SURFACE MORPHOLOGY AND OPTICAL PROPERTIES OF COPPER NITRIDE THIN FILM SYNTHESIZED BY DC SPUTTERING

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Specially dedicated to

My beloved husband, En. Hanezan bin Hanaffi

For supporting and encouraging me to believe in myself

My parents, En. Ma'ajih bin Ismail and Pn. Narizan binti Mohd

My parents in law, En. Hanaffi bin Hj. Kesman and Pn. Azizah binti Hj. Muhamad

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You are my strength

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ABSTRACT

The purpose of this research is to study the surface morphology and optical properties of copper nitride thin films. Copper nitride thin films were deposited on corning glass substrates by using DC sputtering technique. Five samples were prepared with five different deposition time to obtain samples of different thicknesses. Ellipsometer was used to measure thickness and refractive index. The surface morphology images were obtained by using Atomic Force Microscopy (AFM). Both transmission spectra and photoluminescence spectrum were obtained from UV-Vis-NIR spectrophotometer and Photoluminescence spectrometer, respectively. The films obtained were yellow to reddish-brown depending on increasing deposition time. The thickness of the samples increased as the deposition time increased. Thicknesses of films, d obtained were in range of 1092.38 nm to 1331.03 nm. Refractive index decreased as deposition times increased. The Atomic Force Microscopy images showed that the films were a smooth morphology and were seen like pyramidal islands when deposition time increased. Transparency of copper nitride thin film was very low in the visible region, but it slowly increased in the infrared range. The absorption coefficient, α of copper nitride thin films increased with increasing of photon energy. The average optical band gap energy, E_g obtained in range of 1.56 eV to 2.06 eV. The best emission peak for maximum intensity was about 380 nm obtained in photoluminescence emission for all samples, which refer to ultra-violet light in visible light region of electromagnetic spectrum.

ABSTRAK

Penyelidikan ini bertujuan untuk mengkaji permukaan morfologi dan sifat optik saput tipis kuprum nitrida. Kuprum nitrida telah dipendapkan pada permukaan substrat kaca dengan menggunakan kaedah percikan arus terus. Lima sampel telah disediakan pada lima masa pemendapan yang berbeza untuk menghasilkan sampel yang mempunyai ketebalan yang berbeza. Ellipsometer digunakan untuk mengukur ketebalan dan indeks biasan saput tipis. Imej 3D morfologi bagi semua sampel diperoleh daripada *Atomic Force Microscopy (AFM)*. Kadar penghantaran sampel diukur dengan menggunakan *UV-Vis-NIR Spectrophotometer* dan analisis foto luminescence diukur menggunakan *Photoluminescence Spectrometer.* Saput tipis yang terhasil adalah berwarna coklat kemerahan bergantung kepada masa pemendapan. Ketebalan sampel bertambah apabila masa pemendapan bertambah. Ketebalan filem, d yang terhasil dengan julat antara 1092.38 nm hingga 1331.03 nm. Indeks biasan adalah berkurang apabila ketebalan sampel bertambah. Imej yang dihasilkan oleh AFM adalah permukaan morfologi seragam dan kelihatan seperti piramid apabila masa pemendapan bertambah. Kadar penghantaran kuprum nitrida adalah rendah dalam cahaya nampak, tetapi mula meningkat dalam julat sinar merah. Pekali penyerapan, α bertambah apabila tenaga fonon bertambah. Purata jurang tenaga optik, E_g adalah antara julat 1.56 eV hingga 2.06 eV. Panjang gelombang puncak maksimum terbaik bagi pancaran foto luminescence adalah 380 nm yang merujuk kepada warna *ultra-violet* berdasarkan kepada spektrum cahaya nampak.

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LIST OF ABBREVIATIONS

AC	-	Alternating Current
AES	-	Auger Electron Spectroscopy
AFM	-	Atomic Force Microscopy
CL	-	Cathodoluminescence
DC	-	Direct Current
EL	-	Electroluminescence
IBAD	-	Ion Beam Assisted Deposition
NIR	-	Near Infrared
PL	-	Photoluminescence
RF	-	Reactive Frequency
RMS	-	Root Mean Square
SEM	-	Scanning Electron Microscopy
SPM	-	Scanning Probe Microscopy
UV	-	Ultraviolet
VIS	-	Visible
XPS	-	X-Ray Photoelectron Spectroscopy
XRD	-	X-Ray Diffraction

LIST OF SYMBOLS

A	-	Absorbance
Ar	-	Argon
B	-	Band tailing constant
Cu	-	Copper
d	-	Thickness
E_g	-	Energy band gap
E_{opt}	-	Optical band gap energy
I	-	Intensity
I_0	-	Intensity of incident light
I_A	-	Intensity of absorbed light
I_R	-	Intensity of reflected light
I_T	-	Intensity of transmitted light
N	-	Nitrogen
n	-	Refractive index
O	-	Oxygen
PbS	-	Plumbum Sulfide
R	-	Reflectivity

T	-	Transmittance
α	-	Absorption coefficient
Θ_1	-	Angle of incidence
Θ_2	-	Angle of refraction

CHAPTER 1

INTRODUCTION

This chapter consists of some general information about background of research definition of thin film, problem statement, research objectives and the scope of the research.

1.1 Background of Research

Any solid or liquid object with one of its dimensions very much less than that of the other two may be called a “thin film” (George, 1996). The most commonly observed phenomenon associated with thin films, which attracted the attention of physicists as early as the second half of seventeenth century, is the fascinating colours on a thin film of oil coating on the surface of water.

Thin films of metals were probably first prepared in a systematic manner by Micheal Faraday, using electrochemical methods (George, 1996). In the earlier stages, scientific interest in thin solid films centered on antireflection coatings for lenses, multilayer interference filters, automobile headlights and decorative coatings.

An application of thin film technology has revolutionized the field of optics and electronics. The need for new and improved optical and electrical devices has stimulated the study of thin solid films of elements, as well as binary and ternary systems, which controlled composition and specific properties, and has consequently accelerated efforts to develop different thin film deposition techniques. Among advantages of thin films devices are low power consumption, relatively small and reduction occupied space and higher speed performance (Sakrani, 2004).

In recent years, copper nitride thin film has been attracting considerable attention as a new material applicable for optical storage devices and high-speed integrated circuits (Maruyama *et al.,* 1996 & Dorranian *et al*, 2012). It is a promising material for write - once optical recording media devices and microscopic metal links in ultra large scale integrated circuits due to its excellent properties such as nontoxicity and thermal decomposition at lower temperature (100 ~ 470 °C).

It is also an indirect band gap semiconductor with low reflectivity and high electrical resistivity at room temperature. Additionally, this material can also be used as the candidates for an insulating barrier in magnetic tunnel junctions and the electrode material of Li-ion batteries (Xing *et al.*, 2007).

However in these past ten years, an experiment conducted to study the properties of copper nitride increases. Work by Yue *et al*. (2005) shows that the copper nitride phase is very unstable. It can be completely decomposed into Cu and N_2 through vacuum annealing treatment at a temperature of 200ºC. Yuan *et al*. (2006) studied the influence of nitrogen content on the properties of the as-deposited copper nitride thin films. They found that films deposited at higher nitrogen content have relatively smaller grains. The optical energy gap were measured to be in the range of 1.34 – 1.75 eV.

Many research groups have been synthesized copper nitride thin films by various methods, such as molecular beam epitaxial, DC magnetron sputtering, RF magnetron sputtering, pulsed laser deposition, and ion assisted vapor deposition (Arrabal *et al.*, 2010). However, the phenomenon of sputtering has several advantages in film deposition compared to others. There is no direct heating of the material as in evaporation methods.

Therefore, there is no reaction between the source and crucible place. This method is commercially advantageous, since they are relatively easy to scale up, offer high deposition rates, and are comparatively gentle to the substrate (Liljeholm, 2012). The popularity of DC sputtering from elemental targets can be attributed to several factors, like it is capable of producing thin compound films of controllable stoichiometry and composition at high deposition rates and on an industrial scale and high-purity films can be produced due to the elemental targets are usually more easily purified.

1.2 Problem Statement

The study on properties of copper nitride thin films has become one of the interests in investigations among the researchers for many years due to its potential in the electronic industry as well as applications for microelectronics devices. Although the copper nitride has been a subject of research for a long time, its optical properties are still not very clearly understood. In this investigation an attempt is made in the deposition of copper nitride thin films and it will be synthesized by using a self-assemble DC sputtering method. The samples were deposited at different deposition times. The surface morphology and optical properties of copper nitride thin films would be investigated.

1.3 Research Objectives

The objectives of this study are:

1. To synthesize the copper nitride thin film by using DC sputtering method.

2. To determine the surface morphology and grain size of copper nitride thin film by Atomic Force Microscopy (AFM).

3. To characterize the absorption of the copper nitride thin film by means of UV-Vis-NIR spectroscopy.

4. To characterize the emission properties of the copper nitride thin film by means of PL spectroscopy.

1.4 Scope of the Study

The scope of study has been focus on following:

1. Preparation of copper nitride thin film samples using DC sputtering technique in five different deposition times at 60 min, 90 min, 120 min, 150 min, and 180 min.

2. Determination the thickness and refractive index of copper nitride thin film by using Ellipsometer.

3. Determination of surface morphology and grain size of copper nitride thin film by using Atomic Force Microscopy (AFM).

4. Characterization of transmission spectra by using UV-Vis-NIR spectrophotometer and determination of absorption coefficient and optical band gap energy.

5. Characterization of emission properties by using Photoluminescence spectrometer.

1.5 Significance of the Study

The results of this study may discover the new one or improve the existence of optical properties. Hence the fabrication of semiconductor copper nitride material will be used widely in related applications such as for optical storage devices and high speed integrated circuits. Moreover, the study on the optical properties might be significant in providing a baseline data that can be used for further research and development of copper nitride thin film based on optical devices.

REFERENCES

Arrabal, R. G., Gordillo, N., Martin Gonzales, M. S., Ruiz Bustors, R., and Agullo-Lopez, F. (2010). Thermal Stability of Copper Nitride Thin Films: The Role of Nitrogen Migration. *Journal of Applied Physics*. 107(103513), 1-7.

Barna, P. B. (2005). History of Thin Films: Growth, Techniques, Characterization. *Advanced Materials Science and Electron Microscopy*.

Chen, E. (2004*).* Thin Film Deposition. *Applied Physics*. 298.

Cho, S. (2012). Effect of substrate temperature on the properties of copper nitride thin films deposited by reactive magnetron sputtering. *Current Applied Physics*. 12, 44-47.

Dorranian, D., Dejam, L., Sari, A. H., and Hojabri, A. (2009). Effect of nitrogen Content on Optical Constants of Copper Nitride Thin Films Prepared by DC Magnetron Reactive Sputtering. *Journal of Theoretical and Applied Physics*. 3-3, 37- 41.

Dorranian, D., Dejam, L., and Mosayebian, G. (2012). Optical characterization of Cu_3N thin film with Swanepoel method. *Journal of Theoretical and Applied Physics.* 6, 13.

Eckertov'a, L. (1986). *Physics of Thin Films (Second Revised Edition).* New York: Springer-Verlag.

Gallardo-Vega, C., and de la Cruz, W. (2006). Study of the structure and electrical properties of the copper nitride thin films deposited by pulsed laser deposition. *Applied Surface Science*. 252, 8001-8004.

George. J., (1996). "*Preparation of Thin Film*". United State of America.

Ghosh, S., Singh, F., Choudharya, D., Avasthia, D. K., Ganesanb, V., Shah, P., and Gupta, A. (2001). Effect of substrate temperature on the physical properties of copper nitride films by r.f. reactive sputtering. *Surface and Coatings Technology*. 142-144, 1034-1039.

Hayashi, Y., Ishikawa, T., and Shimokawa, D. (2002). Modification of electrical and optical peroperties of metal nitride thin films by hydrogen inclusion. *Journal of Alloys and Compounds*. 330 (332), 348 -351.

Hanewald, K., Glutsch, S, and Bechstedt, F. Theory of photoluminescence excitation spectroscopy in semiconductors. *Applied Physics*.

Ji, A. L., Huang, R., Du, Y., Li, C. R., Wang, Y. Q., and Cao, Z.X. (2006). Growth of stoichiometric Cu_3N thin films by reactive magnetron sputtering. *Journal of Crystal Growth* . 295, 79-83.

Lotfi-Kajlahi, A., and Savaloni, H. (2013). Investigation on the production of copper nitride (copper azide) thin films and their nanostructures. *Journal of Theoretical and Applied Physics*. 72, 1-6.

Liljeholm, L. (2012). Reactive Sputter Deposition of Functional Thin Films. *Digital Comprehensive Summaries of Uppsala Dissertations from the Faculty of Science and Technology*. 945, ISBN 978-91-554-8403-3.

Kitabatake, M., Wasa, K., and Adachi, H. (2004). Thin Film Materials Technology. Japan.

Maruyama, T., and Morishita, T. (1995). Copper Nitride Thin Film Prepared by RF Reactive Sputtering. *Journal Applied Physics*. 78 (4104).

Maruyama, T., and Morishita, T. (1996). Copper Nitride and Tin Nitride Thin Films forWriteonce Optical Recording Media. *Applied Physics Letters*. 69(7).

Mech, K., Kowalik, R., and Zabinski, P. (2011). *Cu Thin Films Deposited by DC Magnetron Sputtering for Contact Surfaces on Electronic Components.* 56(4).

Mikula, M. (2001). *Electrical and Optical Properties of Copper Nitride Thin Films Prepared By Reactive DC Magnetron Sputtering.* 51 (1), 35-43.

Noor Azizun, M. A. *Optical properties and Photoluminescence of Copper Nitride Thin Film prepared by Reactive DC Sputtering*. Master of Science Thesis. Universiti Teknologi Malaysia; 2013.

Nosaka, T., Yoshitake, M., Okamoto, A., Ogawa, S., and Nakayama, Y. (1999). Copper nitride thin films prepared by reactive radio-frequency sputtering. *Thin Solid Films*. 348, 8-13.

Odeh, I. M. (2008). Fabrication and Optical Constants of Amorphous Copper Nitride Thin Films Prepared by Ion Beam Assisted DC Magnetron Reactive Sputtering. *Journal of Alloys and Compound.* 454, 102-105.

Pierson, J. F. (2002). Structure and properties of copper nitride films formed by reactive magnetron sputtering. *Vacuum*. 66, 59-64.

Reddy, K. V. S., Reddy, A. S., Reddy, P. S.,and Uthanna, S. (2007). Copper nitride films deposited by dc reactive magnetron sputtering. *J Mater Sci: Mater Electron*. 18, 1003-1008.

Sakrani, S. (2004). *Lecture Note: Thin Films technology*. Universiti Teknologi Malaysia.

Shinde, K.N. (2013). Basic Mechanisms of Photoluminescence. *Springer Series in Materials Science.* 174.

Subbareddy, K. V., Subramanyam, K., and Uthanna, S. (2007). *Optoelectronics and Advanced Materials – Rapid Communications.* 1 (1), 31-35.

Wang, D. Y., Nakamine, N., Hayashi, Y. (1998). Properties of Various Sputter Deposited Cu-N Thin Films. *Journal of Vacuum Science and Technology*. 16, 2084-2092.

Wang, J., Chen, J. T., Yuan, X. M., Wu, Z. G., Miao, B. B., and Yan, P. X. (2006). Copper Nitride Thin Films Deposited by RF Magnetron Sputtering. *Journal of Crystal Growth*. (286), 407-412.

Xiao, J., Li, Y., and Jiang, A. (2011). Structure, Optical Property and Thermal Stability of Copper Nitride Films Prepared by Reactive Radio Frequency Magnetron Sputtering. J. Mater. Sci. Techno. 27(5), 403-407.

Xing, L., Zuli, L., Anyou, Z., Zuobin, Y., Jianping, Y., and Kailun, Y. (2007). Properties of Al-doped Copper Nitride Films Prepared by Reactive Magnetron Sputtering. *Journal of Wuhan University of Technology Mater Sci. Ed*. 22 (3).

Yuan, X. M., Yan, P. X., and Liu, J. Z. (2006). Preparation and characterization of copper nitride films at various nitrogen contents by reactive radio-frequency magnetron sputtering. *Materials Letters*. 60, 1809-1812.

Yue, G. H., Yan, P. H., and Wang, J. (2005). Study on the Preparation and Properties of Copper Nitride Thin Films. *Journal of Crystal Growth*. 274, 464-468.