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The Effect of Substrate on Structural and Electrical Properties of Cu_3N Thin Film by DC Reactive Magnetron Sputtering

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The aim of this paper is to study the effect of substrate on the Cu_3N thin films. At first, Cu_3N thin films are prepared using DC magnetron sputtering system. Then, structural properties, surface roughness, and electrical resistance are studied using X-ray diffraction (XRD), the atomic force microscope (AFM) and four-point probe techniques, respectively. Finally, the results are investigated and compared for glass and Si substrates. The results show a phase transition in orientation from (111) and (100) planes to (200) plane when the substrate of the sample is changed from glass to Si. Also, the grain size of deposited particles on films is increased by changing the substrate from glass to Si. Then, AFM results show that surface roughness on Si substrate is more than that on the glass substrate. Finally, four-point probe techniques show that surface electrical resistivity is increased sharply by changing the substrate from silicon to glass.

Keywords: DC reactive magnetron sputtering, Thin films, Cu_3N, X-ray diffraction, Atomic force microscopy

INTRODUCTION

The Cu_3N is a semiconductor with an indirect energy band gap of 0.9 eV, on the basis of theoretical calculations, and 1.2 eV - 1.9 eV on the basis of experiments [1-3]. Juza and Hahn obtained Cu_3N powder by heating powder of CuF_2 at 280 °C in NH_3 for the first time in 1939 [4]. Also, at first time, Terao studied the structure of Cu_3N by X-ray diffraction in 1973 [5]. Over the last decade, Cu_3N thin films have been the subject of many studies [6-9]. The thermal, structural, electrical and optical properties of Cu_3N thin films were the main focus of these studies [9-14].

The thin films of Cu_3N were deposited using different experimental methods such as chemical vapor deposition (CVD) [15], sputtering [16], pulsed laser [17], and Atomic layer deposition (ALD) [18].

The sputtering method is among the well-known methods used for the deposition of Cu_3N [11-16]. This technique is very controllable and exact for making thin films [19]. The DC reactive [20,21] and RF [22-24] are different methods of the sputtering method.

The Cu_3N thin films are very interesting because they have attractive properties and a unique crystal structure [8]. The Cu_3N has a cubic anti-ReO_3 type crystal structure and a lattice constant equal to 3.815 Å [24-25]. The Cu atoms do not occupy exactly the closely packed sites on (111) planes in this structure, therefore, this structure has a large number of empty sites [24] leading to the higher tunable properties of this material. The optical and electrical properties of Cu_3N will be changed considerably if other atoms stay on these empty sites. The Cu_3N has been doped with different elements such as Ti [26,27], La [28], O [15], Zn [29], H [30] and N [31]. Therefore, researchers have focused on this material in recent years and investigated structural [32,33], optical [32,34], electrical [32,34] and thermal [35] properties.

Because of its small indirect optical band gap, Cu_3N has been introduced as a new material for optical storage and high-speed integrated circuits devices [22]. The optical reflections of this material are in the visible and infrared

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range [15]. Since the optical reflections of Cu_3N are smaller than pure copper [15], this material is suitable for generating microscopic copper lines by laser writing using electron beam without photolithography process [36]. Since Cu_3N is decomposed in low temperatures (100-470 °C), it is converted to metal with the laser beam radiation locally. Therefore, it can be used in microelectronics and printing industry [15]. Most recently, it was found that this material can be used as a cathode catalyst in alkaline fuel cells [37] or as a negative electrode in the lithium-ion rechargeable battery because it has a good lifetime [38]. This material, as a semiconductor, is used as a substrate for hybrid organic-inorganic solar cells [15].

Many research activities have been carried out on important parameters such as thermal stability, optical gap and electrical resistance of copper nitride. For example, through changing the sputtering parameters, electric resistance values of 2×10^{-3} Ω cm to 10^3 Ω cm and optical band gap values of 0.8 eV – 1.9 eV have been reported [15]. In this paper, we study the effect of substrate on structural, morphological and electrical resistance properties of Cu_3N nanolayers. To do so, we prepared Cu_3N thin films with different substrates (glass and Si) using DC reactive magnetron sputtering. Then, we studied structural, morphological and electrical resistance properties using XRD, AFM, and four-point probe analysis, respectively.

EXPERIMENTAL METHOD

The Cu_3N thin film is prepared as follow. At first, a pure 99.95% copper target with 101.6 mm diameter and 8 mm thickness is polished using soft sanding and cleaned by aston and ethanol. Then, it is installed on the magnetron of the sputtering system. The substrates (glass, Si), with 1 cm × 1 cm size and 1 mm thickness, are cleaned perfectly in ethanol and aston solution using an ultrasonic cleaner. In this process, *Ar* gas (99.99%) with different pressure ratios is used as the working gas and N_2 gas (99.99%) as the reactive gas. The chamber pressure is reduced to vacuum mod (3.8×10^{-4} mbar) and *Ar* gas is imported to the chamber with 4.12×10^{-4} mbar pressure. The plasma is created in 4.5×10^{-3} mbar pressure, and the reactive N_2 gas is imported into the chamber with 4.2×10^{-3} mbar pressure. During sputtering, the power of the system is 0.13 kW and chamber work pressure is 8.7×10^{-3} mbar (P (Ar + N_2)) and temperature of the substrates is 50 °C. Table 1 shows the details of this process.

Thin films are deposited and their crystal structures are analyzed using grazing angle X-ray diffraction (XRD) with Cu Ka radiation (D8 advance model by Brucker Company). The morphology of the films is analyzed using AFM (AFM: DME DS-95-50) and finally, the electrical resistance properties are analyzed using a four-point probe (196 sys DMM model by the keithley company).

RESULTS AND DISCUSSIONS

Structure Properties

XRD analysis. To investigate the structure of these thin films and calculate their crystallization structure, the X-ray diffraction measurement was carried out using an X-Pert Brucker, in 2θ range 10°-100° using Cu Kα radiation of wavelength λ = 1.5406 Å operating.

The size of crystal was calculated using the Scherrer equation [39].

$$D = \frac{k\lambda}{\beta \cos\theta} \qquad (1)$$

where *D* is the average crystalline size, λ is the applied X-ray wavelength, k = 0.98 is a constant, θ is the diffraction angle in degree and β is the full width at half maximum (FWHM) of the diffraction peak observed in radians. Figure 1 shows the XRD patterns of the samples deposited on silicon and glass substrates. The main peaks of diffracted X-Ray photons can be seen from (100), (111) and (200) planes of Cu_3N, at 2θ equal to 23, 41 and 47 degrees, respectively.

By changing the substrate from glass to Si, the intensity of the peaks related to X-ray photon diffraction was decreased in (100) and (111) planes and was increased in (200) plane. Table 2 shows the grain size of Cu_3N thin films deposited on the silicon and glass substrates.

Analysis of the results (obtained by the xpert Highscor plus software) shows a phase transition in orientation from (111) and (100) planes to (200) plane when the substrate of the sample is changed from Si to glass. Also, the grain size of deposited film increases with changing substrate from

Table 1. Working Terms for Deposition of Cu_3N Thin Films

Scale	N_2 pressure (mbar)	Ar pressure (mbar)	Power (W)	Substrate temperature (°C)	Working pressure $P(Ar+N_2)$ (mbar)
Value	4.2×10^{-3}	4.12×10^{-4}	0.13	50	8.7×10^{-4}

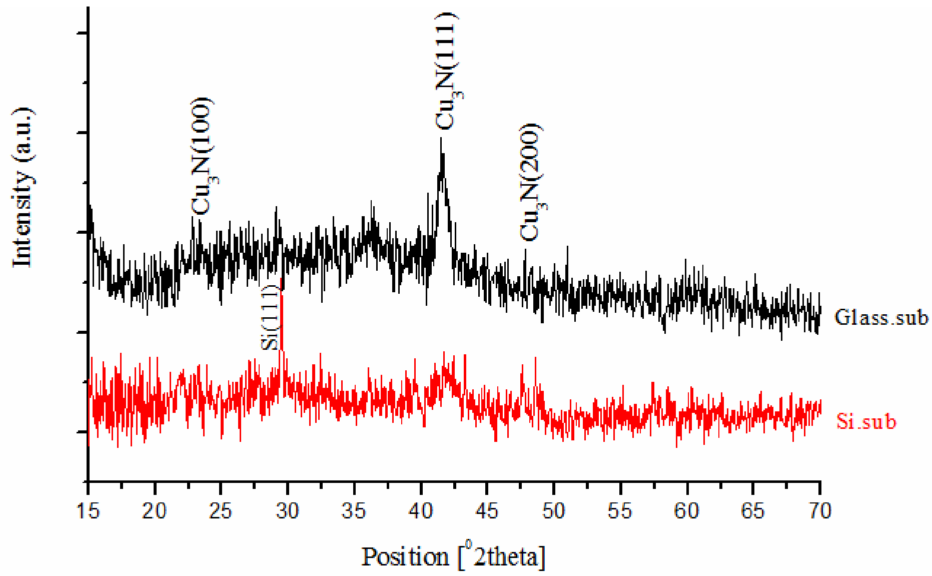

Fig. 1. X-ray diffraction spectrums from the deposited films on silicon and glass substrates.

Table 2. Lattice Constant and Grain Size of the Cu_3N Thin Film Deposited on Glass Substrate

Substrate	Angle	Grain size (nm)	lattice constant (Å)
Si	23 41 47	7.6	3.79
Glass	23 41 47	11.3	3.79

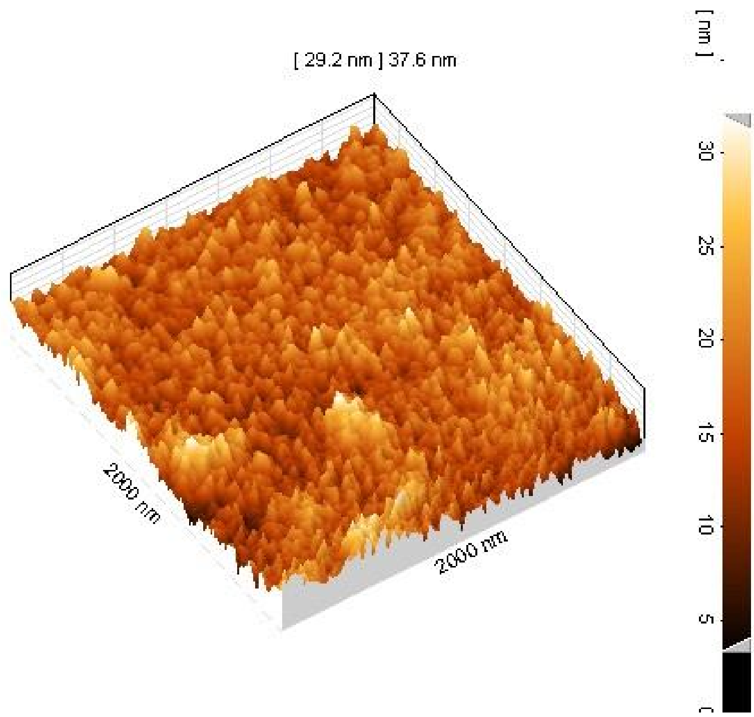

Fig. 2. AFM image of Cu_3N thin film deposited on glass substrate.

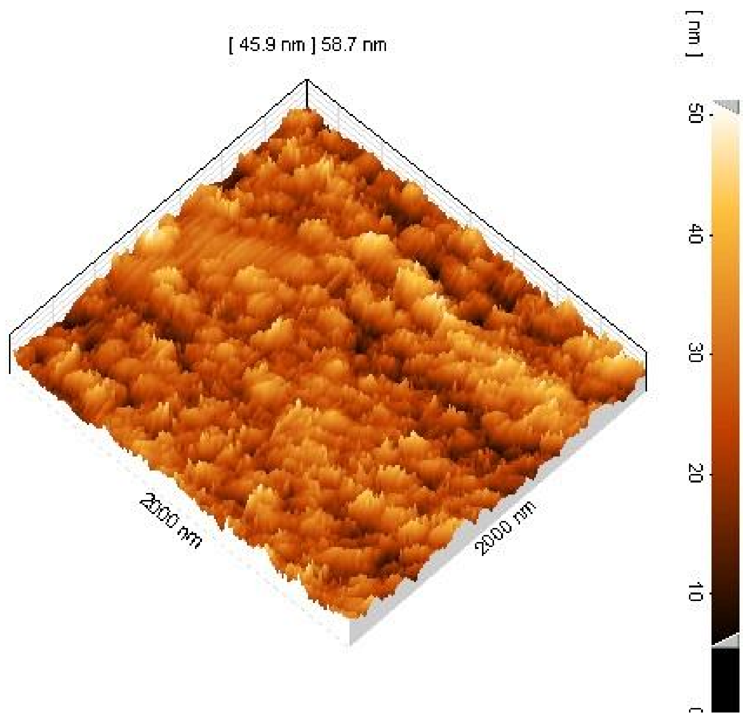

Fig. 3. AFM image of Cu_3N thin film deposited on Si substrate.

Table 3. AFM Analysis Image of Cu_3N Thin Film Deposited on Si Substrate

Substrate	S_a (nm)	S_q (nm)	S_{dq}	S_{tr}	S_{dr}
Si	5.67	7.16	0.48	0.23	10.90%
Glass	3.30	4.22	0.35	0.73	5.78%

Table 4. Surface Resistivity of Cu_3N Thin Film Deposited on Si Substrate

Substrate	Rs (Ω Cm)	Current (A)	Voltage (v)
Si	3.07629×10^3	10^{-3}	0.7
Glass	4.3947×10^3	10^{-3}	1

glass to Si.

In the present study, the lattice constant is the same for the samples that Cu_3N thin films deposited on silicon and glass substrates. This result may be due to the difference in nature of two substrates; an amorphous for glass substrate and non-amorphous for silicon substrate.

AFM analysis. The surface morphology of the samples was studied using atomic force microscopy (AFM). The scanning area is 2 × 2 µm. The results of Cu_3N thin films deposited on silicon and glass substrates are shown in Figs. 2 and 3, respectively.

Figures 2 and 3 show the surface roughness of Cu_3N thin film deposited on the glass and Si substrate, respectively. The figures show that surface roughness and the surface area are changed with changing the substrate. Table 3 shows the AFM analysis details of the Cu_3N thin film deposited on the glass and Si substrates, where S_a is the average roughness, S_q is the standard deviation (root mean square), S_{tr} is the surface isotropy, S_{dq} is the gradient of root mean square, and S_{dr} is the percentage of surface area.

The AFM analysis shows that roughness of Cu_3N thin film deposited on Si is more than that deposited on glass. Furthermore, Table 3 shows that the silicon substrate will cause the grain size to be increased, subsequently the density increases that leads to increasing the layer density. So, the refractive index of the layer increases. A layer of the glass substrate is more regular texture, so it has a more isotropic surface than the silicon substrate layer. Furthermore, the silicon substrate attracts more light and has a harder surface.

The results of Table 3 show that samples with glass substrate have smaller the average roughness, the standard deviation, the gradient of root mean square and the percentage of surface area compared to the samples with Si substrate. Also, the results indicate that the surface isotropy of the samples on the glass substrate is more than that of the samples with Si substrate. We think this observation originates from the fact that glass is an amorphous material.

Electrical Properties

Four-point probe techniques. The surface electrical resistivity of Cu_3N thin films prepared at various substrates was measured at room temperature. The surface resistivity of the films is shown in Table 4 for both samples. The surface electrical resistivity is increased sharply with changing the substrate from silicon to glass. We think this observation may be due to the difference in nature of two substrates which is insulator for a glass substrate but semiconductor for a silicon substrate.

CONCLUSIONS

The Cu_3N thin film is prepared using reactive DC sputtering, then the effect of the substrate is studied on properties of these thin films. The results of XRD analysis show a phase transition in orientation from (111) and (100) planes to (200) plane when the substrate of the sample is changed from glass to Si. Also, the grain size of deposited film increases with changing substrate from glass to Si. The results of AFM analysis show that roughness and the grain size of the Cu_3N thin film deposited on Si are more compared to the Cu_3N thin film deposited on glass. Therefore, the layer density is increased. Also, the refractive index of these thin films is increased with increasing the density. The thin film with silicon substrate has a more isotropy compared to thin film with the glass substrate. Also, the silicon substrate attracts more light and has a harder surface. The surface electrical resistivity of Cu_3N thin films is increased sharply with changing substrate from silicon to glass, because the glass substrates are insulator but the silicon substrates are semiconductor.

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