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ELECTROCHEMICAL PERFORMANCE OF SILVER-DOPED ZINC OXIDE THIN FILMS

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Article Info

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Abstract

Zinc oxide (ZnO) has garnered significant attention as a II-VI semiconductor with a direct band gap of approximately 3.2 eV, making it suitable for near ultraviolet applications. This compound exhibits unique properties, such as an exciton binding energy of about 60 meV, making it appealing for optoelectronic devices. The natural n-type behavior of ZnO can be attributed to its deviation from stoichiometry, leading to the presence of interstitial Zn atoms (Zni) and oxygen vacancies (Vo) within the crystal lattice. Background donors like hydrogen (H) and aluminum (Al) also contribute to its n-type characteristics by forming donor levels around 0.05 eV.

In this study, we explore the wurtzite crystal structure of ZnO, where oxygen atoms are arranged in a hexagonal close-packed lattice, and zinc atoms occupy half the tetrahedral sites. The relative openness of the ZnO structure, with empty octahedral sites and half the tetrahedral sites, allows for the incorporation of external dopants, enhancing its applicability for diverse technological advancements.

During the 1950s, Zinc oxide experienced intensive research focusing on topics such as bulk and surface polarons, luminescence, and lasing. However, this interest waned in the following decades, mainly due to the challenges in achieving p-type doping in ZnO. As research interests shifted towards reduced dimensionality structures, such as the GaAs/Al1-yGayAs system, ZnO took a backseat in the scientific community.

In recent years, there has been a resurgence of interest in ZnO due to its potential in various applications, including optoelectronics, sensors, and transparent electronics. This renewed interest stems from advancements in doping techniques and a deeper understanding of its defect-related properties. This review explores the current state of research on ZnO, focusing on the latest advancements in material synthesis, doping strategies, defect engineering, and emerging applications. We discuss the challenges faced in achieving p-type doping and the innovative approaches proposed to overcome these limitations. Additionally, the promising developments in reduced dimensionality structures, such as ZnO nanowires and thin films, are presented, showcasing their potential for future electronic and optoelectronic devices.

INTRODUCTION

Zinc oxide (ZnO) is a II–VI semiconductor with a direct, dipole allowed band gap around 3.2 eV i.e., in the near UV and an exciton binding energy of about 60 meV. ZnO is naturally an n-type semiconductor partially due to its deviation from stoichiometry i.e., due to the presence of interstitial Zn atoms (Zni) in large voids and the presence of oxygen vacancies (Vo) in the crystal and partially due to the presence of background donors such as H and Al. These defects form donor levels at ~ 0.05 eV.

According to Gupta 1990 ZnO has a wurtzite structure (as seen in Figure 1.1) in which the oxygen atoms are arranged in a hexagonal close-packed type lattice with zinc atoms occupying half the tetrahedral sites. The two types of atoms, Zn and O, are tetrahedrally coordinated to each other and are therefore equivalent in position. The ZnO structure is thus relatively open with all octahedral sites and half the tetrahedral sites empty. It is therefore relatively easy to incorporate external dopants into the ZnO lattice.

Several decades ago (1950s), intensive research on Zinc oxide (ZnO) started gradually and peaked towards the end of the seventies and the begininig of eighties. The attention then was on topics such as bulk and surface polarons, luminescence and lasing. There was a drift from the interest due to partly the inability to achieve p-type doping in ZnO and partly due to interest moved to structures of reduced dimensionality especially the GaAs/Al1-yGayAs system (Nickel and Terukov 2005).

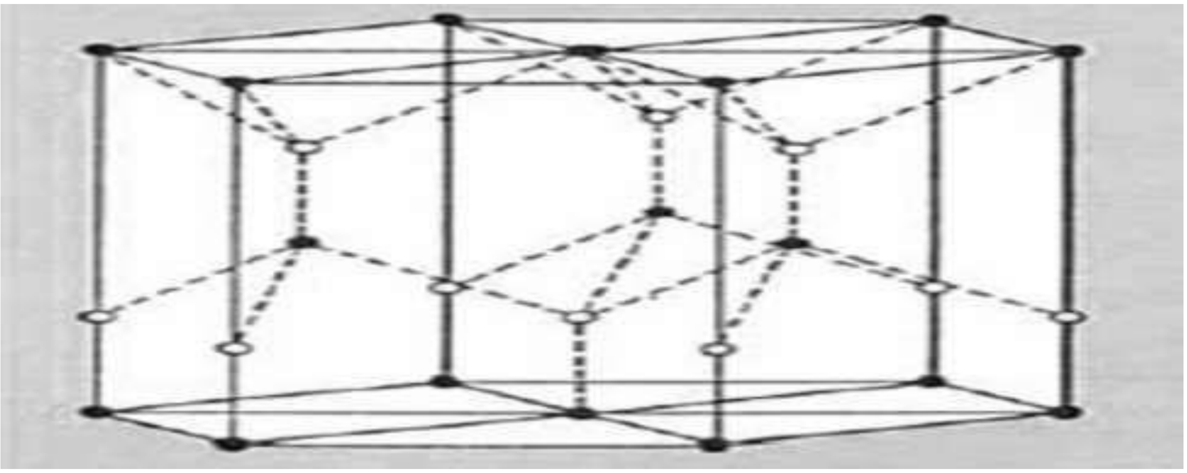

Figure 1.1 The crystal structure of ZnO (shaded circles indicate the positions of oxygen atoms while the open circles indicate the positions of the zinc atoms) Source: Gazene 2006

There has been a renaissance of ZnO research in recent times based on the successful achievement of p-type doping in ZnO and on the possibility to grow epitaxial layers, quantum wells, nano-rods, quantum dots and related objects. According to Klingshirn et al 2005 much of the renewed interest has been focused on ZnO because it is:

- a material for transparent thin film transistors
- a material for blue/UV lasers, LEDs and other optoelectronic devices in addition to (or instead of) the GaN based structures.
- a radiation-hard material for electronic devices in a corresponding environment
- a diluted or ferromagnetic material, when doped with Co, Mn, Fe, V etc., for spintronics

- a transparent, highly conducting oxide (TCO), when doped with/alloyed with Al, Ga, In etc., as a cheaper alternative to indium tin oxide (ITO)

Silver ions have two characteristic features and can be used in the places of substitution and interstitial; hence, they can act as an acceptor in ZnO. However, previous studies on Ag-doped ZnO by Yan et al. 2004 suggested that substitutional sites were more energetically favourable than interstitial sites. Most studies have examined the effects of silver doping on the photocatalytic activity and antibacterial properties of ZnO. It is also possible to form a dilute magnetic semiconductor by silver doping in ZnO wurtzite structure and ferromagnetic behavior of the compound has been investigated experimentally16 and theoretically, which can be used in spintronic applications by both degrees of freedom of electron spin and charge. The ferromagnetic properties are due to the formation of impurity band which interacts with the d orbital of nonmagnetic element. However, the origin of ferromagnetic properties is still under investigation (Hosseini et al. 2015).

Statement of the Problem

An important issue in developing ZnO-based electronics is the formation of p-type material and rectifying junctions. Studies have indicated that Ag can act as an amphoteric dopant, yielding an acceptor state for substitution on the Zn site, and a donor state for interstitial defects.

Aim and Objectives

The aim of this study is to investigate the effect of silver doping on the optical properties of ZnO thin films

Objectives:

a. To synthesize the composites of silver doped zinc oxide.
b. Characterize the synthesized composites using **UV-VIS SPECTROPHOTOMETER**.
c. To generate other optical parameters such as transmittance, reflectance, energy bandgap.
d. To analyse the data obtained using relevant software.

Scope of the Study

The study is limited to the synthesis of zinc oxide thin films doped with Silver and characterization of its optical properties only at varying concentrations.

Significance of Study

The fast development in our society due to the industrialization and wide use of electronics led us to a great challenge to decrease the pollution and fossil fuel usage through deployment of efficient, reliable, durable, economical and environmental friendly energy storage systems such as supercapacitors. The investigation of optical properties of solids such as reflectivity, transmission, absorption, optical energy will improve the fabrication of electrode materials for super capacitor applications.

REVIEW OF RELEVANT LITERATURE

Thin Film Technology

As a part of nanotechnology a thin film is a layer of material ranging from fractions of a nanometer (monolayer) to several micrometers in thickness.

Thin films are created through a process called '**Deposition**'. Deposition means a thin film coating process, which is achieved by modifying the four states of matter i.e. Solid, Liquid, Gas and Plasma.

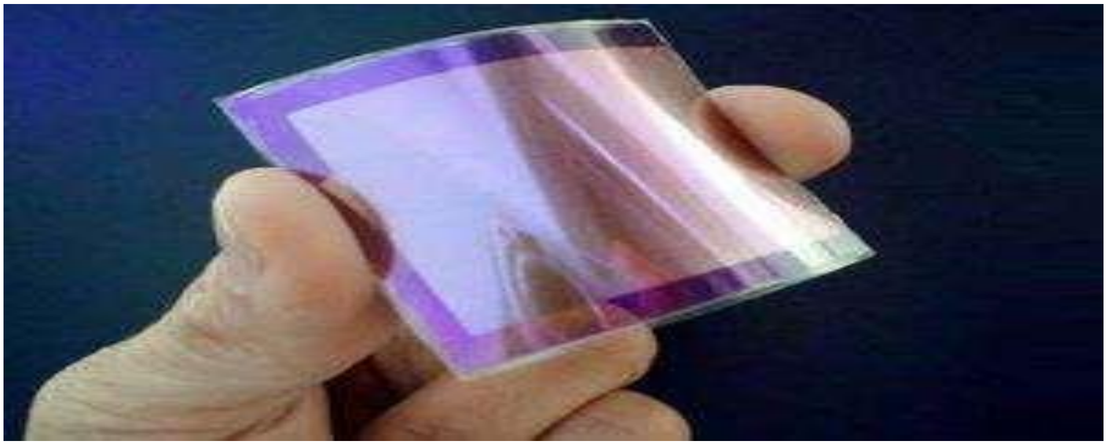

Figure 2.1: Sample of a thin film (Panden and Arora 2020)

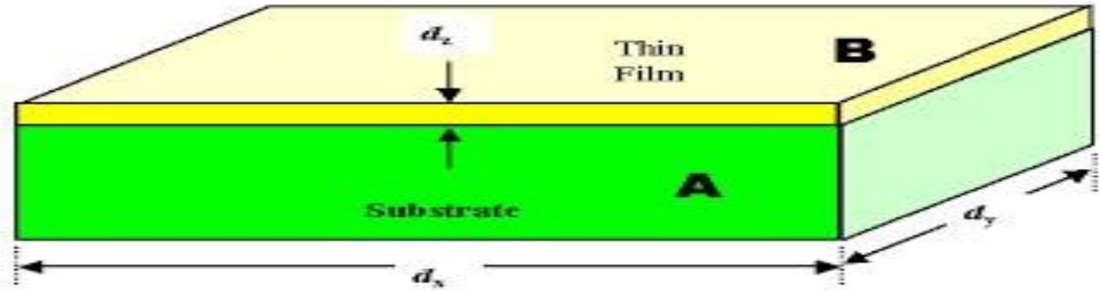

Figure 2.2: Sample of a thin film (Panden and Arora 2020)

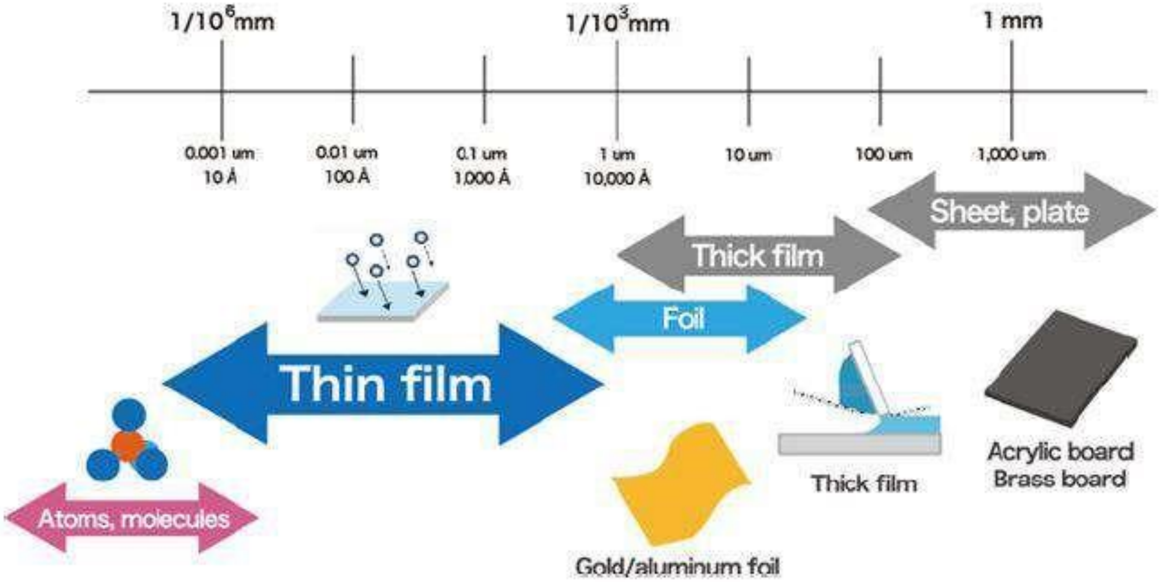

Figure 2.3: Mode of operation of a thin film (Panden and Arora 2020)

History of thin films

1850: Development of first deposition techniques (M.Faraday; W.Grove; T.A.Edison) and of methods of thickness determination (Arago, Fizeau; Wernicke; Wiener)Commercial introduction of electrochemistry (Galvanics) for gold plating of uniform- accessories

▪1931: First TEM was demonstrated by Max Knoll and Ernst Ruska

▪1940: vacuum and thin film (PVD) techniques, Industrial manufacturing of coatings mostly for military.

▪1965: Mass manufacturing processes in semiconductor and optical industry.
▪1990: Thin films of High Tc-Superconductors.
▪2006: Investigation of organic coatings leads to the emergence of organic electronics (OLED, printable circuits).
▪2010: Preparation and characterization of the prototype two dimensional (2d) material, Graphene. Introduction of reliable solid state touch screens to communication media (Smartphone).
▪2015: Generation of heterostructures made from 2d materials. Approaches to manufacture flexible electronic devices consisting of ultrathin materials.

METHOD OF DEPOSITION

Electrodepostion

Electrodeposition is formation of a thin film material on a conductive surface of a substrate using a conductive solution containing the ionic species of that material. Deposition on the conductive surface is enabled by submersing the substrate and a counter electrode into the solution and applying a potential difference between them to cause a reaction of the ionic species on the substrate surface. Although electrodeposition can be carried out in anodic (substrate voltage is positive with respect to the counter electrode) or cathodic (substrate voltage is negative with respect to the counter electrode) mode, successful results for the materials of interest in this paper have been obtained by the cathodic deposition approach (Heintzkill, 2018).

In the batch electroplating technique, multiple substrates are processed in parallel where each substrate is individually contacted and electroplated. Roll-to-roll process may be employed to electrodeposit materials on long and flexible substrates in a continuous manner. Selection of the electroplating approach for a specific application depends on several factors including the nature of the substrate (i.e. flexible or rigid), surface conductivity of the substrate and the material deposition rate, which is related to the deposition current density (Idep). For electroplating processes with slow growth rate, a batch plating technique is more advantageous, whereas processes with high deposition rates may utilize the rollto- roll approach if the substrate is flexible and substantially conductive.

A well designed electrodeposition process may provide several benefits compared to the standard vacuum processes such as evaporation and sputtering. First of all, electrodeposition is an atmospheric process that employs low cost, simple equipment. The technique typically operates at temperatures below 100 °C, and therefore is highly energy efficient. In an electroplating process, the lifetime of the electrolyte is virtually infinite and the materials utilization is near 100%, especially if the solution is free from additives that may disintegrate in time and negatively impact the coating quality (Basol 2011).

Doping of ZnO Thin Films

According to Ganesan 2006; Lugo 2010, doping of a semiconductor is defined as the addition of a small percentage of foreign atoms in its regular crystal lattice with the intent of producing dramatic changes in its properties (when large percentages are involved this process is referred to as alloying). Doping is a routine process generally associated with the fabrication of silicon based semiconductor devices. N type doping is achieved when group VA impurity elements such as P, As and Sb get introduced into the silicon lattice, thus providing easily ionized electrons for electrical conduction. Group IIIA elements such as B and Al act as Mp-type dopants in silicon since they supply positively charged carriers (holes).

Pandene and Arora 2020 stated that in recent times, ZnO has become an important wide band gap semiconductor with a number of potential applications because of its distinctive properties (wide direct bandgap, a large exciton binding energy, chemical etchability etc.). In the optoelectronic industry, for example, there is a huge demand for materials that can be used in short wavelength devices, as transparent electrodes and as windows for displays and solar cell.

However, for any of the aforementioned applications, it is important to control the physical (e.g., the lattice parameters), electronic, (e.g., band gap, conductivity) and optical properties (optical transmission) of the compound, and this can be done via doping. Also, the incorporation of dopants can sometimes lead to the development of some rather unique properties useful for the fabrication of devices. For example, Cddoped ZnO nanowires prepared by a co-evaporation technique were found to possess a positive coefficient of resistance and humidity-sensing properties (Ganesan 2006).

N-type Doping

ZnO is easily doped n-type by cation substitution using group III elements or anion substitution using group VII elements. The most frequently used dopants are Al, Ga, and In, which have resulted in high quality, and highly conductive films. Lugo 2010 reported resistivities as low as $6.2x10^{-4}$ and $1.2x10^{-4}$ Ω/cm for ZnO films doped with Al and Ga, respectively. Films with carrier concentrations of up to 10^{21} cm^{-3} have been realized, which have led to their use as n-type layers for LEDs and transparent Ohmic contacts.

P-type Doping

It is well known that n-type ZnO is easily fabricated, while p-type still remains a major obstacle. This is common in wide bandgap semiconductor because of the low formation energies for compensating defects (Lugo 2010). Candidates for p-type doping include group V anions on oxygen sites or group I or IB cations on Zinc sites. Most research efforts have focused on group V dopants, namely, N, As, P, and Sb. First principle calculations predicted that group I elements are shallow acceptor, while group V elements, for the most part, are deep acceptors. Defect energy levels relative to the valance band maximum (VBM) for each cation and anion substitution were calculated. The VBM is made of anion p-orbitals with small mixing of cation p-d orbitals. Therefore, group I doping results in smaller 21 perturbation and shallower defects than group V doping. However, group I elements rather occupy interstitial sites mitigated by their small size. Both P and As have significantly larger bond length and therefore are more likely to form antisites to avoid lattice strains. Theoretically, N is favored among group V elements because it has a similar bond length to ZnO, low ionization energy, and unlikely antisite formation (NZn).

Nitrogen Doping

As mentioned above, N is the most promising candidate for p-type ZnO and a good deal of effort has been focused in using it as a shallow acceptor dopant. Several studies have been devoted to find the right source for Nitrogen doping during film growth. P-type conductivity, with carrier concentrations ranging from 10^{15} to 10^{18} cm^{-3}, using NO as its dopant source was reported; both NO and N_2O, obtained similar carrier concentrations and resistivities as low as 3.02 Ω-cm. Z-Z. P-type films using NH_3-O_2 were grown and carrier concentrations of $3.2x10^{17}$ cm^{-3} and 1.8 $cm^2V^1s^{-1}$ mobilities obtained.

Oxygen-poor growth conditions are required to incorporate dopants into O sites, which promotes
"hole killer" defects and compensation. The low solubility of N is well known. Only about 0.1 % of the dopant seems to be electrically active, while the remaining inactive N acts as scattering centers resulting in low carrier mobility. In order to increase the N solubility, codoping methods have been engineered using reactive donor dopants such as Ga, Al, and In. N-codoping lowers the acceptor level in the bandgap due to strong interaction between acceptors and donors codopants. SIMS results showed an increase of N-solubility by a factor of 400 when using Ga as the reactive donor codopants. Furthermore, using N Ga codoping via pulsed laser deposition (PLD), successfully grew p-type films. For these films the hole concentration was $4x10^{19}$ cm^{-3} with 2.0 Ω-cm

resistivity. However, the carrier mobility did not improve. Sing et al. 2005, showed a relation between VO, oxygen partial pressure and carrier type. Results showed that at ratios of oxygen partial pressure to total pressure ($4x10^{-4}$ Torr) below 40% films were n-type, while films grown at ratios above 50% showed p-type conductivity. Further increase of pressure, above ratios of 60%, resulted in high resistivities and low mobilities due to crystal degradation by oxygen related defects. P-type ZnO was also achieved using Al and In as codpants, however, high carrier concentrations and incredibly high (~150 $cm^2V^{-1}s^{-1}$) mobilities bring the validity of the results into question. In other studies, despite achieving high concentration of N incorporation, codoping yielded only n-type ZnO (Lugo 2010).

Supercapacitors

Supercapacitors or electrochemical capacitors (ECs) or ultracapacitors are capacitors that depend on charge storage in high surface area materials and the market for these devices rose to about US$470 million in 2010 (Bakker et al., 2015). Previously, supercapacitors are used largely in electronics but due to their rating of 10-year lifetimes and 500,000 duty cycles, they are now proposed to be largely used in energy and transportation. A superconducting magnetic energy storage system is capable of storing electrical energy in the magnetic field generated by direct current flowing through it (Sylvanus and Nwaokoro 2021).

RESEARCH AND DEVELOPMENT

Supercapacitor Energy Storage Systems (SCES)

The first experiment on supercapacitor was done in 1957 by the Engineers at General Electric GE; they found commercial applications in portable electronics, transportation and aerospace industry but GE did not further research on this development. In 1970, Standard Oil of Ohio (SOHIO) patented an electrolytic capacitor based on carbon and this was licensed and marketed by Nippon Electric Company (NEC), thereby promoting supercapacitors as backup memory for electronics (Kim et al., 2015; Wang et al., 2015).

Over the years, there has been an in-depth research on the basic components (electrodes, electrolyte and separator) of a supercapacitor which has improved its performance and reduced the cost of manufacturing (Sylvanus and Nwaokoro 2021). Currently the use of graphene or carbon based anthraquinone as cathode materials is on the increase; this improves the energy density of supercapacitors (Johnson, 2019); the use of graphene yielded an energy density of 85Wh/kg as observed in independent laboratories and a special type of graphene called curved graphene yielded the highest energy density by creating pores accessible to the electrolyte hence increasing the number of reaction sites (Bakker et al., 2011).

According to Halper and Ellenbogen 2006, the high equivalent series resistance in supercapacitors can be lowered by methods such as the use of colloidal thin film suspension, polishing the surface of the current collector and chemically bonding the electrode to the current collector. Also the self discharge problem of supercapacitors can be solved by improving the purity of electrode materials.

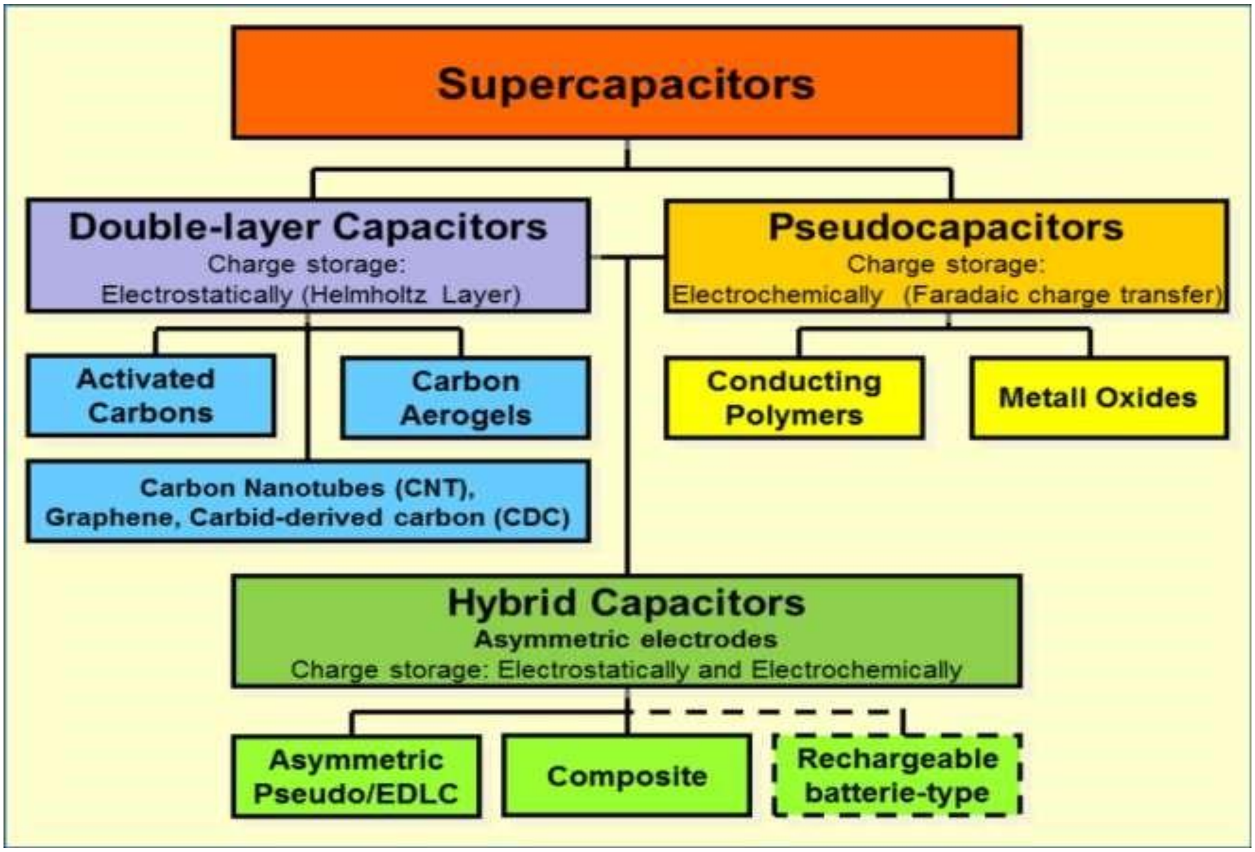

Figure 1: Taxonomy of a Supercapacitor (Source: Sylvanus and Nwaokoro 2021).

Buckle and Zhao, 2014 show that hybrid supercapacitor from Yunakso has an energy density greater than 30Wh/kg and a 95% efficient power capacity of 3120W/kg, hence it was confirmed the best performance of any supercapacitor device among all tested at UC Davis as at then. Recent studies reveal the rare performance of supercapacitors in transportation tools when used with batteries in electric vehicles (EVs), hybrid electric vehicles (HEVs) and cranes (Wang et al., 2015). These are:

- 60% and 30% reduction in the weight and volume respectively of the energy storage systems (ESS): this makes it possible for the ESS to be located under the hood instead of in the trunk of the vehicle.
- Life span of the ESS can be extended: the supercapacitor can enable a battery supply average load and meet short power pulses by giving the required yield power.

The design of STATCOMs with supercapacitor has improved the energy storage systems; it can exchange both reactive and real power with the grid (Sylvanus and Nwaokoro 2021).

MATERIALS AND METHODS

The experimental work was performed in the Nano Research laboratory at the University of Nigeria Nsuka; the precursor materials were synthesized (prepared) followed by characterizations of the obtained materials and evaluation of their optical properties. In the following part of this chapter, experimental technicalities are presented, including the materials and chemicals used in the research project, typical materials, basic materials characterization techniques, cell assembly details, and optical testing specifications.

Materials

A list of the names of materials, chemicals along with their formula and supplier, and equipment used in the research are shown in the table 3.1 below

Table 3.1: Materials and chemicals with chemical formula and name of supplier

S/N	CHEMICALS	CHEMICAL FORMULA	MANUFACTURES	PURITY%
1	Zinc tetraoxosulpate (vi) heptahdrate	$ZnSO_4.7H2O$	Merck	99.999
2	Silver nitrate	$AgNO_3$	Merck	99.999
3	Potassium hydroxide	KOH	Merck	99.999
4	Ammonia solution	NH_3	Merck	99.999
5	Fluorine doped tin oxide	FTO	Merck	99.999
6	Hydrochloric acid	HCl	Merck	99.999
7	Sodium nitrate	$NaNO_3$	Merck	99.999
8	Distilled water	H_2O	Merck	99.999
9	Hot Plate & Magnetic stirrer			
10	UV spectrometer			
11	Reaction bathe			
12	Beaker			
13	Carbon electrode			
14	Conducting glass slides			
15	DC power supply, multimetre			
16	Digital hand held PH metre			

Synthesis

The method of synthesis employed in this study is electrochemical deposition (electrodeposition). According to Ganessan 2006, an electrodeposition can be defined as the deposition of a substance on an electrode by the action of electricity (an electric current is applied between two electrode separated by an electrolyte). The reaction essentially takes place at the electrode interface known as the electrical double layer. The electrochemical system, on the whole, is heterogeneous since the distribution of electrons and reactant species in the bulk and at the interfaces differ significantly.

Fluorine doped tin oxide (FTO) substrates for the electrodeposition of silver doped zinc oxide substrates consisted of F-doped tin oxide (Merck) coated on soda-lime glass. They were nominally calibrated 400 nm thick and had a sheet resistance of 10.3 Ω/m. Strips (0.70 cm x 2cm) were cut and cleaned in 15 min steps of cleansing by ultrasonication in acetone, ethanol and put in an oven to dry before being kept in an air-tight container to avoid contamination. All solutions in this study were prepared from deionized water. 0.1mol solution of $ZnSO_4.7H_2O$ was prepared by dissolving

2.8754 g of $ZnSO_4$ in 100 ml of deionized water. The molar weight of $ZnSO_4.7H_2O$ is 287.54 g/mol. It dissolved completely in water and is colorless.

The electrodeposition bath system is composed of a source of cation (i.e $AgNO_3$, $ZnSO_4.7H_2O$ for Ag2^+, Zn^{2+}), a source of anion (i.e Potassium hydroxide for O^{2-}), deionized water all in 100ml beaker, magnetic stirrer was used to stir the reaction bath. The thin films were cathodically electrodeposited from baths containing different molar ratios (Table 3.2) of AgNO3 and ZnO in 0.1 M KCl as supporting electrolyte.

Table 3.2 Electro deposition bath compositions

SAMPLE NO	$AgNO_3$ concentration in baths (mM)	$ZnSO_4$ concentration in baths (mM)
1	0.00	0.1
2	0.01	0.1
3	0.02	0.1
4	0.03	0.1
5	0.04	0.1

MATERIAL CHARACTERIZATION TECHNIQUE

The experimental set up is shown in the figure 3.1 below.

Absorbance, Transmittance and Reflectance

Optical absorption spectra of the silver doped zinc oxide samples were measured by UV-vis spectrophotometer in the range 200-1200 nm. The different optical and solid state properties are shown in table 4.1. Beer Lamberts law states that the Law says that the fraction of the light absorbed by each layer of solution is the same (Hosseni 2015). Mathematically given as

$$A = \varepsilon bc \qquad 3.1$$

Where A is the absorbance, ε is the molar absorptivity the absorbing specie, b is tha path length, c is the concentration of the absorbing specie. Since the absorbance data is given by the UV-VIS spectrometer, the transmittance can then be calculated using the equation

$$T = 10^{-A} \qquad 3.2$$

. Generally when light is incident on a thin film material, there is an interplay of reflection, transmission and absorption. Hence the reflectance is given by the equation:

$$R = 1 - (A + T) \qquad 3.3$$

According to Hosseni 2015, the absorption coefficient α is given by:

$$\alpha = \frac{2.302A}{t} \qquad 3.4$$

Where t is the film thickness. Absorption coefficient gives information on the extinction coefficient k, and is related as;

$$k = \frac{\alpha\lambda}{4\pi} \qquad 5$$

Optical conductivity is given by

$$\sigma = \frac{\alpha nc}{4\pi}$$

Where c is the speed of light and n is the refractive index given by

$$n = \frac{1+\sqrt{R}}{1-\sqrt{R}} \qquad 6$$

In this study, we are only concerned with the absorbance, transmittance, reflectance and optical energy of the deposited samples.

EXPERIMENTAL SET UP

Figure 3.1 a) Electro deposition Machine b) UVs Spectrometer, C) Glass slides.

RESULTS AND ANALYSIS

The results of the peak absorbance spectra for the samples are shown in table 4.1.

Table 4.1 PEAK VALUES OF ABSORBANCE OF THE DEPOSITED SAMPLES

WAVE LENGTH λ (nM)	ABSORBANCE (AU)	TRANSMITTANCE (T)	REFLECTANCE (R)
298	0.524323002	0.299004	0.176672998
321	0.7221296	0.189614	0.0882564
308	1.500148027	0.031612	-0.531760027
308	1.400947027	0.039724	-0.440671027
294	1.110082317	0.07761	-0.187692317

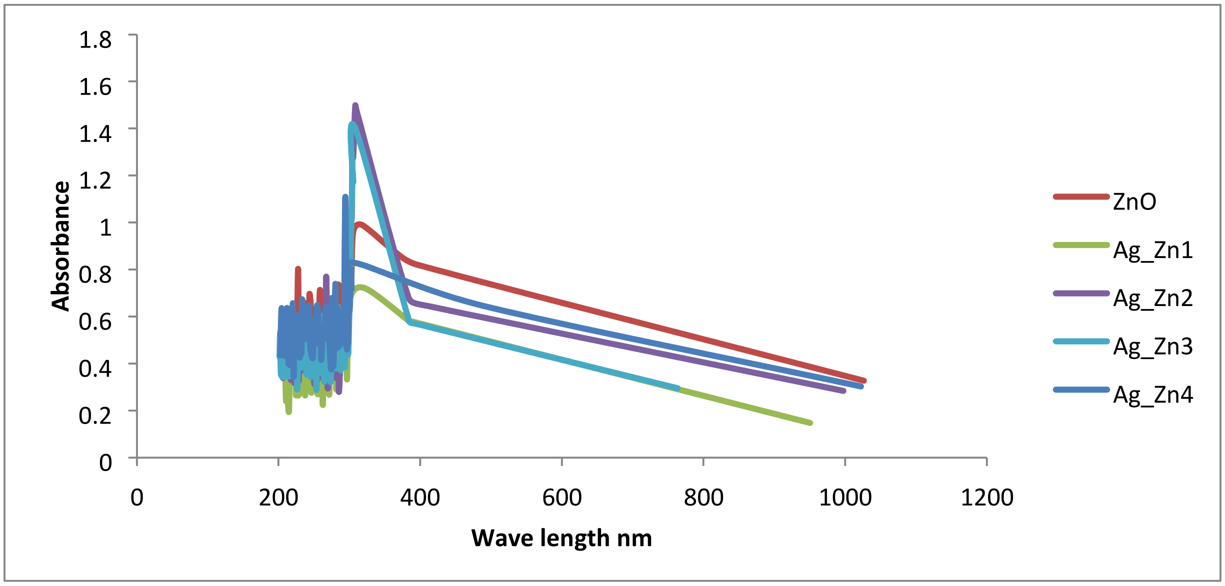

Figure 4.1 UV-VIS absorption spectra of ZnO thin films at different concentrations

Figure 4.1 shows the absorbance spectra as a function of wavelength for Ag- ZnO thin films deposited on glass substrates prepared by electrochemical deposition. It can be seen that increase of Ag concentrations makes slightly shifts of absorption edge to higher wavelengths. In addition, the nearly flat spectra shown in the higher wavelength area according to Sutanto et al., 2016, is due to the larger amount of Ag i.e increasing the substitution of Zn ion by Ag ions. Also the abrupt change in absorption edge for the doped samples at 308nm, means that doping influences drastically the optical properties, and so the absorption edge. . Optical properties of Ag-ZnO thin films show that transparency decreases along 200- 320 nm with increase of Ag content. The absorbance spectra of thin films are slightly shifted to higher wavelengths; these peaks in pure and Ag doped ZnO films might be attributed to intrinsic defects, such as oxygen and zinc interstitials

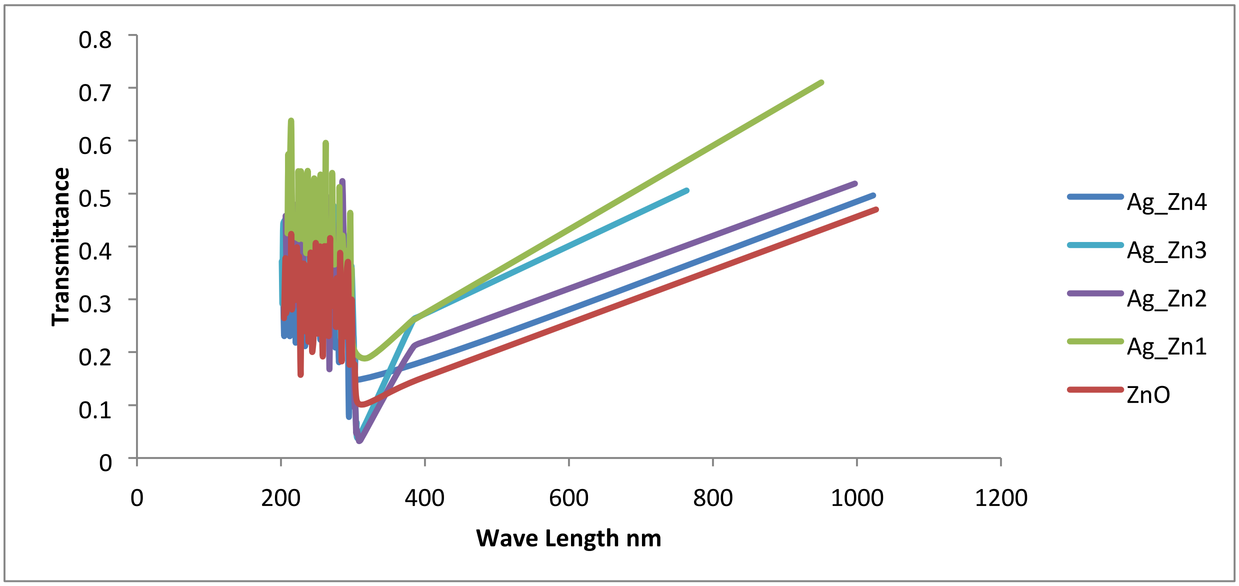

Figure 4.2 Transmittance Spectra of ZnO thin films at different concentrations

The optical transmission spectra of pure and Ag doped ZnO thin films are shown in Figure 4.2. It can be seen that the optical transmission of pure ZnO is about 47 % at 1026 nm in the visible region and after doping it increased to 71 % at 950 nm. According to Machado 2005, a weak fluctuation in the spectra between 200 – 300 nm is due to interference phenomena in the thin film. The abrupt decrease in UV intensity at 308 nm was due to the interactions between the excited ZnO thin films and Ag particles in the grain boundaries. These kinds of interactions via the Schottky contact, metal-semiconductor diode effect, decrease the recombination of electrons and holes generated from UV light irradiation and improved the photocatalytic activities essential for supercapacitor applications Hosseni et al., 2015.

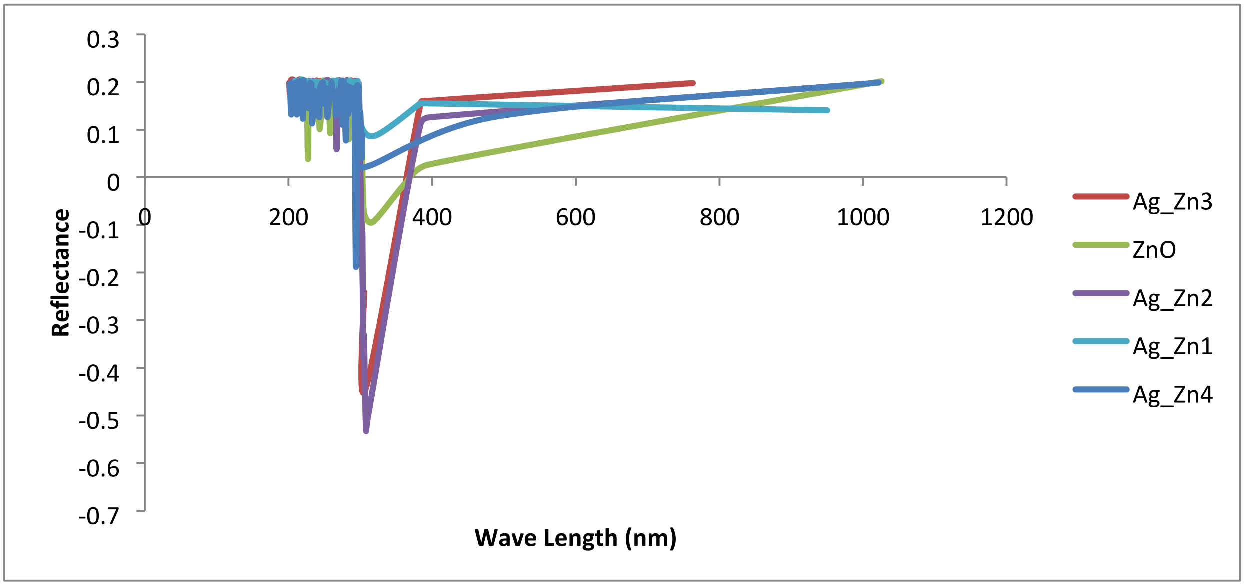

Figure 4.3 Reflectance Spectra of Ag-ZnO thin films for all samples

The reflectance spectra (DRS signal) for samples grown at different electrodeposition concentration are represented in Figure. 4.3. For all samples, the reflectance in the low wavelength <300 nm (high photon energy) region of the spectrum is higher than in the high wavelength >380 nm (low photon energy) region, which shows that these reflectance spectra decrease also for wavelengths well into the infrared region. Though all samples showed a negative reflectance within 300-380 nm well into the infrared region except Ag_Zn1 and this could be due to the travelling of the incident and refracted wave in the same direction (Bedia 2014). Even the ‘‘milky’’ appearance of ZnO films was visually evident after the deposition process and the smooth reflectance between 384 and 1019 nm can then be more correctly assigned to an amorphous structure present on the film rather than to any typical crystalline structure (Machado 2005). More importantly is the smooth increase of reflectance for the samples grown at higher concentrations of dopant (Ag).

Optical Band Gap

The optical band gap is the threshold for photons to be absorbed. The transport gap is the threshold for creating an electron –hole pair that is not bound together. The optical band gap is at a lower energy than transport gap. A band gap is the distance between the valence band of electrons and the conduction band. Essentially, the band gap represents the minimum energy that is required to excite an electron up to a state in the conduction band where it can participate in conduction. In this study, the optical band gap is represented by a Tauc plot which typically shows the quantity hv (photon energy) on the abscissa (x-axis) and the quantity $(\alpha hv)^{1/2}$ on the ordinate, where α is the absorption coefficient of the material. Extrapolating this linear region to the abscissa yields the energy of the optical band gap of the crystalline material. The figures 4.4, 4.5 4.6, 4,7 and 4.8 shows the Tauc plot for the different samples.

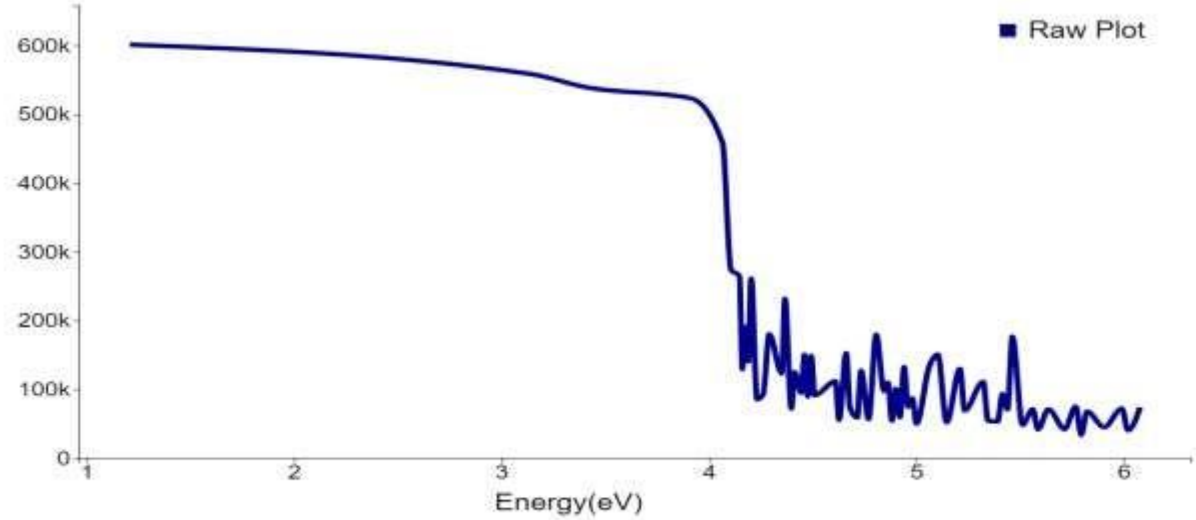

Figure 4.4 Tauc plot of optical band gap of ZnO thin films for sample 1

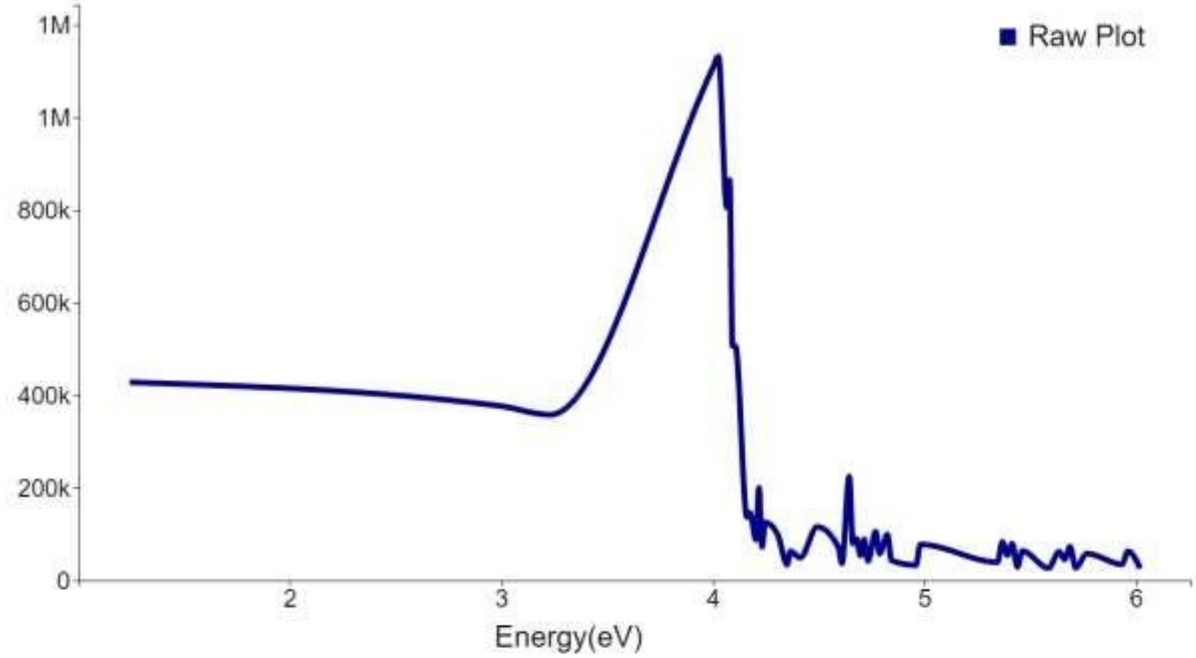

Figure 4.5 Tauc plot of optical band gap of Ag_ZnO thin films for sample 2

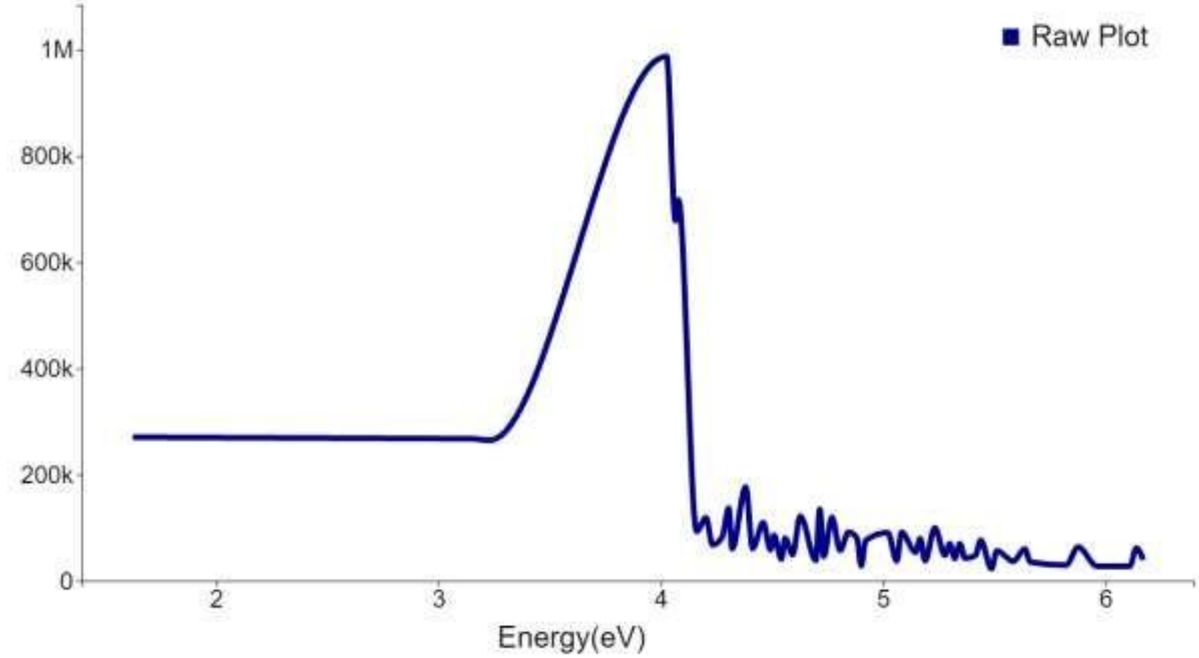

Figure 4.6 Tauc plot of optical band gap of ZnO thin films for sample 3

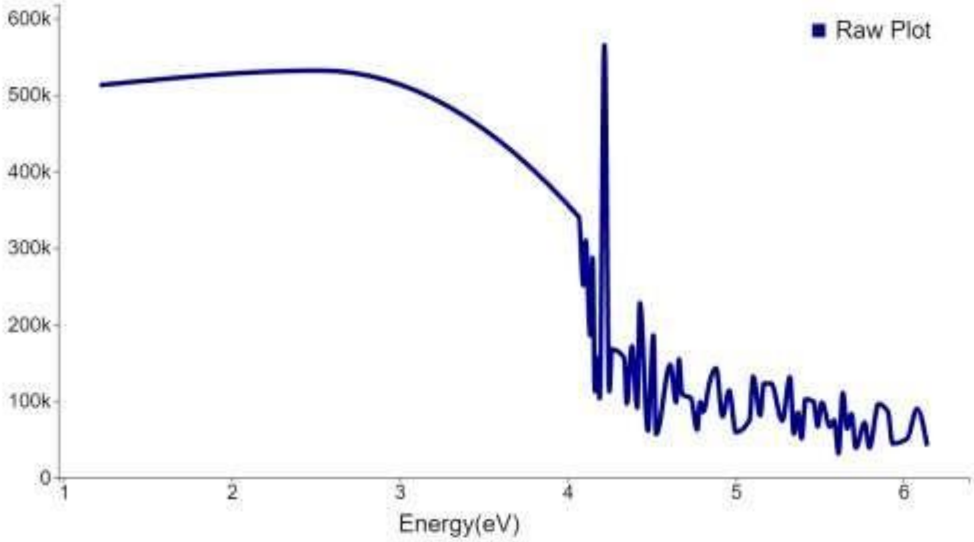

Figure 4.7 Absorbance as a function of energy band gap for sample 4

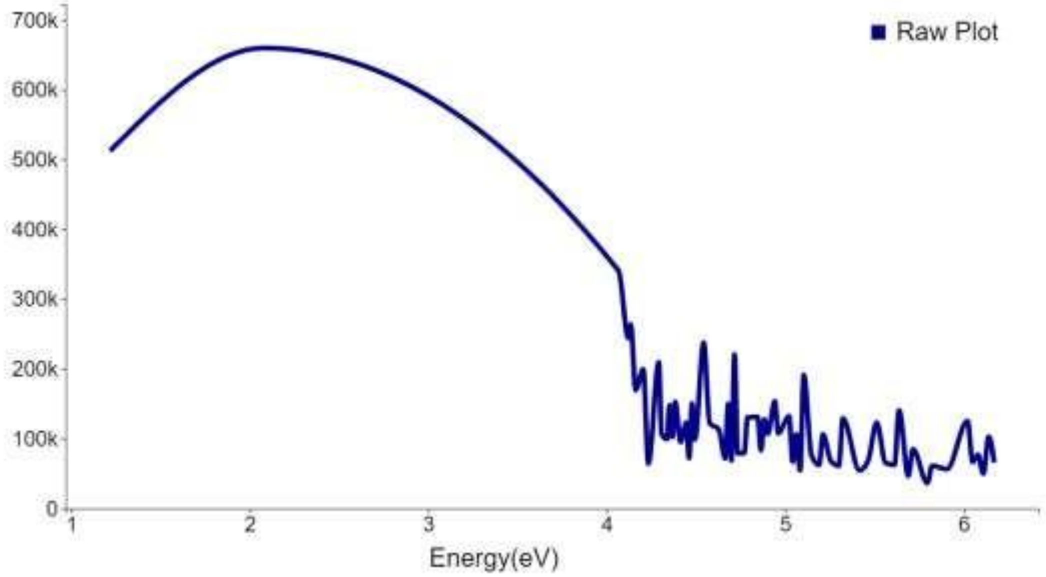

Figure 4.8 Absorbance as a function of energy band gap for sample 5

For the pure ZnO, a value of 3.2 eV was obtained while the corresponding values for the doped samples are 3.32 eV, 3.35 eV, 3.37 eV, and 3.43 eV respectively. It can be seen that the energy band gap of the pure ZnO thin films increased with the Ag doping in line with the findings of Ganesan 2006 on the characterization of Indium doped zinc oxide by Electrodeposition (from 3.37 eV to 3.47 eV). This increase in the energy band gap is known as the Moss-Burstein shift as reported in the study of Ag doped ZnO thin films by Sol gel method (Syed Mansoor ali et al, 2015). Because of this, at high doping level in zinc oxide thin films, the donor electrons occupy the states at the lower edge of conduction band. Therefore, the optical band gap of Ag doped zinc oxide is greater than that of pure zinc oxide films. On the contrary, the shrinking of the band gap in previous study of candium (Cd), Lithium (Li) and indium (In) doped ZnO using Spray Pyrolysis, electrodeposition has been observed and it was attributed to the method of deposition and nature of the dopant. (Ganesan 2006)

CONCLUSION AND RECOMMENDATION

Conclusion

Ag-ZnO thin films have been successfully synthesized onto glass substrates by electrodeposition technique. The effects of Ag doping on the optical properties of ZnO thin films were investigated through the UV-VIS spectrometer machine; the use of metal chlorides (instead of the commonlyused metal nitrate salts in combustion synthesis) as dopant precursors was found to facilitate dopant incorporation into the ZnO lattice. The Ag behavior as a p-type dopant of ZnO enahanced optical transmission which is good for the realization of low energy density devices such as supercapacitors.

Recommendations for Further Study

The properties of the doped powders need to be studied in further detail and material parameters such as the degree of dopant incorporation, carrier concentration and mobility need to be ascertained. Also the need to confirm the reason for negative reflectance is required. Also other optical and solid state properties like extinction coefficient, refractive index, dielectric constant, electrical conductivity etc can be determined.

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