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Effects of Annealing and Oxygen/Nitrogen Ratio on Transmittance of Copper Oxynitride Thin Films

Abraham Kirwa Tuwei[1*], *Daniel Kipngetich Ketui* [2] *and Samson Muriuki Njogu*[1].

[1] Department of Physical Science, Chuka University P.O. Box 109- 60400 Chuka. Kenya
[2] Harbin Engineering University, Heilongjiang Province, 145 Nantong Street, Harbin, 150001, P.R. China.

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Abstract: Copper oxynitride (CuO_yN_x) thin films were deposited on glass substrates by dc reactive magnetron sputtering at room temperature and a pressure of 5 x 10^{-3} mbar with varying oxygen and nitrogen concentrations concurrently on each film for 10 minutes. The oxygen concentration was increased from 2 sccm, 4 sccm, 6 sccm, 8 sccm and 10 sccm while that of nitrogen was reduced from 8 sccm, 6 sccm, 4 sccm, 2 sccm and 0 sccm. The copper oxynitride thin films formed were annealed at 200 ^{0}C and 300 ^{0}C and their optical properties measured. We observed that at oxygen to nitrogen ratio of 8:2, there is a pronounced shifted of transmittance peak of CuO_yN_x from 610 nm to 810 nm for As-deposited and those annealed at 300 ^{0}C. We concluded that CuO_yN_x has tunable optical properties.

Keywords: Copper oxynitride, annealing, transmittance, dc magnetron sputtering.

1 Introduction

There is a growing interest among material science researchers on studying a new class of materials, metallic oxynitrides [1-3] due to their remarkable thermal stability, optical and mechanical properties. It is also reported that some of metallic oxynitride materials benefits from the properties of oxides, nitrides and metallic phases [4]. Copper oxynitride (CuO_yN_x) is among such materials and its transition from a single phase, simple cubic structure Cu_3N through a mixture of two phases, Cu_3N and Cu_2O to a single phase, simple cubic structure Cu_2O has been studied [5] and was prepared by reactive dc magnetron sputtering. It has also being grown using chemical vapour deposition, controlled by the ratio of H_2O and NH_3 as studied by [6]. The decomposition temperature of CuO_yN_x thin films determined from annealing the films has been reported to be 360 ^{0}C [7].

It is well known that copper oxide is a good semiconductor material for solar cell applications [8, 9]. On the other hand, copper nitride is a suitable material for optical storage devices [10-12]. The advantage that comes with the blend of the two properties has promising applications in optical storage devices. We report in this paper, the effects of annealing temperature and oxygen/nitrogen ratio on the optical properties of CuO_yN_x deposited by reactive dc magnetron sputtering on glass substrate at room temperature.

2 Experimental procedures

2.1 Apparatus

Edward Auto 306 sputtering machine was used to deposit CuO_yN_x thin films on a microscope glass substrate (25 mm × 25 mm × 1 mm) with target material being copper (99.99 % purity). UV/VIS/NIR 3700 double beam Shimadzu spectrophotometer was used to determine transmittance of thin films. Tub furnace for annealing with 2 Hot Zones model (XY-1200OTF-2) from Nanyang Xinyu Electric Components Co. Ltd was used to anneal the samples.

2.2 Preparation of CuO_yN_x thin films

Glass substrates were soaked for 30 minutes in dilute nitric acid bath prepared by adding 150 ml of nitric acid to 300 ml of deionized water in a polypropylene container. After 30 minutes, the glass substrates were rinsed with deionized water and ethanol to remove any nitric acid residues then blow dried. The glass substrates were then placed onto the substrate holder in the vacuum chamber with the distance between the copper target and the glass substrate being 15 cm. The deposition chamber was evacuated to a base pressure of 1 x 10^{-5} mbar and then the dc deposition power supply was switched on to start the deposition of copper oxynitride films for 10 minutes at sputtering power of 200 W. At the same time, oxygen (99.99% purity) and nitrogen (99.99% purity) gases were introduced into the sputter chamber at flow rate of 10 sccm and 0 sccm respectively. The deposition power supply, the chamber temperature and

*Corresponding author E-mail: atuwei@chuka.ac.ke

the chamber pressure were maintained at 200 W, 25 ^{0}C and 5 x 10^{-3} mbar respectively. The same procedure was followed and deposition parameters held constant to prepare various copper oxynitride films at different flow rate of oxygen (99.99% purity) and nitrogen (99.99% purity) see table 1. At the end of deposition process, samples were divided into three groups: those that were left As-deposited (without annealing), those that were annealed at 200 ^{0}C and the last group that were annealed at 300 ^{0}C. Finally, transmittance for each group was measured.

Table 1. Sample composition

Sample	Oxygen (sccm)	Nitrogen(sccm)
O2N8	2	8
O4N6	4	6
O6N4	6	4
O8N2	8	2
O10N0	10	0

2.3 UV - NIR spectroscopy measurement.

The transmittance of the three groups of copper oxynitride films were measured independently using UV/VIS/NIR 3700 double beam Shimadzu spectrophotometer in the spectral range of 300 nm - 1200 nm. The resulting data were analysed and compared as discussed in the section 3.

3 Results and discussions

3.1 Effects of oxygen/nitrogen ratio (O: N) on CuN_xO_y films transmittance

Measured transmittance for As-deposited CuO_yN_x samples with varying oxygen to nitrogen ratios are presented in figure 1. From the figure, sample O2N8 with the lowest oxygen to nitrogen ratios shows maximum transmittance of about 50% above 900 nm with its transmittance decreasing to less than 1% below 500nm, a property of Cu_3N [13, 14]. For sample O4N6, transmittance dropped to about 43% at high wavelengths with a shift of maximum transmittance to 700 nm compared to 900 nm for sample O2N8. Sample O6N4 is not affected significantly by oxygen to nitrogen ratios for wavelengths below 760 nm; however, above 760 nm, its transmittance is decreased to about 40%. Samples O8N2 and O10N0 with the highest oxygen to nitrogen ratios shows a sudden increase in their transmittance and their shift to visible region. Sample O8N2 shows transmittance of about 58% above 590 nm while sample O10N0 shows a continuous increase in transmittance from low to high wavelengths, a property of copper oxide.

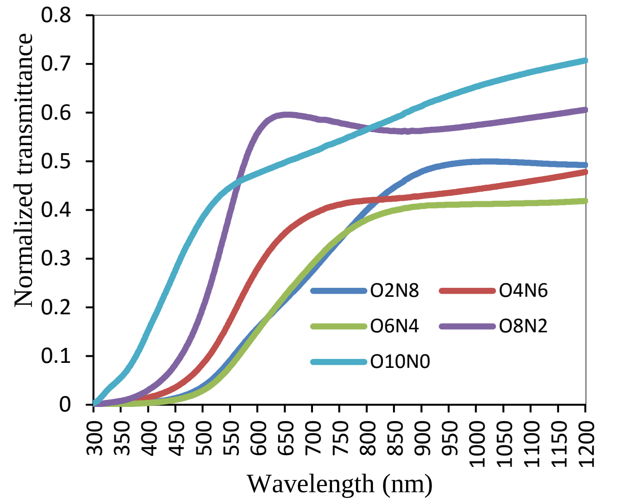

Figure 1. Transmittance of As-deposited thin film

3.2 Effects of annealing on CuO_yN_x films transmittance

Figure 2 to Figure 6 shows comparison between the measured transmittance of CuO_yN_x thin films, As-deposited, annealed at 200 ^{0}C and at 300 ^{0}C. Except for sample O10N0 of Figure 6, increasing the annealing temperature to 200 ^{0}C for the rest of the samples increases their transmittance irrespective of oxygen nitrogen ratio. Figure **4** shows minimal change in transmittance of sample O4N6 in the wavelengths below 650 nm while Figure 5 shows sample O6N4 with the highest increase in transmittance of above 35% at wavelength of 800 nm as compared to that of As-deposited.

On the other hand, Figure 6 shows a very slight drop in transmittance of sample O10N0 across all wavelengths when annealed at this temperature. Increasing annealing temperature to 300 ^{0}C also has varied effects on a number of samples. In sample O2N8 of Figure 2, such increase in annealing temperature lowers the sample transmittance even below that of the As-deposited films for wavelengths lower than 780 nm. Transmittance of samples O2N6 and O6N4 of Figure **3** and Figure **4** is found to be in between that of As-deposited and that annealed at 200 ^{0}C. Annealing temperature for samples O8N2 shows a shift of its transmittance peak from 610 nm to 810 nm. Figure 6 shows the results of O10N0 film which indicate that annealing the film shift the transmittance peak to 820 nm from 550 nm.

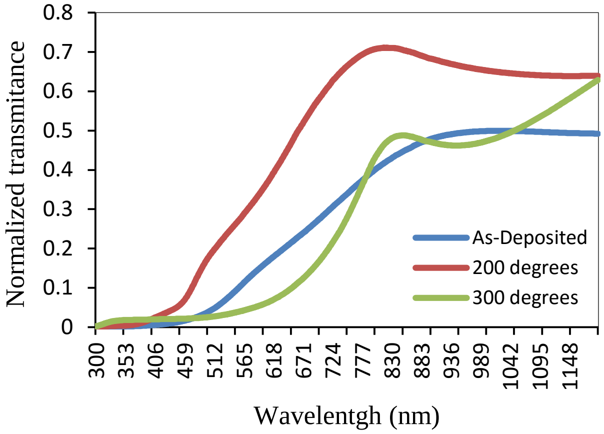

Figure 2. Transmittance for (O2N8) thin films.

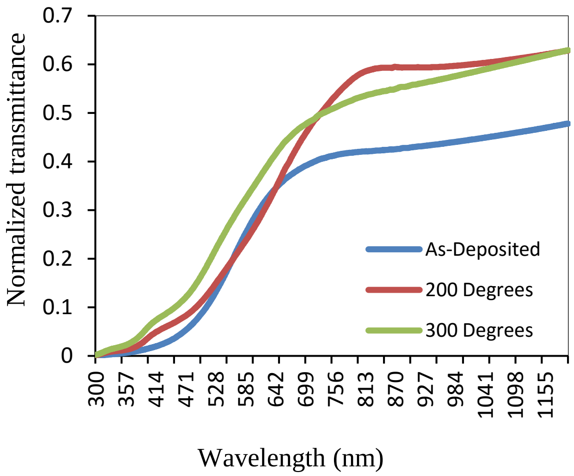

Figure 3. Transmittance for (O4N6) thin films.

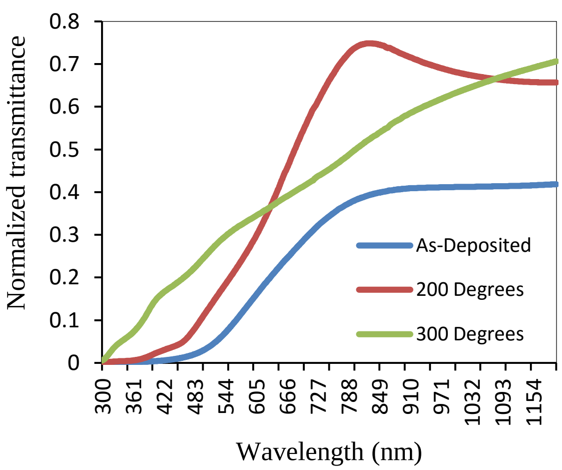

Figure 4. Transmittance for (O6N4) thin films.

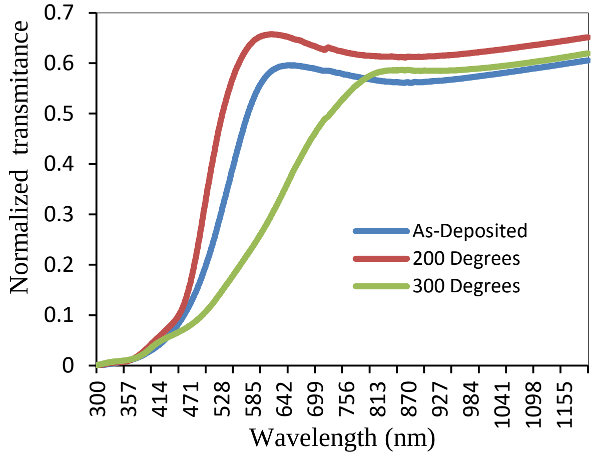

Figure 5. Transmittance for (O8N2) thin films.

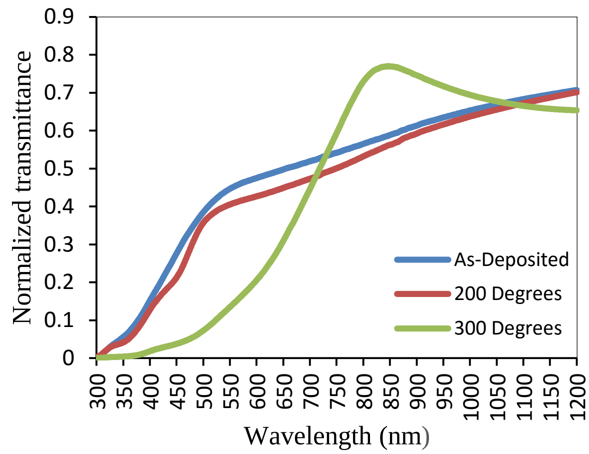

Figure 6. Transmittance for Cu_2O (O10N0) thin films.

This is a property of Cu_2O as reported by [15, 16]. From these observations, we concluded that CuO_yN_x thin films properties can be tuned between those of Cu_2O and Cu_3N in the visible region. We are therefore investigating these results further to confirm the structural composition of the films in order to explain clearly their underlying behaviour.

4 Conclusion

CuO_yN_x thin films with different oxygen to nitrogen ratios were deposited using dc reactive magnetron sputtering. By grouping thin film samples into three: As-deposited, those annealed at 200 ^{0}C and those annealed 300 ^{0}C, their optical properties were studied. Findings indicate that, CuO_yN_x has tunable optical properties that are obtained by annealing and varying oxygen/nitrogen contents. It was found that annealing CuO_yN_x samples with high oxygen to nitrogen ratio at 300 ^{0}C lowers sample's transmittance. At temperature, a pronounced shift of transmittance peak from 610 nm to 810 nm was observed at oxygen to nitrogen ratio of 8:2. We are further investigating these features to explore the applicability of this material.

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