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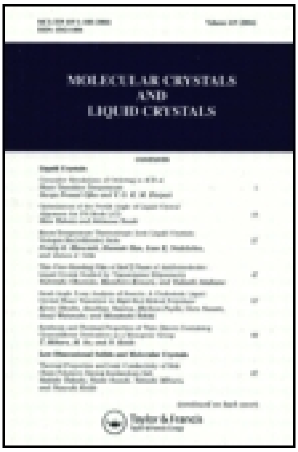

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Effect of Surface Microstructure on the Oxidation Stability of Cu_3N Thin Film

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Characteristics of Cu_3N thin films after deposition and 8 months after deposition are studied and compared experimentally. Films were produced by reactive magnetron sputtering mechanism and have been stayed in natural condition at room temperature for 8 months. It is observed that copper nitride thin films with conical microstructures on surface are oxidized while films with nodule like microstructures on surface remain unchanged. X-ray spectrum shows that some nitrogen atoms of N-rich planes at Cu_3N films are substituted by oxygen atoms after 8 months. The root mean square (RMS) roughness and sheet resistance of samples are increased significantly. The amount of oxygen in the structure of copper oxynitride thin films leads to increasing their band gap energy. It is found that the surface morphology is the most important parameter in stability of Cu_3N thin film in natural condition.

Keywords Copper oxide; copper nitride; energy gap; magnetron sputtering; sheet resistance; thin film

1. Introduction

Copper nitride (Cu_3N), one kind of excellent semiconductors with many extraordinary properties due to its small indirect band gap, has obtained considerable attention in recent years as a new material applicable for optical storage devices and high-speed integrated circuits [1–3]. Cu_3N with the structure of cubic anti-ReO_3 in which Cu atoms do not occupy perfectly the closely packed sites on (111) planes, is nontoxic and is stable at room temperature, but it can decompose into Cu and N_2 by simple heating treatment. The low decomposition temperature and discriminating optical properties of the compound Cu_3N are applicable for optical read-only memory discs by generating microscopic Cu-metal spots on Cu_3N film by performing local laser heating [4].

Low decomposition temperature of copper nitride and high tendency of copper to compose with oxygen motivated us to study the characteristics of Cu_3N thin films 8 months after deposition. The goal was to understand the effective mechanisms which may make Cu_3N unstable in natural condition at room temperature. Copper oxynitride is another important semiconductor with different properties from copper nitride and

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copper oxide. The oxynitrides of various transition metals such as Hf, Ta, and Zr possess improved thermodynamic, structural, and electrical properties compared to the corresponding oxides [5–9]. Beside this, a diversity of applications exists owing to the high variability of deposition parameters, which leads to oxynitride films with physical properties varying between those of the corresponding nitrides and oxides. In this regard the ratio of oxygen to nitrogen enables the preparation of oxynitride films with a multitude of atomic compositions. Therefore, it is possible to prepare films with designed physical properties including band gap and electrical resistance tuning. Further application is the field of decorative coatings along with scratch resistance and corrosion stability [10,11]. Moreover, transition metal oxynitrides are employed as solar absorber, dielectric layers, biocompatible, antireflection, mirror coatings, and beam splitters [12,13].

The purpose of this work is to investigate the effect of aging on the properties of Cu_3N thin films. This manuscript is organized as follow: after introduction the experimental detail is described in Section 2. Section 3 is devoted to results and discussion and conclusion is presented in Section 4.

2. Experimental Details

Copper nitride thin films were prepared on BK7 glass substrates, by using a cylindrical direct current reactive magnetron sputtering system. Before deposition, substrates were cleaned by ultrasonic waves in acetone and alcohol, and finally dried by blowing air. The chamber of sputtering system was vacuumed to less than 4×10^{-4} mbar with rotary and diffusion pumps combination. During the sputtering experiment, pressure was maintained at 6×10^{-2} mbar. A pure copper (99.99%), 30 mm diameter and 195 mm in height, was used as the target. The working gas was a mixture of 99.999% pure nitrogen and 99.999% pure argon. The distance between the substrate and the target was 30 mm. The discharge current was 200 mA at the voltage difference of about 600 V and deposition time was 12 minutes for all samples. Uniform magnetic field of 400 Gauss was generated by a solenoid parallel to the axis of cylindrical chamber. In the deposition process, no external heating was provided. The content of nitrogen in working gas for different samples is presented in Table 1. After film deposition, X-ray diffraction (XRD) was performed on STOE-XRD diffractometer using Cu-K_α line (l = 0.15406 nm). Change in absorbance spectrum of the samples was measured by a Varian Cary-500 spectrophotometer at room temperature. A DEKTAK3 profilmeter was employed to measure the thickness of the growth films. The FPP-5000 Miller Inc. four-point probe resistivity meter was used to measure the electrical resistivity of films. Atomic force microscopy (AFM) micrographs were taken using Auto probe CP from Park Scientific Instrument. The results of deposition process are reported in Ref. 2. For the next part of the study, deposited films were left in a closed opaque box in atmospheric pressure at room temperature for 8 months.

Table 1. The relative nitrogen contents in working gas for deposited films

Sample	1	2	3	4	5
$N_2/(N_2 + Ar)$	0.1	0.3	0.5	0.7	0.9
Film thickness (nm) (standard error ±5 nm)	486	521	414	318	335

3. Results and Discussion

3.1 Structure of Films

The XRD patterns of deposited thin films formed at various nitrogen partial pressures on glass substrates exactly after deposition and 8 months after deposition are shown in Figs. 1(a) and (b), respectively. X-ray spectrum of the sample 1 shows two peaks at $2\theta = 43.2^\circ$ and $2\theta = 50.4^\circ$ related to the (111) and (200) planes of Cu. In other words, Cu_3N is not formed in this film which can be due to small amount of nitrogen in working gas. As can be seen in Fig. 1, the XRD patterns of other films have several peaks corresponds to different preferred orientation of Cu3N planes. They are polycrystalline in nature with cubic structure that are confirmed with Powder Diffraction File (PDF). Card number [47–1088]. As the nitrogen content in the working gas is increased to 30% for the case of sample 2, copper nitride with (111) preferred orientation and cubic structure with lattice constant of 3.810 Å is formed on the BK7 substrate. Lattice constants are calculated from d-spacing magnitude provided by XRD apparatus using the know relation $d = a/\sqrt{h^2+k^2+l^2}$. After 8 months in natural condition, the XRD pattern of this film has not been changed which shows the high stability of this structure of Cu_3N at room temperature. At higher nitrogen content, the density of N atoms in the atmosphere of deposition reactor was increased and the absorbed N atoms could possess appropriate kinetic energy to react with Cu atoms, which leaded to high density of Cu-N bonds for the preferential growth along the (100) direction. By increasing the amount of nitrogen in working gas lattice constant of Cu_3N (100) was increased [14,15]. On the other hand, with increasing the nitrogen partial pressure in the working gas, the intensity of the peak diffracted from (111) planes is decreased. It can be seen in the XRD spectrum of samples 3–5 in Fig. 1(a). The preferred orientation of Cu_3N films was changed from (111) to (100) for these samples. Comparing Figs. 1(a) and (b) confirms that after 8 months in natural condition noticeable amount of Oxygen is added to the structure of samples 4 and 5 while the structure of sample 3 is remained unchanged with out any oxygen. As can be seen after 8 months, the intensity of XRD peaks of samples 4 and 5 at 41.05° corresponds to Cu_3N (111) planes are not decreased while a considerable decrease is occurred for the Cu_3N (100) peaks at 23.3°, and instead of them a new peak corresponds to Cu_2O (111) is formed at 36.52°. From one point of view, Cu_3N (111) is Cu-rich planes while Cu_3N (100) is N-rich planes. It can be claimed that one reason for instability of Cu_3N film is due to high amount of nitrogen in their structure. As will be studied, this is not only the preferred crystalline orientation which affects oxidation but morphological microstructure of the surface of thin film also governs oxidation process.

3.2 Morphology of Films

The surface morphology of samples is studied using AFM micrographs. In Figs. 2(a) and (b), the AFM images of the surface of deposited films exactly after deposition and 8 months after deposition are shown and their RMS roughness of samples that obtained with AFM are plotted in Fig. 3. Films with two kinds of morphologic microstructure were formed on substrates due to different nitrogen content in the working gas. For sample 2, a nodule like structure was formed, which is remained unchanged after 8 months. The size of nodules was increased for sample 3 and after 8 months it is remained. But for the case of samples 4 and 5 with conical microstructures on the surface, morphological changes are noticeable. Some shears are formed on the surface of sample 4 and the conical microstructure of sample 5 is completely changed to nodule like structure. We believe that the microstructure

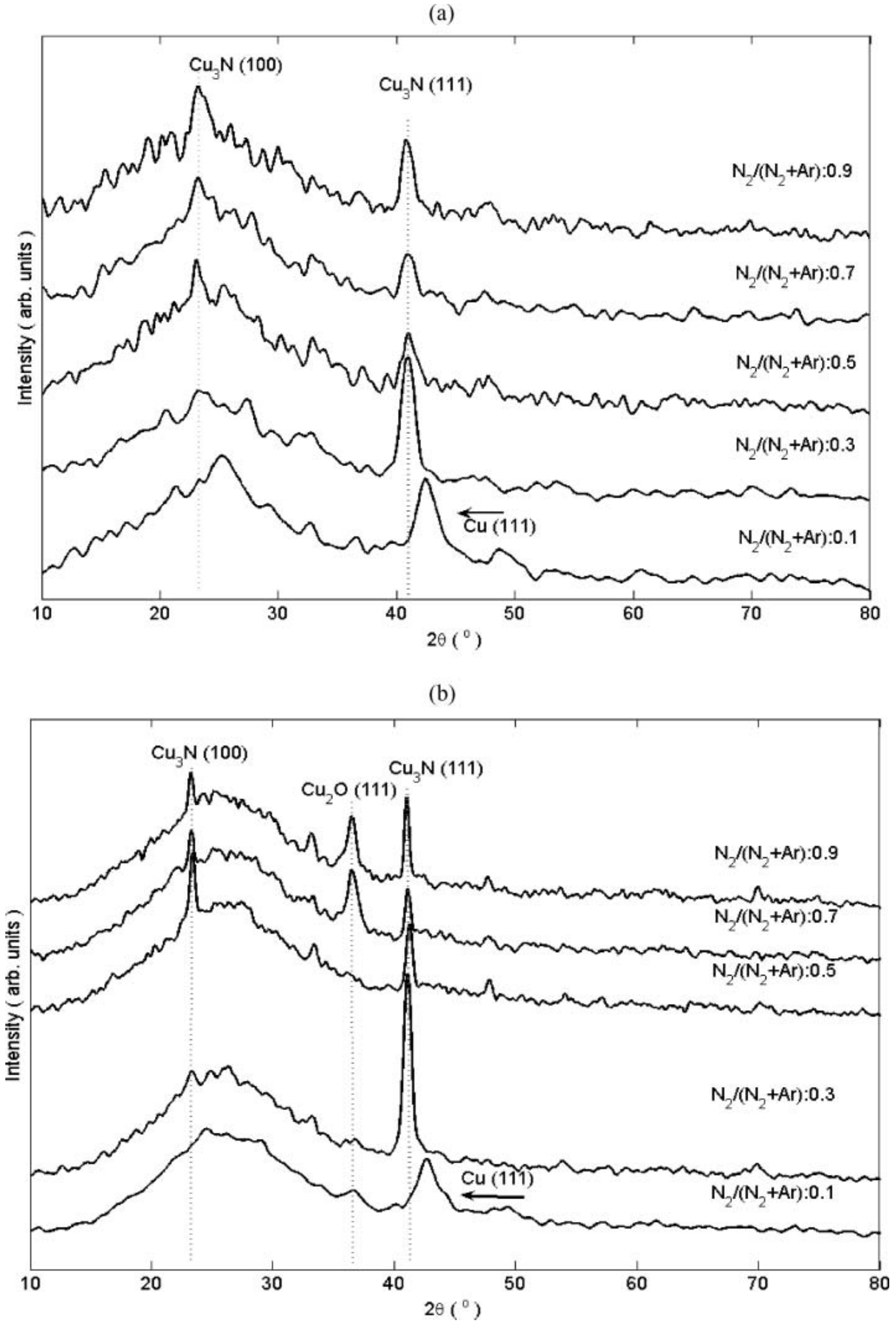
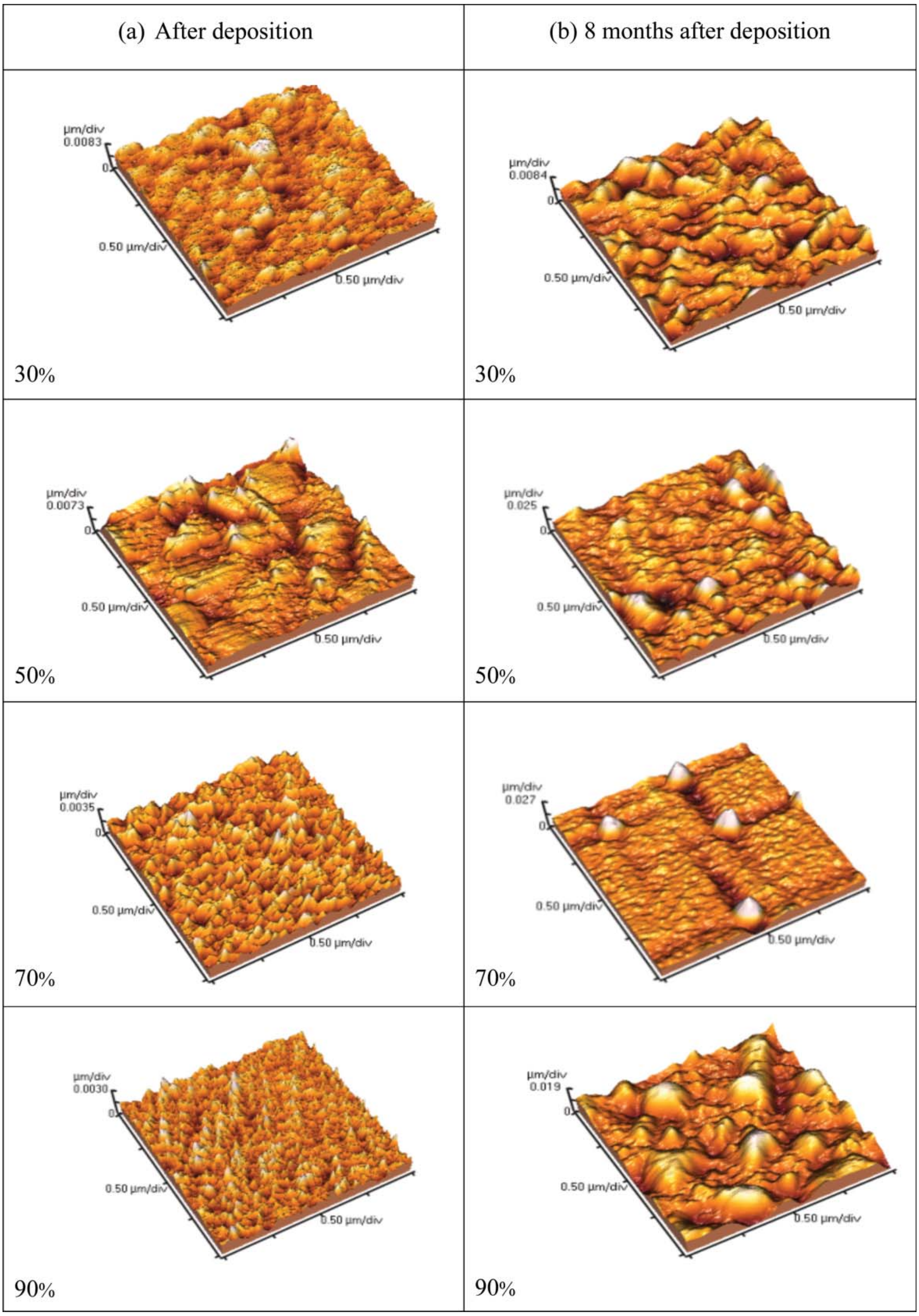


Figure 1. XRD patterns of Cu$_3$N films after deposition (a) and after 8 months (b).


(a) After deposition

(b) 8 months after deposition

Figure 2. AFM micrograph of deposited films after deposition (a) and 8 months after deposition (b).

of deposited Cu_3N films can be one of the main reasons for oxidation. Samples 4 and 5 with conical microstructure had larger effective microscopic contact surface with air leads to substitution of their nitrogen atoms with oxygen. In other words,s surface microstructure of Cu_3N thin films is an important effective parameter on the oxidation stability of the films and

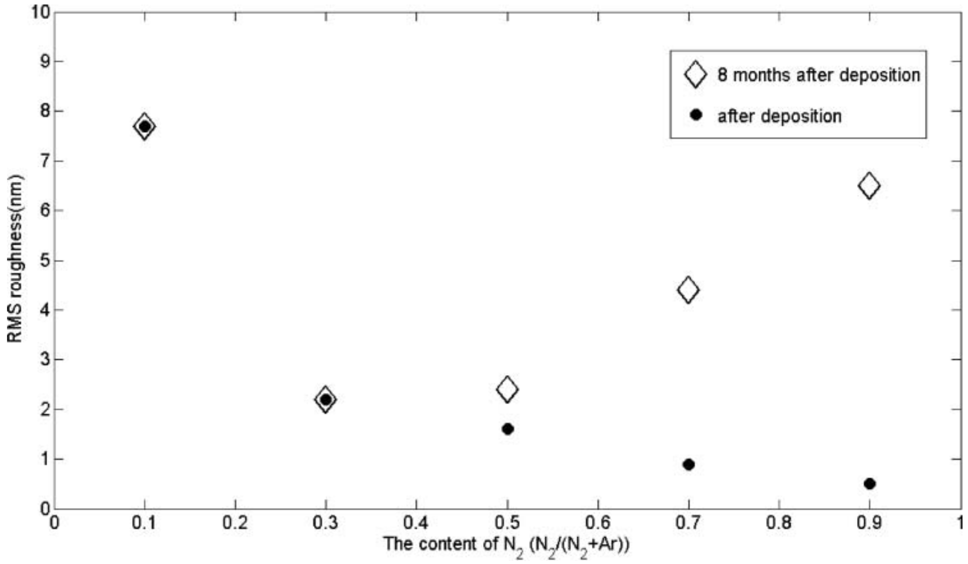


Figure 3. RMS roughness of samples after deposition and 8 months after deposition.

a nodule like microstructure is more stable against oxidation than a conical microstructure. Eight months after deposition, RMS roughnesses of oxide samples are also changed. RMS roughnesses of samples 1 and 2 are not changed but for samples 3–5 RMS roughnesses are changed. Oxidation process is associated with etching process on the surface of copper nitride thin films which increases the roughness of their surface.

3.3 Sheet Resistance

Another quantity which may be changed due to oxidation of copper nitride thin film is their electrical resistivity. Using a four-point probe device, the sheet resistance of samples was measured after sputtering and 8 months after it at room temperature, which are presented in Table 2. After 8 months, significant difference is appeared in the sheet resistance of samples 4 and 5. It is completely discussed in Refs. 2 and 3 that the sheet resistance of thin films is strongly affected by surface morphological microstructure of thin films. The results of study on copper nitride thin films show that variation of sheet resistance is very similar

Table 2. Sheet resistance of copper nitride thin films after deposition and 8 months after deposition at room temperature

The content of $N_2/(N_2 + Ar)$	0.1	0.3	0.5	0.7	0.9
Film thickness (nm) (standard error ±5 nm)	486	521	414	318	335
Sheet resistance (Ω/□) after deposition	0.2×10^2	0.58×10^5	10^9	1.67×10^3	3.6×10^3
Sheet resistance (Ω/□) (8 months after deposition)	0.19×10^2	1.483×10^5	10^9	0.27×10^6	0.4×10^6

Table 3. Optical band gap energy of samples after deposition and 8 months after deposition

The content of $N_2/(N_2 + Ar)$	0.1	0.3	0.5	0.7	0.9
Film thickness (nm) (standard error ±5 nm)	486	521	414	318	335
Band gap energy after deposition (eV)	–	1.4	1.75	1.9	1.95
Band gap energy 8 months after deposition (eV)	–	1.4	1.75	2.1	2.05

to RMS roughness. Increasing the RMS roughness of films leads to increasing their sheet resistance. There are two kinds of nodule like and conical structures formed on the surface of deposited films. RMS roughness of surface in the case of nodule like microstructure is larger than the surface with conical microstructure. In the processes of measuring sheet resistance with four-point probe device charge carriers should current on the surface of films but they are diffracted on the voided boundary of grains. So larger RMS roughness leads to more diffraction of charge carriers at the voided boundaries and in turn leads to smaller surface current and larger sheet resistance. Of course, sheet resistance of copper oxynitride thin film is larger than copper nitride but we believe that oxidation of copper nitride thin film are not so much to cause so large increase in their sheet resistance. Sheet resistance of these oxynitride thin films is strongly affected by their RMS roughness.

After film deposition, sheet resistance of samples 2 with nodule-like structure were larger than sheet resistance of samples 4 and 5 with conical structure on their surface, leads to larger sheet resistance. After 8 months, conical microstructure on the surface of samples 4 and 5 is changed to nodule-like microstructure with larger nodule size in comparison with samples 2 exactly such as their sheet resistance.

3.4 Optical Band Gap Energy of Cu_3N Films

Optical band gap is an important parameter of semiconductors. After film deposition, the optical band gap energy of copper nitride thin films was calculated to be 1.4–1.95 eV with Tauc method from their transmission spectrum [16], which is presented in Table 3. As was reported, optical band gap energy of samples was increased with increasing the amount of nitrogen in working gas during sputtering process. Actually, the film thickness is effective in the magnitude of optical band gap. Increasing the amount of nitrogen in working gas leads to formation of thinner film in which valance and conduction bands are narrower and the gap between them is wider.

The thickness of samples is not changed after 8 months, so difference between magnitudes of band gap energy of films after deposition and 8 months later is not due to a morphological reason such as thickness. The most effective parameter for this difference is the amount of oxygen in the new copper oxynitride films. Optical band gap energy of samples 8 months after deposition is presented in Table 3. These are unchanged for samples 2 and 3 since these two samples did not oxide but for the cases of samples 4 and 5 the band gap energy is tend to about 2.1 eV which is the reported magnitude for the band gap energy of bulk Cu_2O. Obviously, the band gap energy of Cu_2O thin film should be larger, but our films are not pure copper dioxide [17,18].

4. Conclusions

The Cu_3N films were deposited on BK7 glass by reactive direct current magnetron sputtering of a pure Cu target at various Ar and N_2 partial pressures. We have investigated the effect of different parameter on the stability of Cu_3N in the natural condition. XRD measurement shows that Cu_3N with N-rich planes are more unstable than Cu_3N with Cu-rich planes. Two forms of nodule-like and conical surface microstructures were observed on the surface of samples. In microscopic scale, the effective contact surface of conical structures with air is larger and this is the main reason for increasing the probability of oxidation. Oxidation of copper nitride thin films changed surface microstructure of films from conical shape to nodule like leads to increasing the RMS roughness of surface and in turn their sheet resistance. Effect of surface microstructure in band gap energy of samples is just due to addition of oxygen atoms to copper nitride. In this case, depends on the amount of oxidation, the magnitude of band gap energy of samples tends to >2 eV.

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