Characterization of Copper Nitride Nanostructures Synthesized by DC Reactive Plasma Sputtering Technique

Mahdi S. Edan

Department of Pathological Analysis,
Al-Rasheed University College,
Baghdad, IRAQ

In this work, copper nitride nanostructures were synthesized by dc reactive magnetron plasma sputtering technique. These nanostructures were grown on silicon substrates in order to fabricate anisotype heterojunctions. The nitrogen content was varied in the gas mixture in order to introduce its effect on the characteristics of the synthesized nanostructures. For nitrogen content of 10%, the synthesized nanostructures were polycrystalline and the minimum particle size was about 18 nm with approximately spherical shape. As the nitrogen content was increased in the gas mixture, the particles got larger and the electrical resistivity reasonably increased to reach its maximum at nitrogen content of 60% before slightly decreased with further increasing of nitrogen content. The synthesized nanostructures show high absorption in the spectral range of 200-500nm while their absorbance was highly decreased at the longer wavelengths. The energy band gap of these nanostructures was determined to be 1.856 eV. These heterojunctions can be successfully employed for optoelectronics and gas sensing applications.

Keywords: Copper nitride; Thin films; Nanostructures; Reactive sputtering
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1. Introduction

Copper nitride is an n-type semiconductor with an indirect energy band gap in the range of 1.1-1.9 eV [1-3]. It has a cubic anti-ReO_3 crystal structure with a lattice constant of 3.815-3.841 Å [4,5]. In this type of crystal structure, shown in Fig. (1), the copper atoms are located at the center of edges of the cubic cell while nitrogen atoms are located at the corners of the cell [6]. Research works have showed that the copper nitride with lattice constant larger than 3.841Å is a conductor while that with lattice constant smaller than 3.815Å is an insulator [7].

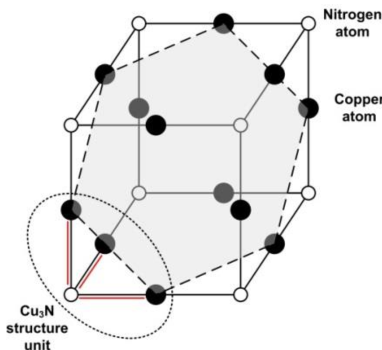

Fig. (1) The crystal structure of copper nitride (Cu_3N) molecule

Copper nitride is thermally metastable material and decomposes at temperatures of 100-470 °C [8]. This thermal metastability makes copper nitride very important for innovative applications such as optical storage devices (OSDs), maskless laser or e-beam writing as metal links, cathode catalyst in alkaline fuel cells, and in low resistance magnetic tunnel junctions as barrier layer [9-11].

Different methods and techniques, such as chemical vapor deposition, molecular beam epitaxy, atomic layer deposition, pulsed-laser deposition, dc-triode sputtering, and mostly rf magnetron sputtering, were used to prepare copper nitride thin films of good quality [12-16].

In this work, nanostructured copper nitride thin films were prepared by dc reactive plasma sputtering technique and deposited on silicon substrates to fabricate anisotype heterojunction.

2. Experimental Part

Highly-pure (99.99%) copper target was sputtered in presence of nitrogen gas by plasma generated between two electrodes employing a novel design of the closed-field unbalanced dual magnetron (CFUBDM) assembly [??]. Figure (2) shows the spatial distribution of the plasma generated between the discharge electrodes. The optimum pressure of nitrogen was $2x10^{-2}$ mbar and the electrodes were separated by 4 cm. The cathode, on which the copper target was maintained, was cooled down to 4°C to prevent the emission of secondary electrons while the anode's temperature was kept at 20-23°C.

Spectroscopic measurements were performed on the prepared samples by a SpectraAcademy UV-Visible spectrophotometer within the range of 200-1100nm with accuracy of ~2.0 nm full width at half

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maximum (FWHM). As well, structural tests such as x-ray diffraction (XRD) (Bruker, 1.54.5Å CuKα radiation), scanning electron microscopy (SEM) (TESCAN Vega3 EasyProbe), and scanning probe microscopy (SPM) (Angstrom AA3000 SPM), and Fourier-transform infrared (FTIR) microscopy (Shimadzu FTIR-8400S), were performed on the prepared samples to introduce the structural and spectroscopic properties of the copper nitride nanostructures prepared in this work. Also, electrical characteristics, such as electrical resistivity and Hall mobility, of the prepared samples were determined as functions of nitrogen content as well as the temperature.

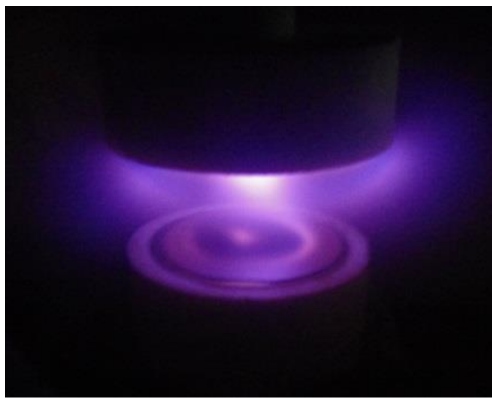


Fig. (2) Spatial distribution of the plasma generated by the CFUBDM system

3. Results and Discussion

Figure (3) indicate the XRD pattern of the copper nitride sample prepared in this work. It is clear that this sample is polycrystalline, typical cubic and five peaks are observed – as shown in table (1) – without any impurities in addition to the corresponding Miller indices of the grown crystal planes. Consequently, the structural phase of copper nitride is Cu_3N. Some small peaks can be seen and they are belonging to the copper not bonded to nitrogen. The amount of unbound copper depends on the partial pressure of nitrogen gas in the gas mixture used in sputtering system. According to Scherrer's formula, the crystallite size (D) was determined too. The average value of microstrain was determined to be 0.822.

Table (1) Structural parameters of copper nitride sample

2θ (deg)	(hkl)	Inter-planar Distance (Å)	FWHM (rad)	D (nm)	Microstrain (ε)
23.00	(100)	3.815	0.698	11.60	0.847
32.90	(110)	2.716	0.988	8.38	0.835
40.50	(111)	2.222	1.216	6.96	0.822
42.50	(200)	1.898	1.435	6.06	0.808
52.80	(210)	1.732	1.582	5.59	0.797

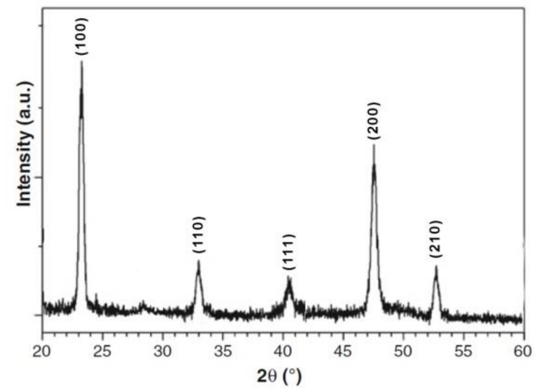
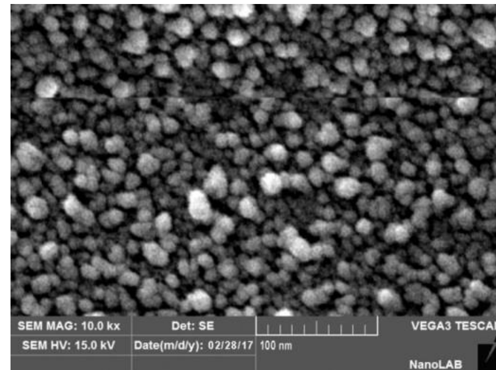
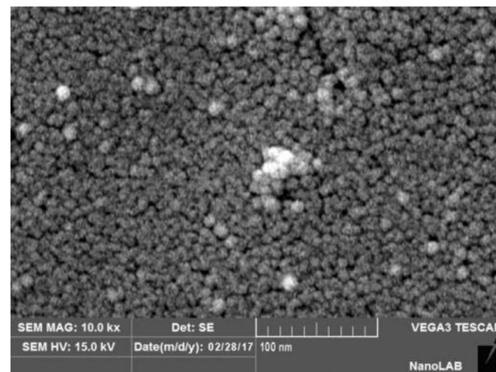


Fig. (3) The XRD pattern of Cu_3N sample prepared in this work using 40:60 mixing ratio of $Ar:N_2$

Figure (4) shows the SEM images of two copper nitride samples prepared using two different $Ar:N_2$ gas mixing ratios (90:10 and 40:60). For the 10% N_2 mixture, it is clear that the particles are relatively large with spherical shape and homogeneous distribution. Increasing the partial amount of N_2 in the gas mixture lead to produce smaller, much more homogeneous distribution of spherical particles. This is attributed to the role of higher rates of bonding between sputtered copper atoms and nitrogen atoms on their path towards the substrate. However, increasing the amount of nitrogen in the gas mixture may have a disadvantage of poisoning the copper target.



(a) 10% N_2



(b) 60% N_2

Fig. (4) The SEM images of (a) sample prepared using 90:10 mixing ratio, and (b) sample prepared using 40:60 mixing ratio

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Figure (5) shows the SEM image of the boundary region of the copper nitride film deposited on the substrate using Ar:N_2 gas mixing ratio of 40:60. The thickness of this film can be uniformly determined to be 130 nm. This value is very coinciding to that measured by laser interferometry (≈133nm).

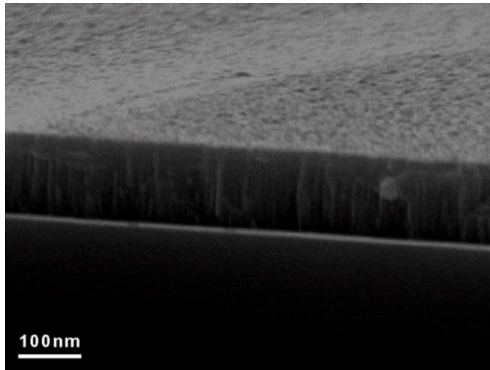

Fig. (5) The SEM image of the boundary region

Figure (6) shows the transmission spectrum of the Cu_3N thin film deposited on the substrate using Ar:N_2 gas mixing ratio of 40:60. This film shows low transmittance in the range 200-500nm, linearly increasing transmittance beyond 500nm to reach its maximum in the IR region (1000-1100nm). Accordingly, this film can be successfully used for photonic and optoelectronic devices those require moderate absorption in the spectral range 350-500nm. For applications requiring high absorption in the UV region (e.g., photocatalysts), this film can be used with considering the varying absorbance for wavelengths shorter than 350nm. With good thermal and chemical stabilities, this material can be efficiently used for energy storage applications.

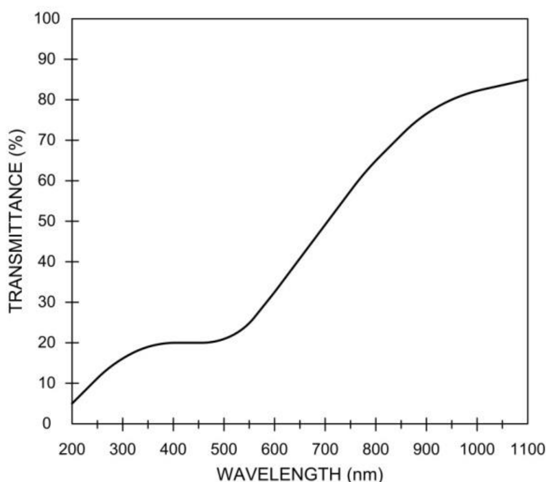

Fig. (6) Transmission spectrum of Cu_3N sample prepared in this work using 40:60 mixing ratio of Ar:N_2

In order to determine the energy band gap of the prepare Cu_3N films, the relationship between $(\alpha h\nu)^2$ and photon energy ($h\nu$) is shown in Fig. (7) (According to Tauc's relation). By extrapolating the linear part of this curve, energy band gap (E_g) can be determined to be 1.856eV, which makes this material good candidate for solar conversion devices and applications as its cutoff wavelength is about 668nm (red wavelengths of visible region).

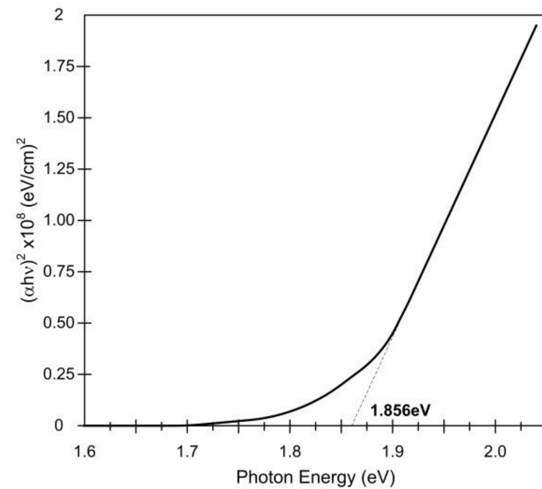

Fig. (7) Relationship of $(\alpha h\nu)^2$ versus photon energy ($h\nu$) to determine the energy band gap of the prepared samples

In order to introduce the effect of varying nitrogen amount in the gas mixture used to prepare copper nitride thin films in this work, this amount was varied from 10 to 90% and the electrical resistivity of the prepared film was measured, as shown in Fig. (8). As the amount of nitrogen is increased from 10 to 40%, a linear increase in the electrical resistivity is observed from 0.1 to 50 Ω.cm, which is normal due to the increase in the density of copper nitride particles formed within the deposited film. With further increase in nitrogen amount in the gas mixture beyond 40%, a slight increase is measured in the electrical resistivity before start to decrease at partial amount of 60%. This behavior can be attributed to the increasing bonding rate of sputtered copper atoms to nitrogen atoms and hence more copper nitride nanoparticles are formed. These nanoparticles tend to exhibit electrical conductivity like metals due to the transitional oxidation states of copper as well as the electronegativity of nitrogen.

It is important to determine the relationship between the partial content of nitrogen (in its atomic state) in the prepared samples as a function of the partial amount of nitrogen gas in the gas mixture, as shown in Fig. (9). At low nitrogen pressures in the gas mixture, the nitrogen content in the prepared sample is approximately constant (0.23) as the bonding rate of copper atoms to nitrogen atoms is independent of partial amount of nitrogen in gas mixture. When this partial amount is increased from 20 to 40%, the nitrogen content increased from 0.23 to 0.26, which is ascribed to the increasing bonding rate. As the partial amount is increased from 40 to 80%, the nitrogen content is approximately constant (0.26), which indicate a constant bonding rate as increasing

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the partial amount of nitrogen in the gas mixture may decrease the sputter yield because the partial amount of argon gas in decreased too. At higher partial amount (>80%), the available number of copper atoms is certainly lower and hence all copper atoms are expected to bond to the available nitrogen, whose content is consequently increased in the final sample.

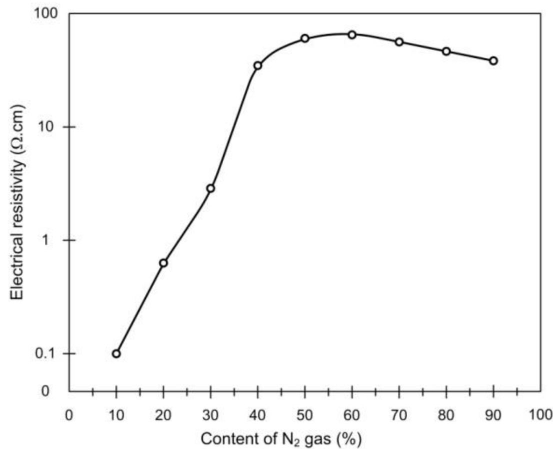

Fig. (8) Variation of electrical resistivity (ρ) of the prepared thin films with the percentage content of nitrogen gas in the gas mixture

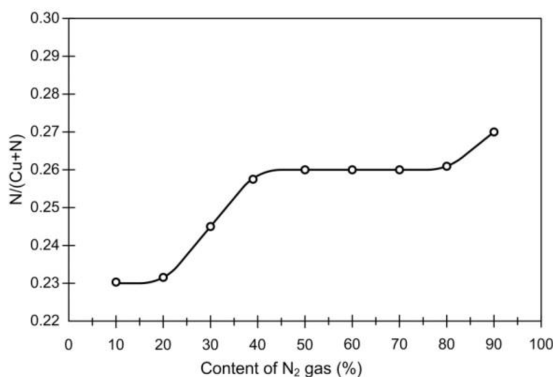

Fig. (9) Variation of partial content of the nitrogen gas in the prepared sample with the partial amount of nitrogen gas in the gas mixture

5. Conclusion

In concluding remarks, a successful attempt to prepare nanostructured copper nitride thin films by dc reactive plasma sputtering technique is presented. The prepared films are polycrystalline with cubic structures. The nanoparticle size was found dependent to the partial amount of nitrogen gas in the gas mixture used for sputtering. Similarly, the electrical resistivity of the prepared films and nitrogen content in the final samples were found sufficiently dependent to the partial amount of nitrogen in the gas mixture.

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