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Properties of Copper nitride thin films deposited using a pulsed hollow cathode discharge

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Abstract

Copper nitride (Cu_3N) thin films were deposited on a glass substrates using pulsed hollow cathode discharge (PHCD). The deposition was performed at 4kV charging voltage, and nitrogen gas pressure of 10^{-2} torr. The structure of the thin films was identified by X-Ray diffraction (XRD) technique. The XRD measurements indicated that the thin films have a nanocrystalline nature and exhibit orientation at (111) phase of Cu_3N. The grain size of the nanocrystalline films ranged from 41 nm to 80 nm. The optical band gaps were measured using U V–Vis–NIR spectrophotometer and Touc's equation. The optical band gaps of the films decreased from 2.55 eV to 2.25 eV by increasing the number of deposition shots from 20 to 80 shots. The surface morphology was studied by scanning electron microscopy (SEM). SEM image indicates that the film have facetted surface morphology packed particles.

1. Introduction

In recent years, among the nitrides of the 3d transition metals, copper nitride (Cu_3N) received more attention as a new material applicable for optical storage devices as write-once optical recording storage media, and high-speed integrated circuits [1-2]. Cu_3N has a cubic structure, where nitrogen atoms are positioned at the corners of the cell and copper atoms are positioned at the centre of the cube edges [3].

Pulsed DC power sources have been proved to provide an efficient way to produce thin films either by reactive or non-reactive sputter deposition [4–5]. Pulsed sputtering allows reducing the substrate temperature during deposition and considerably increasing plasma density in the pulse-on time at constant average discharge power. The increase in the plasma density can promote formation of more dense and stable thin film structure that leads to improvement of the thin films properties [6]. On the other hand, the pulsed hollow cathode discharge (PHCD) combines two important processes, i.e. sputtering and excitation/ionization of the sputtered atoms [7]. In the hollow cathode, due to its geometry, the electrons are electro-statically confined within the volume of the source and losses are minimized, the high-density plasma can be maintained [8]. Various thin film deposition techniques such as ion assisted deposition, pulsed laser deposition; dc and rf sputtering, rf plasma chemical reactor, and PHCD were employed for the growth of Cu_3N films [9]. PHCD serves as an excellent plasma source suitable to investigate anomalous glow discharge plasma and deposition of thin films. This plasma source produces stable discharge and sufficient sputtering rate. PHCD produces relatively thin plasma channel and it makes deposition on the substrates much easier [10]. The incoming working gas forces the plasma of this discharge supersonically from the nozzle into the substrate leading to enhancement of the deposition process.

We have successfully constructed and characterized a PHCD source, in this source the electron temperature ranges from 10-20 eV, and the plasma density in the order of 10^{18} m^{-3} [11, 12]. The present investigation is aimed to deposit the Cu_3N thin films employing pulsed hollow cathode discharge, and study the effect of the number of deposition shots of PHCD on the properties of copper nitride thin film. The structure, surface morphology and optical properties of Cu_3N were investigated.

2. Experiment

Schematic diagram of the used experimental setup is shown in figure (1). Cu_3N thin films were prepared on glass substrates by PHCD sputtering method with a base pressure of 10^{-3} torr. The hollow cathode is made from copper metal of cylindrical shape of diameter 25 mm and inner diameter 5 mm. The distance between the substrate and the nozzle is 20 mm. During deposition, the nitrogen gas pressure in the vacuum chamber was kept at approximately 10^{-2} torr, and the charging voltage was 4 kV. The PHCD device generates a maximum discharge current of 6.7 kA. The current waveform showed damped oscillations with half periodic time 40 µSec [11].

The crystal structures of the films were analyzed using XRD CuKα radiation. The optical properties of the thin films were identified using the UV–Vis–NIR spectrophotometer within the wavelength range of 300-1100 nm. The optical energy gap was obtained by extrapolating the absorption edge line to the abscissa as per the standard Tauc's plot technique [13]. The morphology of the deposited films was investigated by SEM. Experimentally it has been found that the contaminations in the deposited thin films depend strongly on the purity of the hollow cathode surface nozzle. In order to decrease the contaminations in the deposited thin films, the surface of the nozzle must be cleaned before the deposition process. The nozzle surface was chemically cleaned by etching in 38% chloride acid (HCl). The etching of the nozzle surface was then supplemented by ultrasonic cleaning in alcohol in order to remove the oxides and the surface contaminates.

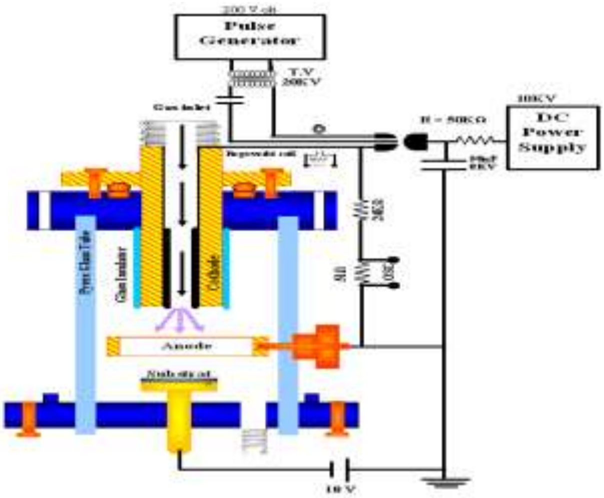


Figure 1: The schematic diagram of the pulsed hollow cathode discharge.

3-Results and Discussion

A. X-Ray Diffraction analysis

Figure (2) shows the X-Ray diffraction (XRD) patterns of the Cu_3N thin films deposited on a glass substrate at nitrogen gas pressure of 10^{-2} torr. The Cu_3N films are taken at different number of deposition shots 20, 40, 60 and 80, in pure nitrogen gas 10^{-2} torr, and at 4 kV charging voltage. For every sample the diffraction pattern containing Cu_3N (100), Cu_3N (110), Cu_3N (111), and Cu_3N (200), corresponding to four diffraction angles at 23.7°, 33°, 41° and 48° degrees, respectively. The structure of the deposited Cu_3N thin films is a cubic anti-Re03 structure [14]. The crystalline nature of the Cu_3N films mainly depends on the mobility of Cu and N atoms reacting in the film growth. The substrate was heated to a high temperature under the effect of bombardment by the hot plasma gas. Cu atoms sputtered from the inner surface of the nozzle react with Nitrogen ions to form the crystalline Cu_3N thin films.

The XRD spectrum also shows that the film prefers (100) orientation along with others. The increase of deposition shot numbers of PHCD leads to formation of more cupper nitride. Figure (2) shows that the intensity of the diffraction peaks increased by increasing the number of deposition shots. The increase of the peak intensity can be attributed to the increase in Cu3N deposition rates, and to the incident high energy atoms which cause a high temperature of the substrate hence forwardly increases the crystallinity of the thin films.

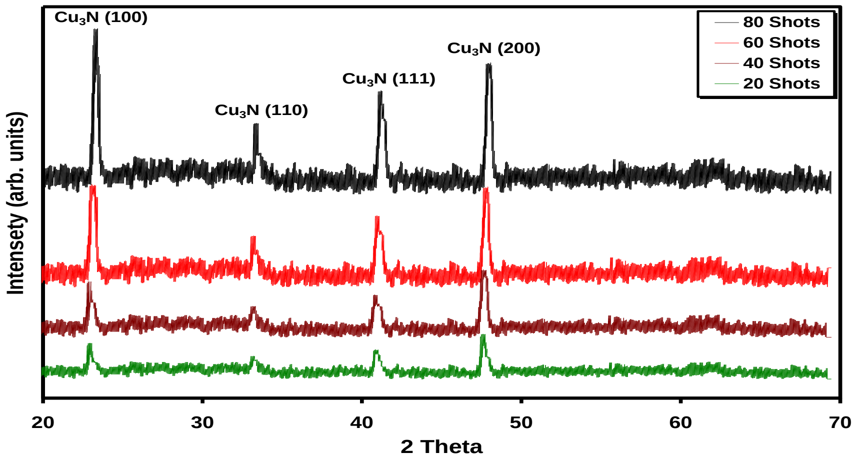


Figure (2) X-Ray patterns for copper nitride prepared at different number of shots.

Figure (3) shows the evolution of the crystal size calculated from the Cu_3N (100) diffraction peak versus number of deposition shots using the modified Scherrer formula [15].

$$D=0.9\lambda/\beta\cos\theta$$

Where λ is the wavelength of the Cu Kα radiation, θ is the diffraction angle and β is the FWHM of the diffraction line adjusted by pseudo-Voigt function, including the instrument peak width [16]. The calculated grain size of the deposited films ranges from 41 nm to 80 nm, when the number of shots increased from 20 to 80 shots.

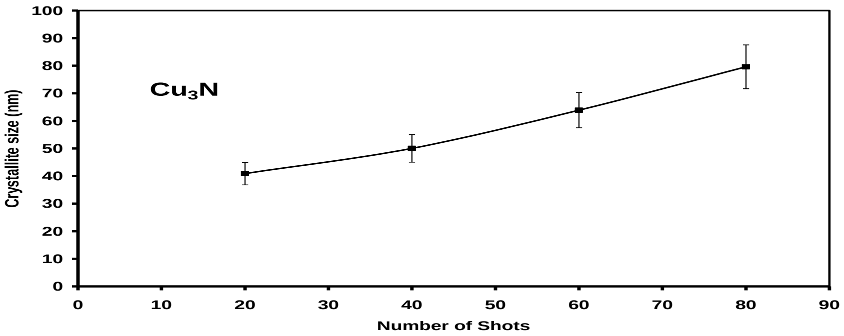


Figure (3): Influence of number of deposition shots on grain size of Cu3N films

B- Optical properties analysis

The results of XRD patterns of Cu_3N thin films indicate that the positive ions bombardment with the inner surface of hollow cathode is the main process for determining the optical properties of the deposited thin films [17, 18]. Figure (4) shows the optical transmittance curve of Cu_3N thin films deposited at different shots prepared using the PHCD source at 4 kV charging voltage. The film shows low optical transmission in visible light range, and yet shows high optical transmission in near-infrared regions. The optical transmission decreases by increasing the number of shots.

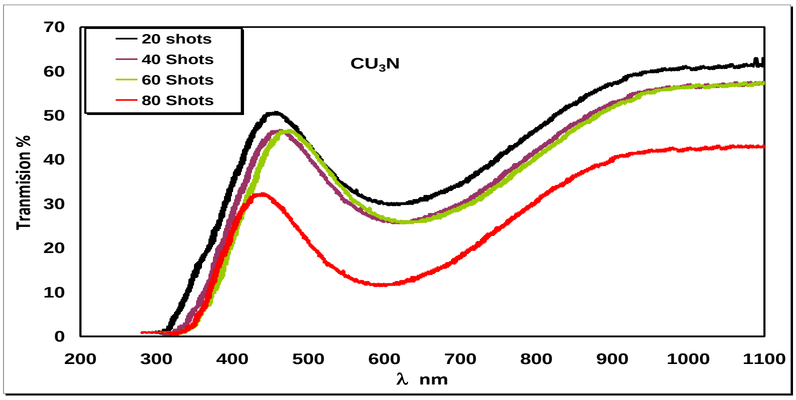


Figure (4): The optical transmission spectra for Cu3N thin films deposited onto glass substrate at different number of shots.

Optical band gap (E_g) determination is based on UV-visible transmission measurements considering copper nitride as an indirect semiconductor. Thus, Eg is determined using the plot ὁ$(\alpha h\nu)^{1/2}$ versus hν by extrapolating the full line to the abscissa (α denotes the absorption coefficient and hν the photon energy). Figure (5) shows the values of $(\alpha h\nu)^{1/2}$ versus hν of the Cu_3N films formed at different number of deposition shots. The optical band gap decreases from 2.55 to 2.25 eV, when the number of shots increases from 20 to 80 shots. This may be attributed to semiconductor character. Values of the experimentally measured optical band gap (Eg) are high compared to those published in the literature [19]. Such high value of the optical band gap may be caused by the quantum confinement of semiconductor nanocrystals [8].

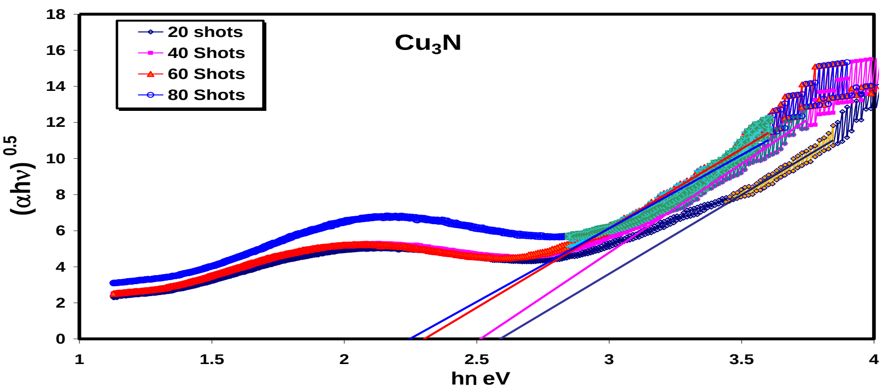


Figure 5: $(\alpha h\nu)^{1/2}$ versus hν of the Cu_3N films formed at different number of Shots.

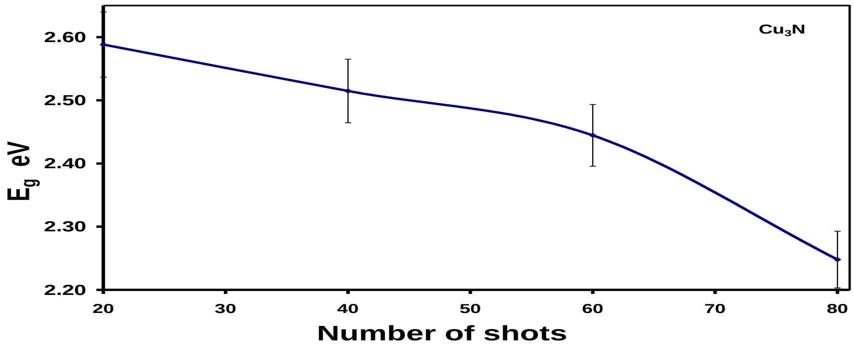
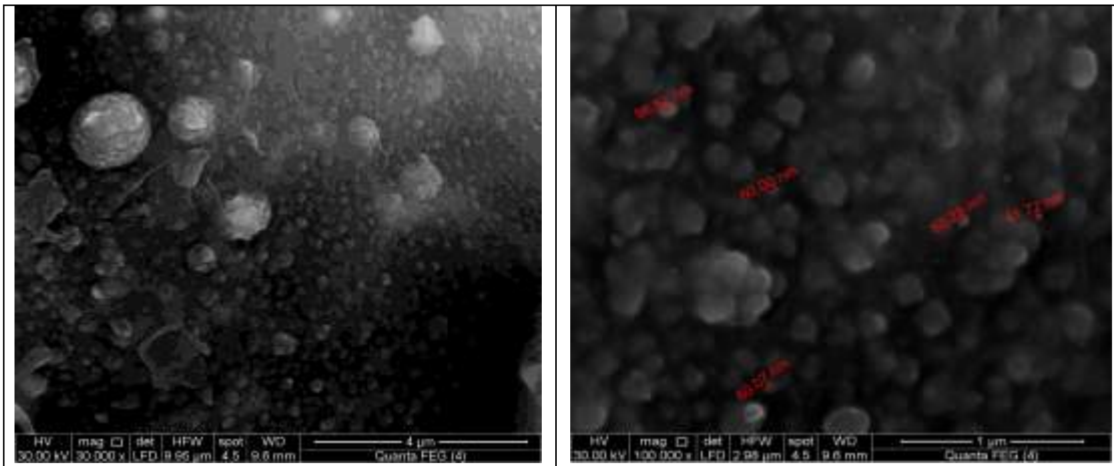


Figure 6: Influence of number of shots on the optical band gap of Cu_3N at V_{ch}=4 kV, and nitrogen pressure 10^{-2}torr

C- Surface morphology of the film

Figure (7) shows the surface morphology of Cu_3N thin film obtained using SEM. It can be seen that there are many uniform cavities in the surface of the film. The deposited thin film indicated a highly facetted morphology which may be due to its preferred orientation in the (111) direction [19]. The images show that the Cu_3N film consists of tightly packed particles. Grain size of the film is determined from SEM image, where the radius of each spherical grain along XY plane is determined. The effective grain size is calculated by taking the average of 5 grains in SEM image. The effective grain size of Cu_3N lattice is about 63 nm.



a b

Figure (7): The SEM of the surface morphology image film of Cu_3N film at nitrogen pressure 10^{-2} torr, V_{ch}=4kV, and 80 shots. a) at lower magnification b) at higher magnification

Conclusion

This paper is devoted to study the Cu_3N thin films deposited on a glass substrate using PHCD source at different number of deposition shots. The deposition was performed using nitrogen gas at pressure of 10^{-2} torr, charging voltage 4kV. The structure and optical band gap of the deposited films have been investigated. The X-Ray diffraction and SEM show that the films grow with preferred orientation in the (111) direction and have facetted surface morphology. The grain size was calculated with Scherrer's formula. The grains size of the deposited films ranges from 41 nm to 80 nm, when the numbers of deposition shots increased from 20 to 80 shots. Cu_3N films have a nanocrystalline nature. The optical band gap of Cu_3N thin films is determined using Touc's equation. The optical band gap decreases from 2.55 to 2.25 eV, when the number of shots increased from 20 to 80 shots.

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