People's Democratic Republic of Algeria Ministry of Higher Education and Scientific Research

Echahid Hamma Lakhdar University of El-Oued

FACULTY OF TECHNOLOGY

MECHANICAL ENGINEERING DEPARTMENT

End of study thesis

Presented for the graduation of

ACADEMIC MASTER

Field: Technologies

Sector: Mechanical engineering

Specialty: Renewable Energies

Theme:

The effect of Ni doping on the properties of ZnO thin films produced by solar pyrolysis spray

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Acknowledgement

First of all, we thank Allah for giving us success and patience to complete this work.

We also thank our Supervisor Abdelbaki Nid for standing with us and guiding us with his experience which without it, this work would not have been possible

Mr. President and Gentlemen of the jury, also all the staff of the Faculties of Technology and Exact Sciences of the Echahid Hamma Lakhdar University of ElOued, thank you all.

We cannot forget to thank our professor, Dr. Yassin Aoun, for his support, care and advice, as they helped us a lot.

We also thank anyone who contributed even a little to help us complete the access we are in now.

Dedication

Our dedication goes to ourselves

Before everything and then our supporters,

And our role models our beloved parents,

Who have been side by side through

The road leading to this moment. Thank you

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Abbreviation

Notation	Unites
MW: megawatt	
BCE:	
CSP:	
LFR:Linear Fresnel Reflector	
PTC:Parabolic Trough Collector	
HFC:Heliostat Field Collector	
PDC:Parabolic Dish/Engine Collector	
LED:Light-emitting diode	
ARC: Anti-reflection coating	
ZnO: Zinc oxide	
PES: photoelectron spectroscopy	
ARPES:Angular resolved photoelectron spectroscopy	
Eg: band gap energy (optical gap)	[eV]
UV: Ultraviolet	
Ni: Nickel	
PVD: Physical vapor deposition	
CVD:Chemical vapor deposition	
APCVD: atmospheric-pressure chemical vapor deposition	
LPCVD: low-pressure chemical vapor deposition	
PACVD: plasma-assisted chemical vapor deposition	
LECVD: laser-enhanced chemical vapor deposition	
SPT: Spray Pyrolysis Technique	
XRD: X-ray diffraction	
FWHM: full width at half height	

σ: Electrical conductivity	[Ω-1cm-1]
ε: Dielectric constant	[F / m]
dhkl: Inter-reticular distance	[Å]
a: Mesh parameter	[Å]
θ: Angle of incidence (angle of reflection)	[degree]
λ: Wavelength of incident X photons	[Å]
n: Order of diffraction	(whole number)
D: Size of crystallites	[nm]
α: Absorption coefficient	[m-1]
h: Planck constant is $6,63.10^{-34}$	[J.s]
ν: Wave frequency	[Hz]
Eu: Urbach energy	[J]
Rs: Surface resistance	
: Electrical resistivity □	[Ω.cm]
I: Current intensity	[A]
U: Current voltage	[V]
T : Transmittance	[%]
t: Thickness	[nm]

General Introduction

General Introduction

Solar energy is the most widely used renewable energy because its source is available forever (the sun) and its multiple applications, and one of the most important and most important applications is the heating efficiency using parabolic plate capacitors, which in turn has multiple uses, for example, the production of thin films, which in turn has many fields such as electronics For example, they are used for interconnections between the various remote components of the chip. In optics, thin layers make anti-reflective films, for eyeglasses or car windshields, or even to make reflective films. Thin layers may also have the purpose of protecting surfaces from corrosion so as to create corrosion-resistant surfaces or surfaces that make it possible to strengthen the materials to be deposited on them, or even decorative surfaces.

Zinc oxide (ZnO), for example, is an n-type semiconductor with versatile applications such as ultraviolet optical devices, piezoelectric transducers, transparent electrodes for solar cells, and gas sensors. The ZnO thin film has high field-effect mobility, is insensitive to visible light and has a low processing temperature. Moreover, its film and device quality can be improved very easily by doping with materials such as In, Ga, Al or Ni.

The aim of this thesis is to apply the spray pyrolysis process to manufacture zinc oxide films, and to verify that the activation of these films by nickel has an effect on the structural, optical, and electrical properties using parabolic solar capacitors.

After a general introduction, the thesis is organized as follows:

The first chapter includes information about solar energy and its use in the production of thin films, then we touched on the components and properties of the components that we will deposit on the substrate (zinc oxide, nickel).

The second chapter is devoted to the applied part of our experiment as well as to the different characterization techniques used to analyze and quantify the different structural, optical and electrical properties of the resulting thin layers of Ni-doped ZnO (1- DRX, 2- UV-visible spectroscopy 3- Quad-dot technique was introduced). Thin layers of Ni-doped ZnO were deposited by spray technique on glass substrates heated with a solar furnace.

The third chapter combines the characterization results that we obtained in our layers and discussions on the results obtained during this study.

Finally, a general conclusion retraces the main part of the research work carried out as well as the perspectives.

Chapter I:

General Information about Solar Energy and Thin Films

I.1. Introduction

Day after day we notice that the world is hungry for the energy industry, especially after knowing that there is a new and renewable sources of energy, such as solar energy, wind energy, hydropower, Biomass… specifically solar energy, has witnessed a wide development in its field. Solar energy is energy that gained from the sun and can be declared by two systems: solar thermal systems (heat) such as solar thermal collectors and solar photovoltaic systems (electricity) such as solar photovoltaic collectors (solar panel).

This study is focused on the heat utilization of solar energy make use of a parabolic solar collector (furnace).

As well, in this chapter we are willing to discuss solar energy and its uses specifically regarding thin films before citing specific techniques of their physical and chemical deposits, as well as the features of the chosen substances.

I.2. Solar Energy

I.2.1. The Sun (the source of energy)

The sun is an ordinary star, one of about 100 billion in our galaxy, the Milky Way. The sun has extremely important influences on our planet: it drives weather, ocean currents, seasons, and climate, and makes plant life possible through photosynthesis. Without the sun's heat and light, life on Earth would not exist. [1]

Figure I. 1: Image of the Sun [2]

The hydrogen, which takes roughly three-quarters of its overall mass, and helium, which makes up roughly a quarter of its total mass. The rest of its bulk (little under 2%) is made up of other elements such as Carbon, nitrogen, oxygen, magnesium, neon, sulfur, silicon, and iron. The surface of the Sun has a temperature of 5778 K (5505°C). [3]

I.2.2 Solar Radiation

Solar radiation is made up of electromagnetic waves which travel from the sun to the earth with the speed of light. The quantity of short wave radiant energy emitted by the sun passing through a unit horizontal area in unit time is referred generally as global solar radiation. This incoming solar radiation is modified as it travels through the atmosphere and again once it hits the surface. So the three main components of solar radiation are the direct, the diffused and the reflected solar radiation.

Direct radiation is intercepted unimpeded, in a direct line from the sun. Diffuse radiation is scattered by atmospheric constituents, such as clouds and dust. Reflected radiation is reflected from surface features. [4]

I.2.3. Solar field

The solar field is a set of data describing the evolution of the solar radiation available during a given period. It is used to simulate the operation of a solar energy system and to make the most exact sizing possible given the demand to be satisfied. The study of solar radiation is necessary for the choice of the best site for the installation of a solar capture system.

I.2.4. Solar field in Algeria

According to its geographical location, Algeria holds one of the highest solar potential. Indeed, following an assessment by the satellites, the German Aerospace Center (DLR) concluded that Algeria has the largest solar potential in the Mediterranean basin: 169,440 TWh / year. Sunshine duration on almost all the country over 2000 hours per year and can reach 3900 hours in the Highlands and the Sahara. The daily energy obtained on a horizontal surface is about 5 kWh on most of the national territory, about 1700 kWh / m² / year for the North and 2263 KWh / m² / year for the South, [5]. The climatic conditions in Algeria are favorable for the development of solar energy due to the abundant sunshine throughout the year, especially in the Sahara region, (Fig. I.2).

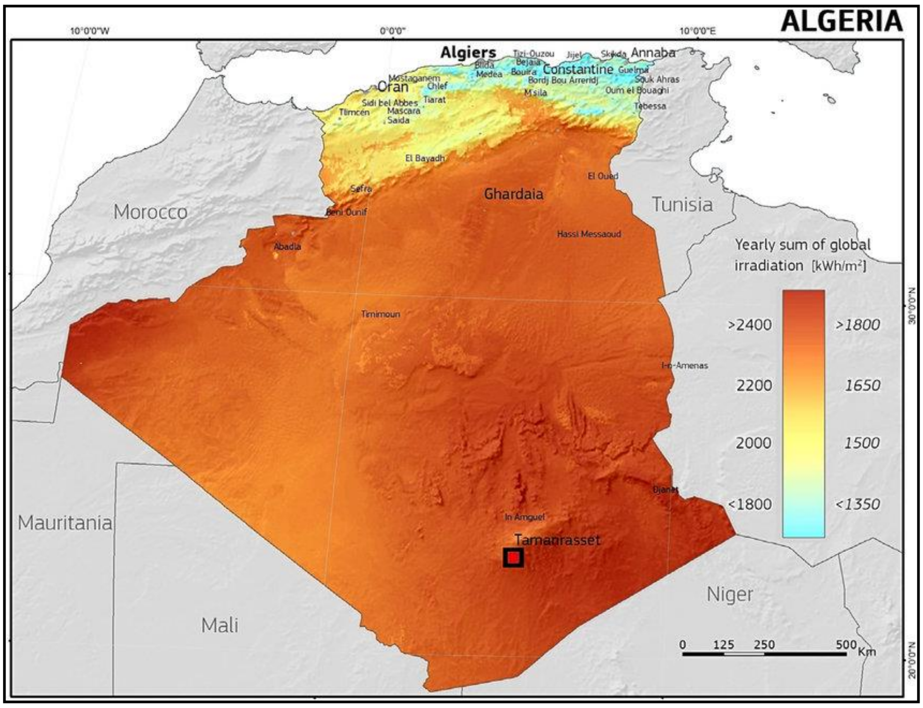

Figure I. 2: Solar energy potential in Algeria**.**

- 80% of the area of Algeria is desert. The duration of the sun's brightness exceeds 3000 hours annually. These features make Algeria possess a large stock of solar energy, which is considered one of the largest reserves in the world, if exploited.

Table I. 1: Solar potential in Algeria [6]

Area	Coastal Area	High plateaus	Desert
Surface	4%	10%	86%
Average duration of sunning (h/ year)	2659	3000	3500
Average energy obtained (kwh/m^2/year)	1700	1900	2650

- Algeria's largest investments in renewable energies were in Hassi Al-Raml and Ghardaia, a hybrid power plant powered by gas and solar energy as one, at a production rate of 150 megawatts in Hassi Al-Raml, and 1.1 megawatts in Ghardaia.
- Algeria aims to reach 15,000 megawatts (MW) of electricity generation capacity based on renewable resources by 2035, with a growth rate of 1000 MW/year. Furthermore, around 1000 MW of off-grid renewable energy installations are expected to be put on stream by 2030. A new law on energy transition is being prepared.[7]

I.2.5. Solar energy applications

People have harnessed solar energy for centuries. As early as the seventh century BCE, they used basic magnifying glasses to focus light from the sun to make fire. Over a century ago, solar also used to make steam to power an engine by solar collector. And here're other uses for solar energy:

a) Solar Space Heating

Space heating means heating the space inside a building. There are two basic types of solar space heating systems: passive and active.

- ✓ **Passive Solar Design**

A passive solar home is designed to let in as much sunlight as possible. It is a big solar collector. Sunlight passes through the windows and heats the walls and floor inside the house. [8]

- ✓ **Active Solar Design**

Active solar heating systems use solar energy to heat a fluid -- either liquid or air -- and then transfer the solar heat directly to the interior space or to a storage system for later use. (Mechanical equipment is used like electric fans or pumps to distribute the thermal energy through the building). [8]

b) Solar Water Heating

A solar water heater works a lot like solar space heating. A solar collector is often mounted on the south side of a roof where it can capture sunlight. The sunlight heats water and stores it in a tank. The hot water is piped to faucets throughout a house.

c) Solar pumping

Usually solar powered pumping system consists of a solar panel array that powers an electric motor, which in turn powers a surface pump. The water is often pumped from the ground or stream into a storage tank that provides a gravity feed, so energy storage is not needed for these systems. [10]

d) Solar Drying

In this case, we heat the air in the solar collectors using solar energy, and conduct the hot air from the collector to an attached enclosure. We can use this technic to dry agricultural, animal products and meat. [9]

e) Solar cooking

Using direct sunlight energy to cook and heat food. Its tempter can goes up to 400 degrees F (204 degrees C), which is hot enough to fry food or bake bread. Here's an example for that. [11]

f) Solar distillation

Solar water distillation is the process of using energy from the sunlight to separate freshwater from salts or other contaminants. The untreated water absorbs heat, slowly reaching high temperatures. The heat causes the water to evaporate, cool, and condense into vapour, leaving the contaminants behind. Solar stills can be used for low capacity and self-reliant water supplying systems. [12]

g) Producing of electricity by radiant energy

Solar energy can be used too to produce electricity. And there are two ways to do that, photovoltaic systems and using thermal energy.

✓ **Photovoltaic systems**

The photovoltaic cell is an energy conversion device that converts solar photons directly into electricity. It is built of semi-conductors, which absorb photons from the sun in order to produce electric current. [13]

✓ **Thermal energy**

Solar thermal power generation is the process of converting solar energy into electricity via thermal energy. This operation takes place in 3 steps:

- Heat up a working fluid (water, oil, gaz...) by solar radiation.
- Turbines convert thermal energy (steam) into mechanical energy.
- Mechanical energy is converted into electrical energy using generator.

This category includes many technics among them:

- Linear Fresnel Reflector (LFR).
- Parabolic Trough Collector (PTC).
- Heliostat Field Collector (HFC).
- Parabolic Dish/Engine Collector (PDC).

h) Producing thin films

Producing thin films using a parabolic dish collector: it's a new and unique method to produce thin films, where a piece of glass is placed on the receiver (the hottest place in the device) and focus the sunlight on it while spraying the solution we want to fixed on the surface of the piece of glass.

I.3. Thin films

I.3.1. Definition of Thin Film

A thin film is a layer or layers of material ranging from nanometre (monolayer) to several micrometres in thickness. Protecting the substrate, changing its appearance (decorative purposes), changing the substrates' optical or electrical properties are some of the layer aspects. [14]

We can say that the thin film deposition process is applying a thin layer of any kind of substance on a surface, whether a basic substrate or already deposited layers.

Applications of thin films in our everyday life are undeniable, and a simple example is a mirror we use daily to see our features. The mirrors typically consist of a sheet of glass that its back is covered by a thin film of metals such as aluminium or silver using deposition techniques, i.e., spray coating or sputtering, to form a reflective surface. (Fig.I.3).

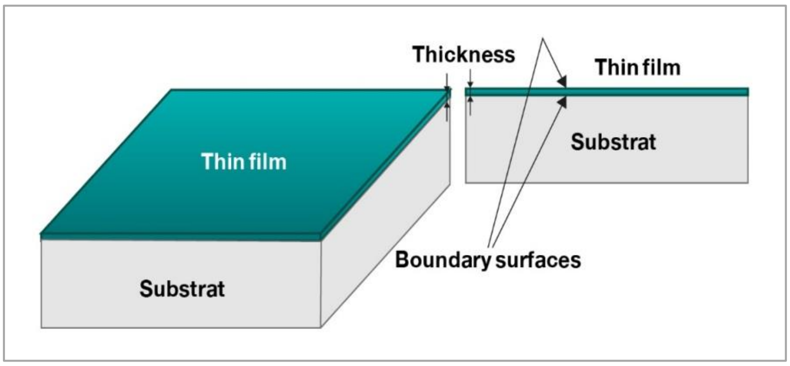

Figure I. 3: Schematic of thin film deposited on a glass substrate.

Another essential characteristic of a thin film is that, whatever the procedure used for its manufacture, a thin film is always integral with a support on which it is built. Consequently, it will be imperative to take this major fact into account in the design, namely that the support has a very strong influence on the structural properties of the layer deposited thereon. Thus, a thin layer of the same material, of the same thickness may have substantially different physical properties depending on whether it is deposited on a monocrystalline silicon substrate or an amorphous insulating substrate such as glass for example.

I.3.2. Applications of Thin Film

Due to the advances in thin film deposition techniques during the 20th century, there has been a wide range of technological breakthroughs in various areas such as :

a) Electric and optoelectronic

- ✓ Light-emitting diode (LED).
- ✓ Thin film solar cell.
- ✓ Thin-film batteries.

b) Optical coatings

- ✓ Anti-reflection coating (ARC).
- ✓ Low emissivity panes of glass for houses and cars.

c) Biomedical

- ✓ Artificial limbs or joints.
- ✓ Implantable sensors such as pacemakers.

d) Corrosion and oxydation protection

I.3.3. ZnO thin films

I.3.3.1. Definition of ZnO

When we say Zinc oxide, most people might think that it's a rare metal or something toxic but on the opposite, ZnO is white powder inorganic compound we use it as an extra in numerous materials and products including cosmetics, food supplements, glass and many others.[15]

Figure I. 4: Zinc oxide. [16]**.**

Good transparency, high electron mobility, wide band gap, and strong room-temperature luminescence. Those features make ZnO worthy for difference emerging applications such as:

- ✓ Transparent electrodes in liquid crystal displays.
- ✓ Energy-saving or heat-protecting windows.
- ✓ Electronics as thin-film transistors and light-emitting diodes.

I.3.3.2. Properties of Zinc metal

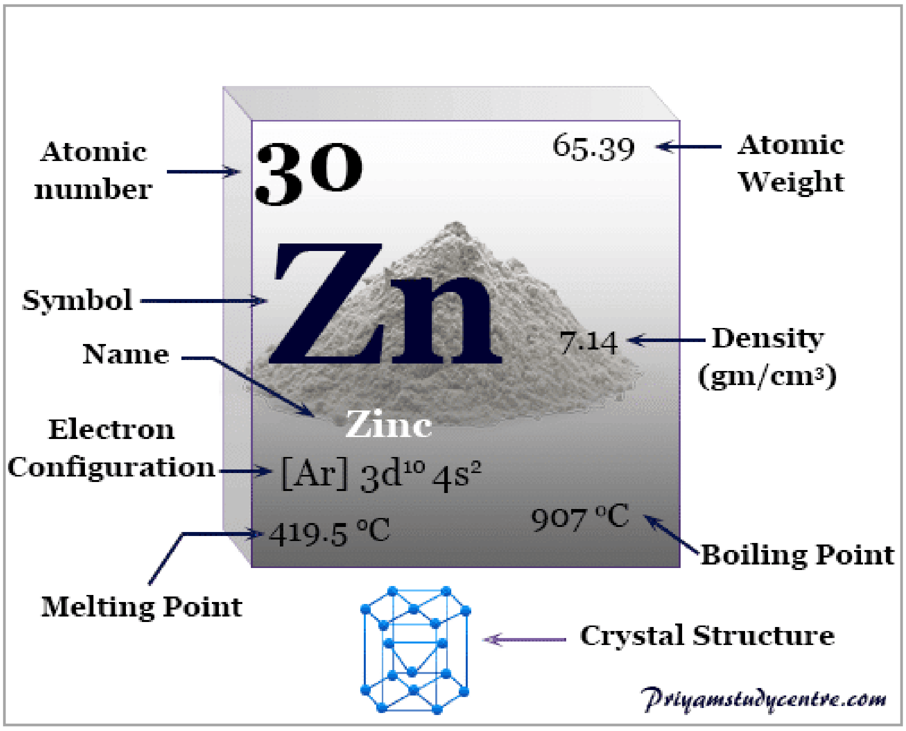

Figure I. 5: Properties of Zinc metal. [17]

Zinc has a closed-packed hexagonal crystal lattice with elongated distances between the layers makes the metal denser than those of copper and silver. The low melting and boiling point of the metal reflects the weak participation of the outer ns electron for metallic bonding. [17]

Table I. 2: Percent composition by element (zinc oxide). [18]

Element	Atomic Mass	Mass Percent
Zinc	65.38	80.340%
Oxygen	15.9994	19.660%

ZnO is a large-band gap semiconductor of the II-VI semiconductor group. The native doping of the semiconductor due to oxygen vacancies or zinc interstitials is n-type. This is what made us pay attention to its Physical and structural properties, to put it in the following table.

Table I. 3: Physical and structural properties of ZnO.[19]

Property	ZnO
Band-gap (eV)	3.2
Melting point (°C)	1975
Specific gravity	~ 5.6
Light absorption (nm)	< 375
Mohr's Hardness	4.5
Lattice constants (Å)	a = 3.25
	c = 5.21
Density (g/cm^3)	5.606
Crystal structure	wurtzite
Refractive index	2.0041
Dielectric constant	~ 40
Zn–O bond length (Å)	1.985

I.3.3.3. ZnO Crystallographic and Structural features

Crystalline ZnO has a wurtzite (B4) crystal structure, having a hexagonal unit cellwith two lattice parameters a and c. In this wurtzite hexagonal structure each anion is surrounded by four cations at the corners of the tetrahedron, which shows the tetrahedral coordination and hence exhibits the sp3 covalent bonding. The tetrahedral configuration of ZnO gives rise to a non-centrosymmetric structure (fig.I.6). [20-21]

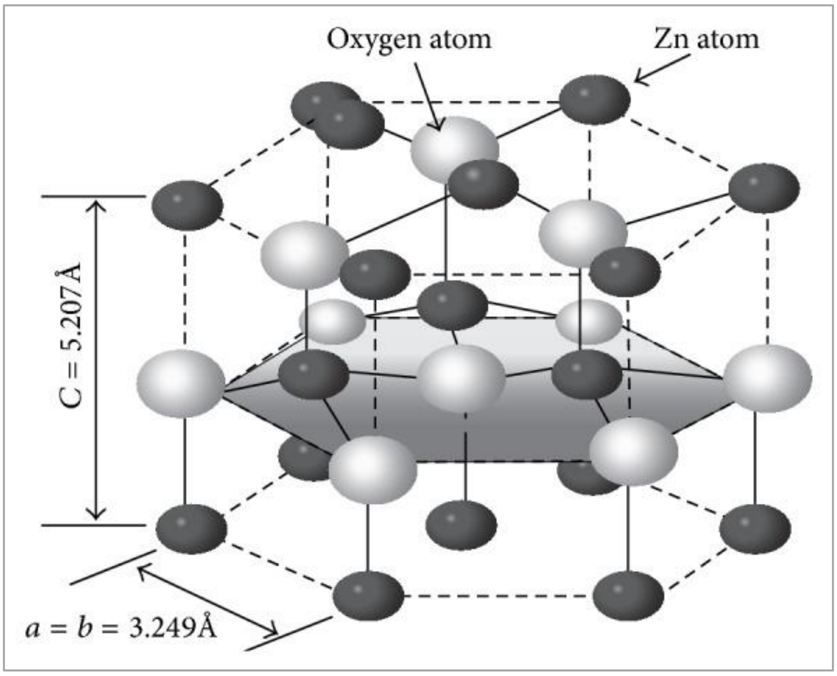

Figure I. 6: Crystallographic and Structural features. [22]

I.3.3.4. Electrical properties

Band structure, the very important property of any given semiconductor because many important properties such as the band gap and effective electron and hole masses are derived from it. ZnO is considered the most favorable semiconductor in his family for ultraviolet lasing at room temperature, device application as well as possibilities to engineer the band gap, for this reason a clear understanding of the band structure is important to explain the electrical properties and many other phenomena because it determines the relationship between the energy and the momentum of the carrier. UV and X-ray reflection/absorption/ emission all this techniques let us define band structure, to measure the electronic core levels in solids we use photoelectron spectroscopy (PES) and angular resolved photoelectron spectroscopy (ARPES). All this methods of measurements measure the energy difference by inducing transitions between different electronic levels (transitions from the upper valence-band states to the upper conduction states, and the lower valence-band states for example). a direct band gap is The most important aspect of the band structure of ZnO, Optical band gap (Eg) of ZnO is about 3.2eV. [23]

I.3.3.5. Optical properties

The optical properties of a semiconductor are associated with both intrinsic and extrinsic effects. Between the electrons in the conduction band and holes in the valence band, there is where the intrinsic optical transitions happen. The main condition for exciton formation is that the group velocity of the electron and hole is equal. Excitons are classified into free and bound excitons. In high quality samples with low impurity concentrations, the free exciton can also exhibit excited states.

ZnO films are transparent in the wavelength range of 0.3 and 2.5 µm, and plasma edge lies between 2 and 4 µm depending on the carrier concentration. The shift in the band gap edge appears with an increase in the carrier concentration. Room temperature PL spectrum of ZnO is usually composed of a near UV emission band (375 nm) and a green emission band (510 nm) although a yellow-orange band (610 nm) can also be observed in some situations. [22]

I.3.4. Nickel oxide thin films

I.3.4.1. Definition of Nickel

Nickel is a naturally-occurring metallic element with a silvery-white shiny appearance, discovered in 1751. It is the fifth-most common element on earth and occurs extensively in the earth's crust and core. Nickel, is a common element in meteorites and can even be found in plants, animals and sea water but in small quantities .It is attractive and very durable as a pure metal.

Nickel's concentration in earth's crust is 80 parts per million, the earth's core consists mainly of a nickel-iron alloy. [23]

Figure I. 7: *Nickel metal.[24]*

Nickel is a Substantial element in hundreds of thousands of products with its chemical and physical properties, and the largest use of it is in the manufacture of alloys, especially if it is mixed with chromium and other metals to produce high-temperature and rust-resistant steel.

I.3.4.2. Properties Of Nickel

- ✓ Nickel is silvery-white, hard, malleable, and ductile metal.
- ✓ It is a good conductor of heat and electricity.
- ✓ It is bivalent that is it has a valency of two.
- ✓ The metal dissolves slowly in dilute acids.
- ✓ Its melting point is 1453 °C and boiling point is 2913 °C. [25]

I.3.5. Thin-Film Deposition

Thin films have become one of the most important industries and unique technologies as they have been able to penetrate into all applications such as optical, electrical, optoelectronic and so on, the structure of thin films is divided into amorphous and polycrystalline structure depending on the preparation conditions as well as the material nature.

There are two deposition techniques help us to reach the good quality of thin films: physical vapor & chemical vapor depositions.

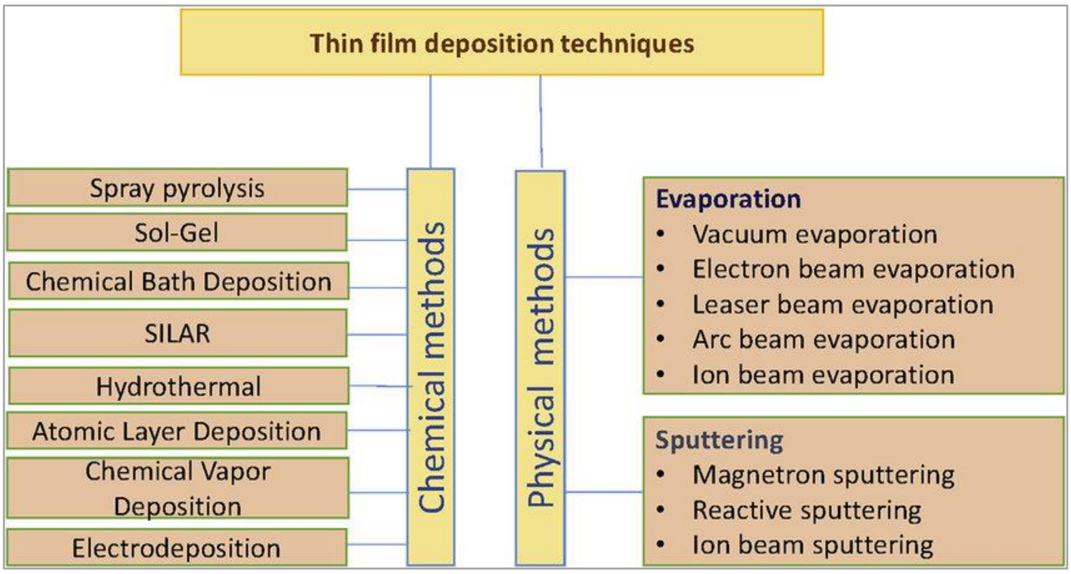

Figure I. 8: Thin films deposition techniques.

I.3.5.1. Physical vapor deposition (PVD)

PVD is a vaporization coating technique, involving the transfer of material on an atomic level under vacuum conditions. It is fundamentally a vaporization coating process in which the basic mechanism is an atom by atom transfer of material from the solid phase to the vapor phase and back to the solid phase, gradually building a film on the surface to be coated. In the case of reactive deposition, the depositing material reacts with a gaseous environment of co-deposited material to form a film of compound material, such as a nitride, oxide, carbide or carbonitride. The process involves four steps:

- ✓ Evaporation of the material to be deposited by a high energy source such as an electron beam or ions–this evaporates atoms from the surface.
- ✓ Transport of the vapor to the substrate to be coated.
- ✓ Reaction between the metal atoms and the appropriate reactive gas (such as oxygen, nitrogen or methane) during the transport stage.
- ✓ Deposition of the coating at the substrate surface.[26]

Table I. 4: Characteristics of the main PVD method

SAM Sputter Target	Evaporation	Sputtering	Ion Plating
Particle energy eV	0.1-1	1-10	0.1-1
Deposition Rate um/min	0.1-70	0.01-50	0.1-50
Adhesion	Poor	Good	Very Good
Density	Low	High	Very High

Among the above three methods, although Ion plating's film adhesion and density are better, due to technical limitations, the other two methods (evaporation and sputtering) are currently more widely used. In general, sputtering is the best PVD technology.[27]

I.3.5.2. Chemical vapor deposition (CVD)

CVD is a method to make thin films by chemical reaction on the surface of substrates by using one or more gaseous compounds or elemental substances containing thin-film elements. CVD is a crucial material preparation method, which plays an essential role in precious metal thin films and coatings.

PVD usually uses evaporation and sputtering techniques and does not involve chemical reactions. CVD is widely used in industry for the production of organic and inorganic films on metals, semiconductors, and other materials.

CVD contains variable processes like atmospheric-pressure chemical vapor deposition (APCVD), low-pressure chemical vapor deposition (LPCVD), plasma-enhanced chemical vapor deposition (PECVD), or plasma-assisted chemical vapor deposition (PACVD), and laser-enhanced chemical vapor deposition (LECVD).

In the late 1970s, it was first found that CVD could deposit diamond films at a pressure lower than 1 atm. Since then, the research on the formation of thin films on different biomaterials by the CVD method has been deepened.

In addition, in order to deposit diamond film directly on metal, Baek et al demonstrated that a thin TiC buffer layer could be formed on the Ti-6Al-4V substrate by combustion-assisted CVD, and then the diamond film can be deposited on it. Andreazza & al. also used an intermediate TiC layer to store diamond films on titanium through PECVD. Subsequently, the researchers also found that polycrystalline diamond films deposited on titanium substrate by CVD method can improve not only the tribological properties but also the biocompatibility.[28]

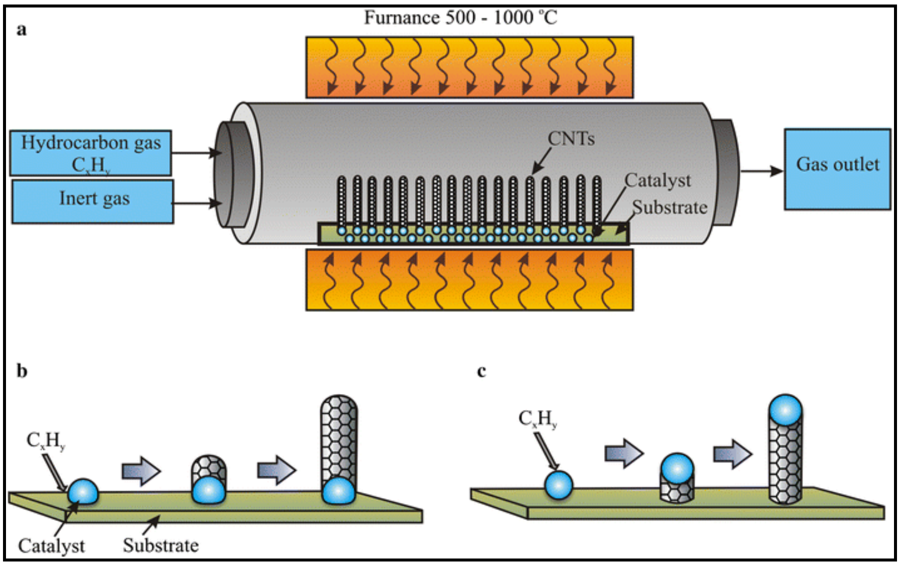

Figure I. 9: Chemical vapor deposition process.

I.3.5.3. Spray Pyrolysis Technique (SPT)

Spray pyrolysis is a process in which a thin film is deposited by spraying a solution on a heated surface, where the constituents react to form a chemical compound. The chemical reactants are selected such that the products other than the desired compound are volatile at the temperature of deposition.

Spray pyrolysis is a very inexpensive processing technique (especially in consideration of equipment costs). It offers a very simple technique for creating films of any composition. Spray pyrolysis does not require the use of expensive substrates or chemicals. Spray pyrolysis is very efficient, cost effective, and utilizes simple equipment.

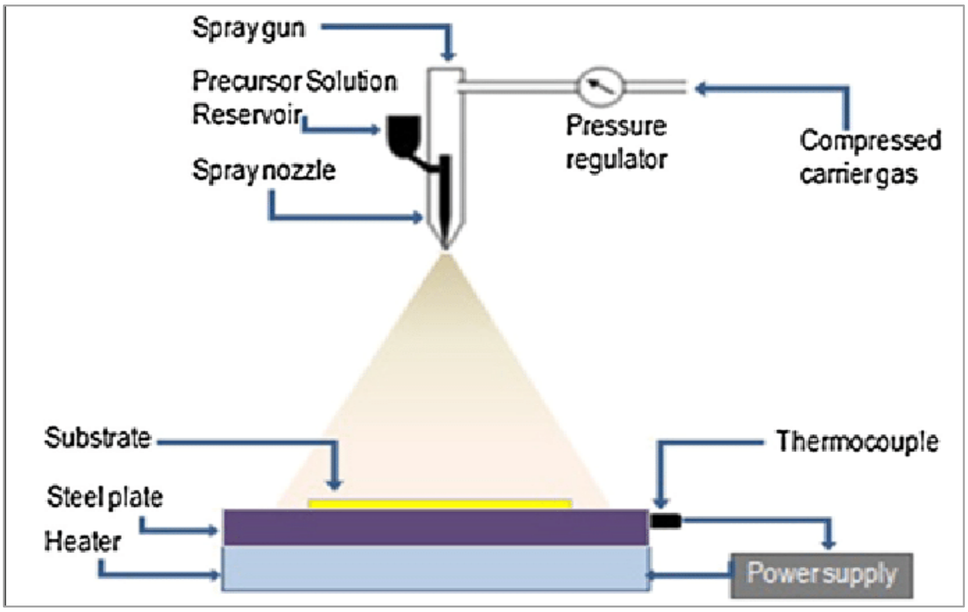

Figure I. 10: Spray pyrolysis technique.

I.3.5.3.a. Models for Film Deposition by Spray Pyrolysis

Precursor solution atomization, Droplet transport and evaporation, Spreading on the substrate, Drying and Decomposition of the precursor salt. All of these operations happen either sequentially or simultaneously by spray pyrolysis So that the thin films are evenly distributed. Understanding these operations will help improving film quality.

Thin-film deposition using spray pyrolysis can be classified into three prime steps: atomization of the precursor solution, transportation of the resultant aerosol and decomposition of the precursor on the substrate.

I.3.5.3.b. Spray Pyrolysis Device

Solar oven (furnace):

It is one of the new and innovative methods in the field of thin films, where the heating process takes place by shedding sunlight on the substrate and spraying the material to be fixed on it. The solar oven consists of five basic components:

- Reflector, - Receiver, - Support, - Tracking system & - Mirror.

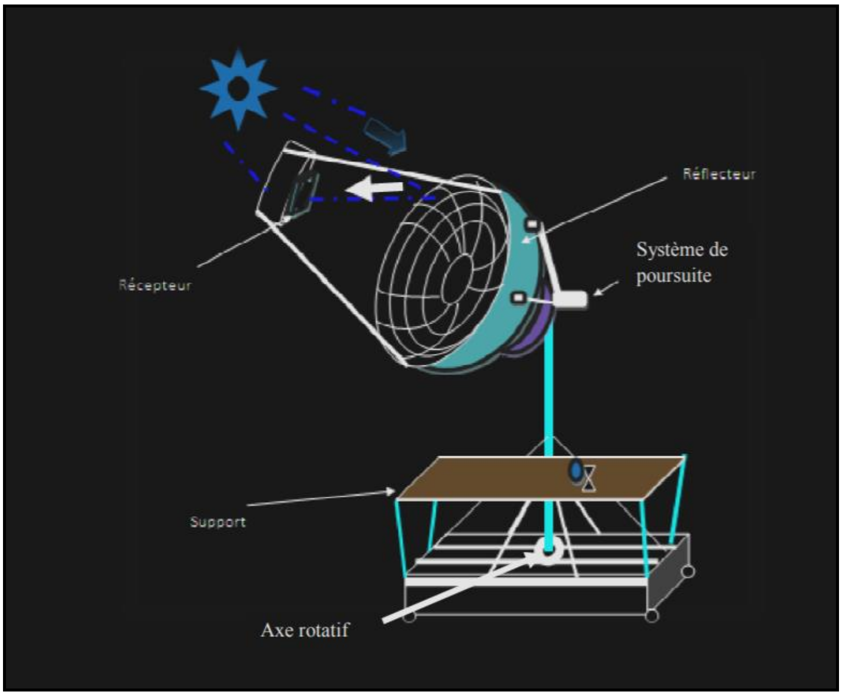

Figure I. 11: Solar oven components.

I.4. Conclusion

In this chapter, we started talking about renewable energies, especially solar energy and its uses in Algeria, and their unlimited characteristics and uses. We also discussed the electrical, optical and Structural features of ZnO and NiO components. As well, we talked about thin film deposition methods and went deep in solar spray pyrolysis technique.

In the following chapter, we steel going to see more details about solar spray pyrolysis and elaboration techniques & characterization devices for Ni- doped ZnO thin films.

Chapter II

Elaboration Techniques and characterization devices for Ni-doped ZnO thin films

II.1 Introduction:

In this chapter, we will talk about the experiment part for elaborate Ni- doped ZnO thin films and the equipment we used for that, without forgetting the used techniques to characterize the obtained films.

II.2 Elaboration Technique of Ni- doped ZnO thin films:

II.2.1 The used experimental montage:

It is a frame produced in the mechanical engineering laboratory n° 22 of El Oued University. It is made of simple elements. We have modified this to produce Ni-doped ZnO thin films in a new way.

The solar concentrator (oven) consists of the following components:

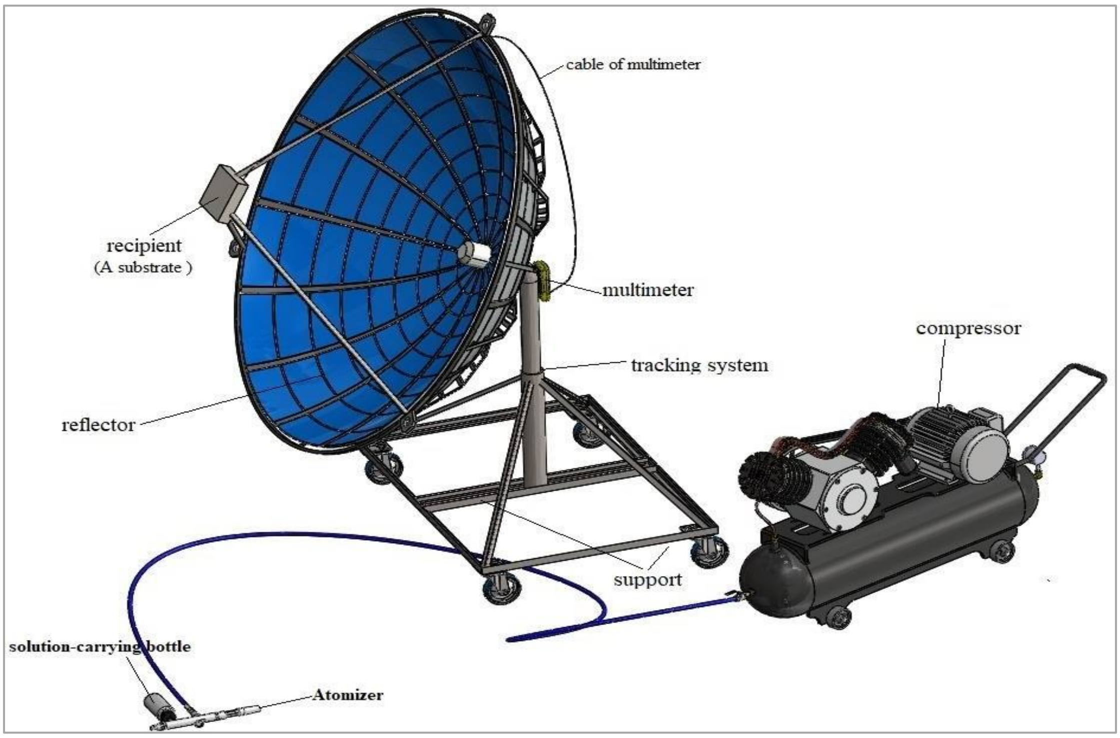

Figure II. 1: Complete assembly of the solar oven used.(Designed by Solidworks). [29]

- **Reflector**

As its name suggests, its role is to collect solar energy (solar rays) and direct it to a specific point (receiver).the reflector is formed by the rotation of a parabolic curve around its axis. There is several kinds of materials that used for reflector surface to be reflective .The most common one is anodized aluminum because its reflectivity in the range of 75–95 %, in our case we used mirrors since its availability, cheap and its ability to reflect rays is large too.

Figure II. 2: General view of the used reflector

- **Receiver**

It receives the solar radiation coming to it from the reflector and works to convert it into heat that can be used in many applications (water heating, cooking, fix the solution on the surface of a piece of glass).

The efficiency of the receiver is measured by its ability to convert the largest amount of radiation emitted to it into heat and with least loss.

In our experiment, a metal plate is our receiver, on which we fix the piece of glass (substrate) and spray it with the solution. This plate is called the heating plate.

Our heating plate must have a Good conductivity and thermal diffusion, also an absorption factor as close as possible to unity to fit the experiment.

Table II. 1: Geometric characteristics of the receiver.

Length	L =0.15 m
Depth	h =0.02 m

Figure II. 3: Real photo of the used receiver.

- **Support structure**

Our device can do nothing without the support structure, because its drive and help the reflector tracking the solar radiation. As shown in figure II.4.

Figure II. 4: Photo of oven support structure.

- **Tracking system**

Tracking system, It is a system that tracks the course of the sun so the collector remain perpendicular to the Sun's rays .Tracking system adjust the direction that the reflector is facing according to the position of the Sun in the sky, by keeping the reflector perpendicular to the Sun, the more sunlight strikes the reflector, the more energy (heat) is absorbed from the receiver.

Tracking system can improve the efficiency by 30 to 40%. In our experiment, we rely on jacks and a rotary axis to be our tracking system, as shown in (figure .II.5).

Figure II. 5: Photo of the tracking system containing a cylinder and a rotary axis.

- **Atomizer**

The atomizer is a device that turns the solution into droplets such as the diffuser pumps on a perfume bottle but with higher pressure. We use the atomizer to create a layer of our solution on the piece of glass by spraying on it from a certain distance.

- **Compressor**

A compressor is a mechanical device that rises the pressure of gas by reducing its volume. In our experiment, we use it to supplies the pressure to the atomizer in order to operate it.

Figure II. 6: The compressor.

II.2.2. Selecting and preparing of the glass substrates:

Substrate selection depends on:

- Substrate cleanliness, one of the most important criteria that must be observed is the cleanliness of the substrate because that will define the quality of both deposits and samples.
- The substrate and the deposited film should have similar crystal structure, so they can fit together.
- Substrate must be free of scratches and spots to maintain its efficiency.
- The substrate should give mechanical support to the film to provide sufficient adhesion.

We used glass type (CITOPLUS-REF-0302-0004) as a substrate. (Figure II.7)

We cleaned the glass following these steps:

- Wash in an acid bath from 5 to 6 min.
- Wash with distilled water.
- Wash with acetone for 15 min.
- Again with distilled water.
- Dry the glass substrates.

Figure II. 7: Type of the used substrate in the experiment.

II.2.4. Measurements and used devices:

There are several essential factors can influence the thin films deposition, among them, weather condition (sunny, cloudy, partly cloudy…), the speed of surrounding air, the working pressure, The mass of the chemical samples used in the experiment, the temperature of the sputtering target (heating plate), and so on. All this factors play a main role to obtain reproducible thin films and with good adhesion.

So, in this part, we are focusing on the measuring devices and measurements taken in the experiment that leads to good thin films deposition.

II.2.5. Measuring instruments:

II.2.5.1. The temperature:

We used a digital multi-meter (VC61A) has the following characteristics:

- Direct voltage: 200 mV - 1000V
- AC voltage: 2V - 750V
- Direct current: 2 mA - 20A
- Alternating current: 20 mA - 20A
- Resistance: 200 Ohm – 200 M Ohm
- Temperature: 40 - 1000 °C.

Figure II. 8: Digital multimeter (VC61A)

II.2.5.2. Pressure measurement:

Our compressor has the following characteristics:

- Model DAC 24D.
- Power consumption: 1.5 kW.
- Performance: 169 l/min.
- Maximum pressure: 8 bar.
- Tank volume: 24 l.

Figure II. 9: Compressor gauge.

II.2.5.3. Wind speed:

We counted on a digital Thermo-Anemometer (AMPROBE) has the following characteristics:

- Model: TMA5
- Wind speed range: 0.5 – 44.7 MPH, 1.1 → 20.0 m/s.
- Air Temperature range: 32 °F → 122 °F (0 – 50°C).
- Wind speed response: Averaging every 2 seconds

Figure II. 10: Digital Thermo-Anemometer.

II.2.5.4. Mass:

We used a digital scale with the following characteristics:

- Model: MH-999
- Weight: 351.0 grams.
- Operating temp range: 10 – 30°C.
- Accuracy: from 0.02 to 0.04 points on the corners.

Figure II. 11: Digital scale

II.2.6. Experimental conditions :

- Solution volume : 5 ml (5 samples).
- Solution concentration : 0.1 mole. l^{-1}.
- Substrate temperature : (400 °C).
- The distance between the spout and the substrate: less than 10 cm.
- Pressure: 2 bar. As shown in figure II.9.

Figure II. 12: The substrate temperature was heated between (375 – 425 °C).

The solution was prepared according to the relations:

$$n = C \times V \qquad \text{(II.1)}$$

$$n = \frac{m}{M} \qquad \text{(II.2)}$$

$$m = M \times C \times V \qquad \text{(II.3)}$$

n: $materialquantity$ (mol)

m : mass (g)

M: $Molarmass$ (g.mol^{-1})

C: $concentration$ (mol.l^{-1})

V: $volume$ (l).

II.2.7. Steps of the experiment:

In this experiment, we made thin layers with ZnO deposited using solar concentrators, where the process took place in several stages:

- **Prepare the solution :**

We bring 1.3628 g of zinc chloride $Zncl_2$ and put it in a beecher containing 100 ml of distilled water and mix them using a magnetic mixer for 30 minutes at a temperature of 20 ° C to obtain solution with 0.1 mole.l-1.

The same experiment steps with nickel chloride hexahydrate $Cl_2H_{12}NiO_6$ (2.3769 g in 100 ml of distilled water)

Figure II. 13: Zinc chloride.

We mixed the two prepared solutions to obtain doped solutions of Ni-doped ZnO: 0, 5, 10, 5 and 20 at. %.

- **Setting the oven :**

The oven is at its most tender when the solar radiation is parallel to its axis of the substrate holder.

We use a solar tracking system, which helps to keep the oven efficiency high.

In our experience, the tracking system was manually, where we make sure that the oven works well by measuring the temperature in thermometer or when the shadow of the heating plate is in the centre of the oven.

Figure II. 14: Setting the oven manually.

- **Multimeter probe location :**

So, we can measure the temperature reached on the surface of the oven, we set the multimeter probe on the surface of the heating plate (receiver).

Figure II. 15: Temperature measuring device and the detector.

- **Preparation of substrates :**

The process is done by washing the substrate in an ethanol solution and then in distilled water to remove any organic traces that may affect the results of the experiment.

- **Spraying process :**

We Measure using a graduated syringe 10 ml of the mixed solution, then pour it into the solution-carrying bottle, using the atomizer we spray the solution on the substrate at distance less than 10 cm at a specified temperature (375 – 425 °C).

II.2.8. Problems encountered:

The production of the thin films process using parabolic concentrator prototype been through some problems among them:

- Holding the spray system (atomizer) in front of The scorching heat that comes from the mirrors was a bit problem.
- Fixing the temperature in certain value because of the wind speed and the moving clouds.
- Spraying the solution on the substrate in light of the past two problems.

II.3. Characterization techniques:

Now we go to study the various techniques used for characterize and measure structural, electrical and optical properties.

II.3.1. Structural Characterization: X-ray Diffraction (XRD)

Sir W.H. Bragg and his son W.L. Bragg (English physicists), has developed new relationship in 1913 to explain why the cleavage faces of crystals appear to reflect X-ray beams at specific angles of incidence (theta, θ).This observation is an example of X-ray wave interference, commonly known as X-ray diffraction (XRD). XRD is a major technique for characterization of compounds based on deviation pattern. Since the discovery of X-rays Many developments and inventions have been achieved through the application of these methods to characterize materials, especially in the domain of materials science and engineering.

II.3.1.1. Principle of XRD analysis:

XRD techniques are lean on the elastic diffusion of X-rays from structures that have long range order. The X-rays get deviated by a crystal because the wavelength of X-rays is much the same the inter-atomic spacing in the crystals (Figure II.16). [30]

X-ray diffraction finds the geometry (shape) of a molecule by X rays.XRD also gives information on how the real structure deviates from the perfect one, because of the internal stresses and defects [31].

XRD is a non-destructive technique which can be done at room temperature and pressure.

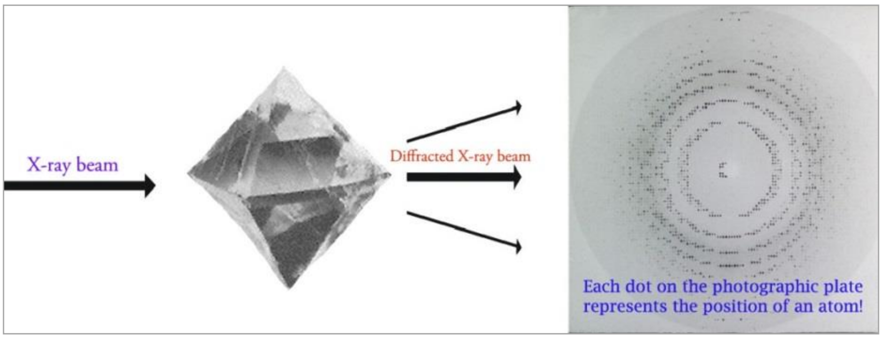

Figure II. 16: X-ray diffraction picture of a crystal**.**

When the X-ray beam encounters the regular three-dimensional arrangments of atoms in a crystal, most of the X-rays will destructively interfere with each-other and eliminate each-other out, but in some specific directions the X-ray beams interefere constructively and reinforce one another. It is these reinforced diffracted X-rays that produce the characteristic X-ray diffraction pattern that is used for crystal structure determination. [30]

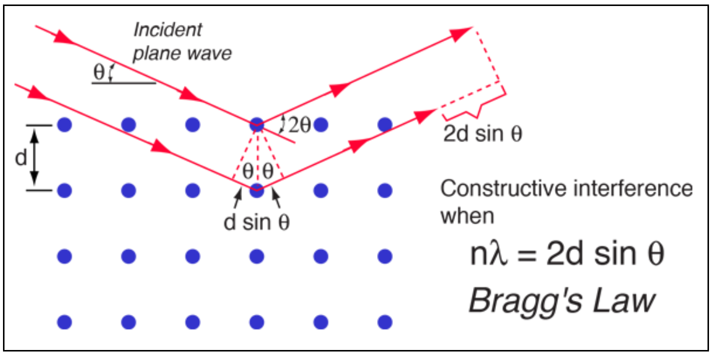

Figure II. 17: Schematic diagram of Bragg equation.

After the x-rays are scattered from a crystal lattice, we observe peaks of dispersed density and also the angle of scattering in this case equal to the angle of incidence.

By using Bragg law we can measure the wavelengths and determine the lattice spacing of crystals:

$$2d_{hkl}\sin\theta = n\lambda \qquad \text{(II.4)}$$

d_{hkl}: is the inter-reticular distance, that is the distance between two crystalline-graphic planes,

θ: the angle of incidence and therefore the angle of reflection in relation to these planes,

λ: the wavelength of photons X incidents,

n: the diffraction order (integer).

II.3.1.2. Determination of crystalline size:

To calculate the crystallite size of the deposits we usually use Scherrer formula which states that: the full width at half maximum (FWHM) of the most intense diffraction line.

And the law is as follows

$$D = \frac{0.9\,\lambda}{\beta cos\theta} \qquad \text{(II.5)}$$

D: the size of the crystals.

λ: the wavelength of the X-ray beam.

β: the half-height width of the diffraction line, expressed in radian (figure II.18).

θ: the diffraction angle.

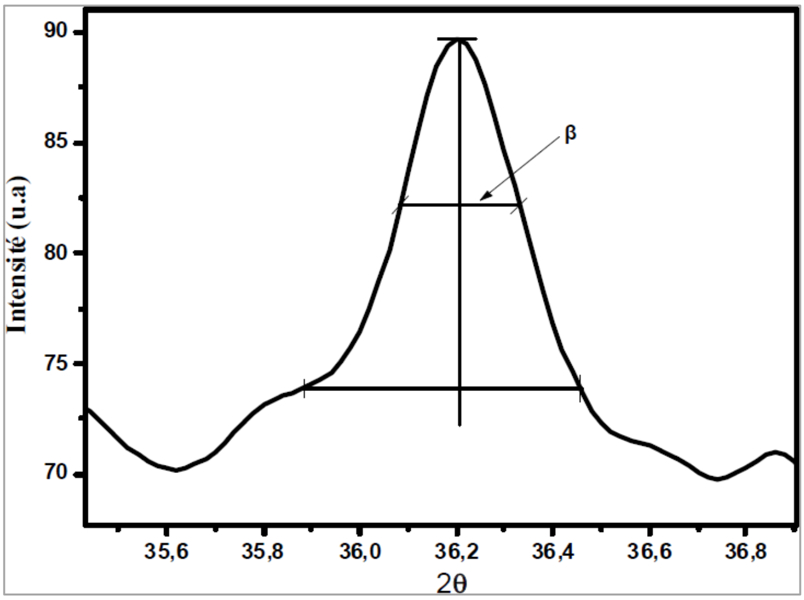

Figure II. 18: The definition of β (the half-height width of the X-ray diffraction line). [32]

II.3.2. Electrical characterization:

Temperature plays an important role in electrical properties as:

The stiffness of the cross-resistive layer increases at high temperatures (depending on the properties of the layer we choose the temperature) this action can be caused by a large number of clear boundaries between the crystalline ZnO columns (in our case).

in our experiment we used KEITHELY SRM 2400 device to determine the surface resistance Rs. this latter has a probe contains of four aligned and regularly spaced contacts (figure II.20), A source supplies a current I passes out of the terminals exterior. The voltage U is sized at the ends of the two inside tips. The use of four contacts instead of two makes it possible to control the resistance of the tips and just measure the resistance of the sample. When the thickness of the thin film "d" is nothing comparing to the distance "a" between the terminals, the lateral dimensions can be considered infinite. In this case, we consider the two-dimensional model of conduction:

$$\frac{U}{I} = K\frac{\rho}{d} \qquad \text{(II.6)}$$

ρ : the resistivity of the layer

d : the thickness.

The ratio characterizing this layer is represented by **RS** and **Ω**. For the readiness factor **K**, **R** is the ratio of voltage **U** to current **I**. Considering the cylindrical propagation of the field lines in the film, the coefficient **K** is **(ln2 /π)**.

From the relation (II.7), we have the formula (II.8) to deduce the resistivity of the four-point measurement knowing the thickness d of the thin film:

$$\rho = \left(\frac{\pi}{\ln 2} \times \frac{U}{I}\right) d = Rs \times d \qquad \text{(II.7)}$$

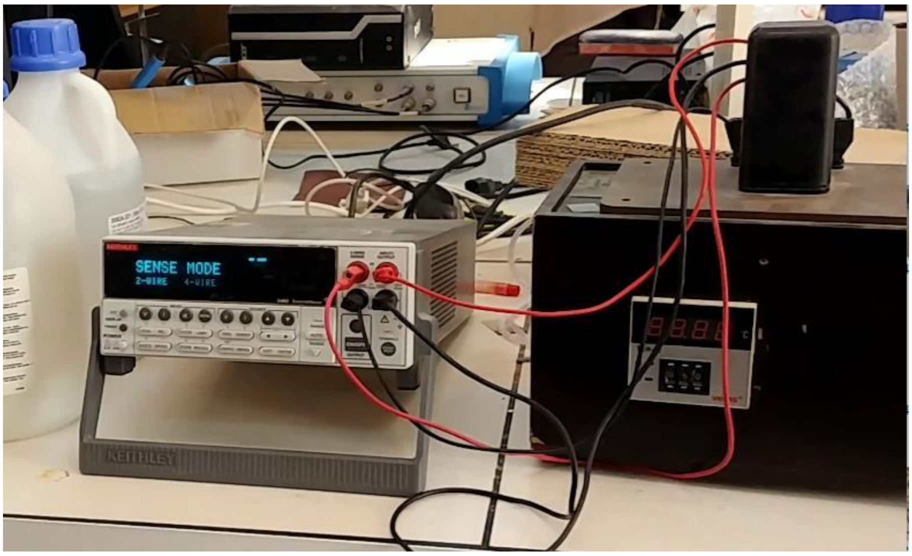

Figure II. 19: The experimental setup of the equipment using the four-probe method (Laboratory n°22, Echahid Hamma Lakhdar University, El Oued).

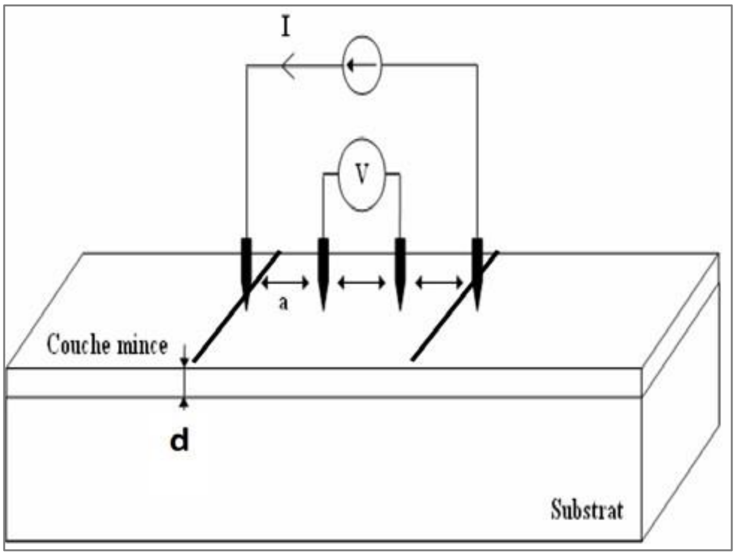

Figure II. 20: Diagram of a four-point device.

II.3.3. Optical characterization:

if we are looking to parameters and its characterisation ,then the optical method is better than the electrical method in the amount of parameters that characterize ,because it is non-destructive and also does not require the reaction of ohmic contacts like electrical methode does.

There are two types of optical methods:

• Methods that study the optical reaction of the material to an excitation such as photo and cathodo-luminescence.

• Methods that examine the optical characteristics of the material like; transmittance, reflectance measurements and ellipsometric measurements. These spectroscopic measurements make it possible to define the optical refractive index, the thickness of the material and the gap.

II.3.3.1. UV-Visible spectroscopy:

Reflectivity (R) and transmission (T) measurement are new developed methods that we use to examine the optical properties of thin films .Fresnel's law say that the reflectivity of a thin-film coated surface lean on the wavelength of the impinging photons.

The light that goes through a material can either be reflected (R), transmitted (T), or absorbed (A). In a standard UV–vis experiment, the intensity of incident light at a specific wavelength is compared with the intensity of the reflected light and that of transmitted light , and the absorbed light is then derived from the difference between input signal and R+T signal.

In our experiment we used a UV-Visible spectrophotometer (SHUMATZU 1800) .it is a double beam spectrometry [one for the reference (glass) and the other is for our sample (the thin layer of zinc oxide + glass)] and whose spectral range extends from UV-Visible (λ = 300-900 nm). The next picture (Figure II.21) helps understand the principle of operation of this device. [33]

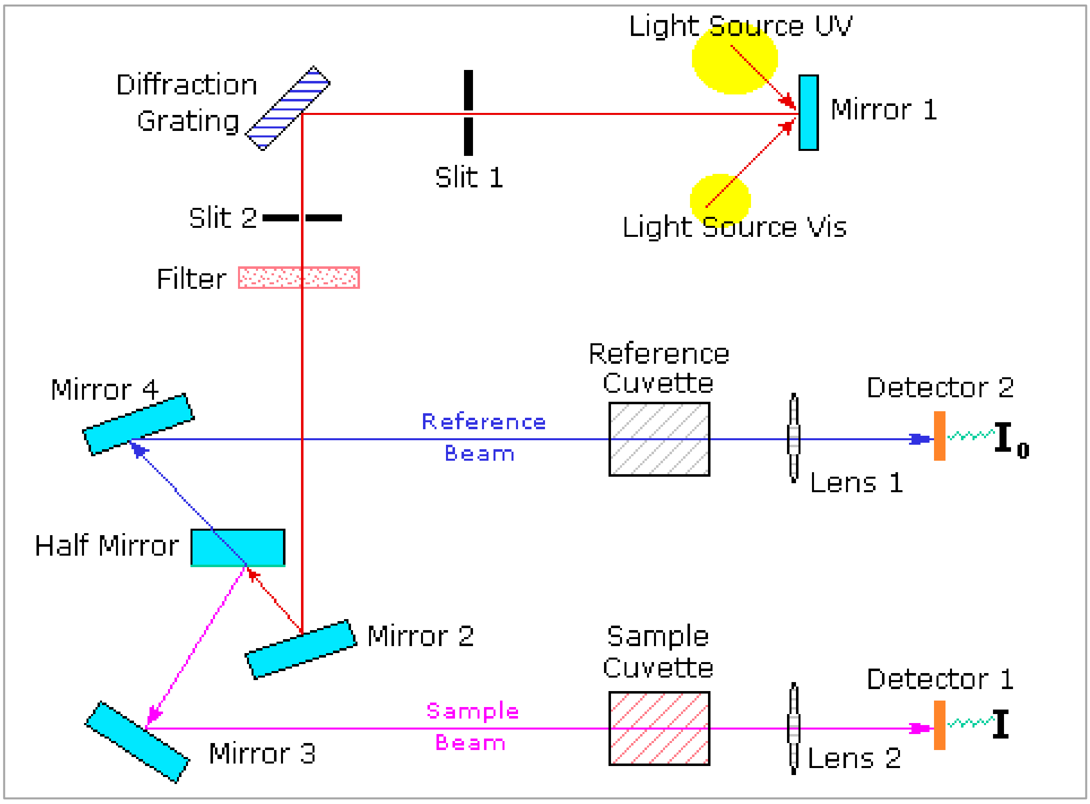

Figure II. 21: Schematic representation of the UV-Visible spectrophotometer. [34]

Figure II. 22: UV-visible spectroscopy device that used (laboratory n°22, Echahid Hamma Lakhdar University, El-Oued)

The light path is indicated by a dashed line. The components are represented as follows:

HL = Halogen lamp.

DL = Deuterium lamp.

M = Mirror.

F = Filter wheel.

S = Slit.

G = Grating.

RM = Rotating mirror.

PMT = Detector (photomultiplier tube).

II.3.3.2. Thickness measurement of thin layers:

Through the transmittance spectrum we can find the thickness of the thin layers, by using "Fit" software. This allows a specific number of parameters to be diverse like the thickness, the refractive index and optical gap and to use the least squares method to fit a simulated transmittance curve to the measured one.

There is also another method to determine the thickness of a sample which is the interference fringe method (layer deposited at 5 min). Using this technique requires you to be in knowledge of the interfering in the transmission spectra.

II.3.3.3. Determination of the optical gap:

Ni-doped ZnO material has a direct and wide band gap in the near-UV spectral region. So we can express the coefficient absorption (α) as a function of the optical gap (Eg) and the energy (hν) of the photons by using the form of (Tauc equation) [35]:

$$\alpha h\nu = (h\nu - Eg) \quad \text{(II.8)}$$

Where:

A: a constant,

Eg: the band width prohibited (or optical gap expressed in eV).

hυ: the energy of a photon in eV.

α: the absorption coefficient.

n: equals to 1/2 for allowed direct transition.The optical band gap energy value Eg is calculated by extrapolating the linear region of (αhν) 2 versus hν plot.

II.3.3.4 Determination of Urbach energy:

In the optical properties field, to define the state of disturbance of the material we should calculate the energy of Urbach (Eu). Actually, the absorption coefficient α according to the law of Urbach comes in the form of: [36, 37]:

$$\alpha = \alpha_0 + \exp(\frac{h\upsilon}{E_u}) \quad \text{(II.9)}$$

α: is the absorption coefficient.

E: is the photon energy andis equal to

And hν: is the Urbach energy.

II.4. Conclusion:

In this chapter, we talked about the deposit system that we used in the laboratory and the role of each of its elements, then we touched on the measuring devices used for samples, after that we moved to count the different characterization techniques used to analyze and define the different structural, optical and electrical properties of Ni-doped ZnO thin film.

Chapter III
Results and Discussion

III.1. Introduction

In this chapter, we analyze and discuss the results obtained from X-ray diffractometer (XRD), a UV-vis spectrophotometer as well as a four probe technique for the obtained Ni-doped ZnO thin films that were deposited on glass substrates fixed on oven receiver under temperature between 375 - 425 °C using spray pyrolysis process.

III.2. Results and discussion

We used the X-ray diffraction (XRD) with an X diffractometer (BRUKER-AXS type D8) equipped with a CuKα radiation source, with a wavelength equal to 1.540593 Å while the scanning range of (2θ) was between 20 and 70 °, to perform structural characterization.

By using SHIMADZU 1800, which a device that measures the UV-visible spectrophotometer, we managed to measure the optical transmittance of the deposited thin films in the range of 300 to 900 nm.

Seebeck effect and the four-point probe were used to confirm the conductivity and its variation with the precursor concentration. 2 × 1 cm was sheets for all the samples.

III.2.1. Structural properties:

X-ray diffraction (XRD) patterns of Ni-doped ZnO thin films were recorded by spray pyrolysis of various proportions of Ni, and illustrated in Figure III.1.

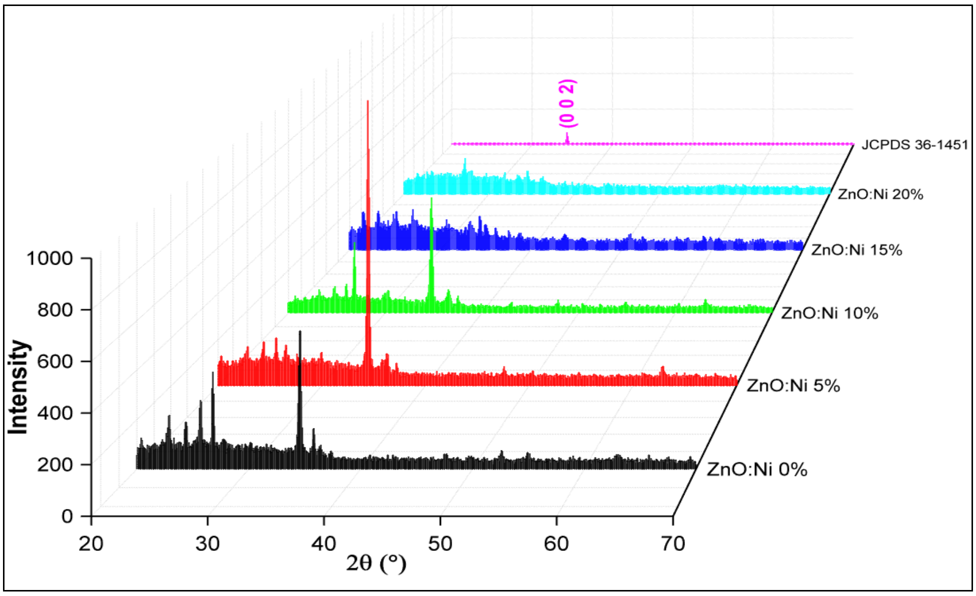

Figure III. 1: X-ray diffraction patterns of Ni-doped ZnO films prepared with various percentages of nickel.

III.2.1.1. X-Ray Diffraction Studies:

Figure I shows the diffraction of X-rays on thin layers of zinc oxide doped with different concentrations of nickel, prepared in temperature between 375 - 425°C. Through these data, we note that ZnO films are polycrystalline and showed the hexagonal Wurtzite structure of ZnO. The layers exhibited the (002) crystal plane as the predominant orientation. The spectra showed different peaks that were related to the (002), (100), (101), (102), and (103) orientations.

The XRD peaks for all the samples are in good agreement with the JCPDS data (JCPDS 36-1451). The high intensity values of (002) peak indicate the improvement in the crystalline quality of the layers. The relative intensities of the other peaks are very low when compared to the (002) peak of the hexagonal phase.

For more structural information, different structural parameters such as lattice parameters a and c, inter-lattice spacing d_{hkl}, grain size D, average strain ε and density of dislocation δ of thin layers of Ni-doped ZnO coated on different percentages of Ni have been calculated.

In the case of a hexagonal structure, the lattice parameters a and c for Ni-doped ZnO are calculated by this equation:

$$\frac{1}{d_{hkl}^2} = \frac{h^2+k^2}{a^2} + \frac{l}{c^2} \quad \text{(III.1)}$$

Where hkl are Miller indices and d_{hkl} is the inter-reticular spacing given by Bragg's law [38]:

$$2d_{hkl} \sin\theta = n\lambda \quad \text{(III.2)}$$

We can say that n is the diffraction order taken equal to unity (first order),and λ is the wavelength of the radiation (λ = 1.540593 Å) for the CuKa radiation and θ is the Bragg diffraction angle of peak (in radian). Using the Scherrer equation, we calculate the grain size D of the films for the plane:

$$D = \frac{0.9}{\beta \cos\theta_{hkl}} \quad \text{(III.3)}$$

Where β is the full width at half height (FWHM) which corresponds to the diffraction angle 2θ and λ is the X-ray wavelength of the incident radiation (1.540593 Å).

The dislocation density δ, defined as the dislocation line per unit volume, was calculated using the following relation [39]:

$$\delta = \frac{1}{D^2} \quad \text{(III.4)}$$

Table III. 1: Values of Bragg angle 2θ, interplanar spacing d_{hkl}, full width at half maximum β, grain size D, and dislocation density δ deduced from Ni-doped ZnO thin films prepared at 400 °C with different proportions of Ni.

Ni Doping Concentration (%)	2θ (deg)	Interplanar spacing d_{hkl} (Å)	β (deg) FWHM	D (nm)	δ x10^{15} (lines/m^2)
Undoped (0)	**34,576**	**2,592**	**0,240**	**35,900**	**0,776**
5	**34,447**	**2,601**	**0,197**	**44,000**	**0,517**
10	**34,765**	**2,578**	**0,300**	**28,500**	**1,231**
15	**34,348**	**2,609**	**0,360**	**23,600**	**1,795**
20	**34,562**	**2,595**	**0,295**	**29,000**	**1,189**

III.2.1.2. Optical properties

Figure III shows the optical transmittance spectra of films prepared with different Nikel dopant concentrations, which recorded in the wavelength range of 300 - 900 nm. All layers showed good transmittance in the visible region and the optical transmittance of Ni-doped ZnO was decreased with increasing of Ni dopant percentage.

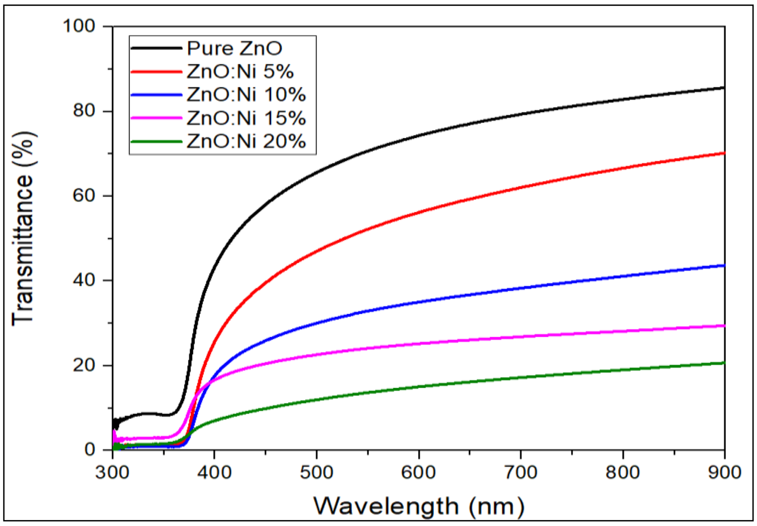

Figure III. 2: Transmission spectra of Ni-doped ZnO prepared at 400°C with different Ni percentages.

For all obtained films, spectra show two regions:

- The first region: Wavelength higher than 500 nm

  In this region the average transmission was between 17 and 78% and revealing a decrease by increasing Ni concentration.

- The second region: Wavelength lower than 500 nm Transparence decreases rapidly exhibit the fundamental absorption because of the transition between the valence band and the conduction band. As shown in table III.2.

Table III. 2: Values of thickness t, average transmittance, band gap energy E_g, Urbach energy E_u of Ni-doped ZnO thin films prepared at 400 °C with different percentages of Ni.

Ni Doping Ratio (%)	*Thickness t (nm)*	*Average transmittance (%)*	*Gap energy Eg (eV)*	*Urbach energy Eu (eV)*
0	**163,42**	**70,705**	**3,22**	**0,179**
5	**233,76**	**52,278**	**3,23**	**0,155**
10	**405,25**	**32,967**	**3,24**	**0,174**
15	**657,01**	**24,136**	**3,17**	**0,299**
20	**1379,59**	**13,696**	**3,05**	**0,594**

For more investigation, we used Swanepoel's method so we can define the transmittance measurements, and from that we can determine the absorption coefficient (α) of Ni-doped ZnO thin films [40, 41]:

$$\alpha = \frac{1}{t} \ln \frac{1}{T} \qquad \text{(III.5)}$$

Where t and T are the thickness and transmittance of the layer, respectively.

The energy gap values generally depend on the crystal structure of the layer (disorder and regularity). Also (α) and incident photon energy (hυ) are related as they are given in Tauc's equation:

$$(\alpha h\upsilon) = A(h\upsilon - E_g)^n \qquad \text{(III.6)}$$

well, A is a constant, Eg is the band gap of the material, and n is an exponent that depends on the type of transition; n = 1/2, 2, 3/2 and 3 correspond respectively to authorized direct, authorized indirect, prohibited direct and prohibited indirect. plotting a graph between $(\alpha h\upsilon)^2$ and hυ and extrapolating the line to $(\alpha h\upsilon)^2 = 0$ is what define The direct energy gap , the values of the direct band gap of the various concentrated thin layers of Ni-doped ZnO clarified in figure IV .3.

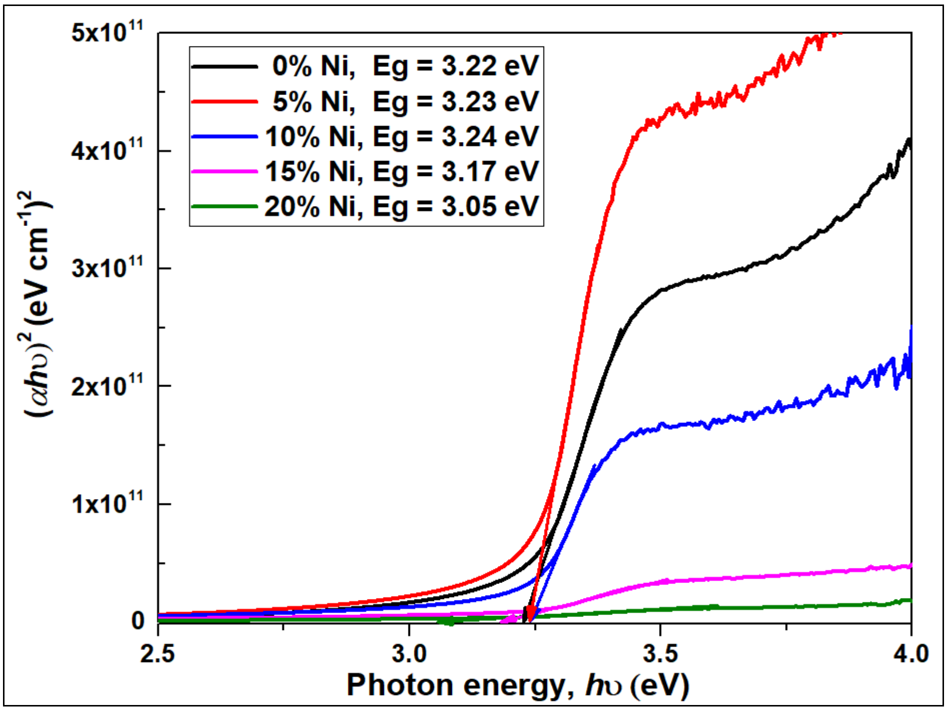

Figure III. 3: Estimation of the optical gap (E_g) of Ni-doped ZnO films prepared at 400 °C with different percentages of Ni.

For more examination its structure has been made.

This width of the localized states is directly related to a similar exponential tail for the density of states near the band edges and can be clarified by the following relationship:

$$\alpha = \alpha_0 \exp(\frac{h\upsilon}{E_u}) \quad \text{(III.7)}$$

Well, hυ is the photon energy, α_0 is constant and Eu is the Urbach energy which refers to the width of the exponential absorption edge. The variation of lnα as a function of the photon energy (hυ) for the layers is showed in Figure IV.4.

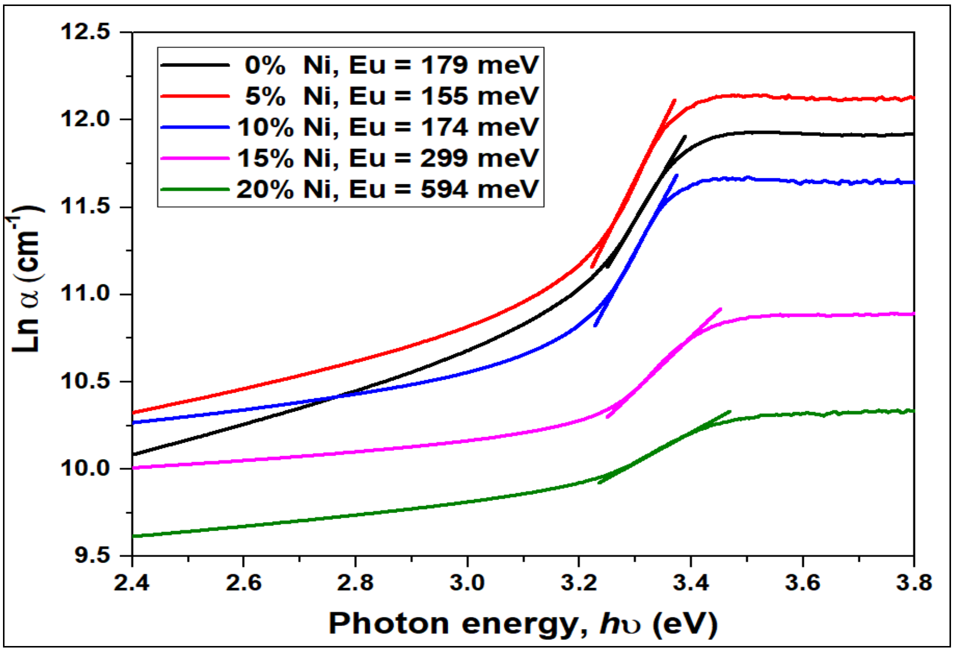

Figure III. 4: Anisotropy of lnα as a function of hυ to determine Urbach energy for Ni-doped ZnO thin layers prepared at 400°C with different percentages of Ni.

The comparison between the optical gap (E_g) and Urbach energy (E_u) of the thin films as a function of Ni percentages is shown in figure III.5. We can see that both E_g and E_u go inversely for different Ni ratios. With the increasing of Ni percentages, the decrease of band gap energy may be attributed to the decrease of structural disorder and defects in the films as observed from Urbach energy analysis (Figure III.5).

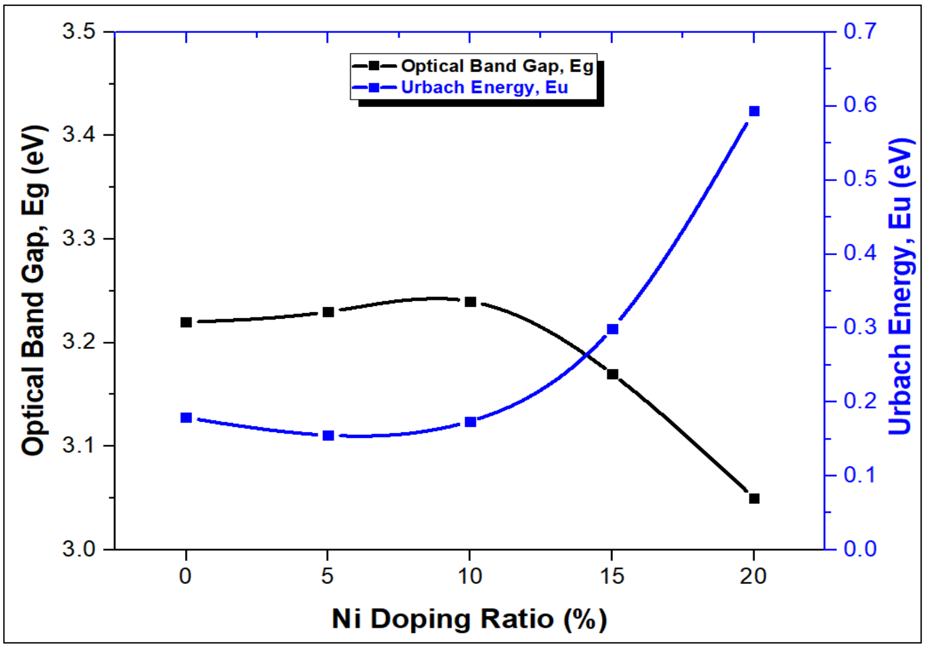

Figure III. 5: Comparison of optical gap values and Urbach energy values for Ni-doped ZnO thin films as a function of Ni percentages.

III.2.1.5. Electrical properties

As it's known that ZnO is N-type semiconductor due to the vacancies of O^{+2}[42], which is the defect considered for its n-type conductivity. The Seebek effect was treated on all samples and confirmed their n-type conductivity. Electrical conductivity was calculated using a four-point probe.

Figure III.6 shows the evolution of electrical conductivity and thickness of Ni-doped ZnO films as a function of Ni percentages. This curve shows that the conductivity of the samples decreases when the thickness of film increases with the increase in the Ni percentages.

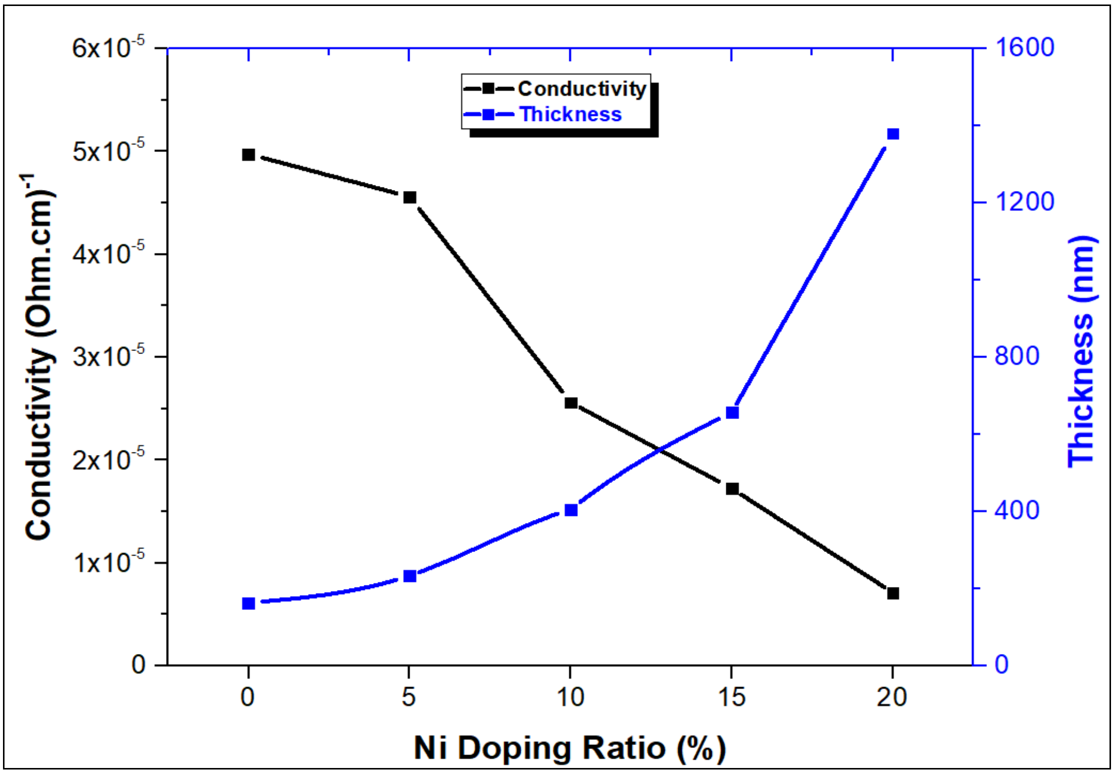

Figure III. 6: Variations of conductivity and thickness (t) of Ni-doped ZnO films as a function of Ni percentage.

III.3. Conclusion

In this part, we deposited thin layers of zinc oxide doped with nickel (ZnO: Ni) with doping concentration varying in the range 0 - 20%, on glass substrates heated using a solar oven between 375 - 425 °C using spray pyrolysis process. Structural Studies using X-ray diffraction (XRD) showed a strong (002) orientation with hexagonal Wurtzite structure.

The transmittance spectra showed a decrease in the transparency and bandgap energy of the obtained films decreased from 71 to 14% and from 3.24 to 3.05 eV respectively with increasing of Ni contents.

Whereas, the electrical conductivity (σ) of obtained films is having N-type character, was correlated of the film thickness revealing the inverse behavior upon the Ni contents.

General conclusion

General conclusion

We started our topic by understanding the sun's structure, properties and the energy it provides. Then we moved on to talk about Algeria and its potential in the world of solar energy. After that we talked about Algeria and its potential in the world of solar energy, and we touched on the applications of this energy, including the production of thin films using the solar furnace coupled with spray pyrolysis technique. We delved into the thin films of zinc oxide and its structural, electrical and optical properties, and finally we saw the effect of nickel doping on the properties of ZnO thin films.

In this case, the purpose of this work is to study the effect of nickel doping on the properties (structural, optical and electrical) of zinc oxide (ZnO) thin films. We use solar furnace at high temperature (between 375 °C and 425 °C) to develop zinc oxide thin films doped with nickel (0, 5, 10, 15 and 20%) on heated glass substrates through the solar spray pyrolysis method. After that, we analyzed the obtained results for each of the structural, optical and electrical properties.

Structural Studies using X-ray diffraction (XRD) showed that Ni-doped ZnO films are polycrystalline and showed the hexagonal Wurtzite structure. Whilst, optical studies showed that the transmittance of obtained layers was decreased with increasing of Ni percentage and bandgap energy ranged from 3.05 to 3.24 eV. For electrical studies, the results exhibit that the conductivity decreases with Ni percentage and films thickness increase.

In the end, we say that these experiments are not finished, as every time the metal or the solution concentration differs, the results also differ. We look forward to more experiments in this domain in the coming time.

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Resume

تأثير نسبة التخدير بالنيكل على خواص الشرائح الرقيقة لاوكسيد الزنك المحضرة بالرش الحراري الشمسي

ملخص:

الهدف من هذه الدراسة هو استخدام الطاقة الشمسية لإنتاج طبقات رقيقة من أكسيد الزنك (ZnO) بتقنية الرش الحراري الشمسي، ثم دراسة تأثير التغير في نسب التخدير بالنيكل (0, 5, 10, 15, 20 %) على خصائصها البنيوية والبصرية والكهربائية. لهذا الغرض، تم ترسيب طبقات رقيقة على ركائز زجاجية مسخنة الى درجات حرارة تتراوح بين 375 و 425 درجة مئوية باستخدام فرن شمسي. وأجريت دراسة لفحص خصائص هذه الطبقات باستخدام تقنية حيود الأشعة السينية (الخصائص البنيوية) والأشعة فوق البنفسجية والتحليل الطيفي المرئي (الخصائص البصرية) وكذلك طريقة المجسات الأربعة (الخصائص الكهربائية).

أظهر التحليل بالأشعة السينية أن عيناتنا تتبلور وفق بنية سداسية حيث تعتمد بلورات الشرائح المحضرة اتجاهًا مفضلاً على طول المستوى (002).

بينما أظهر التحليل المرئي للأشعة فوق البنفسجية أن نفاذية الشرائح تنخفض بزيادة النسبة المئوية للنيكل. أظهر الحساب عمومًا أن طاقة Urbach تتناسب طردا مع نسبة النيكل حيث يمكن تفسير ذلك بانخفاض العشوائية والعيوب في هذه الشرائح. بالإضافة إلى ذلك ، تنخفض الفجوة الضوئية المانعة (Eg) للشرائح مع زيادة نسبة النيكل في الشريحة.

تنخفض الموصلية الكهربائية (σ) للشرائح - المستخلصة بواسطة تقنية المصابر الأربعة - بزيادة نسبة النيكل إلى الحد الأدنى لقيمة ($0.7 .10^{-5}$ اوم$^{-1}$ سم$^{-1}$) عند رش الشريحة بنسبة نيكل قدرها 20 %.

الكلمات المفتاحية: الرش الحراري ؛ الطبقات الرقيقة ؛ أكسيد الزنك (ZnO) ؛ نسبة التخدير؛ فرن شمسي ؛ الأشعة فوق البنفسجية والمرئية ؛ النفاذية ؛ طاقة Urbach ؛ الفجوة الضوئية المانعة .

The effect of Nickel doping on the properties of ZnO thin films elaborated by solar spray pyrolysis

Abstract:

The aim of this study is the using of solar energy to elaborate zinc oxide thin films (ZnO) by solar spray pyrolysis technique, then the study of the effect of nickel doping ratio (0, 5, 10, 15 and 20%) on their structural, optical and electric properties. For this purpose, thin films were been deposited on glass substrates heated to temperatures between 375 and 425°C using a solar oven. A study was conducted to examine the properties of these films using X-ray diffraction (structural properties), UV-visible (optical properties) as well as the four probes method (electrical properties).

X-ray analysis showed that our samples crystallize according to a hexagonal Wurtzite structure, where the crystals of the prepared films adopt a preferred orientation along the plane direction (002).

While the UV visible analysis showed that the transmittance of the films decreases with the increasing of nickel percentage. The calculation generally showed that Urbach energy (E_u) is directly proportional to nickel percentages as this can be explained by the decrease of structural disorder and defects in these layers. In addition, the optical gap (E_g) decreases with the increase of the nickel percentage in the films.

The electrical conductivity (σ) of the films - deduced by four probes method - decreases by increasing of nickel percentage to a minimum value of ($0.7\ .10^{-5}$ $ohm^{-1}cm^{-1}$) for sprayed film with 20% of Ni.

Keywords*:* Solar spray pyrolysis ; Thin films ; Zinc oxide (ZnO); doping ratio ; Solar oven ; UV-visible ; Transmittance ; Urbach Energy (Eu) ; optical band gap enegrgy(Eg).

L'effet de dopage de Nickel sur les propriétés des couches minces de ZnO élaborées par spray pyrolyse solaire

Résumé:

L'objectif de cette étude est l'utilisation de l'énergie solaire pour élaborer des couches minces d'oxyde de zinc (ZnO) par la technique de spray pyrolyse solaire, puis l'étude de l'effet du dopage au nickel (0, 5, 10, 15 et 20 %) sur leurs propriétés structurelles, optiques et électriques. A cet effet, des films minces ont été déposés sur des substrats de verre chauffés à des températures comprises entre 375 et 425°C à l'aide d'un four solaire. Une étude a été menée pour examiner les propriétés de ces films en utilisant la diffraction des rayons X (propriétés structurales), l'UV-visible (propriétés optiques) ainsi que la méthode des quatre points (propriétés électriques).

L'analyse par DRX a montré que nos échantillons présentent une structure hexagonale ‘’Wurtzite’’, où les cristaux des films préparés adoptent une orientation préférentielle suivant la direction du plan (002).

Alors que l'analyse UV visible a montré que la transmittance des films diminue avec l'augmentation du pourcentage de nickel. Le calcul a généralement montré que l'énergie d'Urbach (E_u) est directement proportionnelle aux pourcentages de nickel car cela peut s'expliquer par la diminution des désordres et défauts dans ces couches. De plus, le gap optique (E_g) diminue avec l'augmentation du pourcentage de nickel dans les films.

La conductivité électrique (σ) des films - déduite par la méthode des quatre sondes - diminue en augmentant le pourcentage de nickel jusqu'à une valeur minimale de (0,7 $.10^{-5}$ $ohm^{-1}cm^{-1}$) pour le film pulvérisé avec 20% de Ni.

Mots-clés : Spray pyrolyse solaire ; Films minces ; Oxyde de zinc (ZnO) ; dopage ; four solaire ; UV-visible ; Transmittance ; Urbach Energie (E_u) ; Gap optique (Eg).