# Electrical and optical properties of copper oxide thin films on plastic substrates fabricated by helicon plasma sputtering

Doctoral program, department of electrical engineering and electronics

Anmar Hassan, Shukor

In recent years, a variety of metal oxide thin films have been attracting attention in the field of energy conversion devices. Among them, copper oxides were introduced as a rectifier diode in the 1920s, and its properties make it an old and new material that is still being researched today. There are two major groups of copper oxides, namely cupric oxide (CuO) and cuprous oxide (Cu2O), p-type Cu2O films have a cubic structure with a lattice parameter of 4.27 Å and direct band gaps from 2.1 to 2.6 eV. The n-type CuO films are monoclinic crystal structure semiconductor with direct band gap of 1.2 to 2.1 eV and show good electrical and optical properties. Because of their specific unique properties, they have been used as a solar cell, cathode in lithium primary cells, gas sensors, electrochromic devices, or electronic devices. In addition to the good characterizations, copper oxides are considered as nontoxic and cheap materials and those are why the copper oxides have been chosen to study.

On the other hand, transparent semiconductor materials are becoming increasingly important as the level of living in modern society improves. For example, one technological application is smart windows that add electronic functions to glass. These have been applied in variable light transmitting windows that include automatic switching from transparent to dark, automobile windshields that project important road information as virtual images, automobile windshields that include transparent heaters, and windows that incorporate solar cells. Furthermore, the increasing demand for foldable and wearable electronics has led to need for flexible optoelectronic components. Some applications include skin sensors for healthcare, foldable screens for smartphones, rollable electronic papers, and large-sized curved screens to improve side vision. Other important characteristics for the production of optoelectronic devices are raw material and production costs, scalability of the fabrication method, stability or environmental friendliness of materials.

For the above applications, transparent plastic and glass were selected as substrates in this study. In order to fabricate highly crystalline copper oxide thin films on plastic substrates by the sputtering method, the low temperature formation is required. Therefore, in this study, the helicon sputtering method, which has the characteristics of long-throw sputtering, was utilized in the maximum extent. As a result, it was found that only sputtering power and substrate heating temperature can be controlled to fabricate copper oxide thin films. The helicon plasma

DC magnetron sputtering method was shown to be suitable for the preparation of thin films with good properties at low temperatures.

In this study, CuO and Cu<sub>2</sub>O thin films were prepared by reactive DC magnetron sputtering using helicon plasma. Since the helicon wave provides electromagnetic waves to the plasma in addition to the magnetron power, the helicon plasma can be maintained at a low gas pressure without contacting to the substrate. The crystal structure could be determined by the actual substrate temperature during the deposition. For the substrate, plastic substrates of polymethylmethacrylate (PMMA) and polycarbonate (PC) with high transparency and glass were used as a comparison.

This research consists of 6 chapters, and the outline of each chapter is described below.

Chapter 1 is the introduction to this paper and presents the physical characteristics, crystal structures of CuO and Cu<sub>2</sub>O, and various methods for improving the optical and electrical functions.

In Chapter 2, the deposition process, the configuration and features of the multi-process coating system used for deposition are described.

In Chapter 3, the evaluation methods used in this thesis are described. The physical properties of the copper oxide thin films were measured by X-ray diffraction (XRD) for crystal structure, X-ray photoelectron spectroscopy (XPS) for composition and chemical bonding states, atomic force microscopy (AFM) and laser microscopy (LM) for surface morphology, and Hall effect measurement system for semiconductor properties. The optical band gaps measured from absorbance and transmittance by an UV-Visible spectrophotometer are also described.

In Chapter 4, the electrical and optical functional properties of copper oxide thin films prepared by reactive DC magnetron sputtering using the helicon plasma are described. In this chapter, the effects of DC sputtering power on the structural, electrical and optical properties of the fabricated CuO and Cu<sub>2</sub>O thin films are investigated. By varying the sputtering power, CuO and Cu<sub>2</sub>O thin films with high crystallinity could be fabricated.

In Chapter 5, the crystal structure and semiconducting properties of CuO and Cu<sub>2</sub>O thin films were investigated at different substrate temperatures. The main point of this chapter is the fabrication of CuO thin films with high crystallinity at low temperatures to accommodate low melting point substrates. As a result of careful investigation of the preparation conditions, it was found that CuO and Cu<sub>2</sub>O thin films can be formed at a room temperature without infrared heating.

Chapter 6 focuses on the investigation of the crystal structure and optical properties of CuO and Cu<sub>2</sub>O thin films fabricated on plastic substrates. The CuO and Cu<sub>2</sub>O thin films were fabricated on highly transparent plastic substrates (PMMA and PC) at low temperatures based on the conditions obtained in Chapter 5. The actual temperature during fabrication was measured by a non-reversible temperature measurement sticker, and it was found that the

radiation heat from the sputtering cathode was involved. In the present method, highly crystalline thin films were successfully fabricated on PMMA and PC substrates at temperatures below 100°C without affecting the plastic substrates.

This work demonstrates the new technique for the deposition of CuO and Cu<sub>2</sub>O thin films on transparent plastic substrates at low deposition temperatures. These thin films can be used for a variety of optical applications requiring high transparency and flexibility. This technique is also expected to be applied to other oxide thin films that require a low temperature deposition.

Chapter 1 Introduction	2
1.1 Copper oxide thin films	2
1.1.1 Crystal structure	3
1.1.2 Chemical characteristics	4
1.1.3 Semiconductors characteristics	5
1.2 Thin films	5
1.2.1 Thin film formation method and general thin film features	6
1.2.1.1 Drive process	8
1.2.1.2 Vacuum deposition method and sputtering method	10
References	
Chapter 2 Film deposition equipment	
2.1 Multi-process coating devise	
2.1.1 Summary	
2.1.2 Preparing room	
2.1.3 Plasma room	
2.1.4 Film formation room	
2.1.4.1 Sputtering technique	
2.1.4.2 Magnetron sputtering method	
2.1.4.3 Bipolar sputtering technique and RF sputtering technique	
2.1.4.4 Helicon plasma sputtering system	
2.1.5 Exhaust system specifications	26
2.1.5.1 Exhaust principle of rotary pump (R.P)	27
2.1.5.2 Exhaust principle of turbo molecule pump (T.M.P)	28
2.1.5.3 Exhaust principle of diffusion pump (D.P)	30
References	31
Chapter 3 Thin film evaluation methods	33
3.1 X-ray diffraction (XRD)	
3.1.1 X-ray properties	
3.1.2 X-ray scattering	
3.1.3 X-ray diffraction by crystal	
3.1.4 Crystalline size	
3.2 X-ray photoelectron spectroscopy (XPS)	
3.2.1 X radioactive source	
3.2.2 Composition and chemical state analysis	42

	42
3.3 Surface morphology and cross-section measurement method	42
3.3.1 Measurement principle of atomic force microscope (AFM)	42
3.3.2 Measurement principle of scanning electron microscope (SEM)	43
3.3.3 Laser Scanning Microscope (LSM)	45
3.4 Hall Effect measurement	45
3.4.1 Summary	45
3.4.2 Principle	46
3.5 UV-Vis absorption spectrophotometry	48
3.5.1 Summary	48
3.5.2 Photo energy	49
3.5.3 Visible and violet absorption	49
3.5.4 Calculation method of optical band gap	51
3.5.5 Calculation method of transmittance	51
3.5.6 Adhesion evaluation	53
References	54
Chapter 4 Electrical and photo-functional characteristics for copper oxide th fabricated by reactive dc magnetron sputtering	
fabricated by reactive dc magnetron sputtering	55
fabricated by reactive dc magnetron sputtering	5 <b>5</b> 55
fabricated by reactive dc magnetron sputtering	5 <b>5</b> 55 56
fabricated by reactive dc magnetron sputtering	55 55 56
fabricated by reactive dc magnetron sputtering	55 55 56 57
fabricated by reactive dc magnetron sputtering	55 55 56 57
fabricated by reactive dc magnetron sputtering ————————————————————————————————————	55 55 56 57 57
fabricated by reactive dc magnetron sputtering ————————————————————————————————————	55 55 56 57 57 57
fabricated by reactive dc magnetron sputtering ————————————————————————————————————	55 55 56 57 57 57
fabricated by reactive dc magnetron sputtering ————————————————————————————————————	55 55 56 57 57 57 57
fabricated by reactive dc magnetron sputtering ————————————————————————————————————	55 55 56 57 57 57 57 58 58
fabricated by reactive dc magnetron sputtering  4.1 Introduction	55 55 56 57 57 57 57 58 58
fabricated by reactive dc magnetron sputtering	55 55 56 57 57 57 58 58 58
fabricated by reactive dc magnetron sputtering ————————————————————————————————————	55 55 56 57 57 57 58 58 58 59 60
fabricated by reactive dc magnetron sputtering ————————————————————————————————————	55 55 56 57 57 57 58 58 58 59 60 61
fabricated by reactive dc magnetron sputtering  4.1 Introduction	55 55 56 57 57 57 58 58 58 59 60 61
fabricated by reactive dc magnetron sputtering ————————————————————————————————————	55 55 56 57 57 57 58 58 58 59 60 61 62 62

Chapter 5 Crystal structure and semiconductors properties of c	copper oxides thin
films at low temperature	66
5.1 Introduction	66
5.2 Experimental and measurement methods	66
5.2.1 Experimental methods	66
5.2.2 Measurement methods	67
5.2.2.1 Crystal structure measurement	67
5.2.2.2 Evaluation optical properties	67
5.2.2.3 Calculation of electrical properties	68
5.3 Film characterization	68
5.3.1 X-ray diffraction analysis	68
5.3.2 Optical properties	70
5.3.2.1 Optical Absorbance	70
5.3.2.2 Transmittance	72
5.3.2.3 Bandgap	73
5.3.3 Electrical properties	74
5.4 Conclusion	76
References	77
Chapter 6 Structural and optical properties of copper oxides thi on plastic substrates	
6.1 Introduction	
6.2 Experimental and measurement method	
6.2.1 Experimental method	
6.2.2 Characterization methods	
6.2.2.1 Crystal structure measurement	
6.2.2.2 Surface laser micrographs measurement	
6.2.2.3 Adhesion evaluation	
6.2.2.4 Photoconductivity	82
6.2.2.5 Optical properties calculation	
6.2.2.6 Electrical properties calculation	
6.3 Film characterization and discussion	
6.3.1 Film structure	
6.3.2 Surface laser micrographs	
6.3.3 Optical transmittance	

6.3.4 Optical bandgap	89
6.3.5 Electrical properties	91
6.4 Conclusion	92
References	93
Chapter 7 Conclusions of this paper	94
Acknowledgements	