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Tuning Some Optical Parameters of $(PbO)_{1-x}$ $(ZnO)_x$ Prepared by Spray Pyrolysis Technique .

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Abstract: In the last few decades, the world energy requirement is ever growing owing to the growth in the world population and the techno-economic growth of the countries .This work is focused on a way of utilizing the Sun to provide sustainable energy source for the future. Different thin films of average thickness 152nm were prepared from nanoparticles of $(PbO)_{1-x}$ $(ZnO)_x$ precursorson borosilicate glass substrate by spray pyrolysis techniques at 250^0C temperature . Investigations on some optical constants of the films investigated revealed;refractiveindices within1.28- 1.76, extinction coefficients in the range 0.28 – 3.89 , and the energy gap(E_g) in the range 1.50eV to 3.5eV i,e, a bit below PbO(2.90eV)and a little above ZnO(3.37eV) the stating materials.in all, sample F had the peak value of all the optical constants investigated. The wide band gaps displayed by the film as revealed by Spectroscopic measurements depicts their solar technology applications

Keywords: Population, Sun, Nanoparticles, Precursors, Substrate, Optical constants,Refractive indices, Extinction coefficients.

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I. INTRODUCTION

The Chalcogenide , Lead(II) oxide or Lead monoxide (PbO) is an amphoteric oxide with two polymorphs namely; litharge having a tetragonal crystal structure and massicot having an orthorhombic crystal structure, Litharge the lower temperature type of the two crystalline is red, with a tetragonal layered Tin-Oxide structure. It is produced by heating Lead(Pb) to about 600°C in air or O_2.Massicot is the higher temperature phase of PbO. It is yellow, with an orthorhombic chain structure and is stable above 488°C [1] .

However, the relative phase stability of litharge andmassicot is very sensitive to impurities and discrepancies exist in the literature concerning phase transition temperatures [2]. PbO is a toxic material and when doped to strontium titanate (ST) is found experimentally to be a glass ceramic material. Glass ceramics have been commercially used at wide range and limited work has been done over the borosilicate glass ceramic system, in spite of its wide range of applications.

In the industrial production of lead-acid batteries, lead oxide (PbO) is used as initial active material of both anode and cathode of the batteries. In formation process, lead oxide can be converted to spongy lead in anode and lead dioxide in cathode. Lead-acid batteries developed as widespread articles of commerce in over a century [18]. Lead oxide can be prepared by various methods including chemical bath deposition [2]and Spray pyrolysis [3] which is applicable in this work.

Zinc oxide (ZnO) is a transparent conducting oxide (TCO). It is a II-VI semi conductor, mostly n-type, with a band gap of 3.3eV that could be obtained with resistivity as low as $10^{-6}\Omega$.

Owing to a direct wide band gap , large exciton binding energy (60 meV), and superior conducting properties based on oxygen vacancies, the wurtzite-structured [4,5,6,7,8] Zinc oxide (ZnO) has become one of the most promising materials andhas lots of research interest due to their unique structure and size dependent electrical, optical and mechanical properties. ZnO nanostructures were studied extensibly owing to their potential applications in nano-devices and optical materials [9].

Different techniques to synthesized nano and Micro range phosphor such as spray plasma-enhanced chemical vapour deposition [10], sol gel [4], sputtering [11]; pyrolysis [12], solid state reactions [13,14,15], co-precipitation [16] and combustion [17] etc have been used, but in recent times much interest has been generated

ZnOis a candidate material in gas sensor, in electronic displays, in the fabrication of blue light emitting diodes (LEDS) in the surface acousticwave device and more[18] .

Despite all these efforts, which cell material or production technology will ultimately succeed in the commercially competitive technologies especially the field of Solar technology is still anybody's guess, therefore this research is aimed at fabricating new thin films $(PbO)_{1-x}(ZnO)_x$ from existing materials (ZnO and

PbO) using spray pyrolysis technique .The products of our investigations is expected to compare favourably with existing thin film solar cells in the area of solar cell devices application and production technologies .

II. EXPERIMENT

2.1 Substrate Preparation

Owing to rigidity,hardness , chemical inertness, flat and smooth surface with good transmission characteristics of the substrate needed for this investigation , borosilicate glass was used . The substrates were first washed with detergent and distilled water to remove contaminant and glass-stains, then ultrasonically cleaned for ten minutes with isopropyl alcohol. Dried and kept in desiccator for a later use

2.2 Preparation of the precursors.

The starting materials used in this work are 99.99% pure lead acetate and Zinc acetate purchased from BDH chemical vendors . 0.1M Zinc acetate and0.1M Lead acetate solutions in 50% ethanol were prepared separately by dissolving masses of 2.195g Zinc acetate and 3.790g Lead acetate in 100ml of solution respectively.

The different precursors prepared were combined by volume to 100ml in six different beakers as depicted in ‘‘table 1’’. Each mixture was placed on magnetic stirrer with two drops of anhydrous acetic acid (complexing agent) added and stirred for five minutes in order to achieve a complete homogenous solution.

Table 1, Ratio of the two precursors combined by volume in the six beakers.

Beaker + content	A	B	C	D	E	F	G
Precursor **I** (*ml*)	---	20	40	50	60	80	100
Precursor **II** (*ml*)	100	80	60	50	40	20	---

The content of the beakers were adopted as resultant precursors for samples A-G as prepared**.**

2.3Deposition technique

The spray pyrolysis technique consists of a thermally stimulated chemical reaction between clusters of liquid or vapour atoms of different chemical species. It involves spraying of a solution usually aqueous containing soluble salts of the containing atoms of the desired compound aided by carrier gas (Argon, Neon, e.t.c) onto preheated substrates as shown in ‘‘fig I’’

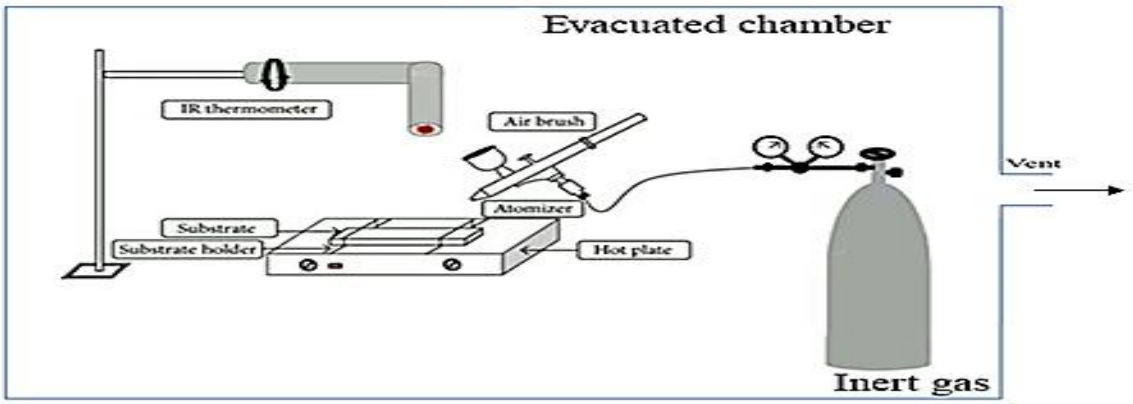


Figure 1. Spray pyrolysis set-up [12]

The spraying of the precursors onto the cleaned substrate surface was done at substrate temperature of 250^{o}C and at a nozzle sample distance of 25cm, during which there was fume resulting from some volatile components of the precursor given off in the vapour phase. This was well accommodated by the fume chamber where the experiment took place.

The nozzle was inclined at an oblique angle to the substrate surface so that escaping by-product of the reaction taking place on the substrate surface does not mix with the fresh spray precursor from the nozzle.

The burner which accommodate the substrate is electrically powered and controlled to give the desired depositing temperature which is recorded by an infra-red thermometer held on a retort stand the fume cupboard .

However,every sprayed droplet reaching the surface of the hot substrate undergoes pyrolytic (endothermic) decomposition and form a single crystalline or cluster of crystallites as a product.Futheremore,The substrates provided thermal energy for the thermal decomposition and subsequent

recombination of the constituent species . Moreover, other volatile by-products and solvent escape in the vapour phase via the vent.

After the deposition ,the film / substrates were allow to cool down gradually / in step to avoid cracking of the substrates. At the end of each deposition, the spraypyrolysis set up and the fume chamber were cleaned and dried up before re-used to avoid contamination or introduction of unwanted impurities into the film.

2.3 Post-deposition Heat treatment and preservation

The as-deposited thin films were annealed in open air at 450^0C for 1 hour to allow for adhesion of film unto the glass surface and elimination of void that may be present in the films. This treatment equally enhanced further crystallization of the cluster of crystal that could bring about homogeneous thin film required. They were cool down in step after the heat treatment and kept in a desiccators for a later use.The average film thickness deposited determined was 152nm .

III. MEASUREMENTS

In both crystalline and amorphous semiconductors, the absorption coefficient near the fundamental absorption edge is dependent on photon energy. In the high absorption region, the absorption coefficient takes on the following more general form as a function of photon energy ;

$\alpha hf = A(\alpha hf - E_g)^n$ *where; n=1/2 for direct transitions and* *2.1*

$\alpha hf = B(\alpha hf - E_g)^n$ *Where; n=2 for indirect transitions* *2.2*

where ; f is the frequency of the incident photon, h is the Planck's constant, A and B are constants, and E_g is the optical energy gap . α is the absorption coefficient given by;

$\alpha = \frac{Absorbance}{optical\ \ density} = 2.303(A/t)$ 2.3

where; A is absorbance and t is the film thickness.

The optical transmittance T is related to the absorption coefficient α and Refractive index n by ;

$T = (1-R)2exp(-\alpha d)/(1-R_2)exp(-2\alpha d)$ *2.4*

The extinction coefficient K is related to α by ;

$K = \alpha\lambda/4\pi$ *2.5*

The optical conductivity σ_o is given by ;

$\sigma_o = \alpha nc/4\pi$ *2.6*

Where; c is the velocity of light , In metals, σ_o and k are very high as reflectance approaches unity.

The dielectric constant ε is defined as the response of the material towards the incident electromagnetic field. It is related to K and n , The dielectric constant of a compound is divided into two parts: real and imaginary, and can be written as ;

$\varepsilon^* = \varepsilon_r + i\varepsilon_I$ *2.7*

Thickness of thin film is calculated by the formula.

$t = m / A\rho$ *2.8*

where;

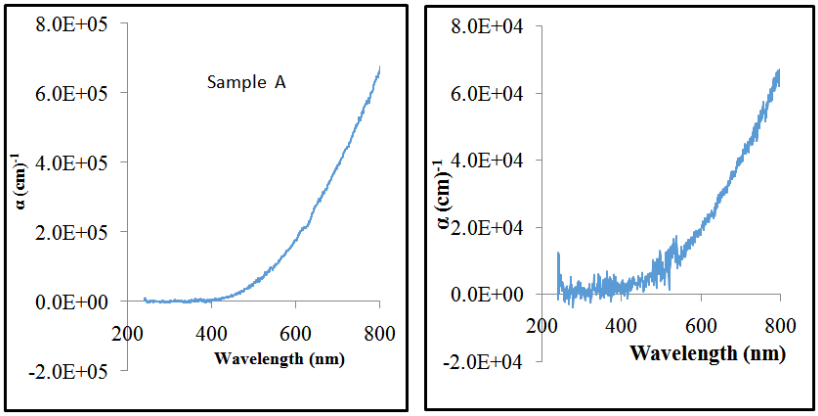
m = mass of deposited thin- film material

A = Surface area of thin -film

ρ= density of material of thin-film

IV. RESULTS AND DISCUSSION

''Fig II'' shows the absorbance plot as a function of wavelengths as obtained from the UV-Vis spectrophotometer.



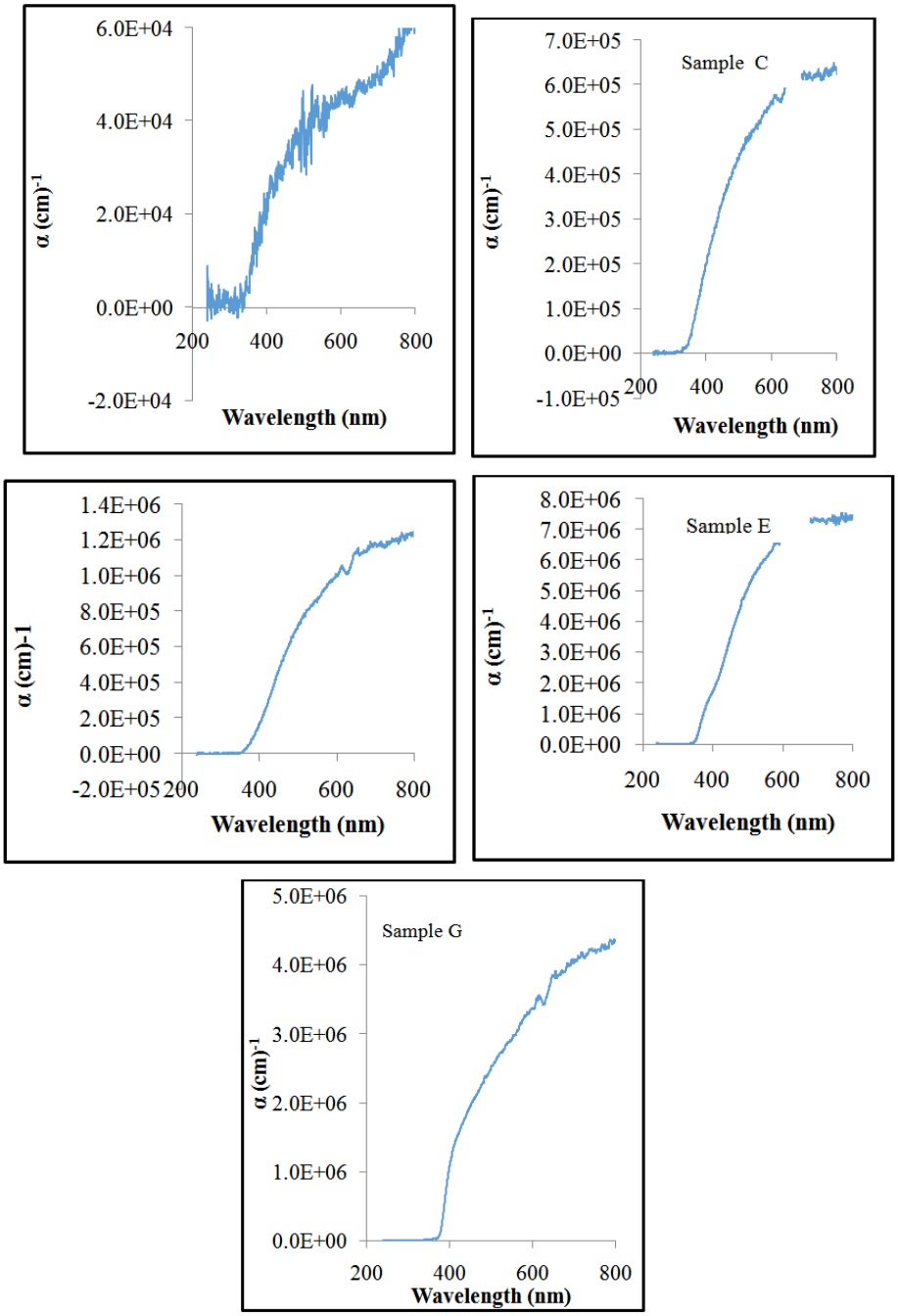


Figure II. Absorption spectra for samples A-G

Transmittance and reflectance of the films were obtained using Beer Lamberts law and by assuming negligible scattering, all the samples showed high absorption in the visible region with absorption edges in the violet region of the electromagnetic spectrum. Photo activation of $(PbO)_{1-x}(ZnO)_x$in this region causes transition from the ground to excited state.

There was a slight decrease in the absorption as ***x***increases in the composition $(PbO)_{1-x}(ZnO)_x$. The samples also show low absorption in the near infrared region .This indicates that the film are not good material for warming applications in low temperate regions ,therefore it could not be used as window glazing to create warmth inPet-house, especially chicken in a poultry farm**.**

The noise level of the optical absorption spectra was observed to be very high in samples B and sample C despite repeated readings, this may be due to the improper alloying between ZnO and PbO in the samples or unforeseen deposition conditions.

These absorption spectra, which are the most direct and perhaps the simplest method for probing the band structure of semiconductors are employed in the determination of the energy gap, E_g. The E_g was

calculated using the well-known Talc's relation (equation 2.1) . The line of best fit of the experimental curve to a band gap semiconductor absorption function was obtained for n=1/2 to obtain direct band gap energy values.

The films displayed energy gaps which varies within the range 1.50eV to 3.5eV as x in $(PbO)_{1-x}$ $(ZnO)_x$ increases as shown in ''fig 2''. This revealed that all the film samples are wide band-gap material that could be useful in photovoltaic technology.

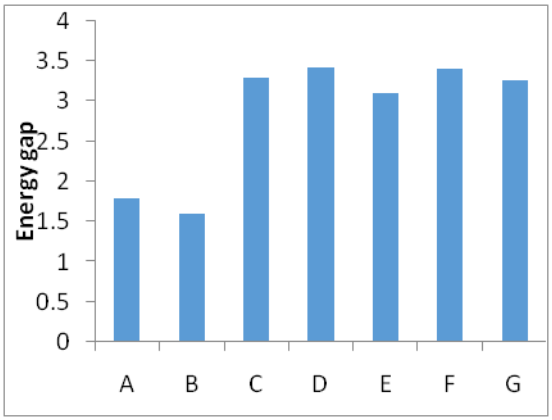


Figure III. Variation in bandgap in Samples A-G

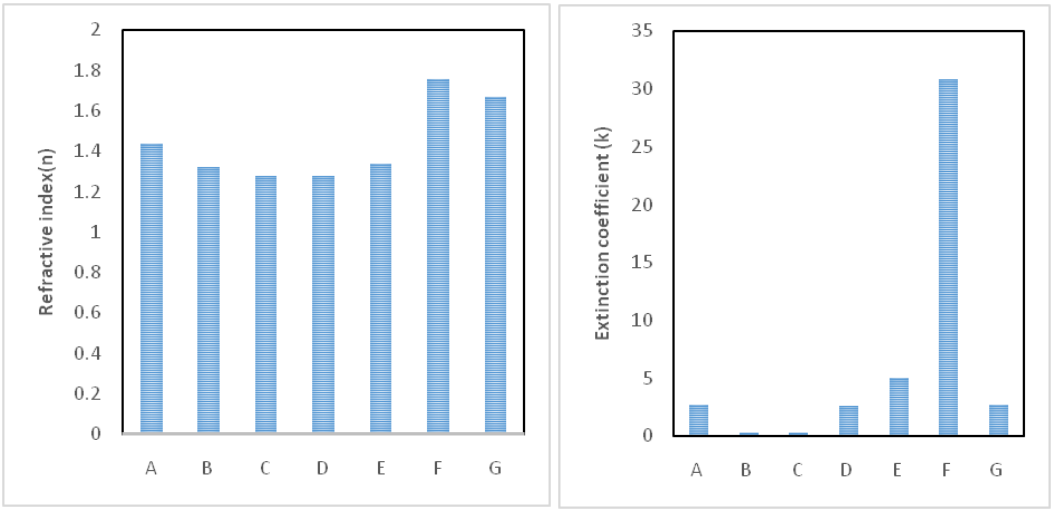


Figure IV. Average values of refractive indeces andextinction coefficients for samples A-G

The refractive index (*n*) and extinction coefficient (*k*)of thin films are related to the interaction between a material of the film and incident light and are associated with refraction and absorption (respectively). Thin film material coatings on various substrates usually provide important functionalities for the microfabricationindustry. Thethe *n*, *k*, as well as the thickness, *t*, of thin film constituents if controlled could allow for repeatable manufacturing

In this study the refractive indices obtained''figure iv '' are within the range 1.28 -1.76 with sample F having the highest and ,C and D with the least meaning that on the average the electromagnetic radiation is 1.28- 1.76 time slower in the films than in the free space. However, the Low refractive index occurs due to successive internal reflection or due to the trapped photon energy with the grain boundary. It could also be attributed to the variety of impurities and defects with the increase of x in $(PbO)_{1-x}(ZnO)_x$of the film and this implies that there is a strong optical scattering in the samples . In summary, the value of the refractive index attested to the usefulness of the films in photovoltaic applications.

The extinction coefficient takes value from 0.28 – 3.89 , sample F had the highest ,C and D the least. The rise in the extinctioncoefficient is directly related to the absorption of light in the film materials as seen in ''fig II'' in relation to ''fig IV''.

V. CONCLUSION

Generally, the optical properties of thin-film ; transmission *T*, reflection *R* and absorption A are determined by its refractive index n, extinction coefficient *K*,bandgap*Eg* and geometry . Geometry include ; film thickness , thickness uniformity and film surface roughness. *T*, *R* and *A* are intrinsic - depending on the chemical composition and solid structure of the material, whereas the geometry is extrinsic[19].

In this study for the first time, the optical behaviour of $(PbO)_{1-x}(ZnO)_x$ thin films deposited on soda lime glass were studied. $(PbO)_{1-x}(ZnO)_x$films have been successfully prepared by spray pyrolysis methodat a temperature of 250^0C from existingPbO and ZnO materials combined chemically in varying proportions. The wide band gaps displayed by the film asrevealed by Spectroscopic measurements depicts their solar technology applications. Thefilms show high absorbance in the visible region and low absorbance near infra-red region of electromagnetic spectrum also with low refractive index and fairly high extinction coefficient .sample F had the widest forbidden gap and the highest value of other optical constants investigated

The energy bandgaps exhibited by the films fall within the energy range required for a semiconductor to effectively function as either buffer or window layers for photovoltaic applications.

Moreover, much is still needed to be done by researchers on the structural and electrical properties of this thin films to compliment this research findings for industrial applications.

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