

Characterization of Al-doped Conductive Layer of ZnO Thin Film Solar Cell

M.S. THESIS



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A thesis on

Characterization of Al-doped Conductive Layer of ZnO Thin Film Solar Cell

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By

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Dedication

Dedicated to *My Parents*

Declaration

It is hereby declared that this thesis or any part of it has not been submitted elsewhere for the award of any degree or diploma.

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Abstract

Zinc Oxide (ZnO) is a group II-VI semiconductor thin film with a hexagonal wurtzite crystal structure. Its direct wide band gap of $E_g = 3.2\sim 3.7\text{eV}$, low electrical resistivity, high optical transmittance characteristics within the visible range and high resistance to degradation under normal operating conditions. These characteristics distinct itself from other semiconductors with similar crystal structure to widely use in optoelectronic industries. ZnO doped with impurity is a potential choice for transparent conducting oxide (TCO) in commercial area as a transparent electrode in flat panel displays (FPDs) and solar cells. As it is regarded a good transparent conductive oxide (TCO) due to its opto-electro properties, non-toxicity, relatively abundance and low cost; Attention of this is to analyze materials thickness, surface morphology, electrical characteristics, crystal structure and orientation. In execution to this purpose, the sol-gel process of producing Zinc Oxide (ZnO) has chosen which is doped by impurities of Aluminum (Al) to make Al doped Zinc Oxide (Zno:Al) on a glass substrate, using 2-methoxyethanol as solvents and monoethanolamine (MEA) as stabilizer. This combination further increases its optical transmittance and band gap of the thin film material. The sole purpose was to optimize the characteristics of this material by focusing on its several characteristics followed by changing the duration of solution preparation, changing the deposition level on substrates, variation in annealing atmosphere and temperature to observe the characteristics changes occurred in the film. In each stage of observation significant characteristics of the film have found which the main execution of this thesis.

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Chapter 1: Introduction

The world in mostly rely on energy, in fact, it can be said that this world run on energy. Over the past two hundred years mankind has managed to do more damage to the environment through exorbitant use of fossil fuels. Many of the earth's natural resources are beginning to deplete. The world faces an oil shortage and increase of fuel prices. Over the years the demand for natural resources and fossil fuels has outnumbered their availability. Additionally, the burning of these fossil fuels has damaged much of our environment including forests and wildlife. When burning these fuels harmful gases are released into the air which produces acid rain and carbon monoxide. Due to these negative results global warming has become a huge concern as well. If we can turn to alternative energy sources we can reduce pollution and decrease the damage that is being done to planet earth.

The earth has always had a protective layer in the atmosphere which protected the plant from too much heat entering or exiting our planet. The carbon emissions have caused a hole that is still increasing in the ozone area. This has caused increased warming of our planet. The second concern is the need to find replacement fuels because the people on earth are rapidly using up resources that cannot be replaced. Trees are being harvested at a rapid rate leaving topsoil uncovered and causing run off. The fuels like coal and oil are going to run out for future generations if something is not done. The fuels were made by species that no longer exist after millions of years of time to decay and transfer. Time is no longer on mankind's side. The last primary concern is the condition of the ozone layer. The damage to our water system has been a result of pollution and the hole in the ozone layer. The hole in the ozone has caused ice bergs to melt. The ice bergs are a source of fresh water supply. Because of the damage of ice in the Polar Regions, species are losing their environment and dying off. Fossil fuel use has also led to damage for species on the planet. For example; the oil spills that have happened have caused the death of many different species, polluted the water system, and destroyed habitats. Air pollution also affects animals. It is vital for mankind to find cleaner fuel resources to replace fossil fuels because of the reasons that I listed. Alternative energy possibilities include but are not limited to hydro energy produced by water movement, wind energy harnessed from moving air, thermal energy found in underground heated systems, and plant related fuels.

Energy development is the ongoing effort to quest for alternative energy source to provide sufficient primary energy sources and secondary energy forms to fulfill civilization's needs. Technologically advanced societies have become increasingly dependent on external energy sources for transportation, the production of many manufactured goods, and the delivery of energy services. This energy allows people who can afford the cost to live under otherwise unfavorable climatic conditions through the use of heating, ventilation and air conditioning. All

terrestrial energy sources are from current solar insolation or from fossil remains of plant and animal life that relied directly and indirectly upon sunlight, respectively.

Alternative energy is a term used to refer to any energy source other than fossil fuels. An ongoing debate exists over what forms of alternative energy are the safest, most cost-efficient, and most practical to replace and/or subsidize fossil fuels. Some activists believe that government agencies and powerful lobbyists are hindering investigation into alternative energy in an effort to support the fossil fuel industry. As a source of energy, fossil fuels are limited and cause numerous harmful environmental effects. Many modern energy companies are studying and developing alternative fuel sources. In recent years, governments have increased the resources dedicated to the development of alternative energy.

By alternative energy sources we mean the energy sources other most widely used source of energy today. These commonly used sources of energy are broadly divided in to groups - fossil fuels and hydro-power. Fossil fuel refers to basically coal, petroleum, and natural gas based fuels. All these fuels have been formed by natural processes from the vegetation over millions of years. The total accumulated reserves of such fuel is limited, and at the rate we are consuming them in ever increasing quantities, the humanity will run out of these resources in foreseeable future. Hydro power is the power generated from the flowing water created as a part of natural water cycle of evaporation of water from seas and other water bodies, precipitation of this water in form of rain, and the water from rain again flowing back to the water bodies. While supply of energy from this source will never run out as it is a renewable source of energy, The total capacity of generating hydro-power is limited. Thus, it is not possible to increase the rate of hydro-power generation indefinitely to meet the future increased requirement of energy. Therefore, if we want to continue to sustain and improve upon our lifestyle based on heavy use of energy, we have to find alternative sources of energy to supplement and replace the conventional sources of energy wit alternative non-depletable sources.

Another important reason to develop and use more of alternative energy source is to control and reduce the pollution caused by burning of fossil fuel. This pollution, poses serious threats, particularly in the form of global warming, to health and even life of large sections of humanity. So we have to find and use alternative sources of energy that do not cause global warming or other kinds of pollution. Hence, for alternative options renewable energy sources could be the best possible environment friendly option for mankind to scale up their energy needs.

Chapter 2: Renewable Energy

2.1 Renewable Energy as Alternative Source

Renewable energy is generally defined as energy that comes from resources which are naturally replenished on a human timescale, such as sunlight, wind, rain, tides, waves, and geothermal heat. Renewable energy replaces conventional fuels in four distinct areas: electricity generation, air and water heating/cooling, motor fuels, and rural (off-grid) energy services.

Renewable energy resources exist over wide geographical areas, in contrast to other energy sources, which are concentrated in a limited number of countries. Rapid deployment of renewable energy and energy efficiency is resulting in significant energy security, climate change mitigation, and economic benefits. In international public opinion surveys there is strong support for promoting renewable sources such as solar power and wind power. At the national level, at least 30 nations around the world already have renewable energy contributing more than 20 percent of energy supply. National renewable energy markets are projected to continue to grow strongly in the coming decade and beyond. Some places and at least two countries, Iceland and Norway generate all their electricity using renewable energy already, and many other countries have the set a goal to reach 100% renewable energy in the future. For example in Denmark the government decided to switch the total energy supply (electricity, mobility and heating/cooling) to 100% renewable energy by 2050. While many renewable energy projects are large-scale, renewable technologies are also suited to rural and remote areas and developing countries, where energy is often crucial in human development.

Renewable energy is reliable and plentiful and will potentially be very cheap once technology and infrastructure improve. It includes solar, wind, geothermal, hydropower and tidal energy, plus biofuels that are grown and harvested without fossil fuels. Nonrenewable energy, such as coal and petroleum, require costly explorations and potentially dangerous mining and drilling, and they will become more expensive as supplies dwindle and demand increases. Renewable energy produces only minute levels of carbon emissions and therefore helps combat climate change caused by fossil fuel usage. Renewable energy sources are so named because, aside from geothermal and tidal energies, they are replenished constantly by sunlight. Uneven solar heating of the Earth's surface causes wind. Sunlight also fuels the water cycle, which is harnessed through hydropower, including hydroelectric dams and less invasive systems that harness streams or ocean currents. Biofuels are grown using sunlight. Geothermal energy is considered renewable because radioactive decay in the Earth's core, which isn't expected to cool down any time soon, produces it. The gravitational pull of the sun and moon causes the tides.

Coal, natural gas and oil reserves are finite and hidden. An unknown and limited amount of each resource is buried deep underground or under the ocean. As more is harvested, finding new sources becomes more difficult and more expensive, and exploiting them becomes more challenging and sometimes dangerous as well. Marginal reserves, such as oil sands, require the burning of huge amounts of natural gas to refine them into usable oil. Drilling under the ocean

floor can lead to catastrophic accidents, such as the British Petroleum oil spill of 2010. Renewable energy, by contrast, is as easy to find as wind or sunlight.

The daily price of oil depends on many factors, including political stability in historically volatile regions. Political strife has caused energy crises, including those that occurred in 1973 and 1979. Renewable energy can be locally produced and therefore is not vulnerable to distant political upheavals. Many of the safety concerns surrounding fossil fuels, such as explosions on oil platforms and collapsing coal mines do not exist with renewable energy.

Renewable energy is far cleaner than fossil fuels. Coal mining and petroleum exploration and refinement produce solid toxic wastes, such as mercury and other heavy metals. The burning of coal to produce electricity uses large quantities of water often discharges arsenic and lead into surface waters and releases carbon dioxide, sulfur dioxide, nitrogen oxides and mercury into the air (see References 4). Gasoline and other petroleum products cause similar pollution. These pollutants cause respiratory illnesses and death in humans, produce acid rain that damages buildings and destroys fragile ecosystems, and deplete the ozone layer.

2.2.1 Major Renewable Energy Sources

2.2.1.1 Solar Energy

Solar energy, radiant light and heat from the sun, is harnessed using a range of ever-evolving technologies such as solar heating, photovoltaics, concentrated solar power, solar architecture and artificial photosynthesis. Solar technologies are broadly characterized as either passive solar or active solar depending on the way they capture, convert and distribute solar energy. Passive solar techniques include orienting a building to the Sun, selecting materials with favorable thermal mass or light dispersing properties, and designing spaces that naturally circulate air. Active solar technologies encompass solar thermal energy, using solar collectors for heating, and solar power, converting sunlight into electricity either directly using photovoltaics (PV), or indirectly using concentrated solar power (CSP).



Figure 2.1: Solar Panels to capture solar energy and produce electricity

A photovoltaic system converts light into electrical direct current (DC) by taking advantage of the photoelectric effect. Solar PV has turned into a multi-billion, fast-growing industry, continues to improve its cost-effectiveness, and has the most potential of any renewable technologies together with CSP. Concentrated solar power (CSP) systems use lenses or mirrors and tracking systems to focus a large area of sunlight into a small beam. Commercial concentrated solar power plants were first developed in the 1980s. CSP-Stirling has by far the highest efficiency among all solar energy technologies.



Figure 2.2: Concentrated Solar Power (CSP)- Solar Tower

In 2011, the International Energy Agency said that "the development of affordable, inexhaustible and clean solar energy technologies will have huge longer-term benefits. It will increase countries' energy security through reliance on an indigenous, inexhaustible and mostly import-independent resource, enhance sustainability, reduce pollution, lower the costs of mitigating climate change, and keep fossil fuel prices lower than otherwise. These advantages are global. Hence the additional costs of the incentives for early deployment should be considered learning investments; they must be wisely spent and need to be widely shared". In 2013 solar generated less than 1% of the world's total grid electricity.

2.2.1.2 Bio Energy

Biomass is biological material derived from living, or recently living organisms. It most often refers to plants or plant-derived materials which are specifically called lignocellulosic biomass. As an energy source, biomass can either be used directly via combustion to produce heat, or indirectly after converting it to various forms of

biofuel. Conversion of biomass to biofuel can be achieved by different methods which are broadly classified into: thermal, chemical, and biochemical methods. Wood remains the largest biomass energy source today; examples include forest residues – such as dead trees, branches and tree stumps, yard clippings, wood chips and even municipal solid waste. In the second sense, biomass includes plant or animal matter that can be converted into fibers or other industrial chemicals, including biofuels. Industrial biomass can be grown from numerous types of plants, including miscanthus, switchgrass, hemp, corn, poplar, willow, sorghum, sugarcane, bamboo, and a variety of tree species, ranging from eucalyptus to oil palm (palm oil).

Plant energy is produced by crops specifically grown for use as fuel that offer high biomass output per hectare with low input energy. Some examples of these plants are wheat, which typically yield 7.5–8 tonnes of grain per hectare, and straw, which typically yield 3.5–5 tonnes per hectare in the UK. The grain can be used for liquid transportation fuels while the straw can be burned to produce heat or electricity. Plant biomass can also be degraded from cellulose to glucose through a series of chemical treatments, and the resulting sugar can then be used as a first generation biofuel.



Figure 2.3: Biomass Gasification base Power Plant

Biomass can be converted to other usable forms of energy like methane gas or transportation fuels like ethanol and biodiesel. Rotting garbage, and agricultural and human waste, all release methane gas – also called landfill gas or biogas. Crops, such as corn and sugarcane, can be fermented to produce the transportation fuel, ethanol. Biodiesel, another transportation fuel, can be produced from left-over food products like vegetable oils and animal fats. Also, biomass to liquids (BTLs) and cellulosic ethanol are still under research. There is a great deal of research involving algal fuel or algae-derived biomass due to the fact that it's a non-food resource and can be produced at rates 5 to 10 times those of other types of land-based agriculture, such as corn and soy. Once harvested, it can be fermented to produce biofuels such as ethanol, butanol, and methane, as well as biodiesel and hydrogen. The biomass used for electricity generation varies by region. Forest by-products, such as wood residues, are common in the United States. Agricultural waste is common in

Mauritius (sugar cane residue) and Southeast Asia (rice husks). Animal husbandry residues, such as poultry litter, are common in the United Kingdom.

Biofuels include a wide range of fuels which are derived from biomass. The term covers solid, liquid, and gaseous fuels. Liquid biofuels include bioalcohols, such as bioethanol, and oils, such as biodiesel. Gaseous biofuels include biogas, landfill gas and synthetic gas. Bioethanol is an alcohol made by fermenting the sugar components of plant materials and it is made mostly from sugar and starch crops. These include maize, sugarcane and, more recently, sweet sorghum. The latter crop is particularly suitable for growing in dryland conditions, and is being investigated by International Crops Research Institute for the Semi-Arid Tropics for its potential to provide fuel, along with food and animal feed, in arid parts of Asia and Africa.

With advanced technology being developed, cellulosic biomass, such as trees and grasses, are also used as feedstocks for ethanol production. Ethanol can be used as a fuel for vehicles in its pure form, but it is usually used as a gasoline additive to increase octane and improve vehicle emissions. Bioethanol is widely used in the United States and in Brazil. The energy costs for producing bio-ethanol are almost equal to, the energy yields from bio-ethanol. However, according to the European Environment Agency, biofuels do not address global warming concerns. Biodiesel is made from vegetable oils, animal fats or recycled greases. It can be used as a fuel for vehicles in its pure form, or more commonly as a diesel additive to reduce levels of particulates, carbon monoxide, and hydrocarbons from diesel-powered vehicles. Biodiesel is produced from oils or fats using transesterification and is the most common biofuel in Europe. Biofuels provided 2.7% of the world's transport fuel in 2010.

Biomass, biogas and biofuels are burned to produce heat/power and in doing so harm the environment. Pollutants such as sulphurous oxides (SO_x), nitrous oxides (NO_x), and particulate matter (PM) are produced from the combustion of biomass; the World Health Organization estimates that 7 million premature deaths are caused each year by air pollution. Biomass combustion is a major contributor. The life cycle of the plants is sustainable, the lives of people less so.

2.2.1.3 Biogas

Biogas typically refers to a mixture of different gases produced by the breakdown of organic matter in the absence of oxygen. Biogas can be produced from raw materials such as agricultural waste, manure, municipal waste, plant material, sewage, green waste or food waste. It is a renewable energy source and in many cases exerts a very

small carbon footprint. Biogas can be produced by anaerobic digestion with anaerobic bacteria, which digest material inside a closed system, or fermentation of biodegradable materials. Biogas is primarily methane (CH_4) and carbon dioxide (CO_2) and may have small amounts of hydrogen sulfide (H_2S), moisture and siloxanes. The gases methane, hydrogen, and carbon monoxide (CO) can be combusted or oxidized with oxygen. This energy release allows biogas to be used as a fuel; it can be used for any heating purpose, such as cooking. It can also be used in a gas engine to convert the energy in the gas into electricity and heat.



Figure 2.4: Biogas Plant

Biogas can be compressed, the same way natural gas is compressed to CNG, and used to power motor vehicles. In the UK, for example, biogas is estimated to have the potential to replace around 17% of vehicle fuel. It qualifies for renewable energy subsidies in some parts of the world. Biogas can be cleaned and upgraded to natural gas standards, when it becomes bio methane.

2.2.1.4 Wind Energy

Airflows can be used to run wind turbines. Modern utility-scale wind turbines range from around 600 kW to 5 MW of rated power, although turbines with rated output of 1.5–3 MW have become the most common for commercial use; the power available from the wind is a function of the cube of the wind speed, so as wind speed increases, power output increases up to the maximum output for the particular turbine. Areas where winds are stronger and more constant, such as offshore and high altitude sites are preferred locations for wind farms. Typically full load hours of

wind turbines vary between 16 and 57 percent annually, but might be higher in particularly favorable offshore sites.

Globally, the long-term technical potential of wind energy is believed to be five times total current global energy production, or 40 times current electricity demand, assuming all practical barriers needed were overcome. This would require wind turbines to be installed over large areas, particularly in areas of higher wind resources, such as offshore. As offshore wind speeds average ~90% greater than that



Figure 2.5: Wind Power Plant

of land, so offshore resources can contribute substantially more energy than land stationed turbines. In 2013 wind generated almost 3% of the world's total electricity.

2.2.1.5 Hydro Energy

Since water is about 800 times denser than air, even a slow flowing stream of water, or moderate sea swell, can yield considerable amounts of energy. There are many forms of water energy:

- i) Hydroelectric energy is a term usually reserved for large-scale hydroelectric dams. The largest of which is the Three Gorges Dam in China and a smaller example is the Akosombo Dam in Ghana.
- ii) Micro hydro systems are hydroelectric power installations that typically produce up to 100 kW of power. They are often used in water rich areas as a remote-area power supply (RAPS).



Figure 2.6: Hydro Power Plant

- iii) Run-of-the-river hydroelectricity systems derive kinetic energy from rivers without the creation of a large reservoir.

Hydropower is produced in 150 countries, with the Asia-Pacific region generating 32 percent of global hydropower in 2010. For countries having the largest percentage of electricity from renewables, the top 50 are primarily hydroelectric. China is the largest hydroelectricity producer, with 721 terawatt-hours of production in 2010, representing around 17 percent of domestic electricity use. There are now three hydroelectricity stations larger than 10 GW: the Three Gorges Dam in China, Itaipu Dam across the Brazil/Paraguay border, and Guri Dam in Venezuela. In 2013 hydropower generated almost 16% of the world's total electricity.

2.2.1.6 Geothermal Energy

Geothermal energy is from thermal energy generated and stored in the Earth. Thermal energy is the energy that determines the temperature of matter. Earth's geothermal energy originates from the original formation of the planet and from radioactive decay of minerals (in currently uncertain but possibly roughly equal proportions). The geothermal gradient, which is the difference in temperature between the core of the planet and its surface, drives a continuous conduction of thermal energy in the form of heat from the core to the surface. The adjective geothermal originates from the Greek roots *geo*, meaning earth, and *thermos*, meaning heat. The heat that is used for geothermal energy can be from deep within the Earth, all the way down to Earth's core – 4,000 miles (6,400 km) down. At the core, temperatures may reach over 9,000 °F (5,000 °C). Heat conducts from the core to surrounding rock. Extremely high temperature and pressure cause some rock to

melt, which is commonly known as magma. Magma convects upward since it is lighter than the solid rock. This magma then heats rock and water in the crust, sometimes up to 700 °F (371 °C).

From hot springs, geothermal energy has been used for bathing since Paleolithic times and for space heating since ancient Roman times, but it is now better known for electricity generation.

2.2.1.7 Other Energy Sources

- **Wave Energy**

Wave power, which captures the energy of ocean surface waves, and tidal power, converting the energy of tides, are two forms of hydropower with future potential; however, they are not yet widely employed commercially. A demonstration project operated by the Ocean Renewable Power Company on the coast of Maine, and connected to the grid, harnesses tidal power from the Bay of Fundy, location of world's highest tidal flow. Ocean thermal energy conversion, which uses the temperature difference between cooler deep and warmer surface waters, has currently no economic feasibility.



Figure 2.7: Wave to Energy Conversion

- **Tidal Energy**

Tidal power, also called tidal energy, is a form of hydropower that converts the energy obtained from tides into useful forms of power, mainly electricity. Although not yet widely used, tidal power has potential for future electricity generation. Tides are more predictable than wind energy and solar power. Among sources of renewable energy, tidal power has traditionally suffered from relatively high cost and limited availability of sites with sufficiently high tidal ranges or flow velocities, thus constricting its total availability. However, many recent developments and improvements, both in design (e.g. dynamic tidal power, tidal lagoons) and turbine technology (e.g. new axial turbines, cross flow turbines), indicate that the total availability of tidal power may be much higher than previously assumed, and that economic and environmental costs may be brought down to competitive levels.

- **Heat pump**

A heat pump is a device that provides heat energy from a source of heat to a destination called a "heat sink". Heat pumps are designed to move thermal energy opposite to the direction of spontaneous heat flow by absorbing heat from a cold space and releasing it to a warmer one. A heat pump uses some amount of external power to accomplish the work of transferring energy from the heat source to the heat sink.

- **Grid Energy Storage**

Grid energy storage (also called large-scale energy storage) is a collection of methods used to store electrical energy on a large scale within an electrical power grid. Electrical energy is stored during times when production (especially from intermittent power plants such as renewable electricity sources such as wind power, tidal power, solar power) exceeds consumption, and returned to the grid when production falls below consumption.

2.2.2 Solar Energy Technology

Solar energy systems are two types: Solar photovoltaic system (Uses photon energy from sun to generate electricity) and Concentrated solar power system (uses thermal energy from sun).

▪ Solar Photovoltaic System

Photovoltaic (PV) materials and devices convert sunlight into electrical energy, and PV cells are commonly known as solar cells. Photovoltaics can literally be translated as light-electricity.

First used in about 1890, "photovoltaic" has two parts: photo, derived from the Greek word for light, and volt, relating to electricity pioneer Alessandro Volta. And this is what photovoltaic materials and devices do—they convert light energy into electrical energy, as French physicist Edmond Becquerel discovered as early as 1839.

Becquerel discovered the process of using sunlight to produce an electric current in a solid material. But it took more than another century to truly understand this process. Scientists eventually learned that the photoelectric or photovoltaic effect caused certain materials to convert light energy into electrical energy at the atomic level.

PV systems are already an important part of our daily lives. Simple PV systems provide power for small consumer items such as calculators and wristwatches. More complicated systems provide power for communications satellites, water pumps, and the lights, appliances, and machines in some homes and workplaces. Many road and traffic signs also are now powered by PV. In many cases, PV power is the least expensive form of electricity for these tasks.

Photovoltaic system consists of solar module, which is comprises with many solar cells. To obtain electricity solar cell plays a vital role in the system. Hence various research are going on to develop optimize level solar cell to get best possible electricity. As in concern to that, this research is conducted to get viable cell performance using unorthodox solar cell technology.

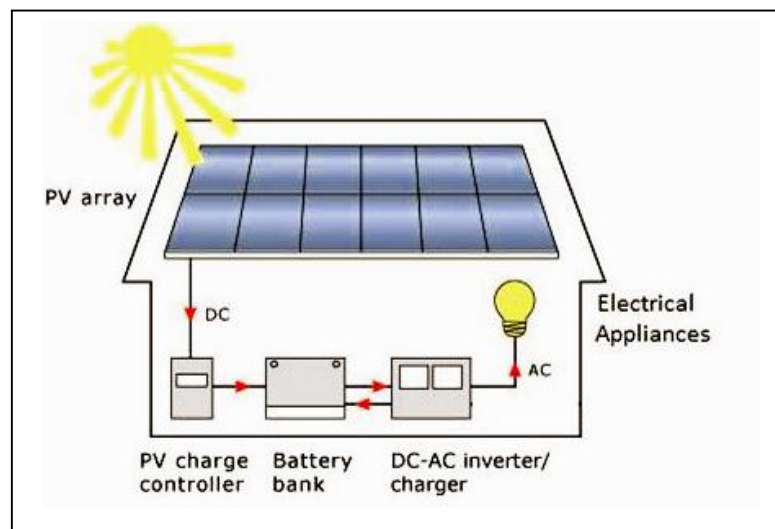


Figure 2.8: Solar Photovoltaic System for Household Electricity Production

Chapter 3: Solar Cell

3.1 Solar Cell

A solar cell or photovoltaic cell is a device which generates electricity directly from visible light by means of the photovoltaic effect, which is a physical and chemical phenomenon. It is a form of photoelectric cell, defined as a device whose electrical characteristics, such as current, voltage, or resistance, vary when exposed to light. Solar cells are the building blocks of photovoltaic modules, otherwise known as solar panels.

3.2 Different Generations of Solar Cells

Solar cells are usually divided into three main categories called generations. The first generation contains solar cells that are relatively expensive to produce, and have a low efficiency. The second generation contains types of solar cells that have an even lower efficiency, but are much cheaper to produce, such that the cost per watt is lower than in first generation cells. The term third generation is used about cells that are very efficient. Most technologies in this generation is not yet commercial, but there is a lot of research going on in this area. The goal is to make third generation solar cells cheap to produce.

3.2.1 First Generation Solar Cells

The first generation includes cells consisting of Silicon or Germanium that are doped with Phosphorus and Boron in a pn-junction. This generation is dominating the commercial market. Silicon cells have a quite high efficiency, but very pure silicon is needed, and due to the energy-requiring process, the price is high compared to the power output.

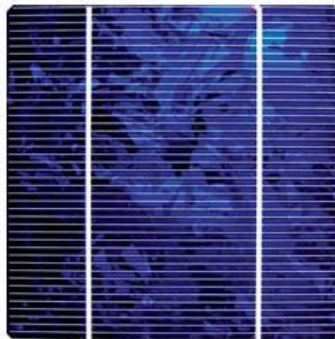


Figure 3. 1: Multicrystalline silicon solar cell

3.2.2 Second Generation Solar Cells

3.2.2.1 Amorphous Silicon Solar Cells

In Amorphous Silicon Cells, hydrogen is introduced to the silicon to make it possible to dope the silicon with boron and phosphorus. The cells are built up in this sequence from bottom to top: metal base contact, n-layer, intrinsic layer, p-layer, transparent contact, glass substrate. These cells experience a drop in efficiency when they are exposed to sunlight, and this effect is created in the intrinsic layer. The effect can be reduced by, instead of one layer, using several thinner layers.

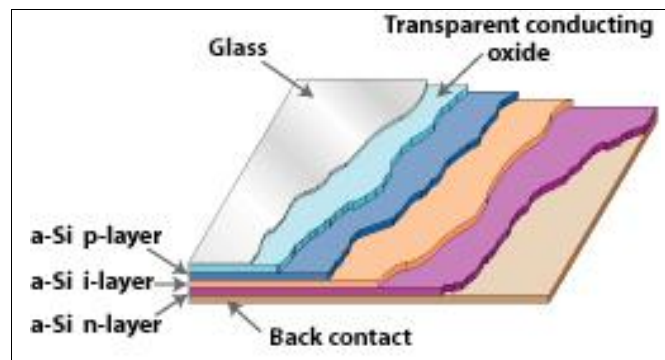


Figure 3. 2: Amorphous Silicon Solar Cell

3.2.2.2 Polycrystalline Silicon on Low Cost Substrate

These cells use antireflection layers to capture lightwaves with wavelengths several times greater than the thickness of the cell itself. This can be done by using a material with a textured surface both in front and back of the cell, rather than a flat surface. This causes the light to change directions and be reflected, and thus travels a greater distance within the cell than the cell thickness.

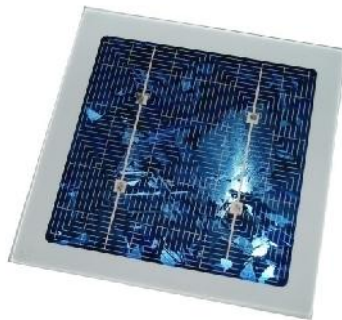


Figure 3. 3: Polycrystalline Silicon Solar Cell

3.2.2.3 Copper Indium DiSelenide (CIS) Cells

Copper Indium Diselenide consists of CuInSe_2 . This material is one of the best light absorber known, and about 99% of the light is absorbed before reaching $1 \mu\text{m}$ into the material. There have been made homojunctions of CIS, but a heterojunction with cadmium sulfide (CdS) has been found to be more stable and efficient.

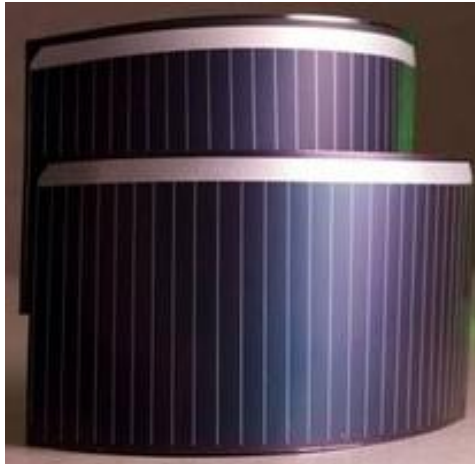


Figure 3. 4: Flexible Copper Indium Gallium diSelenide solar cells

3.2.2.4 Cadmium Telluride Solar Cells

These cells are made from a heterojunction with cadmium sulfide, just like the copper indium diselenide. Cadmium telluride cells also have an ideal bandgap (1.44eV).

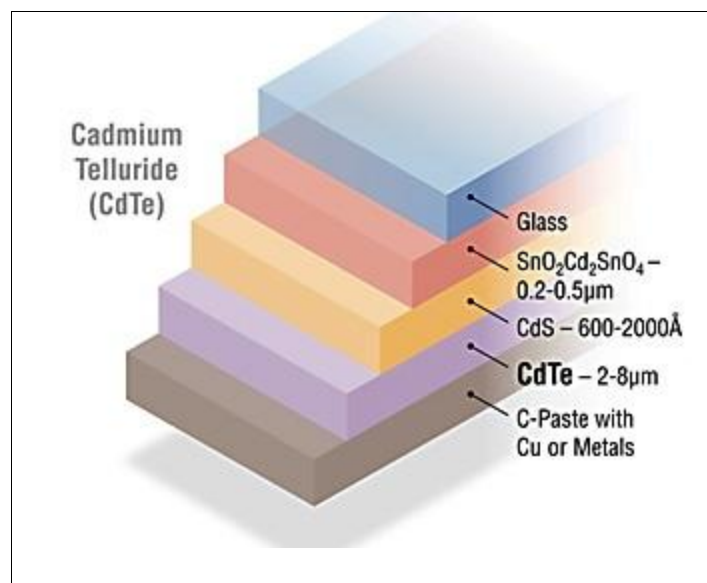


Figure 3. 5: Schematic of Cadmium Telluride Solar Cells

3.2.3 Third Generation Solar Cells

3.2.3.1 Quantum Dot (QD) Solar Cells

There are several technologies in this generation. One of them is Quantum Dot (QD) Solar Cells. These are built up of a semiconductor (silicon) coated with a very thin layer of quantum dots. Quantum dots is just a fancy name of crystals in the size range typically a few nanometers in diameter. These crystals are mixed into a solution and placed on a piece of silicon which is rotated really fast. The crystals are then spread out due to the centrifugal force. The reason these quantum dots are given so much attention is that normally one photon will excite one electron creating one electron-hole pair. The energy loss is the original energy of the photon minus the energy needed to excite the electron (also called the band gap) However, when a photon hits a quantum dot made of the same material, there may be several electron-hole pairs created, typically 2-3, but 7 has been observed.

Another way to increase the efficiency is to use several layers solar cells with different band gaps in a stack. Each layer will utilize light with different wavelengths, and in this way we can get cells with a higher efficiency.

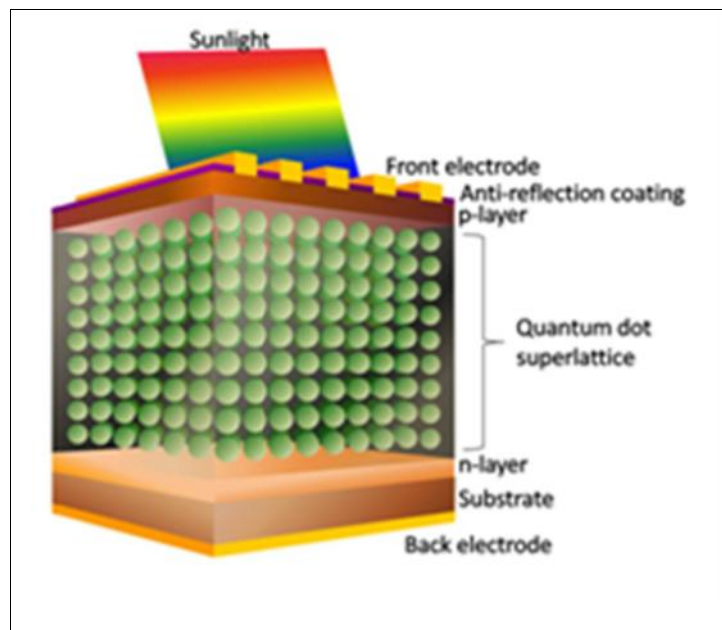


Figure 3. 6: Schematic of Quantum Dot (QD) Solar Cells

3.2.3.2 Multijunction Solar Cells

Another way to increase the efficiency is to use several layers solar cells with different band gaps in a stack. Each layer will utilize light with different wavelengths, and in this way we can get cells with a higher efficiency.

3.2.3.3 Dye-Sensitized Solar Cells

M. Grätzel of the Swiss Polytechnic of Lausanne discovered a thin-film titanium dioxide system that is sensitive to ultraviolet radiation can be made to respond to ordinary light. A layer of light-responsive dye overlays the semiconductor and the charge is transferred back to the dye from an electrolyte. The cells have reasonable efficiencies ($\sim 10\%$) in hazy light conditions, and the cost is projected to be very low, since the materials can be worked on at low temperatures in contrast to most other semiconductor solar cell arrays.

A new idea to harvest solar energy uses dyes on a metal substrate, quite different from what occurs in normal silicon solar cells. The device developed by McFarland and Tang has multiple layers on ultrathin metal films that constitute a Schottky diode (a diode that works by quantum tunneling).

Electrons excited to a higher state by incident light can jump the Schottky barrier and so provide a current. The efficiency is higher than expected. As McFarland and Tang say, “This alternative approach to photovoltaic energy conversion might provide the basis for durable low-cost solar cells using a variety of materials.”

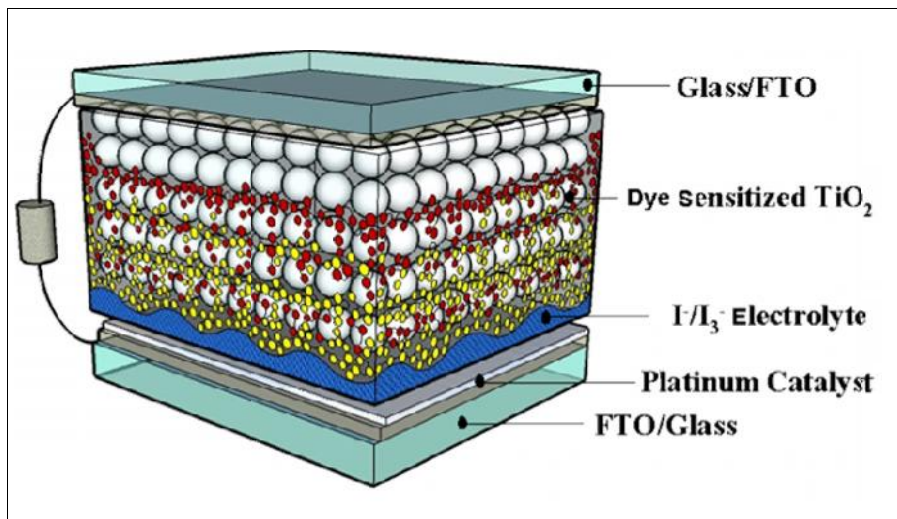


Figure 3. 7: Schematic of Dye Sensitized Solar Cell

Chapter 4: ZnO Thin Film

4.1 Thin Film Solar Cell

The Thin Film technology is based on the deposition of a thin (μm) layer of active materials on large-area (m^2 -sized or long foils) substrates of materials such as steel, glass or plastic. Thin Film technologies use small amounts of active materials and can be manufactured at a lower full cost than c-Si. They have short energy pay-back times (i.e. $<1\text{yr}$ in southern Europe) despite their lower efficiency, good stability and lifetimes comparable to c-Si modules. Plastic Thin Film are usually frameless and flexible and can easily adapt to different surfaces. Standard Thin Film modules have a typical 60-120Wp capacity and a size between 0.6-1.0 m^2 for CIGS and CdTe, and 1.4-5.7 m^2 for silicon-based Thin Film. In comparison with c-Si modules, Thin Film module efficiency (i.e. 4-12%) is significantly lower. The operational experience is also lower. A typical Thin Film manufacturing process includes:

- Coating of the substrate with a transparent conducting layer
- TCO deposition of the active layer by various techniques (e.g. chemical/physical vapour deposition)
- Back-side metallisation (contacts) using laser scribing or traditional screen-printing
- Encapsulation in a glass-polymer casing. Roll-to-roll (R2R) techniques are often used with flexible substrates to reduce production time and costs.

Research efforts focus on materials with higher absorption and efficiency, thin polymer substrates, high-stability TCO, deposition techniques (e.g. plasma enhanced chemical vapour deposition, PECVD), hetero-structures, electrical interconnection, low-cost manufacturing (i.e. R2R coating, sputtering, cheap and durable packaging), quality control and aging tests. In a few years, the typical manufacturing plant-scale has increased from less than 50 MW to hundreds of MW per year. However, the Thin Film manufacturing industry is undergoing significant changes at the moment and the outlook is quite uncertain because Thin Film's share in the PV market is being challenged by the current low costs of c-Si modules. Various Thin Film solar cells current efficiencies are given below:

Table 4- 1: Efficiency of Thin Film Solar Cells

Thin Films	Maximum Efficiency (%)	Commercial Efficiency (%)
a-Si	15	10-11
CdTe	16.5	14
CIGS	20	15

4.2 Advantages of Thin Film over Crystalline Solar Cell

- Technology is relatively simple and inexpensive for a-Si:H
- For a given layer thickness, a-Si:H absorbs much more energy than c-Si (about 2.5 times)
- Much less material required for a-Si:H films, lighter weight and less expensive
- Can be deposited on a wide range of substrates, including flexible, curved, and roll-away types
- Overall efficiency of around 10%, still lower than crystalline silicon but improving
- Can be produced at lower temperatures

4.3 ZnO Thin Film

ZnO thin film is one of the II-VI compound semiconductors and is composed of hexagonal wurtzite crystal structure. ZnO thin film presents investigating optical, acoustical and electrical properties which meet extent applications in the fields of electronics, optoelectronics and sensors. ZnO thin film is applied to the transparent conductive film and the solar cell window because of the high optical transmittance in the visible region. It has excellent piezoelectric properties. Zinc Oxide has a large band gap ($E_g=3.37\text{eV}$), large excitation energy of 60 meV and categorized as a semi-conductor material. In particular, ZnO forms a technologically important class of material, exhibiting exceptional UV attenuation characteristics: blocking 95% of all UV radiation, excellent transmittance in the long wavelength region and outstanding antimicrobial properties. One area of great interest is the application of ZnO as a transparent conducting oxide (TCO). Impurity-doped ZnO is a candidate for transparent conducting oxide (TCO), for potential application as a transparent electrode in flat panel displays (FPDs) and solar cells. ZnO is nontoxic, abundant, and inexpensive and impurity-doped ZnO has electrical and optical properties that may be comparable to those of the expensive indium tin oxide (ITO), which is currently being used commercially in liquid crystal displays (LCDs), plasma display panels (PDPs), and organic light-emitting displays (OLEDs). Transparent conducting thin films require low electrical resistivity, high optical transmittance within the visible range, and high resistance to degradation under normal operating conditions. ZnO thin films have interested as transparent conductor, because the n-type ZnO thin film has a wide bandgap semiconductor and high transmission in the visible range. ZnO thin films can take place of SnO_2 and ITO because of their electrical and optical properties and its excellent stability which has been mentioned widely.

ZnO can be an n-type and a p-type semiconductor determined by the dopant nature. Practically n-Type doping of ZnO is relatively easy compared to p-type doping and reproducible p-type conductivity in Coatings ZnO is still a challenge. However, p-type doping in ZnO may be possible by substituting either group-I elements (Li, Na, K, etc.) for Zn-atoms or group-V elements (N, P, As, Sb, etc.), and for O-atoms [1, 2, 4, 8]. For n-type [2–4,7,8,39], doping with group-III elements (B, Al, Ga, In), as substitutional elements for Zn, has been attempted by many groups, resulting in high-quality, optically transparent, and highly conductive ZnO films as this substitution of divalent Zn^{2+} by a trivalent ion generates an excessive free electron. Especially, Al-doped ZnO (AZO) thin films have attracted a considerable amount of interest due to their good electrical conductivity with reasonably low optical loss. On the other hand, n-type

semiconductors may also be synthesized by substituting O-atoms by group-VII elements (F, Cl, I). The optical constants of the semiconductors play an important role, both from a fundamental and a technological viewpoint. Refractive index is one of the fundamental properties for an optical material, because it is closely related to the electronic polarizability of the ions and to the local field inside materials. The evaluation of refractive indices of optical materials is highly important for applications in integrated optic devices, such as switches, filters, modulators, etc., where refractive indices are the key constants for device design. With a refractive index of about 1.9, ZnO allows the fabrication of waveguiding layers of high transparency from the near UV to middle infrared spectral range.

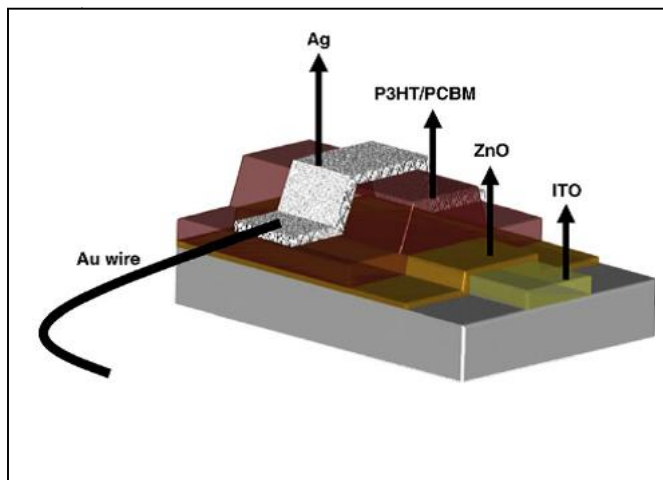


Figure 4.1: ZnO Thin Film

Zinc oxide (ZnO) has distinct advantages over other competitors, e.g., abundance in earth crust, non-toxicity, low material costs, chemical stability, high transparency in the visible and near infrared spectral region, etc. It is a direct wide band gap semiconductor ($E_g = 3.37$ eV at 300 K) with a similar crystal structure to gallium nitride (GaN), another wide gap semiconductor ($E_g = 3.3$ eV at 300 K) and from this direct wide band-gap comes a wide interest in its prospects in optoelectronic applications. For some of these, the interest in ZnO overlaps with that of GaN, which is widely used for production of green, blue-ultraviolet, and white light-emitting devices and lasers. However, ZnO has some advantages over GaN, among which are the availability of fairly high quality ZnO bulk single crystals and a large excitons binding energy (ZnO: $E_{ex} = 60$ meV, GaN: $E_{ex} \sim 18\text{--}28$ meV). On the other hand, ZnO has been investigated intensively due to its unique characteristics that may enable its efficient utilization in/as: varistors, piezoelectric devices such as surface-acoustic wave (SAW) and piezoelectric sensors, transparent conducting oxide (e.g., electrode of solar cells), antireflection coatings, field-effect transistors, phosphors (green phosphors in displays), chemical and biological sensors, gas sensors in electronic noses, etc. Furthermore, because of its transparency, its electro-optical and elasto-optical properties, ZnO is attractive for integrated photonic devices. The conductive layer of ZnO can be doped using Aluminum that is preferably known as AZO.

Chapter 5: Methodology

5.1 Literature Review

Several researches have been conducted on AZO based thin film to observe structural, optical, electrical properties of the materials. Also we have studied some scientific papers on which research have been conducted to observe the characteristics change of the film behavior when its properties have been changed. Also some changes have been notified by changing film preparation process such as doping concentration, doping level and annealing atmosphere. These all helped us to find some initial ideas and knowledge about the film character which was our predecessor to forward our work. The findings on the literatures we have reviewed are given in a nutshell on the below table:

Table 5-1: List of reviewed Literatures

Paper Notification		Materials Used	Observation	
			Purpose	Result
		Starter: Zinc Acetate Dihydrate Solution: mono-ethanol-amine Stabilizer: 2-methoxyethanol Dopant Precursor: Aluminum Nitrate		
1.	s. ilican, y. caglar, m. caglar, Preparation and characterization of ZnO thin films deposited by sol-gel spin coating method , Journal of optoelectronics and advanced materials vol. 10, No. 10, October 2008, p. 2578 - 2583	<ul style="list-style-type: none"> Significant Execution: Spin coating of 3000rpm, 4000rpm and 5000rpm was maintained 	<ul style="list-style-type: none"> Effect of chuck rotation rate on the structural, optical and electrical properties of ZnO thin films 	<ul style="list-style-type: none"> The film thickness changes inversely with increasing or decreasing chuck rotation
2.	Ans Farooq and Muhammad Kamran, Effect of Sol Concentration on Structural and Optical Behavior of ZnO Thin Films Prepared by Sol-Gel Spin Coating , International Journal of Applied Physics and Mathematics, Vol. 2, No. 6, November 2012	<ul style="list-style-type: none"> Significant Execution: Sol concentration varying by 0.1M, 0.3M, 0.5M to observe the changes 	<ul style="list-style-type: none"> Effect of Sol Concentration on Structural and Optical Behavior of thin films 	<ul style="list-style-type: none"> Grain size increases with increase in molar concentration of the deposited thin films

Paper Notification		Materials Used	Observation	
		Starter: Zinc Acetate Dihydrate Solution: mono-ethanol-amine Stabilizer: 2-methoxyethanol Dopant Precursor: Aluminum Nitrate	Purpose	Result
3.	Gil Mo Nam and Myoung Seok Kwon, Al-doped ZnO via Sol-Gel Spin-coating as a Transparent Conducting Thin Film , Journal of Information Display, Vol. 10, No. 1, March 2009 (ISSN 1598-0316)	Significant Execution: <ul style="list-style-type: none"> Al concentration varies by 0.25, 0.5, 0.8, 1.0, 2.0, 3.0, 5.0 at % respectively first post-heat treatment was performed in air at 530°C, and the second at 500°C 	<ul style="list-style-type: none"> Variation of Al dopant concentrations and post-heat-treatments to observe the effect of 	<ul style="list-style-type: none"> Crystallite size of the ZnO:Al thin film decreases with increasing Al concentration Electrical resistivity increased with increasing Al concentration Resistivity became lower after each post heat treatment than the former
4.	Mounir Alhamed, Wael Abdullah, Structural and optical properties of ZnO:Al films prepared by the sol-gel method , Journal of Electron Devices, Vol. 7, 2010, pp. 246-252 [ISSN: 1682 -3427]	Significant Execution: <ul style="list-style-type: none"> Film heated in furnace at 550°C for 1h & 200°C for 15min Dopant concentration changes by 1,2,3,4 wt.% 	<ul style="list-style-type: none"> Structural and optical properties of ZnO:Al to increase band gap and optical transmittance effect of Al concentration on the structural and optical properties 	<ul style="list-style-type: none"> Increasing Al concentration leads to an amorphous stage of the film appears higher than 2 wt.% of concentration

Paper Notification		Materials Used	Observation	
		Starter: Zinc Acetate Dihydrate Solution: mono-ethanol-amine Stabilizer: 2-methoxyethanol Dopant Precursor: Aluminum Nitrate	Purpose	Result
5.	Samia Tabassum, Eiji Yamasue, Hideyuki Okumura, Keiichi N. Ishihara, Damp heat stability of AZO transparent electrode and influence of thin metal film for enhancing the stability , J Mater Sci: Mater Electron (2014) 25:3203–3208	Significant Execution: <ul style="list-style-type: none"> • DH stability was investigated for AZO thin films under DH condition for 7 days • Thin Cr or Ti layer was deposited by sputtering on AZO for protecting them against O/H₂O absorption 	<ul style="list-style-type: none"> • Structural, optical and electrical stability of the film in damp heat (DH) condition • Effect of sputtered thin metal film (Ti and Cr) encapsulation for enhancing the electrical stability of AZO films 	<ul style="list-style-type: none"> • Annealing in hydrogen atmosphere made oxygen annihilation and formed oxygen vacancies which act as carrier increase of carrier concentration, resistivity decreases • mobility decreased with increasing Al concentration (for 3,4 wt% Al) • high degradation of the resistivity was observed under DH (85 <hr/> C and 85 % RH) condition

Paper Notification		Materials Used	Observation	
		Starter: Zinc Acetate Dihydrate Solution: mono-ethanol-amine Stabilizer: 2-methoxyethanol Dopant Precursor: Aluminum Nitrate	Purpose	Result
6.	V.I. Kondratiev, I. Kink, A.E. Romanov, Low Temperature Sol-Gel Technique For Processing Al-Doped Zinc Oxide Films , Materials Physics and Mechanics 17 (2013) 38-46	Significant Execution: <ul style="list-style-type: none"> Before deposition the glass and Si substrates were ultrasonically cleaned in acetone and/or methanol for 10 minutes and dried in a flowing nitrogen gas 	<ul style="list-style-type: none"> Dependence of resistivity and transmittance of Al-doped films from aluminum content Study on time/temperature of annealing and annealing environment 	<ul style="list-style-type: none"> Film resistivity is strongly dependent on dopant concentration and annealing temperature With each annealing concentration of oxygen increased and concentration of carbon decreased in the films Annealing in Ar decreases the resistivity up to ~50-100 times than annealing in air

5.2 Prospect of the Work

- To observe the technology for improving conductivity by Al doping on ZnO layer which is relatively simple and inexpensive for thin film
- Observe the layer thickness and relative characteristic change in the substrate
- Identify dopant material requirement for optimization of layer resistivity
- Impact of deposition on a fixed range of substrates
- Observing affect of surface roughness produced at fixed temperatures

5.3 ZnO Film Preparation Process

The ZnO thin film is prepared using various methods such as spray pyrolysis, sol-gel spin coating, Physical Vapor Deposition (e.g., Sputtering and Pulsed Laser Deposition), Chemical Vapor Deposition (CVD), electro-deposition, aqueous solutions, evaporation. Also both undoped and doped ZnO thin films have been made by a variety of methods among which Successive Chemical Solution Deposition (SCSD), Plasma Enhanced CVD (PECVD), Single-Source CVD (SSCVD), Metalorganic CVD (MOCVD), Molecular Beam Epitaxy (MBE), RF or DC Magnetron Sputtering, Thermal Oxidation of Zinc or ZnS and Atomic Layer Deposition (ALD) are commonly used. In spite of few studies regarding to the sol-gel method, the sol-gel method has some merits for which we have chosen sol-gel method for our work. These advantages are such as:

- This process allows excellent compositional control with controlled dopants, a high degree of homogeneity on the molecular level and a low crystallization temperature, also performing well in atmospheric pressure without the need for expensive vacuum equipment,.
- Process allows easy control of chemical components and fabrication of thin film at a low cost to investigate structure and optical properties of ZnO thin films
- It is an easy to understand procedure, uniform film thickness and large area deposition can be possible
- The simplicity, easy control of doping or growth parameters characteristics prevails this method to other deposition techniques

5.4 Sol-gel Method

The sol-gel process is a method for producing solid materials from small molecules. The method is used for the fabrication of metal oxides, especially the oxides of silicon and titanium. The process involves conversion of monomers into a colloidal solution (sol) that acts as the precursor for an integrated network (or gel) of either discrete particles or network polymers. Typical precursors are metal alkoxides.

In this process, the sol (or solution) evolves gradually towards the formation of a gel-like network containing both a liquid phase and a solid phase. Typical precursors are metal alkoxides and metal chlorides, which undergo hydrolysis and polycondensation reactions to form a colloid.

The basic structure or morphology of the solid phase can range anywhere from discrete colloidal particles to continuous chain-like polymer networks.

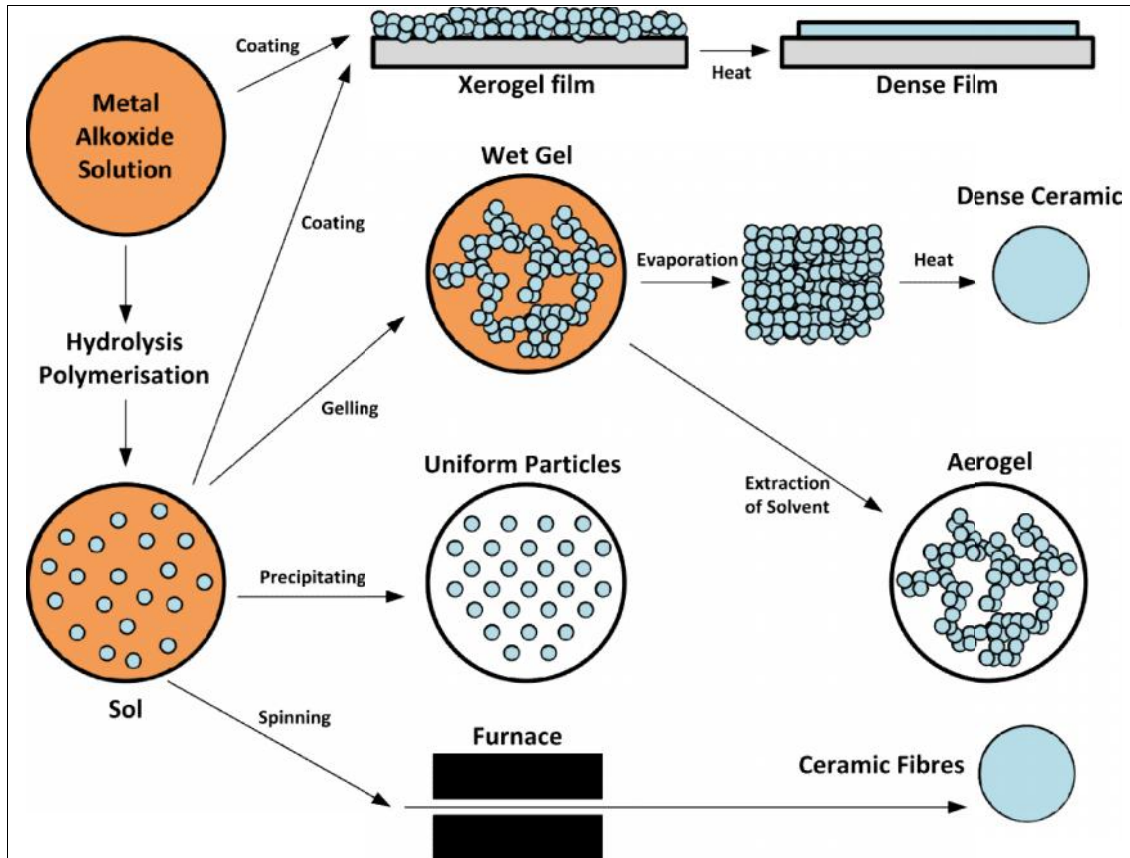


Figure 5. 1: Sol-gel process

The most widespread commercial use of sol-gel is in the fabrication and deposition of coatings. The role of the coating may be to provide one or more of a number of functions:

- chemical protection (e.g. corrosion protection)
- mechanical protection (e.g. abrasion resistance)
- optical properties (e.g. anti-reflective, optoelectronic)
- electronic properties (e.g. ferroelectric, conductive)
- catalytic activity (usually associated with high surface area)

Stages involve in sol-gel process are:

- **Hydrolysis**

In this step the AZO solution are deposited in the sample slides. After preparing the solution and slides, solution is deposited on the slides using spin coater aiming to uniformly distributed layer on the glass slide. This process is done after each deposition.

- **Condensation**

After deposition of the solution the slides is then kept in air for certain time to condense the solution on the substrate. The major concern is uniformity in air for certain time to condense the solution on the substrate. This helps improving uniformity of AZO solution on the substrates and increases the stability of the solution.

- **Gelation**

This step involves solidification of the solution on slide. This improves the stable condition more than the previous stages.

- **Ageing**

After gelation, the slides are kept in a hot furnace where it is stacked on to make robust bonding. The samples are kept for certain time with a predetermined temperature (300°C) which improves the stick condition with maintaining this temperature.

- **Drying**

The hot slides are then kept in ambient air for reducing the temperature to surroundings. This is important to move hot slide safely to avoid fracture on slide while placing for drying.

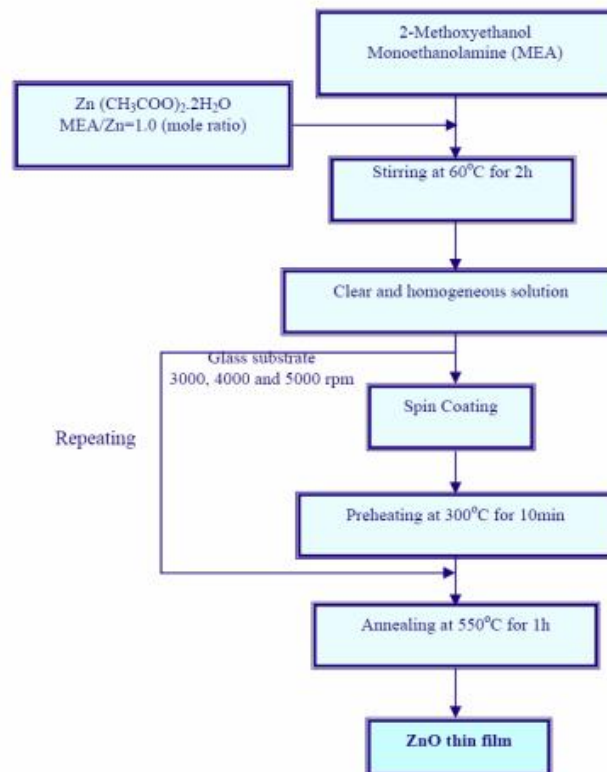


Figure 5.2: Steps of Sol-gel process

- **Densification**

This stage slides are kept for annealing process for densification. The process can be done by using air or vacuum.

Chart showing process of Al doped ZnO thin film preparation process using sol-gel method

5.5 Experimental Film Preparation

5.5.1 Sample Slide Cleaning

Biological glass slides were used as substrate for deposition of Zinc Oxide thin films. The size of the glass slides used as substrate is of 1 inch×1 inch. The substrate was cleaned by Ultrasonic Bath (USB) process. In this process, first the sample slides are cleaned by brush with de-ionized water and washed by methanol as mechanical scrubbing. Then slides were placed in DTPLCSP Ultrasonic Bath machine, firstly in a methanol solution for 10 minutes and then in acetone for 10 minutes.



Figure 5.3: Ultrasonic Bathing Process using DTPLCSP Ultrasonic Bath machine

Those were then placed in methanol and de-Ionized water sequentially for 10 and 15 minutes respectively. Then the samples are kept in open air for drying.

5.5.2 AZO Solution Preparation

Sol-gel method was used to prepare zinc oxide thin films using zinc acetate dehydrate $[\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}]$. Zinc acetate dehydrate was dissolved in 2-methoxy ethanol ($\text{C}_3\text{H}_8\text{O}_2$) to prepare ZnO sol and mono-ethanol-amine $[(\text{HOCH}_2\text{CH}_2)\text{NH}_2]$ was added drop wise in MEA: Zn ratio of 0.75 as a stabilizer. Below is the amount of Zinc acetate dehydrate, 2-methoxy ethanol ($\text{CH}_3\text{OCH}_2\text{CH}_2\text{OH}$), Aluminum nitrate nonahydrate $[\text{Al}_2(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}]$ and mono-ethanol amine $[(\text{HOCH}_2\text{CH}_2)\text{NH}_2]$ which are used for preparing ZnO sol of different concentrations:

Table 5-2: Elements of AZO solution

Elements	Role	Amount
Zinc acetate dehydrate [$\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$]	Starting Material	5.39g
2-methoxy ethanol ($\text{CH}_3\text{OCH}_2\text{CH}_2\text{OH}$)	Solvent	46.93g
mono-ethanol-amine [$(\text{HOCH}_2\text{CH}_2)\text{NH}_2$]	Stabilizer	1.5ml
Aluminum nitrate nonahydrate [$\text{Al}_2(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$]	Doping Material	0.11g

5.5.3 Magnetic Stirring of the Solution

Taking all elements in a 100ml beaker according to the measured amount the magnetic stirring was done with 78-1 MAGNETIC STIRRER HOTPLATE for 2hr at 60°C and then the solution was allowed to aged for 24 hr in room temperature.

5.5.4 Deposition & Spin Coating of the Sample Slides

After that the aged solution was deposited on glass substrate and slides are placed in coater for spin coating at 3000RPM for 30 seconds using DTPLCSP SPIN150 Spin coater and put it into the laboratory Oven DTPLCSP BINDER with is pre-heated at 300°C for evaporation of the residual solvent and any other containment.



Figure 5.4: Spin Coating of the slides with DTPLCSP SPIN150 Spin coater



Figure 5.5: Ageing at 300°C in DTPLCSP BINDER machine

This cycle was done for 5, 10 & 15 times to yield a smooth and uniform surface of thin films and for testing variation in surface dept and reduction of resistivity with layer growth. After each spin coating procedure the deposited thin films are put into an Oven for raising the temperature to complete ageing process.

5.5.5 Drying in ambient temperature & Annealing for Densification

Then the substrates are kept in ambient temperature to make them cool and afterwards they are placed in annealer/high temperature furnace using GSL 1100X Vacuum machine for annealing at 500°C for 1 hour or air annealing DTLCSP C-1000 machine using N₂ purging.



Figure 5.6: Air annealing of samples with machine DTLCSP C-1000



Figure 5.7: Vacuum annealing of samples with machine GSL 1100X

After annealing the ZnO thin films, furnace is then left to cool down to ambient temperature again. Then it is kept for 24 hours for making it stable and thus the substrate preparation process has accomplished and samples are ready for testing.



Figure 5.8: Prepared substrate samples for testing

Chapter 6: Experiments

6.1 Thin Film Characterization

Major quality measures used in the wafer fabrication are:

- Film thickness
- Sheet resistance
- Film stress
- Refractive index
- Dopant concentration
- Unpatterned surface defects
- Patterned surface defects
- Critical dimensions
- Step coverage
- Overlay registration
- Capacitance-Voltage
- Contact angle

Among them we have done thickness measurement, surface morphology test and hall effect measurement for testing film thickness, film stress, dopant concentration, unpatterned surface defects, step coverage and sheet resistance of the cell.

6.1.1 Thickness Measurement

In case of solar cells, the coating thickness of the optical materials and its uniformity has to be monitored. The layer thickness is influencing the efficiency and, in addition, the surface color, defining the appearance. Hence, measuring the right thickness and composition of active layers is important for determining the solar cell performance. Being too thin can affect efficiency and durability, while being too thick can increase cost. The wrong composition can drastically decrease efficiency and manufacturing yield. Profilometer is used to measure the surface thickness of the film. Profilometer is a measuring instrument used to measure a surface's profile, in order to quantify its roughness. It is a device similar to a phonograph that measures a surface as the surface is moved relative to the contact profilometer's stylus, this notion is changing with the emergence of numerous non-contact profilometry techniques.

6.1.2 Surface Morphology Test

Surface Morphology testing is a subset of Analytical Imaging test, which is an advanced form of high spatial resolution imaging that uses sophisticated microscopes to produce images of products, samples and objects that cannot be seen with the naked eye. Such images originate from the exposed surface of the sample or product. For solar cell this test is performed for detecting surface defect and roughness. This has huge impact to determine cell performance when it exhibits to sunlight due its surface character. Surface Imaging Information are required for:

- Surface structures & defects
- Atomic or Nano-scale structures & defects exposed by cross-section or FIB

Analytical Imaging Techniques used in Surface morphology testing are:

- Field Emission Scanning Electron Microscopy (FE-SEM)
- Focused Ion Beam – Scanning Electron Microscopy (FIB-SEM)
- High Resolution Optical Microscopy
- Scanning Transmission Electron Microscopy (STEM)
- Transmission Electron Microscopy (TEM)
- Ultra High Resolution-SEM (UHR-SEM)

For the cell characterization 1, 10 and 20 times layered samples have been prepared and performed several test. As on testing we have found

6.1.3 Hall Effect Measurement

Hall effect measurements have been valuable tools for material characterization. Essentially, the Hall effect can be observed when the combination of a magnetic field through a sample and a current along the length of the sample creates an electrical current perpendicular to both the magnetic field and the current, which in turn creates a transverse voltage that is perpendicular to both the magnetic field and the current. Hall effect measurements are useful for characterizing virtually every material used in producing semiconductors, such as silicon (Si) and germanium (Ge), as well as most compound semiconductor materials, including silicon-germanium (SiGe), silicon-carbide (SiC), gallium arsenide (GaAs), aluminum gallium arsenide (AlGaAs), indium arsenide (InAs), indium gallium arsenide (InGaAs), indium phosphide (InP), cadmium telluride (CdTe), and mercury cadmium telluride (HgCdTe). They're often used in characterizing thin films of these materials for solar cells/photovoltaics, as well as organic semiconductors and nano-materials like graphene. They are equally useful for characterizing both low resistance materials (metals, transparent oxides, highly doped semiconductor materials, high temperature superconductors, dilute magnetic semiconductors, and GMR/TMR materials used in disk drives) and high resistance semiconductor materials, including semi-insulating GaAs, gallium nitride (GaN), and cadmium telluride (CdTe).

Chapter 7: Results & Discussions

7.1 Thickness Measurement

To measure the thickness of the prepared samples, first the samples have been etched to remove solution from a side of the substrate. Mainly wet etching process have been used.

7.1.1 Wet Etching Process

This is the simplest etching technology. All it requires is a container with a liquid solution that will dissolve the material in question. Unfortunately, there are complications since usually a mask is desired to selectively etch the material. In this process mask should be used that will not dissolve or at least etches much slower than the material to be patterned. Secondly, some single crystal materials, such as silicon, exhibit anisotropic etching in certain chemicals. In this work we used HNO_3 based etching process as it is most general etching component in laboratory work. For the etching process 0.32 ml weak solution of HNO_3 (70% share) with molarity 15.7M has been used.

The etching steps followed are given below:

7.1.2 HNO_3 Solution Preparation

- 125ml of De-Ionized (DI) water had taken in a beaker
- 0.32ml of HNO_3 had poured into it
- Then again DI water had poured on the mixture until the liquid level reaches upto 500ml

7.1.3 Etching the Substrates

- Mask tap had been used to cover aside to keep solution on glass
- Then the substrates were kept drenched in the solution for 10 minutes
- After removing from solution its been rinsed by DI water and dried for another 10 minutes
- Mask tap were released and as it, the AZO layer been removed from that side of the glass; the substrates are ready for thickness & morphology testing.

7.1.4 Thickness Testing

Thickness measurement was done at Institute of Electronics, Atomic Energy Research Establishment (AERE), Savar, Dhaka. Stylus Surface Profilometer,

Model: Detak-150 was used for the testing. Substrates with layer of 1, 10 & 20 times were experimented to observe the variation of thickness in the substrates regarding layer increment.



Figure 7.1: Stylus Surface Profilometer, Model: Detak-150

7.1.5 Test Results

The layer thickness are:

- For 1-layer: 504 μ m
- For 10-layer: 5851.9 μ m
- For 20-layer: 10311.8 μ m

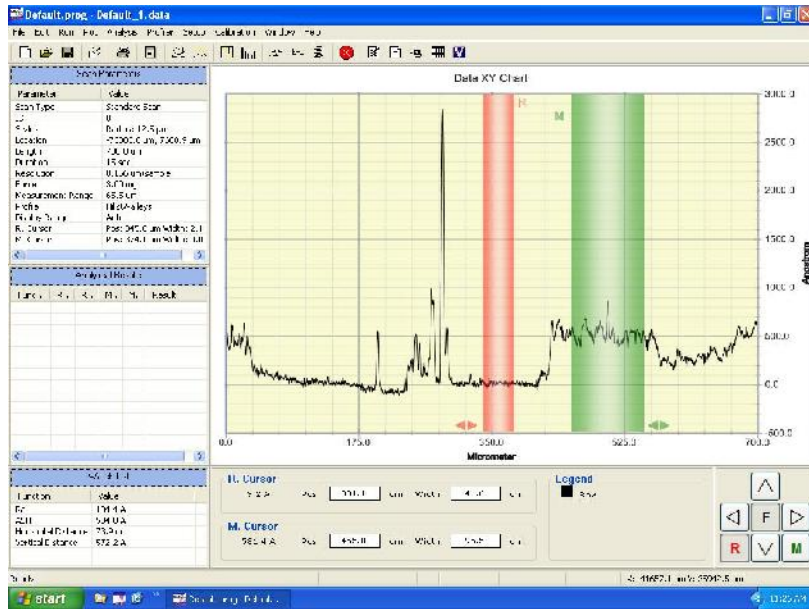


Figure 7.2 (a): Thickness test result from Profilometer for 1-layer

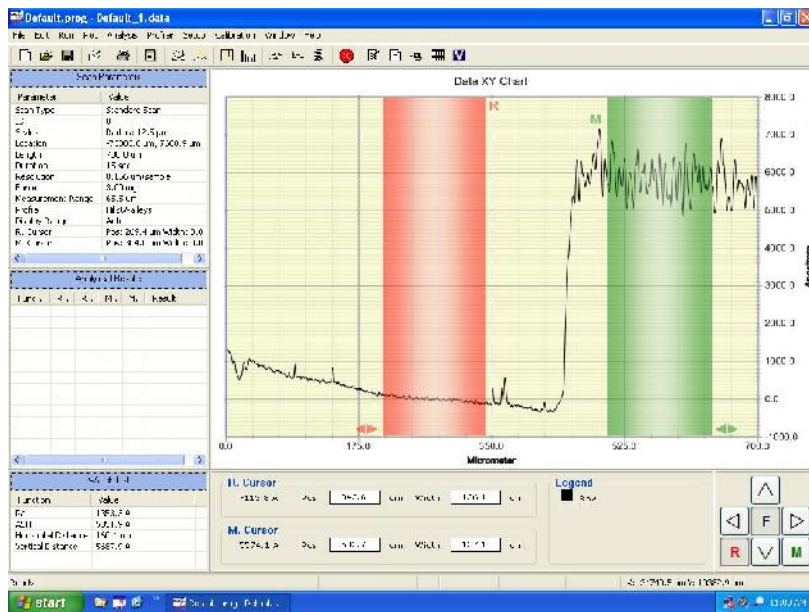


Figure 7.2 (b): Thickness test result from Profilometer for 10-layer

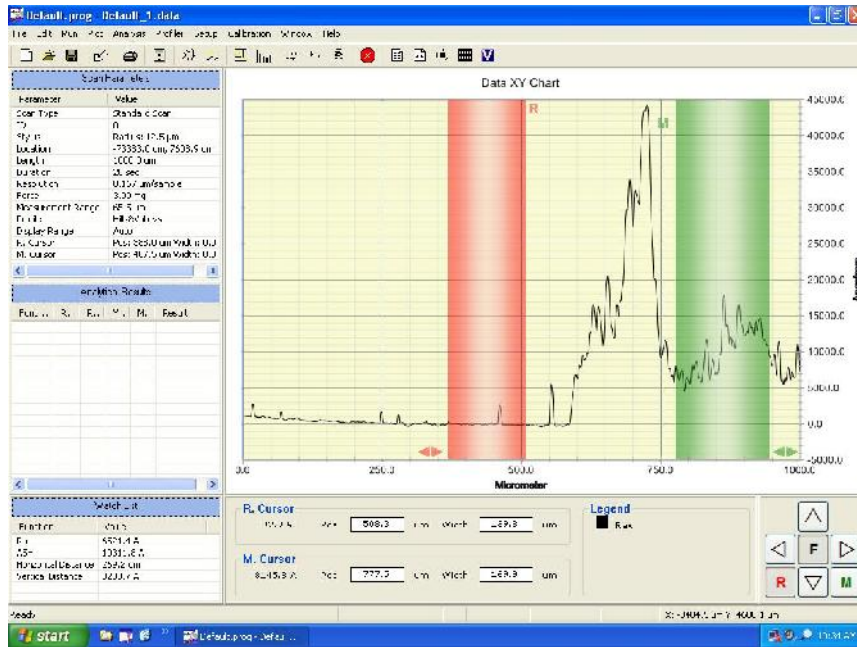


Figure 7.2 (c): Thickness test result from Profilometer for 20-layer

7.1.6 Discussion

It is been observed that a huge improvement in layer thickness with each deposition. For single deposition of AZO the layer thickness was found 504 μm , which is quiet regardable. At 10 times deposition, the layer thickness improved significantly, 5851.9 μm which is almost 11times greater than the thickness found for 1 time deposition.

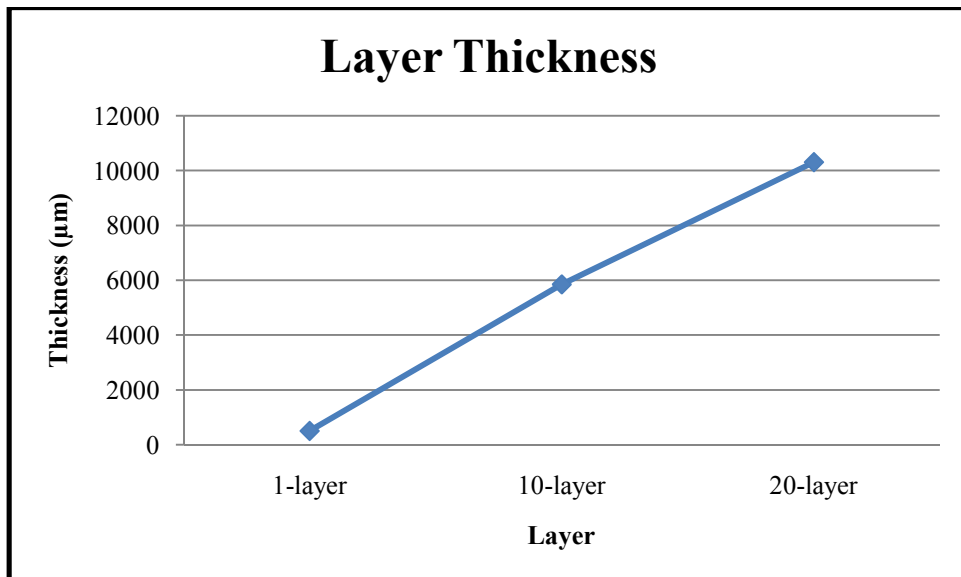


Figure 7.3: Improvement trend of layer thickness with deposition

Likely, when the status of 20 times layer deposition observed its been found that the layer thickness is 10311.8 μ m, almost 20 times higher than the initial stage. From this observation its can be said that with each deposition significant improvement in layer thickness can be obtained.

7.2 Morphology Test

It is mainly to observe the surface roughness of the substrates which has a strong influence on the properties of the deposited film, in particular its adhesion, microstructure and final topography.

7.2.1 Testing

Similarly morphology test has been conducted for 1-layer, 10-layer and 20-layer substrates. This test was also done at Institute of Electronics, Atomic Energy Research Establishment (AERE), Savar, Dhaka using Stylus Surface Profilometer, Model: Detak-150.

7.2.2 Results

The layer roughness are:

- For 1-layer, Ra: 45.3nm
- For 10-layer, Ra: 11545.1nm
- For 20-layer, Ra: 1885.1nm

The surface roughness obtained by the Profilometer for 1-layer, 10-layer and 20-layer substrates are given later.

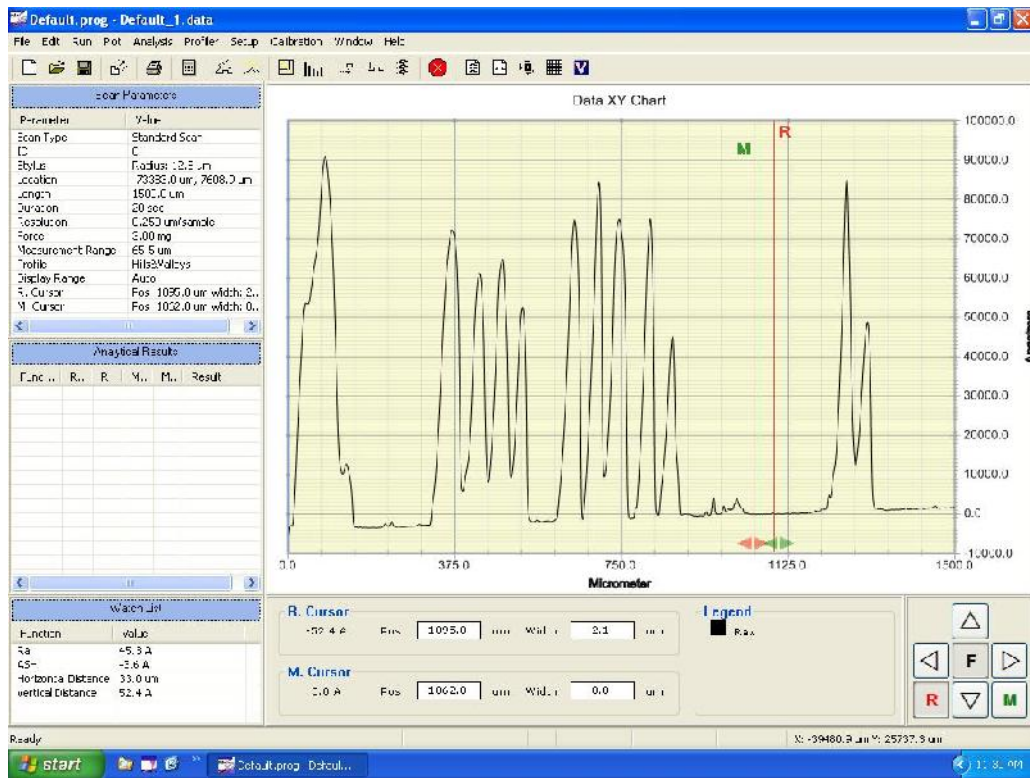


Figure 7.4 (a): Surface Roughness Pattern for 1 time deposited layer

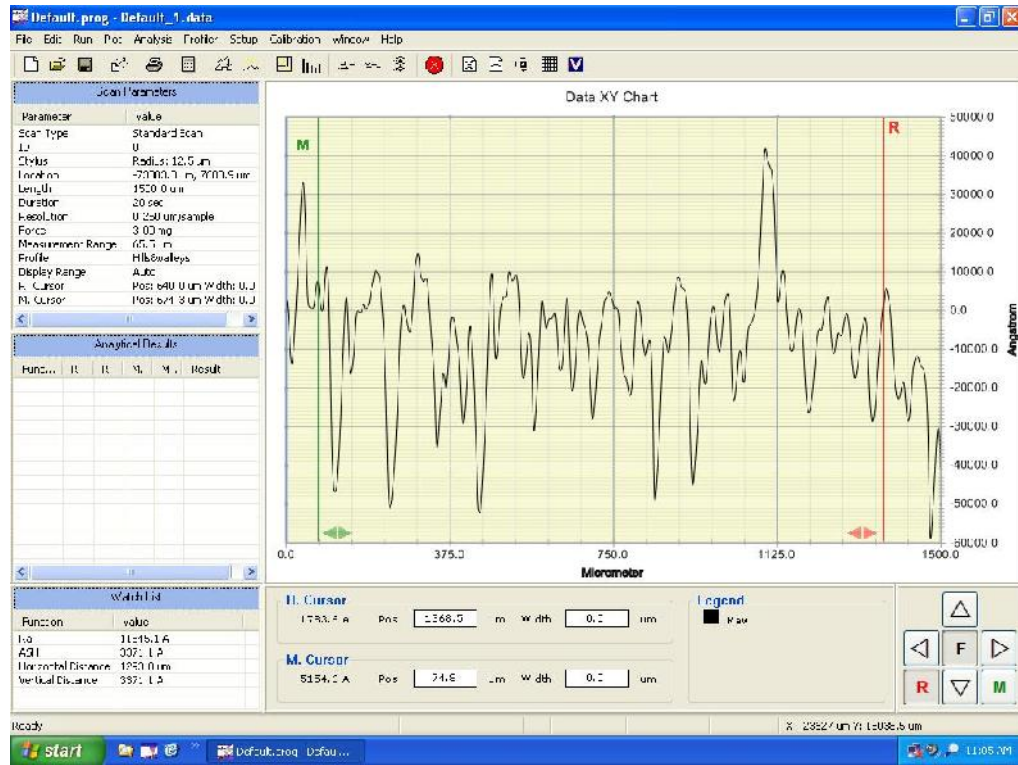


Figure 7.4 (b): Surface Roughness Pattern for 10 times deposited layer

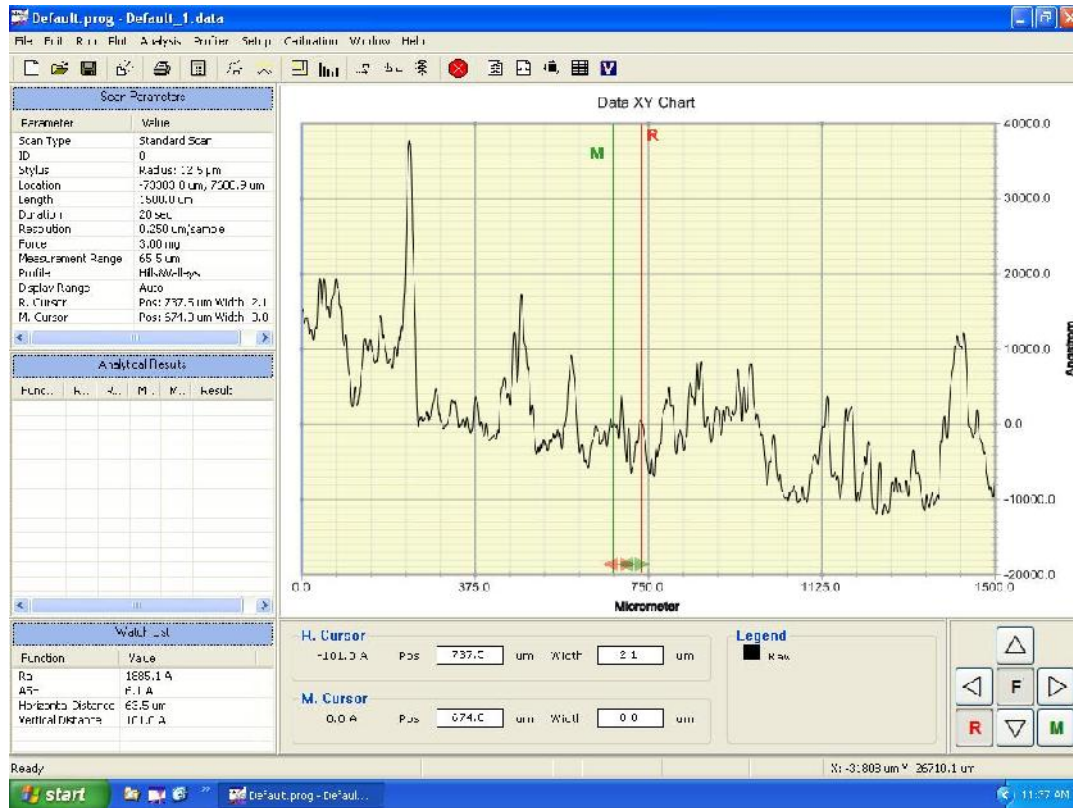


Figure 7.4 (c): Surface Roughness Pattern for 20 times deposited layer

7.2.3 Discussion

It has been found that the roughness of the surface increased with the number of layers from 1 to 10, and then it decreased. For a single deposition, the roughness is so small that it does not affect the surface (grain size) at all. But when the deposition reaches 10 layers, the surface roughness reaches an optimistic level. The smoothest surface (grain size) for Al impurities in ZnO: Al films, together with a first decrease of microstructures when increasing Al impurities for 20 layers of deposition, the roughness decreases, meaning that increasing the doping concentration does not increase the smoothness of the surface a lot.

7.3. Hall Effect Measurement

To measure the Hall Effect of the AZO base glass substrates we took a sample of 10times deposition. All necessary steps have been followed to prepare the samples and vacuum annealing process (500°C) has been done for densification of the samples.



Figure 7.5: Hall Effect Measurement of 10 times deposited layer using ECOPIA HMS-3000

7.3.1 Testing

Hall Effect measurement has been conducted at Institute of Fuel Research & Development (IFRD), Bangladesh Council of Scientific and Industrial Research (BCSIR), Dr. Qudrat-I-Khuda Road, New Elephant Rd, Dhaka using ECOPIA HMS-3000.

7.3.2 Result

The layer various measures are:

- Bulk Concentration: $-9.675 \times 10^{10} / \text{cm}^3$
- Mobility: $1.564 \times 10^3 \text{ cm}^2/\text{VS}$
- Resistivity: $4.126 \times 10^4 \Omega\text{-cm}$
- Magneto-Resistance: $2.698 \times 10^8 \Omega$
- Sheet Concentration: $-6.627 \times 10^6 / \text{cm}^2$
- Conductivity: $2.423 \times 10^{-5} / \Omega\text{-cm}$
- Average Hall Coefficient: $-6.452 \times 10^7 \text{ cm}^3/\text{C}$

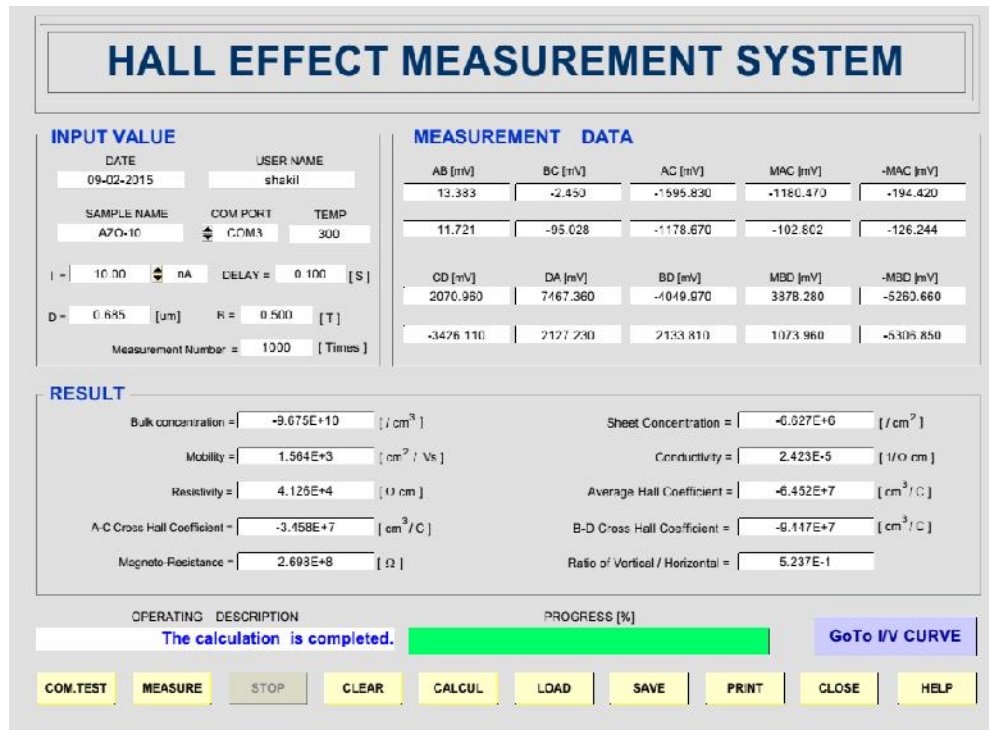


Figure 7.6: Hall Effect Measurement result

7.3.3 I-V Curve

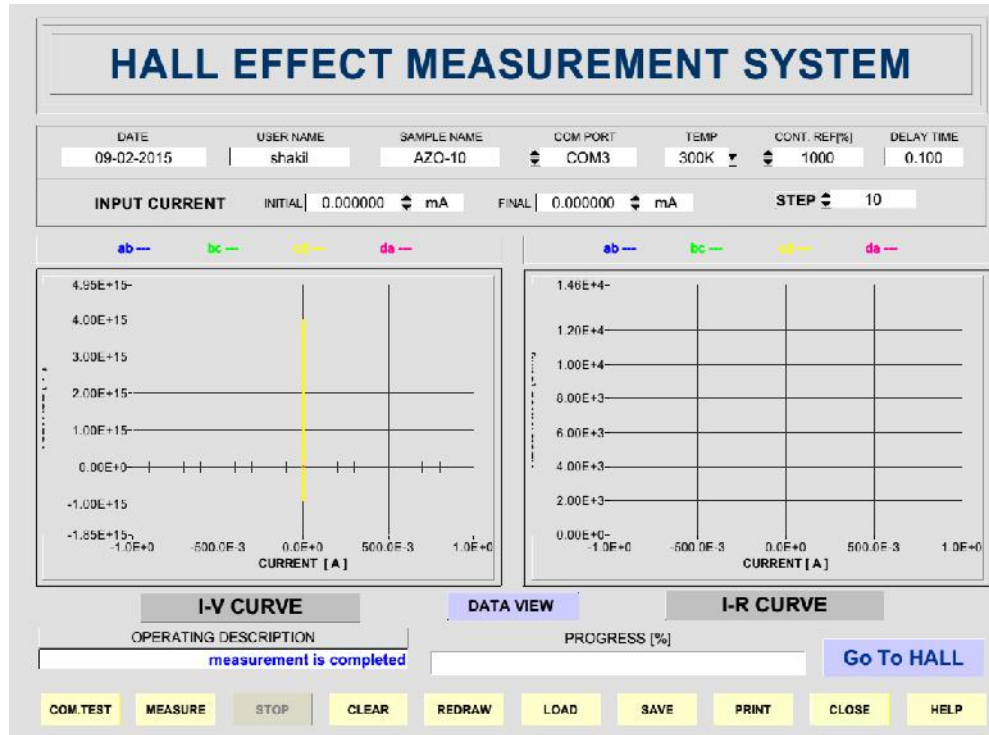


Figure 7.7: Respective I-V Curve for 10 times AZO deposited substrates

7.3.4 Discussion

The Hall Coefficient value was measured as $-6.452 \times 10^7 \text{ cm}^3/\text{C}$. The negative sign of the Hall coefficient shows that Al-doped ZnO thin films are n-type, with electrons as charge carriers. The activated carrier density does not seem to be proportional to the Al dopant concentration. The carrier density decreased with higher Al concentrations. The mobility is $1.564 \times 10^3 \text{ cm}^2/\text{Vs}$. This mobility suggests that it is the grain-boundary scattering mechanism rather than ionized impurity scattering. The conductivity is $2.423 \times 10^{-5} \text{ } \Omega\text{-cm}$ which means the substrates has optimized conductivity. As after the vacuum annealing the resistivity is measured $4.126 \times 10^4 \text{ } \Omega\text{-cm}$, which indicates the post-heat-treatment in a reducing environment efficiently reduced the electrical resistivity of the Al-doped ZnO thin film and affected mainly the oxygen vacancy concentration. The electron density could be increased, probably due to the increased donor concentration (i.e., oxygen vacancies), but the Al addition in the sol-gel process beyond the optimal Al concentration did not increase the carrier density.

Chapter 8: Conclusion

Transparent conducting oxides (TCOs) based on ZnO are promising for application in thin film solar photovoltaic cells (PVCs) and various optoelectronic devices. Desired parameters of ZnO and doped ZnO: Al (AZO) thin films are given by their role in superstrate configuration of tandem Si solar cell: the light enters the cell through the glass substrate where two pin absorber thin-film structures are placed between two TCO layers with back metal contact. The upper front contact AZO layer should fulfill several important requirements: high transparency in VIS/near IR solar spectrum; high electrical conductivity; suitable surface texture in order to enhance light scattering and absorption inside the cell; high chemical stability and adhesion to silicon. Moreover, bottom ZnO interlayer between Si and metal (usually Ag) contact is acting as barrier and adhesion layer as well as optical matching layer to Ag back contact to improve its reflection of radiation, particularly in near IR region. Optimization of the front contact TCO has proven to be crucial for getting the high cell.

Though there are many parameters to characterize the thin film solar cell, most of them couldn't be executed because of limitation of time and availability of testing instruments in the laboratory. However, it's been tried to perform most common norms of characterization which can at least give some conceptions on the AZO substrates prepared. Though faults have been identified in this assignment, best attempt have been given to do it.

Future Work Scope

From this thesis we get informed that AZO base conductive layer is one of the promising conductive layer for thin film. As it is very common material and have the scope of its efficiency improvement to use it as transparent conductive oxide (TCO) it can gain commercial aspect. In this work improvement of conductivity has been observed by varying the layer thickness. The target was to optimize the layer thickness best possible for conductivity. That will ultimately improve the efficiency of the thin film cell. Moreover, this improvement of efficiency will make thin film solar cell to commercially popular and ensure wide range of utilization in different sectors. Hence, attempt should be taken to take this work ahead to explore the optimize layer thickness of the AZO layer for using it as TCO material in thin film technology.

Reference

- [1] Renewable Energy, About Renewable Energy Technologies.
(https://www.google.com/url?sa=t&ret=j&q=&esrc=s&source=web&cd=6&cad=rja&uact=8&ved=0ahUKEWjuveq6sL_KAhVLCY4KHWmhDcoQFghSMAU&url=http%3A%2F%2Fwww.renewableenergyworld.com%2Findex%2Ftech.html&usg=AFQjCNEkjQWfyFk9dN3MZwPRITgqBEOOdA)
- [2] About Thin Film. (<http://www.google.com/patents/WO2013119550A1?cl=en>)
- [3] About Generation of Solar Cell. (<http://org.ntnu.no/solarcells/pages/generations.php>)
- [4] Thin film. (https://en.wikipedia.org/wiki/Thin-film_solar_cell)
- [5] Sol-gel Process. (<http://www.twi-global.com/technical-knowledge/faqs/process-faqs/faq-what-is-sol-gel-processing/>)
- [6] CdTe Cell. (<http://www.nrel.gov/pv/thinfilm.html>)
- [7] QDSC. (http://mbe.rcast.u-tokyo.ac.jp/index_eng.html)
- [8] Dye Sensitized. (<https://schanze.chem.ufl.edu/research/dye-sensitized-solar-cells/>)
- [9] Sol-gel. (<https://en.wikipedia.org/wiki/Sol-gel>)
- [10] Morphology Test. (<http://www.leica-microsystems.com/science-lab/characterization-of-thin-films-using-high-definition-confocal-microscopy/>)
- [11] A. Talbi, F. Sarry, M. Elhakiki, L. Le Brizoual, O. Elmazria, P. Nicolay, P. Alnot, Sensors and Actuators A 128, 78 (2006).
- [12] J. J. Chen, F. Zeng, D.M. Li, J.B. Niu, F. Pan, Thin Solid Films 485, 257 (2005).
- [13] J.-B. Lee, D.-H. Cho, D.-Y. Kim, C.-K. Park, J.-S. Park, Thin Solid Films 516, 475 (2007).
- [14] A. N. Banerjee, C.K. Ghosh, K.K. Chattopadhyay, H. Minoura, A.K. Sarkar, A. Akiba, A. Kamiya, T. Endo, Thin Solid Films 496, 112 (2006).
- [15] J. Yoo, J. Lee, S. Kim, K. Yoon, I.J. Park, S.K. Dhungel, B. Karunagaran, D. Mangalaraj, J. Yi, Thin Solid Films 480, 213 (2005).
- [16] M. Caglar, Y. Caglar, S. Ilican, J. Optoelectron Adv. Mater. 8, 1410 (2006).
- [17] F. Yakuphanoglu, Y. Caglar, S. Ilican, M. Caglar, Physica B 394, 86 (2007).
- [18] Young Yi Kim, Si Woo Kang, Bo Hyun Kong, Hyung Koun Cho, Physica B 401–402, 408 (2007).
- [19] G. Srinivasana, N. Gopalakrishnanc, Y.S. Yud, R. Kesavamoorthy, J. Kumara, Superlattices and Microstructures in press.
- [20] L. H. Van, M.H. Hong and J. Ding, Journal of Alloys and Compounds, 449, 207 (2008).
- [21] F. Yakuphanoglu, S. ilican, M. Caglar, Y. Caglar, J. Optoelectron. Adv. Mater. 9(7), 2180 (2007).
- [22] Y. Caglar, M. Zor, M. Caglar, S. Ilican, J. Optoelectron. Adv. Mater. 8(5), 1867 (2006).

- [23] S. Ilican, Y. Caglar, M. Caglar, B. Demirci, *J. Optoelectron. Adv. Mater.* 10(10), 2592 (2008). Joint Committee on Powder Diffraction Standards, Powder Diffraction File, card no: 36-1451.
- [24] B. D. Cullity, S.R. Stock, *Elements of X-Ray Diffraction*, Prentice Hall, 2001, 3rd ed.
- [25] G. B. Williamson, R.C. Smallman, *Philos. Mag.* 1, 34 (1956).
- [26] X. S. Wang, Z.C. Wu, J.F. Webb, Z.G. Liu, *Applied Physics A* 77, 561 (2003).
- [27] C. S. Barret, T.B. Massalski, *Structure of Metals*, Pergamon Press, Oxford, 1980.
- [28] J. I. Pankove, *Optical Processes in Semiconductors*, Prentice-Hall Inc., Englewood Cliffs, NJ, 1971.
- [29] F. Urbach. *Phys. Rev.* 92, 1324 (1953).
- [30] Tauc, J. *Amorphous and Liquid Semiconductors*, Plenum Press, New York 1974.
- [31] D. C. Look “Recent advances in ZnO materials and devices” *Materials Science and Engineering B80*, 383-387 (2001)
- [32] F. K. Shan and Y. S. Yu “Band gap energy of pure and Al-doped ZnO thin films”, *Journal of the European Ceramic Society* 24, 1869-1872 (2004).
- [33] B.ABBAS, Ph.D Thesis "Linear and Nonlinear Optical Phenomena in Thin Sol-Gel Organic-Inorganic Films" . The University of Reading-1999 United Kingdom
- [34] P. Zu, Z. K. Tang, G. K. L. Wong, M. Kawasaki, A. Ohtomo, H. Koinuma and Y. Segawa
- [35] “Ultraviolet spontaneous and stimulated emissions from ZnO microcrystallite thin films at room temperature” *Solid State* 103, 459-463 (1997).
- [36] S. B. Majumder, M. Jain, P. S. Dobal and R. S. Katiyar “Investigations on solution derived aluminium doped zinc oxide thin films” *Materials Science and Engineering B* 103, 16-25 (2003).
- [37] S. Bandyopadhyay, G. K. Paul and S. K. Sen “Study of optical properties of some sol–gel derived films of ZnO” *Solar Energy Materials and Solar Cells* 71, 103-113 (2002).
- [38] Young-Sung Kim, Weon-Pil Tai, Su-Jeong Shu “Effect of preheating temperature on structural and optical properties of ZnO thin films by sol–gel process” *Thin Solid Films* 491, 54–60 (2005).