Structural, morphological and Optical properties of copper Oxide thin film

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ABSTRACT

From this work we conclude the following mean outcomes:

- Copper oxide thin films have been prepared by low cost using pulsed laser deposition technique on glass slide substrate.
- Polycrystalline structure with three phases cubic Cu, monoclinic CuO and cubicCu2O were obtained from using X-ray diffraction (XRD) analysis
- Homogeneous distribution nano particles with average diameter 68.86 nm and root mean square roughness of 0.67 nm were found from the atomic force microscope measurement .
- The optical characteristics showed that the prepared CuO thin film has a direct allow electronic transition with 2.5 eV optical energy gap (Eg)
- These properties make the material more prominent for device applications of various optoelectronics and photonic devices.

Keywords: Morphological , properties , chopper Oxide

Introduction

This chapter includes theoretical part for thin films semiconductor properties

- **Semiconductor and Thin Films**

The field of semiconductor physics has entered in all daily life aspects and still in continued progress and contributes a great deal in technological scientific development. Thin films technique is considered to be one of the most important techniques that contributed in the development of semiconductor's study [1].

Investigation on the basic properties of the thin films can be grouped roughly into two categories. The first is concerned with change of the physical properties, mean free path effects on the electrical conduction of thin metal films, studies of magnetization of thin films of ferromagnetic materials as function of film thickness, electron tunneling effects and effects due to the adsorption of gases are example of this category [2].

Most physical properties of films; such as optical, magnetic, chemical, and electrical are importance properties in of industrial, scientific and technical applications. At the same time studies of the fundamentals of film formation and of the basic reasons for differences in behavior of films and bulk materials are being pursued with increasing vigor. The structure and properties of many films are known to depend considerably on the state of the surface on which they are deposited to know exactly what kind of surface is being used for deposition of films, whether it is crystallographically oriented or not [3].

The abundance of its source material (Cu) together with other features such as low-cost production, good thermal stability, and electrochemical properties make CuO a promising material in various applications. Furthermore, the ionicity of the Cu-O bonds increases when the size of the material approached the nanodomain. This property combined with the relatively large aspect ratio of CuO nanomaterials is very attractive for applications such as gas sensing and catalyst for degradation of hazardous chemicals,also the synthesis of CuO with another oxide such as ZnO and their application as fast and sensitive humidity sensor was accomplished[4].

Copper has two known stable oxides, cuprous (Cu_2O) and cupric (CuO) oxides. The physical properties of these two copper oxides are different since they have different crystal structures, optical and electronic properties. Studies on cupric oxide nano materials have grown substantially in recent years due to its direct band gap and intrinsic p-type behavior together with low cost fabrication and good electrochemical properties. These interesting properties made CuO among the best materials for electrical, optical, catalytic, and sensing applications to name a few [5]. Due to the high ionicity of the Cu-O bonds in CuO, this material found considerable attention for applications in catalysis, gas sensors, and solar cells. CuO nanomaterials and bulk were used in the preparation of a number of organic-inorganic composites that possess excellent characteristics such as high electrical and thermal conductivities, mechanical strength and high temperature stability [6].

1-4 The Aim of the Work:

Preparing CuO pellet and thin film using pulsed laser deposition technique, then study the characterizations such as structural and morphological and optical properties for fabrication CuO thin film.

1-5 Copper oxide

Recent studies, which depend on copper oxide, have increased because of its many advantages. Copper oxide possesses two phases, namely Cu_2O and CuO. Copper (II) oxide (CuO) is a solid black material with a density of 6.4 g/cm^3. It has a high melting point of 1330 ° C; and insoluble in water. It is a semiconductor of the metal oxide type, which possesses many properties that attracted many researches and studies. These properties include the natural abundance of its primary materials; the ease of production through oxidation of copper; and its good electrical and photovoltaic properties. The semiconductor has a p-type and a band-gap ranging from 1.21 to 1.51 eV, and a monoclinic crystalline structure, whereas copper oxide (Cu_2O) has a band gap of 2.0 eV and cubic shape crystals [7].

As mentioned earlier, copper oxide has two types of polymorphism, namely, cuprous oxide (Cu_2O) and cupric oxide (CuO). These oxides are the two most important stoichiometric compounds in the Cu-O system. Both oxides are intrinsic p-type semiconductors with relatively small band gaps and show many attractive properties that can be utilized in a diversity of applications. The potential applications of copper oxides include solar cells[8] , Li-ion battery where they have been used as negative electrode material[9] , superconductor [10] , magnetic storage, gas sensors [11] , and photoconductive systems [12] . Cupric oxide (CuO) is an intrinsic p-type semiconductor .The CuO has a C_2/c monoclinic crystal structure[13,14] as shown in Fig. (1-1).The unit cell of CuO comprises Cu^{+2} ions which are coordinated by four O^{-2} ions in an approximately square planar configuration.Some of the basic properties of CuO bulk material are tabulated in Table 1.2.

Table (2-2): Some physical properties of CuO [15].

Property	Value
Lattice constants (300K)	a = 0.468 nm , b = 0.342 nm , c = 0.513 nm
Density	6.31gm/cm^3
Melting point	1975 C°
Stable phase at 300 K	Monoclinic
Dielectric constant	18.1
Refractive index	1.4
Band gap (Eg)	1.21-1.58 eV, direct
Hole effective mass	0. 24 mo
Hole mobility	0.1-10 $cm^2/V s$

1-6 Thin Film Preparation Methods

A thin film is defined as thin layer built up on a solid support by controlled condensation of the individual atomic, molecular, or ionic species, either directly by a physical process, or via a chemical and / or electrochemical reaction. Since individual atomic, molecular, or ionic species of matter may exist either in the vapor or in the liquid phase, the techniques of the thin film deposition can be broadly classified under two main categories [1,16]:

- Vapor phase deposition.
- Liquid-phase / solution deposition.

In the thin films, deviations from the properties of the corresponding bulk materials arise because of their small thickness, large surface -to- volume ratio and unique physical structure which is direct consequence of the growth process.

Thin films technique is one of the most resentfully-fledged technologies that greatly contribute to developing the study of semiconductors by giving a clear indication of their chemical and physical properties. Thin films are also particularly important for their use in a great number of the optical field such as manufacturing of ordinary and thermal mirrors of high specialized filters, photo detectors and solar cells [17].

Investigation on the basic properties of the thin films can be grouped roughly into two categories. The first is concerned with change of the physical properties as thickness decreased, mean free path effects on the electrical conduction of thin metal films, studies of magnetization of thin films of ferromagnetic materials as function of film thickness, electron tunneling effects and effects due to the adsorption of gases are example of this category. These investigations all have the film thickness as the principle parameters. The second category of investigations is the study of the film structures [18].

Most physical properties of thin films are optical, magnetic, chemical and electrical which are importances in an ever widening sphere of industrial, scientific and technical applications. At the same time studies of the fundamentals of film formation and of the basic reasons for differences in behavior of films and bulk materials are being pursued with increasing vigor. The structure and properties of many films are known to depend considerably on the state of the surface on which they are deposited to know exactly what kind of surface is being used for deposition of films, whether it is crystallographic oriented or not [19]. Solid solution series are especially qualified for investigations of relationships between structures and physicochemical properties of crystals because their physical and chemical properties show dependences of chemical composition element ordering and microstructures as well as stability parameters as temperature and pressure [19].

1-6-1 Pulsed Laser Deposition (PLD)

With the pulsed laser deposition (PLD) method, thin Films are prepared by the ablation of one or more targets illuminated by a focused pulsed-laser beam. This technique was first used by Smith and Turner [20] in 1965 for the preparation of semiconductors and dielectric thin films and was established due to the work of Dijkkamp and coworkers [21] on high temperature superconductors in 1987. Pulsed laser deposition (PLD) is a thin-film deposition method, which uses short and intensive laser pulses to evaporate target material. The ablated particles escape from the target and condense on the substrate. The deposition process occurs in vacuum chamber to minimize the scattering of the particles. In some cases, however, reactive gases are used to vary the stoichiometry of the deposit [22] . The pulsed laser deposition technique involves four main steps: laser radiation interaction with the target, ablation of the target material, formation of a highly energetic plume, and the growth of the film on the substrate. A high-power laser is used as an energy source to vaporize a target containing components of the desired film. When the laser radiation is absorbed by a solid surface, electromagnetic energy is converted into electronic excitation as well as chemical, mechanical, and thermal energy to cause evaporation and plasma formation.

1.6.1.1 Mechanisms of PLD

The principle of pulsed laser deposition, in contrast to the simplicity of the system set-up, is a very complex physical phenomenon. It involves all the physical processes of laser-material interaction during the impact of the high-power pulsed radiation on a solid target. It also includes the formation of the plasma plume with high energetic species, the subsequent transfer of the ablated material through the plasma plume onto the heated substrate surface and the final film growth process. Thus PLD generally can be divided into the following four stages.

- Laser radiation interaction with the target
- Dynamic of the ablation materials
- Decomposition of the ablation materials onto the substrate
- Nucleation and growth of a thin film on the substrate surface

In the first stage, the laser beam is focused onto the surface of the target. At sufficiently high energy density and short pulse duration, all elements in the target surface are rapidly heated up to their evaporation temperature. Materials are dissociated from the target and ablated out with stoichiometry as in the target. The instantaneous ablation rate is highly dependent on the fluences of the laser irradiating on the target. The ablation mechanisms involve many complex physical phenomena such as collisional, thermal and electronic excitation, exfoliation and hydro dynamics.

During the second stage the emitted materials tend to move towards the substrate according to the laws of gas dynamic and show the forward peaking phenomenon [23] . R.K. Singh [24] reported that the spatial thickness varied as a function of $cos^{n}ph_{i}$, where n>>1. The laser spot size and the plasma temperature have significant effects on the deposited film uniformity. The target-to-substrate distance is another parameter that governs the angular spread of the ablated materials. Hanabusa [25] also found that a mask placed close to the substrate could reduce the spreading.

The third stage is important to determine the quality of thin film. The ejected high-energy species impinge onto the substrate surface and may induce various type of damage to the substrate. The mechanism of the interaction is illustrated in the following figure. These energetic species sputter some of the surface atoms and a collision region is established between the incident flow and the sputtered atoms. Film grows immediately after this thermalized region (collision region) is formed. The region serves as a source for condensation of particles. When the condensation rate is higher than the rate of particles supplied by the sputtering, thermal equilibrium condition can be reached quickly and film grows on the substrate surface at the expense of the direct flow of the ablation particles (see Fig.(1.3)[26].

Although the pulsed laser deposition process is conceptually simple, controlling the dynamics of the film growth is not an easy issue, because of the large number of interacting parameters that govern the growth process and hence the film properties, such as:

- The laser parameters (working wavelength, fluence, pulse duration, and repetition rate).
- The substrate type, orientation and temperature.

- The structural and chemical composition of the target material.
- The chamber pressure and the chemical composition of the buffer gas.
- The geometry of the experiment (incident angle of the laser, incident angle of the plume, distance between target and substrate).

These mechanisms are commonly thought to be:

- Phonon and electron excitation within the lattice.
- Free carrier excitation.
- Excitation of the resulting plasma and subsequent transfer of energy to the material.

1.6.2 Advantage of PLD

- Fast: high quality samples can be grown reliably in 10 or 15 minutes.
- Flexibility in choice of material, background atmosphere, etc., due to the fact that energy source (laser) is located outside of the deposition chamber. Also the evaporation without any melt phase gives room for experimental design freedom.
- Operated under any ambient gas (pressure range 0 - 1 Torr).
- High kinetic energies of plume particles and high degree of ionization stimulate crystalline film growth at lower substrate temperatures relative to other physical vapor deposition (PVD) techniques and increased surface mobility or improved adhesion and the quality of the deposited film.
- The PLD technique is found to be very effective and well suited for developing epitaxial films, and allows fabrication of multi-layers simply by switching between several different targets [27] .

PLD is a clean process because the films are able to be deposited in vacuum or with background gases.

1-7 Optical Properties of Semiconductors:

The spectrum in the absorption edge exhibits much useful information about the material under investigation, such as the type of transition, energy gap (E_g), permittivity and other optical properties of semiconductor [28].

Absorption occurs during the propagation if the frequency of the light is resonant with the transition frequency of the atoms in the medium. In this case the beam will be attenuated as it progresses . The transmission of the medium is clearly related to the absorption because only unabsorbed light will be transmitted . The absorption of light by an optical medium is quantified by its absorption coefficient (α) . This is defined as the fraction of the power absorbed in a unit length of the medium . The absorption and refraction of a medium can be described by a single quantity called the complex refractive index. This is usually given by the symbol N* and is defined through the equation [29].

$$N^{*} = n + iK \quad \text{... (1-1)}$$

The real part of N* ; namely n is the real refractive index .The imaginary part of N* namely K, is called the extinction coefficient which is directly related to the absorption coefficient α of the medium.

1-7-1 Optical Absorption and Absorption Edge:

An important technique for measuring the band gap energy of semiconductors is the absorption of incident photon by material [3]. The fundamental absorption refers to all band-to- band transition. This process in which a photon absorbed and electron excited from an occupied valence band state to unoccupied conduction band state , which used to determine the value of the optical band gap . The fundamental absorption edge is one of the most important features of the absorption spectrum of semiconductors [30].

When a semiconductor is illuminated with light, the photons may be absorbed through the semiconductor, depending on the photon energy (hυ); where h is Plank's constant υ is the incident photon frequency, and the electronic transition between the valence band (V.B.) and the conduction band (C.B.) in the crystal start at the absorption edge which corresponds to minimum energy difference between the lowest minimum of the C.B. and the highest of the V.B. i.e. the E_g . If $h\upsilon \geq E_g$ the photon can interact with a valence electron, elevate the electron into the C.B. and creates an electron-hole pair, the minimum wavelength (λ) of the incident photon which creates the electron-hole pair is defined as [29].

$\lambda(\mu m) = hc/E_g = 1.24/E_g(eV)$ ………………………….. (1-2)

where c is the speed of light. The intensity of the photon flux decreases exponentially with distance (t) through the semiconductor which is the thickness of it according to the Beer-Lambert equation [29].

$I = I_o \exp(-\alpha t)$ ……………………………………………………… (1-3)

where I_o and I are the incident and the transmitted photon intensity respectively and α is the absorption coefficient, which is defined as the relative number of the photons absorbed per unit distance of a semiconductor, and t is the thickness of the material.

In polycrystalline and amorphous semiconductors there are localized states in their energy gaps, then the absorption edge becomes wide. The width of these localized states can be calculated by using Urbach equation [31]:

$\alpha = \alpha^o \exp(hc/E_u)$ …………………………………………(1-4)

where E_u is the width of the localized states inside the E_g and creating a further mechanism for enhance absorption in polycrystalline films.

1-7-2 Optical Transition:

The electronic transition type between the V.B. and the C.B are divided into direct and indirect [16] it is obeying the following Tauc equation [29]:

$\alpha h\upsilon = \text{cons.} (h\upsilon - Eg)^r$ ……………………………………..(1-5)

where r=1/2, 3/2, 2, 3 for allowed direct, forbidden direct, allowed indirect, forbidden indirect transitions respectively.

1-7-2-1 Direct Transitions:

In general it occurs between initial and final states of the same wave vector value of electron occurs, $\Delta k=0$ for conservation momentum. The absorption coefficient for this transition takes the values from 10^4 to 10^5 cm^{-1}. This transition takes place in crystalline and polycrystalline semiconductors. Allowed direct transition occurs when an electron makes direct transition from the top of the V.B. to the bottom of the C.B. and the wave vectors of initial and final states are equal to zero as shown in figure (1-2 a) . Forbidden direct transition occurs between the state of the same wave vector but the wave vector does not equal zero, i.e. the allowable transition occur at different positions of C.B. and V.B. [29,30], as shown in figure (1-2 b)

1-7-2-2 Indirect Transitions:

Indirect transitions occur when the C.B. minima are not at the same value of the k as the V.B. maxima, the assistance of phonon is necessary to conserve the crystal momentum, therefore $h\upsilon = E_g \pm E_p$ where E_p is the emitted or absorbed phonon energy [17], α takes the values 1 to 10 cm^{-1}. Allowed indirect transitions occur from the top of the V.B. to the bottom of the C.B [30] as shown in figure (1-2 c) Forbidden indirect transitions occur from any point that the top of V.B. to any point other than the bottom of the C.B., as shown in figure (1-2 d)

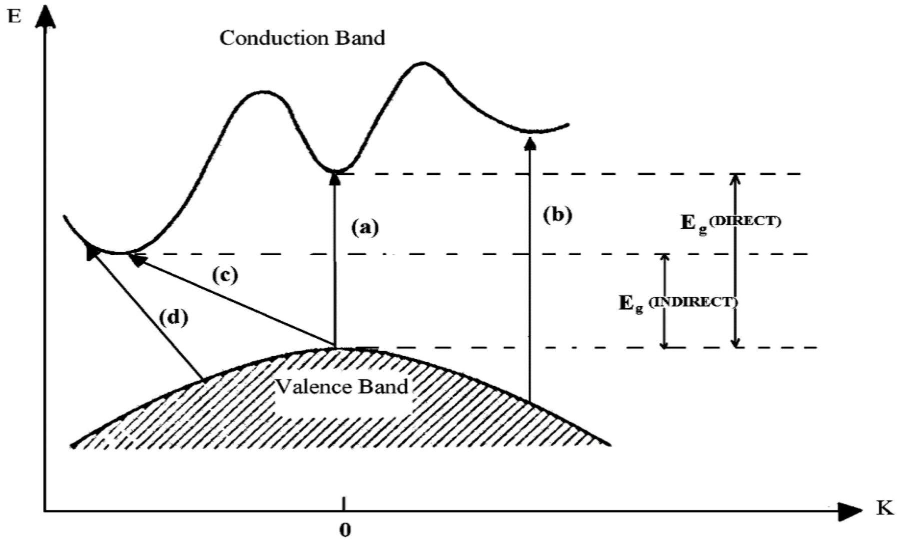

Figure (1-2): The optical transitions (a) Allowed direct, (b) Forbidden direct; (c) Allowed indirect, (d) Forbidden indirect [29].

The reflection at the surface is described by the coefficient of reflection or reflectivity (R) , which is defined as the ratio of the reflected to the incident power on the surface. The coefficient of transmission (T) is defined likewise as the ratio of the transmitted power to the incident power, the absorption of light by an optical medium is quantified by its absorption coefficient (α), which defined as the fraction of the power absorbed in a unit length of the medium [3].The relation between absorption (A) and Transmission (T) is:

$A = \log_{10} 1/T$ .... (1-6)

For very small R , we can write the absorption coefficient as :

$\alpha = 2.303 A / t$ .... (1-7)

(R+1)

½

The refractive index was determined by the relationship [28]

4R

(R-1)

2

(R-1)

$n = [\ – \ - k^2] + –$ ..... (1-8)

where the reflectance (R) has been found by using the relationship

$R + T + A = 1$ ......(1-9)

The extinction coefficient k is given by :

$k = \alpha\lambda/4\pi$ .... (1-10)

where **λ** is the wavelength of the light.

The real part of dielectric constant is given by [29]:

$\varepsilon_r = n^2 - k^2$ ....(1-11)

The imaginary part of dielectric constant is given by

$\varepsilon_i = 2nk$ ....(1-12)

1-8 Structural Properties

The arrangement of atoms in a material is determined mainly by the strength and directionally of inter atomic bonds. Thus one needs, to distinguish between strong or weak and directional or non-directional bonds. The local arrangements of atoms in a solid may be either regular (crystalline) or irregular (amorphous). The regular three-dimensional arrangement of atoms or ions in space constitutes the crystalline structure. These highly ordered structures of atoms or ions in a space lattice arise from geometrical conditions which are imposed by directional bonding and close packing with the aim of minimizing the energy of the solid [30] .

A solid may also contain more than one phase. There are many ways in which crystalline and non-crystalline aggregate of atoms and molecules can be arranged a solid . The crystal structure determine by x-ray diffraction. An x-ray on a group of atoms transmits its electric field to the electrons of the atoms, so that these start to oscillate. However a vibrating electric charge is always a source of electromagnetic waves, the wave length of which is identical with that of the impinging ray , hence every atom acts as an emitter, the wave radiated from the various atomic layers (crystals planes) causing interference effects. This means that the wave train constrictively interferes, in certain directions, and in others destructively , depending on whether or not, the wave are in phase. These events cause diffraction phenomena which can be described with the classical Bragg equation [23]:

$$m\lambda = 2d\sin\theta \quad \ldots\ldots\ldots\ldots\ldots (1\text{-}13)$$

where λ, θ and m represent X-ray wavelength from Cu target (1.5406 Å), diffraction angle and diffraction order respectively .

The Scherrer equation is a formula that relates the size of crystallites in a solid to the broadening of a peak in a diffraction pattern. It is used in the determination of size of particles of crystals i.e, crystallite size (*C.S*) [30,32].

References

[1] K. Chopra and I. Kaur “ Thin film Device Application, Plenum Press “ ,New York (1983).

[2] S. Al-Naimi and M.N. AL-Dileamy“ Determination of the Optical Constants of Cadmium Stannate (Cd_2SnO_4) Films” ,International Jour. Pure and App. Phys. Vol.3 No.1pp.30-39. (2007).

[3] A.N.Donald, " Semiconductors Physics and Devices" ,University Mexico,(1992).

[4] H. Wu, D. Lin, and W. Pan, “Fabrication, assembly, and electrical characterization of CuO nanofibers,” Appl. Phys. Lett. Appl. Phys. Lett., vol. 89, no. 13, p. 133125, 2006.

[5] X. Wang, C. Hu, H. Liu, G. Du, X. He, and Y. Xi, “Synthesis of CuO nanostructures and their application for nonenzymatic glucose sensing,” Sensors Actuators B. Chem., vol. 144, no. 1, pp. 220–225, 2010.

[6] C.-L. Huang, R. E. Partch, and E. Matijevic, “Coating of Uniform Inorganic Particles with Polymers. II. Polyaniline on Copper Oxide,” J. Colloid Interface Sci., vol. 170, no. 1, p. 275, 1995..

[7] G. Papadimitropoulos, N. Vourdas, V. E. Vamvakas and D. Davazoglou, "Deposition and characterization of copper oxide thin films", J. Phys. Conf. Ser., Vol. 10, pp. 182–185, (2005).

[8] A. Mittiga, E. Salza, F. Sarto, M. Tucci, and R. Vasanthi, “Heterojunction solar cell with 2% efficiency based on a Cu[sub 2]O substrate,” Appl. Phys. Lett. Appl. Phys. Lett., vol. 88, no. 16, p. 163502, 2006.

[9] D.-W. Zhang, T.-H. Yi, and C.-H. Chen, “Cu nanoparticles derived from CuO electrodes in lithium cells,” Nanotechnology, vol. 16, no. 10, pp. 2338–2341, 2005.

[10] J. B. Goodenough, “Bond-length fluctuations in the copper oxide superconductors,” J. Phys. Condens. Matter, vol. 15, no. 7, pp. R257–R326, 2003.

[11] S. Y., Z. Y., Z. W., L. B., Z. B., and Y. H., “Synthesis of polyhedron hollow structure Cu2O and their gas-sensing properties,” Sens Actuators, B Chem Sensors Actuators, B Chem., vol. 171–172, pp. 135–140, 2012.

[12] E. Fortin and F. L. Weichman, “PHOTOCONDUCTIVITY IN CUPROUS OXIDE SINGLE CRYSTALS,” Can. J. Phys., vol. 40, no. 12, pp. 1703–1713, 1962.

[13] F. Marabelli, G. B. Parravicini, and F. Salghetti-Drioli, “Optical gap of CuO,” Phys. Rev. B Phys. Rev. B, vol. 52, no. 3, pp. 1433–1436, 1995.

[14] F. A. B. F.P. Koffyberg, “A photoelectrochemical determination of the position of the conduction and valence band edges of p-type CuO’’,” J Appl Phys, pp. 1173–1177, 1982.

[15] B. Raton, CRC Handbook of Chemistry and Physics, 86th Ed. CRC Press, (2005).

[16] R. A. Smith, "Semiconductors", Cambridge University Press, (1987).

[17] D. A. Newman "Semiconductor Physics and Devices", Basis Principles, Richard D. and Irwin, Inc., USA, McGraw-Hill companies (1990).

[18] G. Hass, R. E. Thun “Physics of thin film”, Vol. 2, (1964).
[19] O.S. Heavens “Thin Film Physics”, John Wiley and Sons , New York , (1970)
[20] H. M. S. and A. F. Turner, “No Titl,” Appl. Opt., p. 147, 1965.

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