Sudan University of Science and Technology
College of Graduate Studies

Preparing and Study of Optical Properties of Nano Copper Oxide (CuO) by Sol-Gel Method

تحضير ودراسة الخصائص البصرية لأكسيد النحاس النانوي بإستخدام طريقة التكوين الجلاتيني

A Thesis submitted in partial for requirement of the Degree of Master in physics (solid state)

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بسم الله الرحمن الرحيم

VERSE

قال تعالي:

⁽⁽قَالُوا سُبْحَانَكَ لَا عِلْمَ لَنَا إِلَّا مَا عَلَّمْتَنَا إِنَّكَ أَنْتَ الْعَلِيمُ الْحَكِيمُ (32)
قَالَ يَا آدَمُ أَنْبِئْهُمْ بِأَسْمَائِهِمْ فَلَمَّا أَنْبَأَهُمْ بِأَسْمَائِهِمْ قَالَ أَلَمْ أَقُلْ لَكُمْ إِنِّي أَعْلَمُ
غَيْبَ السَّمَوَاتِ وَالْأَرْضِ وَأَعْلَمُ مَا تُبْدُونَ وَمَا كُنْتُمْ تَكْتُمُونَ (33)⁾⁾

صدق الله العظيم

سورة البقرة الأيات(32-33)

DEDICATION

To the Jasmines bouquet whose fragrance spreads all over everywhere…

My mother….

To the courageous strong man who took the trouble and suffering for me ….

My father…

To the most beloved …..

My Brothers and sisters….

To those who took our hands down the path of knowledge as life role models…

Our Glorious Teachers….

To those who are even more pure and true than all of us ….

The Martyrs of the Glorious…

December 2018 Revolution….

For Sudan: one flag, one land, one heart, one land, one nation evermore….

Those who sleep under the sun and the bitter cold...**the Displace...**

The friend of exile…….

To the one who I could never describe him…my soul mate….

Khalid Dahawi…

To the beloved who is my trouble…….

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In the first and last place an infinite gratitude goes to his Almighty Al-Moniem, his majesty (**Allah**)…

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Abstract

This study is focused on the optical properties of p-type semiconductor Nano copper oxide (CuO) prepared by Sol-gel method. The optical characteristics have been investigated by UV/V_{is} spectrophotometer in the wavelength range (200 – 900) nm. The Nano copper oxide exhibits high absorbance values atultraviolet region which they decrease rapidly in the visible/ near infrared region .The Nano copper oxide have a direct allow electronic transition with optical energy (Eg) values increased from (2.271) eV to (2.416) eV for allowed energy gap. The maximum value of the refractive index (n) for all Nano copper oxides are given about 2.15.

الخلاصة

ركزت هذة الدراسة علي الخصائص البصرية لأكسيد النحاس النانوي شبة الموصل من النوع الموجب بإستخدام طريقة التكوين الجلاتيني (الهلامي)، تم فحص الخصائص البصرية بواسطة مقياس الطيف الضوئي فوق البنفسجي في مدي الطول الموجي (200-900) نانومتر، واظهرت النتائج امتصاصية عالية في المنطقة فوق البنفسجية وبعدها تتناقص في المنطقة المرئية والقريبة من المنطقة تحت الحمراء. يمتلك اكسيد النحاس النانوي إنتقال الكتروني مباشر مع زيادة قيم الطاقة الضوئية من (2.271)الكترون فولت الي (2.416) الكترون فولت لفجوة الطاقة المسموح بها، والقيمة القصوي لمعامل الانكسار لجميع أكاسيد النحاس النانوية حوالي (2.15).

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Chapter one

Introduction

1.1 Preface

Thin film is a layer of material having thickness of the order of few nanometers in the past couple of decades, a large amount of research is carried out on semiconducting thin films for various device applications. A good amount of literature is available on the preparation and characterization of semiconductor materials the development of semiconductor thin films is one of the key technologies for pn-junction based devices such as diode, transistors, and light emitting diodes. Copper oxide (CuO) has unique features such as low cost, non-toxicity, the abundant availability of copper, high efficiency and relatively simple formation of the oxide layer, etc.

Copper oxides materials are known to be p-type semiconductors in general and hence potentially useful for constructing junction devices such as p-n junction diodes a part from the semiconductor applications, these materials have been employed as heterogeneous catalysts for several environmental processes solid state gas sensor heterocontacts and microwave dielectric materials ,their use in power sources has received special attention. Thus, in addition to photovoltaic devices one of the important advantages of using CuO in device applications is that it is non-toxic and its constituents are available in abundance Because the chemical and physical properties of CuO are strictly dependent of its size and morphology thin films of copper oxide have been prepared by a number of techniques including spray pyrolysis, sol–gel synthesis and electro deposition, sol-gel synthesis ,chemical vapor deposition pulsed laser deposition and electro deposition.

In this study CuO thin films prepared by a spray pyrolysis technique , which is a well-known nanostructured thin film preparation method with excellent features such as the need for no sophisticated equipment, and quality targets or substrates, as well as film thickness and stoichiometry are easy to control and the resulting films are well compacted .

Copper oxide was one of the oldest and first semiconductor material that discovered and characterized, but then was overtaken by the fast development of silicon, Copper oxide thin films could be used for several applications in catalyst, semiconductor, solar cells and electronics. It has direct optical band gap energy in the range of (2.271 - 2.416) eV. The transparent conductive copper oxide thin films had been developed by several techniques such as electrodeposition, thermal evaporation, sol-gel technique, and wet chemical method, which could be deposited on various substrates, However, the common technique used is sol-gel method due to its simplicity, lower cost, reproducibility, ease of composition control and large area deposition, In addition, sol gel method also easily to deposit on different type of substrates that could be performed under no vacuum environment.

Therefore in this research sol-gel method was used to form the solution of copper oxide which then deposited on quartz substrates using spin coating technique. The main goal of this paper is to study the effects of different spin coating speeds on the electrical and optical properties of the copper oxide thin films on quartz substrates. In this work, the samples were characterized using UV-Vis spectrophotometer and two-point probe method for the optical and electrical properties respectively.

However, sputtering is known to provide thin films that are highly uniform physically for use in semiconductor development and many research fields. It is simple to deposit thin films with a controllable thickness by changing the deposition time and with a controllable crystalline phase by changing the deposition atmosphere and temperature [1, 2, 3, 4, and 5].

1.2 Research Problem

The organic/inorganic composite materials consisting of polymers doped with metal or semiconductor thin film such as CuO, are quite interesting and play important role in the technological industries. Exploring their crystal structure along with the optical properties provide valuable information.

1.3 Aim of the Research

1. Prepare a layer of copper oxide in thin film.
2. Study of optical properties of copper oxide.

1.4 Importance of Research

This research is conducted to assess the literature review on CuO thin films. The optical properties are of the greatest importance, therefore, the study enriches the CuO thin films technologies, such as photovoltaic cells and solar energy conversion systems.

1.5 Thesis Layout

The thesis consists of the four chapters, chapter one is the introduction. Chapter two is Literature review. Chapter three is concerned method and materials. Chapter four is devoted results, analysis, reference, discussion beside conclusion and recommendations.

Chapter Two

Literature Review

2.1 Introduction

There are many studies carried out by scientists in this area in order to identify some of the results you get and review the results and a summary of their results.

2.2 Study of optical properties of copper oxide (CuO) thin film prepare by SPD technique. Shymaa K. Hessian.

This study is focused on the optical properties of thin films of p-type semiconductor CuO prepared by spray pyrolysis deposition technique (SPD). This film is grown at 350°C on glass substrate. The optical properties are considered because of its application as photovoltaic cells and solar energy conversion. These properties are evaluated from UVVIS spectra. The results are shown high absorbance at UV region, which decreases rapidly in VIS-IR region whereas they show direct transition energy gap of 2.094 Eve.

CuO thin film was deposited on to glass substrate at temperature (350°C), has been prepared using SPD technique with a solution of $CuCl_2.2H_2O$. The film exhibits high absorbance values at ultraviolet region which they decrease rapidly in the visible/ near infrared region, the film shows a direct transition which was (2.094) eV for allowed energy gap. The film has high values of absorption coefficient ($\alpha \geq 10^4$ cm^{-1}). The spray pyrolysis method for the production of thin solid films is a good method for the preparation of thin films which are suitable for scientific studies and for many applications in technology and industry, equally [1].

2.3 Preparing of Copper Oxides Thin Films by Chemical Bath Deposition (CBD) for Using in Environmental Application.

NASSER. Saadaldin, Alsloum M.N, Hussain N

Thin films of copper oxide were prepared by chemical bath deposition (CBD) method on substrates of glasses by Alternate immersions method (AI) at room temperature for 20 second using heated liquid of sodium hydroxide up to $70c^0$. and copper thiosulfate complex. The substrates were annealed at different temperatures $(200\text{-}300\text{-}400)c^0$ in the air; the crystalline structure of prepared samples was studied by using XRD and (SEM) technologies. The results were indicated to; the crystalline structure of prepared films was related to temperature of annealing of copper-oxide (Tenorite), cubic of CuO (Cuprite). Optical studies showed that the prohibited rang between (1.3-2.4)ev was related to annealing temperature (monoclinic). Therefore, application of solar cells is very promising as a suitable material for conversion of photovoltaic energy with high absorbency solar and low thermal issue. Real and imaginary dielectric constants were calculated ($\varepsilon_1$and ε_2). Significant improvement in structure as a follower of annealing temperature required by oxide layer, SEM image showed that porous structure were distinctive materials for the manufacture of gas sensors.

Perfect thin films of copper oxide material were prepared by using copper sulphate and solution of sodium sulphate with sodium hydroxide as the X-ray measure showed at perfect preparing conditions for a high degree of uniformity and adhesion on the substrate. The permitted and prohibited electronic transitions were directly.

Increase value the real dielectric constant of the material leads to increase susceptibility of the material of polarization Porous structure images of samples were shown by using morphology study by electron microscope (SEM). Furthermore, the control on crystalline grains size and blanks was by changing of temperature, thus, use efficiently copper oxide for sensors gas industry [2].

2.4 Electrical and Optical Properties of Copper Oxide Thin Films by Sol-Gel Technique. H. Hashim, S. S. Shariffudin, P. S. M. Saad and H. A. M. Ridah

Copper oxide were prepared by sol-gel technique and deposited onto quartz substrates as thin films using spin coating method. The aim of this research was to study the effects of different spin coating speeds of copper oxide thin films on the electrical and optical properties of the thin films. Five samples of copper oxide thin films with different spin coating speeds of 1000, 1500, 2000, 2500 and 3000 rpm were annealed at 600°C for 30 minutes. UV Vis spectrophotometer and two-point probe technique were used to characterize the optical and electrical properties of the deposited films. Based on the results obtained, it revealed that the electrical conductivity of the copper oxide thin films reduce as the spin coating speeds increase. The calculated optical band gap and the resistivity of the copper oxide thin films also, Copper oxide thin films were deposited on quartz substrates by spin coating technique. The thicknesses of thin films, surface topology, optical and electrical properties were investigated. In this work, the goal has been achieved to study the effects of varying the spin coating speeds of copper oxide thin films. From the results obtained, copper oxide thin film that deposited at 1000 rpm shows the highest thickness and the lowest of surface roughness. At 1000 rpm of spinning rate also shows the highest of transparency. However, at copper oxide thin film that deposited at 3000 rpm shows the lowest optical band gap. Besides, it was found that at 1000 rpm of spinning rate shows the best of electrical conductivity. Future investigation should be done on the crystallinity of the thin film by using XRD. Besides that, the investigation on the electrical and optical properties of the copper oxide thin films could be performed using doping technique [3].

2.5 Optical and structural properties of nanostructured copper oxide thin films as solar selective coating prepared by spray pyrolysis method, M. ASADI,

Copper (II) oxide thin films were prepared by spray pyrolysis method on soda- lime glass substrates using copper acetate precursor solution. Influence of substrate temperature on structural and optical properties was investigated. Structural analysis of these layers were carried out by X-ray diffraction (XRD). Single phase nature and high crystallinity of CuO nanostructures were observed on XRD patterns. The general appearance of the films was uniform and black in color. FT-IR transmittance spectra confirmed the results from the XRD study. Selective solar absorber coatings of copper oxide (CuO) on stainless steel substrates was prepared by spray pyrolysis method. Effect of deposition temperature on optical properties of thin films was investigated. Optical parameters, absorbance (α) and emittance were evaluated from reflectance data. It can be deduced that the porous structure, such as a light traps, can greatly enhance absorbance, while the composition, thickness and roughness of thin films can greatly influence the emissivity. Single phase nature and high crystallinity of CuO nanostructures were observed by XRD patterns. Solar absorbance of thin films were in the range of (85 - 92) %.

Single-phase CuO thin films with monoclinic structure were produced from precursor solutions prepared by dissolving copper acetate in water and ethanol followed by spray pyrolysis on glass and stainless steel substrates. Optical band gap of the thin films, measured by using an UV-Vis scanning spectrophotometer was about 1.7 eV. As a result, the thin films showed absorption in the visible region. For thin films prepared on stainless steel substrates, selectivity of the films was affected by variation of substrate temperature. The best selectivity was achieved for the sample prepared at $400c^0$ substrate temperature [4].

2-6 Dielectric and optical properties for (Poly vinyl alcohol-Carboxymethyl Cellulose –Copper Oxide) Nano composites and their Applications. Raheem G. Kadhim, Majeed A. Habeeb and Qayssar M. Jebur

Nano composites are new materials important for several applications as humidity sensors, antibacterial etc. So, to fabricate a humidity sensor as application will make perpetration anew kind of (Poly vinyl alcohol - Carboxymethyl Cellulose –Copper Oxide) Nano composites with different concentrations to test it's for this purpose. From the results we note that the dielectric constant, dielectric loss and AC. Electrical conductivity of (PVA-CMC) blend increase with the increasing of the copper oxide nanoparticles concentrations at 100HZ. Whereas dielectric constant and dielectric loss decrease with increased frequency but AC. Electrical conductivity increases with increased frequency. The optical measurements are showed the absorbance of (PVA-CMC-Copper Oxide) Nano composites is increased with increase of the concentrations of copper oxide nanoparticles. The indirect energy gap (Eg) of (PVA-CMC) blend decreases with the increase of the concentrations of copper oxide nanoparticles. All the optical constants as absorption coefficient, extinction coefficient, and refractive index, real and imaginary dielectric constants of Nano composites are variation with the increase of the weight percentages of copper oxide nanoparticles. Surface resistance of (PVA-CMC-Copper Oxide) Nano composites variation with increase relative humidity. Volumetric electrical conductivity of (PVA-CMC-CuO) Nano composites increases with increasing the temperature and concentration of copper oxide nanoparticles. Activation energy of (PVA-CMC-CuO) Nano composites decreases with increases concentration of copper oxide nanoparticles.

The transition electronic of (PVA-CMC-CuO) Nano composites was indirect. Because of the absorption coefficient of less than (10^4). Each of (extinction coefficient, refractive index, real and imaginary part) increases with increase weight percentage of copper oxide nanoparticles for (PVA-CMC-CuO) Nano composites. With higher photon energy, optical conductivity for (PVA-CMC-CuO) Nano composites is increased and decrease with low photon energy. For humidity sensor application, surface resistance for (PVA-CMC-CuO) Nano composites decrease with increase copper oxide nanoparticles. Surface resistance for (PVA-CMC-CuO) Nano composites decrease with increase relative humidity (RH%) [5].

2.7 Copper Oxide Nanomaterial's Prepared by Solution Methods, Some Properties, and Potential Applications: Thi Ha Tran and Viet Tuyen

Cupric oxide (CuO), having a narrow band gap of (1.2)ev and a variety of chemophysical properties, is recently attractive in many fields such as energy conversion, optoelectronic devices, and catalyst. Compared with bulk material, the advanced properties of CuO nanostructures have been demonstrated; however, the fact that these materials cannot yet be produced in large scale is an obstacle to realize the potential applications of this material. In this respect, chemical methods seem to be efficient synthesis processes which yield not only large quantities but also high quality and advanced material properties. In this paper, the effect of some general factors on the morphology and properties of CuO nanomaterial's prepared by solution methods will be overviewed. In terms of advanced nanostructure synthesis, microwave method in which copper hydroxide nanostructures are produced in the precursor solution and sequentially transformed by microwave into CuO may be considered as a promising method to explore in the near future. This method produces not only large quantities of Nano products in a short reaction time of several minutes, but also high quality materials with advanced properties.

In conclusion, CuO nanostructures have been widely studied and are receiving more and more attention from material scientists and engineers recently because of their interesting properties and potential applications in various fields. In this study, we make a summary on the influences of different factors of synthesis process, some unique properties, and some promising applications of CuO nanostructures. We focus on the some chemical synthetic strategies along with associated influence of basic factors of synthesizing process for CuO nanostructures, as well as their interesting fundamental properties, and interesting applications. Understanding the synthesizing process as well as the characteristics of CuO nanostructures is fundamental for further purposes to realize application of CuO nanostructures in daily life and technology. Some unique properties of CuO nanostructures which make CuO different from other transition metal oxides were also summarized and highlighted. Some potential applications based on CuO nanostructures are also presented.

Although encouraging developments and fascinating achievements in CuO nanostructures have been obtained as overviewed in this paper, better understanding for controlling morphology, structures, and properties of cupric oxide nanostructures and finding ways to take advantages of these interesting properties of such nanostructures still require much effort from scientists but also bring in opportunities for further development [6].

2.8 Growth and Characterization of Cu2O for Solar Cells Applications. A. Ait hssi' , L. Atourki, K. Abouabassi, A. Elfanaoui, K. Bouabid, A. Ihlal,S. Benmokhtar and M. Ouafi

In this work, we investigated the effect of the deposition potential on the morphological, structural, and optical properties of Cu_2O thin films prepared on FTO-coated glass substrates. The potentials of the electrodeposition are -0.3V, 0.4V, -0.5V. The deposition potentials were optimized by cyclic voltammetry experiment for a slow scan rate of 20mV/s. It has been found that the potential of electrodeposition has a significant influence on the Cu_2O thin films. X-ray diffraction revealed that all thin films are crystallized in cubic phase for all potential with a preferential orientation. Scanning electron microscope (SEM) images explored significant variation on morphology of Cu_2O thin films deposited with different applied potential. Transmittance in the visible range was found to be (60 – 80) % for all samples. The energy gap of Cu_2O films was found to be ~ (2-2.3) eV by optical measurements. In this work, we investigated the morphology, structural, optical properties of the Cu_2O thin films deposited by electrodeposition technique at various applied potential. It is found that potential played an important role in orientation and morphology of Cu_2O structure. XRD measurement shows pure Cu_2O films are obtained at (-0.3 to -0.5) v potentials with preferential growth is the (111) direction. SEM images shows that the morphology of the Cu_2O is changed from granular to cubic by increasing of applied potential. All the films exhibit high transmittance (60 – 80) % in visible region from (500 to 800) nm. Optical band gap of the films is found to be in the range of (2.10 - 2.30) eV, which is match well with the optimum for photovoltaic solar conversion [7].

2.9 Investigations of Cuprous Oxide and Cupric Oxide Thin Films by Controlling the Deposition Atmosphere in the Reactive Sputtering Method. Jinyan Pan, Chengfu Yang, and Yunlong Gao

Cu_2O is a direct and narrow band-gap material; hence, it serves as an important candidate material for applications such as solar cells. In this study, copper (Cu) metal was used as a target and the reactive sputtering method was used to deposit cuprous oxide (Cu_2O) and cupric oxide (CuO) thin films on indium tin oxide (ITO) glass. The formation of Cu_2O and CuO thin films was controlled by varying oxidation conditions, such as controlling the deposition atmosphere (called the O_2 ratio). The microstructure, crystalline orientation, and optical properties of Cu_2O and CuO thin films were measured using X-ray diffraction and optical spectroscopy, respectively. The results for the deposited thin films indicated that the formation of thin films as Cu_2O and CuO phases was controlled by the flow rate of oxygen during the deposition process. In addition, the $(\alpha h v)^n - hv$ curve plot was used to find the optical energy band gap of the Cu_2O and CuO thin films. Moreover, we found that the crystalline phase and morphology of the deposited thin films affected the properties of the spectral response. This study provides a reference for the possible exploration and application of new, high-performance thin-film photovoltaic solar cells.

Using magnetron sputtering, CuO and Cu_2O were prepared and the phase and regulation of the optical band gap of the deposited thin films were evaluated. When Cu metal was used as the target, the oxygen flux rate controlled the crystalline phase of the deposited thin films. When the gas flux ratio of O_2 and Ar was 1:16, Cu_2O thin films were formed, while a gas flux ratio of O_2 and Ar of 1:2 produced CuO thin films. By optimizing deposition parameters, optical absorption properties of cupric oxide and cuprous oxide thin films were enhanced. The morphologies of the deposited thin films were influenced by heat treatment, and the grain sizes of Cu_2O thin films increased while the grain boundaries blurred. The Cu_2O thin films prepared had a critical absorption edge at a wavelength of around (400) nm and a suitable absorption in the wavelength range of (400–570) nm, while the CuO thin films showed a good absorption spectrum in the region of(500–900) nm and had a large absorption at wavelengths in the near-IR range. From the UV visible light absorption spectra of Cu_2O and CuO thin films, the measured optical band gaps were (2.4 and 1.9) eV, respectively. By modulating the parameters for preparation, the optical band gap of the deposited thin films could be adjusted to enhance different optical properties of the copper oxides [8].

2.10 Structural and Optical Absorption Analysis of CuO Nanoparticles. Asha Radhakrishnan, B. Baskaran Beena

Nanostructured materials have wide range of applications due to their interesting size-dependent chemical and physical properties compared to particles of size in the range of micrometer. Copper oxide Nano materials are of interest on account of their potential uses in many technological fields. In this study CuO nanoparticles were synthesized via simple sol gel method using basic CuSO4 as wet chemically synthesized precursor and NaOH as stabilizing agent. Samples were characterized by X-ray diffraction (XRD), infrared spectrum (IR), scanning electron microscope (SEM), transmission electron microscopy (TEM) and UV-visible spectrum. Using this method CuO nanoparticle could be synthesized without using organic solvent, expensive raw materials and complicated equipments. Besides simplicity, the advantage of produsing nanoparticles by this method are that it is easeful, flexible, fast, cost effective, and pollution free .The CuO nanoparticles prepared in the present study is crystalline and particle size determined using XRD is (19)nm. SEM images shows a homogeneous distribution of spherical CuO nanoparticles. From Optical absorption analysis the direct band gap is higher as compared to indirect band gap which also reveals that the obtained nano CuO is crystalline in nature. The CuO nanoparticles obtained have relatively large band gap due to its small size which results in Quantum confinement effect. Therefore this nanomaterial could be used as a wide band gap semiconductor [9].

2.11 Chemically deposited copper oxide thin films: structural, optical and electrical characteristics M.T.S. Nair, Laura Guerrero, Olga L. Arenas, P.K. Nair

in films of copper oxide with thickness ranging from (0.05–0.45) mm were deposited on microscope glass slides by successively dipping them for (20) s each in a solution of 1 M NaOH and then in a solution of copper complex. Temperature of the NaOH solution was varied from (50–908)C^0, while that of the copper solution was maintained at room temperature. X-ray diffraction patterns showed that the films, as prepared, are of cuprite structure with composition Cu_2O. Annealing the films in air at 350C^0 converts these films to CuO. This conversion is accompanied by a shift in the optical band gap from 2.1 eV (direct). To 1.75 eV (direct). The films show p-type conductivity, $5 \times 10^{-4} \Omega^{-1} cm^{-1}$ for a film of thickness 0.15 mm. Electrical conductivity of this film increases by a factor of 3 when illuminated with $(1\ kwm^{-1})$ tungsten halogen radiation. Annealing in a nitrogen atmosphere at temperatures up to 400C^0 does not change the composition of the films. However, the conductivity in the dark as well as the photoconductivity of the film increases by an order of magnitude. The electrical conductivity of the CuO thin films produced by air annealing at 400C^0, is high $7 \times 10^{-3} \Omega^{-1} cm^{-1}$ these films are also photoconductive.

In this work we reported the deposition and properties of copper oxide thin films prepared by the successive immersion of glass substrates in solutions of NaOH (50–90)^{0}C. And of a copper complex (25)^{0}C. Even though the Cu–Cu_2O is a classic example of the cheapest of Schottky diodes possible and hence created initial interest in its photovoltaic applications, a 1979 study has led to the conclusion that the prospects of such devices are limited. Application of Cu2O film as an electro chromic material is a possibility. Another use for the Cu2O films produced by the present technique may be as a substrate layer for semiconductor thin films deposited by chemical bath deposition technique, primarily to improve adhesion of the second layer to glass substrates. Migration of copper ions during post deposition thermal processing of such films, in oxidizing, reducing or inert atmosphere may lead to interesting properties of the films. Such expectations arise from previous results on the metal sulfide to metal oxide conversion, diffusion of metal into chemically deposited films, as well as formation of new ternary compounds, during post deposition processing of multilayer films [10].

2.12 Optical Analysis of Chemical bath Fabricated Cuo Thin Films Ezenwa I.A. Department of Industrial Physics, Anambra State University Uli, NIGERIA

Copper oxide CuO thin films were deposited on glass substrates using chemical bath deposition technique. The films' growth was based on the decomposition of cupric sulphate in the presence of sodium hydroxide with EDTA disodium salt (CH_2N (CH_2COOH) CH2COONa) $_2 2H_2O$) acting as complexing agent. Optical and morphological investigations were also performed. The films were found to have strong absorption of approximately 0.87 at wavelength range of 300-320nm. The optical absorbance generally reduced with increase in wavelength. The optical band gap of the deposited film was found to be 1.7eV.

The fabrications of CuO thin film with band gap of 1.7 have been successfully carried out using chemical bath deposition technique at 300K. The films were found to have strong absorption of approximately 0.87 at wavelength range of 300-320nm and depreciates as the wavelength increased. Generally all the samples have approximately 80% transmittance throughout the VIS/NIR regions and an average reflectance of 20% in the range of (300-320) nm. The optical micrographs of the CuO show high density of grains and uniformity in the distribution of the grains, the grains are small and regular [10].

2.13 Effect of post-annealing on the properties of copper oxide thin films obtained from the oxidation of evaporated metallic copper. V. Figueiredo a, E. Elangovan a, G. Gonc¸alves a, P. Barquinha a, L. Pereira a, N. Franco b, E. Alves b, R. Martins a, E. Fortunato.

Thin films of copper oxide were obtained through thermal oxidation (100-450) ^{0}C of evaporated metallic copper (Cu) films on glass substrates. The X-ray diffraction (XRD) studies confirmed the cubic Cu phase of the as-deposited films. The films annealed at 100^{0}C showed mixed Cu–Cu_2O phase, whereas those annealed between (200–300)^{0}C showed a single cubic Cu_2O phase. A single monoclinic CuO phase was obtained from the films annealed between (350-450) ^{0}C. The positive sign of the Hall coefficient confirmed the p-type conductivity in the films with Cu2O phase. However, a relatively poor crystallinity of these films limited the p-type characteristics. The films with Cu and CuO phases show n-type conductivity. The surface of the as-deposited is smooth (RMS roughness of (1.47) nm and comprised of uniformly distributed grains (AFM and SEM analysis). The post-annealing is found to be effective on the distribution of grains and their sizes. The poor transmittance of the as-deposited films

(<1%) is increased to a maximum of 80% (800 nm) on annealing at 200^0C. The direct allowed band gap is varied between (2.03-3.02) eV.

Thin films of copper oxide were obtained through oxidization of the metallic Cu films deposited on glass substrates by e-beam evaporation. It is demonstrated that the cubic Cu phase of the as deposited films changes into single cubic Cu2O phase for the annealing between $(200\ -300)^0$C and whereas the films annealed between $(350\text{-}450)^0$C show a single monoclinic CuO phase. The films with dominating Cu2O phase are p-type conducting, but however, a relatively poor crystallinity of these films limited the p-type characteristics. The films with Cu and CuO phases show n-type conductivity. The surface of the as deposited films is smooth (RMS roughness of 1.47 nm) and is comprised of uniformly distributed grains. The post-annealing is found to be effective on the distribution of grains and their sizes. The poor transmittance of the as-deposited films (<1%) is increased to a maximum of 80% (800 nm) on annealing at 200^0C. The direct allowed band gap is varied between (2.03 to 3.02) eV. The p-type characteristics need to be improved to make these films useful for applications like transparent p–n junction based devices [12].

2.14 Characterization of Cu_2O thin films prepared by evaporation of CuO powder V a Gevorkyan, A E Reymers, M N Nersesyan and M A Arzakantsyan

Among the potential photovoltaic devices based on semiconductor oxides as active layer is cuprous oxide (Cu_2O). This oxide semiconductor shows many attractive characteristics useful for solar cells production such as low cost, nontoxicity, high mobility and diffusion length of minority carriers, high absorption coefficient and direct energy gap. In this work we report our results of optical and structural investigations of Cu_2O thin films fabricated by thermal vacuum evaporation of CuO powder. The effects of the deposition velocity on structural and optical properties of Cu_2O films were investigated. The X-ray investigations have shown that at low deposition velocity the films consist only of Cu_2O phase without any interstitial phase and have a Nano-grain structure. The grains have an average dimensions about (25-30) nm and all these grains showed (200) preferential crystallographic orientation. Optical investigations have shown that the absorption edge of prepared films is due to a direct allowed transition. The value of determined optical band gap is 2.05 eV which corresponds to band gap of bulk Cu_2O.

The films of copper oxide were deposited on sapphire substrate by the continuous thermal evaporation of CuO small particles. The effects of deposition velocity on the structural and optical properties of Cu_2O films were investigated. It was shown that at deposition velocity less than 5 nm/min the films deposited on the 700^0C substrate consist only of Cu_2O phase. These films have a nano-grain structure and all these nano-grains have (200) preferential crystallographic orientation with average dimensions about (25-30) nm. It was found that the optical band gap of fabricated Cu_2O films is 2.05 eV which corresponds to the band gap of bulk Cu_2O [13].

4.15 Nanocrystalline copper oxide thin films deposited by SILAR technique: Morphological, Structural, optical and antibacterial studies. K. Dhanabalan A.Vasuhi G. Padma Priyac, A.T. Ravichandran K. Ravichandran P.Karthick S. Valanarasu .

Nanocrystalline copper oxide thin films were deposited onto glass substrates employing successive ionic layer adsorption and reaction (SILAR) technique. The surface morphological, microstructural, optical and antibacterial properties were studied. The structural studies revealed that as-deposited and annealed at 250°C films belong to the cubic Cu_2O

phase with preferential orientation along (111) direction. The antimicrobial assay was tested against Staphylococcus aureus. Nanoparticles are in demand for the usage of medical industries to control pathogens. Results obtained from Cu_2O Nano-thin films possessing significant antimicrobial activity against the tested human pathogen at a maximum inhibition zone of 16 mm. The surface morphological studies showed that the needle-shaped grains play the crucial role in the antibacterial activity of the Cu_2O films. From EDAX, the presence of elements Cu and O in the product was confirmed. Atomic force microscope study depicts that the surface of the film has closely packed nearly uniform sized grains. From the TEM, the film is well oriented after annealing.

Deposition of copper oxide thin films through SILAR technique was successfully demonstrated. The thin films thus grown were systematically characterized for their morphology and optical properties. The SEM characterization of the films has the shown needle-shaped Cu_2O films. The band gap of the film calculated is found to be (2.3 to 2.0) eV which is well matched with the literature of Cu_2O. This Cu_2O nanoparticle deposited on glass plates have exhibited moderate antimicrobial activity against Staphylococcus aureus. The AFM and TEM images are clearly shown, that the crystalline quality of the film is improved for the annealed film at 250^0C. Further work is underway to check the effect of the bactericidal activity of Cu_2O nanoparticles against S. aureus and other gram positive and gram negative bacterial and fungal pathogens [14].

4.16 Characterization of copper oxide nanoparticles for antimicrobial applications. Dawei Hub, Eileen W.C. Chengb, Miguel .AVargas-Reusc, Paul Reipd, Robert P. Allakerc.

Copper oxide (CuO) nanoparticles were characterized and investigated with respect to potential antimicrobial applications. It was found that Nano scaled CuO, generated by thermal plasma technology, contains traces of pure Cu and Cu_2O nanoparticles. Transmission electron microscopy (TEM) demonstrated particle sizes in the range (20–95) nm. TEM energy dispersive spectroscopy gave theratio elements as (54.18 - 45.26) %.The mean surface area was determined as 15.69m^2/gby.Brunau–Emmet–Teller (BET) analysis. CuO nanoparticles in suspension showed activity against a range of bacterial pathogens, including methicillin-resistant Staphylococcus aureus (MRSA) and Escherichia coli, with minimum bactericidal concentrations (MBCs) ranging from (100 – 5000)g/mL. The ability of CuO nanoparticles to reduce bacterial populations to zero was enhanced in the presence of sub-MBC concentrations of silver nanoparticles. Studies of CuO nanoparticles incorporated into polymers suggest release of ions may be required for optimum killing [15].

Chapter Three

Material and Methods

3.1 Introduction to Nanotechnology

Nanotechnology is the science that deals with matter at the scale of 1 billionth of a meter (10^{-9} m = 1 nm), and is also the study of manipulating matter at the atomic and molecular scale. A nanoparticle is the most fundamental component in the fabrication of a nanostructure, and is far smaller than the world of everyday objects that are described by Newton ' s laws of motion, but bigger than an atom or a simple molecule that are governed by quantum mechanics. The United States instituted the National Nanotechnology Initiative (NNI) back in 2000, which was soon followed (2001) by a plethora of projects in nanotechnology in nearly most of the U.S. Departments and Agencies. About 20 Research Centers were subsequently funded by the Nationa1 Science Foundation (NSF), an agency responsible solely to the President of the United States and whose mandate is to fund the best of fundamental science and technology projects. NSF was the lead U.S. agency to carry forward the NNI [17].

The word nanotechnology soon caught the attention of various media (TV networks, the internet, etc.) and the imagination and fascination of the community at large. In general, the size of a nanoparticle spans the range between (1-100) nm. Metallic nanoparticles have different physical and chemical properties from bulk metals (e.g., lower melting points, higher specific surface areas, specific optical properties, mechanical strengths, and specific magnetizations), properties that might prove attractive in various industrial applications. However, how a nanoparticle is viewed and is defined depends very much on the specific application. In this regard, summarizes the definition of nanoparticles and nanomaterial by various organizations. Of particular importance, the optical property is one of the fundamental attractions and a characteristic of a nanoparticle. For example, a (20) nm gold nanoparticle has a characteristic wine red color. A silver nanoparticle is yellowish gray. Platinum and palladium nanoparticles are black. Not surprisingly, the optical characteristics of nanoparticles have been used from time immemorial in sculptures [18].

3.2 Material

3.2.1 Copper (II) nitrate

Cu $(NO_3)_2$, is an inorganic compound that forms a blue crystalline solid. Anhydrous copper nitrate forms deep blue-green crystals and sublimes in a vacuum at (150-200) °C. Copper nitrate also occurs as five different hydrates, the most common ones being the rehydrate and hex hydrate. These materials are more commonly encountered in commerce than in the laboratory. Anhydrous copper (II) nitrate has been crystallized in two solvate-free polymorphs α- and β-Cu $(NO_3)_2$ are fully 3D coordination polymer networks. The alpha form has only one Cu environment, with [4+1] coordination, but the beta form has two different copper centers, one with [4+1] and one that is square planar. The nitro methane solvate also features "[4+ 1] coordination", with four short CuO bonds of approximately 200 pm and one longer bond at 240 pm. they are coordination polymers, with infinite chains of copper (II) centers and nitrate groups. In the gas phase, copper (II) nitrate features two bidentate nitrate ligands (see image at upper right). Thus, evaporation of the solid entails "cracking" to give the copper (II) nitrate molecule.

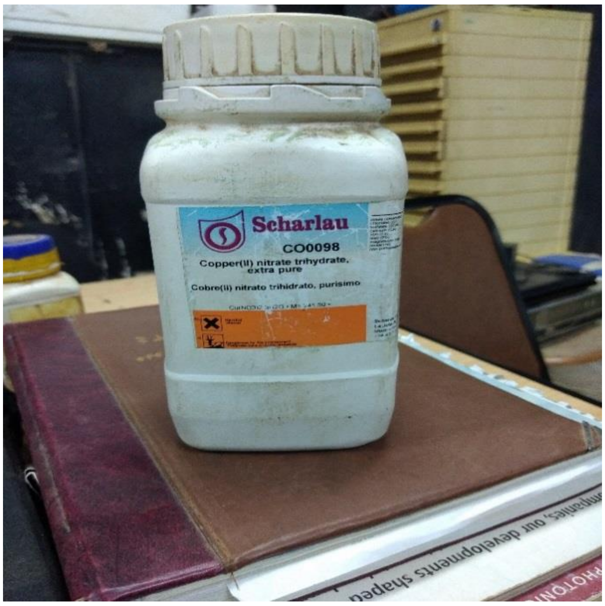

Figure (3.1) copper (II) nitrate

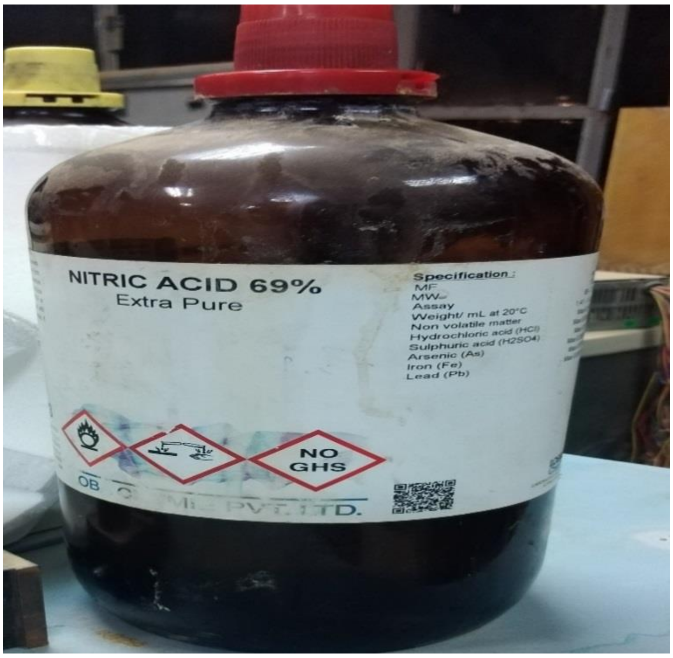

Figure (3.2) Nitric Acid 69%.

3.3 Methods

3.3.1 The sol-gel method

Sol-gel processing is a soft-chemistry method to obtain function materials at low temperatures. This route can be used to produce very sophisticated nanomaterials and to tailor the materials to very specific applications. Adsorption and detection of pollutants, water purification and soil remediation represent challenging fields of application that can be exploited by sol-gel materials.

CuO thin films were prepared by the sol-gel method with different concentrations. The optical properties of the CuO thin films were investigated. In particular, optical parameters such as the optical band gap, absorption coefficient, refractive index and extinction coefficient, real and imaginary dielectric constant were comprehensively studied in order to investigate the effects of $Cu(NO_3)_2 3H2O$ doping on the optical properties of CuO thin films.

3.3.2 Synthesis of copper oxide thin film

The synthesis of copper oxide thin film was synthesized through the sol-gel process with the Following fundamental steps. Initially, 4.93g (0.1M), 7.61g (0.3M), 8.34g (0.5M), 6.18g (0.7M), of Nano hydrated copper nitrate $Cu(NO_3)_2 3H2O$, in 57ml(0.1M), 88ml(0.3M), 97ml (0.5M), 72ml (0.7M) of deionized Water solvent and 30ml nitric acid 69% in the glass beaker. Then the solution on magnetic stiller for 60 min at 80°C until they get solution. The four mounts of solutions have been leaved in lab's temperature about 24 hours, then we filter it, and we obtained the Sol ready to be used, the samples were placed in a water bath foe four hours at 100c0 to evaporate the water from the solution. The deposited film is preheated at

200 c^0. For 30 min to evaporate the water and then at for 30 min to200 c^0 of the furnace for 40 min get powder this powder is copper oxide.

NO	Sample	Copper Nitrate(g)	Deionized water (ml)	Nitric Acid 69%(ml)
1	0.1	4.93	57	30
2	0.3	7.61	88	30
3	0.5	8.34	97	30
4	0.7	6.18	72	30

Figure (3.3) shows the copper (II) nitrate on magnetic stiller

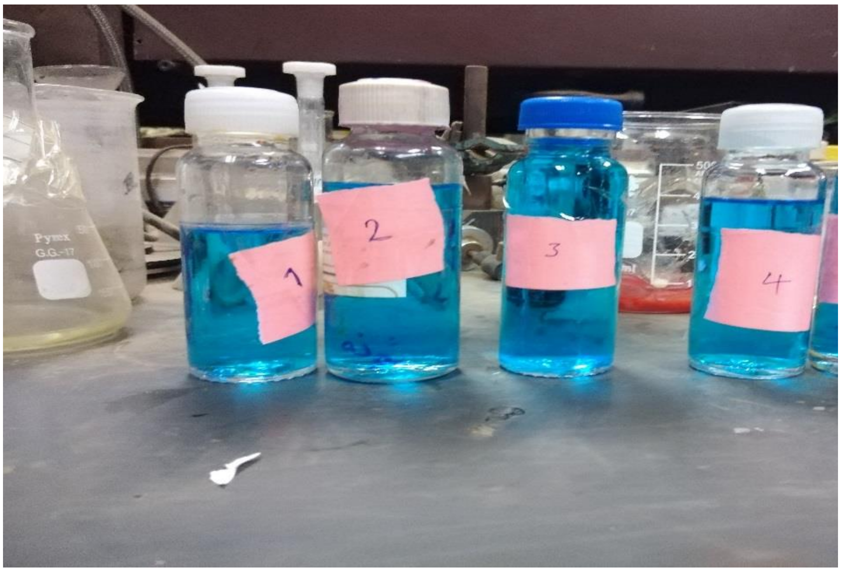

Figure (3.4) shows the for all sample of copper (II) nitrat.

Figure (3.5) shows the copper (II) nitrate on Water Bath.

Figure (3.6) UV- visible absorption.

Figure (3.7) shows evaporation furnace.

Figure (3.8) shows the sample inside the furnace.

Figure (3.9) shows the samples inside the test tubes.

Figure (3.10) shows the samples of copper oxide CuO inside the test tubes.

Chapter Four

Results and Discussion

4.1 Introduction

In this part of research, the main results that have been obtained from the experiments made of CuO where (0.1, 0.3, 0.5 and 0.7) Molar are prepares by using sol gal method to ensure good quality of the samples. The data of UV-visible used to evaluate optical properties and energy band gap.

4.2 Result

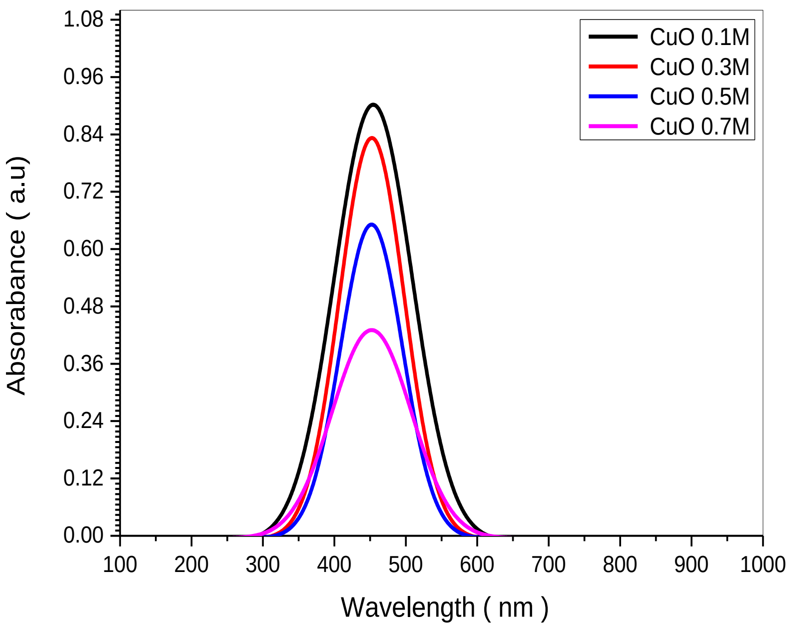

Fig (4.1) relation between absorbance and wavelengths of copper oxide CuO (0.1, 0.3, 0.5 and 0.7) Molar samples.

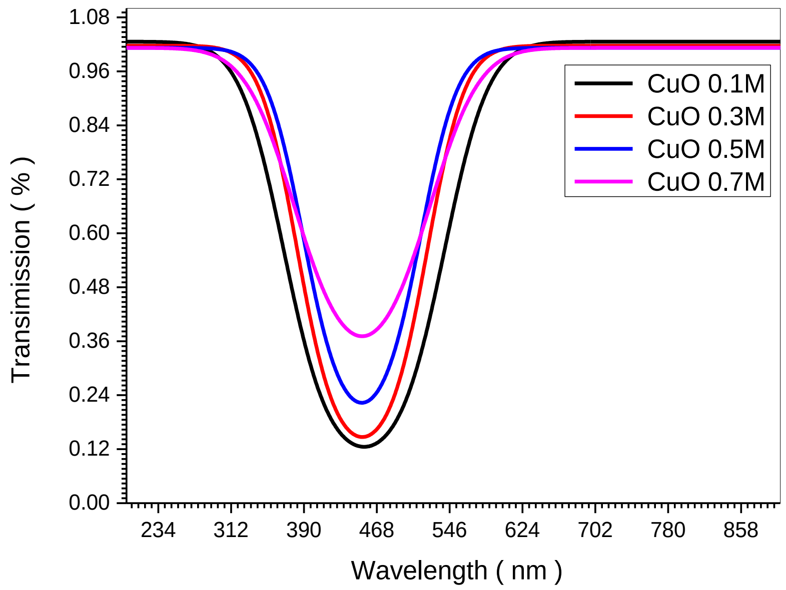

Fig (4.2) relation between transmission and wavelengths of copper oxide CuO (0.1 ,0.3 ,0.5 and 0.7) Molar samples.

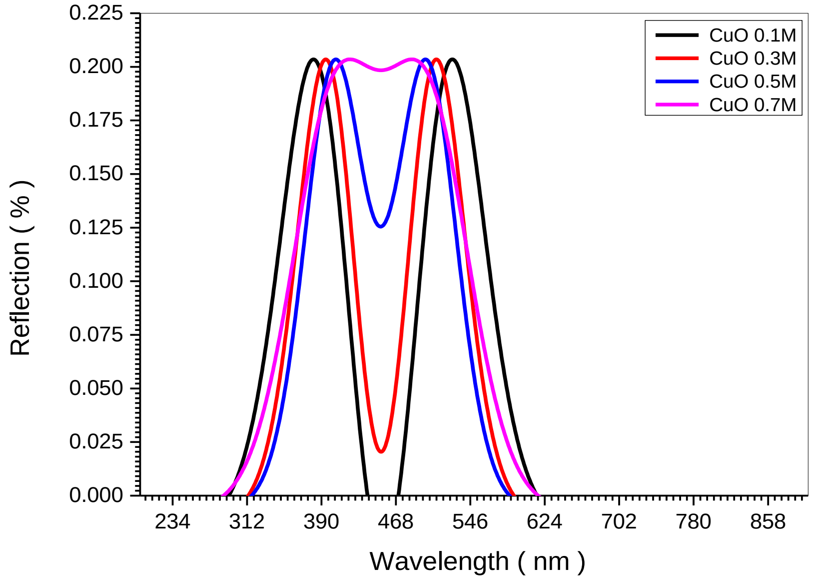

Fig (4.3) relation between reflection and wavelengths of copper oxide CuO (0.1 ,0.3 ,0.5 and 0.7) Molar samples.

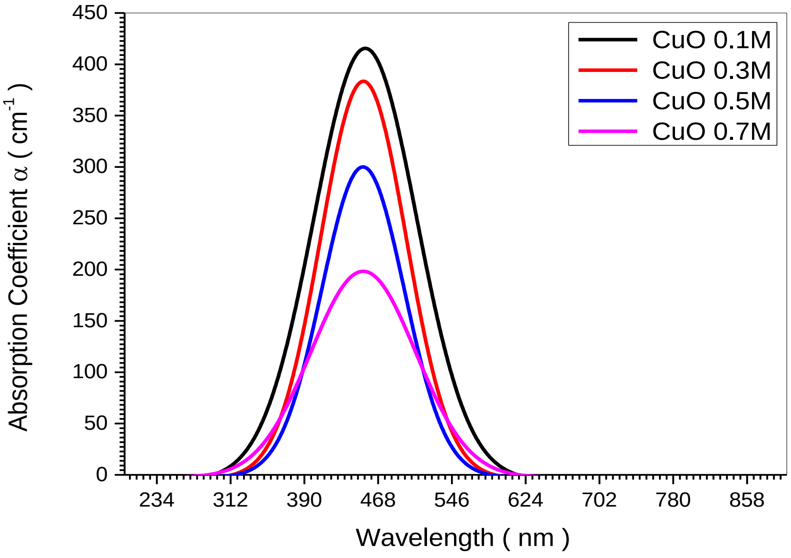

Fig (4.4) relation between absorption coefficient and wavelengths of copper oxide CuO (0.1, 0.3, 0.5 and 0.7) Molar samples.

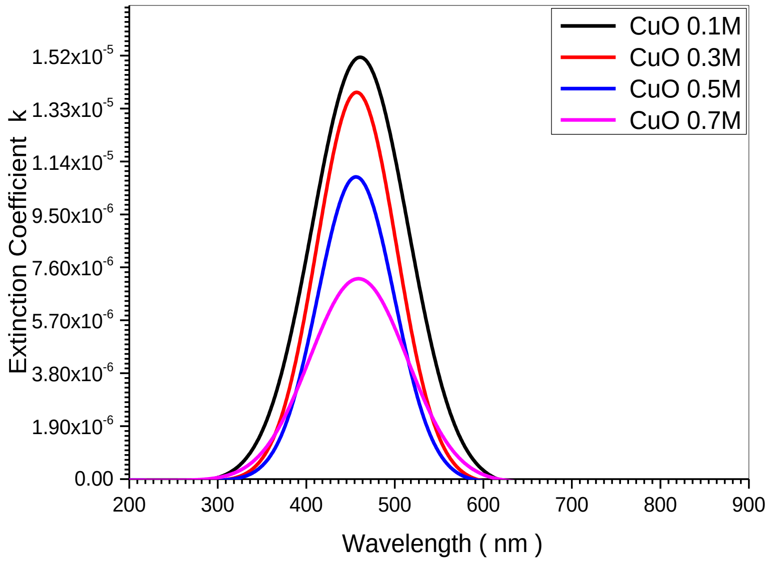

Fig (4.5) relation between extinction coefficient and wavelengths of copper oxide CuO (0.1, 0.3, 0.5 and 0.7) Molar samples.

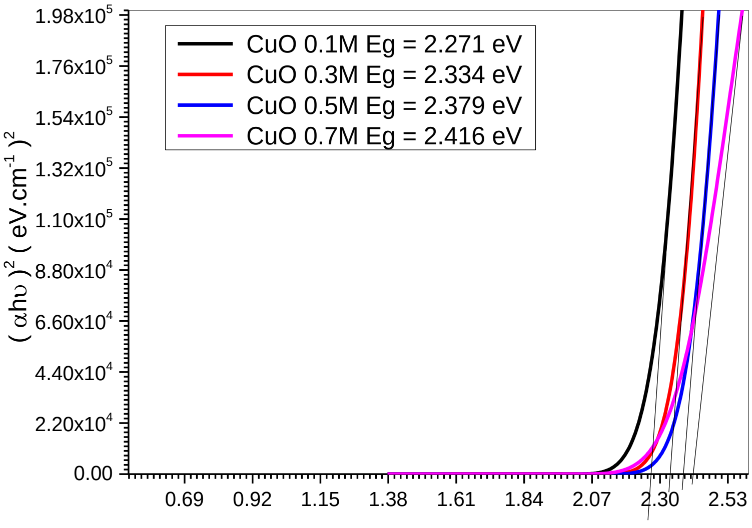

Fig (4.6) optical energy band gap of copper oxide CuO (0.1, 0.3, 0.5 and 0.7) Molar samples.

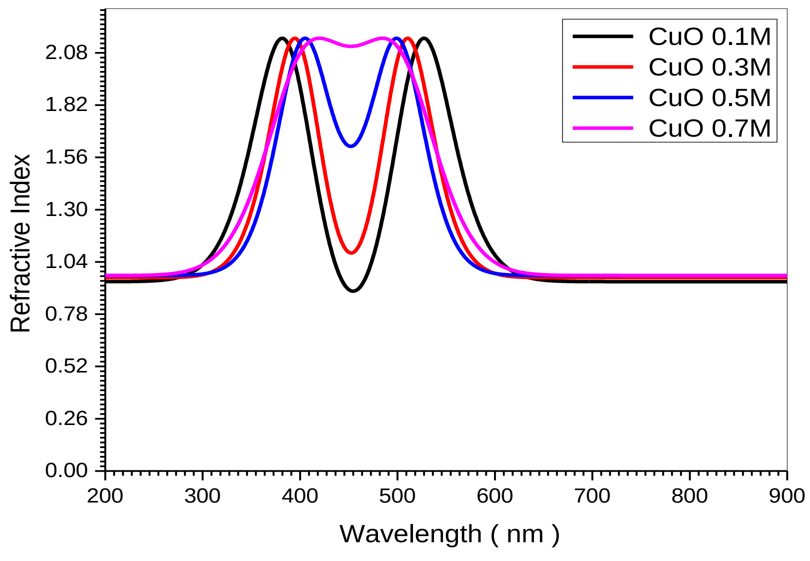

Fig (4.7) relation between refractive index and wavelengths of copper oxide CuO (0.1, 0.3, 0.5 and 0.7) Molar samples.

4.3 Discussion

4.3.1 Absorbance

An absorbance we found the behavior of curves is the same with four samples of CuO (0.1, 0.3, 0.5 and 0.7) Molar studied using UV-VS min 1240 spectrophotometer. Show all resolute of absorbance in fig (4.1). In fig. (4.1) shows the relation between absorbance and wavelengths f or four samples of CuO the rapid decrease of the absorption at wavelengths 454 nm. The mean effects on the absorbance value was rated of molar, when the rated of molar increased the absorbance value decrease.

4.3.2 Transmission

Transmission of four CuO (0.1, 0.3, 0.5 and 0.7) Molar samples we found in fig (4.2) the rapid increase of the transmission at wavelengths 454 nm. The mean effects on the absorbance value was rated of molar, when the rated of molar increased the absorbance value increase.

4.3.3 Reflection

In fig (4.3) show that relation between reflection and wavelengths of CuO (0.1, 0.3, 0.5 and 0.7) Molar samples, and in fig (4.3) high value of reflection in the ranged (379 to 531) nm.

4.3.4 Absorption coefficient (α)

The absorption coefficient (α) of four prepared CuO (0.1, 0.3, 0.5 and 0.7) Molar samples by equation $\alpha = \frac{2.303xA}{t}$ where (A) is absorbance and (t) is the optical length on the samples. In fig (4.4) shows the plot of (α) with wavelength (λ) of four sample was treatment by CuO (0.1 ,0.3 ,0.5 and 0.7) Molar, which obtained that the value of α = $4.16x10^{2}$ cm^{-1} for CuO 0.1 M in the Visible region(454 nm), but for CuO 0.7 M equal 1.9 $x10^{2}$ cm^{-1} at the same wavelength , this means that the transition must corresponding to a direct electronic transition, and the properties of this state are important since they are responsible for electrical conduction. Also, fig.(4.4) shows that the value of (α) for the four samples of CuO increase while the molar of CuO decreased .

4.3.5 Extinction coefficient (α)

The extinction coefficient (α) of four prepared CuO (0.1, 0.3, 0.5 and 0.7) Molar samples by equation $k = \frac{\alpha\lambda}{4\pi}$. The variation at the (K) values as a function of (λ) are shown in fig. (4.5) of four sample was treatment by CuO (0.1, 0.3, 0.5 and 0.7) Molar, and it is observed that the spectrum shape of (K) as the same shape of (α). In fig (4.5) which obtained that the value of k = 1.5×10^{-5} for CuO 0.1 M in the Visible region (454 nm), but for CuO 0.7 M equal 7.2×10^{-6} at the same wavelength. Also, fig.(4.5) shows that the value of (α) for the four samples of CuO increase while the molar of CuO decreased.

4.3.6 The optical energy gap (Eg)

The optical energy gap (E_g) has been calculated by the relation $(\alpha h\upsilon)^2 = C (h\upsilon - E_g)$ where (C) is constant. By plotting $(\alpha h\upsilon)^2$ vs photon energy (hυ) as shown in fig.(4.6) with four prepared sample was by CuO (0.1 ,0.3 ,0.5 and 0.7) Molar. And by extrapolating the straight thin portion of the curve to intercept the energy axis, the value of the energy gap has been calculated. In fig (4.6) the value of (E_g) 0.1M CuO sample was (2.271) eV while for 0.7 M CuO sample was (2.416) eV. The value of (E_g) was increased from (2.271) eV to (2.416) eV. The increasing of (E_g) related to increase of molar on the samples. It was observed that the different molar confirmed the reason for the band gap shifts.

4.3.7 The refractive index (n)

The refractive index (n) is the relative between speeds of light in vacuum to its speed in material which does not absorb this light. The value of n was calculated from the equation $n[\left(\frac{1+R}{1-R}\right)^2 - (1+k^2)]^{\frac{1}{2}} + \frac{(1+R)}{(1-R)}$ Where (R) is the reflectivity. The variation of (n) vs (λ) for the four samples was treatment by CuO (0.1, 0.3, 0.5 and 0.7) Molar was shown in fig. (4.7). Fig (4.7) Show that relationship of four prepared sample by CuO $_{\text{refractive}}$ index (n) spectra ,which shows that the maximum value of (n) is (2.15) for all samples at the differences wavelength which is agreement with increased of molar on all samples.

4.4 Conclusions

CuO thin film deposited by Sol-gel method with a solution of Cu $(NO_3)_2$ $3H_2O$. The film exhibits high absorbance values at ultraviolet region which they decrease rapidly in the visible/ near infrared region, the film shows a direct transition which was the value of (E_g) was increased from (2.271) eV to (2.416) eV for allowed energy gap. The film has high values of absorption coefficient which obtained that the value of $\alpha = 4.16 \times 10^2$ cm^{-1} for CuO 0.1 M in the Visible region (454 nm), but for CuO 0.7 M equal 1.9 $\times 10^2$ cm^{-1} at the same wavelength. The sol-gel method for the production of thin solid films is a good method for the preparation of thin films which are suitable for scientific studies and for many applications in technology and industry, equally.

4.5 Recommendation

1. The state interest in scientific research and researchers.
2. Encouraging the scientific researcher to discover and innovate.
3. The state should pay attention to scientific research because it has the benefits of the nation's patronage.
4. The state universities to prepare the scientific environment to be suitable for scientific research.
5. The state should like to provide practical equipment that enables the researcher to complete his scientific research.

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