TIME DEPENDENCE OF MORPHOLOGICAL AND OPTICAL PROPERTIES OF DC SPUTTERING GROWN COPPER OXIDE THIN FILM

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To my beloved parents, brothers, sisters and supervisor.

To all my dearest friends and lecturers.

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ABSTRACT

Copper oxide thin films with five different deposition times (30 min, 60 min, 90 min, 120 min and 150 min) had been successfully growth by dc sputtering technique. The thickness of copper oxide thin film was measured by using ellipsometer. The optical properties of copper oxide thin films were characterized by UV-Vis-NIR spectrometer and Photoluminescence spectrometer while the morphology images were determined by Atomic Force Microscopy (AFM). The copper oxide thin film thicknesses were found around 11.6 nm, 122.1 nm, 129.7 nm, 142.4 nm and 144.2 nm with respect to the five different depositions time at 30 min time interval. The absorption and transmission spectra obtained from UV-Vis-NIR spectroscopy revealed five absorption edges of copper oxide thin film in the ultraviolet region. The optical absorption intensity was increased with increase the thickness while the transmission intensity was decreased with increase the thickness. The transmission intensity was increased to 90% for copper oxide with deposition time 30 min, 60 min, 90 min, and 120 min while the transmission intensity of copper oxide with deposition time 150 min was increased up to 75%. Based on the absorption coefficient measurements, the optical band gap energy have been determined by Tauc plot relation around E_g= 4.63 eV to 4.18 eV for 30 min to 150 min of deposition time. The photoluminescence spectra of copper oxide thin film was found in violet region (400 nm and 402 nm) for copper oxide thin film with deposition time 30 min and 60 min while the blue region (435 nm) was found for copper oxide thin film at deposition time 90 min, 120 min and 150 min. The root mean square roughness (RMS) was confirmed that the surface roughness of copper oxide thin film was increased with increase the deposition time and compatible with the images shown by Atomic Force Microscopy (AFM).

ABSTRAK

Oksida tembaga filem nipis dengan lima masa pemendapan yang berlainan (30 min , 60 min , 90 min , 120 min dan 150 min) telah berjaya dihasilkan oleh teknik percikan arus terus. Ketebalan oksida tembaga filem nipis diukur dengan menggunakan ellipsometer . Ciri-ciri optik oksida tembaga filem nipis telah di uji oleh UV- Vis -NIR spektrometer dan Photoluminescence spektrometer manakala imej morfologi ditentukan oleh 'Atomic Force Microscopy' (AFM). Ketebalan filem nipis oksida tembaga didapati sebanyak 11.6 nm, 122.1 nm, 129.7 nm, 142.4 nm dan 144.2 nm mengikut urutan masa pemendapan pada julat 30 min. Penyerapan dan penghantaran spektra yang diperolehi daripada UV- Vis -NIR spektroskopi menunjukan lima puncak penyerapan tembaga oksida filem nipis berada di kawasan ultraungu. Keamatan penyerapan optik meningkat dengan meningkatnya ketebalan oksida filem nipis manakala keamatan penghantaran adalah menurunan dengan menurunnya ketebalan oksida filem nipis. Keamatan penghantaran meningkat kepada 90% untuk oksida tembaga dengan masa pemendapan 30 min , 60 min , 90 min, dan 120 minit sementara intensiti penghantaran oksida tembaga dengan masa pemendapan 150 min meningkat sehingga 75 %. Berdasarkan ukuran pekali penyerapan , jalur optik jurang tenaga yang ditentukan oleh hubungan Tauc plot berada di antara Eg = 4.63 eV sehingga 4.18 eV untuk masa pemendapan selama 30 min hingga 150 min. Jalur photoluminescence oksida tembaga filem nipis didapati berada di rantau ungu (400 nm dan 402 nm) untuk masa pemendapan 30 min dan 60 min manakala kawasan biru (435 nm) ditemui untuk oksida tembaga filem nipis pada masa pemendapan 90 min , 120 min dan 150 min. Punca min kekasaran persegi (RMS) telah mengesahkan bahawa kekasaran permukaan oksida tembaga filem nipis meningkat dengan meningkatnya masa pemendapan dan setanding dengan imej-imej yang ditunjukkan oleh 'Atomic Force Microscopy (AFM).

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LIST OF ABBREVIATIONS

DC	-	Direct Current
AC	-	Alternating Current
AFM	-	Atomic Force Microscopy
NIR	-	Near Infrared
IR	-	Infrared
Vis	-	Visible
UV	-	Ultraviolet
PL	-	Photoluminescence
GMR	-	Giant Magneto-resistance
2D	-	2-Dimension
3D	-	3-Dimension
PVD	-	Physical Vapor Deposition
CVD	-	Chemical Vapor Deposition
Cu_2O	-	Cuprous Oxide
CuO	-	Cupric Oxide
SPM	-	Scanning Probe Microscopy
XRD	-	X-ray Diffraction Analysis

XPS	-	X-ray Photoelectron Spectroscopy
SEM	-	Scanning Electron Microscopy
FT-IR	-	Fourier Transform-Infra Red
RMS	-	Root Mean Square

LIST OF SYMBOLS

λ_{mfp}	-	Mean Free Path Wavelength
$\AA$	-	Angstrom Unit
P	-	Pressure
I_T	-	Intensity of transmitted light
I_A	-	Intensity of absorbed light
I_R	-	Intensity of reflected light
I_0	-	Intensity of incident light
I	-	Intensity
d	-	Thickness
α	-	Absorption coefficient
A	-	Absorbance
T	-	Transmittance
hv	-	Photon energy
E_g	-	Energy band gap
n	-	Refractive index

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CHAPTER 1

INTRODUCTION

1.1 Background of Study

Thin film technologies development is consistently increases with number of publications in this few decades. These researches have been done due to high demands to the nanoparticles technology which can be a fundamental basis of the products. This technology is well established and can be fabricated from organic or inorganic material which greatly applied in electronics components like capacitors, diode, transistor, solar cells, pn junction and also in photovoltaic application (Parreta *et al.,* 1996). They are also widely applied in other scientific applications like optics, biotechnology and manufacturing industry tools which produce anti-reflection coatings, printed circuit board interconnection, bio-compatible films for surgical implants and ultra hard films in machinery parts respectively. Thus, the discovery of thin films that was started around last three decades is absolutely changed our daily life.

Many semiconductor materials can be fabricated into thin films but copper oxide grab the researchers' interest to fabricate it into thin films and extensively studied because of its attractive properties and behaviour. It is the first semiconducting materials to be investigated through work carried out in the 1920s and 1930s (Drobny *et al.,* 1979). Balamurugan and Mehta also chose this semiconductor material in their studies because of natural abundance of copper, low cost production processing, non-toxic to nature also good in electrical and structural properties (Balamurugan *et al.,* 2001). Beside, the copper oxide nanoparticle has special interest in nanofluid heat transfer application which studied have been reported that 4% of additional Copper oxide willimprove 20% of the thermal conductivity of water (Amrut Lanje *et al.,* 2010).

Therefore, many researchers agreed that the materials in thin film geometry present the physical properties that can be more effective than in bulk geometry (Maissel *et al*., 1970). By means, metal presents good characteristic inoptical properties whichgive highest response for the smallest grain size of film. This was confirmed that the enhancement in inner grain reaction was provided by the presence of smaller grain size as reported in journal of alloy and compound by Mani G.K *et al.,*(2014). Usha Rajalaksmi and his friend also were asserted that the copper oxide thin film has interesting optical behaviour. They have found that these films exhibited high absorption in the visible region and optical transition was found to be direct and allowed with optical band gap varies in range 2.4 – 1.8eV (Usha Rajalaksmi *et al.,* 2013).

Further discovery of optical properties of copper oxide is done by Mugwang and friends in their journal wrote that the copper oxide can be promising candidate as solar cell fabrication because of their suitable optical properties (Mugwang *et al.,*2012). Their studies have been convinced by Ogwu reported that copper oxide thin film has band gap energy values was suitable for absorber application for solar energy conversion (Ogwu *et al.,*2005). Theyalso highlighted that the optical property of copper oxide such a range of direct optical band gap energies is varying due to stoichiometric deviation arising from deposition technique and parameter.

Many literatures were reported and reviewed for deposition technique of copper oxide thin film. The best selected preparation method must be considered while producing the thin films and several preparation methods such as thermal oxidation, electro-deposition, chemical conversion, spraying, chemical vapor deposition, plasma-evaporation, molecular beam epitaxy and reactive sputtering have been used to fabricate the copper oxide thin film and were reported in literature to gain best result in application.

The great researchers Uthman Isah K. and friend were synthesized the copper oxide thin film by using thermal evaporation method to study the effect of oxidation temperature on copper oxide thin film and published their papers in 2013 (Uthman Isah *et al.,* 2013). Then followed by Mugwang et al were studied optical characterization of copper oxide thin film which prepared by reactive magnetron sputtering for solar cell application (Mugwang'a *et al.*, 2012). A year back then, Rafie Johan and Amrut Lanje also carried out their experiment on copper oxide thin film by using chemical vapor deposition and aqueous precipitation method respectively (Rafie *.et al.,* 2011) (Amrut Lanje *et al.*, 2010). Their aims were almost the same which to find the best optical properties of copper oxide thin film.

From the review, we can see that many researchers were studied on copper oxide by various preparation methods. However, their research had just restricted only on deposition techniques, characterization methods and parameters applied. Since the reactive dc sputtering technique is not familiar as reactive magnetron technique and the journals also not much published for this technique thus the research on this technique is very crucial and also relevant in order to get better optical properties and morphological of copper oxide as well.

1.2 Problem Statement

The morphological and optical properties of copper oxide thin film have been widely studied due to its efficiency in various behaviour and applications as mentioned before. The copper oxide thin film become a promising semiconductor material for solar cell fabrication due to its suitable optical properties and an attractive material as a selective solar absorber since it has a high solar absorbency and low thermal emittance. There are also some advantages of using copper oxide thin film in device application such it is non-toxic and its constituents are available in abundance. Therefore, many researches have been done in attempt to discover their excellent properties for technological application. However, it is not well reported on the growing of copper oxide thin film by using dc sputtering method with dependence of the deposition time. Therefore, this present work aims to study the time dependence evolution of morphological and optical properties of dc sputtering grown copper oxide thin film.

1.3 Objectives of the Study

The objectives of this study are:

1. To grow the copper oxide thin film for five different deposition time at 30 min time interval (30 min, 60 min, 90 min, 120 min and 150 min) by using dc sputtering.

2. To determine the morphological properties of copper oxide thin film by Atomic Force Microscopy (AFM).

3. To characterize the optical properties of the samples by means of UV-Vis-NIR and PL spectroscopy respectively.

1.4 Scope of the Study

In order to achieve the objectives, the studies have been focused on the given scope. First is preparation of the grown copper oxide thin film samples using dc sputtering technique at five different deposition times of 30 min, 60 min, 90 min, 120 min and 150 min. Second is determination of the thickness and refractive index of grown copper oxide thin film using an ellipsometer. Third is evaluation of morphological properties of grown copper oxide thin film by getting the root mean square roughness value from the Atomic Force Microscopy (AFM). Fourth is characterization of absorption spectra by using UV-Vis-NIR spectrophotometer and determination of optical band gap energy, transmission and absorption coefficient and lastly is characterization of photoluminescence spectra by using photoluminescence spectrometer.

1.5 Significance of the Study

Recently, the grown copper oxide thin film are chosen because their well known as an efficient material used in every device application especially in solar cell and p-n junction based devices likes light emitting diode (LED), photodiode, photo detector and so forth. The results of this study may provide a basis of employing the copper oxide thin film system in more effective behavior and properties in many applications. Thus, the study on the optical properties in this work might be significant in providing a baseline data that can be used for the further research and development of copper oxide thin film based optical devices.

REFERENCES

Amrut, Lanje, S., Staish, Sharma, J., Ramchandara, Pode, B. and Raghumani, N., (2010). Synthesis and Optical Characterization of Copper Oxide Nanoparticles.*Advanced in Applied Science Research*, 2, 36-40.

Balamurugan, B. and Mehta, B. R., (2001). Optical and Structural Properties of Nanocrystalline Copper Oxide Thin Film Prepared by Activated Reactive Evaporation. *Thin Solid Films*, 396, 90-96.

Cristoph E. S. (2014). Technology of Thin Film.Institute of Solid State Physics. Retrieve from http:// www.static.ifp.tuwien.as.

Depla, D., Mahieu, S. and Greene, J. E. (2007). Sputter Deposition Process. *Materials Science and Physics Department and Frederick Seitz Materials Research Laboratory, University of Illinois, Urbana, USA*., 61801.

Dorbny, V. F. and Pulfrey, D. I. (1979). Properties of Reactively Sputtered Copper Oxide Thin Film. *Thin Solid Film,* 61, 89-98.

Greenwood N. N. and Earnshaw, A. (1997).Chemistry of the Elements, 2nd Edition. Butterworth Heinemann, Oxford.

Heinman, D. (2004). Photoluminescence Spectroscopy. *Physics of Waves and Optics*.Northeasten University.

Ibrahim, Y. E. and Gullu, O. (2010). Optical and Structural Properties of CuOnanofilm: Its diode application. *Journal of Alloys and compound.*492, 378-353.

Issa, M. E., Shehata, M. Z., Fawzi, S. K. Mohammed, S., Issabelle, G. and Florence, B. Nanostructured Copper Oxide-Cotton Fibers: Synthesized, Characterization, and Applications. *International Nano Letters Springer Journal*.2, 14.

Jesper Jung, Jacob Bork, Tobias Holmgaard and Niels Anker Kortbek (2004).Ellipsometry. *Institute of Physics and Nanotechnology*.Aalborg University.

John, A. V.(2000). Introduction to Surface and Thin Film Processes, Cambridge University Press.

Juyun Park, Kyounga Lim, Ramsier, D. R. and Yong-Cheol Kang (2011). Spectroscopic and Morphological Investigation of Copper Oxide Thin Films Prepare by Magnetron Sputtering at Various Oxygen Ratios. *Bull. Korean Chem. Soc.* 32, 9.

KasimUthamanIsah, Muhammad Bakeko M., Umar Ahmadu, Uno Essang Uno, Muhammad IsahKimpa and JibrinAlhajiYabaji (2013). Effect of Oxidation Temperature on Properties of Copper Oxide Thin Film Prepared from Thermally Oxidised Evaporated Copper Thin Films. *Journal of Applied Physics*, 2, 61-66

Kasim, A. (2012). Absorption and Upconversion of Doped Tollurite Glass.*IEEE, Engineering & Industrial Applications Colloquium* (BEIAC).

Kumar, S. K., Murugesan, S., Suresh, S. and Paul Raj, S., (2013). Sputtering for Solar Selective Absorbers.*Journal of Solar Energy,* 2013, 6.

Lin, W., Ma, R. X., Shao, W. and Liu, B. (2007) . Structural, Electrical and Optical properties of Gd doped and undopedZnO:Al(ZAO) thin films prepared by RF Magnetron Sputtering. *Applied Surface Science* 253, 5179-5183.

Maissel L. I. and Glang, R.(1970) (eds) Handbook of Thin Film Technology, MC Graw Hill Co., New York, USA.

Mani, G. K. and John, Basco, B. R., (2014). Influenced of Copper Doping on Structural, Optical and Sensing Properties of Spray Deposited Zinc Oxide Thin Films. *Journal of Alloy and Compounds*, 582, 414-419.

Mugwang'a, F. K., Karimi, P. K., Njoeroge, W. K., Omayio, O. and Waita, S. M., (2012). Optical Characterization of Copper Oxide Thin Film Prepared by Reactive dc Magnetron Sputtering for Solar Cell Applications. *International Journal of Advanced Renewable Energy Research*, 1, 474-480.

Mohammad Suleiman, MuathMousa, Amjad Hussein, BelkheirHammouti, Taibi B. Hadda and Ismail Warad. (2013). Copper(II)-Oxide Nanostructures:Synthesis, Characterizations and their Applications-Review. *J. Matter Environmental Sci*. 4, 792-797.

MohdHaiza B. MohdNor@Ghazali (2007). Optical Characterizations Copper Oxide Thin Film Prepared by DC Sputtering. *Master Degree of Science (Physics). Universiti*Teknologi Malaysia.

Muhibullah, M. (2012).Deposition of Copper Oxide Thin Films by Chemical Techniques.*Thesis for Doctor of Engineering Nagoya Institute of Technology Japan*.

Ogwu, A. A., Darma, T. H. and Bouquerel, E. (2007).Electrical resistivity of Copper Oxide Thin Film Prepared by Reactive dc Magnetron Sputtering.*Journal of Achievements in Materials and Manufacturing Engineering*, 24, 172-179.

Ohring, M. (1992).The Material Science of Thin Films. San Diego: Academic Press.

Ozer, N. and Tepehan, F.,(1993) Optical Properties of Copper oxide Thin Films Prepared by Thermal Evaporation Method. *Solar Energy Materials and Solar Cells*, 30, 13.

Paretta, A., Jayaraj, M.K., Di Nocera, A., Loreti, S., Quercia, L. and Agati, A. (1996). Electrical and Optical Properties of Copper Oxide thin films prepared by Reactive RF Magnetron Sputtering. *Solid State Physics,a*. 155, 399-404.

Peter, B. B., Petrov, I., Hultman, L. and Greene, G. E. (2005).Thin Films Growth, Technique, and Characterization.*Research Institute for Technical Physics and Material Science of HAS Budapest, Hungary,* 21, 117.

Podgorsak, E. B. (2005). Radiation Oncology Physics: A handbook for Teacher and Students. Vienna, International Atomic Agency. 84-85.

Rafie, M. J., Shahadan M. S., Nor Liza, H. and Hee, A. C. (2011), Annealing Effect on the Properties of Copper Oxide Thin Films Prepared by Chemical Deposition. *International Journal of Electrochemical Science*, 6, 6094-6104.

Sekhar, C. R..(2001). Preparation of Copper Oxide Thin Film by the Sol-Gel-Like Dip Technique and Study of their Structural and Optical Properties.*Solar Energy Materials and Solar Cell,* 68,307-312.

Serin, T., Yildiz, A., HorzumSahni, S. and Serin, N. (2011). Extraction of Important Electrical Parameters of CuO.*Elsevier Physica B*. 406, 575-578.

Swarnkar, R. K., Singh, S. K. and Gopal, R..(2009). Optical characterizations of Copper Oxide Nanomaterial.*IOCP 2009-International Conference on Optics and Photonics.*

Tan Hang Khume (2007). Synthesis and Characterization of Aluminium Doped Zinc Oxide Thin Film for Solar Cell. Master of Science (Physics). UniversitiTeknologi Malaysia

Usha, Rajalakshmi, P. and Rachel, O. (2013).Structural and Optical Characterization of Chemically Deposited Cuprous Oxide (Cu_2O) Thin Film.*Advanced Materials Research*, 678, 118-122.

Uthman, Isah, K., Muhammad, Bakeko, M., Umar A., Uno, E. U. Muhammad, I. K. and Jibrin, A. Y. (2013).Effect of Oxidation Temperature on the Properties of Copper Oxide Thin Film prepared by Thermally Oxidized Evaporated Copper Oxide Thin Film.*Journals of Applied Physics*, 3, 61-66.

Weston, G. F. (1985). Ultrahigh Vacuum Practice. London Butterworth & Co.

Yakui Bai, Tengfei Yang, Guon Cheng and Ruiting Zeng (2010). A self-assembly mechanism of cuprous oxide nanoparticle in aquous colloidal solutions. *College of Nuclear Science and Technology,* Beijing, 100875.

Yuming, W. and Alfred, W., (1997).An Introduction to Physics and Technology of Thin Films, Vol. 1, *World Scientific*, 1997.

Zangwill A., (1992) Physics of Surfaces and Thin Films, Cambridge University.