



Effect of N₂-gas flow rates on the structures and properties of copper nitride films prepared by reactive DC magnetron sputtering

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ABSTRACT

Copper nitride films were deposited on glass substrates by reactive DC magnetron sputtering at 100 °C substrate temperature. The influence of N₂-gas flow rates on the structure, resistivity and microhardness of deposited films was investigated. X-ray diffraction measurements showed that the films were composed of Cu₃N crystallites with anti-ReO₃ structure and exhibited preferential orientation to the [111] and [100]. The preferred crystalline orientation of the films changed with the N₂-gas flow rate, which should be caused by the variation of Cu nitridation rate with N₂-gas flow rate. Additionally, the N₂-gas flow rate also affected the deposition rate, the resistivity and the microhardness of the Cu₃N films. The optimum N₂-gas flow rate for producing high-quality and well-oriented Cu₃N films on glass substrates is 5–10 sccm, where the substrate temperature is 100 °C and the DC power is 50 W.

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1. Introduction

In recent years, copper nitride (Cu₃N) thin film has been attracting considerable attention as a new material applicable for optical storage devices and high-speed integrated circuits. Copper nitride is semiconductor and its optical reflectivity in the visible and infrared range is far smaller than that of pure Cu [1,2]. It is known that Cu₃N is stable at room temperature but starts to decompose into Cu and N₂ above 300 °C. The low decomposition temperature and discriminating optical properties of the compound compared to those of Cu are applicable for optical read-only memory disks by generating microscopic Cu-metal spots on Cu₃N film under local laser heating [3]. Cu₃N films can also be used as buffer layers for depositing Cu-metal lines on Si wafers to achieve higher signal speed than existing Al-metal lines in integrated-circuit fabrication processes. The crystal structure of Cu₃N is also interesting – it has the cubic anti-ReO₃ structure in which Cu atoms do not occupy the fcc (face centered cubic) close-packing sites. Hence another metallic atom can be inserted into the body center of the cubic unit cell to induce significant changes in the electrical properties [4–7].

The main method to prepare Cu₃N films is RF [8–11] or DC [12] sputtering, molecular beam epitaxy [13] and reactive pulsed laser deposition [14]. In sputtering, some parameters such as gas flow rate, substrate temperature, and sputtering power can significantly affect the structure of the deposited films. In this work, copper nitride thin films were prepared by reactive DC magnetron sputtering of a Cu target at 100 °C substrate temperature in Ar/N₂ gas mixture with various N₂-gas flow rates. The purpose of this study is to optimize N₂-gas flow rate for growing well-oriented and high-quality Cu₃N films on glass substrates.

2. Experiment

The experimental apparatus is JZCK-III multifunction magnetron sputtering system (produced by Shenyang Juzhi Technology Company Limited, China). For preparing Cu₃N films, reactive DC magnetron sputtering was used with a 99.999% pure Cu target with 50-mm diameter and 5 mm thickness. The distance between substrate and target was kept at 60 mm and the DC power at 50 W during the sputtering. The base pressure of the vacuum chamber before the sputtering was less than 8.0×10^{-4} Pa. The working and the reactive gases were 99.99% pure Ar and N₂, respectively. The Ar and N₂ gas flows were adjusted by independent mass-flow controllers and the total sputtering pressure was maintained at 1 Pa. The partial pressures of Ar and N₂ in the chamber were

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estimated by their respective flow rates measured by the mass-flow controllers. The ordinary glass ($\text{Na}_2\text{O} \cdot \text{CaO} \cdot 6\text{SiO}_2$) was used as substrates and substrate temperature was kept at 100°C using a thermostat system. Before deposition, the glass substrates were cleaned by ultrasonic waves in acetone and alcohol respectively, and finally dried by blowing air. Pre-sputtering was performed for 5 min before each deposition process for removing the oxidized surface layer of the target and for maintaining stability during the sputtering, the deposition time of each sample was 10 min.

The crystalline properties of the obtained films were analyzed by XRD measurements with $\text{CuK}\alpha$ line (X'Pert Pro. PANalytical, Holland). The thicknesses of films were measured by a profilometer (DEKTAKII). The resistivity of films was measured using the four-probe method (SZ-82, four-probe measure apparatus, Suzhou, China). The microhardness measurements were carried out on MICROMET2104 apparatus by using the maximum load 0.098N.

3. Results and discussion

3.1. The structure of films

Fig. 1 shows the XRD pattern of Cu_3N films deposited at the N_2 -gas flow rates of 5, 10, 15, 20, 25 sccm. The Ar gas flow rate was maintained at 1 sccm and the total pressure of N_2 and Ar gas mixture maintained at about 1 Pa. The substrate temperature during the sputtering was kept at 100°C . The XRD pattern of the films shows a small fraction of crystalline phase of Cu_3N riding over an amorphous hump. All the diffraction peaks are ascribed to Cu_3N phase, and no copper peaks can be observed in any XRD profiles of deposited films at different N_2 -gas flow rate. The Cu_3N films take on a different texture with different N_2 -gas flow rate. It can be seen that the texture direction of the films changed from [111] to [100] with increase of N_2 -gas flow rate. The films prefer to growth along [111] direction at low N_2 -gas flow rates (5, 10 sccm) and [100] at high N_2 -gas flow rates (15, 20, 25 sccm). The peak height for each film derived from its corresponding XRD curve was shown Fig. 2. The [100] and [111] prefer orientation of Cu_3N films were changed with the N_2 -gas flow rates, indicating that the N_2 -gas flow rate in the sputtering gas mixture significantly affects the orientations growth behavior. In Fig. 2, the peak of [100] has a clearly and enormously increasing with increase of the N_2 -gas flow rates. The increase in peak [100] intensity could be attributed to the enhanced

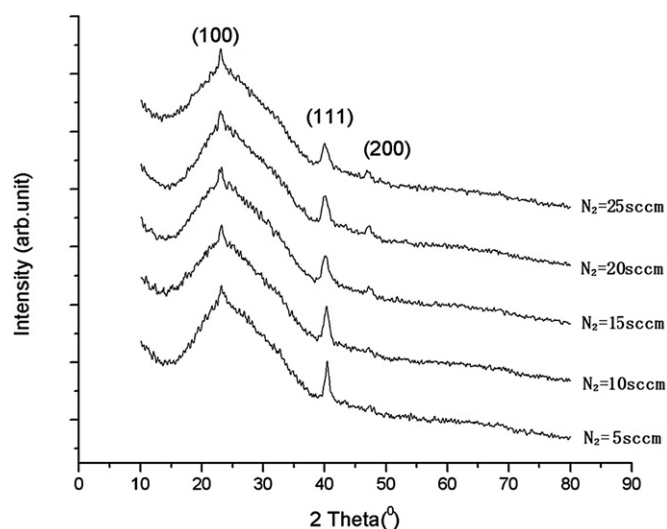


Fig. 1. XRD pattern of Cu_3N films deposited at 100°C substrate temperature with various N_2 -gas flow rates.

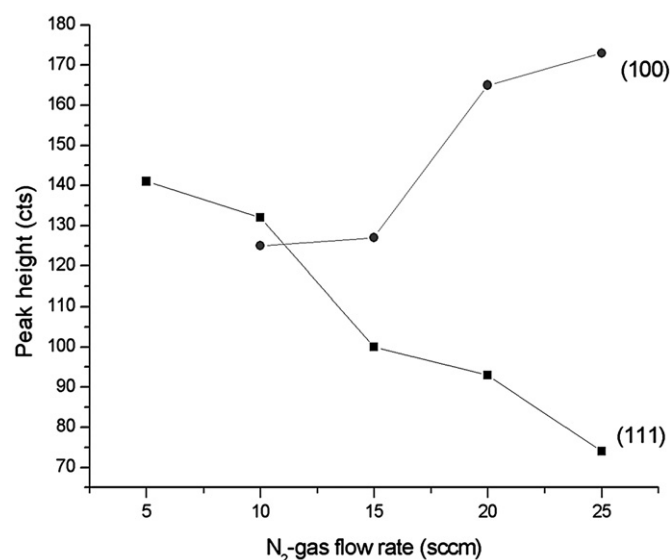


Fig. 2. The (100) and (111) peak height derived from Fig. 1 for each Cu_3N films.

surface diffusion of the adatoms at higher nitrogen partial pressure. The temperature and the activation energy dependence of the diffusivity is proportional to $\exp(-E/k_B T)$, according to the Arrhenius law, where E is the activation energy and k_B is the Boltzmann constant [15]. Therefore, it is believed that the diffusion of Cu and N atoms is more efficient at higher substrate temperatures (100°C) and high N_2 -gas flow rate for producing appreciable density of Cu–N bonds, which is necessary for the growth along the [100] direction. The observed preferential formation of copper nitride phase over any other combination of copper and nitrogen such as copper azide is due to the least free energy of formation and smallest crystallographic volume.

3.2. The thickness and deposition rate of films

The film thickness was measured by a profilometer (DEKTAKII). The deposition rate for each Cu_3N film was calculated by dividing its thickness by deposition time. In this case, the deposition rate of Cu_3N films is 9–28 nm/min, it is little higher than that (10–20 nm/min) of Cu_3N films prepared by RF magnetron sputtering [17]. Fig. 3 shows the deposition rate of Cu_3N films changing with the N_2 -gas flow rate. The deposition rate of Cu_3N film increases with increasing N_2 -gas flow rate and reached the maximum value at 15 sccm, then the deposition rate decrease with further increasing N_2 -gas flow rate. This result indicates that the very high N_2 -gas flow rate is not favorable for the deposition of Cu_3N film. Considering the deposition rate and the resistivity of Cu_3N film changes with the N_2 -gas flow rate can explain the maximum deposition rate as the following.

3.3. The resistivity of films

Fig. 4 shows the resistivity curve of Cu_3N films measured by four-probe method at room temperature. The curve shows that the resistivity of Cu_3N film decreases from 900.67 Ωcm at the N_2 -gas flow rate of 5 sccm to 46.87 Ωcm at 15 sccm, then increases to 299.0 Ωcm at 25 sccm. Hence the minimum resistivity of Cu_3N films at our experiment condition is 46.87 Ωcm . In some reports [12,16], the resistivities of Cu_3N are in the range of $20\text{--}2 \times 10^3 \Omega\text{cm}$. It is interesting to note that the films prepared at lower N_2 -gas flow rate of 5 sccm, which is composed of Cu and Cu_3N mixtures, still showed rather high electrical resistivity values of nearly 900 Ωcm . This

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