Available online at www.sciencedirect.com
SCIENCE DIRECT®
Materials Letters 60 (2006) 1809 – 1812
materials letters
www.elsevier.com/locate/matlet

Preparation and characterization of copper nitride films at various nitrogen contents by reactive radio-frequency magnetron sputtering

X.M. Yuan [a], P.X. Yan [a,b,*], J.Z. Liu [a]

[a] *Institute for Plasma and Metal Materials, Lanzhou University, Lanzhou 730000, PR China*
[b] *Key Laboratory of Solid Lubrication, Institute Chemical and Physics, Chinese Academy of Science, Lanzhou 730000, PR China*

Received 15 October 2005; accepted 8 December 2005
Available online 4 January 2006

Abstract

The semiconducting Cu_3N films were successfully deposited on glass substrates by reactive radio-frequency magnetron sputtering in a mixture gas of nitrogen and argon. The influence of nitrogen content in a fixed total sputtering gas flow on the preferential crystalline orientation, the mean crystalline grains size, the electrical resistivity, and the optical energy gap of as-deposited films were investigated. X-ray diffraction analysis shows that the films were polycrystalline Cu_3N and the preferential orientation is greatly affected by the N_2 content. All the Cu_3N films have smooth surfaces with dense and continuous microstructure. The electrical resistivity and the optical energy gap of these as-deposited Cu_3N films were measured to be in the range of 1.51×10^2–1.129×10^3 Ω cm, and 1.34–1.75 eV, respectively.

Keywords: Copper nitride film; Surface morphology; Electrical resistivity; Optical energy gap

1. Introduction

In recent years, there has been much interest in studying the properties of Cu_3N films. Cu_3N is a promising material which has potential applications in the electronic industry, such as write-once optical recording media devices [1] and high-speed integrated circuits [2]. Until now, Cu_3N films have been prepared with different methods, including ion-assisted vapor deposition [1], reactive rf magnetron sputtering [2–9], and direct current sputtering [10]. The nontoxic semiconductor material of Cu_3N has the cubic anti-ReO_3 structure with lattice constant of 3.815 Å. The electrical and optical properties of Cu_3N could be varied remarkably by inserting Cu or other elemental atom into the body center of anti-ReO_3 structure. However, by reviewing the previous work on study of Cu_3N films [11], some physical properties of Cu_3N films were reported inconsistently. The decomposition temperature of Cu_3N was found to be in the region of 100–470 °C [1,6–10]. The resistivity of Cu_3N films altered from 2×10^{-5} to 2×10^3 Ω cm [5,6,12] and the optical energy gap of Cu_3N thin films was reported to be 0.8∼1.9 eV [1,4–6,13–16].

In our work, Cu_3N films were prepared on glass substrates by reactive rf magnetron sputtering with different nitrogen

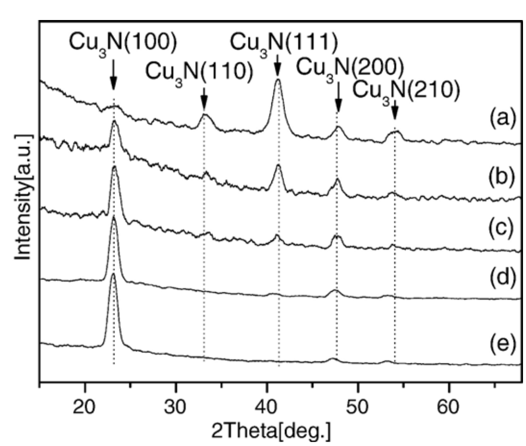

Fig. 1. The X-ray diffraction patterns of films deposited at various nitrogen contents ($N_2/(N_2+Ar)$): (a) 20% N_2; (b) 33% N_2; (c) 47% N_2; (d) 80% N_2; (e) 100% N_2.

* Corresponding author. Institute for Plasma and Metal Materials, Lanzhou University, Lanzhou 730000, PR China. Tel.: +86 931 8912719; fax: +86 931 8913554.
E-mail address: yuanxm03@163.com (P.X. Yan).

0167-577X/$ - see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.matlet.2005.12.028

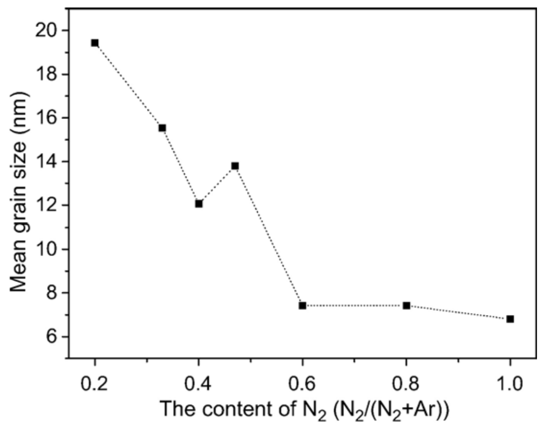

Fig. 2. The mean grain size of Cu_3N films deposited at various N_2 contents.

contents. We focus on the influence of nitrogen content on the structure, the grain size, and the electrical resistivity of the as-deposited films. Moreover, the surface morphology and the optical properties were also studied.

2. Experiment

The copper nitride films were prepared by reactive rf (13.5 Hz) magnetron sputtering equipment using a 99.999% pure copper target. The working gas was a mixture gas of nitrogen and argon, and each of the gas flow rate was controlled by mass flow controllers. Glass sheets (Cat. no. 7101, Feizhou Co., China) were ultrasonically cleaned in a mixture of acetone and ethanol and then used as substrates. The distance between the substrate and target was 40 mm. Before deposition, the chamber was pre-evacuated to less than 1×10^{-3} Pa. During deposition, the rf power was set at 100 W, the temperature was kept at 150 °C, and the total gas pressure was fixed at 1 Pa. A series of films were deposited for 1 h under various nitrogen contents with fixed total gas flux of 15 sccm.

The structure of the films was analyzed by X-ray diffractometer (XRD) using CuKα radiation. The fracture section and surface morphology of the films were studied using the scanning electron microscope (SEM) and the atomic force microscope (AFM). The four point resistivity test system and the UV-VIS spectroscopy were employed to investigate the electrical resistivity and optical properties of the films.

3. Results and discussion

3.1. Structure of Cu_3N films

Fig. 1 shows the typical XRD patterns of copper nitride films deposited at fixed total flow rate of 15 sccm with various nitrogen contents ($N_2/(N_2+Ar)$) changing from 20% to 100%. The XRD patterns of films deposited with the content of nitrogen over 40% are similar, so those corresponding to 50%, 60%, 70% and 90% nitrogen contents are not presented here.

It is noted from Fig. 1 that the N_2 content greatly affects the preferential orientation of the crystalline films. By increasing the N_2 content from 20% to 100%, the original strongest peak of (111) decreased while the peak of (100) increased to be the strongest. The preferential orientation of the grains is a function of stoichiometry, growth rate and the kinetic energy of arriving species, all of which change with the mobility of the Cu and N atoms participating in film growth with alterable sputter gas flow under fixed temperature. It has been reported that the nitrogen density in the sputtering gas mixture significantly affects the growth behavior [2]. At lower nitrogen content, the density of N atoms reaching the substrate with high kinetic energy is rather insufficient for constructing N-rich planes like (100). On the contrary, the Cu-rich plane, such as (111), has a relatively high growth rate. At higher nitrogen content, the density of N atoms increase and the absorbed N atoms can possess appropriate kinetic energy to react with Cu atoms, which leads to high density of Cu–N bonds for the preferential growth along the (100) direction.

The lattice constant calculated from XRD information is irregular with decreasing N_2 content. It oscillates between 3.798 and 3.842 Å, and the largest lattice expansion is about 0.71%. The mean grain size of the films is estimated by Debye–Scherrer formula [18] and the results are represented in Fig. 2. The mean size of grains is in nanoscale and increases from 6.80 to 19.44 nm with decreasing N_2 content. The changes in the grain size with deposition conditions can be ascribed to the competition between grain growth rate and nucleation rate. As the nitrogen content decreases in our experiment, the argon content would accordingly increases, which results in increase of the sputtering rate of Cu target and the N atoms are insufficient to compose with sputtered Cu atoms. Therefore Cu atoms prefer to devote to growth rather than nucleation and the grain size will be larger.

3.2. Morphology of the Cu_3N films

The fracture section and the surface morphologies of Cu_3N films were investigated using SEM and AFM. All the films have clean and smooth surface morphology. Fig. 3 shows the typical SEM and AFM

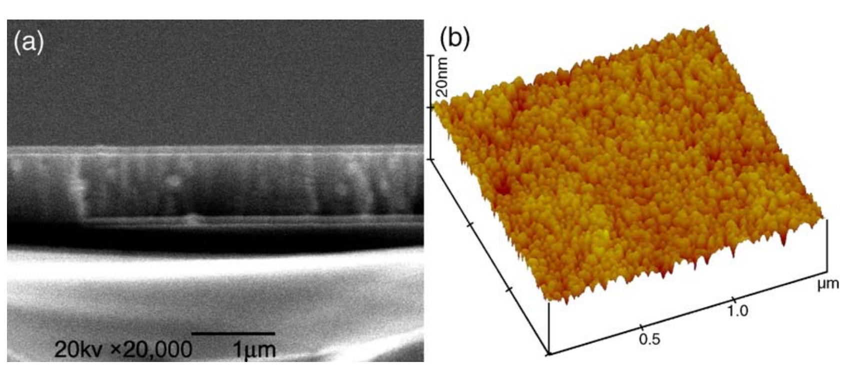

Fig. 3. The typical SEM (a) and AFM (b) images of the copper nitride film deposited on glass with 20%N_2.