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The Effect of Annealing Temperature and Reactive Gases on Optical Properties of Cu_2O Thin Films

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Abstract

The Cu_2O thin films were synthesized by using RF sputtering technique. Comparisons were made with films created by deposition at room temperature followed by thermal annealing between 100˚C and 400˚C and using different gases, oxygen (O_2) (oxidizing and reactive gas) and nitrogen (N_2) (inert gas), besides air. The thickness of the thin films was kept constant, around 2000 Å (Angstrom). In addition, the RF power and pressure deposition were kept constant, as well. The thin films were evaluated for a range of wavelengths between 200 nm and 400 nm (Ultra Violet spectrum), 400 nm and 700 nm (Visible spectrum), 700 nm and 800 nm (Infrared spectrum) for both, optical transmittance and photoluminescence. From the experimental results, the higher annealing temperature and the introduction of nitrogen (N_2) gas produced the following results: the optical bandgap for the Cu_2O was found to be 2.23 eV and photoluminescence peaks were around 551 nm and 555 nm, which matched the theoretical analyses. Overall, there was a decrease in the optical bandgap of the Cu_2O from 2.56 eV at room temperature to 2.23 eV for the film annealed in nitrogen gas at 400˚C. This indicates that the Cu_2O is a potential candidate in solar cell applications.

Keywords

Cu_2O Thin Film, Optical Properties, Bandgap, Photoluminescence

1. Introduction

In general, metal-oxide semiconductors are very popular materials in numerous applications, such as solar cells [1]. Cuprous oxide (Cu_2O) is a p-type semiconductor that has a high absorption coefficient and a low optical bandgap [2]. The intrinsic cuprous oxide (Cu_2O) is present in abundance and has both low toxici-

ty and cost. It has a cubic structure that has a direct optical bandgap between 2.10 eV and 2.60 eV [3]. These characteristics make the cuprous oxide a potential candidate for the manufacturing of low-cost, all-oxide solar cells. The optical properties of this material, like the bandgap and photoluminescence, are dependent on the method of film preparation and deposition [4]. Cu_2O thin films can be synthesized by using a combination of either physical or chemical methods. The most popular examples are thermal oxidation, RF sputtering, DC sputtering, pulsed laser deposition, chemical vapor deposition, and electrochemical deposition [5]. In this paper, the effect of the variation of the annealing temperatures and introduction of the different gases was studied.

Cu_2O is the known copper oxide structure that has Cu^{1+} ionization and formed in a cuprite structure with a lattice parameter of a = 4.268 Å (Angstrom), with a space group of cubic geometry and octahedral Pn-3m symmetry. When the thin film is annealed, it causes the changes in the crystal structure's ionic pattern and its bonding properties [6].

The defect concentration in the cuprous oxide (Cu_2O) thin films can be reduced through several processes. A few examples are annealing or growth in a controlled environment, passivation using a cyanide treatment, or hydrogen diffusion [7]. Raj Kumar *et al.* [7] chose to introduce hydrogen ions during deposition (passivation of materials surface by hydrogen) and annealing (post deposition) of the Cu_2O thin film in hydrogen ambient atmosphere at different temperatures (100˚C through 600˚C). The deposition method was DC magnetron sputtering at 400˚C temperature and hydrogen ion was at 900˚C [7]. The results obtained for the optical bandgap of the Cu_2O film varied between 2.45 eV to 2.55 eV [7]. In our case, the method chosen for improving the quality of the Cu_2O thin films was annealing at different temperatures post deposition.

The Cu_2O forms in a unique cubic crystal structure where Cu^+ ions occupy one-half of the tetrahedral sites of a body-centered cubic packing of O^{2-} ions. The Cu_2O particles tend to have a morphology exposing {100}, {111}, and {110} crystal facets. The intrinsic p-type conduction of Cu_2O is believed to originate from copper vacancies acting as a shallow acceptor level located 0.2 to 0.3 eV above the valence band maximum. Due to earth-abundant constituent elements, low cost and toxicity, the Cu_2O can be used in various applications like solar cells, photo-catalysts, and as a thermoelectric material (direct conversion of waste heat into electricity) [8].

For practical applications of Cu_2O, it is important to consider the stress in the films caused by the substrate. This will affect the electrical and optical properties of the film. A compressive or tensile stress in a film is developed due to the mismatch of the lattice constant or the thermal expansion coefficient between the film and the substrate [7]. If glass is used as a substrate, because it is amorphous, the first mechanism is negligible. The films are not epitaxial grown on the substrate. The thermal expansion coefficient of Cu_2O ($\alpha_f = 1.6 \times 10^{-6}\ K^{-1}$) is much smaller than that of the glass substrate ($\alpha_s = 8 \times 10^{-6}\ K^{-1}$) [7]. Thus, Cu_2O films deposited on the glass substrate at an elevated temperature are sub-

jective to a compressive stress. In our case, the thin film deposition occurs at room temperature; hence, the impact of the compression stress is negligible.

2. Experimental Procedure

In this research, thin films of Cu_2O were deposited on glass slides that were thoroughly cleaned using acetone, methanol and de-ionized water. The Cu_2O films were deposited from a 2-inch powder pressed target with a purity of 99.5% using RF magnetron sputtering technique. The sputter depositions were done in an in-house built sputtering system after a constant base pressure of 4×10^{-5} Torr was achieved between each deposition. Cu_2O films with constant thickness of 2000 Å (Angstrom) were deposited at room temperature using Ar (argon) as the only sputtering gas. The RF power, argon flow and chamber pressure were kept constant for all depositions at 10 SCCM (standard cubic centimeter per minute), 10 mTorr and 50 W respectively. The film thicknesses were identified using a Dektak 150 profilometer. Three sets of Cu_2O films were made by systematically annealing for thirty minutes in an isotemp programmable muffle furnace at temperatures of 100˚C to 400˚C in the presence of oxygen (O_2), nitrogen (N_2) and air respectively. The gas flow into the annealing furnace was kept constant at 100 SCCM (standard cubic centimeter per minute).

The optical transmissions of the deposited Cu_2O thin films were measured in a Carry 100 UV-Vis spectrophotometer from Agilent Technologies. The optical transmission was measured between 200 to 800 nm, however, due to UV absorption only 350 to 800 nm results were analyzed. The optical bandgaps of the Cu_2O films were identified from the transmission data using the Tauc plot method.

The photoluminescence measurements were recorded using a Flame spectrometer from Ocean Insight (formerly known as Ocean Optics) with a wavelength range from 200 nm to 850 nm. The optical resolution of the spectrometer was 1.33 nm at full width half max (FWHM). The detector was a linear silicon CCD array with 2048 pixels and an entrance slit of 25 μm. The software used in association with the spectrometer was the Ocean View from the same company (Ocean Insight). The excitation source was a ThorLabs UV laser diode (L375P70MLD at 375 nm). A 1000 μm fiber optic patch cable (SMA to SMA) from ThorLabs with a numerical aperture of 0.50 completed the setup.

3. Results and Discussion

The Cu_2O thin films had different levels of transparency as a function of annealing temperature (room temperature (RT) – semi-transparent to high temperature (400˚C)—close to opaque). The thin films had an overall strong absorption in the UV region (between 200 nm and 375 nm). The optical transmission spectrums for the Cu_2O thin films annealed in different mediums (air, oxygen, and nitrogen) are shown in **Figures 1-3**.

The transmission spectrum for the first series of Cu_2O thin films (room temperature and annealed in air) is shown in **Figure 1**.

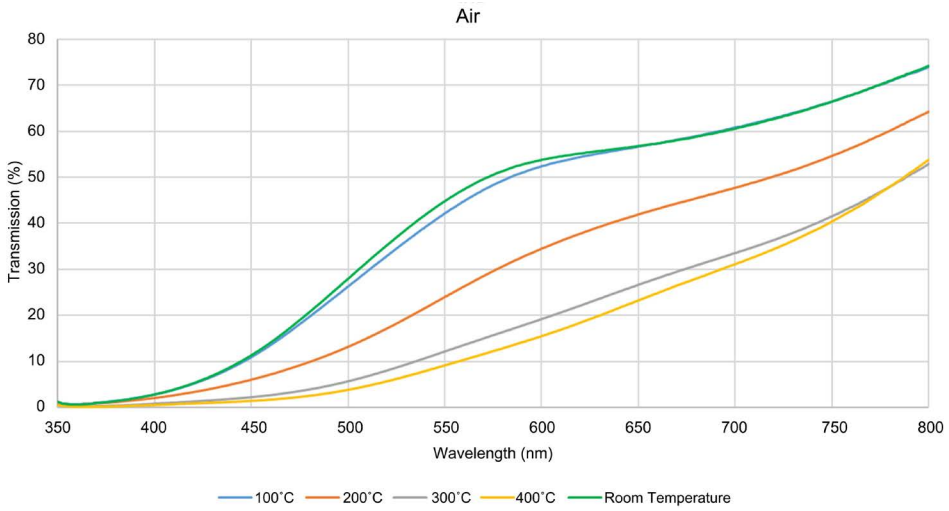

Figure 1. Spectra of Cu_2O thin films annealed in air.

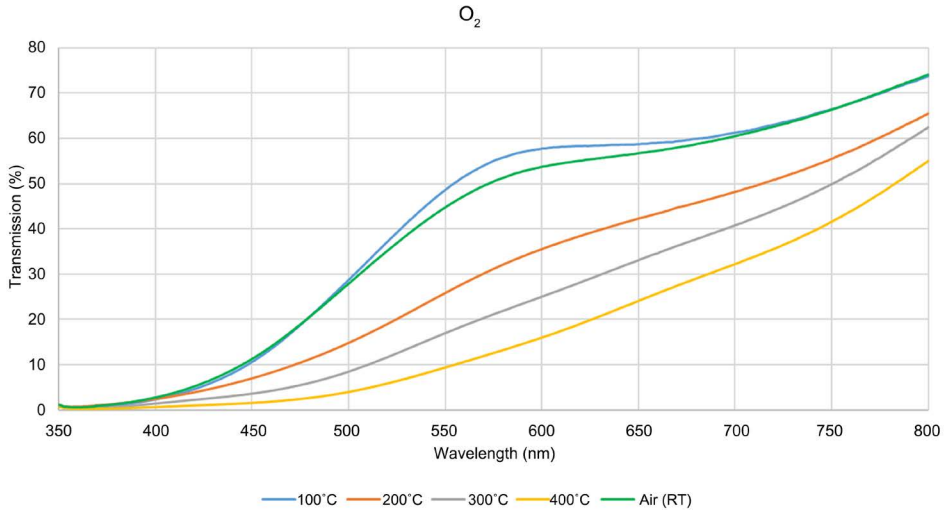

Figure 2. Spectra of Cu_2O thin films annealed in O_2 reactive gas.

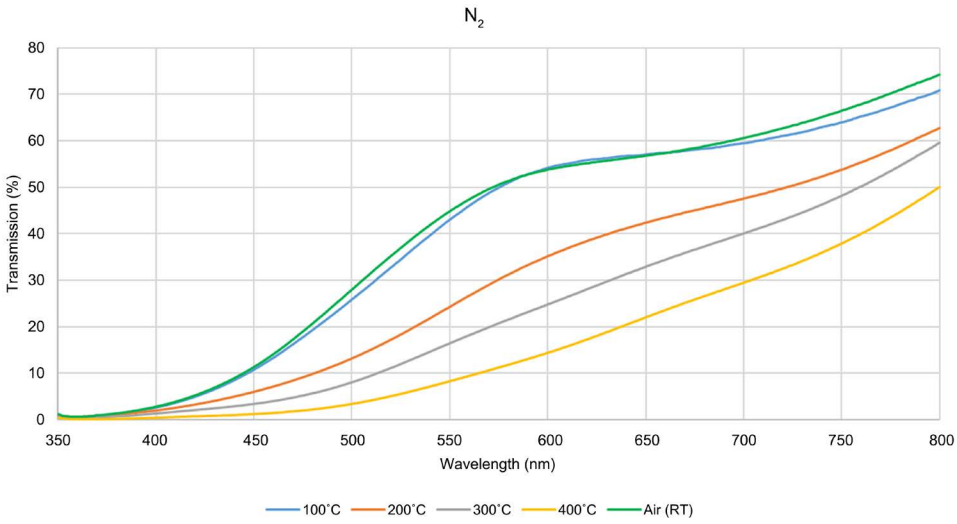

Figure 3. Spectra of Cu_2O thin films annealed in N_2 inert gas.

The transmission varied as function of the annealing temperature (room temperature (RT) – maximum transmission of 74.16% at 800 nm to high temperature (400˚C)—maximum transmission of 53.84% at 800 nm). A similar behavior, the decrease in optical transmission as a function of annealing temperature increase, was observed at the optical bandgap (555 nm). At room temperature (RT) – maximum transmission of 46.14% to high temperature (400˚C)—maximum transmission of 9.80%.

Note: The values for the actual percentages for the optical transmission with respect of the wavelength were obtained from the data provided by the Carry software.

The transmission for the thin film deposit at room temperature and the film annealed in air at 100˚C is very similar with a slight decrease between 500 nm and 600 nm for the annealed film. This can be associated with the temperature impact on the structure of the film.

The transmission spectrum for the second series of Cu_2O thin films (room temperature and annealed in oxygen (O_2)) is shown in **Figure 2**.

The transmission varied as a function of the deposition temperature (room temperature (RT) – maximum transmission of 74.16% at 800 nm to high temperature (400˚C)—maximum transmission of 55.07% at 800 nm). A similar behavior, the decrease in optical transmission as a function of deposition temperature increase, was observed at the optical bandgap (555 nm). At room temperature (RT) – maximum transmission of 46.14% to high temperature (400˚C)—maximum transmission of 9.97%. The transmission for the film annealed in oxygen was slightly increased, in comparison with the film deposit at room temperature, between the 520 nm to 670 nm. For this portion of the visible spectrum, the presence of oxygen in the annealed chamber, allow of the change in structure of the film making it more transparent, hence the somewhat higher transmission percentage.

The transmission spectrum for the third series of Cu_2O thin films (room temperature and annealed in nitrogen (N_2)) is shown in **Figure 3**.

The transmission varied as a function of the deposition temperature (room temperature (RT) – maximum transmission of 74.16% at 800 nm to high temperature (400˚C)—maximum transmission of 50.07% at 800 nm). A similar behavior, the decrease in optical transmission as a function of deposition temperature increase, was observed at the optical bandgap (555 nm). At room temperature (RT) – maximum transmission of 46.14% to high temperature (400˚C)—maximum transmission of 8.93%. The transmission for the air deposited film at room temperature was slightly higher, in comparison to the film annealed at 100˚C in nitrogen, between 470 nm and 560 nm (visible spectrum), and lower between 700 nm and 800 nm (infrared spectrum). This shows the impact of nitrogen on the thin film at the longer wavelengths. The decrease in the transmission is direct proportional with the increase in absorption.

The results obtained for the optical transmission at different temperatures were tabulated in **Table 1**:

Table 1. Cu_2O Thin Films optical transmission results.

Annealing Medium	Wavelength	Transmission				
		RT (no annealing)	100˚C	200˚C	3000˚C	400˚C
Air	800 nm (IR)	74.16%	73.99%	64.25%	52.88%	53.84%
O_2			73.70%	65.48%	62.35%	55.07%
N_2			70.84%	62.69%	59.51%	50.07%
Air	555 nm (VIS)	46.14%	43.46%	25.10%	12.91%	9.80%
O_2			50.14%	29.97%	17.87%	9.97%
N_2			44.50%	25.46%	17.28%	8.93%
Air	400 nm (UV)	2.81%	2.74%	1.99%	0.88%	0.60%
O_2			2.28%	2.44%	1.51%	0.59%
N_2			2.18%	1.94%	1.31%	0.49%

Overall, the results indicated a decrease in optical transmission as a function of increasing the annealing temperatures. Furthermore, the change of the medium in the annealing chamber affected the optical transmission. Air as a annealing medium had the minimum impact of the thin film with the lower results observed for the thin films annealed in the nitrogen gas at 400˚C (8.93% at 555 nm).

Ozaslan *et al.* [6] deposited Cu_2O on a glass substrate at 70˚C by the SILAR (Successive Ionic Layer Adsorption Reaction) method. After the deposition the thin films were annealed in air at different temperatures between 100˚C and 500˚C. The thickness of the film was determined by calculations using the gravimetric weighting method and found to be 488 nm. The researchers found that the optical transmission value of copper oxide thin film to be 37% (at 550 nm – center of visible spectrum), the percentage dropped to 33% for the film annealed at 100˚C, and dropped even further to 23% for the annealing temperature of 300˚C.

The same behavior was detected from the thin films created for this paper. From the three series of films deposited, it was observed that the increase in annealing temperature created a more opaque film that minimized the optical transmission. In **Figure 4**, the graph shows the comparison between the transmissions in the three thin films annealed at 400˚C.

The transmission was minimum between 350 nm and 383 nm (UV spectrum) and less than 10% up to 556 nm (VIS spectrum). Overall, the lowest transmission (highest absorption) was observed in the last series of films at the highest annealing temperature (400˚C) in the presence of N_2 gas.

The absorption coefficient of the thin film was determined using the following formula (Equation (1)) [9]:

$$\sigma_\lambda = \frac{-\ln(T)}{t} \tag{1}$$

where σ_λ = absorption coefficient, T = optical transmission, and t = thickness of

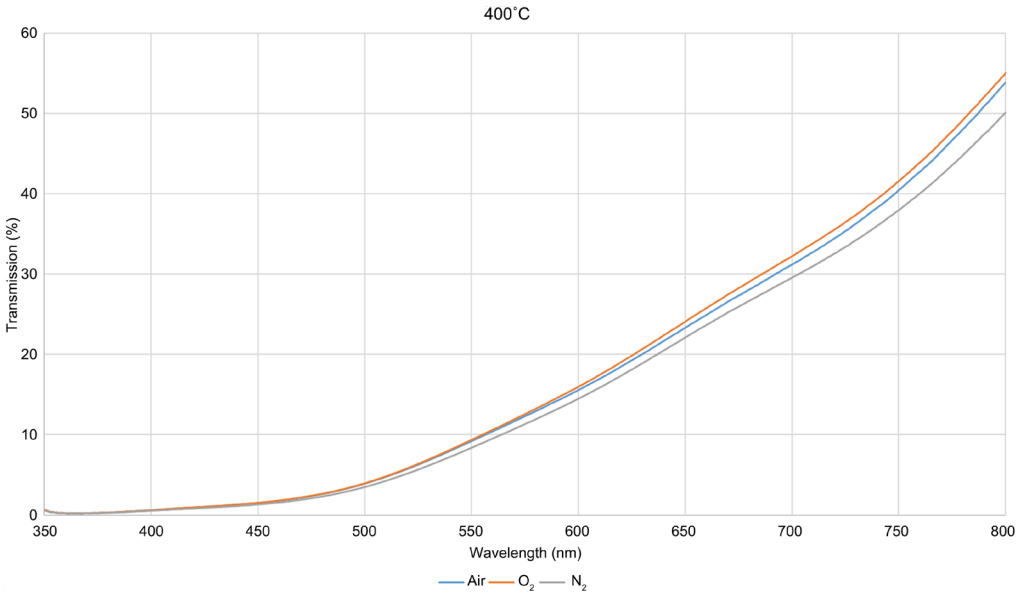

Figure 4. Spectra of Cu_2O thin films annealed at 400˚C.

the film. The absorption coefficient was used to calculate the optical bandgap in the Tauc plot. The Tauc plot was graphed by fitting the data into this equation (Equation (2)) [10]:

$$\left(\sigma_\lambda \cdot h\nu\right)^2 = B\left(h\nu - E_g\right) \tag{2}$$

where $h\nu$ = photon energy, B = constant factor, and E_g = optical bandgap.

The Tauc plot for the absorption coefficient is shown in **Figures 5-9** below from room temperature to 400˚C:

The optical bandgap is extracted by extrapolating the linear region of the Tauc curve to the x-axis. The x-intercept provides the value of the optical bandgap for the Cu_2O thin films. The curve for the film deposited in O_2 almost overlaps the film deposited in air and as a result, no significant difference was observed in the optical bandgap, 2.23 eV. The bandgap for the film annealed in N_2 was 2.25 eV. The optical bandgap for the Cu_2O thin film varied between 2.58 eV (at room temperature) to 2.23 eV (at 400˚C). The bandgap values in **Table 2** are in agreement with the theoretical and experimental values found in the literature, 2.23 eV band-gap [11], 2.10 - 2.30 eV [12].

Sai Guru Srinivasan *et al.* [3] deposited Cu_2O thin films on a glass substrate by RF reactive (controlled argon and oxygen atmosphere) sputtering at room temperature with various deposition times (1, 3, and 5 minutes) which corresponded to the following thicknesses: 112, 304, and 498 nm. The optical bandgaps for the three Cu_2O thin films were 2.54, 2.41, and 2.12 eV. The results show a decrease in the optical bandgap with the increase in the film thickness. The conclusion was that the particle size and lattice defects have a direct influence on the optical bandgap value. The growth in the grain size was observed as a function of high surface to volume ratio of the film with lower thickness. In addition, lattice defects were observed due to oxygen vacancy [3].

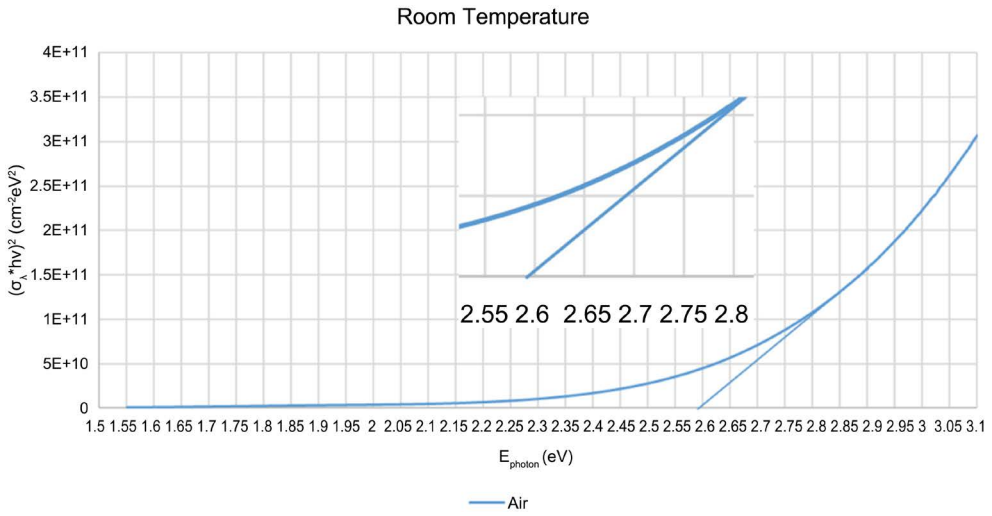

Figure 5. Cu_2O thin films optical bandgap (room temperature).

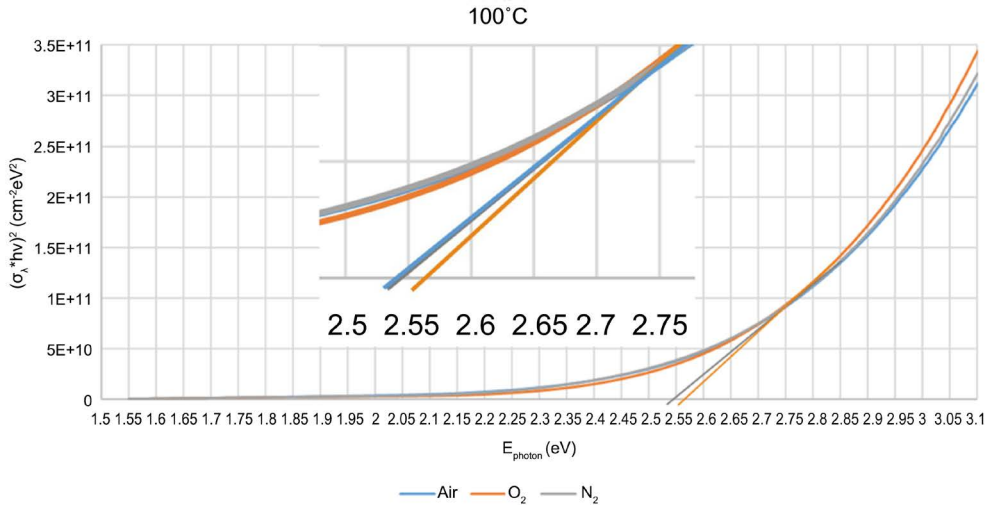

Figure 6. Cu_2O thin films optical bandgap (annealed at 100˚C).

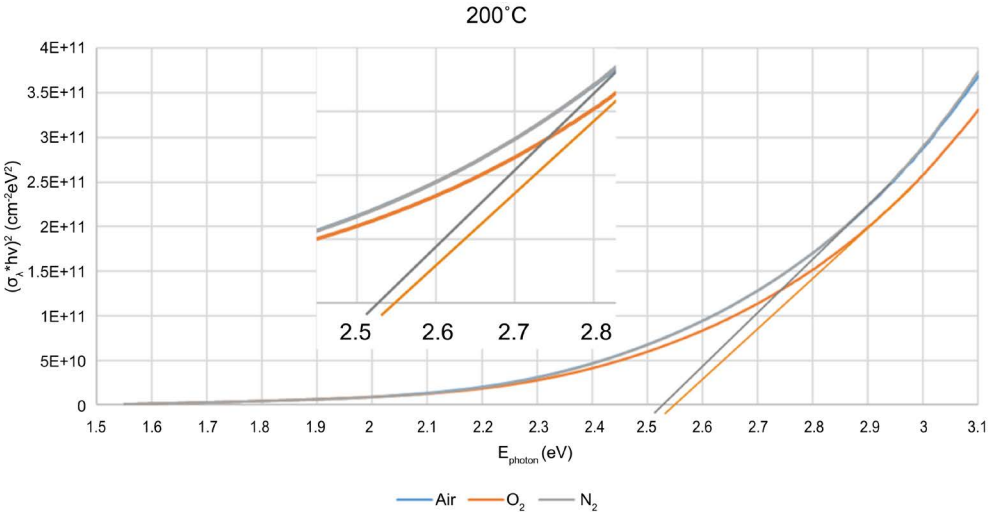

Figure 7. Cu_2O thin films optical bandgap (annealed at 200˚C).

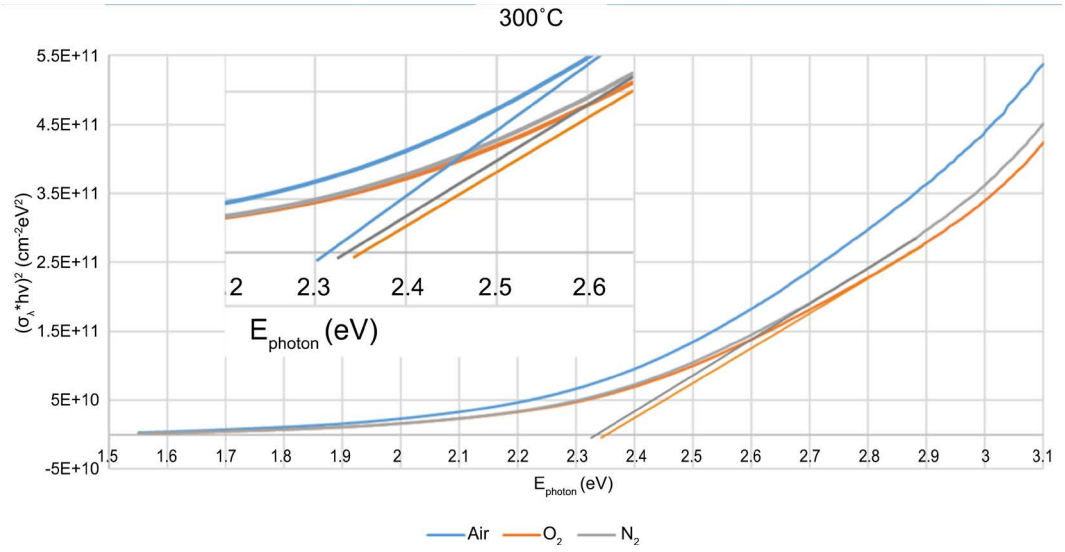

Figure 8. Cu_2O thin films optical bandgap (annealed at 300˚C).

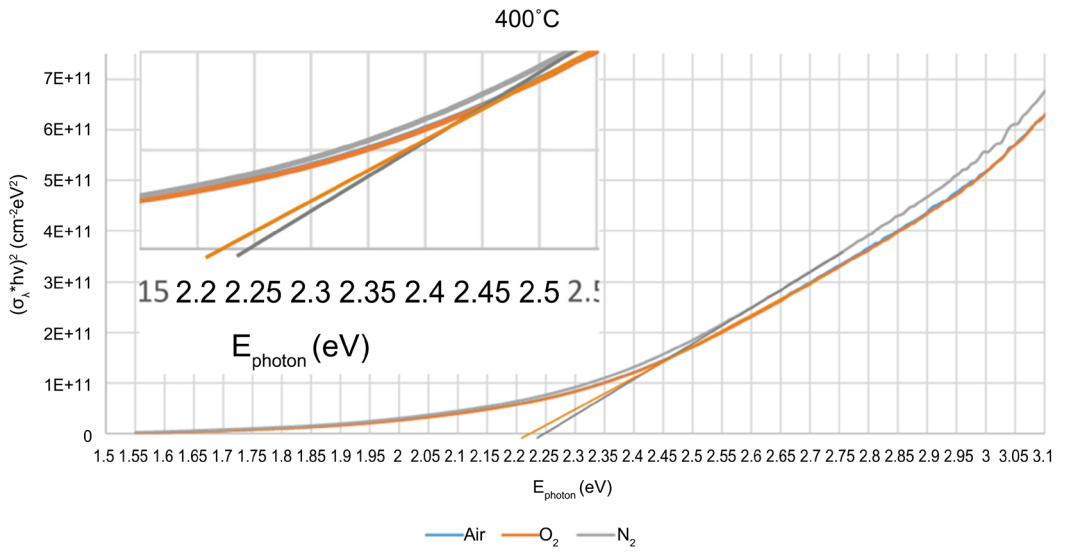

Figure 9. Cu_2O thin films optical bandgap (annealed at 400˚C).

Table 2. Cu_2O thin films optical bandgap values.

Temperature	Optical Bandgap		
	Air	O_2	N_2
Room Temperature		2.58 eV	
100˚C	2.53 eV	2.54 eV	2.56 eV
200˚C	2.53 eV	2.54 eV	2.53 eV
300˚C	2.32 eV	2.35 eV	2.34 eV
400˚C	2.23 eV	2.23 eV	2.25 eV

The increase in the annealing temperature affected the properties of the Cu_2O thin films and one of their effects was a decrease in the optical bandgap. If the

annealing temperature is increased even higher than 400˚C, an even lower bandgap for the Cu_2O thin films can be achieved. Ozaslan *et al.* [6] found that the bandgap for the Cu_2O thin films was reduced from 2.57 eV (at 70˚C) to 1.91 eV (at 500˚C) with the increase in temperature.

The photoluminescence measurement is shown in Figures 10-14 below (from room temperature to 400˚C):

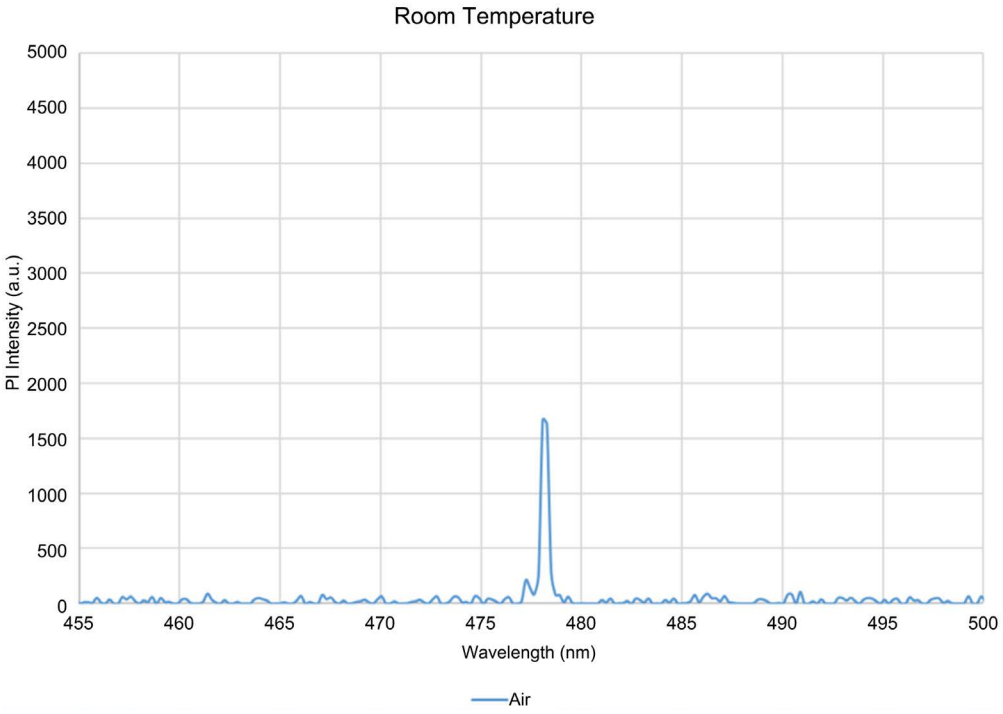

Figure 10. PL Spectra of Cu_2O thin films (room temperature).

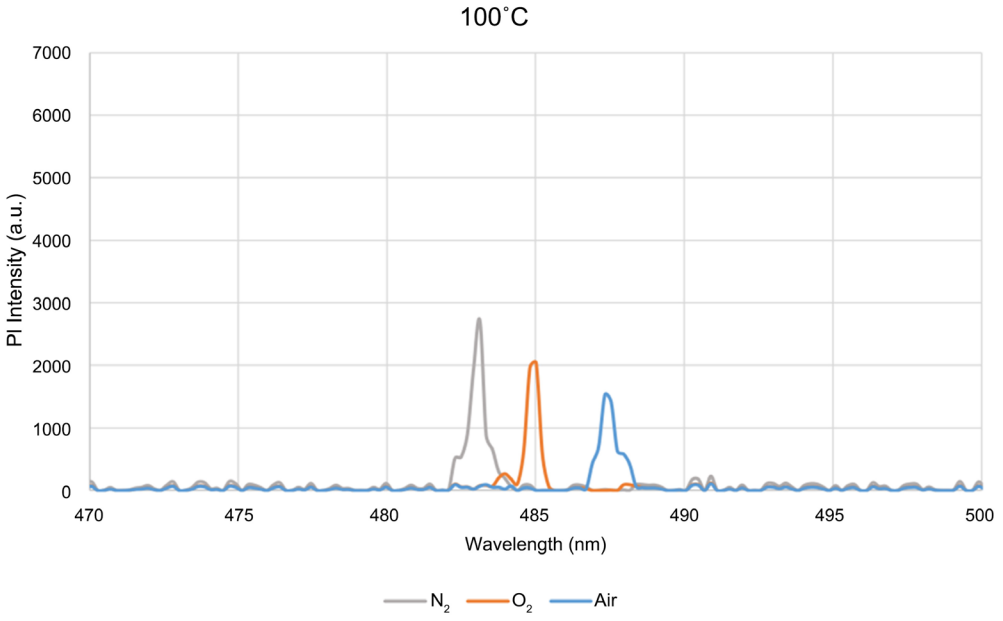

Figure 11. PL Spectra of Cu_2O thin films (annealed at 100˚C).

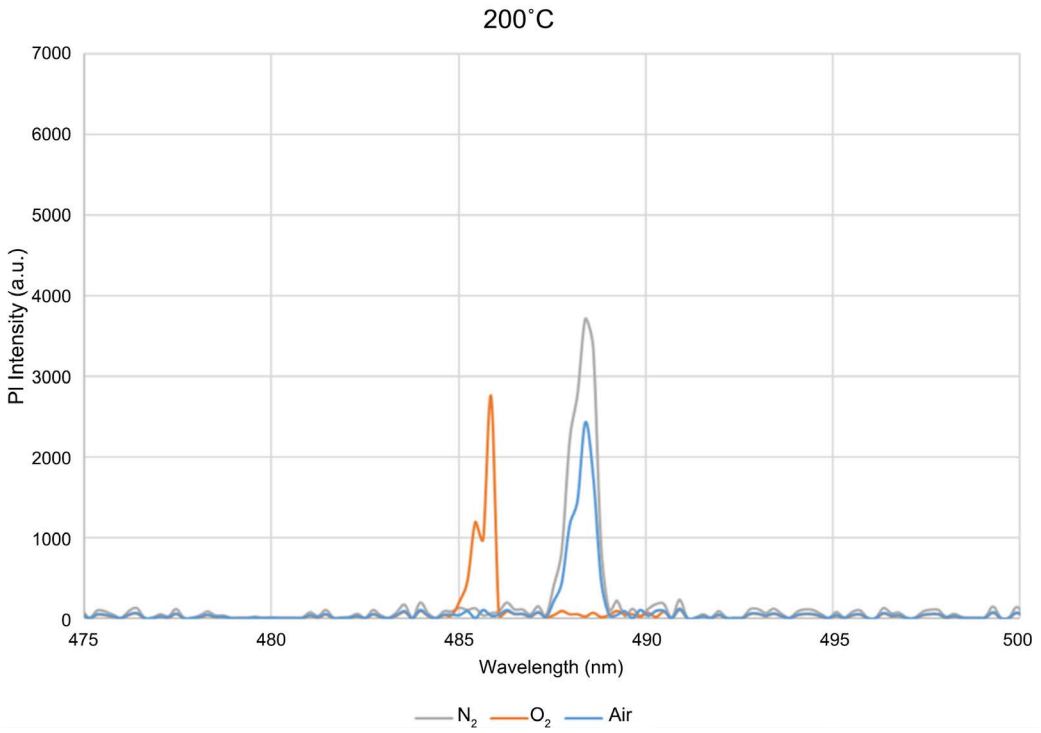

Figure 12. PL Spectra of Cu_2O thin films (annealed at 200˚C).

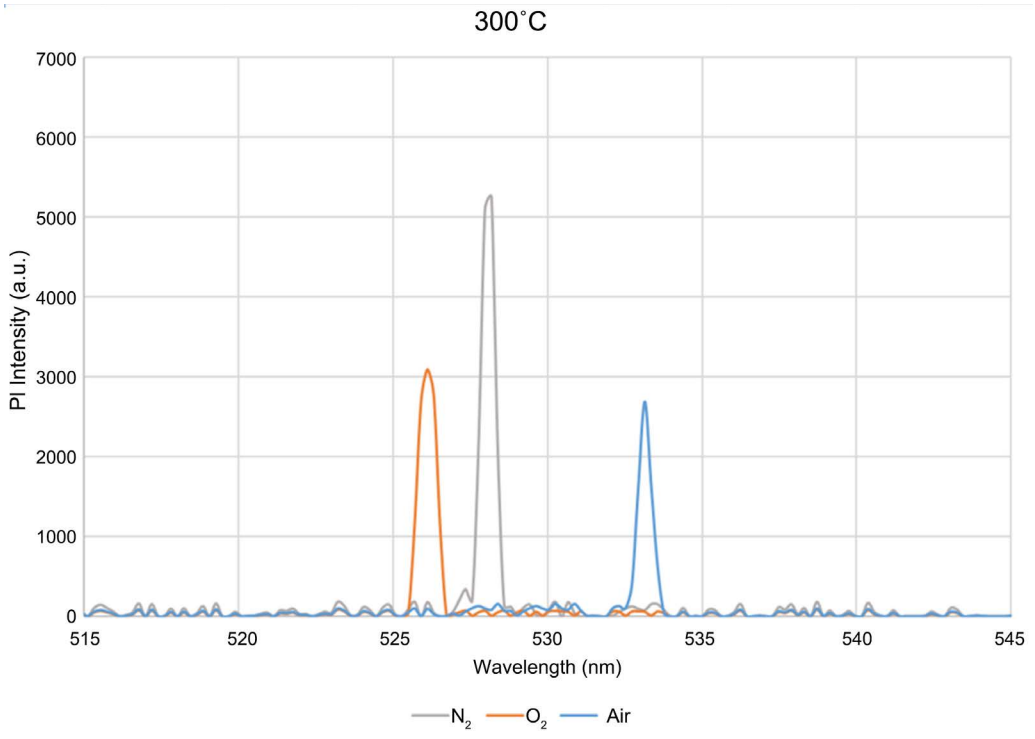

Figure 13. PL Spectra of Cu_2O thin films (annealed at 300˚C).

Using the spectrometer software, the following specs were adjusted: integration time of 400 ms and reference spectrum stored as a background spectrum. The PL peaks results observed are shown in **Table 3**:

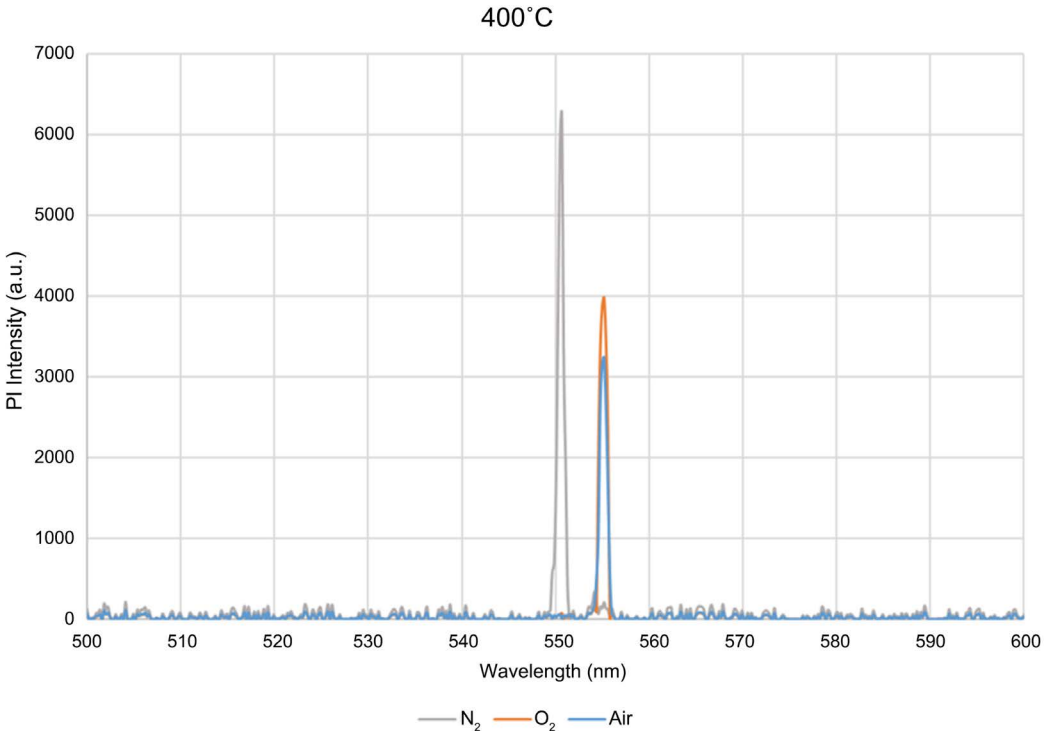

Figure 14. PL Spectra of Cu_2O thin films (annealed at 400˚C).

Table 3. Cu_2O thin films PL peaks.

Temperature	PL Peaks		
	Air	O_2	N_2
Room Temperature		478 nm	
100˚C	488 nm	485 nm	483 nm
200˚C	488 nm	485 nm	488 nm
300˚C	533 nm	526 nm	528 nm
400˚C	555 nm	555 nm	550 nm

The effects of the annealing temperature were noticeable and overall there was shift from a lower spectrum peak (478 nm) for the thin film created in air, to 483 nm at 100˚C and all the way to 550 nm at 400˚C for the film annealed in nitrogen (N_2). If the annealing temperature is increased even higher than 400˚C, an even higher PL peak for the Cu_2O thin films can be achieved, which will transition the output spectrum to upper visible and even infrared. The increase in the annealing temperature induces the formation of a more hard packed structure. The sharper peaks obtained for the thin films annealed at 400˚C indicate a higher uniformity of the composition and strain.

The results are similar with other investigations of similar types of films (300 nm to 700 nm range) [13]. The difference between the three types of films was the following: annealed in air and in oxygen (O_2) produced the lower intensity peaks (orange and blue colors) and the films annealed in nitrogen (N_2) produced

a higher intensity peak (gray color) at almost the same wavelengths. The PL emission peaks are attributed to the recombination of the phonon-assisted excitons in the Cu_2O layer. It corresponds to the transition between ${}^3\Gamma_5^+$ valence band to ${}^2\Gamma_7^+$ conduction band in Cu_2O crystals [14].

Raebiger *et al.* [15] calculations on Cu_2O show that the intrinsically copper-deficient nature is due to formation of copper vacancies (V_{Cu}). These copper vacancies would act as a shallow and efficient hole producer. The Cu_2O is intrinsically p-type because the oxygen vacancies (V_O) which are potential hole destroyers have no transition level in the gap and thus cannot annihilate holes. The other possible hole destroyer copper interstitials (Cu_i) has high formation energy associated with deep transition level and would thus, be incapable to destroy holes efficiently created by V_{Cu} [16].

Photoconductivity and deep level transient spectroscopy studies shows the presence of holes laying between 0.45 eV and 0.55 eV above the top of the valence band. These are due to Cu vacancies and as a result, the PL spectra of Cu_2O films show free excitons and bound excitons in the region between 450 to 650 nm in the visible spectrum [16].

Dolai *et al.* [16] observed PL peaks located at 551 nm (2.25 eV) and 543 nm (2.28 eV). These peaks were assigned to V_{Cu} [16].

4. Conclusion

In this work, the optical properties of the Cu_2O thin films were investigated. The optical bandgap for the Cu_2O thin films was found to be between 2.23 eV and 2.56 eV, which allows for potential applications in photovoltaic solar conversion. The optical bandgap varied as a function of temperature and the gas introduced during the annealing process. The introduction of different gases in the annealing chamber affected the quality and the optical properties of the Cu_2O thin film. The differences between the air and the oxygen (O_2) were minor; however, the largest impact was created by the introduction of the nitrogen (N_2) gas in the annealing process. The annealing temperature had a severe impact on the films as well. The increase in annealing temperature created darker, more opaque films (in the visible spectrum) which shows that by decreasing the optical transmission, the absorption of energy will be increased. The source of this energy can be in the infrared portion of the solar spectrum. For further investigations, an analysis/comparison with copper oxide (CuO) thin films should be explored as well.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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