بسم الله الرحمن الرحيم

Sudan University of Science and Technology

College of Graduate Studies

Effect of Laser Pulse Energy and Repetition Rate on Optical Transmittance Spectra of Fe_2O_3Thin Films

تأثير طاقة الليزر النبضي ومعدل تكرار النبضة في أطياف النفاذية البصرية لأغشية رقيقة من Fe_2O_3

A thesis Submitted As Partial Fulfillment to Satisfy Requirements of Master Degree in Laser Applications in Physics

By:

Altaf Alsaid Mohamed Abdalgader

Supervisor:

Dr. Ali Abdel Rahman Saeed Marouf

October 2015

الآيـة

أعوذ بالله من الشيطان الرجيم

بسم الله الرحمن الرحيم

{لَقَدْ أَرْسَلْنَا رُسُلَنَا بِالْبَيِّنَاتِ وَأَنْزَلْنَا مَعَهُمُ الْكِتَابَ وَالْمِيزَانَ لِيَقُومَ النَّاسُ بِالْقِسْطِ ۖ وَأَنْزَلْنَا الْحَدِيدَ فِيهِ بَأْسٌ شَدِيدٌ وَمَنَافِعُ لِلنَّاسِ وَلِيَعْلَمَ اللَّهُ مَنْ يَنْصُرُهُ وَرُسُلَهُ بِالْغَيْبِ ۚ إِنَّ اللَّهَ قَوِيٌّ عَزِيزٌ}

سورة الحديد الأية 25

Dedication

I dedicate my dissertation work to my family and many friends. Special Feeling of gratitude to my loving my mother and to my father's soul, whose words of encouragement and push for and tenacity ring in my ears.

I also dedicate this dissertation to my many friends for helping me in work.

Acknowledgements

In the first I thank to Allah**,** I would like to express my gratitude to my supervisor Dr. Ali Abdelrahman Marouf for the useful comments, remarks and engagement through the learning process of this master thesis.

Furthermore I would like to thank Dr. Abdalfatah and Ostaz Mahasen from Nileen University, Special thanks to the staff of laser institute.

During the period of the master study, many friends are helpful to color my life; I have to acknowledge all my colleagues in studying fields for their assistance in many aspects that I cannot list them all because of limited space.

Last but not the least important, I owe more than thank to my family members which includes my Mother , an elder sister(Tysser) and my brother(Hassan), for their financial Support and encouragement throughout my life without their support, it is impossible for me to finish my college and graduate education seamlessly.

CONTENTS

List of figures

Abstract

In this work; iron oxide thin films (Fe_2O_3) were fabricated by pulsed laser deposition technique (PLD). Pulsed Nd: YAG laser was used for prepared Fe_2O_3 thin films at wave length 532nm and 10 ns pulse duration with varying both pulse energy and laser repetition rate. The optical transmittance spectrum of Fe_2O_3 thin films was measured experimentally and the effects of laser pulse energy and laser repetition rate on it were studied. An inverse relationship between transmittance spectra and both laser pulse energy and laser repetition rate was observed.

مستخلص

في هذا البحث تم تحضير أغشية رقيقة من أوكسيد الحديديك عن طريق تقنية الترسيب بواسطة الليزر النبضي ، استخدم ليزر النيوديميوم ياج ذو النمط المفتاحي بطول موجي 532 نانوميتر وزمن بقاءالنبضة 10نانوثانية ومع بتغيير كل من طاقه الليزرومعدل تكرار نبضة الليزر.

وبشكل عملي قيس طيف النفاذية لهذه الاغشية الرقيقة ودرس تاثير كل من طاقة الليزر ومعدل تكرار نبضة الليزر على طيف النفاذية البصرية للأغشية الرقيقة ولوحظ أن هنالك علاقة عكسية بين طيف النفاذية البصرية وكل من طاقة الليزر ومعدل تكرار نبضة الليزر.

CHAPTER ONE

INTRODUCTION

1-1Introduction:

Metal oxide thin films have unique characteristics such as good magnetic properties and conductivity, high optical transmittance over the visible wavelength region, excellent adhesion to substrates and chemical stability and photochemical properties. Among magnetic materials, iron oxides, such as (α-Fe_2O_3) and (Fe_3O_4), are the most popular materials and possess many advantages in technological applications. Iron oxide thin film (Fe_2O_3) can be used in several fields .(α-Fe_2O_3) is the most stable iron oxide compound material and is widely used in photo-electrodes, gas sensing, catalysts, magnetic recording, and medical fields. Due to its great sensitivity for flammable gases, its fast speed of response and its long-term stabilities ; Photo electrochemical solar cell, due to its optical band gap, its high optical absorption coefficient; Negative electrode in rechargeable batteries. It is also used for water electrolysis in the presence of sunlight. (S. S. Shinde et al, 2011).

1-2 Literatures Review:

Lackner, J.M., et al., in 2003 used Pulsed laser deposition as a new technique for deposition of amorphous SiO*x* thin films. Their works presents some results on silicon-based PLD-films with reduced density of particulates. Silicon, SiO*x* and SiO_2 thin films were deposited by laser ablation from silicon targets with a high power pulsed Nd: YAG laser of 1064 nm wavelength in argon and oxygen containing atmospheres. The

substrates were arranged in shaded off-axis geometry. They investigated the chemical composition and structure of the films employing transmission electron microscopy (TEM), secondary ion mass spectroscopy, X-ray photoelectron spectroscopy and ellipsometry. The results demonstrate the capability of PLD for the deposition of SiO*x* films with varying composition ($0 < x < 2$) by shaded off-axis PLD. The results of TEM and spectroscopic ellipsometry are indicating amorphous film structures in all cases.

Ekwealor, A.B.C & Ezema, F.I., in April 2013 they studied the effects of precursor concentration on the optical and structural properties of Fe_2O_3 thin films synthesized in polymer matrix by chemical bath deposition and found, The structural composition of the films were determined and confirmed using XRD. The optical properties were studied using spectrophotometer. These films were observed to have low absorbance and reflectance of radiation in the ultraviolet, visible and near infra-red (UV-VIS-NIR) regions of optical spectra. These properties were found to increase with increase in concentration of precursor. They showed high transparency to radiation, which decreased with increase in precursor concentration in the VIS and NIR regions of optical spectra.

Liu Wei et al., in 2014 they characterized zirconium thin films deposited by pulsed laser deposition, Zirconium (Zr) thin films deposited on Si (100) by pulsed laser deposition (PLD) at different pulse repetition rates are investigated. The deposited Zr films exhibit a polycrystalline structure, and the X-ray diffraction (XRD) patterns of the films show the Zr phase. Due to the morphology variation of the target and the laser–plasma interaction, the deposition rate significantly decreases from 0.0431 A° /pulse at 2 Hz to 0.0189 A° /pulse at 20 Hz. The presence of droplets on the surface of the deposited film, which is one of the main disadvantages of the PLD, is

observed at various pulse repetition rates. Statistical results show that the dimension and the density of the droplets increase with an increasing pulse repetition rate. We find that the source of droplets is the liquid layer formed under the target surface. The dense nanoparticles covered on the film surface are observed through atomic force microscopy (AFM). The root mean square (RMS) roughness caused by valleys and islands on the film surface initially increases and then decreases with the increasing pulse repetition rate. The results of our investigation will be useful to optimize the synthesis conditions of the Zr films.

Kadhim A. Aadim, Ali A-K. Hussain & Mohammed R. Abdulameer in 2014 studied effect of annealing temperature and laser pulse energy on the optical properties of CuO films prepared by pulsed laser deposition, copper oxide films (CuO) were fabricated by PLD. The films were analyzed by UV-VIS absorption spectra and their thickness by using profilometer. Pulsed Nd: YAG laser was used for prepared CuO thin films under O_2 gas environment with varying both pulse energy and annealing temperature. The optical properties of as-grown film such as optical transmittance spectrum, refractive index and energy gap has been measured experimentally and the effects of laser pulse energy and annealing temperature on it were studied. An inverse relationship between energy gap and both annealing temperature and pulse energy was observed. The optical transmittance decreased with increasing annealing temperature and decreases with increasing the incident laser pulse energy The refractive index increases with increasing annealing temperature and the refractive index increases with increasing laser pulse energy as well as the effect of laser pulse energy on the morphology of the thin film surface and increase the reflectivity. The results refer to indirect

allowed transition for CuO thin films. Band gap energies values decreases with increasing annealing temperatures for each CuO film prepared by PLD technique due to the growth of Crystallization. Increase in laser pulse energy leads to increasing in laser power density and thus increase the number of nanoparticles and thus band gap energy.

Elttayef, A. K.,et al**.,** in 2015 they studied the Structural and Optical Properties of Fe_2O_3 Thin Films Prepared by RF Magnetron sputtering. (Fe_2O_3) thin films were prepared on glass substrates via reactive radio frequency (RF) magnetron sputtering system using pure iron oxide (Fe_2O_3) target with purity of 99.99%. The glass substrates were cleaned chemically and ultrasonically, the glass substrate was cleaned by ethanol followed by distilled water rinse, subsequently samples are placed in beaker contain distilled water inside ultrasonic device for 2 hour at 353K The substrates and target were fixed in the chamber of magnetron sputtering system . The base pressure of the deposition chamber was kept at 6×10^{-5} Torr, they observed from transmittance spectrum of Fe_2O_3 films for different thickness (50,100,370 nm.), the transmission increase when thickness decrease and energy gap increase with increasing of thickness. Energy gap increased after the annealing.

1-3 Research Objectives:

- To deposit Fe_2O_3 thin films on glass substrate by pulsed laser deposition technique.
- To study the optical transmittance spectra of the Fe_2O_3 Thin films deposited as a function of different laser pulse energy and different repetition rates.

1-4 Problem of Study:

This research focused on the study the effect of the laser pulse energy and repetition rate on optical transmittance spectra of Fe_2O_3 thin films.

Fe_2O_3 thin films can be prepared by pulsed laser deposition process. The laser pulse energy and repetition rate have clear effect on transmittance spectra of thin films. This effect can be increase or decrease transmittance spectra. Thus in future work can determine appropriate parameters for each material to give suitable transmittance spectra for the application in question.

This study was done to the importance of the transmittance characteristic of the thin films his kind to be used in many applications such as solar energy conversion, electrochromism, photo catalysis, interference filters, and photo-oxidation of water. Fe_2O_3 thin films have high optical transmittance over the visible wavelength region thus it can be used in solar cells .from literature review this material has low transmittance spectra over ultra violet wavelengths region and thus can be used as filters from harmful rays.

1-5 Thesis Outline:

This thesis contains four chapters, chapter one contains introduction of research (objectives and problems of research, Literatures review), chapter two contains, laser in synthesis thin films, pulsed laser deposition of thin films, then describe characterization of thin film techniques and application of thin films .Chapter three describe experimental part, finally chapter four discuss the results, conclusions and then finished by references.

CHAPTER TWO

BASIC CONCEPT

2-1Introduction:

Fe_2O_3 thin film has been prepared by various methods such as chemical vapor deposition, sol- gel method, and pulsed laser deposition. In this study pulsed laser deposition technique was used. One of the most important and enabling characteristics in PLD is the ability to realize stoichiometric transfer of ablated material from multication targets for many materials. This arises from the non-equilibrium nature of the ablation process itself due to absorption of high laser energy density by a small volume of material. For low laser fluence and/or low absorption at the laser wavelength, the laser pulse would simply heat the target, with ejected flux due to thermal evaporation of target species. In this case, the evaporative flux from a multi-component target would be determined by the vapor pressures of the constituents. As the laser fluence is increased, an ablation threshold is reached where laser energy absorption is higher than that needed for evaporation. The ablation threshold is dependent on the absorption coefficient of the material and is thus wavelength dependent. At still higher fluences, absorption by the ablated species occurs, resulting in the formation of plasma at the target surface. With appropriate choice of ablation wavelength and absorbing target material, high-energy densities are absorbed by a small volume of material, resulting in vaporization that is not dependent on the vapor pressures of the constituent cations. (D. Yokoyama et al, 2007).

2-2 Laser in Synthesis Thin Films:

The field of material science and engineering community's ability to conceive the novel materials with extraordinary combination of chemical, physical and mechanical, properties has changed the modern society. There is an increasing technological progress. Modern technology requires thin films for different applications. Thin film technology is the basic of astounding development in solid state electronics. The usefulness of the optical properties of metal films, and scientific curiosity about the behavior of two-dimensional solids has been responsible for the immense interest in the study science and technology of the thin films. Thin film studies have directly or indirectly advanced many new areas of research in solid state physics and chemistry which are based on phenomena uniquely characteristic of the thickness, geometry, and structure of the film (A.R. West, 2003).When we consider a very thin film of some substance, we have a situation in which the two surfaces are so close to each other that they can have a decisive influence on the internal physical properties and processes of the substance, which differ, therefore, in profound way from those of a bulk material. The decrease in distance between the surfaces and their mutual interaction can result in the rise of completely new phenomena. Here the one dimension of the material is reduced to an order of several atomic layers which creates an intermediate system between macro systems and molecular systems, thus it provides us a method of investigation of the microphysical nature of various processes. Thin films are especially appropriate for applications in microelectronics and integrated optics. However the physical properties of the films like electrical resistivity do not substantially differ from the properties of the bulk material. For a thin film the limit of thickness is considered between tenths of nanometer and several

micrometers. Thin film materials are the key elements of continued technological advances made in the fields of optoelectronic, photonic, and magnetic devices. The processing of materials into thin films allows easy integration into various types of devices. The properties of material significantly differ when analyzed in the form of thin films. Most of the functional materials are rather applied in thin film form due to their specific electrical, magnetic, optical properties or wear resistance. Thin film technologies make use of the fact that the properties can particularly be controlled by the thickness parameter. Thin films are formed mostly by deposition, either physical or chemical methods. Thin films, both crystalline and amorphous, have immense importance in the age of high technology. Few of them are: microelectronic devices, magnetic thin films in recording devices, magnetic sensors, gas sensor, A. R. coating, photoconductors, IR detectors, interference filters, solar cells, polarizer's, temperature controller in satellite, superconducting films, anticorrosive and decorative coatings.

2-2-1 Pulsed Laser Deposition of Thin Films

In this thesis we used the pulsed laser to deposit thin films. As a materials processing technique, laser ablation was utilized for the first time in the 1960's, after the first commercial ruby laser was invented (H.M Smith &A.F Turner, 1965). Nevertheless, as a thin film growth method it did not attract much research interest until the late 1980´s, when it has been used for growing high temperature superconductor films. Since then, the development of the pulsed laser deposition technique has been more rapid and the amount of research devoted to this topic has increased dramatically. The advantages of PLD are the simplicity and versatility of the experiments. By using high-power pulsed UV-lasers and a vacuum chamber, a variety of stoichiometric oxide films can be grown in a reactive oxygen background gas without the need for further processing.

Pulsed laser deposition is deposition process using high power pulsed laser to ablate material from a target which is then deposited onto a substrate PLD can be used to deposit a wide range of materials from polymers to metals. Couples of unique characteristics are the doped particles high kinetic energy (~100 eV) and the wide deposition temperature range (0-1000 c^0). Films made by PLD can be extremely smooth and amorphous, or crystalline depending on the chamber atmosphere**.**

The focused laser pulses are absorbed at the target surface in a small volume. The absorbed energy density is sufficient to break any chemical bonds of the molecules within that volume. What essentially happens is that high-pressure gas is produced in the surface layer. As a result of the pressure gradient, a supersonic jet of particles is ejected normal to the target surface. The particle cloud absorbs a large amount of energy from the laser beam producing an expansion of hot plasma (plume) through the deposition

chamber. The ablated species condense on the substrate placed opposite to the target forming a thin film after some hundreds or thousands of laser pulses. Laser-pulse energy density, fluence [J/cm^2], on the target surface is one of the most important ablation parameters. When the fluence is sufficiently high, rapid evaporation of material occurs in a thin surface layer, which is necessary for stoichiometric transfer of material from a multi-component target. PLD can take place both in vacuum and in the presence of some dilute background gas which is used to influence the composition of the film (E. Morintale et al, 2010). This section discusses mechanism of PLD, Characteristics of PLD growth and Particulates on the film surface.

2-2 -2 Mechanism of Pulsed Laser Deposition Process:

This section presents the current state of understanding of some of the fundamental physic-chemical aspects of pulsed laser ablation and deposition, viewed from the perspectives of, respectively, the target, the plume and the deposited film.

The pulsed laser ablation process is a very complex one. At a superficial level, ablation might be viewed simply as a rapid boiling of material within a localized interaction volume at the surface of the target. Much of this complexity is illustrated, schematically, in figure: (2-1).

If a solid or liquid is irradiated with an intense laser beam, a small amount of material on the surface is vaporized and ejected away from the sample. This vapor is a collection of atoms, molecules, ions and electrons, the exact ratio and kinetic energy of which depend on the laser parameters (intensity, wavelength, pulse width) and to some degree on the target sample. If this vapor comes in contact with another surface it may recondense on the surface. Repeated pulses of laser light and subsequently

repeated vapor plumes might build up material on the surface to form what is termed a thin film.

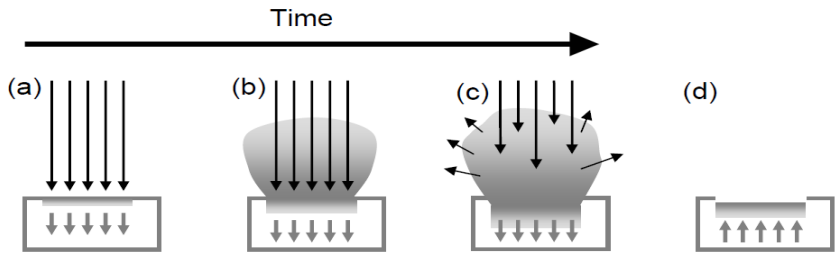

Figure: (2-1) Schematic illustrating key elements of the pulsed laser ablation event.

In figure (2-1) above (a) Initial absorption of laser radiation (indicated by long arrows), melting and vaporization begin (shaded area indicates melted material, short arrows indicate motion of solid–liquid interface), (b) Melt front propagates into the solid, vaporization continues and laser-plume interactions start to become important. (c) Absorption of incident laser radiation by the plume, and plasma formation. And (d) Melt front recedes leading to eventual re-solidification.

The growth and quality of the resulting film will generally depend on a number of fundamental parameters, including the choice of substrate, the substrate temperature T_S, and the absolute and relative kinetic energies and/or arrival rates of the various constituents within the plume. The latter may be affected by the choice of excitation wavelength, by the laser pulse duration, energy and intensity, by the presence (or otherwise) of any background gas, and by any secondary plasma activation in the target–substrate gap.

The PLD process can be divided into the following steps and is shown schematically in figure: (2-2):

1. Laser − target interaction
2. Plume expansion
3. Film deposition

Each step is very material dependent as well as dependent on experimental parameters such as laser wavelength, laser fluence and pulse width, background gas type and pressure, substrate type and temperature, and deposition geometry. Lasers used in PLD studies range in output wavelength from the mid infrared, e.g. *a* CO_2 laser, 10.6 μm, through the near infrared and visible, e.g. the Nd-YAG laser, with fundamental and second harmonic outputs at 1064 nm and 532 nm, respectively, down into the ultraviolet. Much current PLD work employs excimer lasers, which operate at a number of different UV wavelengths, e.g. 308 nm (XeCl), 248 nm (KrF), 193 nm (ArF) and 157 nm (F_2).

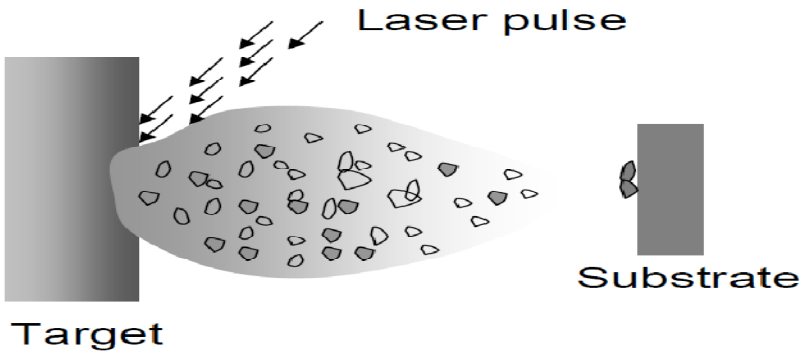

Figure: (2-2) Schematic presentation of the pulsed laser deposition process

The time scales involved in the three process steps are very different. Typically, the laser target interactions occur within nanoseconds, whereas the plume expansion in a background gas takes place within microseconds. Depending on the experimental conditions, the film growth process

following a laser pulse can in principle continue to develop until the next laser pulse occurs milliseconds later.

Laser − target interaction:

We start by considering some of the mechanisms that can contribute to materials loss following irradiation of the target with pulsed photons (laser pulse). According to Kelly and Miotello (R. Kelly & A. Miotello, 1999).these are generally divided into primary and secondary processes. Suggested sub-divisions of the former include thermal, electronic and macroscopic sputtering, their relative importance depending on the nature of the target material and on the laser excitation wavelength and pulse duration; however, the distinctions between them are often not particularly clear-cut. Direct evidence for electronic sputtering contributions in the case of metals and other extended solids is generally harder to discern, but reported examples include the observation of atoms with markedly non-thermal velocity distribution arising in laser induced desorption from nano-sized metal (W. Hoheisel et al,1988) . And from thin metallic films (both findings have been attributed to surface–Plasmon interactions), and even of graphite targets. Most detailed mechanistic considerations of target excitation and sputtering involve electronic initiation. Material interaction with an ultra-short laser pulse is assumed to involve very rapid excitation of the electron distribution, with efficient electron–electron coupling leading to an immediate rise in the electron temperature, subsequent heating of the lattice at a rate dependent upon the electron–phonon coupling strength, and eventual vaporization of the transiently heated target. Electronic contributions will thus tend to be most evident when using very short, *i.e.* sub-picoseconds pulse durations, and can manifest themselves as

unexpectedly large ion yields and/or supra-thermal propagation velocities within the expanding plasma plume.

Thermal contributions will generally dominate when using longer laser pulses, *e.g.* nanosecond pulses, of sufficient duration to allow photon coupling with both the electronic and vibrational modes of the target material. Such thermal contributions will be most favoured in cases where the target has low reflectivity, at the laser wavelength, a large absorption coefficient thus ensuring that the optical penetration depth is small, a low thermal diffusion coefficient and comparatively low boiling point, T_b. Since T_b will always exceed the target melting temperature, T_m, evidence of wavelike structures on the post-irradiated target surface, indicative of localized melting, is often sought as confirmatory evidence for there being a thermal contribution to the ablation yield.

The material ejection mechanism and the total amount of ejected flux can change dramatically when the fluence increases sufficiently to induce explosive boiling of the target material. This process sometimes referred to as phase explosion (A. Miotello & R. Kelly., 1999) .occurs at temperatures approaching the critical point, T_c. It is viewed as an explosive relaxation of the laser induced melt into a co-existent mixture of liquid droplets and vapour. Such hydrodynamic ejection of droplet-like particulates is one illustration of macroscopic sputtering. Exfoliation, whereby macroscopic flakes detach from the target as a result of the repeated thermal shocks, is another example. This type of sputtering can arise when using target materials having high thermal expansion coefficients and a sufficiently high melting point that the thermal oscillations induced by repeated pulsed laser excitation do not exceed T_m. Macroscopic particulate ejection can also arise in the case of porous targets, where in the localized laser induced heating

will cause very rapid expansion of any trapped gas pockets just below the surface and forcible ejection of the surface material.

Plume expansion:

This section attempts to characterize the formation, propagation, and properties of the plasma plumes typically encountered in PLD experiments, as revealed by numerous theoretical and mathematical modeling studies. As the plasma plume typically expands in vacuum or in a background atmosphere, we will treat separately the behavior of the plasma plume for both experimental conditions. Full characterization of the PLD plume requires an understanding of the advantages and limitations of several techniques. Despite the variety of diagnostic experiments designed to study PLD laser plumes, a number of major questions remain to be solved, including: The role of non thermal (electronic) and thermal (evaporation) ejection mechanisms in the ablation of material amounts necessary for film growth, the extent and explanation of laser absorption by the initial ejectants,The etching effects of the laser plasma on the target, The expansion mechanism responsible for the high kinetic energy of the ejectants, the competition between adiabatic expansion and space charge acceleration models, the fractional ionization of the plasma plume and the range of distances over which it can be electromagnetically steered, The role of clusters and particulates in the mass transfer to the substrate, The collision kinetics within the plume in the "collisionless" regime, The role of scattering, diffusion, and hydrodynamics in the slowing and thermalization of the plume by background gases, The major factors, i.e. kinetic energy, deposition rate, etc., determining the optimal film growth distance for various materials, The role of chemistry with the background gas and The

role of target surface morphology and phase on the eject. The plume can expand in vacuum or in a background atmosphere

1- Plume expansion in vacuum:

During a 30 ns PLD laser pulse in vacuum, a bubble of hot plasma is formed at approximately 50 μm from the target surface .As soon as the plasma is created, the plasma particles interact and tend to "lose memory" of the primary ablation mechanisms (A. Miotello & R. Kelly, 1999). Thus the plasma expansion can be described by certain characteristics, i.e. secondary ablation mechanisms (D.B Geohegan, 1993) **.**which to some extent is independent of the primary mechanisms. The expansion characteristics are described below:

A- Knudsen layer formation

Initially the density of ablated particles may be high, in the range of $10^{18} – 10^{20}$ cm^{-3}, and the ablated particles close to the target surface have an anisotropic velocity distribution, all velocity vectors pointing away from the target surface. However, this anisotropic velocity distribution is transformed into an isotropic one by collisions among the ablated particles. This happens within a few mean-free paths from the surface, a region known as the Knudsen layer. It is mainly within this Knudsen layer that laser energy is absorbed in the plasma.

B-Forward-directed plume:

After the laser pulse has terminated, inter-particle collisions can lead to a highly anisotropic expansion of the plasma plume, which will typically be peaked in the forward direction, i.e. normal to the target surface. In a model by (Singh & J. Narayan, 1990).where they model the plasma as a fluid using the equations of gas dynamics followed by an adiabatic expansion; it is shown that during the incidence of the laser pulse, the

isothermal expanding plasma is constantly augmented at its inner surface with evaporated particles from the target. The plasma is assumed to have exponential density gradients, and the velocity of various species vary linearly from the center of the plasma. The acceleration and the expansion velocities in this regime are found to depend upon the initial velocities of the plasma. Consequently, the highest velocities are obtained in the direction perpendicular to the target surface, where the initial plasma dimension is only tens of micrometers (S.I Anisimov et al, 1993).

2-Plume expansion in a background atmosphere

Ambient gases present during PLD scatter, attenuate, and thermalize the plume, changing important film growth parameters such as the spatial distribution, deposition rate, and kinetic energy distribution of the depositing species. In addition, the plume particles can react chemically with the gas particles. In general, raising the background pressure results in the following effects:

A-Increased fluorescence:

An increase in fluorescence from all species due to collisions on the expansion front and subsequent inter-plume collisions compared with the expansion in vacuum can usually be observed (D.B Geohegan, 1993).

B-Sharpening of the plume boundary, indicative of a shock front:

As the plume propagates into the background atmosphere it seems to push the background gas ahead and a sharp plume boundary may be created at the plume front. This plume sharpening indicates the formation of a shock front.

C-Slowing of the plume:

After a few microseconds of expansion and at sufficiently high background gas pressure, the plume slows down relative to the propagation

in vacuum and eventually coalesces with slower moving material. The velocity of the emitted particles is maximum for helium and minimum for argon background gas. This is attributed to larger degree of freedom per unit mass of helium than of any other gas and hence the collisional volume of helium is less as compared to that of other gases. The emitted species cover larger distances in helium atmosphere followed by air, oxygen, and argon. Misra and Thareja studied the ablation of an aluminum target by fast photography and found that particle's velocity is maximum in helium - 7.29×10^4 m/s, followed by air - 6.84×10^4 m/s, oxygen - 6.75×10^4 m/s and argon - 6.21×10^4 m/s, at a pressure of 10 mbar for laser energy of 100 mj.

E-Chemical reactions:

Reactive scattering can result in the formation of molecules or clusters in the plume (D.B Geohegan, 1993).

Film growth:

Film growth processes, i.e. deposition of ejected target material onto a substrate, can be described by the following sequence: the arriving particles must adsorb on the substrate surface, after which they may diffuse some distance before they react with each other and the surface and start to nucleate. The way the particles nucleate may determine the structure or morphology of the growing film. Under certain circumstances, e.g. high substrate temperature, diffusional interactions within the film and with the substrate, beneath the growing film surface, may subsequently modify film composition and film properties. In considering the general theory of film nucleation and growth, there are three conventional modes of nucleation and growth: Three-dimensional island growth − the Volmer-Weber growth, Two-dimensional full-monolayer growth − the Frank-van der Merwe growth and Two-dimensional growth of full monolayer followed by nucleation and

growth of three-dimensional islands − the Stranski-Krastinov growth. The selection of one of these growth modes by a substrate-film system depends on the thermodynamics that relates the surface energies of the film and substrate, and the film substrate interface energy.

1- Volmer-Weber Nucleation and Growth:

Figure: (2-3) illustrates the different processes involved in the nucleation of clusters on a surface by vapour deposition of atoms. Film atoms arrive at a rate dependent on the deposition parameters either on bare substrates areas or on preexisting clusters of film atoms. These film atoms can subsequently diffuse over the substrate or cluster surface, encounter other mobile film atom to form mobile or stationary clusters, attach to preexisting film-atom clusters, be re-evaporated from the substrate or from a cluster, or be detached from a cluster and remain on the substrate surface.

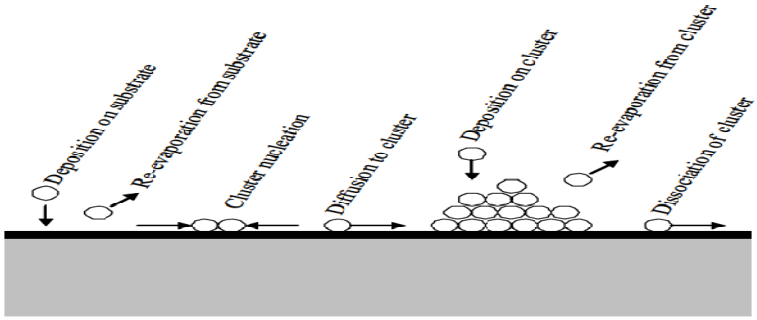

Figure: (2-3) Schematic diagram of atomic processes in the nucleation of three Dimensional clusters of deposited film atoms on a substrate surface.

The balance between growth and dissolution processes for a given cluster will be governed by the total free energy of the cluster, ΔG, relative to an assemble of individual atoms. For three-dimensional cluster growth, ΔG will have a maximum, ΔG^*, at a critical cluster size which means that cluster sizes above this critical size are stable. To a first approximation the nucleation rate is given as the product: [arrival rate of atoms at critical-size

nucleus] × [concentration of critical nuclei] the first term is proportional to the concentration of mobile atoms on the surface and to the surface diffusion coefficient. The second term is a strongly decreasing function of ΔG^*. As a rule, an increased cluster nucleation rate is desired in Volmer-Weber growth. In practice, this can be achieved by increasing the deposition rate or decreasing the substrate temperature, which gives a decrease in ΔG^*. Another possibility is to decrease the net surface/interface free energy (and thereby decrease ΔG^*), e.g. by creating interactions with a background gas.

2-**Frank - van der Merwe Nucleation and Growth:**

Full monolayer growth involves the nucleation and growth of islands that are only one monolayer thick and grow to essentially complete coalescence before significant clusters are developed on the next film layer. In this case there is no free energy barrier to nucleation, i.e. no ΔG^*. If the substrate material is different from the film material, full monolayer nucleation will be promoted by strong film-substrate bonding, low film surface energy and high substrate surface energy.

3-Stranski-Krastinov Nucleation and Growth:

Full monolayer growth may change to three-dimensional island growth after 1-5 monolayer due to a change in the energy situation with successive monolayer. This might be an increase in stress with increasing layer thickness due to mismatched lattice spacing.

2-2-3 Characteristics of PLD Growth:

Qualitatively, a possible event scheme for nucleation during a PLD cycle is as follows (assuming a high instantaneous vapour flux), A vapour pulse causes the nucleation of a high density of small subcritical clusters, i.e. clusters that are much smaller than those that would be stable for a lower instantaneous deposition rate. The subcritical clusters are expected to be

unstable once the vapour pulse has decayed after approximately 1 ms, the subcritical clusters will tend to dissociate into mobile species, The mobile species will nucleate new clusters on a different scale during the time of no vapour arrival - typically 100 ms (laser repetition rate of 10 Hz) and The next pulse will initiate the same sequence with some of the mobile atoms being added to the clusters formed following the first pulse. If the atomic process time constants, Tap, (i.e. the time constants for all the relevant diffusion, accumulation and dissociation phenomena) are much smaller than the period of the PLD cycle, TCycle, the pulsed vapour arrival should not affect the final film result significantly. However, if Tcycle ≈ tap, then the film formation pattern may be altered. If the PLD is performed in a background gas, e.g. oxygen, the background gas may promote stoichiometric film formation as oxide deposition. Furthermore, as mentioned above, the presence of a background gas may change film and substrate surface energies, possibly even the film growth mode. However, it is difficult to predict specific effects since they will depend on sticking coefficients, reaction rates and other factors. Other important process parameters that may influence the film growth are the flux, the energy, the ionization degree and the type of condensing particles. Surely, the physiochemical properties of the substrate are essential for film growth as well. For example, YBCO films are typically grown on non-interacting, nearly lattice-matched crystalline substrates such as MgO, SrTiO3 and LaAlO3 (R.E Zeng Acosta, L.T Romankiw & R. J VonGutfeld, 1982).

2-2-4 Particulates on The Film Surface:

The number of particulates on the surface is another issue that affects the overall film quality. The particulates can be categorized into small droplets (whose diameters range from a few nanometers to one micrometer)

and large, possibly irregularly-shaped outgrowths (diameters up to tens of micrometers). The number density of the particulates depends on the fluence, the number of laser pulses on the target, and on the deposition parameters such as the substrate temperature and the background-gas pressure. The largest particulates are believed to originate directly from the target breaking of protruding surface features, mechanical disintegration of, e.g., cones, craters, or microcracks, ejection of large droplets due to thermal shocks, splashing of a molten surface layer, or violent expansion of gas bubbles under a solid layer are typical explanations for their emergence. Droplets, on the other hand, are either re-solidified objects ejected from the target or other species condensed from the supersaturated vapor on the substrate. By adjusting the deposition parameters properly, the particulate density can be minimized but, simultaneously, the number of so-called precipitates can increase. The precipitates are particulates with a stoichiometry totally different from that of the film matrix and they are a sign of good crystallinity: off-stoichiometric areas are excluded from the otherwise perfect film into a separate phase. The enrichment of the particulates or precipitates with respect to some element is typical for films deposited from metal-alloy targets since elements with a low melting point and a high vapor pressure are evaporated first thus making the target deficient in these components. The particulate density is the highest off the deposition axis but the on-axis particulate density can also be high if the target–substrate distance is too small or the velocity of the species in the plume is too high. A high enough substrate temperature and a moderate background-gas pressure reduce the number of droplets and outgrowths on the film surface; reactive scattering at high pressures may lead to the nucleation and growth of additional particle clusters. The fluence has a

complicated influence on the distribution and size of the particulates: the larger the fluence, the larger the particulates are but the smaller their number is on the deposition axis. Furthermore, the pulse repetition rate should be low enough such that the condensed species would have time to form a smooth layer with the correct stoichiometry but too low a rate should be avoided such that chemical reactions would not take place For example, repetition rates of the order of 1−10 Hz promote the growth of YBCO in the desired orthorhombic high-temperature phase and result in a smooth film surface, whereas in the case of yttrium-iron-garnet films, the repetition rate should be above 20 − 30 Hz to prevent the loss of oxygen from the film matrix . At the moment, there are only a limited number of studies on the effect of the laser-pulse duration on the film quality. Klini et al. have deposited ZnO films using nanosecond and femto-second pulses at 248 nm and concluded that femto-second PLD produces rougher surfaces with a higher number of small crystallites on the surface than nanosecond PLD (TKK Dissertations, 2006).

2-3 Thin Film Characterization Techniques:

In the advancement of science and technology the discovery of novel materials those are having varied characteristics and applications have played an important role. Characterization is an important step in the development of exotic materials. The complete characterization of any material consists of phase analysis, compositional characterization, structural elucidation, micro-structural analysis and surface characterization, which have strong bearing on the properties of materials. This has led to the emergence of variety of advanced techniques in the field of materials science. In this section different analytical instrumental techniques used to characterize our thin films are described with relevant principles of their operation and working. These techniques such as:

2-3-1Thickness Measurements:

The thickness of thin films can be measure by various methods one of this method weight difference method and interference method.

1- Using Weight Difference Method:

Film thickness is an important parameter in the study of the film properties. Amongst different methods for measuring the film thickness, the weight difference method is simple and convenient and thickness't' is measured using the relation.

$$t = m / A \rho_b \qquad (2\text{-}1)$$

Where, 'm' is the mass of the film deposited on area 'A' of the substrate and ρ_b is the density of the material in the bulk form. The mass 'm' of the film has been measured by using a single pan microbalance. As reported in many studies the thin film density varies between 0.74 to 0.87 times the bulk

densities owing to the porosity. (M. Hernández., A. Juárez &R. Hernández., 1999).Hence a correction factor of 0.8 is applied to the bulk density in equation (2-1)

2- Interference measurement:

In the past, measurement of thin film thickness was achieved by our group by using a Talystep-Sloan Dektak II device, through needle sweeping with bi-dimensional displacement .However, it was necessary to develop an alternative method which allows knowing the thickness of the film that has been grown up. The use of an interferometer allows to measure thin film thickness. This method, using a radiation source, has as a limit the wavelength of the radiation applied. In this method can be achieved by making Comparison between two patterns of interference is taken into a count for the measurement of film thickness. These patterns are generated by substrate without and with film. Thus the thin film thickness forming is calculated using the data of the source wavelength and the shift in the interference patterns. Using the equation for the thickness:

$$t = (a/b)(\lambda/2) \qquad (2\text{-}2)$$

Where λ is the laser wavelength, the thickness of the layer grown up can be measured as function of Interference bandwidth (b), shift between bands (a) and wavelength of the source (M. Hernández., A. Juárez &R. Hernández., 1999).

2-3-2 Optical Absorption measurement:

The equilibrium situation in semiconductor can be disturbed by generation of carriers due to optical photon absorption. Optical photon incident on any material may be reflected, transmitted or absorbed. The phenomena of radiation absorption in a material is all together considered to

be due to: inner shell electrons, valence band electrons, Free carriers including electrons and electrons bound to localized impurity centers or defects of some type. In the study of fundamental properties of the semiconductors, the absorption by the second type of electrons is of great importance. In an ideal semiconductor, at absolute zero temperature the valence band would be completely full of electrons, so that electron could not be excited to higher energy state from the valence band. Absorption of quanta of sufficient energy tends to transfer of electrons from valence band to conduction band. The optical absorption spectra of semiconductors generally exhibits a sharp rise at a certain value of the incident photon energy which can be attributed to the excitation of electrons from the valence band to conduction band (may also involve acceptor or donor impurity levels, traps , exactions etc.) The conservation of energy and momentum must be satisfied in optical absorption process. Basically there are two types of optical transitions that can occur at the fundamental edge of the crystalline semiconductor, direct and indirect. Both involve the interaction of an electromagnetic wave with an electron in the valence band, which is rose across the fundamental gap to the conduction band. However, indirect transition involves simultaneous interaction with lattice vibration. Thus the wave vector of the electron can change in the optical transition. The momentum change being taken or given up by phonon. Direct inter-band optical transition involves a vertical transition of electrons from the valence band to the conduction band such that there is no change in the momentum of the electrons and energy is conserved as shown in Figure: (2-4a). The optical transition is denoted by a vertical upward arrow. The forms of the absorption coefficient ‘α’ as a function of photon energy hν depend on

energy of N(E) for the bands containing the initial and final states. For simple parabolic bands and for direct transitions.

$$\alpha = A(h\nu - E_g)^n / h\nu \qquad (2\text{-}3)$$

Where A is a constant depending upon the transition probability for direct transition, n = 1/2 or 3/2 depending on whether the transition is allowed or forbidden in the quantum mechanical sense. E_g is the optical gap. Let's visualize a situation given in Figure: (2-4b) where inter-band transition takes place between different k-states. Since these must satisfy the momentum conservation laws, the only way such transition can take place is through the emission or absorption of a phonon with wave vector q i.e.

$$K' \pm q = k + K \qquad (2\text{-}4)$$

While discussing the optical absorption edges observed in amorphous semiconductors the following assumptions are made: (a) the matrix elements for the electronic transitions are constant over the range of photon energies of interest and (b) K- conservation selection rule is relaxed.

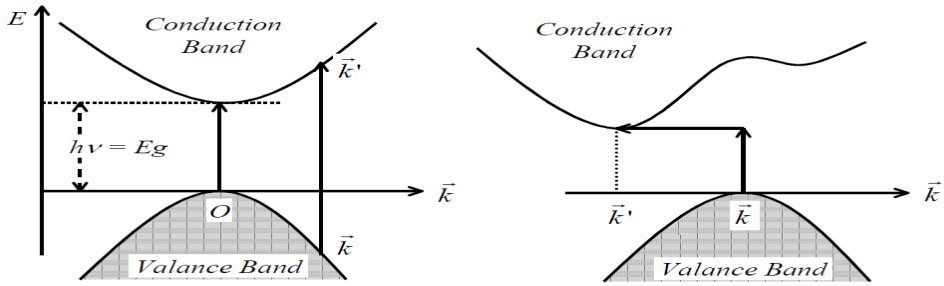

Figure: (2-4) direct inter-band optical transitions for a- direct band and b- indirect band semiconductors. The transitions are represented by vertical arrow.

This assumption is made in amorphous Semiconductors because near the band edges at least, $\Delta k \sim k$ and thus k is not a good quantum number. On E - k diagram such transitions would be non-vertical. However, no phonon absorption or emission processes are invoked to conserve momentum and all

the energy required is provided by the incident photons. Such transitions are termed non- direct as opposed to indirect. Without knowledge of the form of N (E) at the band edges, and under the assumption of parabolic bands. The absorption edge of many amorphous semiconductors can be described by a simple power law, at least over a limited range of the absorption coefficients, which enables an optical gap 'Eg' to be defined.

2-3-3 X- Ray Diffraction (XRD) Technique:

X-ray diffraction (XRD) is a powerful technique for determination of crystal structure and lattice parameters. Figure: (2-5) shows the schematics of X-ray diffractometer. Diffraction in general occurs only when the wavelength of the wave motion is of the same order of magnitude as the repeat distance between scattering centers. This condition of diffraction is nothing but Bragg's law and is given as,

$$2d \sin\theta = n\lambda \quad (2\text{-}5)$$

Where, d = inter-planer spacing, θ = diffraction angle, λ= wavelength of x-ray and n = order of diffraction

For thin films, the powder technique in conjunction with diffractometer is most commonly used. In this technique the diffracted radiation is detected by the counter tube, which moves along the angular range of reflections. The intensities are recorded on a computer system. The X- ray diffraction data thus obtained is printed in tabular form on paper and is compared with Joint Committee Power Diffraction Standards (JCPDS) data to identify the unknown material. The sample used may be powder, single crystal or thin film. The crystallite size of the deposits is estimated from the full width at half maximum (FWHM) of the most intense diffraction line by Scherer's formula as follows (TKK Dissertations, 2006).

$$D=\frac{0.9\lambda}{\beta \cos\theta} \qquad (2\text{-}6)$$

Where, D is crystallite size, λ is wavelength of X-ray used, β is full width at half maxima of the peak (FWHM) in radians, θ and is Bragg's angle. The X- ray diffraction data can also be used to determine the dimension of the unit cell.

This technique is not useful for identification of individuals of multilayer or percentage of doping material

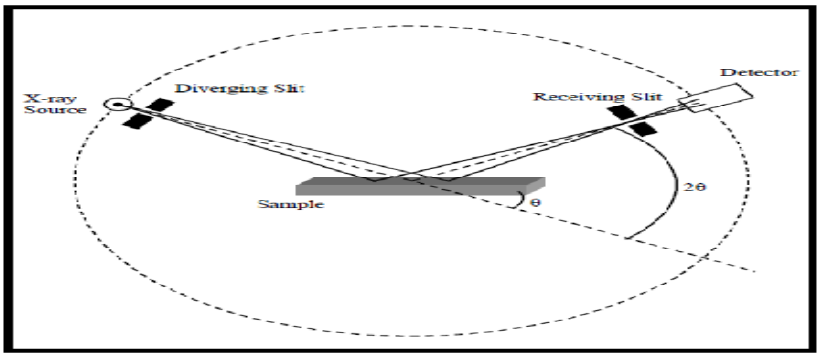

Figure: (2-5) Schematics of X-ray diffractometer

2-3-4 Scanning Electron Microscopy (SEM):

Scanning electron microscope is an instrument that is used to observe the morphology of the solid sample at higher magnification, higher resolution and depth of focus as compared to an optical microscope (T .Silfvast William, 2008). When an electron strikes the atom, variety of interaction products are evolved. Figure: (2-6) illustrates these various products and their use to obtain the various kinds of information about the sample. Scattering of electron from the electrons of the atom results into production of backscattered electrons and secondary electrons. Electron may get transmitted through the sample if it is thin. Primary electrons with

sufficient energy may knock out the electron from the inner shells of atom and the excited atom may relax with the liberation of Auger electrons or X-ray photons. All these interactions carry information about the sample. Auger electron, ejected electrons and X-rays are energies specific to the element from which they are coming.

These characteristic signals give information about the chemical identification and composition of the sample.

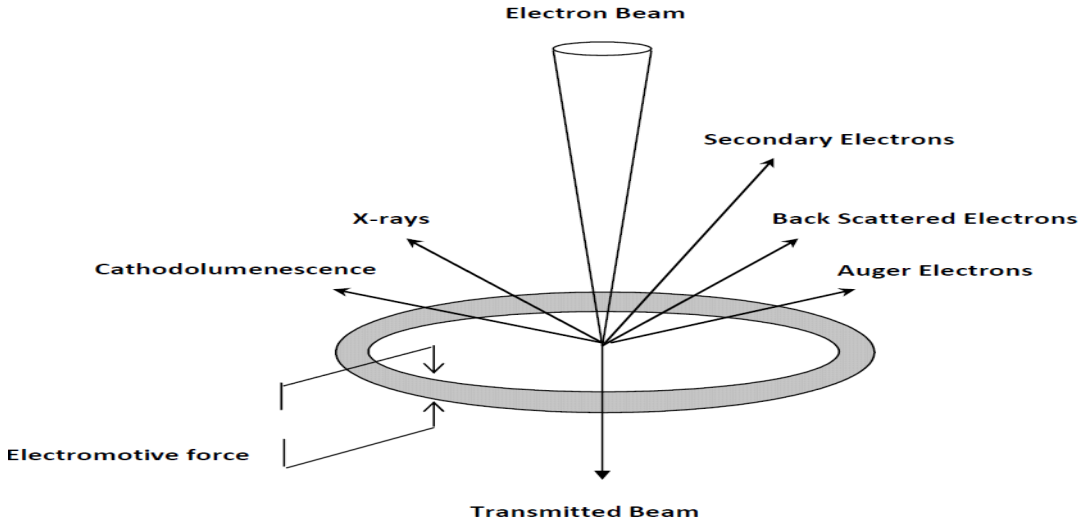

Figure: (2-6) Variety of interaction products evolved due to interaction of electron beam and sample

2-4 Applications of Thin Films:

Although the study of thin film phenomena dates back well over a century, it is really only over the last four decades that they have been used to a significant extent in practical situations. The requirement of micro miniaturization made the use of thin and thick films virtually imperative. The development of computer technology led to a requirement for very high density storage techniques and it is this which has stimulated most of the research on the magnetic properties of thin films. Many thin film devices have been developed which have found themselves looking for an application or, perhaps more importantly market. In general these devices have resulted from research into the physical properties of thin films. The fundamental research has led to a dramatic improvement in understanding of thin films and surfaces. This in turn has resulted in a greater ability to fabricate devices with predictable, controllable and reproducible properties. The cleanliness and nature of the substrate, the deposition conditions, post deposition heat treatment and passivation are vital process variables in thin film fabrication. Therefore, prior to this improvement in our understanding of thin films, it has not really been possible to apply them to real devices. much of the finance for early thin film research originated from space and defense programmes to which the device cost is less important than its lightweight and other advantages, the major applications of thin film technology are not now exclusively in these areas but rather often lie in the domestic sector in which low cost is essential (K. L Chopra, 1969).

Thin film materials have already been used in semiconductor devices, wireless communications, telecommunications, integrated circuits, rectifiers, transistors, solar cells, light-emitting diodes, photoconductors, light crystal displays, magneto-optic memories, audio and video systems, compact discs,

electro-optic coatings, memories, multilayer capacitors, flat-panel displays, smart windows, computer chips, magneto optic discs, lithography, micro electromechanical systems (MEMS), and multifunctional emerging coatings, as well as other emerging cutting technologies. (K. L Chopra, 1969).

CHAPTER THREE
EXPERIMENTAL PART

This chapter describes the experimental part of this work, materials, equipments and tools were used with their specifications, experimental procedure that was followed to deposit the thin films by PLD technique and UV-Vis spectroscopy characterization.

3-1 Materials:

The target of the deposition was Fe_2O_3, supplied from Sudanese Chemicals Import Company; it was brought in powder form with weight 100g. The figure: (3-1) below shows the Fe_2O_3 material in powder form (red color).

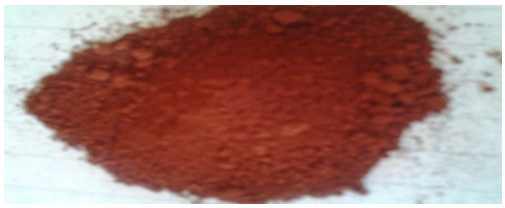

Figure: 3-1 The Fe_2O_3in powder form

Glassy microscope slide was used in this work as substrate to deposit thin films on it, with thickness 1mm, weight 4.9995 g, length 7.5cm and width 3cm.

3-2 Equipments and Tools:

Those equipments were chosen and aligned in this work to prepared Fe_2O_3 in tablets form, deposit the Fe_2O_3 thin films by PLD technique and characterized this films.

3-2-1 Samples Compressor:

The devices used to prepare Fe_2O_3 tablets form.

3-2-2Laser source:

The laser source used in this work was HS220E Nd: YAG Q-switched laser .It was supplied from Apolo Shanghai Medical Technology Company China, (2007). The specifications of this laser are (Portable Dual 1064&532nm, Pulse energy-1064/532nm was 1000/ 500Mj, Pulse duration was <10ns, Aiming beam was 532&1064 nm, Repetition rate was 1~5Hz and Dimension was 38cm*36cm*28cm (L*W*H)). The pulse energy of this laser was adjustable depending on the applied pumping the flash lamps voltage.

3-2-3 UV-Vis Spectrophotometer:

The spectrophotometer used in this work was UV-Vis 1240 spectrophotometer this device was used to measure the transmittance spectra of Fe_2O_3 thin films; it covering wave length from (190-1100) nm, with auto lamp switch from visible to ultraviolet, the UV-Vis spectrophotometer used here was supplied from SHIMADZU.

3-3 Experimental Methods:

Experimental methods in this work contain the sample preparation, Fe_2O_3 thin films synthesis by PLD and characterization Fe_2O_3thin films by UV-Vis 1240 spectrophotometer.

3-3-1 Sample Preparation:

4g from Fe_2O_3 powder material was weighed for seven samples, after that this powder material was compressed for converted from powder form to tablets form by pressure 12 tons ,diameter was 2.5cm and holding time: 2 min).

3-3-2 Thin Films Synthesis by PLD Technique:

Conceptually and experimentally, Pulsed Laser Deposition (PLD) is simple, it was performed at ambient pressure and room temperature .the schematic diagram and setup have been shown in Figure: (3-2) and figure: (3-3) respectively. It consist the Target, Substrate, Holders and Laser source (Nd-yag Q- switched laser). And the experiment procedure was followed by steps:

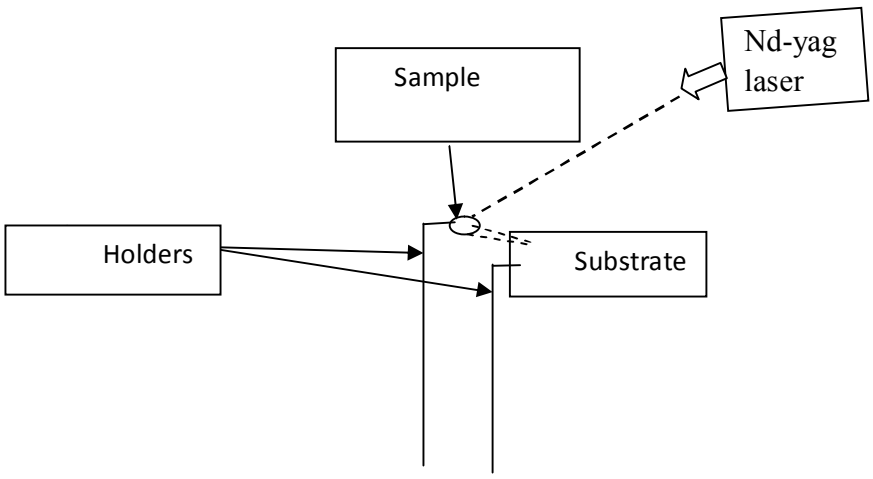

Figure: (3-2) schematic diagram of PLD technique

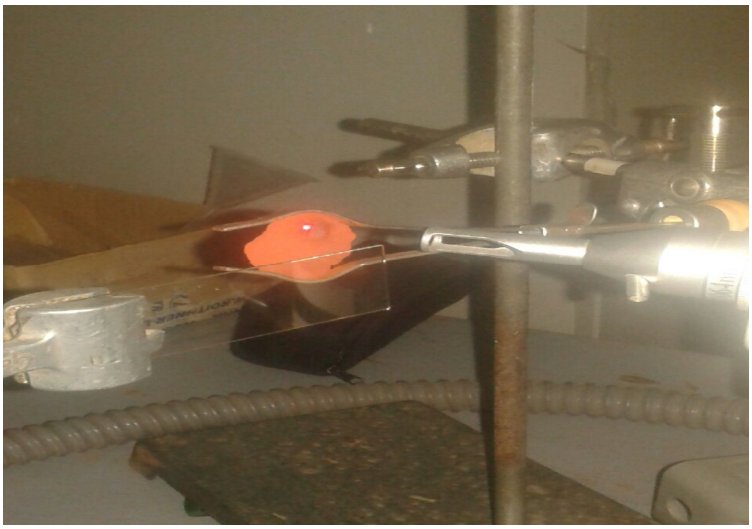

Figure: (3-3) experimental setup of PLD technique

1-The target –substrate distance was fixed at 6 mm.

2-The laser beam was incident on the target by angle of incident 45° , the wave length 532nm was selected (second harmonic generation Nd: YAG laser) and pulse duration 10ns.

3-The laser pulse energy was varied from (250-400) mj with increment 50 mj in each step, and with fixed laser repetition rate 20Hz.

4-The laser repetition rate was varied from (10-30) Hz with increment 10Hz in each step and with fixed laser pulse energy 300mj.

3-3-3 UV-Vis 1240 Spectrophotometer Characterization:

After the thin films synthesized on glass substrates by PLD technique with laser wave length 532nm, pulse duration 10ns ,different laser pulse energy and different repetition rate for all the samples .the transmittance spectra of thin films were obtained by using the UV-Vis 1240 spectrophotometer. In the spectrophotometer the transmittance spectra was selected against the wave length and the spectrum was plotted for all the samples.

CHAPTER FOUR

RESULLTS AND DISCUSSION

This chapter covers and discussed the results of the sample compression, thin films synthesis and effects of laser pulse energy and laser repetition rate on the transmittance spectra of Fe_2O_3 thin films that prepared by pulsed laser deposition technique that were characterized by UV-Vis spectrophotometer. Flowed by conclusion of this work and then finish by references.

4-1 Sample Compression:

After the material was pressed by samples compressor device with pressure 12 tons and diameter was 2.5cm. It obtained cylindrical samples with 2.5 cm in diameter and thickness 2 mm. Figure: (4-1) below show the Fe_2O_3 in tablet shape used as target in this work.

Figure 4-1:Fe_2O_3 tablet

4-2 PLD Technique:

Different Fe_2O_3 thin films were synthesized using PLD technique at laser pulse energy (250,300,350,400) mj with fixed laser repetition rate 20 Hz and at different laser repetition rate (10, 20, 30) Hz with fixed laser pulse energy 300 mj. Figures below shown thin films were synthesized.

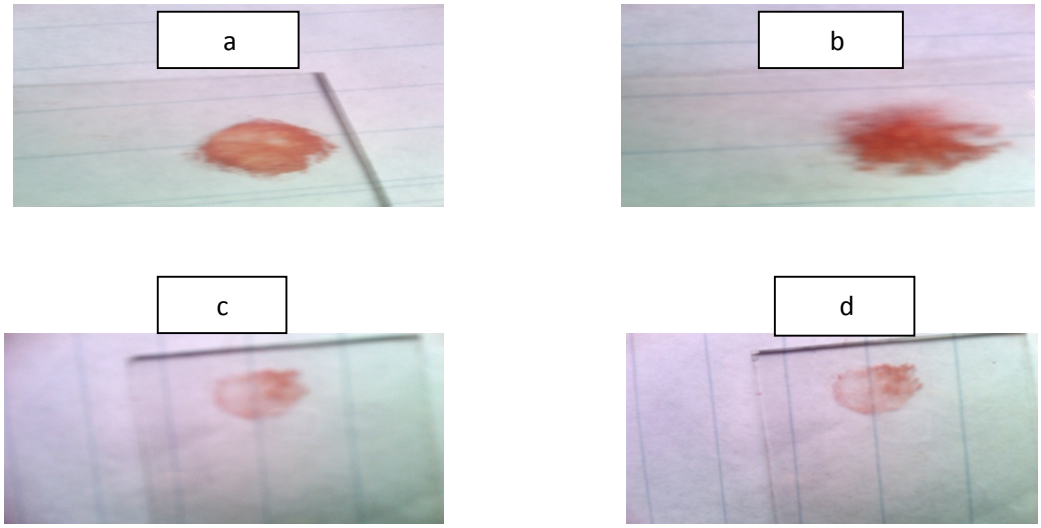

Figure: (4-2) Thin films Synthesized at fixed repetition rate 20 Hz with different laser pulse energy (a) 400mj, (b) 350mj, (c) 300mj and (d) 250mj

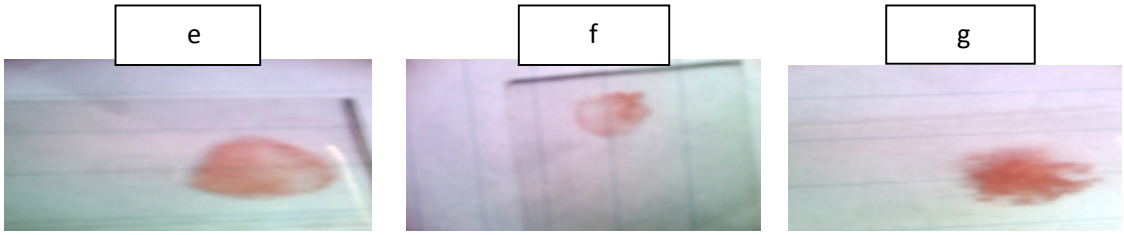

Figure :(4-3) Thin films Synthesized at fixed laser pulse energy 300mj with different repetition rate (e) 10Hz, (f) 20Hz and (g) 30Hz.

From figures above it obvious thin films have small area. Another observation is the lack of uniformity over a large area of the plume, due to the narrow angular distribution of the plume that comes out from the target surface. Also observed the deposition increases with increase incident laser pulse energy thus the thickness of thin films increases. And the droplet increase with increase laser repetition rate.

4-3 UV-Vis Spectroscopy Characterization:

After Fe_2O_3 thin films characterized by UV-Vis spectrophotometer the transmittance spectra of all samples were plotted and it will discuss below.

4-3-1 Transmittance Spectra of Fe_2O_3 Thin Films Prepared by Changing Laser Pulse Energy:

For the purpose of measuring the optical transmittance laser repetition rate has been set constant at 20Hz. UV-Vis optical properties with range of (400nm to 500nm) for different laser pulse energy (250,300,350,400) mj.

Figure 3-8 below shows Optical transmittance spectra of Fe_2O_3 thin films at different laser pulse energy by using Nd: YAG laser wavelength 532nm, laser repetition rate 20Hz,it is obvious from the figure that at certain wavelength the transmittance decreases with increasing the incident laser pulse energy. When the incident laser energy increased the amount of energy absorbed in the target increased, which in turn leads to an increase of particles ejected toward the substrate.

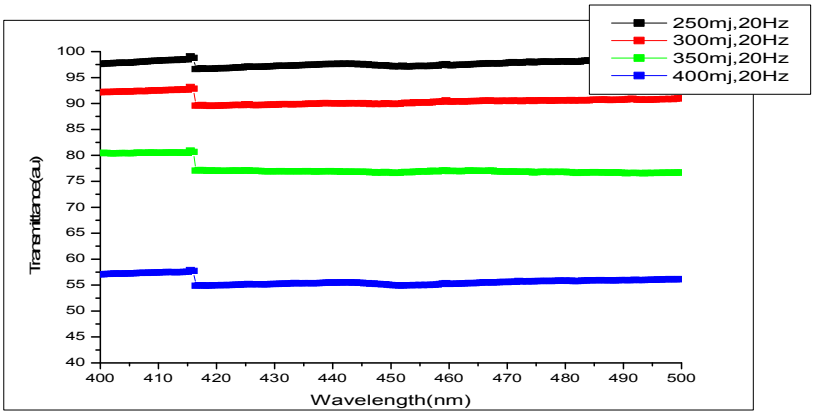

Figure: (4-4) Optical transmittance spectra of Fe_2O_3 thin films at different laser pulse energy by using Nd: YAG laser wavelength 532nm, laser repetition rate 20Hz.

These ejected particles have high kinetic energy when it absorbs the high energy laser and ultimately the density of particles deposited on the substrate increases, and the thickness of the film will increase and thus the transmittance will decrease with increasing thickness.

As a result we can conclude that the optical transmittance measurements depend strongly on the laser pulse energy of Fe_2O_3 thin films prepared by PLD method.

4-3-2 Transmittance Spectra of Fe_2O_3 Thin Films Prepared by Changing Laser Repetition Rate:

For the purpose of measuring the optical transmittance laser pulse energy has been set constant at 300mj and UV-VIS optical properties with range of 400nm to 500nm for different laser repetition rate(10,20,30)Hz. Figure: (4-5) below shows Optical transmittance spectra of Fe_2O_3 thin films at different laser repetition rate by using Nd: YAG laser wavelength 532nm, laser pulse energy 300mj.

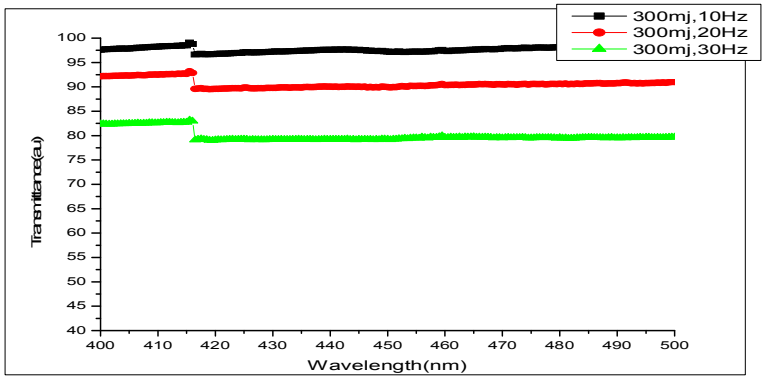

Figure :(4-5) Optical transmittance spectra of Fe_2O_3 thin films at different laser repetition rate by using Nd: YAG laser wavelength 532nm, laser pulse energy 300mj.

It is obvious the optical transmittance spectra of Fe_2O_3 Thin films prepared by PLD method decrease with increase laser repetition rate. The laser repetition rate has effects on the crystalline structures of the films and droplets formation. At higher laser repetition rate the droplets became more and have larger dimensions and at low repetition rate it became less and have smaller dimension.

The amount of energy introduced to the target increases with increasing pulse repetition rate, which makes the target surface rougher However, the energy introduced to the surface of the target per unit area and per unit time decreases because of the target roughening and the plume deflection effect resulting in the decrease of the average deposition rate. For this reason the high repetition rate is causing droplets formation in thin films surface and then the transmittance spectrum of this films decreased with increasing of the laser repetition rate.

As result the optical transmittance measurements depend on the laser repetition rate of Fe_2O_3 thin films prepared by PLD method.

4-4 Conclusions:

Fe_2O_3 thin films were prepared by PLD technique with different laser pulse energy (250,300,350,400)mj at fixed laser repetition rate 20Hz and with different laser repetition rate(10,20,30)Hz at fixed laser pulse energy300mj.thin films were characterized by UV-Vis spectroscopy and transmittance spectra of all samples were obtained. From the results obtained in this work, we can conclude that:

- The Fe_2O_3 thin films grown on glass substrate by PLD at different laser pulse energy and different laser repetition rate are characterized.
- The optical transmittance spectra of Fe_2O_3 thin films prepared by PLD technique depend strongly on deposition condition such as laser pulse energy and laser repetition rate.
- The transmittance spectra decreases with increasing the incident laser pulse energy and transmittance spectra also decreases with increasing the laser repetition rate.
- A smoother films surface can be obtained by changing the pulse repetition rate during the deposition process.

References

A.B.C. Ekwealor & F.I .Ezema. *" Effect of precursor concentration on the optical and structural properties of the Fe_2O_3 thin films synthesized in A polymer matrix by chemical bath deposition "* Journal of Ovonic Research Vol. 9, No. 2, March - April (2013), p. 35 – 43.

A.Giardini et al., "*Thin films deposition in RF generated plasma by reactive pulsed laser ablation*", Appl. Surf. Sci. 197 - 338-342,(2002).

A. Kadhim Aadim, A-K Ali Hussain, R. Mohammed Abdulameer *"Effect of annealing temperature and laser pulse energy on the optical properties of CuO films prepared by pulsed laser deposition*" Iraqi Journal of Physics, (2014) Vol.12, No.23, PP. 97-104.

A.k. Elttayef et al. *"Study the Structural and Optical Properties of Fe2O3 Thin Films Prepared by RF Magnetron sputtering"* International Journal of Application or Innovation in Engineering & Management (IJAIEM) Web Site: www.ijaiem.org Email: editor@ijaiem.org (2015).

A. Miotello and R. Kelly, "*Laser-induced phase explosion: new physical problems when a condensed phase approaches the thermodynamic critical temperature"*, Appl. Phys. A 69- S67-S73, (1999).

A.R. West *"Solid State Chemistry"*, John willey & Sons Singapore, (2003).

A. Y Cho." *Thin Solid Films*", 100-291. (1983).

D.B Geohegan, *"Diagnostics and characteristics of pulsed laser deposition laser plasmas"*, in ref. 3, pp.115-165, (1993).

D. Dijkkamp, et al., *"Preparation of Y-Ba-Cu oxide superconductor thin films using pulsed laser evaporation from high Tc bulk material",* Appl. Phys. Lett. 51619-621 (1987).

D.J Krajnovich, J.E Vazquez and R.J Savoy *"Impurity-driven cone formation during laser sputtering of graphite*", Science 259, 1590-1592. (1993).

D. Oatley McMullan and K. C. A Smith, *"The Development of the Scanning Electron Microscope, in The Beginnings of Electron Microscopy, ed P. W. Hawkes. Advances in Electronics and Electron 1Physics Suppl*" (London: Academic Press) 16-443. (1985).

D. Yokoyama et al.,"*Mössbauer study of films produced by laser deposition of iron oxides"* Journal of Radio analytical and Nuclear Chemistry, Vol. 272, No.3 (2007) 631–638.

E. Morintale, C. Constantinescu and M. Dinescu", *"thin films development by pulsed laser-assisted deposition",* physic AUC, vol.20 (part 1), 43-56, (2010).

H.M. Smith, and A.F.Turner ,*"Vacuum deposited thin films using a ruby laser",* Appl. Opt. 4 147, (1965).

J.M. Lackner et al., *"Pulsed laser deposition: a new technique for deposition of amorphous SiOx thin films*", Elsevier Surface and Coatings Technology 163 –164 (2003) 300–305.

K.L.Chopra, "*Thin Film Phenomena",* McGraw Hill ,NewYork, (1969).

Liu Wei et al., *"Characterization of zirconium thin films deposited by pulsed laser deposition*" Chin. Phys. B Vol. 23, No. 9 (2014) 098103.

M.Chirita and I. Grozescu *"Fe_2O_3 – Nanoparticles, Physical Properties and Their Photochemical and Photoelectrochemical Applications Chem".* Bull. "Politehnica" Univ. (Timisoara) Volume 54(68), 1(2009).

M. Hernández, A. Juárez and R. Hernández, "*Interferometric thickness determination of Thin Metallic Films",* Superficies y Vacío *9,* 283-285. (Diciembre 1999).

P.R.Willmott and J.R Huber *"Pulsed laser vaporization and deposition",* Rev. Mod. Phys. 72 315-328, (2000).

R. Behrisch*,"Sputtering by Particle Bombardment",* Springer, Berlin, (1981).

R.E Zeng Acosta, L.T Romankiw, and R. J VonGutfeld,*"Thin Sol. Films*" 95, 131. (1982).

R. Kelly and A. Miotello, *"Mechanisms of pulsed laser sputtering",* in ref. 3, pp.55-87. (1999).

R.K Singh and J. Narayan, *"Pulsed-laser evaporation technique for deposition of thin films: Physics and theoretical model",* Phys. Rev. B 41 8843-8859, (1990).

S.I Anisimov et al, *"An analytical model for three dimensional laser plume expansion into vacuum in hydrodynamic regime*", Appl. Surf. Sci. 96-98 24-32. (1996)

S.I Anisimov et al., *"Gas dynamics and film profiles in pulsed laser deposition of materials",* Phys. Rev. B 48 12076-12081. (1993).

S. S. Shinde et al, *"Physical properties of hematite Fe2O3 thin films: application to Photoelectrochemical solar cells",* Journal of Semiconductors, Vol. 32, No. 1(2011).

TKK Dissertations 38 Espoo thin film deposition using laser ablation: application to ferromagnetic shape-memory material and methods for spatial shaping of laser beams (2006).

W. Hoheisel et al., "Desorption stimulated by laser-induced surface-plasmon excitation", Phys. Rev. Lett. 601649-1652 (1988).

Y. GAO, H. Niu, and C. Q Chen, Chem. Phys. Lett., 367 (1-2) 141(2003).

Appendixes:

Figure1: The Glassy microscope slide substrate

Figure2: samples compressor device.

Figure 3: Components of samples compressor devices

Figure 4: Q-switched Nd: YAG laser HS220E

Figure 5: UV-Vis 1240 spectrophotometer