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Optical Properties of Cu_2O Thin Films Impregnated with Carbon Nanotube (CNT)

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ABSTRACT

This study investigates CNT-doped Cu_2O thin film deposited by spray pyrolysis technique at a substrate temperature of 100^{o}C. The samples were annealed at temperatures of 200^{o}C and 230^{o}C for 30 minutes. The effect of CNT doping on certain optical properties, such as extinction and absorption coefficients, a refractive index of doped Cu_2O thin films were examined. The absorbance of the doped samples increases within the visible range and decreases in the ultraviolet range of the electromagnetic spectrum (EM). Both absorbance and extinction coefficients increased with temperature making the samples a good candidate for use as absorbance layer in device fabrication. In addition, there was an increase in direct bandgap with the increase in CNT concentration of the thin films. The result of the study revealed that CNT doping has a significant effect on the properties of Cu_2O.

Keywords: Bandgap, Carbon-nanotube (CNT), Copper (I) Oxide (Cu_2O), optical characterization, spray pyrolysis

INTRODUCTION

Semiconducting metal oxides are ideal materials in thin-film technology due to the abundance of their onstituent elements in the earth's crust, ease of manufacturing process, and ecologically friendly existence. Copper oxides are strong absorber materials among the various p-types of metal oxides (Farhad et al., 2019; Ruhle et al., 2012). There are two stable copper oxides, namely monoclinic cupric oxide (CuO) or tenorite with a 1.3–1.5 eV energy bandgap (Farhad et

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al., 2019; Chatterjee et al., 2016; Rafea & Roushdy, 2009; Daoudi et al., 2018) and cubic cuprous oxide (Cu_2O) that is a p-type semiconductor with an energy bandgap of 2.0-2.6 eV depending on its method of fabrication and stoichiometry (Farhad et al., 2018; Oluyamo et al., 2014). In photovoltaic research, Cu_2O gets more publicity compared to CuO because of its direct bandgap nature, high absorption coefficient ($\alpha \sim 10^4 cm^{-1}$) in the visible region, higher mobility ($\mu \sim 100\ cm^2/V.s$) and larger minority carrier diffusion length ($Lp \sim 1–2$ μm) relying on deposition parameters (Farhad et al., 2019). Various endeavors have been made to tune its properties for more innovative applications. Therefore, adding suitable dopants into Cu_2O to maintain multifunctionality is a common occurrence by researchers to overcome the two major drawbacks of Cu_2O, i.e., wide energy bandgap ~ 2.2eV and high resistive capacity.

Carbon nanotubes (CNTs) have triggered enormous worldwide interest due to their unique mechanical, electrical, and thermal properties when incorporated into semiconductor materials, which make them conceivably useful in numerous applications in nanotechnology, electronics, optics, and other fields of materials science (Zhu, 2017; Thostenson et al., 2011). Studies have shown that adding CNT to materials may alter carrier concentration and electrical conductivity despite the reduction in carrier mobility, which is comparable to the function of dopants in semiconductors (Yoo et al., 2011).

Various techniques have been applied to prepare Cu_2O this includes high-temperature oxidation of copper, magnetron sputtering, thermal evaporation, pulsed laser deposition (PLD), spin-derived sol-gel coating, chemical bath deposition, electrodeposition, successive ionic layer adsorption and reaction (SILAR), and spray pyrolysis (Farhad et al., 2019; Musa et al., 1998; Figueiredo et al., 2008; Muhibbullah & Ichimura, 2010; Septina et al., 2011; Nair et al., 1999; Mohammed, 2010). In addition, spray pyrolysis has many leading advantages among the other techniques, such as cheap expense, simplicity of experimental operation, and effective controllable deposition settings (Perednis & Gauckler, 2005).

The spray pyrolysis technique consists of directing straight down the precursor solution on top of heated substrates where a thin film of metal oxide is obtained after decomposition and oxidation phenomena (Perednis & Gauckler, 2005).

In this research work, Cu_2O was doped with various concentrations of Carbon nanotubes (CNTs) from 10% to 40% with respect to volume.

MATERIALS AND METHODS

Materials

Cupric acetate, 1- Methyl 2- Pyrrolidinone, and short single-wall CNT of purities 98%, 99.5%, and 92% respectively were the reagents used. In contrast, microscopy glass slides were used, while microscopy glass slides were used as a substrate for the deposition of the thin films.

Substrate Cleaning Process

The substrates were washed with liquid soap, distilled water, and acetone to eliminate noticeable dust. The substrate was dried for 20 minutes at a temperature of 40°C using a hand dryer.

Preparation of Precursor Solutions

0.15 M of precursor solution was prepared by adding 1.9965 g of Copper (II) acetate (Cu $(CH3COO)_2$. H_2O) in distilled water (20 ml) plus N-Methyl-2-pyrrolidone (NMP) (80 ml) stirred vigorously at room temperature using a magnetic stirrer.

For dispersion, 0.2 g of CNT were added to 80 ml of N-Methyl-2-pyrrolidone (NMP) and sonicated for 12 hours to form a dispersive black solution.

Thin-film Deposition

The substrate temperature for the deposition of all the samples was maintained at 100°C. In contrast, the distance between the spray head and the substrates, precursor flow rate, air pressure were maintained at 10 cm, 500 liter/hr, and 0.05 MPa, respectively. The films were annealed at 200°C and 230°C for 30 minutes. Optical measurements were obtained using a UV-visible spectrophotometer (UV-1601, Shimadzu Corp, Japan) (Nath et al., 2015). The absorption coefficient α was calculated from the transmission spectra using Equation 1.

$$\alpha = -\frac{2.303A}{t} \qquad [1]$$

where, A is the absorbance and *t* is the thickness of the film.

According to (Nath et al., 2015), the corresponding bandgap was determined using Equation 2

$$(\alpha hv)^2 = hv - Eg \qquad [2]$$

where h is Planck's constant, e.g., is the bandgap energy, and v is the frequency of the incident light.

The coefficient of extinction was also obtained with Equation 3

$$k = \frac{\alpha\lambda}{4\pi} \qquad [3]$$

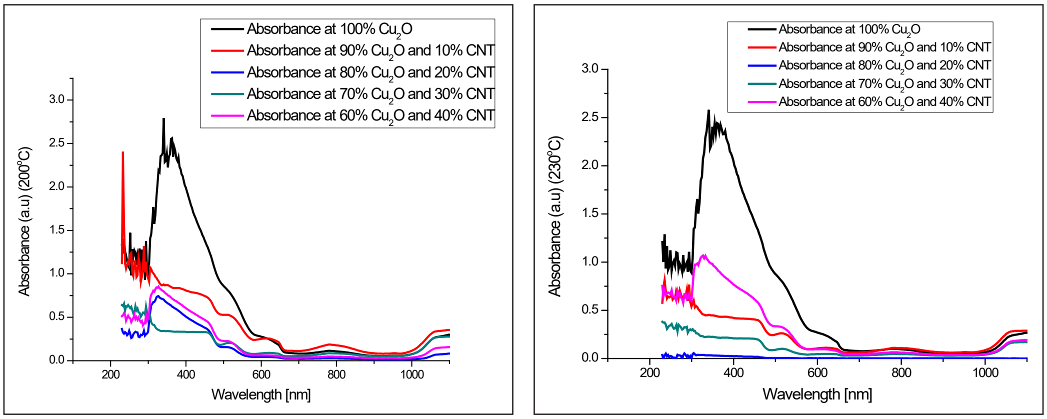
A thin-film material's reflectance (R), transmittance (T), and absorbance (A) are connected by using Equation 4:

$$R = 1 - (Te^A)^2 \qquad [4]$$

RESULTS AND DISCUSSION

Figure 1 shows the variation in absorbance at 200°C and 230°C. The absorbance of the doped sample increases within the visible range of the EM spectrum. As the concentration of CNT increases, the absorption peaks were found to decrease within the visible region (Figure 1). It might be attributed to the absorption of photons by CNT in the doped films. The optical properties in the range of 300 nm to 1100 nm at 230°C prove that absorbance is highly dependent on temperature levels. It is in agreement with (Varughese et al., 2014; Siddiqui et al., 2014).

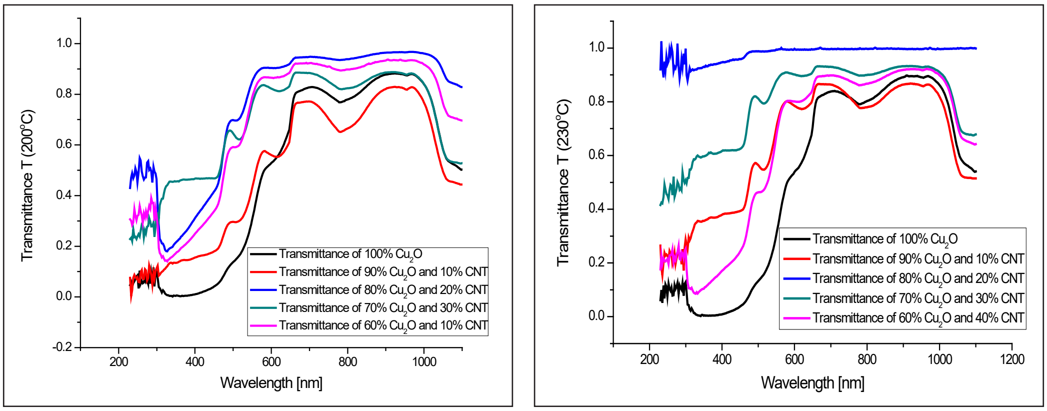
Figure 2 shows the transmittance spectra with a wavelength of the Cu_2O thin films annealed at 200°C and 230°C. All the films displayed high transmittance within the 600–1000 nm wavelength region. On the other hand, CNT-doped Cu_2O thin films have lower



(a)

(b)

Figure 1. Absorbance spectra of CNT doped Cu_2O thin films at (a) 200°C and (b) 230°C for various doping concentrations



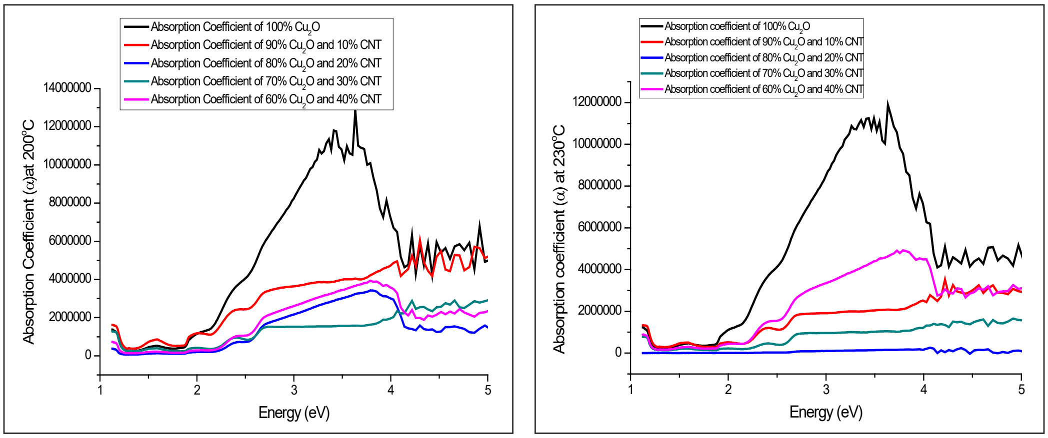
(a)

(b)

Figure 2. Transmittance spectra of CNT doped Cu_2O thin films at (a) 200°C and (b) 230°C for various doping concentrations

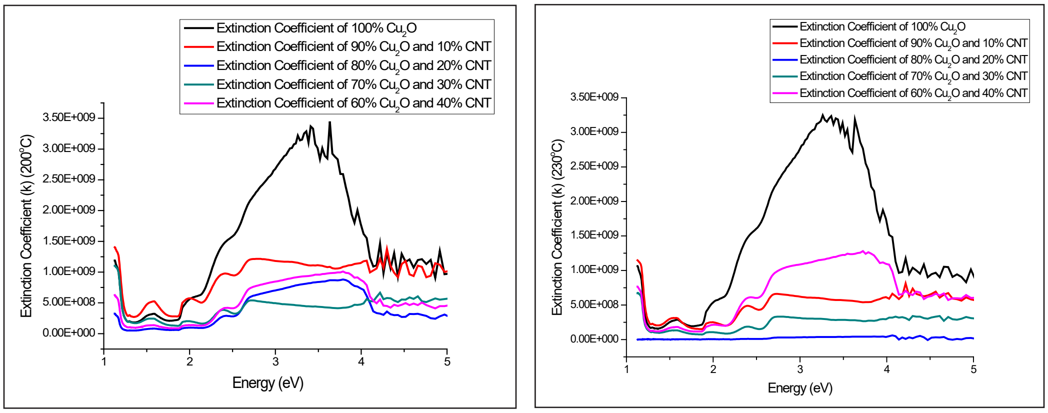
transmittance within the 200–500nm wavelength range. The increase in transmittance might be due to enhancing scattering of photons owing to an increase in the grain size of Cu_2O (Mardare & Rusu, 2002; Zhang et al. 2013a; Zhang et al. 2013b). It is important to note that 20% CNT has the maximum transmittance than any other sample for annealed temperatures. The average transmittance in the visible region was found to be greater than 65%.

Figures 3 and 4 show the variation of absorption coefficient and extinction coefficient with energy for the Cu_2O doped CNT thin films. Both absorption and extinction coefficient increase as the energy increases. The absorption coefficient values were found to be higher than $10^4 cm^{-1}$, which results in an increase in the probability of occurrence of direct



(a) (b)

Figure 3. Absorption coefficient against the energy of CNT doped Cu_2O thin films at (a) 200°C and (b) 230°C for various doping concentrations



(a) (b)

Figure 4. Extinction coefficient against the energy of CNT doped Cu_2O thin films at (a) 200°C and (b) 230°C for various doping concentrations

transition. Furthermore, materials with high absorption coefficients are known to absorb photons, which excite them into conduction bands readily. Hence the thin film could serve as a good absorbance layer in device fabrication. The direct bandgap value for pure deposited Cu_2O was found to be 2.53 eV, while the CNT doped thin films have values of 1.80, 2.17, 2.18, and 2.27 eV for the samples containing 10%, 20%, 30%, and 40% CNT annealed at 200^oC. For film samples annealed at 230^oC the bandgap values were 1.68, 2.09, 2.13 and 2.17 eV for 10%, 20%, 30% and 40% CNT concentration. The reduction in the value of the bandgap of the samples annealed at 230^OC could be attributed to a reduction of trap ions and an increase in grain size, as earlier stated. The increase in bandgap as CNT percentage increase has attributed this phenomenon to the rich CNT content in the films, which is probably associated with the structural change in Cu_2O induced by CNT doping (Nakano et al. 2009; Zhang et al. 2013a; Zhang et al. 2013b).

CONCLUSION

In this study, CNT-impregnated Cu_2O thin films were deposited on a glass substrate using the spray pyrolysis technique at a substrate temperature of 100^oC. The absorbance of the CNT doped Cu_2O samples increased within the visible range and decreased in the ultraviolet range of the electromagnetic spectrum. The absorption and extinction coefficient was found to increase with increases in energy, making the samples a good candidate as absorbance layer in device fabrication. The average transmittance in the visible region is greater than 65%. The maximum value of the transmittance was 70%, while absorption increases in the wavelength range 300–600 nm, and an increase in some optical constants makes it useful in solar cells application. The bandgap of CNT impregnated Cu_2O thin films was observed to range between 1.80–2.38 eV for samples annealed at 200^oC and 1.68–2.17 eV for samples annealed at 230^oC.

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