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The effect of annealing on the optical properties of (Al$_2$O$_3$) thin films prepared by chemical spray pyrolysis

A thesis

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By

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الأهداء

الى بلدي الجريح (العراق) وشهداءه الأحرار....

الى من أفتخر بحمل اسمه...الى من يحرص على راحتي... الى السند و العمد.

والدي الحبيب

الى تلك السفينة التي أثقلتها أمواج الحياة...والتي أتعبتها أعاصير الزمن... فلم تبالي في ايصالي الى شاطئ الأمان.

والدتي الحبيبة

الى الدم الجاري في العروق...ونبضات القلب...أمي الثانية منبع العطف والحنان.

خالتي الدكتورة فاتن

الى النجمة الساطعة في حياتي...الى من تحلو الأيام بوجوده... الى عزيز قلبي الذي أبعدته الأيام عني.

أخي مصطفى

الى الزهور المتفتحة...الى أعز ما أملك...الى شذى المحبة الذي لايغنى.

أخي علي وأخواتي

الى كل أساتذتي وأصدقائي...والى كل قلب ينبض بالحب من أجلي...

أهدي ثمرة جهدي المتواضع هذا

مع حبي وأعتزازي

عبير

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Abstract

The recent study deal with the structural and optical properties of Al_2O_3 thin films prepared by the chemical spray pyrolysis technique at glass substrate(450°C) and studying the effect of annealing at different temperatures (500,550,600) °C on the optical properties.

The results of X-ray diffraction showed that the prepared films are polycrystalline, the study of optical properties included the record of transmittance spectrum of the films with the wavelengths range from (300-900)nm, and then measuring the forbidden energy gap of electronic transitions where it was found that the values of the forbidden energy gap of both allowed and forbidden transitions are (3.4)eV and (2.5)eV successively and it was (1.6)eV for the allowed indirect transition. When annealing the Al_2O_3 thin films, the values of the forbidden energy gap of the allowed and forbidden of direct transitions are (2.7)eV and (3.6)eV and it is (1.9)eV for the allowed indirect transition. Also, absorption coefficient , reflectance and optical constants such as extinction coefficient, refractive index, dielectric constants with it's two parts real and imaginary and optical conductivity as a function of photon energy have been studied, the study showed that the annealing caused an increase in energy gap values, reflectance, transmittance, refractive index and real part of dielectric constant, and a decrease in the values of absorptance, absorption coefficient, extinction coefficient, imaginary part of dielectric constant and the optical conductivity.

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Experimental work

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Results and discussion

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List of symbols

Symbols		Units
A	Absorpance	—
B	constant proportion to the density of state in conduction and valence band	—
c	Velocity of light in vacuum	m/s
d	Distance between two successive crystal planes	Å
e	Electron charge	C
h ν	Photon energy	eV
Ec	Energy of conduction state	eV
Ev	Energy of valence state	eV
E^o_g	Forbidden energy gap(optical energy gap)	eV
E_{ph}	Phonon energy	eV
h	Planck constant	J.s
θ_B	Bragg's angel	Degree
λ	wavelength	nm
k_B	Boltzman's constant	J/k
$I_\circ$	Incident intensity	—
I_x	Transmittance intensity	—
K	Wave vector	—
M	Mass of material film	gm
N	Complex refractive index	—
n	Refractive index	—
k	Extinction coefficient	—
α	Absorption coefficient	cm^{-1}
ε	permittivity constant	—
σ	Conductivity	$(\Omega.cm)^{-1}$
ε	Dielectric constant	—
v	Velocity of light in medium	m/s
t	Film thickness	nm
V	Volume of distilled water	ml
M	molar concentration	mollary
n	degree of refraction	—
T	Transmittance	—

Chapter One

Introduction

1.1 Introduction

The physics of thin films were considered to be an important branch of solid state physics which then became an individual branch in physics.

The expression (film) is using to explain a layer of thickness ranging between tens of nanometers and several micrometers. All researchers participated that the thickness of thin film is very small and less than (1) micrometer [1].

The study of thin films attracted the consideration of numerous researchers since the seventeenth century, a lot of researches were accomplished in this aspect which connected with famous names like Boyle, Hook and Newton. The practical side of thin film was developed during the nineteenth century by the scientist Jamin, and Drude was interested in the theoretical side.

The study of physical properties was first started at the 20th century and the researches made a fast jump in this aspect [2]. Recently, semiconductor thin films have attracted much attention in industrial, practical fields since it contributed clearly in the progress of electronic fields, most parts of electrical circuits were substituted by thin films taking its place and giving the same properties with a better efficiency as in resistance, capacitance, condensers, filters, detectors, transistors and electrical keys.

Also, thin films entered in several industrial applications which contributed effectively in the progress of solar cells, optical detectors, and different kinds of electronic devices , while for optical applications , thin films have been used in interference operations which used in photography, copying apparatus, they have been used as optical filters which itself included designing mirrors and antireflectance [2].

1.2 Method of preparing thin films

The wide and important applications in thin films field incite researchers to introduce different methods to prepare the films, according to the scientific progress, the method of preparing thin films also revoluted and became on a high degree of accuracy in specifying the thickness and homogeneity of film. Some of these methods are suitable to a certain materials and not suitable for others, some of them are simple and the others are complicated. Generally, the method of preparing instead of another depends on many factors such materials used and the field of using thin films can be divided into two principal kinds:

$1^{st.}$ Physical methods which include:

      1. Thermal Evaporation Method in vacuum.

      2. Sputtering method.

2nd. Chemical Methods which include:

      1. Electrical Deposition Method, which includes:

      a. Cathodic Films.

      b.   Anodization films.

      c. Electroless deposition.

     2. Chemical Vapor Deposition (C.V.D).

     3. Chemical Spray Pyrolysis Method.

Chemical spray is considered to be a chemical method, in summary, the solution of the desired material (to be a thin film) sprays on a hot substrate at a certain temperature depends on the kind of material used, a chemical reaction takes place between atoms of the material and the hot substrate, and that moment thin film is formed [3]. It is also possible to control the average of deposition (thickness of thin film) through controlling the number of sprays, and under suitable

circumstance, thin films prepared by this method have a strong adhesion with substrate, also, they are of good properties so that they can be used in many application such as solar cells, detectors and Sensing.

Hottel and Hanger were used this method for the first time in solar cells at 1959, they prepared thin films of blank of cupper deposited on Aluminum substrate [4].

Features of this method are :

    a. It is considered to be commercial since it is low cast.

    b. Can be used under normal atmospheric conditions.

    c. A high melting point thin film can be prepared by this method.

    d. A homogenous thin film with large area can be prepared by this method

    e. This method is considered to be suitable to prepare the oxides and sulfates materials [5].

1.3 The crystalline structure of thin films

The crystalline structures of most solid materials including thin films are polycrystalline. It consists of a large number of a small volume of crystals, and in thin films, the small crystals can be formed as follows:

When the material of thin film becomes cold after heating to a high temperature becomes crystallized where grains of small volume begins to formed in a certain regions in the material, these regions are called centers of collective nuclei and this numbers linearly proportional with the rate of cooling, and each atom takes it`s location (exact location) in the lattice of these centers under the condition that the temperature of the substrate should be at room temperature, but if it`s degree is less than temperature, the motion of atoms become slow which will not allow them to take their right places (exact) in the lattice and then no small crystals performed and the structure of the film will be random [6].

1.4 Crystal Growth

The surface of the substrate consists of a layer of atoms separated by vacancies, and when the atoms of material fall on the substrate they will occupy sites in these vacancies as shown in figure (1-1), these atoms which reach to the surface of substrate and which has taken sites inside vacancies will consist with the atoms of substrate surface the first layer which separate between the next deposited layer and the surface of the substrate, this separation layer has the effect of changing the properties of the material in its shape as a thin film and its shape as material in its ordinary coordinates. The thickness of thin film when deposition completed has an additional effect in the specification the physical properties of thin film, and in a case of a thin film of a semiconductor there will be a number of charge carriers which have a fixed free path, if the average of the free path of charge carriers is greater than the thickness of the film, then the number of collision of carriers with the surface of the film increase and this causes an increment in the average of scattered carriers thus, the thickness of a thin film controls some of electrical properties [7].

Atoms on the surface of
the substrate
The precipitate atoms
Adsorption locations
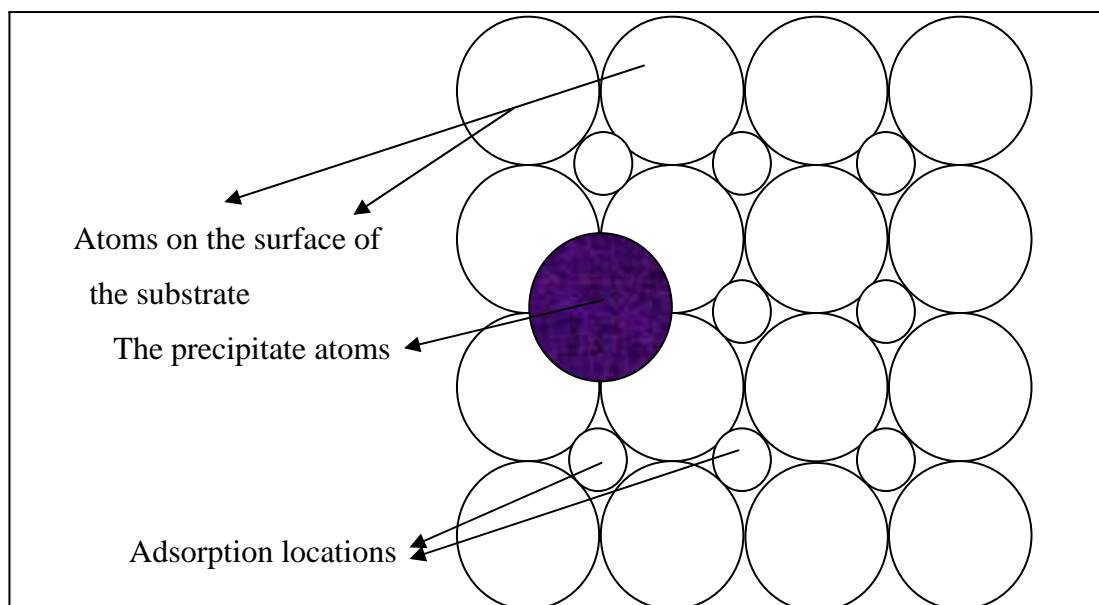
Fig. (1-1): precipitate materials atoms on the surface of the substrate [7].

The atoms of material deposited on the substrate may not stay stable in its place, it may have a chance to evaporate and escaping from the surface of the substrate or it may go to another place. In order that the atoms of precipitate can move to different sites on the surface of the substrate, they should have energy to slide on the surface with knowledge that the passed on the surface does not exceed tens of nanometers. But, in case of evaporation, atoms need more energy to overcome the forces of binding with other atoms and escaping from the surface, and for this, atoms of precipitate of high energy do not stay at one site when they reach the surface of the substrate and have the possibility to collide with other atoms, and as a result of this collision a couple of binding energy may appear that may exposed to separate from or evaporated or it may collide with a third atom consisting a triple bonding which is more stable than the previous one because the bonding energy between it's atoms is greater and increases with the increasing of bonding atoms, and by this method a groups of atoms appear. The continuity operation of groups growing is called (the growing stage) and during this growing, the surface of thin films will not be flat because the shape of atomic groups is limited by two principal effects which are [6]:

A surface effect (analogy to surface tension) which makes the atomic groups spherical, the other effect is the absorption effect in the surface of the substrate which tries to make the surface of the substrate flat, and because of these two effects a stress and strain regions will appear in the film. The growth of atomic groups is continuing so that each group will unites with the other groups which surround it and large single group will appear, and when the substrate be filled by the precipitate material the film becomes full and these stages are called continuity. Figure (1-2) explain the stages of thin film forming.
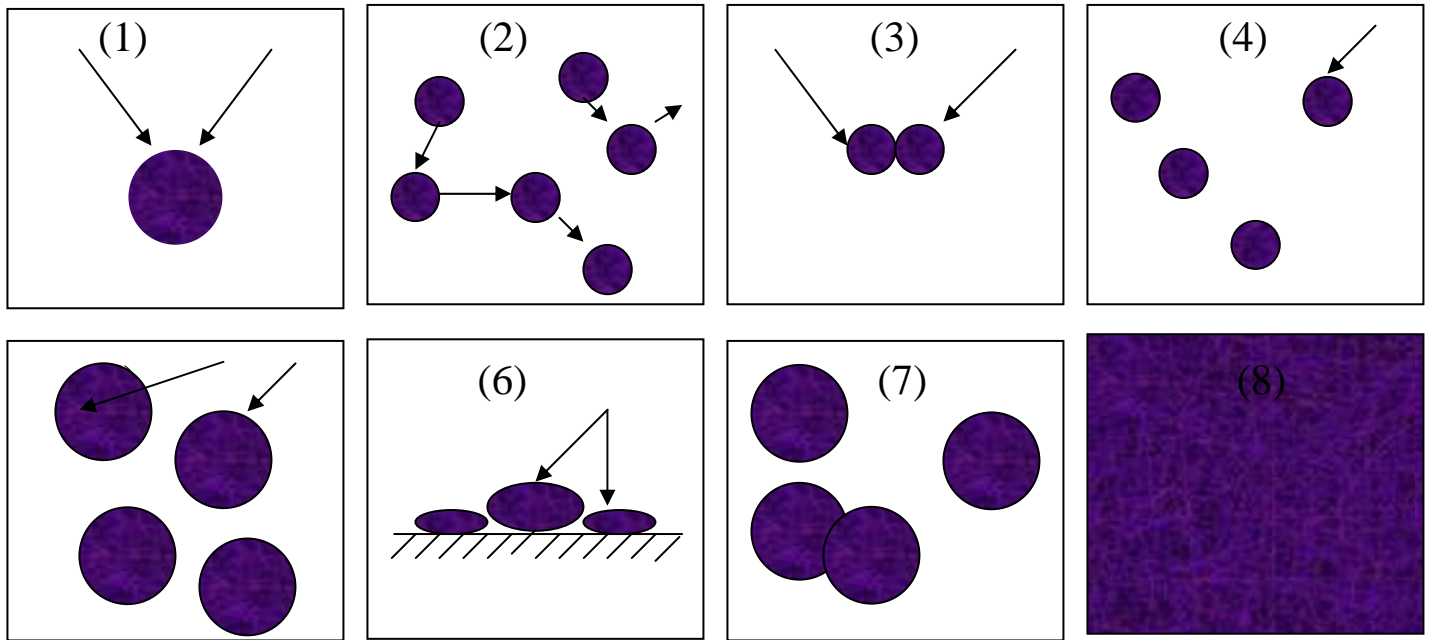
Fig. (1-2): Stages of thin film forming [6]

1.5 The effect of drops size on the nature of the chemical spray pyrolysis films

The size of drops has an important rule in getting a best operation of particip-atation, nevertheless, it is not easy to get the suitable size of drops, also, the thermal behavior depends on it's mass. Fig (1-3) shows different operations which the size of drops coming out from the spraying nozzle.
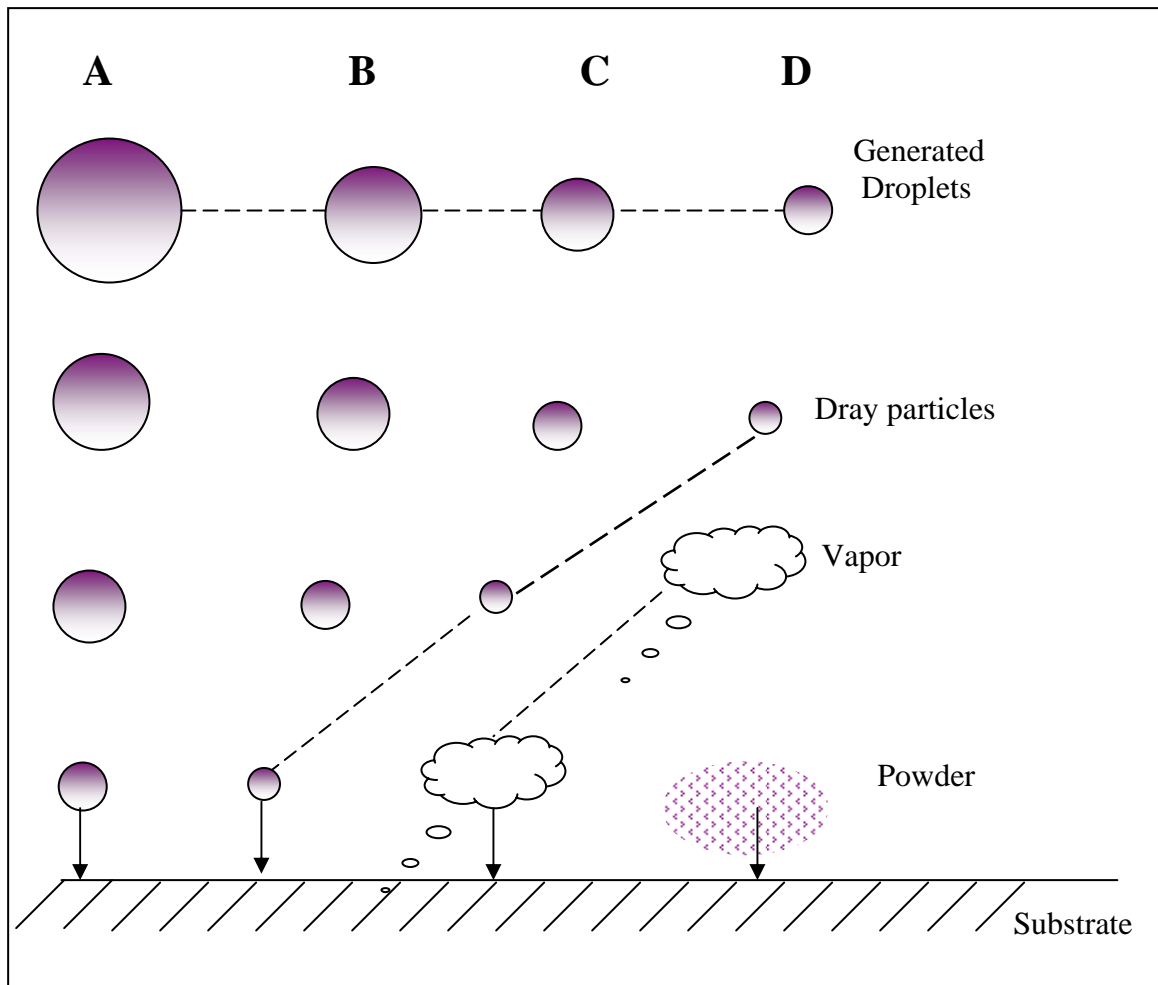
Fig. (1-3): participitate operation of different size of drops [7]

Process (A): the drops are large so that the absorbed temperature from the surrounding medium will not be enough to evaporate the falling solution towards the substrate and at the moment when the drops reach to the substrate, the solution evaporates leaving a dry participitate, and during the evaporation a part of the solution breaks up at this point the temperature decreases and the surface become rough, hence, the formed film will be nonhomogenous.

Process (B): when the drops dry before arriving the substrate, some particles evaporate and this local evaporation of particles breaks up a part of heat less than that in operation (A).

Process (c): this includes the classical chemical vapor deposition process which leads to better properties of films because at this process the solution evaporates at the nearest point of the substrate and before the arriving of particles, the time is enough to increase the temperature to the temperature of the medium where they boil and evaporate or sublime and reaction takes place and includes:

◈ Spreading of reaction particles on the surface .

◈ Adhesion of particle or many particles on the surface.

◈ A surface diffusion, chemical reaction, recombination with the lattice and the spreading of molecules to the vapor space [7].

process (D): represents the behavior of the small drops which the solution mostly evaporate completely away from the substrate and the drops become small crystals forming a participitate look like a powder on the substrate making the film disorder and reduce the efficiency of participitation .

From the previous presentation, it is clear that the best conditions to form a film of high participition efficiency will be when the size of drops as shown in process (C), practically it is not possible to fix the precise conditions of this process, furthermore, transitions happened from the homogeneous reaction to the nonhomogenous reaction because there is nolimited size of drops [8]. In this project, the previous condition was taken carefully into account as much as possible, the product films were so soft, strongly stick and without defects which means passing stages (A) and (B).

1.6 The grain growth

Atoms transfer through grain boundried as well as it`s transfer inside crystals and in both directions, and the transfer number of atoms takes place across the wall of grain boundaries in equilibrium, i.e the number of atoms which passes in one direction equal to that which passes in the opposite direction. But if the wall is curved, there will be two regions arround this curve, one of them is concave and the

other is convex, the concave region is more impaction by atoms rather than that of the convex region, therefore, the number of atoms in the concave region is more than the adjacent atoms and hence their energy is less than that in the concave region as shown in figure (1-4), consequently, the transition of atoms through the grain boundaries is not similar [9]. By this method the production of transition of atoms through the grain boundaries takes place, i.e the transition of the boundaries themselves toward the center of curvature, and the driving force to this transition which reduce the area of the grain boundaris and the atoms energy in the crystal stracture as a whole and as a result of this, the boundaries shrink toward the center of curvature [10]. Since the small grains will expand at the expense of the vanishing of small grains as in fig. (1-5), the operation is called the grain growth [11].

All the crystal materials, metallic and nonmetallic, submit to experience to the grain growth property, so with the increasing of temperture, the grain growth increases since the spreading transition proportional exponentially with the absolute temperture, thus, we find that the increasing of grain growth is larger than the grains which formed at high temperture. However, decreasing the temperture after the grain growth will reduce the speed of grain growth but it does not reverse the operation at all.
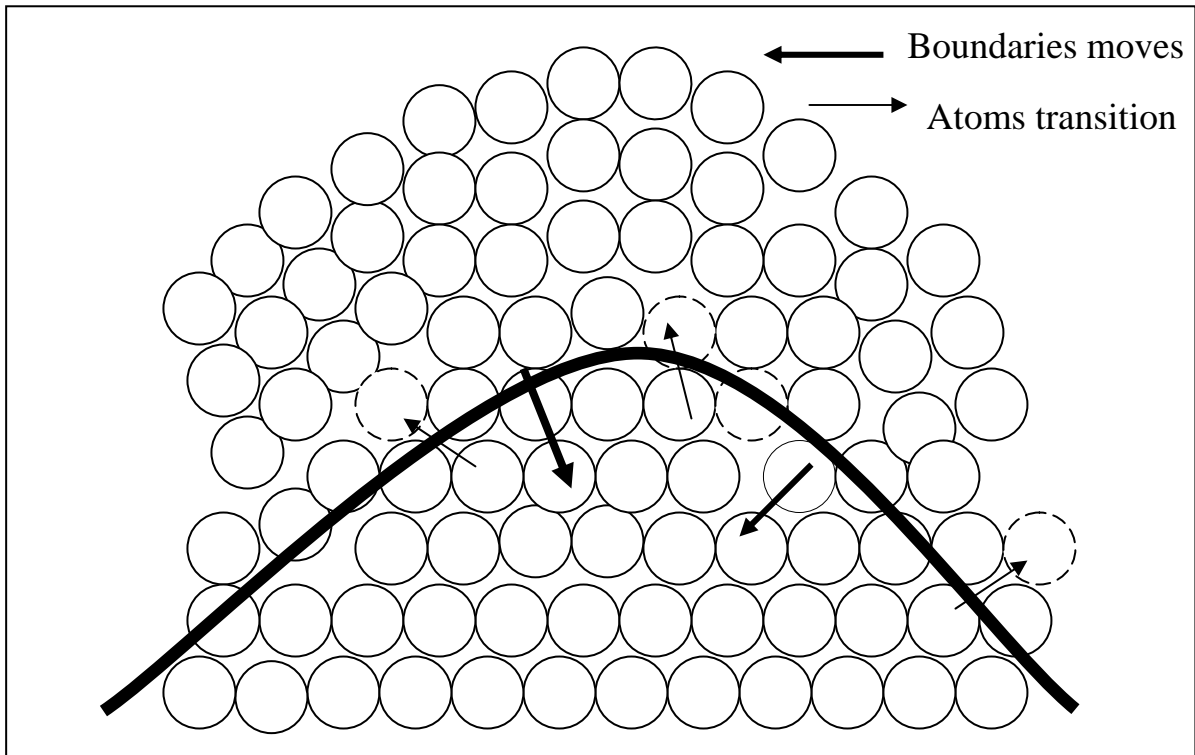
Figure (1-4) the transition of the grain boundaries to the center of curvature, where the atoms moved to the concave surfaces which are more stable [10].
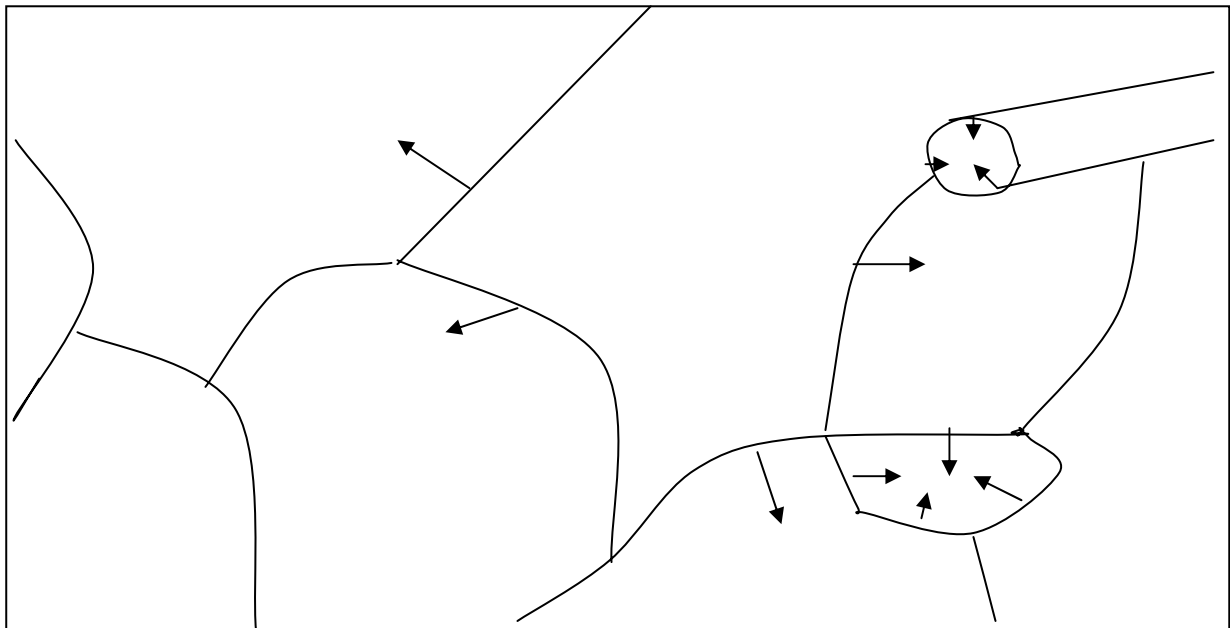
Figure (1-5) the grain growth, since the boundaries moved towards the center of curvature, then small grain vanishes [10].

The growth of crystals is spontaneous growth and this is due to the tendency of metal to reduce it's free energy and make it as low as possible because this will increase it's stability and the growth will be on the expense of small crystals where the large crystals are more stable from the point view of thermal dynamic [12].

1.7 Factor affecting the grains size:

One of the most important result of annealing is the change which takes place in the size of grain boundaries and which limited at the same time the properties of the material (electrical and mechanical), the size of the grain depends on two principal factors which are [13]:

The number of crystalline returning (N) and the linear speed of growing of new crystals (Gc), where N is measured by the number of new crystals which appear per unit time and size unit, while,(Gc) represents the speed of moving of crystal boundaries, therefore, the size of grain depends on the ratio between(Gc /N), so, as (N) increases and Gc decreases, we get small grains become larger because of the grain growth, therefore, it is possible to specified the most important factors which affect to the size of the grain:

Temperature: the increasing of annealing temperature will increase the amount of (N) and (Gc), and this will lead to an increase in the size of the grain until it reaches the limit where it stops because of the approach of grain's size with the thickness of sample [14].

Time: there is a relation between the temperature of annealing and the grain size at the stability of keeping time in oven, where it is clear that in- creasing the period of annealing means increasing the grain size after the recrystalline operation [14].

Effect of impurities: if there are impurities, the chemical structure affect to the grain's size, where the impurities will form a ready center of nuclei which polarize

the atoms to them and this will lead to create a large number of grains of small size[15].

1.8 Aluminum oxide

Aluminum oxide is an amphoteric oxide of aluminum with chemical formula Al_2O_3. It is also commonly referred to as alumina or aloxide [16], in the mining of ceramic and materials science communities. Al_2O_3 is an electrical insulator but has relatively high thermal conductivity, and can obtained it by heating $Al(OH)_3$ .Corundum is the naturally crystalline form of Al_2O_3. The major uses of specialty aluminum oxide are in refractories, ceramics, polishing and abrasive applications. It is widely used in the fabrication of superconducting devices, particularly single electronic transistors and superconducting quantum interference devices (SQUID), where it is used to form highly resistive quantum tunneling barrier. Figure (1-6) shows the crystalline structure of alumina and table (1-1) shows some of physical and chemical properties of Al_2O_3.
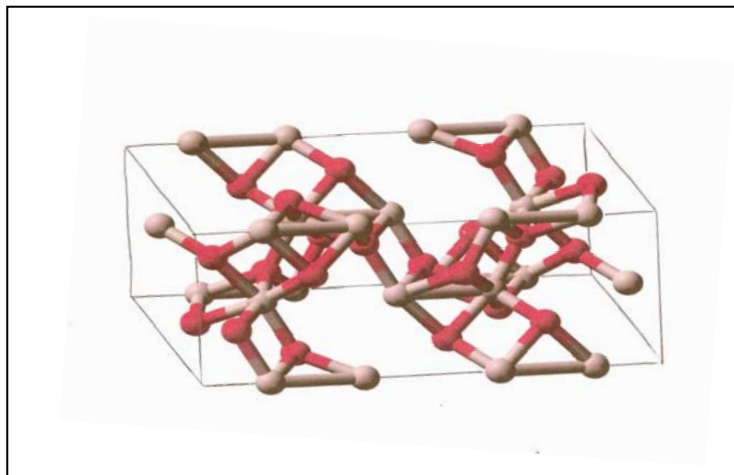
Figure (1-6): the crystalline structure of Al_2O_3 [16]

Table (1-1): some of physical and chemical properties of Al_2O_3 [14]

Colour	Appearance	Melting point (°C)	Boiling point (°C)	Density g /cm³	Molar mass g /mol
White	Solid	2054	2980	3.97	101.96

1.9 (Annealing)

The operation of exposing a film to a specified temperature in a specific limited time is called the thermal treatment, this operation can take place in vacuum or in the presence of a specific gas or in air [18]. The operation can be done either by using thermal oven, then it is called classical thermal annealing or by using the technique of laser and then it is called the fast thermal annealing, and it's influence differs according to the type of material, conditions of heating and the surrounded gas. The thermal heating gives atoms the sufficient kinetic energy to re-order themselves in the crystal lattice, and then lead to the organizing of the crystal structure of the material and reducing the crystal defects inside it, this is why the thermal annealing is used sometimes to get the crystalline state of materials in case that the prepared thin films are amorphous, also, the annealing of thin films may cause a decrease in the resistivity of the film as a result of localized states inside the energy gap hence, increasing the conductivity, or the annealing may cause an increase the resistivity of the film and then reducing the conductivity as a result of reaction of the material of the film with Oxygen during the operation of annealing in air [19]. Several studies have been written about the effect of annealing on some physical properties of thin films Hsiuang and Wang [20] found the effect of annealing on amorphous semiconductors to be on two stages, first includes the reducing of vacancies and the disorder of atoms (which is at low temperature), and the second stage includes the suspended bonds and the relaxation structure (which is at high temperature).

1.10 Literature Survey

The researcher tried hardly to find a researches concern with her project but she did not find any of them expect the research accomplished by Khudheir A.M.

Khudheir A. Mishjil, 2003[21], has prepared a thin films of Al_2O_3 by chemical spray pyrolysis method and studied the optical properties and dc conductivity, the results showed that the film have a direct electronic transition allowed and forbidden of energy gap and have two activation energy for dc conductivity (0.00255 eV and 0.527 eV).

1.11 Aim of the research

The aim of the research is to prepare a thin film of Al_2O_3 by chemical spray pyrolysis method and studying the structural and optical properties and study the effect of annealing on the optical properties and energy gap to know the application fields of these films in solar cells and gas sensors.

Chapter two

Theoretical part

2.1 Introduction

This chapter includes a general description of the theoretical part of the recent study concerning the ideas, theoretical concepts, scientific classification and the relations and mathematical laws which will used to explain the results.

2.2 Bragg's Law

Any comprehensive study to any solid material is for understanding it's electrical behavior and other properties, first we must begin with it's structure which can be known with atomic arrangement by studying X-ray diffraction [22].

X-ray is an electromagnetic waves with wavelengths lies between (0.1-10)nm less than that of ultraviolet wavelength by about (100)nm, it can be effected crystal lattice in which the atoms or molecules are separated by distances approximately to (10^{-10} m), and diffraction is the deviation of any ray from it`s path because of it's interaction with matter, so, if the scattered particle or photon losses a part of it's kinetic energy, then the scattered will be inelastic, and if there is no change in energy, the process will be elastic scattering[22]. W.L Bragg was able to deduce his law which stand on the basis that the difference in path between two scattered rays of the same phase equals to whole numbers of X-ray wavelength, and it can be written as [23]:

$$n \lambda = 2 d \sin \theta_B \qquad \text{----------------(2-1)}$$

where;

θ_B : Bragg's angel

λ : wavelength in nm

d : interplanner spacing

n : spectrum order (n = 1,2,3,…).

The main condition of Bragg's reflection is that($\lambda \leq 2d$) [22]. From equation (2-1), one can notice that two variables which are (θ_B) and (λ) and their values can be well as fixing the defects exist in the crystal structure.

The average grain size (g.s) of crystalline material has an important role in determining the properties of material which can be find from the spectrum of X-ray taking into account full width at half maximum [FWHM] which is given by a Scherer relation [24]:

g.s = (0.9 λ) / (B cosθ)   ...(2-2)

Where:

B: full width at half maximum measured in radian

θ_B: Braggs angel.
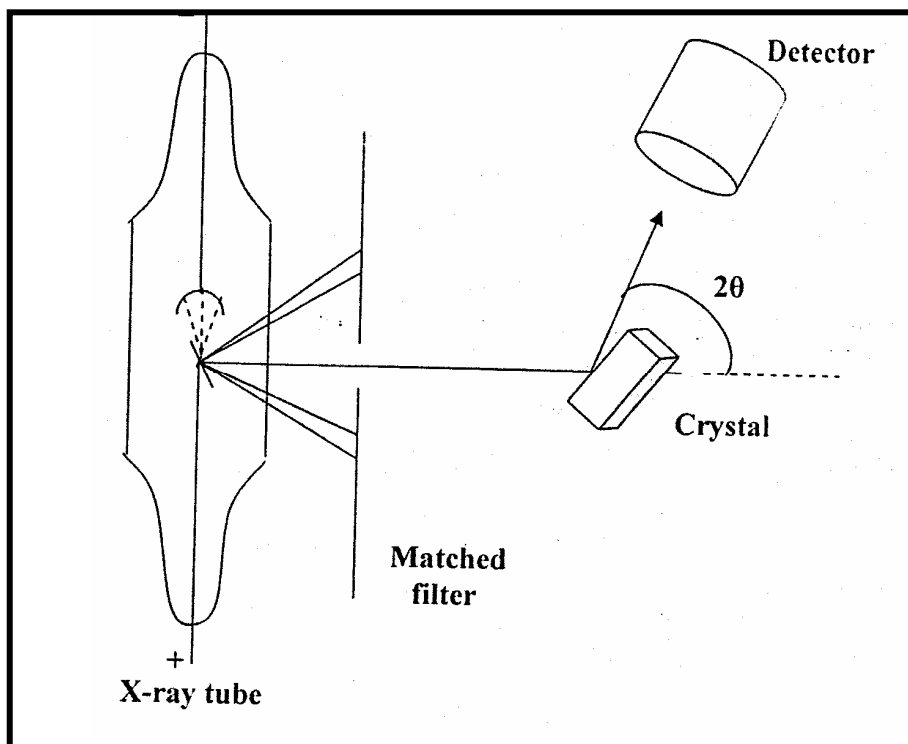
Figure (2-1): analysis by X-ray diffraction [22]

2.3 The crystal structure and direction

In most solid material, the atoms organized in a well-ordered form, so that the material appears as it is built of construction units of organized geometrical shapes, and in this well-ordered composition, it is possible that a complete crystal might be built with a continuous packing of the construction unit, and these units are called the primitive cells, these units include the required information to rebuild the atoms the primitive cells, these units include the required information to rebuild the atoms sites in the crystal, mostly these cells take geometrical shapes differ from one material to another where as they keep the symmetry of the unit cell to the material itself, their repeating units in three dimension will produce a large crystal of a solid material.

This unit cell can be represented in crystal materials by the level of three-dimensional surface and by the facing angles (α,β,γ) as in fig. (2-2). The directions of planes inside the crystal can be expressed in terms of the organization of the unit cell, and by using Miller indices which can be calculated by following successive mathematical steps.
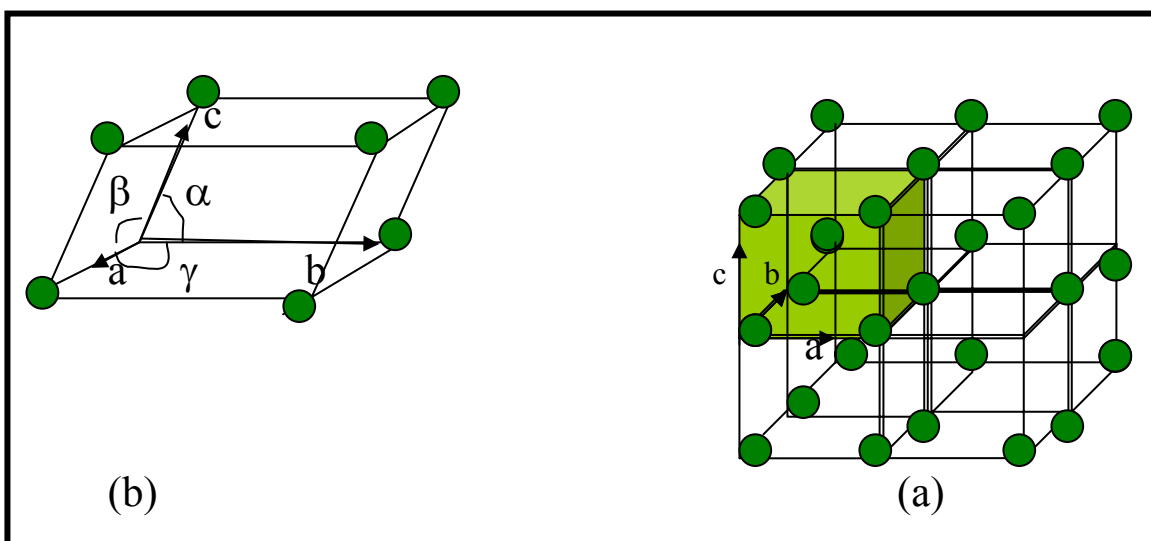
Figure (2-2) :(a) unit cell in a crystalline lattice
(b) unit cell of parallel surface [25].

2.4 Crystal defects

In an ideal crystal of no defects, the material atoms arrange in all directions without any disorder in their sequences, but perfectly there is no crystal without defects, this is why any deviation or disorder in any crystal about it's ideal periodic lattice or it's ideal structure is considered to be a defect or imperfection for this crystal, or it means the discontinuity in the pattern of atoms or the crystals ions, and this is why the word defect or disorder in any crystal refers to irregularity in the crystal structure [22]. Defects formed during the operation of the crystal growth, therefore getting rid of all impurities and defects is considered to be impossible, but, it is possible to reduce it's defects by using an active methods in purification and crystal development, whatever the matter is, in some cases, crystal defects might be interested as in the case of doping by strange atoms or impurities. Researchers to be able to add atom's impurity like Magnesium (Mg) in the crystal structure of Lithium fluoride (LiF) to be used as a probe to measure the amount of expose ray of those who work in this field several times instead of the classic card which can be used for one time only, also, using the crystal(LiF/Mg)which is called thermoluminescence dosimetery TLD-in atomic medicine and measuring the amount of Gamma rays exposed to patient [26]. Controlling most of important properties of the crystal depends on the nature of crystal besides the defects inside it, and to represent that :

(a) Conductivity of some semiconductor crystals being related in a complete view to the chemical impurities concentration in them.

(b) Luminescence of any crystal being combined generally with the   presence of impurities inside it.

(c) the colors that distinguish one atom from another is related to it's constructed defects.

As a summary the crystalline defects can be in different forms [27]:

The occupation of atom to a site which is not a localized to her between atoms (figure 2-3a).

The absence of atom from it's site, thus, leaving a vacancy in the crystal (figure 2-3b).

The absence of long chain of atoms (figure 2-3c), and in this case the atoms rearranged themselves in a way which reduces the distortion of the crystal, where the atoms deviated to close the produced vacancy at which the atoms appear to be at the edges of the crystal as it is seen to be deviated from it's original place.

The presence of atom's impurity in the crystal.
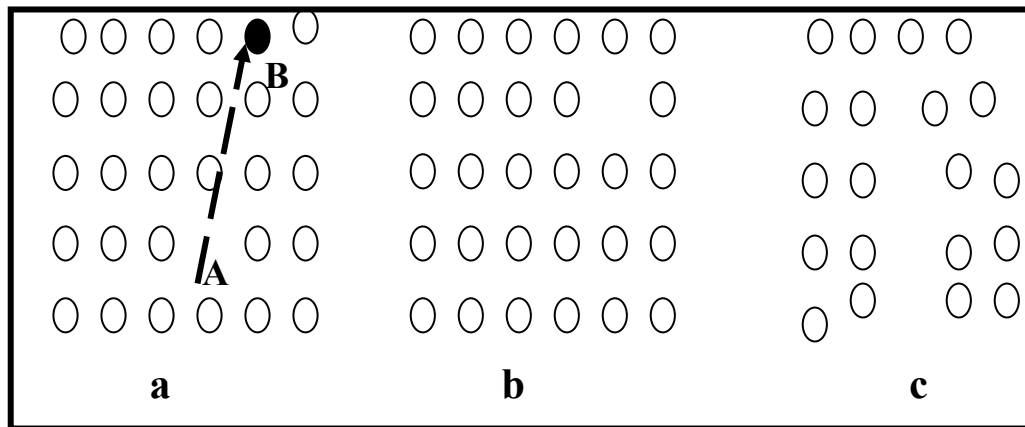
Figure (2-3) some kinds of crystal defects [27].

2.5 Energy bands in solid materials

The energy is considered to be of large useful in specification the properties of any solid material, so as to understand the principle of operation of new electronic model where it clarifies the mode which electron moves in the material [28].

Consider a regular periodic arrangements of atoms in which each atom contains electrons up through the n= 3 energy level. If the atoms are initially very far apart, the electron in adjacent atoms will not interact and will occupy the discrete energy levels, if these atoms are brought close together, the outermost electrons in the n=3 energy shell will begin to interact initially, so that this discrete energy level will split into a band of allowed energies. If the atoms continue to move closer together, the electrons in the n=2 shell may begin to interact and will also split into a band of

allowed energies. Finally, if the atom become sufficiently close together, the innermost electrons in the n=1 level may interact, so that this energy level may also split into a band of allowed energies, the band splitting in the Diamond is shown in fig. (2-4). As the inter atomic distance decreases, states will interact and overlap. At the equilibrium interatomic distance the band have again split, but now four quantum states per atom are in the lower band and four quantum states per atom are in the upper band. At absolute zero temperature, electrons are in the lowest energy states (valence band) will be full and all states in the conduction band (upper band) will empty.
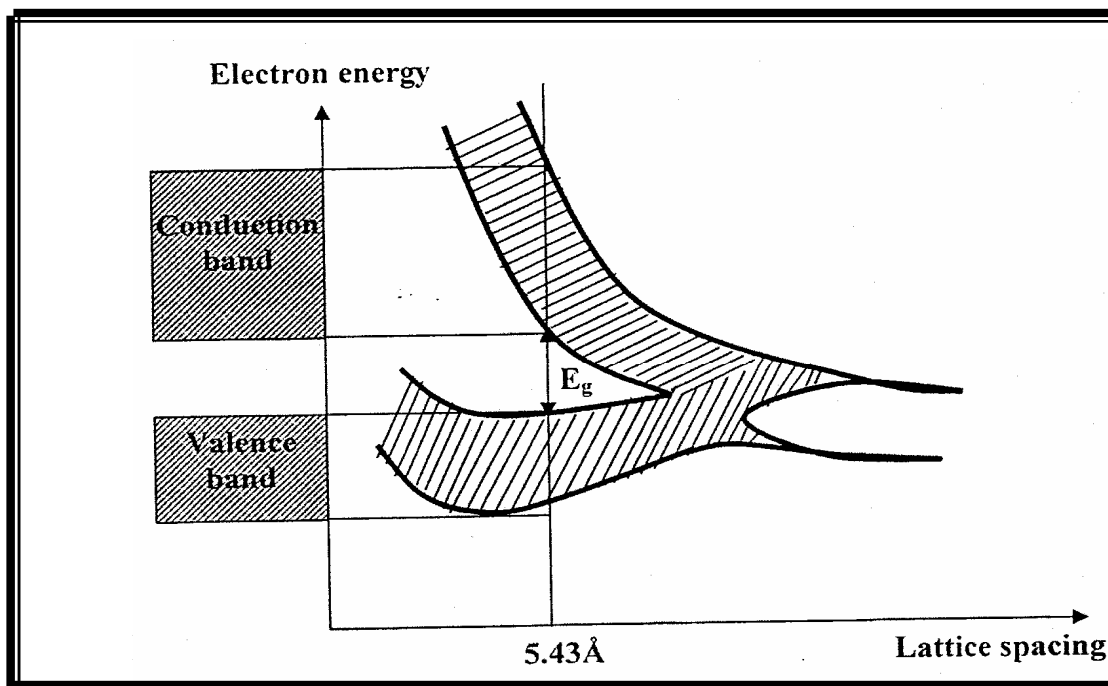
Figure (2-4): forming of bands in solid diamond [29]

Figure (2-5) shows a diagram of energy bands for three kinds of solid materials, conductors, semiconductors and insulators, and as shown from fig. (2-5a), conduction band interfers with valence band in conductors and electrons at the top of valence band can transfer to levels of higher energy when they gain kinetic energy (from the external electric field) and hence the current can move easily and it's conductivity is about $(10^3-10^8)(\Omega.cm)^{-1}$.

For semiconductors which have a relatively variable energy gap about $(0 < Eg < 3.5)$eV [29] as in fig.(2-5b). These materials are considered to be insulators at absolute zero (0K) if the electrons in the valence band have a sufficient amount of energy that can transfer through the forbidden energy gap to the conduction band leaving behind them holes in valence band . The conductivity ranging is about $(10^{-8}-10^{3})$ $(\Omega.cm)^{-1}$.

In insulators, the forbidden energy gap is large, and about (5-10) eV [29] as shown in fig. (2-5c) and have conductivity with about$(10^{-18}-10^{-8})$ $(\Omega.cm)^{-1}$, and all energy levels in valance band are occupied by electrons, whereas all energy levels in conduction band are empty (un occupied), neither the heat energy nor electric field can raise the electrons which are at the top of valance band up to bottom conduction band, that is why these materials can not transfer the electric current [2].
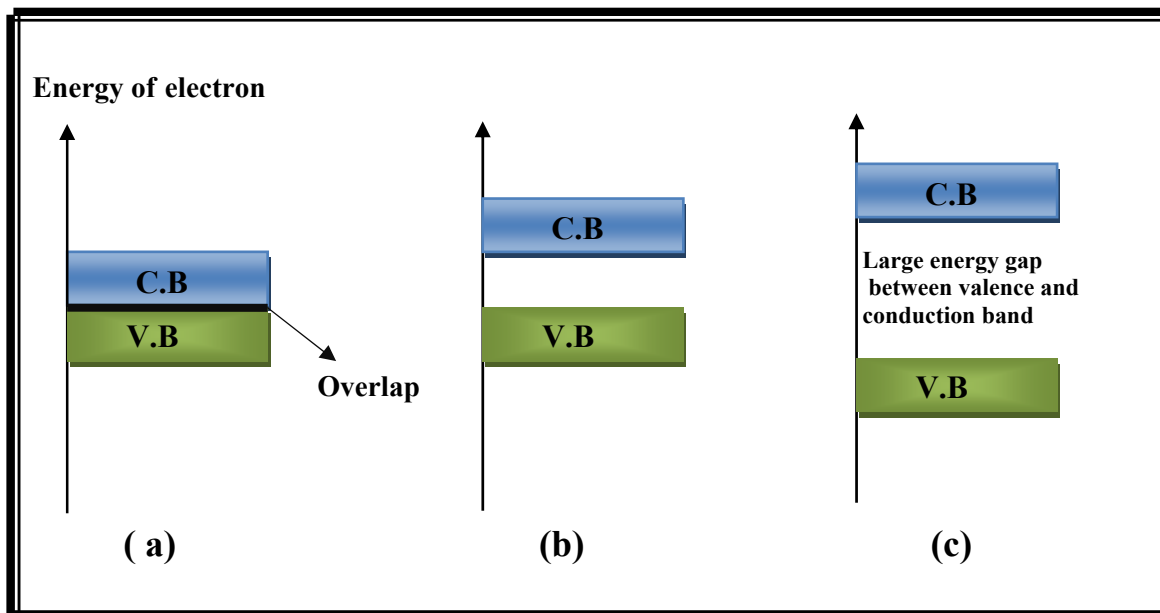
Figure (2-5): energy gaps diagrams in materials [30]

a. Conductors   b. Semiconductors   c. Insulators

2.6 Semiconductors

This branch of science was studied recently during the last few decades, this is because of the requirement of wireless engineering to new materials where the excellent properties of semiconductors arise from the method in which the electric current pass through [30].

Hence, the study of semiconductors become interested by researchers because of the important properties which make them affected by heat, light, magnetic field and the presence of low quantities of impurities which highly affected them. The sensitivity of semiconductors against these factors make them very important materials in electronic applications [31].

2.6.1 Classification of semiconductors

Semiconductors are classified according to it's crystal structure to:

1- Crystalline [32]

(a) Single crystalline

Which is a group of atoms arranged periodically consisting a triple coordinates configuration, and for this it has a kind of symmetry and, it's structure can be considered as a result of a repeated geometrical sample called unit cell which it's structure has a long range order as in fig.(2-6 b).

(b) Polycrystalline

It is a group of crystals which contains a relatively large number of atoms, these crystals are called grains, each one of them has a long-rang order, but as a whole these grains have a short- range order which directed randomly for each other. The region in which the grains meets are called grain boundaries. Polycrystalline semiconductors are thermo- dynamically low stability from that of a single crystalline because the free internal energy is limited by the energies of grain boundaries as in fig.(2-6 a).

2- Amorphous

It's structure characterized as a short range order [33], because they ordered randomly and this is why they do not have the symmetry which exists in crystalline materials and it's structure can not be considered a repetitions of unit cell [33], as shown in figure (2-6 c).
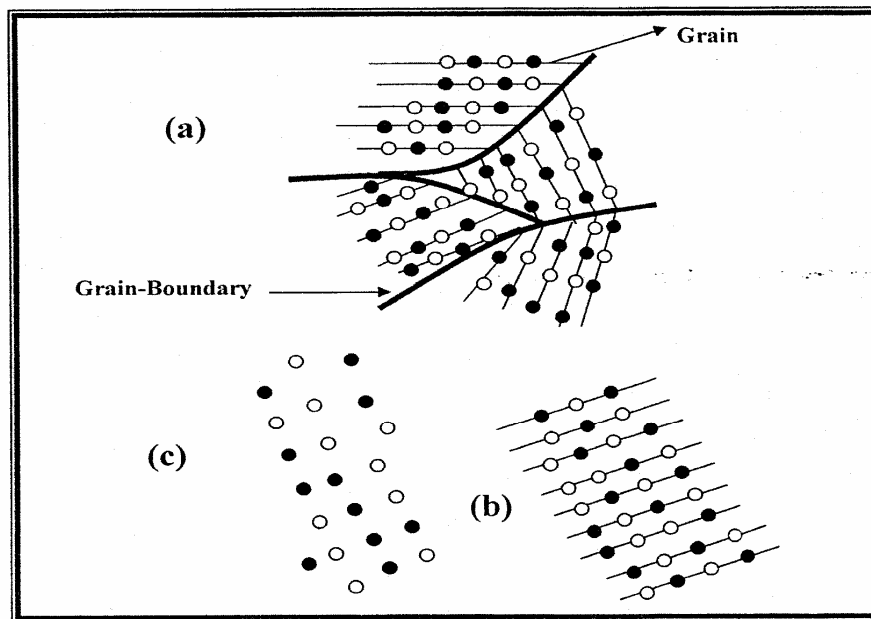
Figure (2-6): characterized of atoms in materials [30]
(a) Poly crystalline   (b) single crystalline   (c) amorphous

From the study of diffraction patterns produced by X-ray diffraction due to materials subjected, it is possible to characterized the crystalline semiconductor from the amorphous semiconductors because the diffraction pattern will be as sharp luminas points in the single crystalline materials [34], as shown in figure (2-7-b) and it will be as thin rings of sharp luminas coincides with each other and concentric in polycrystalline materials, as shown in figure (2-7-c), and as wide rings of low luminas and concentric as shown in figure (2-7-a), and it`s sharpness gradually becomes low and disappeared so fast with the increasing of angle of diffraction for amorphous materials [35].
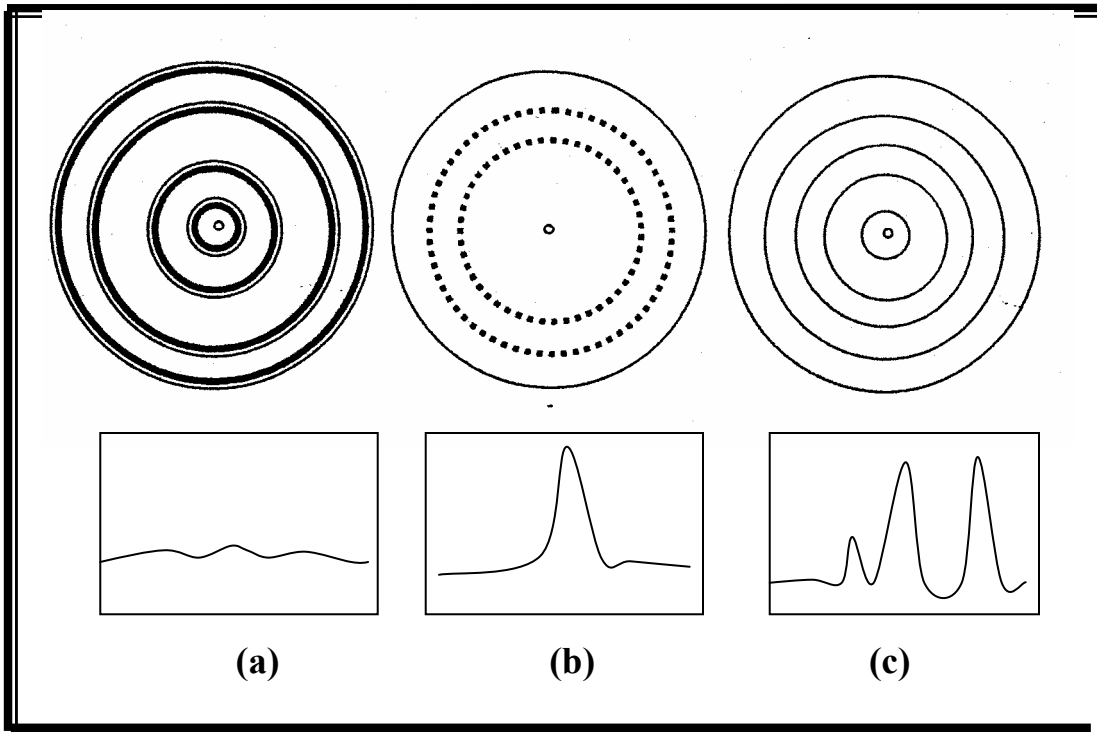
Figure (2-7): X-ray diffraction (XRD) [30].

(a) amorphous   (b) single crystalline   (c) polycrystalline amorphous

2.6.2 intrinsic semiconductors

The materials are insulators at absolute zero temperature but they have an amount of electrical conductivity when their temperature increase or by adding impurities or by making defects in their crystalline structure, these materials have two bands of energy according to the theory of bands in solid materials, one of them is completely filled by electrons which represent the valence band while the other band is empty of electrons and represent the conduction band separated by forbidden energy gap[36], as shown in figure (2-8).

Energy of electrons

Conduction bands

Large energy gap between valence and conduction bands

Valence band

(a) insulator

Conduction band

Fermi level

Valence band

Overlap

Conduction band

Valence band

(b) Semiconductor
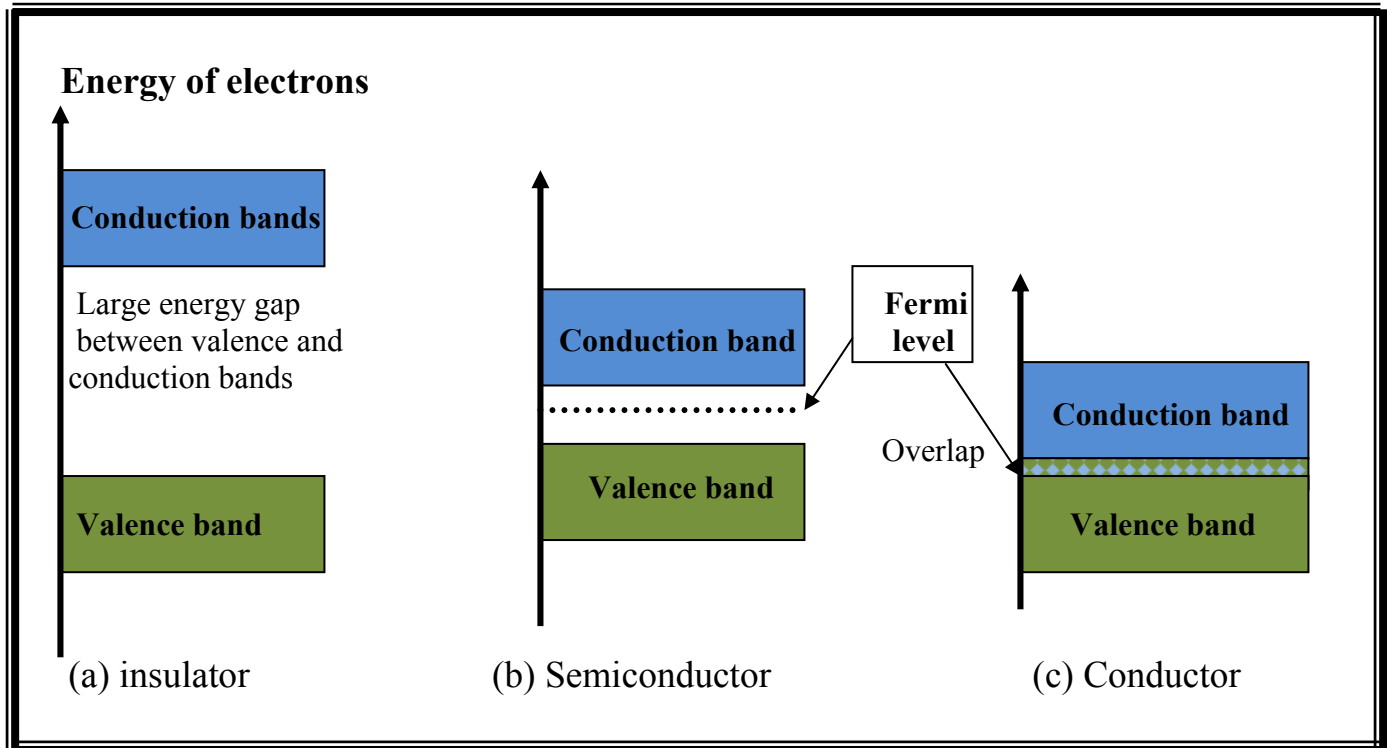
(c) Conductor

Figure(2-8):energy bands diagram in absolute zero temperature for[37]:

(a) insulator,(b) semiconductor ,(c) conductor.

If the temperature increase to a higher degree from absolute zero, some of electrons after gaining a sufficient energy which is equal or greater than energy gap will transfer from valence band to conduction band. When electrons leave the valence band they will make spaces called vacancies [30] these materials are called intrinsic semiconductors which have equal numbers of negative and positive charge carriers {electrons and vacancies}, and figure (2-9) shows the energy gaps of intrinsic semiconductor
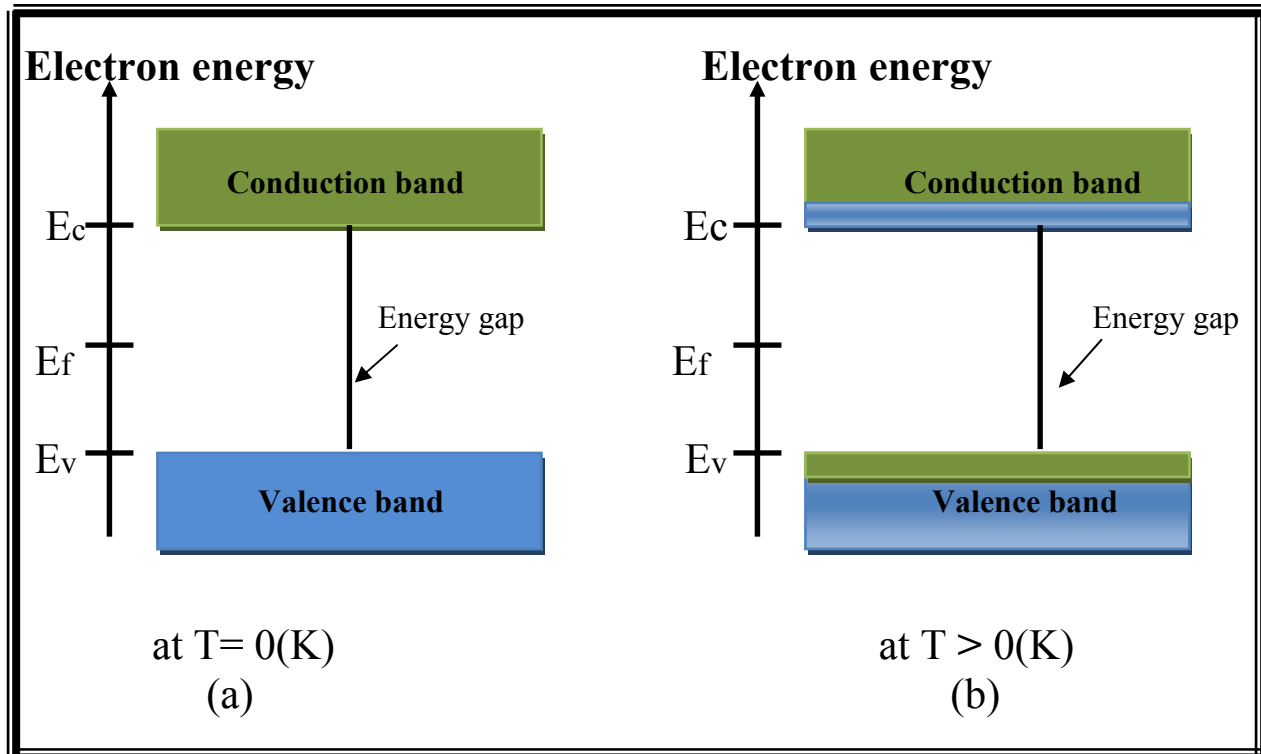
Figure (2-9): the energy gaps of intrinsic semiconductors [38].

2.6.3 Interaction of electromagnetic radiation with matter

When a beam of a monochromatic light incident on a surface of a semiconductor, some of this beam will reflected (R) and the rest of the beam transmitted. The beam of the transmitted light will be absorbed inside the material because it's energy is sufficient to excite the electron, and since there are large number of levels occupied by electrons in valence band and large number of empty level on conduction band separated from each other by forbidden gap, then the probability of the absorbance will be very high when the energy of photon of incident light is larger than the forbidden energy gap, the ratio of photon absorbance is directly proportional with the incident intensity [30], this common physical phenomenon and tends to a decay exponentially in the incident of the monochromatic incident light when it passes through the semiconductor which can be written mathematically as follows [29]:

$I_x = I_\circ \exp(-\alpha t)$ **……** (2-3)

where:

α: is the absorption coefficient and by solving the equation, (α) will be as follows:

$\alpha = 2.303\ (\log I_\circ / I_x)\ /\ t$ **……**(2-4)

Where:

t: is the material thickness.

2.6.4 Temperature and energy gap

The thermal coefficient of semiconductors do not equal zero, thus it's energy gap depends on temperature where it effects the atomic space and then variation of energy gap, it was found experimentally that the energy gap of a semiconductor decrease when temperature increases according to the following equation [39]

$E_g = E_g(0K) - \eta\ T^2 / (T + \mu)$ **……** **(**2-5)

Where :

η and μ: constant and vary from material to another.

2.7 Optical properties

Optical properties of semiconductors are important to understand the mechanism of electron transition between energy bands during the measuring of absorption and transmition of semiconductors. All semiconductor materials common with distinct character which is fast increasing in absorption when absorbed energy of radiation approximately equal to the energy gap which is called the fundamental absorption edge. The absorption edge is the least difference in energy between the highest point in valence band and lowest point in conduction band [36] and it have three regions as shown in figure(2-10)where region A represent high absorptance($\alpha>10$ cm), and B represent exponential region ($1<\alpha<10$)cm , and C represent weak absorption region ($\alpha<1$) cm.

The optical properties of semiconductors films depend on the method and preparation condition, deposition rate, substrate temperature and annealing, since any change in these conditions lead to a deviation of the absorption edge to a higher or lower energies [40].
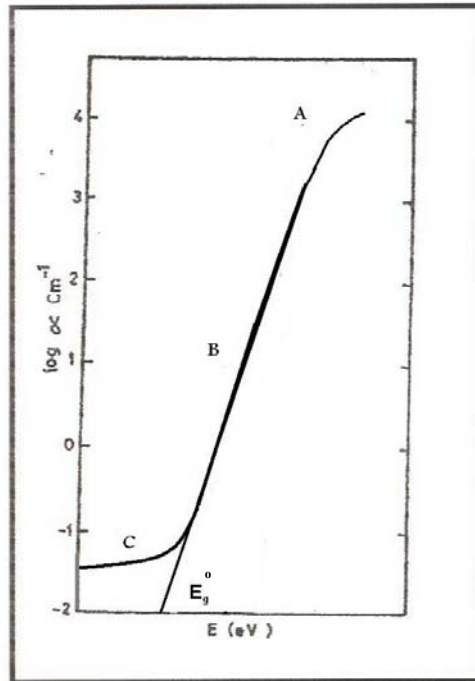
Figure (2-10): base regions on optical absorption edges [40]

2.7.1 Absorption coefficient (α)

Absorption coefficient is defined as the reduction ratio in the flux of the energy of incident ray with respect to distance in the direction of wave propagation inside the medium [41].

Absorption represents the reduction taking place in the energy of electromagnetic radiation when entering a specified medium [37], so, when a light of intensity (I) incident on a film of thickness (t), then the intensity of transmittance ray (I) is given by:

I = I exp($-\alpha$ t)   …… (2-6)

Which defined as Bouger`s equation achieved by him at 1739 which then approved by Lambert, the ratio (I_o / I) represents the intensity of transmittance light through a thickness(t)and connected by the following relation [41]:

$A = \log (I_o / I) = \log (1/T)$ …… (2-7)

Where:

A : represents absorption.

T: represents transmittance.

$\ln (I_o / I) = \alpha t \Rightarrow 2.303 \log (I_o / I) = \alpha t$

$\alpha = 2.303 (A / t)$ ……(2-8)

2.8.2 Electronic transition

When electromagnetic wave interacts with valence electrons, electrons will move to conduction band across the energy gap, the absorption appears when the photon energy absorbed by electron equals or greater than forbidden energy gap ($h\nu \geq E_c - E_v$) and two kinds of transitions occur which are :

2.8.2.1 Direct transitions

Which can be defined as a direct vertical transmission of electron in the space of wave vector of valence band to the conduction band of wave vector values ($\Delta k=0$) where the conservation laws of momentum and energy are achieved [35]. There are two types of direct transitions:

 a- **Allowed Direct Transition**

This transition occurs directly from the top of valence band to the bottom of conduction band and for the same values of wave vector (k) (i.e. the momentum is conserved), the absorption coefficient is given by the relation:

$\alpha h\nu = B \ (h\nu - Eg)^n$ **……(2-9)**

Where : B   constant .

n = 1/2

b- Forbidden Direct Transition

This transition occurs vertically from the areas adjacent to the highest point in the valance band to the points adjacent to the lowest point in the conduction band.

Absorption coefficient is given by the following equation:

$$\alpha h\nu = B \quad (h\nu - E_g)^n \qquad \ldots\ldots(2\text{-}10)$$

Where: B   constant.

n = 3/2

2.7.2.2 Indirect Transitions

The electron transition between valence and conduction bands required a change in crystal momentum, because the momentum variation of electronic transition and this is attributed to the location of energy on the top of the valence band which is far away from the location of energy of the bottom of the conduction band in the wave vector space, so, the transition will not be vertical and it's value does not equal to the wave vector of electron before and after transition ($\Delta k \neq 0$), so the momentum of electron and photon will not be conserved. With the help of a third particle called phonon the system momentum is achieved, this phonon(E_p), gives the momentum needed by the system and the transition occurs from the valence band to conduction band, either by phonon absorption or phonon emission [35] and the absorption coefficient is given by the following relation [42]:

$$\alpha_i (h\nu) = \alpha_e(h\nu) + \alpha_a (h\nu) \qquad \ldots\ldots(2\text{-}11)$$

Where:

α_i: represents the absorption coefficient resulting from the indirect transition.

α_e: represents the absorption coefficient resulting from the emission of phonon

α_a: the absorption coefficient resulting from the absorption of phonon.

When ($h\nu > E_g - E_p$), then $\alpha_e = 0$, i.e. absorption of phonon occurs and the absorption coefficient is given by :

$$\alpha_a (h\nu) = A \quad (h\nu - E_g + E_p)^2 / [\exp(E_p/ k_\beta T) - 1] \qquad \ldots\ldots(2\text{-}12)$$
Where:

A : constant

k_β: Boltzman's constant

T: absolute temperature in (K).

But, if ($h\nu > E_g + E_p$), then $\alpha_a = 0$, a phonon emission occurs, and the absorption coefficient is given by the following relation:

$$\alpha_e\ (h\nu) = A \quad (h\nu - E_g - E_p\ )^2 / [1 - \exp(E_p/\ k_\beta\ T)] \qquad \text{......} (2\text{-}13)$$

Where: A   constant.

There are two types of transitions:

a- Allowed indirect transition

In this type the transition is not vertical from the highest point in the top of valance band to the lowest point in the bottom of conduction band with variation of wave vector, i.e. ($\Delta k \neq 0$).

b- Forbidden indirect transition

In this type the transition is also not vertical but from the adjacent points to the highest point in the valance band to a point in conduction with the variation of wave vector. Figure (2-11) shows these electronic transitions.
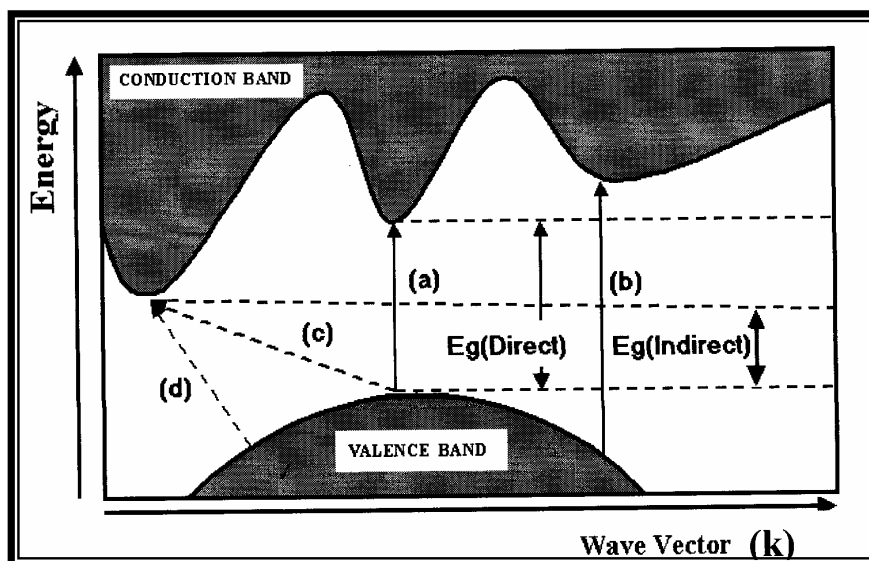
Figure(2-11): electronic transitions [56]:

(a) allowed direct   (b)forbidden direct   ,

(c) allowed indirect   (d) forbidden indirect

2.8 The optical constants

There are many methods to find the optical properties which include (absorption coefficient (α), refractive index (n), extinction coefficient (k), real(ε) and imaginary (ε) parts of the dielectric constant.

2.8.1 Reflectance (R)

The effect of reflectance on the intensity of ray which incident vertically is given by the following relation [41] :

$$R = (n -1)^2 + K ^2 / (n +1)^2 + K ^2 \qquad \ldots\ldots (2\text{-}14)$$

Where:

n : refractive index

K : extinction coefficient, When K =0 then:

$$R = (n -1)^2 /(n +1)^2 \qquad \ldots\ldots (2\text{-}15)$$

If n =0, then R=1 and the semiconductors will be totally reflectance.

The absorbance (A) is connected with reflectance (R) and transmittance (T) as in the following relation [43]:

$$A + R + T = 1 \qquad \ldots\ldots(2\text{-}16)$$

2.8.2 Refractive index(n)

Refractive index is defined as the ratio between wave speed in vacuum to it's speed in medium, i.e.[37]:

$$n = c/v \qquad \ldots\ldots(2\text{-}17)$$

Where: c: speed of light in vacuum , v: speed of light in medium.

Refractive index depends on several factors such as type of materials and crystal structure, where (n) varies according to the granular volume even if the crystalline structure is itself of the material [44].

Refractive index is considered as a complex quantity given by [37]:

$$N = n - ik \qquad \qquad \text{…… (2-18)}$$

Where: N complex refractive index.

It is possible to find the refractive index from reflectance spectrum where:

$$n = [\{(1+R)^2/(1-R)^2\} - (k^2+1)]^{1/2} + (1+R)/(1-R)] \qquad \text{……(2-19)}$$

2.8.3 Extinction coefficient (k)

Extinction coefficient represents the imaginary part of complex refractive index and, it is the exponential decay inside the material [45], i.e. the extinction happened to the electromagnetic wave inside the material, which means that the amount of energy of incident photon absorbed by electrons, it can be measured by the following equation:

$$k = \alpha \lambda / 4\pi \qquad \qquad \text{…… (2-20)}$$

2.8.4 Dielectric constant (ε)

Looking at equation (2-17) represents the refractive index which appears when there is a change in the speed of light between space and medium. i.e. when there is a reduction comes from interaction of light with matter which produce a polarization to the charges of the medium usually described as the complex extinction coefficient (ε) which physically represents the response of electrons to the incident electromagnetic field [46], and is given by the following relations [43]:

$$\varepsilon = \varepsilon + \varepsilon \qquad \qquad \text{…… (2-21)}$$

Where:

ε: complex dielectric constant.

ε : real part of the dielectric constant,

ε : imaginary part of the dielectric constant.

ε is connected with complex refractive index by the relation [37]

$$N = \sqrt{\varepsilon} \qquad \qquad \text{…… (2-22)}$$

and from equations (2-21) and (2-22) can get [37] :

$$\varepsilon_1 = n^2 - k^2 \qquad \dots\dots (2\text{-}23)$$

$$\varepsilon_2 = 2\,n\,k \qquad \dots\dots (2\text{-}24)$$

2.8. 5 Optical conductivity (σ)

The optical conductivity is connected with refractive index and extinction coefficient according to the following relation [47]:

$$\sigma = 2\,n\,k\;\omega\,\varepsilon_0 \qquad \dots\dots (2\text{-}25)$$

where ω is the angular frequency.

Equation (2-25) can be written as [47]:

$$\sigma = \varepsilon_2\;\omega\,\varepsilon_0 \qquad \dots\dots (2\text{-}26)$$

where ε_0 is the permitivity constant.

Chapter three

Experimental work

3.1 Introduction

This chapter includes a full description of preparation method and materials used in this research to obtain thin films with high quality, also includes the methods for the determination the structure and optical properties.

3.2 Chemical spray pyrolysis

This method was employed in the present work, where thin films were prepared by spraying the solution on a hot glass substrate at a certain temperature; the film could be then obtained by the chemical reaction on the substrate. The quality of the prepared thin film by this method might be less than thin film prepared by other method. However, in other applications these thin films could have good properties; for example, it might be used in solar applications.

3.3 System used for fabricated thin films

Chemical spray pyrolysis system consists of many simple apparatus which arranged in such a way to be used in preparing thin film on different substrates. The system used in the present work is of following parts:

3.3.1 Spray Nozzle

One of the basic advantages of the apparatus used is it's simplicity in preparing thin films because it can be made mostly in any glass workshop with a relatively low cost. The apparatus consists of small bulb of about 100 ml in volume opened from the above with circular aperture of 1.5 cm in radius; the height of bulb is 8 cm, the bulb is used as a tank for the solutions that be used to deposit on the substrate. In the bottom of the bulb there is a valve to be used as a control control the descending

solution to a capillary tube of diameter 0.1 cm and 6 cm in length. A glass chamber closed from the upper side because it joints with capillary tube, and it is opened from the bottom surrounds the capillary tube. One side of glass chamber is opened for compressed air which goes out of the chamber through the bottom side, thus the out-coming solution is mixed with compressed air, it will be in a spray form in a direction toward the substrate which thin film is deposit. Fig. (3-1) shows the schematic diagram of the spray nozzle used in our work.
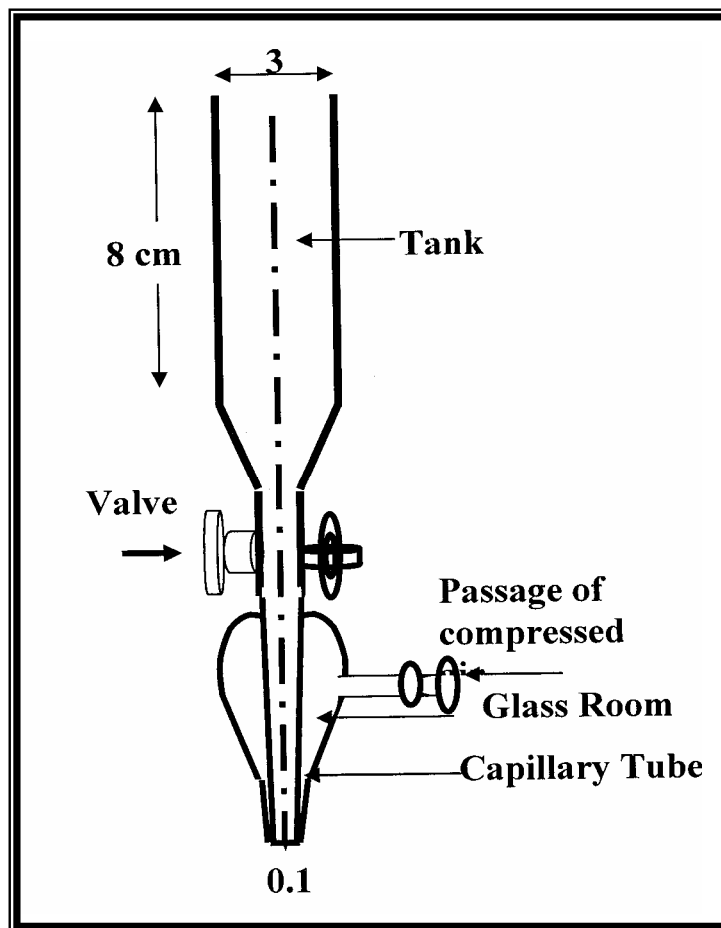

Figure (3-1): schematic diagram of the spray nozzle.

3.3.2 Holder of the sprayer nozzle

Spray pyrolysis apparatus is fixed on a certain height by means of a holder which itself fixed on metal rod, in such away the height of the apparatus above the surface

of the electrical heater can be controlled. In addition to the position of the apparatus can also be controlled because the end of the capillary tube in which the solution coming out should be in a perpendicular position on the substrate.

3.3.3 Electrical Heater

In order to get certain reaction, the substrate be heated to a certain temperature. An electrical heater of thermal range between 323K to 863 K was used. This heater has a circular surface of 15 cm in diameter, it should be noted that before starting of the spray process, the glass substrate should be left on the electrical heater for a period not less than half hour, in order to get the stability of the desired temperature.

3.3.4 Thermocouple

A thermocouple type (NiCr-Ni) which was supplied from (Payne Company) was used for the measurement of the substrate temperature. The thermocouple is consisting of a sensitive thermal probe in contact with the surface of the substrate; and connected to a digital counter showing the temperature degree (in centigrade). In the present work the reading accuracy of the thermocouple was checked by putting the probe of thermocouple in a mixture of ice and distilled water was found to be (276K) which meant the accuracy is about 1%.

3.3.5 Air pump

In order to control the quantity of air entered the nozzle, a rotary pump type (Geblase) supplied from (Phywe company) has been used for compressed air to a certain pressure inside the glass room through the opening side, this can be done by a control gauge connected to the air pump with the nozzle via a rubber tube. When the solution is descending through the nozzle tube it will be mixed with the compressed air under a certain pressure which will make the out coming solution

from the capillary tube which be lie on the substrate surface in the form of fine spray, it should be maintained that the compressed air can be controlled via the valve in such away to get a homogenous films.

3.4 Factors affecting on thin films homogeneity

There are several factors effecting thin film homogeneity which are:

1-Temperature

Temperature is one of the important parameter in homogeneity of thin films; it has significant effect upon the homogeneity of the prepared films, because it is responsible for the varying of the crystal structure of material, which affects the physical properties of materials.

2-Spraying rate

To obtain a homogeneous film, we must keep the spraying rate constant during deposition. That is because this parameter affects the homogeneity and thickness of the prepared films.

One can control this parameter via nozzle valve, taking into account that the increment in sprayer rate might causes a significant decrease in substrate temperature and might lead to crush the substrate.

3- Spraying time

Spraying operation should be uniform, so it is important to control the time period between every spraying, moreover should be constant.

4- Nozzle distance from the substrate

The normal distance from the end of the capillary tube to the substrate is one of the important parameter to obtain uniform film. In our study the best height for the

nozzle spray was (30±1) cm, any excess in this distance caused a scattering for the atomized solution away from the substrate, also any decrease in this distance will cause the collection of solution drops in one spot, and this will affect the film homogeneity.

5- Air pressure

The air pressure inside the glass room must be adjusted to obtain fine atomizes, in order to avoid the rapid decrease in substrate temperature which will cause the glass substrate to be broken [48].

In this work the air pressure was kept at (10^5 N/ m²) to get uniform films.

3.5 Thickness measurements

Thickness is one of the most important thin film parameters, since it largely determine the properties of the film. The thickness of the film usually measured by monitoring the rate of deposition during the coating process or by checking after the deposition, however there are several methods used for measuring the thickness of the film, such as weight, balance, optical, electrical and other methods.

In our study the thickness of thin films were measured by the weight method. This method is an approximated one used to obtain the thickness of thin films. Electronic balance type (Mettler AE- 160) with an accuracy of 10^{-4}g was used. The weight of the glass substrate was measured before and after the deposition of thin film, the difference between them represents the weight of film (Δm). This thickness (t) can be obtained by using the following relation:

t= Δm / ρA **……** (3-1)

Where:

ρ: is the density of the material used.

A: area of the film.

The thickness of Al_2O_3 films was (7254.4) Å

3.6 preparation of thin films

Aquatic aluminum chloride was used to prepare Al_2O_3 films, which is a yellowish green powder with a molecular weight of 241.43g and 96% in purity.

The solution was prepared as standard of 0.1 M, this was done by gradually melting of (2.414g)of the Al_2O_3 in 100 ml of distilled water and at room temperature using a magnetic mixer until getted a light white homogenous solution. The following relation was used to get the weight under consideration [49]:

M = (Wt / Mwt). (100 / V)   **......** (3-2)

Where:

M: represents molar concentration.

V: volume of distilled water.

M_wt: molecular weight of the material ($AlCl_3.6H_2O$).

Wt: weight to be melted.

The desired solution was left for appropriate period after finishing the melting process to make it cool before spray, then, it was put inside the spray device. The solution then sprayed and deposited on a cleaned glass (450 °C) substrate to get the finally Al_2O_3 thin film of white colour according to the following chemical equation:

$$2AlCl_3.6H_2O \xrightarrow[450\,°C]{\text{heat}} Al_2O_3 + 6HCl + 3H_2O \quad \textbf{...} (3\text{-}3)$$
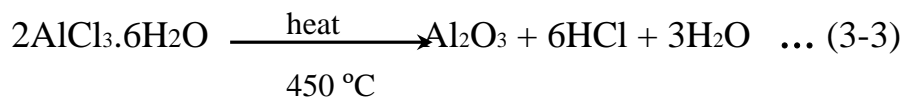
It is necessary to leave the glass substrate on the electrical heater for one hour at least after finishing the operation of spraying to complete it's oxidation and crystalline growth process.

3.7 Thin films deposition

A glass substrate made of borosilicate used to deposit the film on. They must be cleaned carefully by distilled water, then, put in acetone and dry them in oven to get rid of impurities suspended materials which may affect the structure of the prepared film, then changing it's physical properties [48]. The glass substrate is putting under heating after weighting by a sensitive electronic balance and left for one hour until they reach the desired temperature. It was noticed that, if this time is less than 1hour, then the films will not be homogenous enough.

The solution sprays on glass substrate for (5) seconds, then the glass substrate left for (2) or (3) minutes until they return to their original temperature, then the spray to be repeated several times according to the wanted thickness of prepared films. During the operation of spraying, the glass substrate must be moved regularly and the amount of spray should be controlled to get the best homogeneity of the films. As mentioned before, the films should be left under heating for one hour.

3.8 Testing and diagnosing the prepared films

3.8.1 Optical measurements

Optical measurements of thin films depend on, thickness, homogeneity, structure, materials used and the preparation conditions. These factors are responsible for the properties of thin films like optical absorption edges and optical absorption coefficient. These properties depend on the absorption of incident ray by materials, the amount of transmission ray from it and the reflection from it's surface. A spectr-ophotometer (UV-160A UV-visible recording spectrophotometer) supplied by Japanese company (Shimadzu) was used to record the optical measurements in the wavelength range (300-900) nm. This apparatus is of the double beam type, one of them passes through the film under consideration (optical measurements), while the

other passes through the glass slide inside the device, the method of measurement depends on the transmission which will be happened in the sample.

The optical measurements include the absorptance and transmittance of wavelength range (300-900)nm for Al_2O_3 thin films prepared at substrate temperature (450°C). To perform the tests, a clean glass substrate of the same kind as the original one which the film was deposited on, was put in the references window, and then, the sample was putting in the light source window so that the ray can fall perpendicular on the film.

By measuring the absorptance and transmittance spectra one can measure the absorption coefficient, the forbidden energy gap, refractive index, extinction coefficient and the values of optical constants.

3.8.2 Diagnosis using X-ray diffraction techniques

X-ray diffraction pattern were obtained by X-ray diffraction technique with the following properties instrument:

Type: Philips pw 1840

Target: CuKα

Filter: Ni

Wavelength: (1.541) Å

Speed: 3°/ min.

Voltage: (40) Kv

Current: (20) mA

Range: (10°-60°)

Chapter four

Results and discussion

4.1 Introduction

This chapter deals with the results which have been obtained from the study of the structural and optical properties of aluminum oxide films prepared by chemical spray pyrolysis technique and the study of annealing effect on the deposited thin film of thickness (7000)Å and on spraying rate (20 ml/s.).

4.2 Structural analysis

The crystalline structure of Aluminum oxide films was known by studying X-ray diffraction pattern at a substrate temperature (450°C) and annealed by (500,550,600) °C, and by knowing the angle at which peaks comes from a constructive interference when Bragg's conditions exist.

Figure (4-1) represents the X-ray diffraction of the Al_2O_3 thin film at (450°C) it reveals from the pattern the film is a polycrystalline and the film has a monoclinic structure according to ASTM card.

The grain size was calculated by using eq. (2-2) and interplanner spacing (d) was calculated by using eq. (2-1) and the results compared with ASTM card were in a good agreement as shown in table (4-1).

Table (4-1): the values of d, grain size and miller indices for Al_2O_3 films at (450 ºC)

Substrate Temperature (°C)	experimental (d) Å	ASTM (d) Å	Miller indices (hkl)	experimental (g.s) Å
450	2.83	2.837	400,40$\bar{1}$	414.075
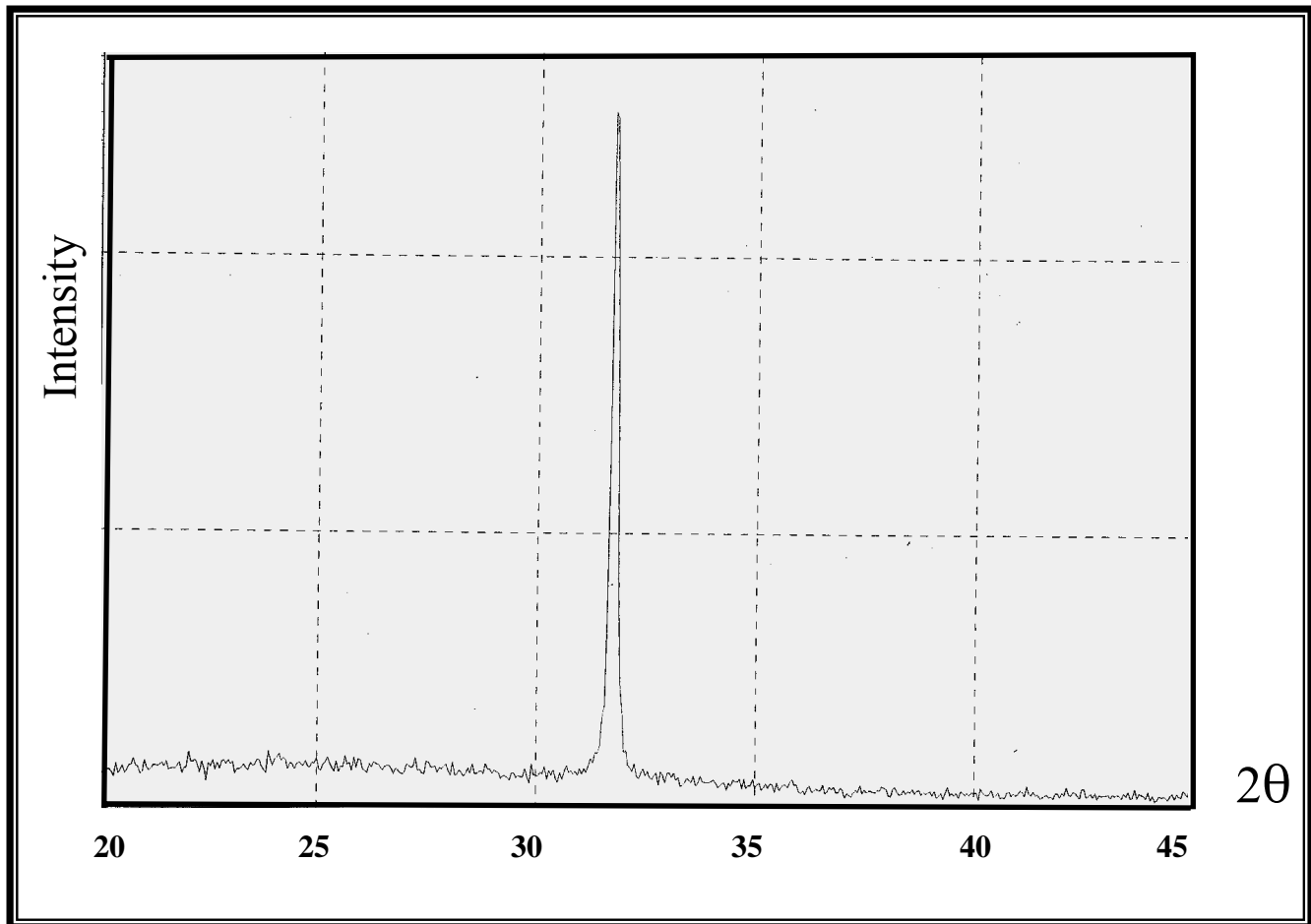
Figure (4-1): Diagram of X-ray diffraction of Al_2O_3 film at substrate temperature (450 °C)

4.3 Measurements of optical properties

This includes the study of the results of optical properties of Al_2O_3 films at different temperatures (450, 500,550, 600) °C, the allowed and forbidden energy gap for all films were obtained and the measurements of optical constants as absorptance, transmittance, reflectance as a function of wavelength and absorption coefficient, refractive index, real and imaginary parts of dielectric constants as a function to photon energy.

(4-3-1)Transmittance

The transmittance spectrum of Al_2O_3 films in the spectral range (300- 900) nm at (450°C) and heat treatment of different annealing temperatures (500,550,600) °C are shown in figure (4-2). It is clear from these figures that the transmittance increased as the wavelength increase, and the spectral characterization are affected by heat treatment. The peaks of transmittance spectrum of thermal annealing for Al_2O_3 films were shifted to the shorter wavelength compared to un annealed films as the temperature is increased. After annealing the interplanner spacing (d) is increased due to heating treatment then the volume of crystal is increased too, thus, he transmittance is increased because the wavelength of incident ray become smaller than the d spacing. According to this real the reflection was reduce as a ratio with transmittance.
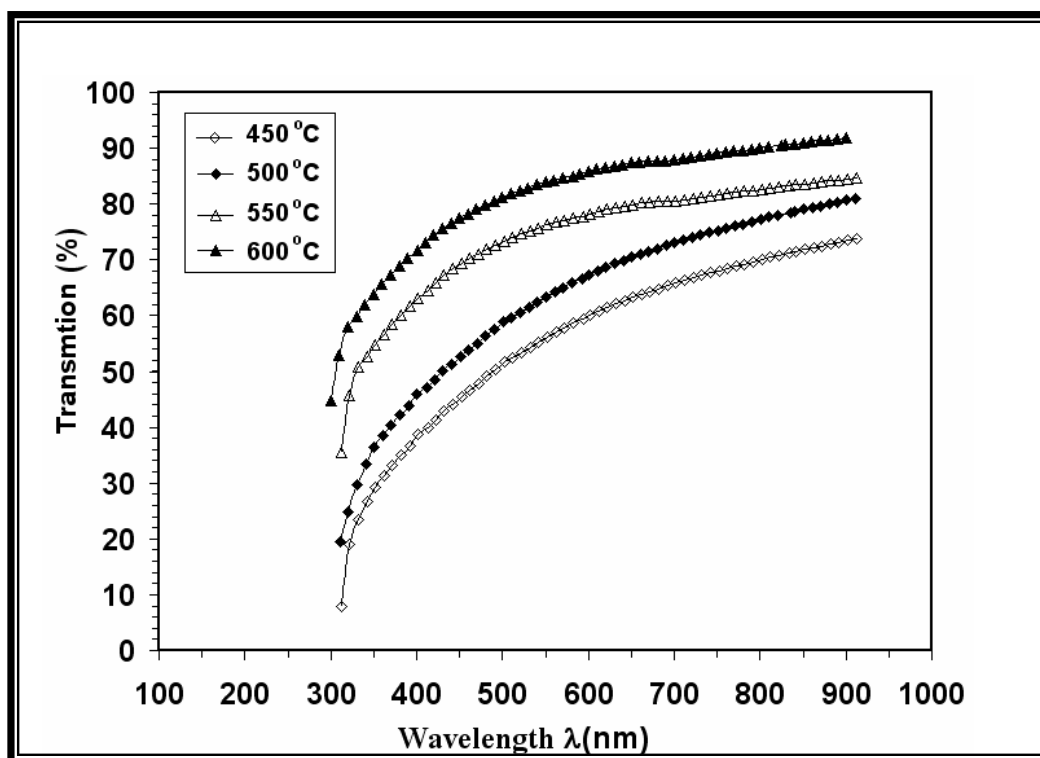

Figure (4-2): Transmittance as a function of wavelength for Al_2O_3 films at substrate temperature (450) °C and after annealing at (500,550,600) °C.

4.3.2 Absorption coefficient (α)

By using eq. (2-8) the absorption coefficient can be calculated. Figure (4-3) shows the absorption coefficient of Al_2O_3 films as a function of photon energy in the range of (1.25-4.2)eV before and after annealing, from this figure the values of absorption coefficient is higher than ($\alpha > 10^4$) cm^{-1} in the region of photon energy (2.8-4.2)eV and these values increase with the increasing of photon energy, this is assist to expect a direct electronic transition occurs in these photon energies, and this does not prevent an indirect electronic transition to occur, where the value of ($\alpha < 10^4$)cm^{-1} leads an indirect electron transition to occur [50]. Also, we can observe from these figures that the fundamental absorption edge has a value around (3.2eV), and the annealing process caused shift the absorption edge toward higher photon energy.
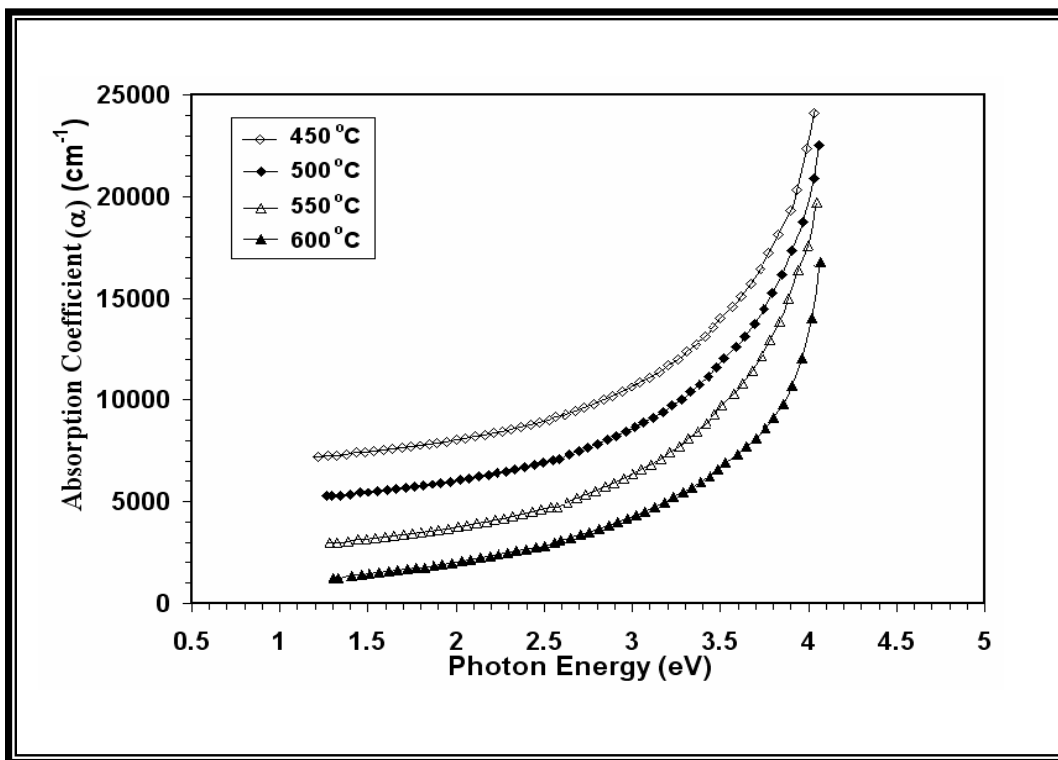

Figure (4-3): Absorption coefficient as a function of photon energy of Al_2O_3 films at substrate temperature (450) °C and after annealing at (500,550,600) °C.

4.3.3 Measurements the forbidden energy gap of the direct allowed transition

Measurement the forbidden energy gap of the allowed direct transition was done and the equation (2-20) which can be written as follows was used:

$(\alpha h\nu) = B (h\nu - E^o_g)$ **......** (4-1)

Where n = 1/2, and at $(\alpha h\nu)^2 = 0$ we get $E^o_g = h\nu$

By drawing a relation between $(\alpha h\nu)^2$ and photon energy (hν), the forbidden energy gap of the direct allowed transition could be obtained under the condition of photon energy is equal to zero [45]. Figure (4-4) show the variation of the relation $(\alpha h\nu)^2$ a function of incident photon energy of the prepared film before and after annealing.

The extracted results from this figures are shown in table (4-2) which clearly show that the value of forbidden energy gap of the allowed direct transition before annealing is (3.40 eV) and which increases as the temperature of annealing is increaing, and the explanation of this is the annealing lead to reduce the local state near the valance and conduction band, hence, increasing the energy gap.

Table (4-2): the values of forbidden energy gap of direct allowed transition of Al_2O_3 films at substrate tem.and after annealing

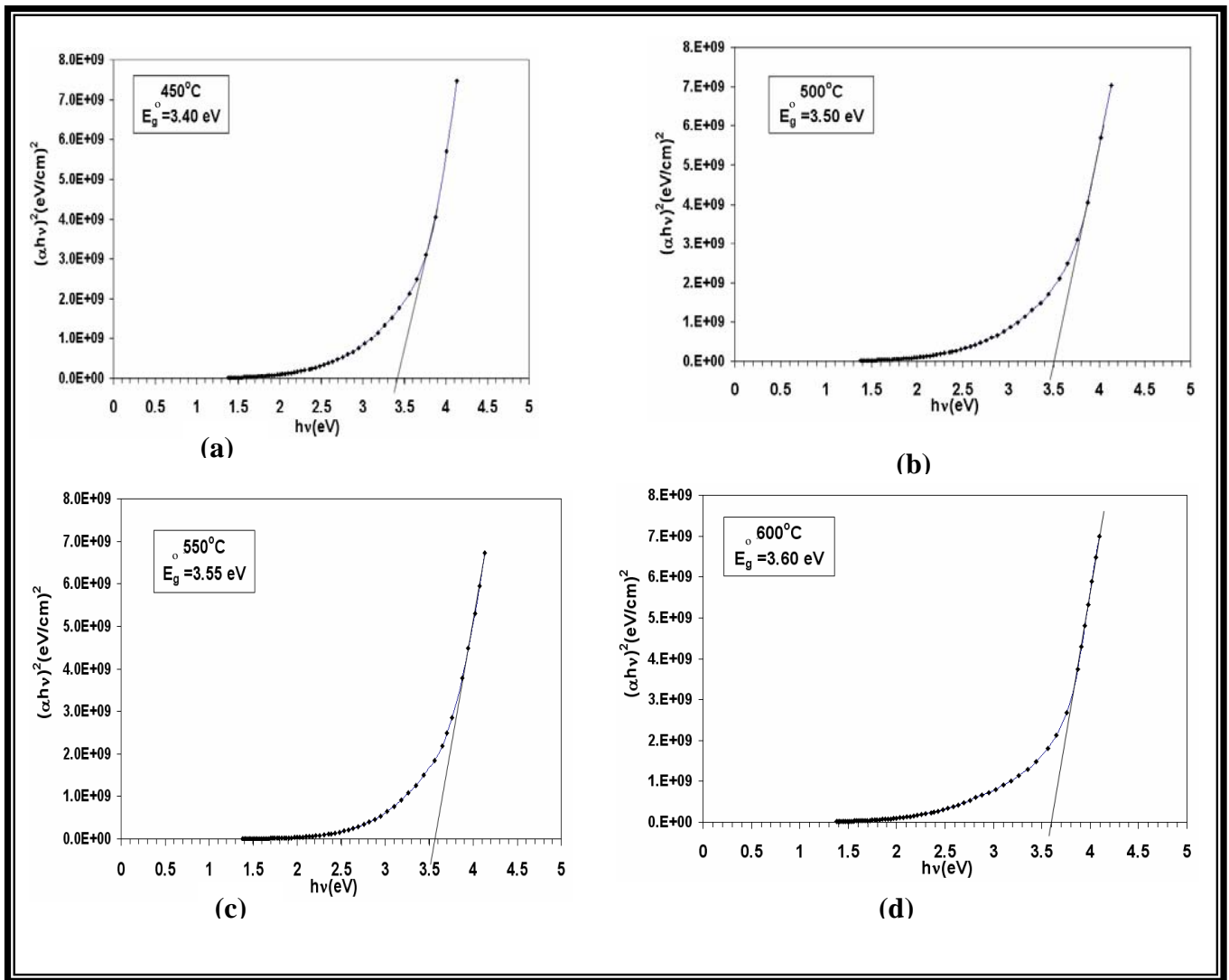|	T(°C)	E^o_g (eV)
Substrate temp.	450	3.40
After annealing	500	3.50
	550	3.55
	600	3.60

Figure (4-4): allowed direct transition as a function of photon energy of Al_2O_3 films at substrate temperature at (a) 450°C and after annealing at {(b) 500, (c) 550, (d) 600}°C

4.3.4 Measurements of the forbidden energy gap of the direct forbidden transition

Measurements of forbidden energy gap of the direct forbidden transition were done by using the equation (2-10) which can be written as follows:

$$(\alpha h\nu) = B\,(h\nu - E^{o}_{g})^{n} \qquad\qquad \dots\dots (4\text{-}2)$$

Where n = 3/2

By plotting a relation between $(\alpha h\nu)^{2/3}$ with photon energy (hν)and by extrapolating the linear part of the curve at a photon energy at $(\alpha h\nu)^{2/3} = 0$ from it one can get the value of forbidden energy gap of forbidden direct transition. Figure (4-5) shows the values of forbidden energy gap of the direct forbidden transition of Al_2O_3 films before and after annealing which is equal after annealing to (2.50eV). By increasing annealing temperature, the values of forbidden energy gap increase until they reach (2.70eV) at 600°C and this means that the increasing temperature leads to shift in the absorption edge toward higher energy. In case of Al_2O_3 before annealing the transition occurred between the peak of valence band and the bottom of conduction band, after annealing the electrons gain energy and the bottom of conduction band become partially filled and the transition to the low state is forbidden and hence the transition which is able to happen for higher photon energy, this means increasing the value of energy gap this called (Buresten-Moss) shift [51].

Table (4-3): the values of forbidden energy gap for the direct forbidden transition of Al_2O_3 films at substratetem. and after annealing

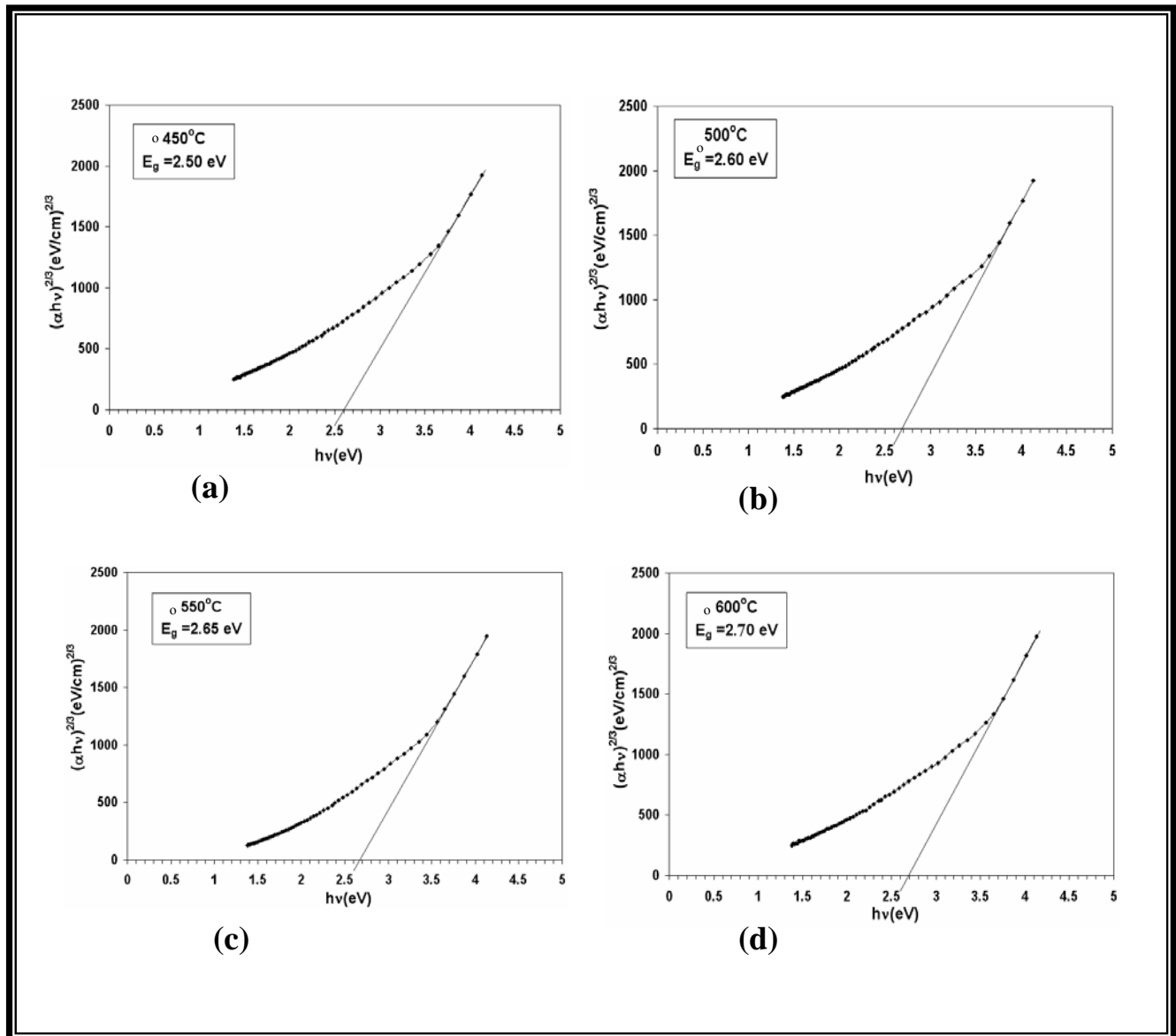|	Temperature(°C)	Eg (eV)
Substrate tem.	450	2.50
After annealing	500	2.60
	550	2.65
	600	2.70

Figure (4-5): forbidden direct electrons transition as a function of photon energy of Al₂O₃ films at substrate tem. (a) 450°C, after annealing at {(b) 500,(c)550,(d)600}°C

4.3.5 Measurements of the forbidden energy gap of the indirect allowed transition

The forbidden energy gap in case of the indirect allowed electronic transitions was measured, and the following relation was used:

$$(\alpha h\nu) = B (h\nu - E^o_g \pm E_{ph})^n \qquad \text{......(4-3)}$$

Where the value of the power (n) is (2) this equation can be written as follows:

$$(\alpha h\nu)^{1/2} = B^{1/2} (h\nu - E^o_g \pm E_{ph}) \qquad \text{......(4-4)}$$

Where: Eph: assistant photon energy.

(+): absorption of phonon.

(-): emission of phonon.

when $(\alpha h\nu)^{1/2} = 0$ then $E^o_g \pm E_{ph} = h\nu$ and to estimate this we draw a relation between $(\alpha h\nu)^{1/2}$ and photon energy (hν), we notice that two parts of the produced curve is a straight line which it's extension cut the photon energy axis at $(\alpha h\nu)^{1/2} = 0$ and this means the verification of equation (4-4), i.e. the cutting point represents the optical energy gap of the indirect allowed transition ($E_g \pm E_{ph}$). Figure (4-6) shows the variation relation of $(\alpha h\nu)^{1/2}$ with the incident photon energy before and after annealing. The extracted results from these figures in table (4-4) show clearly that the value of energy gap of the indirect allowed transition before annealing is equal to 1.60 eV and it increases as annealing temperature increases for the same previous reason.

Table (4-4): the values of forbidden energy gap of the indirect electronic transition of Al_2O_3 films at substrate tem. and after annealing.

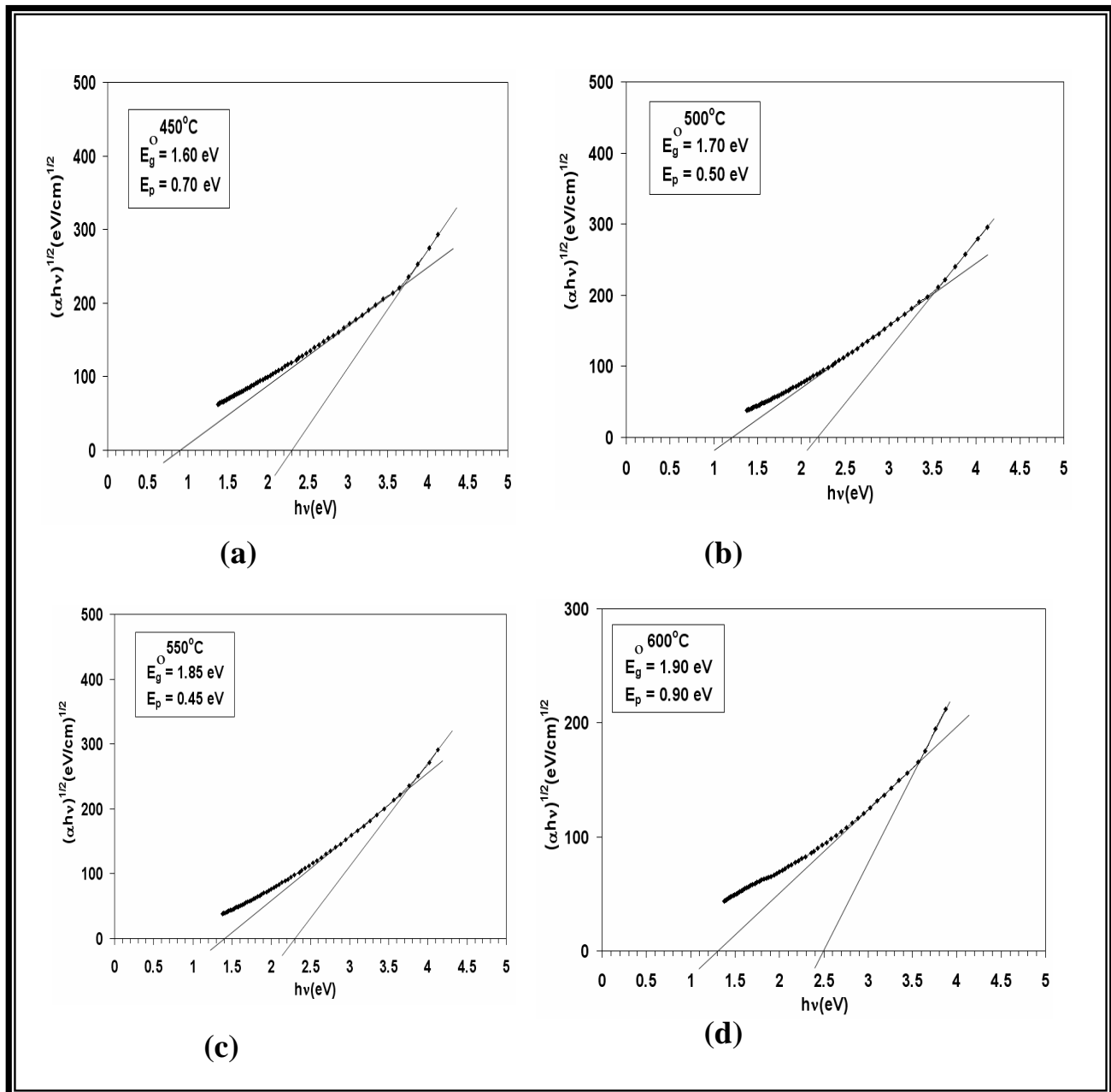|	Temperature (°C)	E_g (eV)
Substrate tem.	450	1.60
After annealing	500	1.70
	550	1.85
	600	1.90

Figure (4-6): indirect electronic transition as a function of photon energy of Al_2O_3 films at substrate tem. (a) 450°C, after annealing at{(b)500, (c)550,(d)600}°C

4.3.6 Reflectance

Figure (4-7) represents the variations of reflectance for Al_2O_3 thin films as a function of photon energy before and after annealing, we notice that the reflectance increases gradually with the increasing of photon energy and it reaches (4-4.2)eV, also the reflectance increases with the increasing of annealing temperature, for explanation of this phenomena is one can expect the absorptance is small in this region so the reflectance increased with the increase of temperature, this means that surfaces of the film affected by annealing.
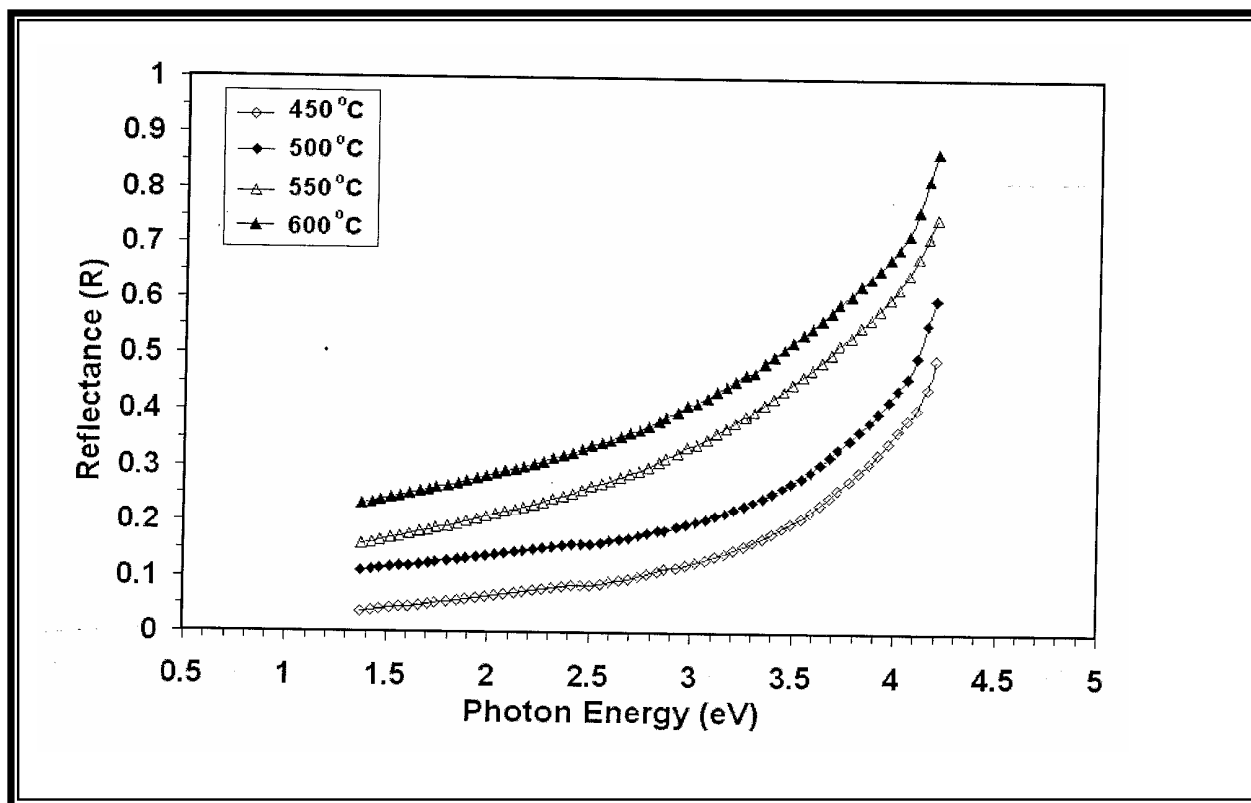

Figure (4-7): reflectance of Al_2O_3 films as a function of photon energy at substrate tem. (450°C) and after annealing at(500,550,600) °C.

4.3.7 Measurements of extinction coefficient (k)

Extinction coefficient is considered to be a scale of absorptance its value depends on the density of free electrons in the material and structure defects [19].

Extinction coefficient was measured from the value of absorption coefficient determined from the spectrum of absorptance within the spectral range (300-900)nm, and according to equation (2-20) for the as deposited film. Figure (4-8) shows the variation of extinction coefficient as a function of photon energy, from this fig. are can find the range of similarity in the nature of these curves with the curve of absorption coefficient for each film, this similarity results from the dependence of the values of extinction coefficient on the values of absorption coefficient. We notice a slowly increment in the values of k with increasing photon energy then increases quickly for all films at the energies nearest to absorption edge. The decreasing in the values of extinction coefficient with the increasing of annealing temperature of Al_2O_3 films is attributed to the decreasing of absorptance with the increasing of annealing temperature, where the temperature leads to overcome from some of local state and then decreasing the absorptance and increasing the transmittance, hence the number of charge carriers producing from the deviation of ideal structure of the film will be less , and then the extinction produce from the absorption of radiation by carriers decreases, so as the extinction coefficient decreases as the time of annealing increases and this behavior is similar to that of absorption coefficient[18].
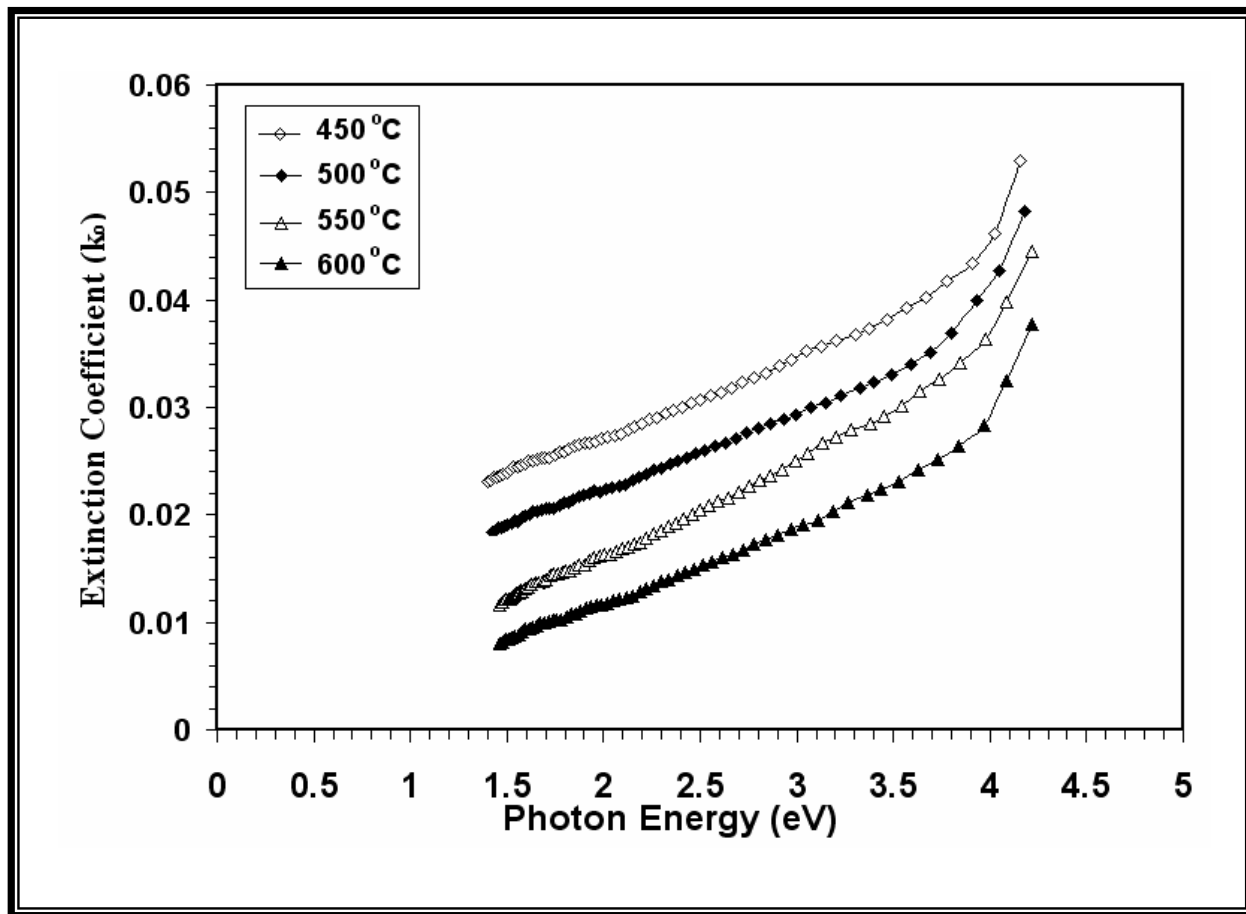
Fig. (4-8): extinction coefficient of Al_2O_3 films as a function of photon energy at substrate tem. (450°C) and after annealing at (500,550,600) °C

4.3.8 Measurements of refractive index (n*)*

The refractive index n   was determined for all films by equation (2-19). Figure (4-9) represent the refractive index as a function of photon energy of Al_2O_3 films deposited at 450°C and annealed at(500,550,600) °C, this fig. shows that refractive index increases as the energy of photon increase, and the nature of refractive index curve is similer to that of reflectance according to equation (2-19), however at annealing we notice from the figure and for all annealing temperatures that the curve of the refraction has been changed in it's value where it increased as temperature increased this increment is due to the annealing temperature which leads to a variation in the fine structure of the film, hence increasing the density of packing

[18] which reduces the speed of light in the material of the thin film and then leads to an increasing in the refractive index according to the relation of (2-17).
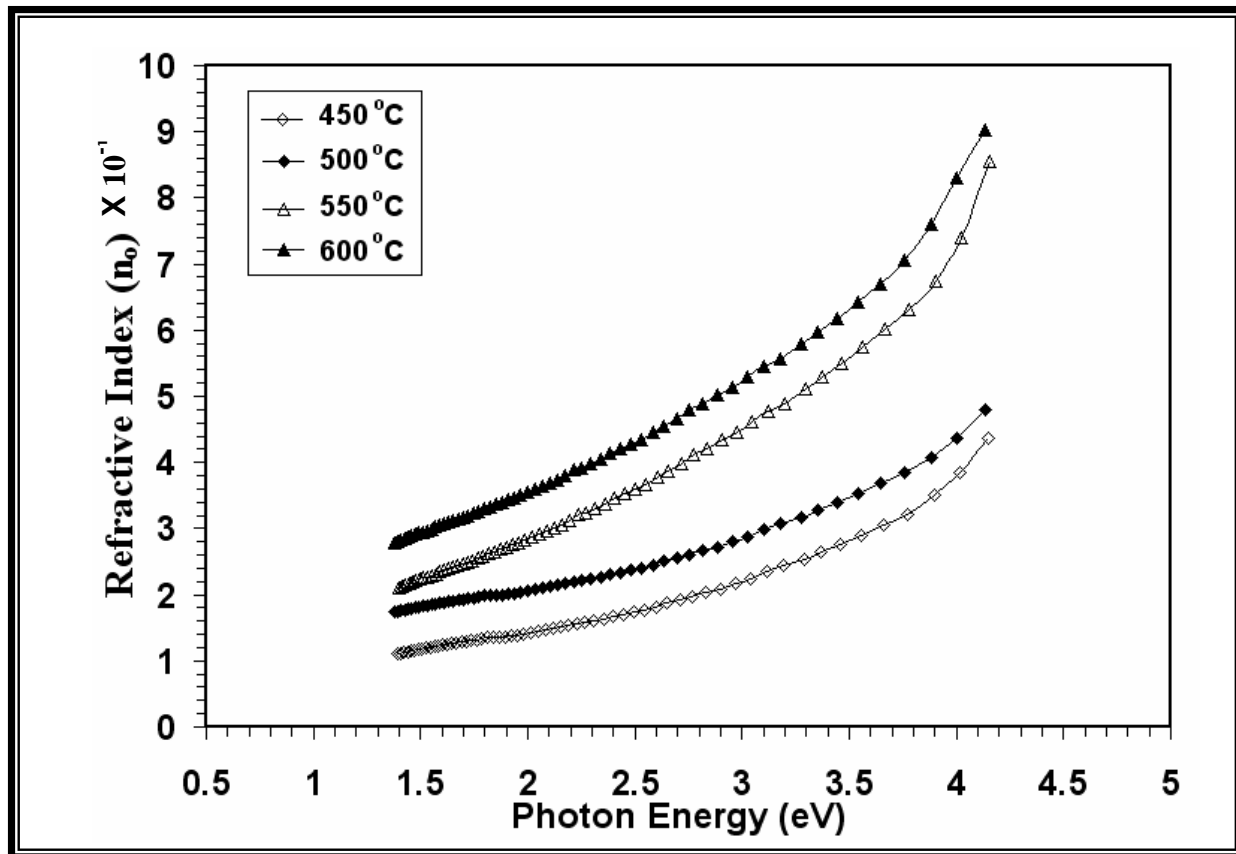

Figure (4-9): Refractive index for Al_2O_3 films as a function of photon energy at substrate tem. (450°C) and after annealing at (500,550,600) °C

4.3.9 Measurements of real part of dielectric constant ($\varepsilon 1$)

The real part ($\varepsilon 1$) of dielectric constant was measured for the prepared films by using equation (2-23). Figure (4-10) shows the variation of the real part of dielectric constant with photon energy, and it is clear from the figure that ($\varepsilon 1$) increases as photon energy increases and also increases as the temperature of annealing increases. The behavior of ($\varepsilon 1$) with photon energy is the same as that of refractive index (n), owing to the dependence of ($\varepsilon 1$) on the refractive index (n) where the effect of extinction coefficient (k) is so less in comparison with the effect of refractive index. The highest value of real part of dielectric constant is at annealing

temperature of (600°C) and it's lowest value before annealing is at deposition temperature of (450°C) and this means that there is a high effect of annealing on the real part of dielectric constant.
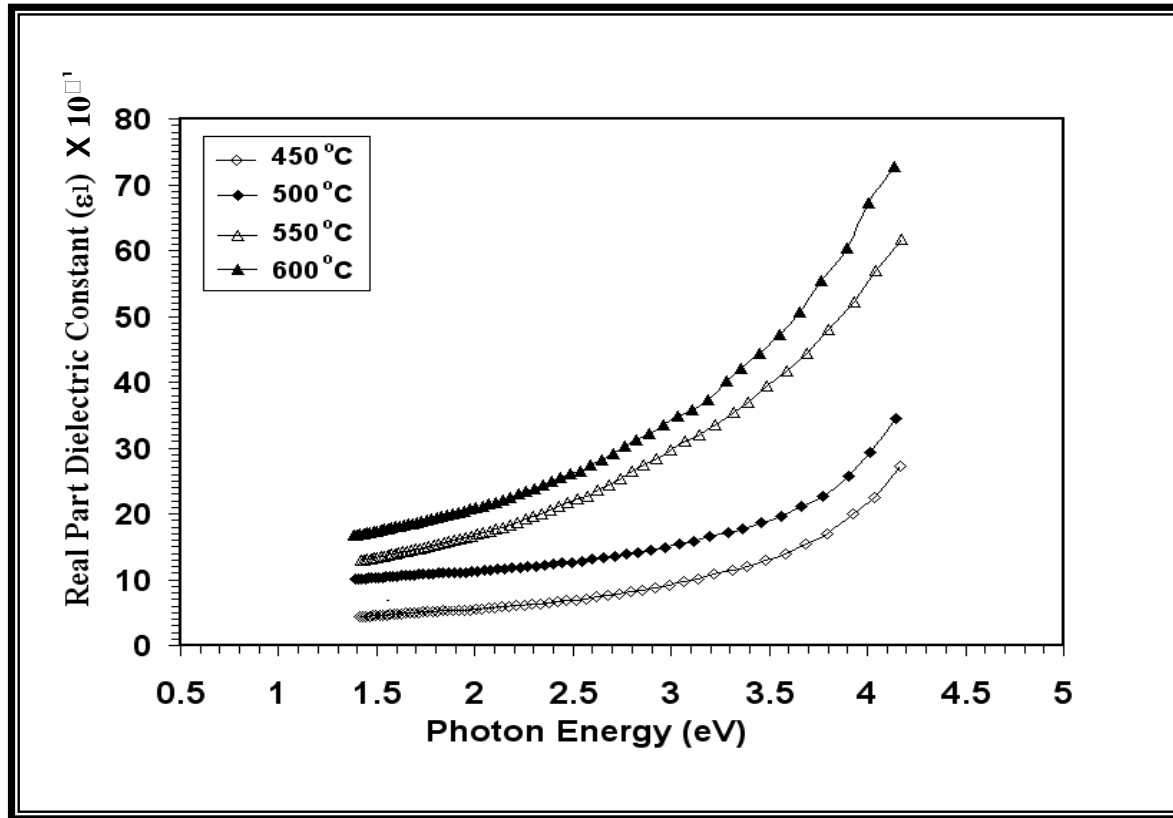

Figure (4-10): Real part of dielectric constant for Al₂O₃ films as a function of photon energy at substrate tem. (450°C) and after annealing at (500,550,600) °C

4.3.10measurement of imaginary part of dielectric constant (ε2)

The imaginary part (ε2) of dielectric constant was measured by using equation (2-24). Figure (4-11) shows the variation of imaginary part of dielectric constant versus photon energy, it is clear from figure that (ε2) increases as the incident photon energy increased but it decreases as the annealing temperature increases. The behavior of (ε2) with the incident photon energy and annealing temperature is the same as that of extinction coefficient (k) owing to the dependence of (ε2) on the

extinction coefficient (k) according to equation (2-24), and this can be explained as that the imaginary part of dielectric constant (ε2) represents the energy loss of incident radiation [18], i.e. it coefficient (k) owing to the dependence of (ε2) on the extinction coefficient (k) according to equation (2-24),and this can be explained as that the imaginary part of dielectric constant (ε2) represents the energy loss of incident radiation [18], i.e. it indicates to absorption of optical radiation energy exerted by the atoms of material and this is concerned by the sense of extinction coefficient (k) of the film.
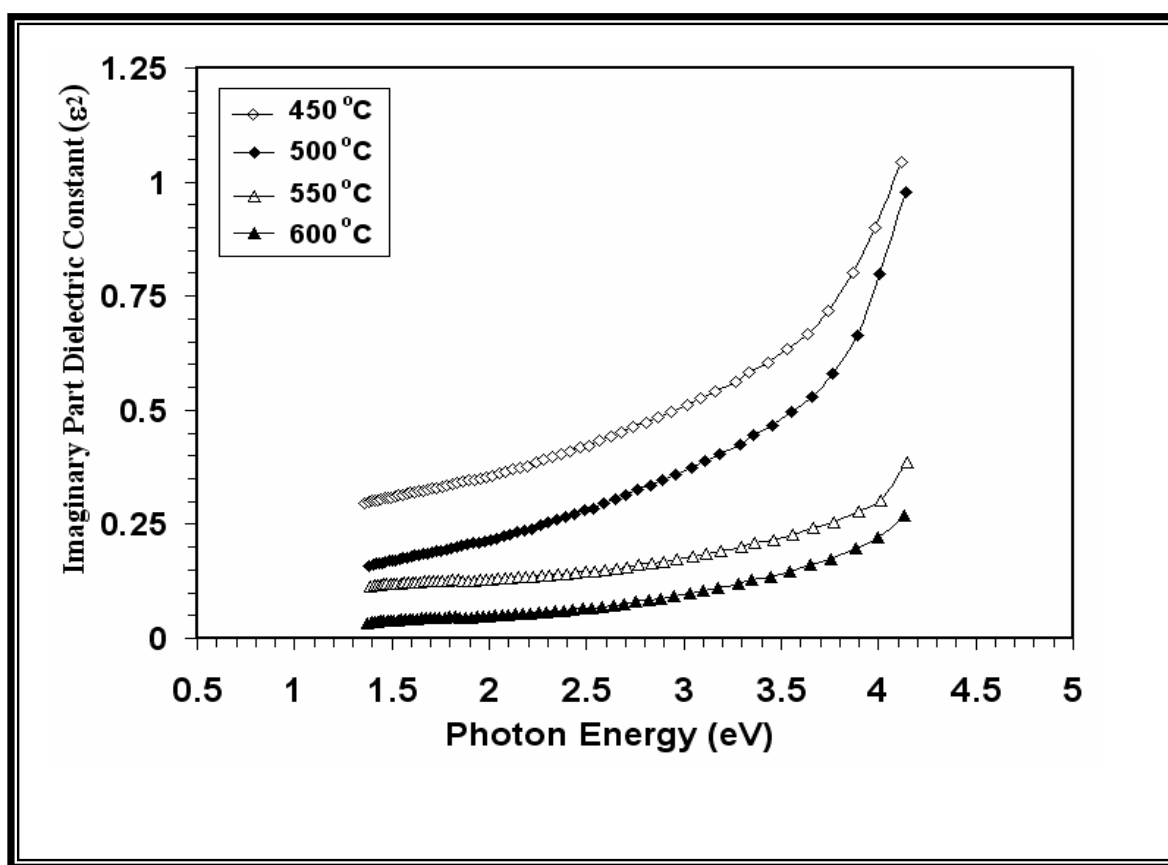

Figure (4-11): Imaginary part of dielectric constant for Al_2O_3 films as a function of photon energy at substrate tem. (450°C) and after annealing at (500,550,600) °C

4.3.11 Measurements of optical conductivity (σ)

Figure (4-12) shows the variation of optical conductivity with photon energy of Al₂O₃ films before and after different temperature annealing, one can notice from this figure that the conductivity increases as photon energy increased and decreases as annealing temperature increase. The reducing in the values of optical conductivity with the increasing of annealing temperature is due to annealing operation which caused an increment in the resistance of the film, and then reducing the conductivity illuminate local states inside the energy gap. The behavior of optical conductivity with annealing temperature is the same as that of the imaginary part of dielectric constant ($\varepsilon2$) and this is due to the dependence of conductivity on ($\varepsilon2$) according to equation (2-25).
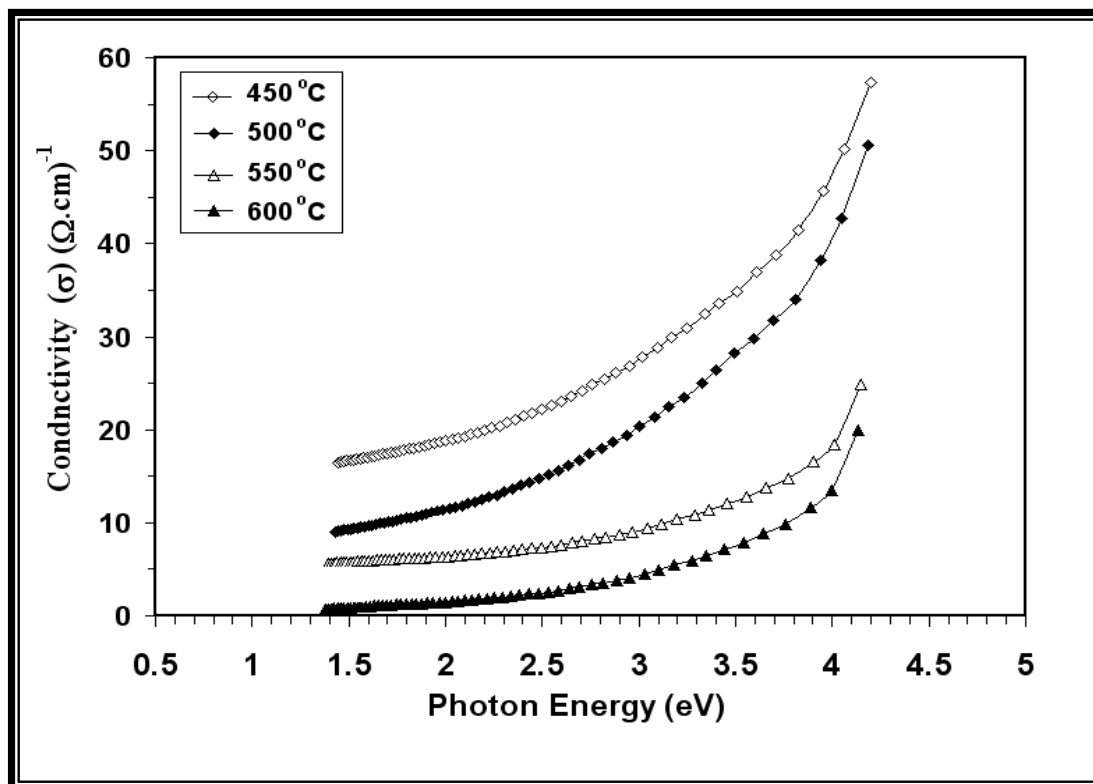

Figure (4-12): optical conductivity for Al₂O₃ films as a function of photon energy at substrate tem. (450°C) and after annealing at (500,550,600) °C

Chapter five

Conclusion and future work

5.1 Conclusions

- ❖ X-ray analysis proved that the Al_2O_3 thin films prepared by chemical spray pyrolysis method and at a substrate temperature (450°C) is a poly crystalline structure.

- ❖ Forbidden energy gap of allowed and forbidden direct electronic transitions before annealing was(3.4)eV and(2.5)eV respectively, and for indirect allowed electronic transitions was (1.6)eV, and after annealing, an increment occurred in the value of the forbidden energy gap for both types of transitions, and the highest recorded increment was (3.6)eV and (2.7)eV at (600)°C for the direct electronic transitions and (1.9)eV for the indirect electronic transitions at (600)°C too.

- ❖ Annealing process caused a decrease in absorptance, absorption coefficient, extinction coefficient, optical conductivity and the imaginary part of the complex dielectric constant. Also, annealing caused an increment in the transmittance, reflectance, refractive index and the real part of the complex dielectric constants.

- ❖ The real part of dielectric constant has the same behavior of the refractive index while could noticed the imaginary part have the same behavior of extinction coefficient.

5.2 Future works

1- Studying the electrical and structural properties of Al_2O_3 thin films prepared by thermal evaporation in vacuum.

2- Studying the electrical properties of un doped Al_2O_3 thin films of different thickness prepared by chemical spray pyrolysis method.

3- Effect of radiation by Neutrons on the optical and structural of un doped Al_2O_3 thin films of different thickness and comparing the results with the results of the recent study.

4- Studying the doping by Halogens on the optical and electrical of Al_2O_3 thin films prepared by chemical spray pyrolysis method.

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الخلاصة

تتناول هذه الدراسة الخواص التركيبية والبصرية لأغشية أوكسيد الألمنيوم(Al_2O_3) الرقيقة المحضرة بطريقة الترسيب الكيميائي الحراري على قواعد زجاجية ساخنة بدرجة حرارة أساس (450^oc) . ودراسة أثر التلدين بدرجات حرارية مختلفة ^oc(500,550,600) على الخواص البصرية للعينات.

فقد أظهرت نتائج حيود الأشعة السينية ان الأغشية المحضرة ذات تركيب متعدد التبلور. وقد اشتملت دراسة الخواص البصرية على تسجيل طيفي الأمتصاصيةو النفاذية للأغشية المحضرة لمدى الأطوال الموجية nm(900-300)

ومن ثم حساب فجوة الطاقة الممنوعة للأنتقالات الألكترونية اذ كانت قيم فجوة الطاقة للانتقال المباشر المسموح والممنوع هي eV(3.4 ,2.5), وللانتقال غير المباشر المسموح هي (1.6eV) أما عند تلدين أغشية Al_2O_3 فأن قيم فجوة الطاقة الممنوعة للأنتقال المباشر المسموح والممنوع هي eV(2.7,3.6) وللأنتقال غير المباشر المسموح هي (1.9 eV).

وكذلك تم حساب ودراسة معامل الأمتصاص, الأنعكاسية, والثوابت البصرية المتمثلة ب(معامل الخمود, معامل الأنكسار, ثابت العزل الكهربائي بجزئيه الحقيقي والخيالي والتوصيلية الضوئية) كدالة لطاقة الفوتون فقد أظهرت الدراسة ان التلدين تسبب في زيادة قيم فجوة الطاقة والأنعكاسية والنفاذية ومعامل الأنكسار والجزء الحقيقي لثابت العزل الكهربائي ونقصان في قيم الأمتصاصية ومعامل الأمتصاص ومعامل الخمود والجزء الخيالي لثابت العزل الكهربائي والتوصيلية الضوئية.

جمهورية العراق
وزارة التعليم العالي والبحث العلمي
جامعة النهرين
كلية العلوم
قسم الفيزياء

أثر التلدين على الخواص البصرية لأغشية أوكسيد الألمنيوم (Al$_2$O$_3$) الرقيقة المحضرة بطريقة الترسيب الكيميائي الحراري

رسالة مقدمة الى
كلية العلوم –جامعة النهرين
وهي جزء من متطلبات نيل درجة ماجستير علوم في الفيزياء

من قبل

عبير كمال جعفر العزاوي
(بكالوريوس علوم في الفيزياء 2006م)

بأشراف

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