study.

Solar cells of p -CuO(Ti)/ n -Si were fabricated by using two-step sputter at a working pressure of 30 mTorr, indicated as HP-two step in Figure 5.10, to reduce the interfacial layer and Cu-rich interfacial layer. Solar cells fabricated by conventional sputtering used a working pressure of 3.3 mTorr, indicated as a LP-one step. Figure 5.10 (a) shows the variation of dark current and photo current for both the cells. From Figure 5.10 (b), it is clearly seen that the open-circuit voltage and short-circuit current significantly improved for the device fabricated at the high working pressure and employing two-step sputter method for Ti-doped CuO solar cells. This is due to the reduction of interfacial layer. It may be noted that the sputtering power of Ti has to be adjusted proportionally to maintain the Ti concentration when the two-step sputtering method at high working pressure is employed.

Figure 5.10. (a) Comparison of photo and dark current of samples prepared using LP-one-step and HP-two-step sputtering and (b) enlarged version of figure (a) to show the variation of short-circuit current and open-circuit voltage.

5.4 Summary

In conclusion, the potential of Ti to serve as a useful dopant in CuO thin film was investigated. It was shown that the Ti content in the deposited films can be controlled by tuning the sputtering power during the film deposition. Microstructural analysis revealed that the crystal quality of samples was not significantly influenced when the Ti content was increased up to 0.099 at %. By tuning the Ti doping, it was found that it is possible to improve the conductivity of the deposited thin films, while retaining the optical properties and crystal quality. The p -CuO(Ti)/ n -Si heterojunction solar cells fabricated using Ti-doped CuO absorber layer exhibited improved solar cell parameters compared with undoped cells. Effects of N incorporation during the CuO sputter deposition were also investigated. Optical and material properties of N-doped CuO were compared with Ti-doped CuO. It was shown that, unlike the Ti dopant, N incorporation significantly induces the structural change and its impact is greatly influenced by annealing temperature. N incorporation widens the optical band gap and increases the optical transmittance and reflectance. Incorporation of N causes the formation of mixed CuO-Cu₂O phase at low annealing temperature and dominant Cu₂O phase at high annealing temperature, instead of CuO. The present work provides a possible solution for the growth of doped CuO for photovoltaic application.

Chapter 6

Design of front surface field using nitrogen and aluminium dopants for CuO-based thin film heterojunction solar cells

- 6.1. Introduction
- 6.2. Experimental
- 6.3. Results and discussion
- 6.4. Summary

6.1 Introduction

The short circuit current density (J_{sc}) and fill factor (FF) of the CuO based heterojunction solar cells are generally very low resulting in poor power conversion efficiency. The FF of CuO-based solar cells is only about 30% - 40%, which is reported to be due to low carrier density in the CuO thin film [36]. As demonstrated in previous Chapters, by introducing nitrogen (N) as dopant, the carrier density in CuO thin films can be increased. Similar approach has been recently reported on the improvement of FF by N-doping the CuO absorber layer. However, due to the deleterious effect of N out diffusion at the interface of heterojunction, this method helped only in the marginal improvement of FF .

On the other hand, incorporation of aluminum (Al) in the atomic structure of CuO can significantly increase the carrier concentration [76]. Utilizing custom designed Al/Cu composite target is one of the widely used techniques to incorporate Al into CuO structure [77-79]. However, this method not only requires specially designed target but also needs very high annealing temperature to get high quality CuAlO₂ thin films. Co-sputtering the Al is also another approach to incorporate the Al into CuO. However, it may degrade the crystal quality and influence the bulk recombination. Therefore, finding suitable technique to increase the carrier concentration of CuO is of great interest.

The performance of CuO-based heterojunction solar cell can also be tuned by increasing the short-circuit current (J_{sc}). One of the key parameters that significantly affects the performance of solar cells with a thin absorber layer is charge carrier collection efficiency [80]. The presence of inner electric field at the front or back surface

of a solar cell can be useful to repel photo-induced minority carriers and reduce the recombination velocity, which significantly influences the charge collection efficiency. Designing of solar cells with back and front surface field (BSF and FSF) is reported to be the efficient method to strength the inner electric field and hence increase the charge collection efficiency, and improve the J_{sc} [81,82]. Employing the FSF also enhances the V_{oc} as the bandgap in the space-charge region expands. It is also an effective method to reduce the front ohmic contact recombination, which influences the fill factor and short circuit current of the solar cells. To employ this technique, the absorber layer requires graded carrier concentration, which is possible by tuning the dopant concentration across the thickness [83]. Indeed, the carrier concentration of the absorber layer has to be changed in such a way that the excess minority-carrier density is reduced at the surface and the minority carriers moved towards the junction, resulting in the reduction of carriers, which recombine at the surface. As shown in chapter 3 and 4 by employing CuO layer followed by N doped CuO as an absorber layer can enhance J_{sc} . However, this method has limitation due to the out diffusion of N into the undoped CuO layer exhibiting almost uniformly distributed carrier concentration, which only results in slight enhancement in the collection efficiency of photogenerated carriers. Therefore, developing a technique to form thin copper oxide absorber layer with graded carrier concentration is crucial.

In this chapter, the FSF was designed by employing Al and nitrogen doping in the CuO absorber layer. A simple approach is presented to create graded carrier concentration in the absorber layer by employing Al and nitrogen dopant. The graded carrier concentration in the CuO layer was formed through controlling the out-diffusion

of Al and nitrogen into CuO. The Al-doped CuO was formed through thermal diffusion of Al, which was inserted between n-Si and p-CuO absorber layer. Nitrogen doped CuO was formed through sputtering of CuO in nitrogen and argon ambient. The absorber layer reported in this investigation has step distribution of carrier concentration, fabricated by integrating the N-doped CuO with Al doped CuO through sputter deposition technique and rapid thermal treatment.

6.2 Experimental

N-type (001) Si wafers with the resistivity of 5-10 Ωcm were used as the substrate. Pure Al and stoichiometric CuO targets were used for deposition. All depositions were performed at room temperature, and a working pressure of 3.3 mTorr was maintained. One control sample and three different kinds of samples were prepared. CuO was deposited using stoichiometric CuO target without N and Al doped with Ar gas flow fixed at 25 sccm, assigned as control device. For the N doped-CuO, firstly, undoped CuO was sputtered in Ar ambient and subsequently, CuO was sputtered in Ar and nitrogen ambient with the flow rate of 20 sccm and 5 sccm, respectively. For Al-doped CuO, a thin layer of Al was first deposited on *n*-Si followed by CuO deposition in Ar ambient with the flow rate of 25 sccm. To fabricate graded layer of CuO, a thin layer of Al was first deposited on *n*-Si followed by undoped CuO deposition in Ar ambient. After that, CuO was deposited in N and Ar ambient with the flow rate of 5 sccm and 20 sccm, respectively. The schematic diagrams of prepared samples are presented in Fig.

6.1. After deposition, all the samples were annealed for 1 min at 300 °C – 400 °C in nitrogen ambient by a rapid thermal processing system.

Figure. 6.1. Schematic diagram heterojunction solar cells: (a) control p -CuO/ n -Si cell (b) Al-doped CuO/ n -Si cell (c) N-doped/ n -Si cell and (d) Graded doped CuO/ n -Si cell.

6.3 Results and discussion

The SIMS depth profile measurement was used to investigate the elemental distribution in the absorber and interfacial buffer layers of the samples with different structures. The distribution of Cu, O, N and Al in the control sample, N-doped CuO, Al-doped CuO and Graded CuO are shown in Fig. 6.2

Figure. 6.2. SIMS depth profiles of (a) control p -CuO/ n -Si (b) Al-doped CuO/ n -Si (c) N-doped/ n -Si and (d) Graded doped/ n -Si heterojunction solar cells. Regions with different carrier concentration are marked with the circles.

The depth profile of the control sample, presented in Fig. 6.2 (a), shows the presence of copper rich interfacial layer (Cu rich IL) between *n*-Si substrate and sputter deposited CuO. As discussed in chapter 3 and 4, the existence of Cu rich IL strengthens the Fermi level pinning effect and affects the solar cell performance. In N-doped CuO, as shown in Fig. 6.2 (b), the out diffusion of N into the bottom undoped CuO layer can be clearly observed. N-distribution is almost uniform in region (I) and (II) except for a small bump at the interface of region (I) and (II). Since the dopant distribution is uniform, it is difficult to form strong inner electric field. Thus, the efficiency improvement in *p*-CuO:N/CuO/*n*-Si heterojunction solar cell reported in chapter 3 and 4 is mainly due to the formation of low-resistivity ohmic contact between the absorber layer and top electrode. The depth profile of Al-doped CuO structure is shown in Fig. 6.2 (c), which shows the Al out diffuses from Al interfacial layer into CuO absorber layer and forms lightly Al doped CuO layer. In Fig. 6.2 (d), the SIMS depth profile reveals the distribution of Al and N within the CuO layer (graded-CuO). The intensity corresponding to N and Al contents is clearly reduced in region (I) and (II), respectively. In fact, a graded doping structure is formed in this sample due to higher carrier concentration of N-doped top layer compared to lightly Al doped bottom layer. It is also aided by the lower out diffusion of N and Al into region (I) and (II).

The XPS measurements were conducted to study the surface chemical composition and understand the out-diffusion of Al due to thermal treatment. Fig. 6.3 presents the Al2p and N1s XPS spectra of samples of N-doped CuO, Al-doped CuO and graded-CuO annealed at 350°C for 1 min. Al2p XPS spectra of Al-doped CuO and graded-CuO samples are compared in Fig. 6.3 (a). While Al-doped CuO sample shows a

small peak at 74 eV, no signature of Al was found in graded-CuO sample. This observation confirms the out diffusion of Al from Al interfacial layer into the undoped CuO layer in the case of Al-doped CuO. However, Al cannot diffuse into top N doped layer of graded-CuO. The N1s XPS spectra of N-doped CuO and graded-CuO are shown in Fig. 6.3 (b). The peak position of N1s spectra in both the cases indicate partial substitution of oxygen with nitrogen and formation of CuO:N at the surface level.

Figure. 6.3. (a) Al2p spectra of Al-doped CuO and graded-doped CuO and (b) N1s spectra of N-doped CuO and graded-doped CuO. Impact of Al out-diffusion and N incorporation on the surface chemical composition of CuO films.

The HR-TEM studies were undertaken to further investigate the impact of N and/or Al doping on the microstructural properties and the influence of Al buffer layer insertion and out-diffusion of Al on the crystal quality of heterojunction solar cell structures. The cross sectional TEM images of *p*-CuO/*n*-Si and *p*-CuO:N/CuO/Al/*n*-Si

layer structures after RTA are illustrated in Fig. 4. It can be seen that the thickness of CuO thin film used is ~60 nm. The existence of Cu rich IL can be clearly observed in Fig. 6.4 (a) and Fig. 6.4 (b). A thin buffer layer of ~10 nm thick is formed at CuO/Si interface for p -CuO:N/CuO/Al/ n -Si heterojunction solar cell.

Figure. 6.4. Cross-sectional transmission electron microscopy image of (a) control p -CuO/ n -Si heterojunction solar cell and (b) Graded doped CuO/ n -Si heterojunction solar cell.

The EDX spectroscopy analysis indicates that the buffer layer is essentially Al_xCu_yO_zSi_t with 45 at.% Al, 25 at.% Si, 13 at.% Cu and 17 at.% O, respectively. This

result indicates that the Al layer deposited initially was oxidized during the thermal treatment resulting in $\text{Al}_x\text{Cu}_y\text{O}_z\text{Si}_t$ buffer layer between n -Si substrate and copper rich IL. The HR-TEM images of p -CuO:N/CuO/Al/ n -Si heretofunction solar cell also reveal that the CuO thin film exhibits no significant change in crystallinity with the Al out diffusion making it lightly Al auto-doped.

The electrical performance of p -CuO/ n -Si heterojunction solar cells were investigated in detail. The dark current density–voltage (J – V) characteristics were measured using a semiconductor parameter analyzer and the photo J – V characteristics were measured using a solar simulator to produce light with AM 1.5G spectrum of power intensity 100 mW/cm^2 . The photo and dark J – V characteristics of the control solar cell annealed at 350°C and Al-doped CuO/ n -Si heterojunction solar cell, which is annealed at 300 , 350 and 400°C , are presented in Fig. 6.5 and the corresponding solar cell parameters are summarized in Table 6.1.

Table 6.1. V_{oc} , J_{sc} , FF and η of the heterojunction solar cells

Solar cell parameters	Control sample	Al- doped CuO	N- doped CuO	Graded doped CuO
V_{oc} (mV)	407	302	435	369
J_{sc} (mA/cm^2)	1.73	6.79	5.10	7.56
FF (%)	33.0	51.2	40.0	68.10
η (%)	0.23	1.05	0.88	1.91

There is significant impact of thermal annealing on the performance of Al-doped CuO based solar cells. As shown in Fig. 6.5 (a), the V_{oc} and efficiency (η) increased significantly as the annealing temperature was increased from 300 °C to 350 °C.

Figure. 6.5. Impact of thermal treatment on Al-doped-CuO/ n -Si heterojunction solar cells (a) photo current-voltage characteristics. (b) Elaboration of Fig. (a) to show the variation of short-circuit current and open circuit voltage, (c) semi-log scale dark current-voltage characteristics and (d) log-log scale plot of dark current-voltage characteristics.

This enhancement of V_{oc} and η is due to the uniform distribution of Al into CuO and partial oxidation of Al interfacial layer and the consequent formation of $Al_xCu_yO_zSi_t$ buffer layer. However, by increasing the annealing temperature to 400 °C, J_{sc} and FF of Al-doped CuO/*n*-Si heterojunction solar cell drastically degraded. The deterioration of J_{sc} and FF is likely due to the enhancement of Al out diffusion, forming heavily doped CuO that significantly degrades the crystal quality and the photovoltaic properties. Clear variation of V_{oc} and J_{sc} of the solar cells are presented in Fig. 6.5 (b), which is the elaboration of Fig. 6.5(a). As shown in Fig. 6.5 (a) and (b), J_{sc} and FF of Al-doped CuO/*n*-Si heterojunction solar cell annealed at 350°C show significant improvement over the control sample. This is attributed to the out-diffusion of Al during annealing and lightly doping the copper oxide to increase the carrier concentration. The improvement may be also due to the formation of thin $Al_xCu_yO_zSi_t$ buffer layer upon thermal treatment. Both these effects were identified using TEM and SIMS studies as discussed earlier. The formation of lightly doped copper oxide is beneficial to enhance the J_{sc} and FF significantly. However, due to recombination effects at the CuO(Al)/ $Al_xCu_yO_zSi_t$ interface, V_{oc} reduced slightly compared to the control sample.

To investigate Al-doped solar cells further on different annealing temperatures used, semi-log plot of dark J-V characteristics are presented in Fig. 6.5 (c). For comparison, the dark J-V characteristic of control sample is also presented. As shown, all the samples exhibit rectifying behavior confirming the formation of p-n junction. However, the rectifying ratio for samples with the Al buffer layer is smaller compared to the control device. The smaller rectifying ratio may be due to the amorphous nature of the buffer layer leading to slightly enhanced interface recombination. The log-log scale

plot of dark J-V characteristics, shown in Fig 6.5 (d), identify three regions corresponding to different conduction mechanisms. While the electrical behavior is ohmic in region (I), the main conduction mechanism in regions labeled II and III are recombination-tunneling and space-charge limited current, respectively [38]. As shown in this figure, the voltage range of region (I), which corresponds to the overall resistance of the solar cell, is significantly lower for Al-doped CuO compared to the control sample. The overall resistance reduction is primarily due to the enhancement of carrier concentration due to Al out-diffusion into copper oxide.

To provide more information about the influence of Al incorporation on the electrical properties of Al-doped CuO and understand its influence on the carrier concentration, a thin layer of Al was sputtered on glass substrate followed by depositing CuO and annealed at 350 °C. The sheet resistance of the sample measured is $\sim 9 \times 10^6$ Ω/square . The sheet resistance of CuO(Al) is much lower than the sheet resistance of CuO, which is $\sim 10^8$ Ω/square , indicating the enhancement of carrier concentration by incorporation of Al. On the other hand, by comparing the sheet resistance of CuO(N) and CuO(Al), it can be seen that the sheet resistance of CuO(Al) is higher than that of CuO(N), indicating that the carrier concentration is lower in CuO(Al). These results further confirm the formation of step distribution of carrier concentration in the CuO absorber layer of *p*-CuO(N)/CuO(Al)/*n*-Si heterojunction solar cell. The distribution of charge carriers along CuO layer also suggests the formation of stronger inner electric field when integrating Al and N doped CuO, which can enhance the charge collection efficiency.

Dark and photo J-V characteristics of N-doped CuO/*n*-Si heterojunction solar cell were compared with control sample in Fig. 6.6. It can be seen from Fig. 6.6 (a) that J_{sc} , V_{oc} and FF of N-doped solar cell show improved performance compared to the control sample. As shown by SIMS depth profiling (Fig. 6.2), nitrogen out diffuses into the undoped copper oxide layer. As a result, this configuration influences the charge carrier collection efficiency and separation of electrons to some extent. Therefore, the improvement of solar cell parameters in N-doped solar cell is mainly due to the formation of low resistivity ohmic contact and reduction of recombination at the top electrode/absorber interface. The dark J-V characteristics were plotted in Fig 6.6 (b). Inset of Fig. 6.6 (b), conduction mechanism of N-doped CuO was presented. The dark current characteristic for N-doped CuO is similar to the control device. From the conduction mechanism study, it was found that the voltage range of region (I) is notably influenced by incorporating the N which is due to the enhancement of carrier concentration and reduction of overall resistance.

Figure. 6.6. (a) Photo and (b) dark current-voltage characteristics of N doped- CuO/n-Si heterojunction solar cells. Conduction mechanism of N-doped CuO/n-Si presented in Inset of (b).

The performance of solar cells was significantly influenced by Al and N-doped CuO compared to the control device. While the Al-doped CuO showed enhanced short-circuit current and fill factor, the open-circuit voltage degraded. On the other hand, for nitrogen doped CuO , the open circuit voltage is found to be similar to that of the control sample, but higher compared to the Al-doped CuO . However, the short-circuit current and fill factor are found lower compared to the Al-doped CuO . Thus, by employing the Al-doped CuO and nitrogen doped CuO , the performance of CuO based solar cells can be tuned. The out-diffusion of Al from the bottom and nitrogen from the top formed graded-doped CuO . The J-V characteristics of graded-doped CuO/n-Si heterojunction solar cell are presented in Fig. 6.7.

Figure. 6.7. Current-voltage characteristics comparison of different heterojunction solar cells studied: graded-doped CuO/*n*-Si, N-doped CuO/*n*-Si, Al-doped CuO/*n*-Si, and control *p*-CuO/*n*-Si.

As shown in this Fig 6.7, the J-V characteristics of graded-doped CuO solar cell shows significant increase in J_{sc} and FF compared to all the other solar cells studied. The enhancement of these parameters can be explained by the formation of highly graded doping absorber layer and creation of strong inner electric field. The step distribution of carrier concentration in graded-doped CuO results in energy-band bending, which aids to reduce the surface recombination velocity and draw the photo-induced minority carriers towards the opposite electrodes. Also, the strong inner electric field formed improves the collection efficiency and effectively drives the charges out of the device. As a result, both FF and J_{sc} show significant improvement.

6.4 Summary

In summary, the integration of N-doped CuO with Al-doped CuO to produce high efficiency CuO based thin film heterojunction solar cells with FSF design have been demonstrated. A significant improvement in J_{sc} and FF from 1.73 to 7.56 mA/cm² and 33% to 68.7% have been achieved, respectively, in the cell with FSF design. The improvement in J_{sc} and FF is attributed to the enhancement of charge carrier collection and increase in the carrier concentration. It has been shown that the enhancement of charge carrier collection is due to the formation of strong inner electric field, which resulted from out diffusion of Al from the Al interfacial buffer layer into undoped CuO layer in conjunction with N doping of the top CuO layer to form graded doping absorber. These results emphasize the importance of engineering the front surface field for efficient charge collection to improve the performance of CuO based thin film heterojunction solar cells.

Chapter 7

A physically based compact model for solar cell parameters extraction

- 7.1. Introduction
- 7.2. Methodology
- 7.3. Results and discussion
- 7.4. Summary

7.1 Introduction

To predict the performance of solar cells accurately it is essential to have a precise set of solar cell parameters [84, 85]. There are many models in the literature to describe the current-voltage characteristic of solar cells. The single exponential model is the simplest one and widely used method to describe the characteristics of large variety of solar cells [86-89]. In the single exponential model (SEM), the current (I) and voltage (V) relation has an explicit form given by the following equation [86]

$$I = I_{ph} - I_0 \left(\exp \left(\frac{V + R_s I}{n V_{th}} \right) - 1 \right) - \frac{V + R_s I}{R_{sh}} \quad (7-1)$$

where I_{ph} is the photocurrent, I_0 represents the saturation current, V_{th} is the thermal voltage, n is the ideality factor, R_s is the series resistance, and R_{sh} is the shunt resistance.

The equivalent circuit model of the SEM is also shown in Fig. 7.1.

Figure 7. 1. The single diode equivalent electrical model of a solar cell.

An accurate estimation of these parameters is very important to precisely evaluate the performance of a solar cell. Various methods have been developed to determine these

parameters of solar cells [84-89]. However, the transcendental nature of SEM increases the complexity of determination of solar cells parameters. In spite of the easy availability of computers, the physically-based compact models aid designer to create preliminary designs and more simply predict the performance of new devices without the need of complex simulation. Compact solar cell models are ideal for predicting the designing parameters of solar cells from I-V characteristics without rigorous simulation. In addition, the compact modeling of solar cell is crucial for shortening the design cycle, which is necessary in today's competitive industry for successful design flow and is particularly helpful to device designers. However, only a few works have attempted to introduce compact model [90-92] for parameter extraction solar cells. Presented compact models by [90,91] are empirical expressions for the solar cell parameters. Also, the accuracy of their predicted results is sensitive to the selection of measured points. One of the useful compact models for determining the physical parameters of solar cells is that of Phang et al [92]. However, in their model, they have assumed R_{sh} is much bigger than the R_s ($R_{sh}+R_s \sim R_{sh}$). Hence, parameters are estimated with errors for the solar cells with high series resistance.

The series resistance of a solar cell is parasitic and is a dominant factor that affects conversion efficiency and current-voltage characteristics under illuminated condition. The energy loss resulting from the series resistance has risen because of the increase in the finger length and handling of large current. Therefore, accurate determination of series resistance becomes important to obtain reliable characterization and optimization of cell designs to minimize such losses [93-100]. In this study, using the Lambert function technique, a new compact formula has been derived for

determining the parameters of solar cells from a single exponential model. The compact model is mainly focused on the improvement of the predicted series resistance. This compact model allows an easy estimation of solar cell parameters from open circuit voltage (V_{oc}), short circuit current (I_{sc}), and maximum power point (V_{mm} , I_{mm}).

The maximum power point and fill factor of a solar cell are the most important parameters for designing high efficiency solar cells [101] and also are considered as the input parameter in our compact model. There are many methods in literature for determining these parameters from experimental I–V measurement, including empirical models [91,101] and curve fitting techniques [86,87,102]. Generally, the polynomial interpolation is used to estimate the maximum power point and fill factor. However, the polynomial technique calls more measured points and very smooth variation of measured points to reduce the Runge-Effect [102] and estimate the accurate data. Also, fluctuations in the measured current voltage curve reduce smoothness of experimental data and cause a large numerical error in the estimated parameters by polynomial method.

To resolve these problems Y. Chen et al [102] presented a subsection polynomial curve fitting technique. In this method, the experimental current voltage curve is divided into several subsections, and for each subsection, low degree polynomial curve fitting is used. However, the accuracy of the estimated parameters by this method is greatly influenced by the position of the selected subsections and experimental points.

Since many factors may influence the measured current-voltage curve and introduce noise to the measured data, finding a curve fitting technique with less

sensitivity to measurement noise and selected experimental points is of great interest and serves to alleviate the extraction error induced by test noise and selected points.

In this study, a curve fitting method based on Thiele interpolation technique is employed to determine maximum power point and fill factor from the measured points of the current-voltage characteristics. It is shown that this method can accurately estimate the maximum power point and fill factor with less sensitivity to the measurement noise and less dependency on the position of the selected experimental points. Also, for further evaluation of suitability of Thiele interpolation method, the results of Spline technique, two degree not-a-knot Spline technique, Polynomial interpolation and Polynomial curve fitting are presented and compared with the results obtained from Thiele interpolation method.

7.2 Methodology

Eq. (7-1) is an implicit equation and it is not possible to solve analytically. However, using the Lambert W function, the solution for current and voltage can be expressed as

$$V = I_{ph}R_{sh} + I_0R_{sh} - I(R_s + R_{sh}) - nV_{th}W\left(\frac{I_0R_{sh}}{nV_{th}}\exp\left(\frac{I_{ph}R_{sh} + I_0R_{sh} - IR_{sh}}{nV_{th}}\right)\right) \quad (7-2)$$

where W represents the Lambert W function.

The short circuit current I_{sc} , by substituting $V = 0$ and $I = I_{sc}$ in Eq. (7-2), and open circuit voltage V_{oc} , by substituting $V = V_{oc}$, $I = 0$ in Eq. (7-2), can be given as

$$I_{sc} = -\frac{nV_{th}}{R_s} W \left(\frac{R_s I_0 R_{sh} \exp \left(\frac{R_{sh} (R_s I_{ph} + R_s I_0)}{nV_{th} (R_s + R_{sh})} \right)}{nV_{th} (R_s + R_{sh})} \right) + \frac{R_{sh} (I_{ph} + I_0)}{R_s + R_{sh}} \quad (7-3a)$$

and

$$V_{oc} = I_{ph} R_{sh} - nV_{th} W \left(\frac{I_0 R_{sh} \exp \left(\frac{R_{sh} (I_{ph} + I_0)}{nV_{th}} \right)}{nV_{th}} \right) + I_0 R_{sh} \quad (7-3b)$$

Using Eqs. (7-3a) and (7-3b), the photocurrent, I_{ph} and saturation current, I_0 can be given by

$$I_0 = \frac{(I_{sc} (R_s + R_{sh}) - V_{oc}) \exp \left(-\frac{V_{oc}}{nV_{th}} \right)}{R_{sh} \left(1 - \exp \left(-\frac{V_{oc} - R_s I_{sc}}{nV_{th}} \right) \right)} \quad (7-4a)$$

and

$$I_{ph} = \frac{V_{oc}}{R_{sh}} + \left(\exp \left(\frac{V_{oc}}{nV_{th}} \right) - 1 \right) \frac{(I_{sc} (R_s + R_{sh}) - V_{oc}) \exp \left(-\frac{V_{oc}}{nV_{th}} \right)}{R_{sh} \left(1 - \exp \left(-\frac{V_{oc} - R_s I_{sc}}{nV_{th}} \right) \right)} \quad (7-4b)$$

By substituting Eqs. (7-4a) and (4b) in Eq. (7-2) and making the assumption of $\Delta \equiv \exp \{ -(V_{oc} - R_s I_{sc}) / nV_{th} \} \ll 1$, which is generally valid for a large variety of solar cells [86,87], the Eq. (7-2) is simplified to

$$V = I_{sc} (R_s + R_{sh}) - I (R_s + R_{sh}) - nV_{th} W \left(\frac{(I_{sc} (R_s + R_{sh}) - V_{oc}) \exp \left(-\frac{V_{oc}}{nV_{th}} \right) \exp \left(\frac{I_{sc} (R_s + R_{sh}) - IR_{sh}}{nV_{th}} \right)}{nV_{th}} \right) \quad (7-5)$$

Using the reverse of Lambert function, the current and voltage relation can be expressed

as

$$V = (I_{sc} - I)(R_s + R_{sh}) - (I_{sc}(R_s + R_{sh}) - V_{oc}) \exp\left(\frac{V - V_{oc} + IR_s}{nV_{th}}\right) \quad (7-6)$$

From Eq. (7-6), the derivative of V with respect to I is:

$$\frac{dV}{dI} = \frac{-(R_s + R_{sh}) + \frac{R_s}{nV_{th}}(V - (I_{sc} - I)(R_s + R_{sh}))}{1 - \frac{V - (I_{sc} - I)(R_s + R_{sh})}{nV_{th}}} \quad (7-7)$$

The short circuit dynamic resistance R_{sho} , by substituting $v = 0$ and $i = I_{sc}$ in Eq. (7-7), and open circuit dynamic resistance R_{so} , by substituting $v = V_{oc}$, $i = 0$ in Eq. (7-7), can be written as:

$$\left. \frac{dV}{dI} \right|_{V=0} = -R_{sho} = -(R_s + R_{sh}) \quad (7-8a)$$

and

$$\left. \frac{dV}{dI} \right|_{I=0} = -R_{so} = \frac{-(R_s + R_{sh}) + \frac{R_s}{nV_{th}}(V_{oc} - I_{sc}(R_s + R_{sh}))}{1 - \frac{V_{oc} - I_{sc}(R_s + R_{sh})}{nV_{th}}} \quad (7-8b)$$

For a maximum power $\partial(I.V)/\partial I = 0$, so that the equation (7-7) becomes

$$\left. \frac{dV}{dI} \right|_{V=V_m, I=I_m} = -\frac{V_m}{I_m} = -\frac{-(R_s + R_{sh}) + \frac{R_s}{nV_{th}}(V_m - (I_{sc} - I_m)(R_s + R_{sh}))}{1 - \frac{V_m - (I_{sc} - I_m)(R_s + R_{sh})}{nV_{th}}} \quad (7-9)$$

where I_m represents the maximum power current and V_m represents the maximum power voltage. By substituting the Eq. (7-8a) into Eqs. (7-8b) and (7-9), we have the following relations for the R_{so} and maximum power:

$$R_{so} = -\frac{-R_{sho} + \frac{R_s}{nV_{th}}(V_{oc} - I_{sc}R_{sho})}{1 - \frac{V_{oc} - I_{sc}R_{sho}}{nV_{th}}} \quad (7-10)$$

and

$$\frac{V_m}{I_m} = \left(-R_{sho} + \frac{R_s}{nV_{th}} (V_m - (I_{sc} - I_m)R_{sho}) \right) / \left(1 - \frac{V_m - (I_{sc} - I_m)R_{sho}}{nV_{th}} \right) \quad (7-11)$$

Eq. (7-10) can be rewritten as:

$$n = \left(\frac{R_{so} - R_s}{R_{sho} - R_{so}} \right) \left(\frac{I_{sc}R_{sho} - V_{oc}}{V_{th}} \right) \quad (7-12)$$

The closed form expression for n in terms of the measured parameters can be represented by substituting Eq. (7-12) in Eq. (7-11) as:

$$n = \frac{\beta}{\alpha V_{th}} \quad (7-13a)$$

where

$$\beta = -V_m R_{sho} (I_{sc} - I_m) + V_m^2 + I_m (R_{sho} (I_{sc} - I_m) - V_m) R_{so} \quad (7-13b)$$

$$\alpha = V_m - R_{sho} I_m - \frac{I_m (R_{sho} (I_{sc} - I_m) - V_m) (R_{so} - R_{sho})}{R_{sho} I_{sc} - V_{oc}} \quad (7-13c)$$

Substituting Eq. (7-13a) in Eq. (7-10), R_s can be given by

$$R_s = \frac{(R_{so} - R_{sho})\beta + \alpha R_{so} (R_{sho} I_{sc} - V_{oc})}{(R_{sho} I_{sc} - V_{oc})\alpha} \quad (7-14)$$

Substituting Eq. (7-14) in Eq. (7-8a), R_{sh} becomes:

$$R_{sh} = R_{sho} - \frac{(R_{so} - R_{sho})\beta + \alpha R_{so} (R_{sho} I_{sc} - V_{oc})}{(R_{sho} I_{sc} - V_{oc})\alpha} \quad (7-15)$$

Substituting Eqs. (7-13), (7-14) and (7-15) in Eqs. (7-4a) and (7-4b), the I_0 and I_{ph} can be written as:

$$I_0 = \left(I_{sc} + \frac{R_s I_{sc} - V_{oc}}{R_{sh}} \right) \exp \left(-\frac{\alpha V_{oc}}{\beta} \right) \quad (7-16)$$

and

$$I_{ph} = I_{sc} - \left(I_{sc} + \frac{R_s I_{sc} - V_{oc}}{R_{sh}} \right) \exp \left(-\frac{\alpha V_{oc}}{\beta} \right) + \frac{R_s I_{sc}}{R_{sh}} \quad (7-17)$$

The Eqs. (7-13), (7-14), (7-15), (7-16), and (7-17) can be used to determine the corresponding values of n , R_s , R_{sh} , I_0 and I_{ph} from the measured parameters.

7.3 Results and discussion

The accuracy of the presented equations for determining the parameters of solar cells depends on the accuracy of determined I_m , V_m , R_{so} , and R_{sho} . The values of I_m , V_m , R_{so} , and R_{sho} are determined from the rebuilt current voltage curve by curve fitting techniques. Therefore, the accurate rebuilding of current voltage curve is crucial for precise extraction of the parameters. To find the more accurate curve fitting technique for rebuilding the current voltage curve of solar cell and parameter extraction, the I_m and V_m of control solar cell were extracted and compared using the rebuilt I-V characteristics by Spline technique, two degree not-a-knot Spline technique, Polynomial interpolation, Polynomial curve fitting and Thiele techniques.

Fig. 7-2 compares the rebuilt I-V curves generated using the Spline technique, two degree not-a-knot Spline technique, Polynomial interpolation, Polynomial curve fitting and Thiele technique. Three different groups of data points of a silicon solar cell measured at a temperature of 50°C [103] were used to evaluate the the sensitivity of each method to the positions of the selected data points. For comparison, the ideal I-V curve obtained by the exact numerical method [87] is also plotted. The estimated maximum

power points and fill factor, using the aforementioned techniques have been also tabulated in Table 7-1, 7-2 and 7-3. The derivation percentage (DP) is also presented in the tables. The DP is a factor, which differentiates between the estimated results by curve fitting technique and exact numerical model for parameter extraction.

Figure 7.2.a. Comparison of rebuilt I-V curves of a silicon solar cell @ $T=50^{\circ}\text{C}$ by Spline technique, Low degree Spline technique, Polynomial interpolation, Polynomial curve fitting and Thiele technique for well-picked data points of experimental results.

It is clear from Fig. 7. 2a that, for the well-picked data points, the rebuilt I-V curves using various interpolation techniques are very close to the ideal one. As also shown in Table 7-1, the estimated maximum power points and fill factor for all the cases are close to the results obtained by the exact numerical model.

TABLE 7.1: Estimated maximum power point and fill factor by Spline technique, Low degree Spline technique, Polynomial interpolation, Polynomial curve fitting and Thiele technique for well-picked data points of a silicon solar cell @ T=50°C and the results obtained by exact numerical method.

Method	ST	TDST	PI	PCF	TT	numerical
$V_m(V)$	0.41	0.41	0.425	0.424	0.42	0.42
$J_m(\text{mA}/\text{cm}^2)$	-24.11	-24.04	-23.85	-24.15	-23.95	-23.99
FF (%)	71.32	71.11	73.13	73.87	72.5	72
DP of V_m	2.38%	2.38%	1.19%	1%	0%	0%
DP of J_m	0.5%	0.3%	0.58%	0.66%	0.16%	0%
DP of FF	0.94%	1.23%	1.5%	2.5%	0.6%	0%

Figure 7.2. b Comparison of rebuilt I-V curves of a silicon solar cell @ T=50°C by Spline technique, Low degree Spline technique, Polynomial interpolation, Polynomial curve fitting and Thiele technique for randomly pick up of bias point of experimental results.

Figure 7.2. c Comparison of rebuilt I-V curves of a silicon solar cell @ $T=50^{\circ}\text{C}$ by Spline technique, Low degree Spline technique, Polynomial interpolation, Polynomial curve fitting and Thiele technique for selected measured points which have equal space in I axis.

The rebuilt I-V curves using the various interpolation techniques are compared in Fig. 7-2b and Fig. 7-2c for randomly-picked data points and selected points with equal space in the I axis, respectively. As shown, the rebuilt I-V curves using the polynomial and Spline method are more sensitive than the Thiele curve fitting technique to the position of selected point. The presented data in Table 7-2 and 7-3 also confirm the less sensitivity of Thiele curve fitting technique to the position of selected point.

TABLE 7.2: Estimated maximum power point and fill factor by Spline technique, Low degree Spline technique, Polynomial interpolation, Polynomial curve fitting and Thiele technique for randomly measurement of bias point of a silicon solar cell @ T=50°C and the results obtained by exact numerical method.

Method	ST	TDST	PI	PCF	TT	numerical
$V_m(V)$	0.4	0.4	0.43	0.43	0.42	0.42
$J_m(mA/cm^2)$	-24.18	-24.1	-23.8	-24.2	-23.9	-23.99
FF (%)	70	69.55	75.05	75.07	72.4	72
DP of V_m	4.76%	4.76%	2.38%	2.38%	0%	0%
DP of J_m	0.8%	0.45%	0.79%	0.87%	0.37%	0%
DP of FF	2.77%	3.4%	4.23%	4.2%	0.55%	0%

TABLE 7.3: Estimated maximum power point and fill factor by Spline technique, Low degree Spline technique, Polynomial interpolation, Polynomial curve fitting and Thiele technique for selected points have equal space in I axis of bias point of a silicon solar cell @ T=50°C and the results obtained by exact numerical method.

Method	ST	TDST	PI	PCF	TT	numerical
$V_m(V)$	0.386	0.37	0.435	0.435	0.421	0.42
$J_m(mA/cm^2)$	-25.3	-25.6	-24.8	-24.9	-23.9	-23.99
FF (%)	70.5	68.6	77.8	78.1	72.65	72
DP of V_m	8.09%	11.9%	3.6%	3.6%	0.23%	0%
DP of J_m	5.46%	6.7%	3.34%	3.8%	0.37%	0%
DP of FF	2.3%	4.8%	8.1%	8.6%	0.9%	0%

To further investigate the sensitivity of our adopted technique to the fluctuations in the measured data or noise, the data with added random noise have been used in the employed technique to estimate maximum power point and fill factor.

Figure 7.3 Comparison of rebuilt I-V curves of a silicon solar cell @ T=50°C by Spline technique, Low degree Spline technique, Polynomial interpolation, Polynomial curve fitting and Thiele technique for measured bias point with added random noise.

TABLE 7.4: Estimated maximum power point and fill factor by Spline technique, Low degree Spline technique, Polynomial interpolation, Polynomial curve fitting and Thiele technique for measured bias point with added random noise of a silicon solar cell @ T=50°C and the results obtained by exact numerical method.

Method	ST	TDST	PI	PCF	TT	numerical
V_m (V)	0.402	0.398	0.409	0.4	0.423	0.42
J_m (mA/cm ²)	-28	-27.7	-26.6	-26.3	-23.2	-23.9
FF (%)	81.2	79.5	78.49	75.9	71	72
DP of V_m	4.3%	5.5%	2.8%	4.76%	0.7%	0%
DP of J_m	16.74%	15.5%	10.99%	9.63%	2.5%	0%
DP of FF	12.77%	10.41%	9%	5.44%	1.3%	0%

As illustrated in Fig. 7.2, the fitted curve using the Thiele curve fitting technique is in good agreement with the ideal one. As given in Table 7.4, the estimated maximum

power point and fill factor using the Thiele technique are accurate for the data with random noise. It may also be noted that, in specific situations, the algorithm for constructing of Thiele interpolation may produce division-by-zero error. It is produced for two successive points with same dependent value or for three successive collinear points. To resolve this problem, the data points should be perturbed slightly. In the rest of the study, the Thiele curve fitting technique is employed to precisely estimate the values of I_m , V_m , R_{so} , and R_{sho} from the measured current-voltage curve.

To investigate the reliability of our present compact model, the physical parameters of a large variety of solar cells have been predicted and compared with the numerical results. The presented compact model is used to predict the parameters of silicon solar cells (@ $T= 33^{\circ}\text{C}$), silicon solar module (@ $T= 45^{\circ}\text{C}$), P3HT cell (27°C), PCPDTBT cell (27°C), and Multi-junction small molecule cell under different illumination. The predicted parameters by our model have been tabulated in Table V, VI and VII. The results have also been compared with the results obtained by numerical method [86] and presented compact model by [92]. As summarized in the tables, our predicted results are close to the numerical results, and DP of the predicted parameters by our method is around 1%, which is much better than the reported results by Phang et al [92]. It is mainly because of considering the R_s which significantly influences the solar cell performance.

TABLE 7.5. Predicted parameters by our model and Phang et al [92] and extracted parameters by Zhang et al [86] of a multi-junction small molecule cell under different illumination @ T=27°C

Parameters	58 mW/cm ² (27°C)					116 mW/cm ² (27°C)				
	This work	Zhang et al	Phang et al	DP of This work	DP of Phang et al	This work	Zhang et al	Phang et al	DP of This work	DP of Phang et al
R _s (Ωcm ²)	50.3	50.9	43.5	1%	14.5%	47.0	46.9	42.02	0.35%	10.4%
R _{sh} (kΩcm ²)	2.91	2.9	3.01	0.34%	3.79%	1.4	1.4	1.4	0.37%	3.2%
I _{ph} (mA)	2.32	2.3	2.4	0.8%	4.34%	4.7	4.7	4.85	0.014%	3.2%
I ₀ (mA)	1.73×10 ⁻³	1.7×10 ⁻³	2.53×10 ⁻³	1.6%	49.4%	1.07×10 ⁻³	1.045×10 ⁻³	1.9×10 ⁻³	2.1%	81.4%
N	6.3	6.3	6.5	0.03%	3.46%	5.8	5.8	6.2	0.58%	5.90%
I _{sc} (mA/cm ²)	-2.27	-2.2	—	0.169%	—	-4.5	-4.5	—	0.003%	—
V _{oc} (V)	1.12	1.12	—	0.015%	—	1.22	1.2	—	0.08%	—

TABLE 7.6. Predicted parameters by our model and Phang et al [92] and extracted parameters by Zhang et al [86] of a silicon cell @ T=33°C, and a silicon solar module @ T=45°C

Parameter s	Silicon solar cells (33°C)					Silicon solar module (45°C)				
	This work	Zhan g et al	Phan g et al	DP of This work	DP of Phang et al	This work	Zhan g et al	Phan g et al	DP of This work	DP of Phang et al
R _s (Ω)	0.0302	0.03	0.031	0.66%	3.33%	1.31	1.31	1.35	0.01%	3.5%
R _{sh} (kΩ)	0.0405	0.04	0.043	1.25%	7.5%	0.61	0.60	0.64	0.2%	6.6%
I _{ph} (A)	0.76	0.76	0.78	0.004%	2.5%	1.02	1.03	1.06	0.97%	2.97%
I ₀ (μA)	0.242	0.24	0.255	0.88%	6.25%	1.58	1.59	1.67	0.63%	4.6%
N	1.46	1.45	1.5	0.67%	3.44%	45.81	45.8	46.9	0.09%	2.4%
I _{sc} (A)	-0.76	-0.76	—	0.00013%	—	-1.03	-1.03	—	0.0009%	—
V _{oc} (V)	0.57	0.57	—	0%	—	16.78	16.7	—	0.0005%	—

TABLE 7.7. Predicted parameters by our model, Phang et al [92] and extracted parameters by Zhang et al [86] of a P3HT standalone polymer solar cell and a PCPDTBT standalone polymer solar cell @ T=27°C

Parameters	P3HT cell (27°C)					PCPDTBT cell (27°C)				
	This work	Zhang et al	Phang et al	DP of This work	DP of Phang et al	This work	Zhang et al	Phang et al	DP of This work	DP of Phang et al
$R_s (\Omega\text{cm}^2)$	1.21	1.2	1.14	0.83%	5%	5.4	5.41	4.46	0.18%	17.2%
$R_{sh} (\text{k}\Omega\text{cm}^2)$	0.67	0.68	0.71	1.47%	4.41%	0.17	0.17	0.18	0.094%	3.1%
$I_{ph} (\text{mA})$	10.7	10.8	11.1	0.92%	2.8%	9.43	9.4	9.54	0.4%	1.5%
$I_0 (\text{mA})$	3.35×10^{-6}	3.4×10^{-6}	4.1×10^{-6}	1.4%	2.5%	3.75×10^{-7}	3.8×10^{-7}	4.9×10^{-7}	1.4%	28.9%
N	1.64	1.65	1.68			1.74	1.74	1.82	0.017%	4.7%
$I_{sc} (\text{mAcm}^{-2})$	-10.8	-10.8	—	0%	—	-9.2	-9.22	—	0%	—
$V_{oc} (\text{V})$	0.6	0.63	—	0.015%	—	0.66	0.66	—	0%	—

A series of annealed heterojunction solar cell of $p\text{-CuO}/n\text{-Si}$ at different temperatures ranging from AsD to 600°C were investigated by our proposed compact model to further evaluate the accuracy of this model and its suitability for predicting the parameters of heterojunction devices. In Fig. 7.4 the rebuild J-V characteristics and experimental results are compared. As shown in this figure, there is an excellent agreement between the experimental data and modelling results.

Figure 7.4. Comparison of experimental data presented by symbols and rebuilt J-V curves of *p*-CuO/*n*-Si solar cells annealed @ AsD, 300°C and 600°C. The rebuild data was obtained by Thiele technique and presented by lines.

The predicted parameters of the prepared solar cells are listed in Table 7.8. As shown in this table, R_{sh} and R_s of the samples increase by increasing the annealing temperature.

TABLE 7.8. Predicted parameters by our model of heterojunction solar cell for *p*-CuO/*n*-Si annealed at @ AsD, 300°C and 600°C.

Parameters	AsD	300°C	600°C
R_s (Ωcm^2)	1.02	2.21	3.1
R_{sh} ($\text{k}\Omega\text{cm}^2$)	0.67	0.8	1.8
I_{ph} (mAcm^{-2})	1	4	20
I_0 (mA)	2.22×10^{-6}	2.12×10^{-6}	2.02×10^{-6}
n	1.12	1.03	1.64
J_{sc} (mAcm^{-2})	-0.44	-1.2	-1.9
V_{oc} (V)	0.08	0.41	0.44

The enhancement of R_{sh} by increasing the annealing temperature is mainly attributed to the improvement of crystal quality of the annealed samples at higher temperature as experimentally shown by XRD measurement in Chapter 5. The enhancement of R_s might be due to degradation of the interface properties of CuO/Si due to thickening of the amorphous isolation layer of Si_xO_y between the CuO and Si substrate. To further investigate this hypothesis, the HR-TEM images of the AsD and annealed samples at 600°C are presented in Fig. 7.5. As shown in this figure, the thickness of Si_xO_y isolation layer has increased by increasing the annealing temperature from around 2 nm for the AsD sample to around 5 nm for the sample annealed at 600 °C, which confirms our hypothesis.

Figure 7.4. HR-TEM images of heterojunction solar cell of $p\text{-CuO}/n\text{-Si}$ annealed at (a) AsD and (b) 600°C.

7.4 Summary

In summary, a new compact model, focusing on the improvement of predicted series resistance, has been presented for predicting the physical parameters of solar cells. The equations are directly derived from a single exponential model and are useful for easily determining the physical parameters of solar cells. It has been shown using several examples that the presented compact model could predict physical parameters with high accuracy. In addition, it has been demonstrated that Thiele interpolation appears to be more accurate for predicting maximum power point and fill factor with less sensitivity to measurements noise.

Chapter 8

Chapter 8 Conclusion and future work

8.1. Summary

8.2. Future work

8.1 Summary

In this thesis, systematic investigation of optical, electrical, structural, and interface properties of sputter deposited CuO based heterojunction solar cells have been reported. The focus of this work is to develop cost effective p -CuO/ n -Si heterojunction solar cells. In particular, four main factors that limit the efficiency of p -CuO/ n -Si heterojunction solar cell were considered: (a) the presence of high degree of traps and the poor interface properties between p -CuO absorber layer and n -Si substrate, (b) poor bulk material and crystal quality of CuO (c) low carrier concentration and high series resistance of CuO absorber layer, and (d) low charge collection efficiency of CuO absorber layer.

Reducing the thickness of amorphous like isolation layer between p -CuO absorber layer and n -Si substrate was found as the effective method to mitigate the poor interface properties in p -CuO/ n -Si heterojunction solar cell. In Chapter 3, it was shown that the crystalline quality and interface quality can be improved by increasing the working pressure during sputter deposition. The impact of interface traps on the performance of CuO based solar cells was studied, and it was shown that charge carrier recombination rate can be reduced by increasing the working pressure. Improvements in the V_{oc} and J_{sc} of p -CuO/ n -Si heterojunction solar cell were achieved through interface engineering.

To increase the efficiency of p -CuO/ n -Si heterojunction solar cells, both the crystal quality of the absorber CuO layer and heterojunction interface properties have to be improved. In Chapter 3, it was shown that Cu-rich IL forms during sputter deposition of

CuO layer on Si substrate. It has significant impact on the performance of p -CuO/ n -Si heterojunction solar cells. In Chapter 4, CuO films deposited on Si at different RF-power levels using single and two-step RF-sputtering techniques were studied including the fabricated p -CuO/ n -Si heterojunction solar cells. Systematic characterization using XPS, AFM, XRD, Raman, and HR-TEM reveal that two step RF-sputtering technique offers better crystal quality CuO film with thinner Cu-rich IL layer. PV properties with higher V_{oc} and J_{sc} have been achieved for the solar cells prepared by this method. The PV properties were further improved by depositing CuO films at higher working pressure with nitrogen doping.

As described, low carrier concentration and high series resistance of CuO absorber layer are some of the limiting factors of CuO based solar cells. In Chapter 5, the potential of titanium (Ti) incorporation into CuO was demonstrated. The optical, electrical, microstructural, material quality, chemical composition, surface morphology, and photovoltaic properties of Ti doped CuO, CuO(Ti), have been systematically investigated. It was shown that Ti doped CuO exhibits reduced sheet resistance and improved charge transport properties. Furthermore, by tuning the Ti concentration, the conductivity of CuO(Ti) can be improved, while retaining the optical properties and crystallinity of the samples. The optical and structural properties of Ti-doped CuO were compared with nitrogen (N) doped CuO. It was found that the incorporation of N into CuO causes structural change, while Ti-doped CuO maintains structural quality. Heterojunction solar cells of p -type Ti doped CuO on n -type silicon (Si) substrate, p -CuO(Ti)/ n -Si, were prepared by conventional sputter deposition at room temperature

followed by rapid thermal annealing at 300°C to investigate the impact of Ti doped CuO on the performance of photovoltaic properties. The short circuit current and efficiency of p -CuO(Ti)/ n -Si heterojunction cells showed significant improvement compared to the cells without Ti doping in CuO.

In Chapter 6, a novel method has been proposed to demonstrate CuO based thin film heterojunction solar cells with front surface field (FSF) design. The FSF design was created by aluminium (Al) doped CuO layer followed by nitrogen (N) doped CuO layer by sputter deposition. The Al doped CuO was created through thermal diffusion of Al. The short-circuit current and fill-factor obtained are significantly higher for the FSF device compared to devices without FSF. The fill-factor of the device improved to 68% through the FSF design and an efficiency of ~2% was achieved. The enhancement of the properties is attributed to the creation of energy-band bending and formation of strong inner electric field, which results in the reduction of surface recombination due to the increase of doping concentration at the top surface. The strong field is found to aid in the separation of electrons to enhance the charge carrier collection.

To optimize the performance of solar cell system, extraction of accurate parameter values of solar cell is important. An accurate current-voltage (I–V) model of solar cells is inherently implicit, which calls for iterative calculations to obtain the solar cell parameters. In Chapter 7, using a systematic approach, a new physically based compact model for more accurate determination of solar cell parameters was derived from the single diode model. To validate the accuracy of the presented model, the predicted

results of the compact model were compared with the other compact and numerical models. Since the experimental outcomes have significant impact on the precision of extracted parameters, a simple approach based on the Thiele interpolation technique was also employed to minimize the impact of measurement noise and determine the maximum power point and fill factor from the less measured points of I–V characteristics. This was further verified by the good agreements between the experimental results of fabricated solar cell and the fitted I–V curve.

8.2 Future work

8.2.1 Interface engineering to improve the efficiency of *p*-CuO/*n*-Si heterojunction solar cell

The open circuit voltage of solar cell devices fabricated in this thesis was lower than the predicted open circuit voltage of around 700 mV. It was shown that the performance of *p*-CuO/*n*-Si heterojunction solar cell is significantly affected by the presence of native oxide, and performance enhancement can be achieved by the reduction of its thickness. The open circuit voltage of *p*-CuO/*n*-Si heterojunction solar cell can be further improved by breaking the amorphous like isolation layer between the deposited CuO and Si substrate or by inserting an interracial buffer layer between the CuO absorber layer and Si substrate.

8.2.2 Improving the efficiency of p -CuO/ n -Si heterojunction solar cell by employing textured CuO absorber layer

One of the main limiting factors of p -CuO/ n -Si heterojunction solar cell is the low short circuit current. The short circuit current of the solar cells fabricated in this study is much lower than the predicted theoretical results, mainly because of the small grain size of prepared solar cell. Grain size can be increased by increasing the annealing temperature of prepared solar cells. However, annealing at higher temperature may significantly degrade the interface properties. Employing textured structure is one of the useful methods to overcome this problem.

List of Publications Resulting from this Thesis

- Journal Publications
- Conference Publications

Journal papers

- [1] **Saeid Masudy-Panah**, K Radhakrishnan, Hui Ru Tan, Ren Yi, Ten It Wong, Goutam Kumar Dalapati, “Titanium doped cupric oxide for photovoltaic application” *Solar Energy Materials and Solar Cells* vol. 140, 266–274, 2015.
- [2] **Saeid Masudy-Panah**, Goutam Kumar Dalapati, K Radhakrishnan, Avishek Kumar, Hui Ru Tan, Elumalai Naveen Kumar, Chellappan Vijila, Cheng Cheh Tan, DongZhi Chi “*p*-CuO/*n*-Si heterojunction solar cells with high open circuit voltage and photocurrent through interfacial engineering” *Progress in Photovoltaics: Research and Applications*, vol 23, 637–645, 2015
- [3] **Saeid Masudy-Panah**, Goutam Kumar Dalapati, A. Kumar, K Radhakrishnan, Hui Ru Tan, “Reduction of thin Cu-rich interfacial layer and improvement of bulk CuO property through two step sputtering for *p*-CuO/*n*-Si heterojunction solar cell” *Journal of Applied Physics*. vol. 116, 074501. 2014.
- [4] **Saeid Masudy-Panah**, Goutam Kumar Dalapati, K Radhakrishnan “A New Compact Model for Solar Cell Parameters” *under peer review*.
- [5] **Saeid Masudy-Panah**, Goutam Kumar Dalapati, K Radhakrishnan, Hui Ru Tan, “Design of Front Surface Field Using Nitrogen Dopant and Al Passivation for the *p*-CuO/*n*-Si Heterojunction Solar Cells” *under peer review*.
- [6] **Saeid Masudy-Panah**, K Radhakrishnan, Ten It Wong, Goutam Kumar Dalapati “Phase transformation and optical bandgap widening of nitrogen doped cupric oxide” *under peer review*.
- [7] **Saeid Masudy-Panah**, Roozbeh Siavash, Ten It Wong, Goutam Kumar Dalapati, “Sputter deposited CuO thin film for photocatalytic water splitting” *under revision Nanoscale*.

- [8] Goutam Kumar Dalapati, **Saeid Masudy-Panah**, Avishek Kumar, Cheng Cheh Tan, Hui Ru Tan, and Dongzhi Chi, “Alpha-phase $\text{FeSi}_2(\text{Al})$ ternary alloy for low cost industrial compatible environmental-friendly photovoltaic technology” *under revision Nano energy*.

Conference papers

- [1] **Saeid Masudy-Panah**, Vinay Kumar, Cheng Cheh Tan, K Radhaknshnan, Dongzhi Chi, Goutam Kumar Dalapati “Impact of metal contact on the performance of cupric oxide based thin film solar cells” Nanoelectronics Conference (INEC), 2013 IEEE 5th International, 378-380, 2013.
- [2] Vinay Kumar, **Saeid Masudy-Panah**, Cheng Cheh Tan, TKS Wong, Dongzhi Chi, Goutam Kumar Dalapati “Copper oxide based low cost thin film solar cells” Nanoelectronics Conference (INEC), 2013 IEEE 5th International, 443-445.

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