The influence of nitrogen plasma on characteristics of Cu thin film deposited on Si substrate by DC magnetron sputtering technique

A. Hojabri¹, N. Haghghian¹, K. Yasserian¹, M. Ghoranneviss²

¹Physics Department, Islamic Azad University, Karaj Branch, Iran.
²Plasma Physics Research Center, Islamic Azad University, Iran.

Abstract
In the present experiment, firstly, copper (Cu) thin films were deposited on silicon substrates at constant pressure by means of the DC cylindrical magnetron sputtering. Then we investigate the effect of nitrogen plasma on Cu thin films under various time durations. The structural properties, morphology and conductivity of the copper nitride films are investigated by X-ray diffraction (XRD), atomic force microscopy (AFM) and four-point probe techniques respectively. The results show that the nitrogen plasma results to the modifying of the crystalline phase of the thin films. In addition, the dependence of the conductivity of thin films on the time duration as well the surface morphology and structural properties are measured.

Keywords: copper nitride, nitrogen plasma, thin film, conductivity, surface morphology.

1. Introduction
Pure copper nitride has attracted much attention as a novel semiconductor material [1] with narrow indirect band gap which is reported experimentally in the range of 1.2-1.9 eV [2] and high resistivity at room temperature [3]. The density of the sample is 5.84g/cm³ and its molecular weight is 204.63. The color of material is dark green and stable at room temperature [4]. Cu₃N readily decompose in to N₂ and Cu at the temperature range 350-460 C⁰ [5]. Notably, the thermal decomposition of Cu₃N also brings about remarkable change in its optical properties which also provide the possibility of being used in write–once optical recording applications [6]. Also, Cu₃N films have wide applications in optical storage device and high-speed integrated circuits. As reported by Borsa [7], Cu₃N in an interesting candidate as an insulating barrier in magnetic tunnel junction.

The crystal structure of Cu₃N is of the anti-ReO₃ type with a simple cubic unit cell of lattice constant 3.817 Å. In this structure, copper atoms occupy the center of the cubic edges forming collinear bonds with two nearest neighbor anions instead of occupying the face-centered cubic close-packing sites. As a consequence, this crystal structure has many vacant interstitial sites. This open crystal structure is suited for the interposition of other element, like Cu or Pd. In addition, with the insertion of Cu atoms, the Cu₃N lattice undergoes a small expansion, and the Cu₄N phase is formed [8].

There are several methods to prepare copper nitride thin films such as ion beam assisted DC magnetron reactive sputtering [9], DC magnetron sputtering [10], RF magnetron sputtering method [11,12], molecular beam epitaxy (MBE) [8] and reactive pulsed laser deposition (RPLD) [13].

In this work, we are going to investigate the influence of nitrogen plasma on Cu thin films. The copper nitride films have been prepared on silicon substrates by DC cylindrical magnetron sputtering at various time depositions.
Firstly, Cu films have deposited on silicon substrate via the argon plasma for 7 min at room temperature. Then these Cu films have been exposed to the nitrogen plasma and then, the characteristics of thin films such as morphology, structure and electrical properties are investigated.

2. Experimental

In this experiment firstly, Cu films are deposited by DC cylindrical magnetron sputtering on silicon substrate. The Si substrates geometry were approximately 1 Cm x 1 Cm and were cleaned ultrasonically in acetone and alcohol. Our cylindrical magnetron consists of two coaxial cylinders as cathode (inner one) and anode (outer one). The diameters of the outer and the inner cylinders are 3cm and 10cm, respectively and 20cm in length. Before the operation, the chamber was evacuated to less than 4.7x10^{-5} Torr, by means of a rotary pump and diffusion pumps. In the first step, the argon gas is used as working gas to sputter copper thin films at a fixed condition. The sputtering parameters are as follow:

<table>
<thead>
<tr>
<th>Table 1: Deposition condition in first step</th>
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<tr>
<td>Substrate-to-target distance</td>
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<tr>
<td>Substrate</td>
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<tr>
<td>Base pressure</td>
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<tr>
<td>Final pressure</td>
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<tr>
<td>Current</td>
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<tr>
<td>Deposition time</td>
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In the second step Cu thin films have been exposed to the nitrogen plasma at different time depositions which is shown in table 2.

Finally, the effect of nitrogen plasma on surface morphology, root mean square (RMS) roughness, microstructure and resistively of the films are studied by means of atomic force microscopy (AFM) (park scientific instrument, auto probe CP ), the X-ray diffraction (XRD) analyses in the θ/2θ mode using Cu Kα X-rays and conventional four-point-probe method (FPP5000) respectively.

<table>
<thead>
<tr>
<th>Table 2: Deposition condition in second step</th>
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<tbody>
<tr>
<td>Final pressure</td>
</tr>
<tr>
<td>Current</td>
</tr>
<tr>
<td>Deposition time</td>
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3. Result and discussion

3.1. Structure of the films

Fig.1 shows the effect of the plasma nitrogen on the X-ray diffraction pattern of Cu films deposited on silicon substrates. In Fig.1a we have shown the XRD pattern of copper thin films. This figure vividly shows the (111) peak of copper structure. By exposing the copper thin films into the nitrogen plasma, intensity of the (111) copper changes. From Figs. 1b, 1c and 1d, it can be seen that by introducing the nitrogen plasma leads to decrease of the copper peak intensity and eventually in high time duration disappears and Cu$_3$N phase emerges.

![Fig.1 XRD pattern of cu thin film](image)

Fig.1 XRD pattern of cu thin film (a) have been exposed to nitrogen plasma at 2 min (b) 4 min (c) and 6 min (d).
3.2. Morphology of the films

The influences of nitrogen plasma on the surface morphology of Cu thin films are examined by the AFM, as shown in Fig.2. By comparison of Fig.2a, b and c, it can be deduced that by introducing the nitrogen plasma, the grain size decreases which is accompanying with smoothing of thin films surface. Cu thin film roughness is 8.3188nm Fig.3 shows the RMS roughness decrease by introduce the nitrogen plasma. The results of the figures 1 and 2 are in agreement with the Scherrer's relation [14].

\[ L_{(hkl)} = \frac{k\lambda}{\beta \cos \theta} \]

Where \( k \) is a constant with a value about 0.89 for Cu target, \( \lambda(\text{Å}) \) is the X-ray wavelength, \( \beta \) is the FWHM of \((hkl)\) peak and \( \theta \) is the diffraction angel.

3.3. Electrical properties of the films

The electrical resistivity is studied by employing van der pauw method [15]. The sheet resistance (\( \rho_s \)) of the films is calculated using the equation

\[ \rho_s = \left( \frac{\pi}{\ln 2} \right) f \left( \frac{R_1 + R_2}{2} \right) \]

Where \( f \) is the van der pauw factor, which depends on the position of electrical contacts on the film surface and can be obtained from the following relation.

\[ f = 1 - \frac{\ln 2}{2} \left[ \frac{R_1 - R_2}{R_1 + R_2} \right]^2 \]

Where the electrical resistivity (\( \rho \)) of can be found by

\[ \rho = \rho_s t \]

and \( t \) is the film thickness.

Fig.4 demonstrates the variation of the resistivity of films as a function of plasma nitrogen exposing time. The resistivity is obtained using four-point-probe method.
at room temperature. From this figure, one can deduce that by employing nitrogen plasma, electrical resistivity increases.

The Cu film has the lowest resistivity value of $0.567 \times 10^3 \ \Omega/\square$. When the Cu films are exposed to the nitrogen plasma, the resistivity of films increase up to $1.920 \times 10^4 \ \Omega/\square$. The high resistivity at higher time is due to the semiconductor feature of the Cu$_3$N film. By comparison between resistivity and AFM results, it can be deduced that by enhancement of grain size, the electrical conductivity decreases. As a result, the grain size is inversely proportional to electrical resistivity [16].

**4. Conclusion**

We have investigated the effect of nitrogen plasma on Cu thin films. We firstly make a Cu thin film by cylindrical magnetron sputtering technique. Then we have studied the response of the thin films to the nitrogen plasma. The thin films properties such as crystalline structure, morphology and resistivity are analyzed by XRD, AFM and four point probe method respectively. The results have shown that the nitrogen plasma leads to the diminishing the Cu peak in XRD patterns and amplify the Cu$_3$N peak while the roughness of the films reduces. Furthermore, by exposing the films to nitrogen plasma, the electrical resistivity increase which is due to the feature transition from Cu to Cu$_3$N films.

**References**