ELECTRICAL PROPERTIES OF COPPER NITRIDE THIN FILM PREPARED BY REACTIVE DC SPUTTERING

WAN NOOR EZIANTI BT. WAN MOHD NORAL AZMAN

UNIVERSITI TEKNOLOGI MALAYSIA

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WAN NOOR EZIANTI BT. WAN MOHD NORAL AZMAN

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Faculty of Science
Universiti Teknologi Malaysia

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To my beloved mother and father

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ABSTRACT

The purpose of this research is to study the electrical properties of copper nitride (Cu_3N) thin films. Cu_3N were deposited on corning glass substrates by using reactive DC sputtering technique. Four samples were prepared with different deposition time to obtain samples of different thicknesses. The thickness of the samples increases as the deposition time increase. The electrical conductivity of Cu_3N thin films was measured by using the Van der Pauw method. Results obtained show that the conductivity of Cu_3N films increases as the thickness of the films increases. The effect of temperature on conductivity of the Cu3N thin film was also studied. The conductivity of the samples was measured under high temperature from 313 K to 573 K. The results show that the conductivity of Cu_3N thin films increases as the temperature increases. The activation energy was also calculated. The sample with high conductivity has low activation energy.

ABSTRAK

Penyelidikan ini bertujuan untuk mengkaji sifat elektrik saput tipis Cu_3N. Cu_3N telah dipendapkan pada permukaan substrat kaca dengan menggunakan kaedah percikan reaktif arus terus. Empat sampel telah disediakan pada masa pemendapan yang berbeza untuk menghasilkan sampel yang mempunyai ketebalan yang berbeza. Ketebalan sampel bertambah apabila masa pemendapan bertambah. Kekonduksian elektrik bagi saput tipis Cu_3N diukur dengan menggunakan kaedah Van der Pauw. Keputusan yang diperolehi menunjukkan bahawa kekonduksian bagi saput tipis Cu_3N meningkat apabila ketebalan saput bertambah. Kesan suhu terhadap kekonduksian saput tipis Cu_3N juga turut di kaji. Kekonduksian bagi sampel telah diukur pada suhu tinggi dari 313 K hingga 573 K. Keputusan telah menunjukkan bahawa kekonduksian Cu_3N meningkat dengan peningkatan suhu. Tenaga pengaktifan telah di kaji. Sampel yang kekonduksiannya tinggi mempunyai tenaga pengaktifan yang rendah.

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LIST OF SYMBOLS

f	-	Coefficient factor for Van der Pauw.
J	-	Current density
σ	-	Conductivity
k_B	-	Boltzmann's constant
d	-	Sample thickness
E_g	-	Optical energy gap
R_s	-	Sheet resistance
eV	-	Electron Volt
μ	-	Mobility
m	-	Mass
Ω	-	Ohm (SI unit for resistivity)
ρ	-	Resistivity
ω	-	Frequency
Å	-	10^{-10} m
θ	-	Angle
K	-	Kelvin (1 ºC = 273 K)
t	-	Deposition time
T	-	Temperature (Kelvin, K)
E_{a1}	-	Activation energy at higher temperature.
E_{a2}	-	Activation energy at lower temperature.
$R_{AB,CD}$	-	Resistance when current flows across AB point and voltage across CD point.

$R_{CD,AB}$ - Resistance when current flows across CD point and voltage across AB point.

$R_{AD,BC}$ - Resistance when current flows across AD point and voltage across BC point.

$R_{BC,AD}$ - Resistance when current flows across BC point and voltage across AD point.

LIST OF ABBREVIATIONS

Al	-	Aluminium
Al_2O_3	-	Aluminium oxide
Ar	-	Argon
CdS	-	Cadmium sulfide
Cu	-	Copper
DC	-	Direct current
EHP	-	Electron-hole pair
GaAs	-	Galium arsenide
Mo	-	Molybdenum
N_2	-	Nitrogen gas
ReO_3	-	Rhenium trioxide
Si	-	Silicon
Ta	-	Tantalum
Ti	-	Titanium
nm	-	nanometer
TaN	-	Tantalum nitride
TiC	-	Titanium carbide
ZnS	-	Zinc sulphide
W	-	Tungsten
AES	-	Auger electron spectroscopy
XPS	-	X-ray photoelectron spectroscopy
AFM	-	Atomic force microscopy
SEM	-	Scanning electron miscoscope

MBE	-	Moleculr beam epitaxy
CVD	-	Chemical vapour deposition
PVD	-	Physical vapour deposition
RF	-	Radio frequency
Y	-	Sputtering yield

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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

Thin film is one of the areas in material science which study the low dimensional properties of artificial layers in comparison to their bulk properties. The first phenomena observed which related to thin film was in 1838 by Faraday during the electrolysis process. Then in 1927, electron diffraction on thin film was observed by Davison-Germer. Since then, rapid development of thin film technology started in many areas including electronics, optoelectronics, and laser.

Thin film technology is important due to miniaturization of mainly in the electrical area like hand phone, laptop, etc. Until today, researcher keeps on studying to find ways to improve the characteristics of thin film. Among the advantages of thin film devices are relatively small in size, low power consumption, cheaper, faster and more effective in performances.

In recent years, there has been much interest in studying the properties of copper nitride thin films which have a potential in the electronic industry. However in these past ten years, an experiment conducted to study the properties of copper nitride increases. In 2006, Gallardo-Vega and de la Cruz prepared copper nitride films by pulsed laser deposition and concluded that the electrical resistivity increases when the lattice parameter is decreased.

Work by Yue *et al*. (2005) shows that the Cu_3N 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 electrical resistivity and optical energy gap were measured to be in the range of $1.51 \times 10^2 – 1.129 \times 10^3$ Ω, and 1.34 – 1.75 eV, respectively.

1.2 Definition of Thin Film

The thin film is simply defined as the layer of material (metal, semiconductor and insulator) deposited on a substrate at a film thickness less than 1000 nm. A familiar application of thin film for example in the household is a mirror, which typically has a thin metal coating on the back of a sheet of glass to form a reflective interference.

1.3 Copper Nitride Thin Films

In recent years, copper nitride has attracted much attention from both research groups and in the electronic industry. This was due to its properties which is thermally unstable and decomposes into copper and nitrogen. The facile decomposition of this compound, though absolutely troublesome of the film growth practitioners are still promises many innovative applications such as fabrication of optical storage devices and microscopic metal links with mask less laser or electron beam writing.

Copper nitride films deposited by Nosaka *et al*. (1999) present a reddish dark brown colour. It is a metastable semiconductor material with a cubic anti-ReO_3 type crystal structure with a lattice constant of 3.815 Å. In this structure, nitrogen atoms are positioned at the corner of the cell and copper atoms are positioned at the center of the cube edges as shown in Figure 1.1. Copper atoms do not occupy perfectly the sites in (111) plane, so the crystal structure has many vacant interstitial sites that can be filled with contaminants with remarkable changes of the electrical and optical properties.

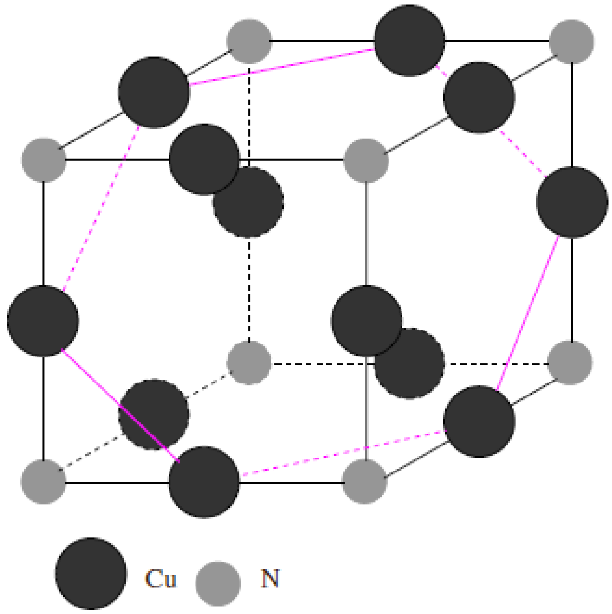

Figure 1.1: Structure of Cu_3N. (Wang *et al*, 2006)

Ji *et al*. (2006) reported that the binary compound Cu_3N is an indirect band gap semiconductor which readily decomposes into Cu and N_2 at an elevated temperature. The thermal decomposition was found to be at ~350 ºC which indicated that Cu_3N films have excellent thermal stability. The chemical composition of copper nitride was studied by Gallardo-Vega and de la Cruz (2006) by using Auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS). The result showed that the samples are constituted mainly of copper and nitrogen.

Maruyama and Morishita (1995) produced conductive copper nitride thin film by RF magnetron reactive sputtering. They reported that the films with lattice constants above 3.868 Å were conductors, while films with lattice constants below 3.868 Å were insulators. They also suggested that the conductor behaviour of the copper nitride films is due to the insertion of a copper atom into the body center cubic structure of the anti-ReO_3. Pierson (2002) found from his experiment that both the lattice constant and electrical resistivity increases with the nitrogen flow.

According to Yuan *et al.* (2006), the nitrogen N_2 content greatly affects the preferential orientation of the crystalline films. Then the mean grain size of the films is estimated by the Debye-Scherrer formula. The mean grain size of the grains is in nanoscale and an increase from 6.8 to 19.44 nm with the increasing of N_2 content. This proved that the films deposited at higher nitrogen content have relatively smaller grains. However, Pierson (2002) stated that the size of the grain of copper nitride ranges from 9 nm to 16 nm for all nitrogen flow rates where the mean crystal size was calculated from the copper nitride (100) plane using modified Scherrer formula.

The fracture section and the surface morphologies of copper nitride films were investigated by using Scanning Electron Microscope (SEM) and Atomic Force Microscopy (AFM). The results show that copper nitride films have a clean and smooth surface morphology (Yuan *et al*. 2006). The thickness of the films is about 1 μm and the average diameter of surface grains is approximately 25 nm. In terms of hardness, copper films have a microhardness of 1.7 GPA. The films hardness increase abruptly with the introduction of N_2 in the reactive mixture.

Wang *et al*. (1998) prepared copper nitride films by changing the content of nitrogen gas at various sputtering pressures. They concluded that the band gap of the film could be engineered by controlling the nitrogen gas pressure. A calculation of electronic structure showed that copper nitride is a semiconductor with a small indirect band gap. It was also predicted that the copper nitride is a better conductor when it is rich in copper and that extra copper produces an increase in the lattice constant. (Monero-Armenta *et al*., 2004)

As for the band gap of the semiconductor copper nitride, experimental value reported falls within the range of 1.2 eV to 1.9 eV (Ghosh *et al*., 2001). Whatever the changes in the band gap energy, E_g against the N_2 content, it attributes to semiconductor character. It is observed that the optical band gap decreases along with the resistivity. Work by Venkata Subba Reddy *et al*. (2007) shows that the optical band gap of Cu_3N thin films decreased from 1.89 to 1.54 eV and the electrical resistivity of the films decreases from 8.7 x 10^{-1} to 1.1 x 10^{-3} Ωm with the increase of substrate temperature from 303 to 523 K.

However, Yuan *et al*., 2006 reported that the electrical resistivity increases with increasing of nitrogen content when measured at room temperature. Accordingly, the semiconductor nature of Cu_3N films can be understood by the nonstoichiometry of the films. For example, the low N_2 content in the sputtering process will result in more copper doping in copper nitride and more free carriers. Hence the resistivity of the films decreases with decreasing the N_2 content.

1.4 Problem Statement

In the past years, interest in copper nitride (Cu_3N) thin films is growing because of potential applications of this material like write-once optical recording media. Although researches on copper nitride have been going on for a long time, its properties are still not well understood (Gallardo-Vega and de la Cruz, 2006). This could be due to insufficient information about the stoichiometry of the sample. In this work, copper nitride will be prepared by using the reactive DC sputtering method. The samples were deposited at different duration of time. The electrical properties of copper nitride films would be investigated.

1.5 Research Objectives

The objectives of this study are:

1. To determine the thickness of the copper nitride (Cu_3N) thin films.
2. To measure the conductivity of Cu_3N films at room temperature by using Van der Pauw technique.
3. To measure the conductivity of Cu_3N thin films at higher temperature from 313 to 573 K using Van der Pauw technique.
4. To calculate the activation energy of Cu_3N thin films.

1.6 Scope of the Research

In this work, four sets of copper nitride thin films would be prepared on glass substrates by reactive DC sputtering. The deposition time of each set is different, which are in 1 ½ hours, 2 hours, 2 ½ hours and 3 hours. The main scope of this study is to investigate the electrical properties of copper nitride thin films like resistivity and conductivity by using Van der Pauw technique. For the structural properties, only the thickness of the films is measured.

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