Available online at www.sciencedirect.com
ScienceDirect
Applied Surface Science 254 (2008) 5012–5015
applied surface science
www.elsevier.com/locate/apsusc

The effect of hydrogen on copper nitride thin films deposited by magnetron sputtering

Guangan Zhang [a,b], Pengxun Yan [a,b,*], Zhiguo Wu [a], Jun Wang [a], Jiangtao Chen [a]

[a] School of Physical Science and Technology, Lanzhou University, Lanzhou 73000, China
[b] State Key Laboratory of Solid Lubrication, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, China

Received 1 November 2007; received in revised form 28 December 2007; accepted 30 January 2008
Available online 8 February 2008

Abstract

Copper nitride thin films were deposited on Si (1 0 0) wafers by reactive magnetron sputtering at various H_2/N_2 ratios. X-ray diffraction measurements show that the films are composed of Cu_3N crystallites with anti-ReO_3 structure and exhibit preferred orientation of [1 0 0] direction. Although the relative composition of the films has obviously changes with the H_2/N_2 ratios, the orientations of the films keep almost no changes. However, the grain size, lattice parameter and composition of the films are strongly dependent on the H_2/N_2 ratios. The copper nitride films prepared at 10% H_2/N_2 ratios show poor stability and large weight gain compared to the copper nitride films prepared at 0% H_2/N_2 ratios.

Keywords: Copper nitride; Thin films; Hydrogen; Structure; Thermal properties

1. Introduction

Copper nitrides have attracted considerable attention as a new material for optical storage devices and semiconductor integrate circuit, based on its unique properties, such as the rather low thermal decomposition temperature, semiconductor properties and excellent optical qualities [1–3]. A number of non-equilibrium techniques, such as RF reactive sputtering [4,5], DC magnetic sputtering [6], ion assisted vapor deposition [7], reactive pulsed laser deposition [8] and other methods [9], are currently available for the preparation of copper nitride films. Although these many alternative methods could successfully prepare copper nitride films, the effect of the preparation parameter on the structure and properties of the copper nitride films still have not been well characterized. The hydrogen acts as a sputtering gas like argon not as reactive gas in the film deposition process. And the influence of the light hydrogen ions on the bombardment of target, sputtering rate and the kinetic energies of Cu and N atoms is very low, while the composition of the films could be controlled through the change of the H_2/N_2 ratios. The copper nitride films prepared at nitrogen and hydrogen gas mixture atmosphere may show unexpected structure and properties. In this paper, the copper nitride thin films were prepared at various H_2/N_2 content in order to investigate the structure evolutions. Meanwhile, the thermal properties of the films are also examined.

2. Experiment

Copper nitride thin films were deposited on silicon (1 0 0) substrates using magnetron sputtering Cu (99.99% pure copper) target in nitrogen and hydrogen gas mixture atmosphere at room temperature. The sputtering chamber was evacuated to a pressure of about 10^{-3} Pa with a turbomolecular pump before introducing sputtering gas. The Si substrates were cleaned ultrasonically in acetone and de-ionized water. Prior to the film deposition, the substrate bias voltage was kept −700 V for the Ar glow plasma cleaning. After the Ar glow plasma cleaning, the 20 min film deposition process was carried out at 200 sccm N_2 and various H_2 flow rate (0–20 sccm). We kept the target current at 1.6 A in all the deposition process. The operating pressure was 0.5–0.6 Pa. At all stage of deposition process, no external heat was provided to the substrates.

* Corresponding author. Tel.: +86 931 8912661; fax: +86 931 8913554.
E-mail address: pxyan@lzu.edu.cn (P. Yan).

0169-4332/$ – see front matter
doi:10.1016/j.apsusc.2008.01.156

In this study, the relative Cu and N compositions of the copper nitride films were determined using X-ray photoelectron spectroscopy (XPS) (PerkinElmer PHI-5702 multi-functional photoelectron spectrometer) with Al Kα radiation (1476.6 eV). The XPS spectra were collected with a constant analyzer energy mode, at a chamber pressure of 10^{-8} Pa and pass energy of 29.4 eV, with 0.125 eV/step. X-ray diffraction (XRD) was performed on Philips X'perts diffractometer at Cu Kα wavelength. To obtain the diffraction peak profiles of the thin films along the vertical direction, grazing angle X-ray diffraction (GAXAD) with a grazing angle of 1° was applied for phase identification and qualitative texture characterization. Field emission-SEM (Hitachi, S-4800) was utilized to observe the surface microstructure. The as-deposited Cu_3N films were subjected to thermal analysis using a thermogravimetry analysis (TGA) system, which is equipped on PerkinElmer Thermal Analysis system in air.

3. Results and discussions

The atomic percentage of Cu and N atoms in the as-deposited films was derived from XPS analysis. By using an appropriate curve analysis and known sensitivity factors for both copper and nitrogen, the Cu/N ratios in the films were estimated, and their values are listed in Table 1. The theoretic value of nitrogen atomic percent in copper nitride is ~25%. The most approached value is 23.2% in the sample prepared at 0% H_2/N_2 ratios as showed in Table 1, while the Cu/N ratio is roughly 3:1. For the sample prepared at 2% H_2/N_2 ratios, the N content was a little higher than the theoretic nitrogen content. Further increase the H_2 content, the Cu/N ratio increases (larger than 3:1). And Cu-rich copper nitride films were formed under higher H_2/N_2 ratios. In such case, the hydrogen gas acts as a sputtering gas like argon, and the hydrogen dilutes the nitrogen concentration in the deposition atmosphere. The concentration of nitrogen in the sputter gas decreases with the increase of H_2/N_2 ratios hence there is a decrease in the nitrogen content in the films, which is similar to the result of the decrease of nitrogen partial pressure in argon and nitrogen mixture atmosphere [10,11]. Some remained hydrogen atoms in the copper nitride films deposited under H_2 and N_2 mixture is inevitable. However, the hydrogen content in the films cannot be detected from the XPS analysis because of the special structure of hydrogen atom.

Fig. 1 shows the XRD patterns of copper nitride films prepared on Si (1 0 0) wafer with various H_2/N_2 ratios. The spectra are corresponding to the cubic anti-ReO_3 structure of Cu_3N and no Cu peaks are found in all the as-deposited films. It can be observed that the preferential growth of copper nitride occurs in all films. A strong (1 0 0) texture and very weak

Table 1
The atomic percentage of Cu and N atoms in the films derived from XPS spectra

H_2/N_2 (%)	0	2	4	6	10
Cu (at.%)	76.8	68.8	80.8	89.0	93.9
N (at.%)	23.2	31.2	19.2	11.0	6.1

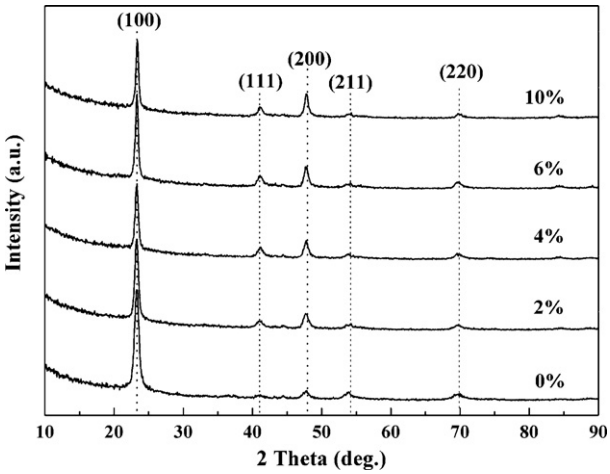

Fig. 1. XRD spectra of copper nitride films deposited at various H_2/N_2 ratios.

(2 0 0), (2 1 1) and (2 2 0) peaks of the copper nitride are observed in XRD pattern (0% H_2/N_2 ratios) corresponding to a pure nitrogen atmosphere. In XRD pattern (2–10% H_2/N_2 ratios) the peak of (1 0 0) is also the strongest one and a small peak of (1 1 1) appears. Although the relatively Cu/N ratios of the films have obviously changes with the H_2/N_2 ratios, the structure of the films only show very small changes even in the films prepared at 10% H_2/N_2 ratios. It gives an indication that the effect of H_2 in the sputtering gas mixture on the growth behavior is rather small. It is considered that the preferred orientation of the grains is interpreted to depend mainly on the mobility of the Cu and N atoms participating in the film growth. Such mobility is expected to be a function of the ratio between the number of N and Cu atoms reaching the substrate and also of the kinetic energies of these atoms [12,13]. While the nitride films deposited under Ar and N_2 mixture atmosphere, the bombardment of the argon towards the target and the film surface, and the ionization of the nitrogen influence the kinetic energies of the Cu and N atoms. Therefore, the argon content influences the film growth processes, and the films always show complicated growth orientations changes with the Ar/N_2 ratios various [10]. However, the bombardment of hydrogen ions towards the copper target and film surface is much lower than that of argon ions, and the sputtering rate of hydrogen ions is also very low, close to zero; this may not strongly influence the kinetic energies of Cu and N atoms. So the influence of the hydrogen on the growth orientation can be ignored. Also, the increase of hydrogen flow rate decreases the nitrogen content in the films and form substoichiometry copper nitride films. And this substoichiometry copper nitride films may influence the growth orientation slightly, and weak [1 1 1] orientation appears. Although the copper nitride films are substoichiometry at high H_2/N_2 ratios, these excessive copper atoms are not forming a separate phase just distributed in crystal boundary. And we can acquire fine (1 0 0) orientation growth Cu-rich copper nitride films under higher H_2/N_2 ratios.

In Fig. 1, it also appears clearly that the diffraction peaks of copper nitride (1 0 0) shift with H_2/N_2 ratios various. The lattice parameter has been estimated from the position of the (1 0 0) diffraction peak. Thus, the lattice constant of copper nitride