Plasma Diagnostics and Characterizations of Reactive Magnetron Sputtered Copper Nitride Thin Films

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Abstract:
The plasma diagnostics of dc magnetron reactive sputtered copper nitride thin films by Optical emission spectrometer (OES) is investigated and argon / nitrogen effect (Ar /N2) mixture ratio on plasma parameters and structural properties of sputtered Cu3N thin films are discussed. Cu3N thin films of 60.30 nm and 105 nm have been formed on glass substrates at room temperature using Ar(70)/N2(30) and Ar(50)/N2(50) working gas discharges respectively. The size of crystallites, grains and particles in the copper nitride thin films have been estimated from X-ray diffractions, Atomic Force Microscope (AFM), and Field Emission Scanning microscope (FESEM) respectively. The properties of sputtered copper nitride thin films are related to the plasma parameter of electrons temperature and density. An increase in optical transmittance and a decrease in absorbance over the wavelength range were found as the nitrogen percentage increased which result on decrease the film thicknesses. The energy of the optical band gap, Eg obtained in the range of 2.6 to 2.7 eV.

Keywords: DC-magnetron sputtering, Optical emission spectroscopy, (CuN3) cooper nitride, Structural properties

INTRODUCTION:
Thin films of metal nitride have many exceptional characteristics and were extensively made. Thin films’ optical characteristics were the interest of many researchers, both thermal stability and electrical conductivity of Cu3N thin films gave huge interest and became the center of attention in semiconductor materials due the special composition & physical chemical properties (1-2). By adding other different atoms in (Cu3N) crystals, the Cu3N thin films’ composition may be changed, thus allowing the Cu3N conversion to be semiconductors or even conductors from dielectrics [3-4]. Cu3N offers promise probability and benefits for uncomplicated elaboration and toxicity. Inorganic phase change materials may be replaced based on one-time optical storage [5-6]. According to the low down temperature of pyrolysis, thin films of Cu3N are expected to be Cu line buffer layer in incorporated circuits, The low-resistance tunnel joints blockade layer, a model of self-assembly materials [7,8–9]. Moreover,
thin films of Cu3N can be used like a new battery material and catalyst additives due to their brilliant chemical action [10,11,12,13-14]. In the emission materials field, They are considered physically powerful competitors because of their excellent characteristics in electronic emission [15,16,17,18]. therefore, Cu3N displays exceptional physical assets, capable of developing, and has special crystalline structures in application prediction. This study, two features have been recognized: Firstly, the Cu3N crystal mechanism (Figure 1) and the structural factors are suitable, they be in the right place to the asymmetric cellular compounds family; As a result, scientists can regulate the Cu3N grid constant by scheming industrial technological factors.

![Figure (1). Diagram of the crystal structure of Cu₃N structure [5].](image)

**Experimental details**

DC magnetron reactive sputtering system has been used for this work, it is a low down pressure gas release unit that contains abandoned chamber, a copper object (cathode & anode) stainless steel disk used to deposited the glass substrates. Cathode is front of the anode, that supply field of electricity for discharging the gas. Fig.2 displays plasma chamber graphic, the electrical electrodes and the linked DC-power provide 3 kV. by means of fixed conditions of (660V of DC) power and 0.08 mbar chamber pressure. Sputtering processes normally utilizes argon gas because has no reaction with the object material permitting thin films to be created. The adding up of a gas that act in response with the target material, such as nitrogen , will form material compounds and the reactant. By using Ar(70)/N₂(30) and Ar(50)/N₂(50) mixture ratio for sputtering Cu₃N thin films.
RESULTS AND DISCUSSION:

Plasma diagnosis

The applied voltage and gas working pressure inside the vacuum chamber play crucial role in homogeneity of the generated plasma. Therefore, these parameters affect directly the discharge plasma spectrum characteristics such as the intensity, electron temperature and electron density.” We can measure electron temperature and electron density, etc., by means of the information from optical emission spectroscopy. There is an evident that the intensities increase with increasing working gas pressure as in Figure(3). Both of (Ar I & Ar II) intensity increases with rising operational pressure. The result may be given details as follow: When there is an increasing of the pressure in the chamber, it can cause increasing in the impact number between electrons and gas atoms [19]. It has determined time-resolved values of the plasma temperature from the Boltzmann plots that has been made from the five observed Cu I spectral lines analysis. The electronic time values have also been determined for the electron density values from the Saha-Boltzmann equation, which connects the electron density with the ratio of the density of the atomic and ionic emission lines. The average electron density value is calculated at a given delay time by looking at the measured intensity ratios for Cu I and Cu II lines at different wavelengths. [19-22].
Figure (3): Spectrum by using copper target at different gas mixtures (Ar/N₂)(70/30) and (50/50).

Figure (4): The plasma emission spectra for Ar/N₂ (70/30) gases mixture at different working pressures.
Table 1. Values of transition probability, upper energy level and statistical weight that used to calculate $T_c$ [20].

| Wavelength (nm) | Transition probability $A_i (S^{-1})$ | Statistical weight energy level $g$ | Upper level energy (eV) |
|-----------------|--------------------------------------|----------------------------------|------------------------|
| Ar I            | 772.3761                             | 349.1244                         | 3 4                    |
| Ar II           | 5.18E+06 1.79E+08                     | 13.1531437 22.8113582            |
| Ar II           | 388.9064 2.21E+05                     | 13.3859609 1                    |
| Cu II           | 600 7.50E+07                          | 16.9553486 2                    |
| Cu II           | 395.585 1.21E+07 2.2148E+05           | 21.5995392 41.477704            |
| Cu II           | 399.5 1.21E+07                        | 21.5995392                       |
Figure (5). The emission spectra for plasma argon and nitrogen(50/50) at different working pressures.

Table (2). Values of transition probability, upper energy level and statistical weight that used to calculate $T_e$

| Wavelength (nm) | Transition probability $A_1(S^{-1})$ | Statistical weight $g$ | Upper energy level $E_i$(eV) |
|-----------------|-------------------------------------|------------------------|-------------------------------|
| ArI 738.398     | 8.47E+06                            | 3                      | 13.30222736                  |
| ArII 35.438     | 3.4E+08                             | 2                      | 23.2581135                   |
| ArI 772.3761    | 5.18E+06                            | 3                      | 13.15314376                  |
| H 388.9064      | 2.2148E+05                          | 2                      | 13.38596091                  |
Table (1&2) show, the minimum campaigning energies for the argon lines are comparatively high, ~12 eV for ArI. This refers to the argon emission lines adoption on the presence of high velocity electrons in the plasma. Some Ar lines can also excite efficiently from the Ar "metastable levels". Evidently, the energy required for excitation is less than that required for ionization because the electron of an stir atom does not remove completely from this atom. For example, the stir energy of argon atoms is 11.8 eV while the ionization energy is 14.6 eV. As well, the stir energy should greater than or equal to the energy of the electronic case in order for the excitation to occur [20,21,22].

Table (3): show the Ar/N₂(70/30) plasma diagnostic parameter with different pressure

| Pressure (mbar) | Te(ev)  | Ne(cm⁻³) | λ_D     | N_D     | Wpe   |
|----------------|---------|----------|---------|---------|-------|
| 0.08           | 1.43E-02| 1.03E+16 | 7.07E-05| 1.53E+04| 5.72E+09|
Tables (3 & 4) depict the temperature and density of the electron as a function of the pressure of working argon at steady provided voltage. As pressure increases, the atoms and molecules number increases, as an alternative of acquiring electron energy from the its field. From the electron to plasma types during the inflexible collision, more and more energy is transferred. The normal free path reduces and the electrons collision rate with the atoms increases. A decreases appears for the energy gained for the electron, so there is an increase for the electron density and a decrease for the electron temperature [23,24].

### XRD analysis:

Figure (6) shows the X-ray diffractions pattern of sputtered Cu$_3$N thin films are discussed. Cu$_3$N thin films of 60.30 nm and 105 nm have been formed on glass substrates at room temperature using Ar(70)/N$_2$(30) and Ar(50)/N$_2$(50) working gas discharges respectively. Is
agreeing well with the monoclinic phase of Cu3N nanoparticles, and the crystallite size of the prepared nanostructure has been determined by the Debbie-Scherer equation, 

\[ D = \frac{0.9\lambda}{\theta \cos \theta} \]

where \( \lambda \) is the wavelength of X-ray radiation, \( \beta \) is the full half-width (FWHM) in radians, \( \theta \) is the Prague diffraction angle. The average size of crystals is around 9.5 to 17.9 nm. Peaks of pure copper are observed in the XRD pattern.

Fig. (6) The XRD pattern of copper oxide (Cu3N) nanoparticles prepared in this work at different gas mixture (Ar/N2) ratio
### Table (5): X-ray diffraction parameters for Cu₃N thin film deposited on glass substrates at different gas mixture (Ar/N₂) ratio

| Gas (Ar/N₂) | 2θ (Deg.) | FWHM (Deg.) | d₁₀₀ | C.S (nm) | d₀₁₁ Std. (Å) | Hkl   |
|-------------|-----------|-------------|------|---------|---------------|-------|
| (50/50)     | 35.1278   | 0.6600      | 2.5526 | 12.6    | 5.7720        | (200) |
| (70/30)     | 21.6383   | 0.6400      | 4.1037 | 12.6    | 4.3830        | (001) |
|             | 24.4521   | 0.4000      | 3.6375 | 20.3    | 2.7685        | (011) |
|             | 34.8430   | 0.6700      | 2.5728 | 12.4    | 5.7720        | (200) |
|             | 38.0753   | 0.8800      | 2.3615 | 9.5     | 4.3830        | (001) |
|             | 21.9077   | 0.4520      | 0.5400 | 17.9    | 4.3830        | (001) |

### Scanning Electron Microscope (FESEM)

Figures [7,8] illustrate the surface shape of a thin film of copper nitride with a different gas Ar/N₂ mixture. Equivalent Cu₃N samples also feature SEM methods. The sample is set at 0.08 mbar. The SEM image exposes a level morphology uniform that is collected from separate morphological areas in a archetypal dimension. The parity SEM image shows a well aligned [0 0 1], confirming the crystal orientation purity's deposition. The planar aircraft distance [0 0 1] and [200], which correspond well to the consequences for the measurement of XRD. Even copper in pure Cu₃N has a slight nitrogen deficiency. That means, in chemical measurement samples, the content of Cu is one way or another larger than 80.0%. From the energy dispersed X-ray analysis and photo-spectral data, the lowest copper content is about 80% of the methods accuracy. The roughly equivalent copper nitride sample has to be typical semiconductor.
Fig. 7. Field emission scanning electron microscopy (FE-SEM) images for copper nitride gas rate mixture (Ar/N₂)=(70/30) %

Fig. 8. Field emission scanning electron microscopy (FE-SEM) images for copper nitride gas rate mixture (Ar/N₂)=(50/50) %
Optical properties:

The optical transmittance spectra of samples are presented in Fig. 9. As it is clear for the reflectance spectrum of the remarkable different from other samples. The sample wave-like behavior of the reflectance spectrum of samples(70/30),(50/50) cannot be seen in the spectrum of the sample(70/30), which is a smooth curve. Also, the reflectance spectrum of the sample (1) is larger than the sample (2). It can explain the content of nitrogen in working gas for deposition of the sample (1) was not enough for the formation of Cu3N atoms. In other words, the reflectance spectrum of the sample (70/30))is a typical spectrum of copper film. But for samples (50/50) the electromagnetic wave is reflected by copper nitride films. The magnitude of reflectance of Cu3N films is smaller than Cu film especially for the wavelength range between 800 to 1200 nm. This is a huge possible for thin films of Cu3N to be utilized as a write-once optical recording media which are typically working at this range of electromagnetic waves The reflection property of the copper nitride thin films have shown that it is apt for this function [25]. The Cu3N films optical transmittance is formed on top of a glass substrate at various nitrogen contents is presented in Fig. 9. Absolute zero transmittance of the sample confirms the formation of pure copper for this sample. The transmittance of copper nitride films increases with decreasing the film thicknesses, which is a natural result of absorption law for semiconductors.

![Graph of optical transmission against wavelength](image)

**Fig. 9. Percentage optical transmission against wavelength of copper nitride films prepared at different gas mixture (Ar/N2) ratio**
Fig. 10: Absorption coefficient and Absorption versus wavelength for copper nitride films prepared at different gas mixture (Ar/N₂) ratio.

Fig. 11: (αhv)² versus hv plot for copper nitride film prepared at different gas mixture (Ar/N₂) ratio.
The UV-visible absorption spectra of the dc reactive magnetron sputtered copper nitride thin films were recorded in the wavelength range between 200 and 1100 nm (Figure 10). The wide absorption range of Cu\textsubscript{3}N thin film presented in (200-900) nm can be ascribed to nanosized grains resulted from dc reactive magnetron sputtering. The deposited high purity Cu\textsubscript{3}N nanostructure film have low energy band gap [fig. 11], which can absorb the low energy photons, thus Cu\textsubscript{3}N nanoparticles have high solar energy selectivity which is essential for solar absorbers. Optical band gap power, $E_g$ obtained in the range of 2.6 to 2.7 eV (table 6) and the refractive index, $n$, was about 1.80, constant for all samples. The Cu\textsubscript{3}N thin film can use as a good absorber material for solar cell application [26].

Table (6) : Optical Constants (at $\lambda=500$ nm) for (Cu\textsubscript{3}N) thin film at different gas mixture (Ar/N\textsubscript{2}) ratio

| Data         | T\%  | $\alpha$ (cm\textsuperscript{-1}) | K    | n      | $\varepsilon_r$ | $\varepsilon_i$ | $E_g$ (eV) |
|--------------|------|----------------------------------|------|--------|----------------|----------------|------------|
| (Ar/O\textsubscript{2})=(70/30) | 82.41 | 18424                           | 0.081| 1.870  | 3.490          | 0.302          | 2.7 ev     |
| (Ar/O\textsubscript{2})=(50/50) | 84.53 | 26559                           | 0.116| 1.801  | 3.229          | 0.419          | 2.6 ev     |

Conclusion:

Discharge plasma spectrum characteristics such as the intensity, electron temperature and electron density were analyzed. We can measure plasma parameters such as electron temperature and electron density, Deby length, and plasma electron frequency by means of the information from optical emission spectroscopy technique. It can be concluded, the temperature of electron and negative glow region density depending on the working gas pressure. The some structural and optical properties of the reactive sputtered CuN\textsubscript{3} structure were investigated. The results pointed to the monolayer CuN\textsubscript{3} is energetically steady in the infrared and visible spectrum. The results suggest that bulk CuN\textsubscript{3} may be a promising candidate for energetic materials.

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