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Photoelectric Properties of ZnO/Si and Ag Doped ZnO/Si Heterojunctions

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Abstract- **A type of semiconductor heterojunctions was fabricated by ZnO thin film layer deposited on Si substrate. The elementary particles were examined by Energy Dispersive X-rays (EDX). X-ray Diffraction (XRD) analysis was described by structural properties of ZnO and Si layer. The study of ZnO growth morphology on Si substrate was determined by Scanning Electron Microscope (SEM). Then, the electrical and optical characteristics for ZnO-Si solar cell was investigated. Thermally simulated current (TSC) and I-V characteristics under different wavelengths in visible regions were also studied. In this work, the ZnO-Si thin film layer was indicated in photovoltaic effect. Moreover, studying silver contact on ZnO-Si heterojunction was purposed for achieving higher efficiency.**
Keywords— **heterojunctions, EDX, XRD, SEM, I-V, efficiency**

I. INTRODUCTION

Solar (photovoltaic) cell is a device that converts photon energy directly into electrical energy. This is achieved by using solid state semiconductor devices. Many semiconductors exhibit changes in some of their physical properties when exposed to appropriate photon energy. This phenomenon is known as photosensitivity. In addition, the phenomenon of incident photon energy modifying the intrinsic resistivity or conductivity of a semiconductor is known as photoconductivity. These photons induced effects have been utilized to produce devices that convert photon energy directly into useful electrical energy; such devices are normally called solar cells. When photon energy coming from the sun, for instance, falls on a solar cell, a fraction of the incident solar energy with appropriate wavelengths is converted into electricity, a photon that is known as solar photovoltaics [1].

The Zinc oxide, as an important semiconductor material, is with a wide band gap energy of 3.37 eV, high exciton binding energy of 60 meV, a wide range resistivity, high electron hall mobility (200 cm^2Vs^{-1}) and high transparency at room temperature [2]. These unique properties make ZnO which has many potential applications; such as ultraviolet (UV) photoconductive detectors [3], solar cells [4], photo catalysts [5], light emitting diodes [6], especially for solar cells. They have been growing research efforts to improve the cell efficiency by optical absorption. These properties and potential applications make this material an attractive subject for theoretical studies for thin film technologies.

Moreover, ZnO; II-VI compound semiconductor, is a cheap, abundant, chemically stable and nontoxicity material with excellent radiation hardness. ZnO has been grown on different substrates such as GaAs, Si, Glass, Sapphire these are used by several techniques for many reasonable applications. For example, light emitting diodes, visitors, optical waveguides and conductive gas sensors are used by several techniques such as pulse laser deposition, spray pyrolysis, dc magnetron sputtering and thermal evaporation method. Thermal evaporation method is widely used and interested due to simple technique, cost effective, easy deposition, enhancing adjusted composition and dopants, and fabricating large area films.

Silver Ag, a soft, white, lustrous transition material, it exhibits the highest electrical conductivity, thermal conductivity and reflectivity of any metal [7]. The conventional Si thin-film solar cell technology depends on textured metal based back reflectors, which typically consists of a silver layer deposited on a thin film transparent conducting oxide (TCO) layer, ZnO [8]. Although silver reflectors exhibit excellent electrical and optical reflectivity properties, they still require a high manufacturing cost. Thus a low cost silver doped thin film is developed as a back reflected layer using Si junction solar cell. Therefore, silver doped ZnO/Si thin film is effectively enhanced the short-circuit current under visible wavelength region and improving efficiency for solar cell fabrication.

II. METHODOLOGY

The development of nanoscience and nanotechnology research on ceramic materials shows a lot of promising applications of ZnO in the manufacturing of nanoscale-based electronic and optoelectronic devices and the fact that it is a wide band gap semiconductor with good carrier mobility. Furthermore, it can also be doped both n-type and p-type [9-11]. Moreover, selection of ZnO film is grown for the realization of excited based photonic devices.

ZnO has some advantages for the short wavelength 3650A˚ applications compared with ZnSe and GaN based materials. The most peculiar point is that ZnO has a large exciton binding energy about three times as large as those of ZnSe and GaN. For this large binding energy, the exciton is stable at room temperature even in the bulk crystal. Another notable property is that it has large bond strength. Hence, ZnO is a hopeful material for exciton-related optical devices.

Amorphous ZnO powder, molecular weight 81.378g and its melting point is about 1800°C. Its high refractive index (n=2) makes it a good white pigment where its main diameter for maximum light scattering is 0.25 µm. Photoconductivity of ZnO has been observed so far only as a surface phenomenon and without sensitization by absorbed foreign substance, merely with light in the spectral region of fundamental absorption and having a penetration depth of about $2x10^{-15}$cm. ZnO which has wurtzite structure and its lattice constants are a=b=3.242°A and c=5.176°A.

In this article, Ag-doped ZnO thin films with various doping concentration are prepared by thermal evaporation method. The p-type Ag solid phase solution is used an appropriate contact on nn^+ ZnO-Si layer to form pnn^+ solar cell structure for two main reasons:

(1) To have low contact resistance and
(2) To create an electric field which reduces carrier.

A. Preparation of ZnO-Si Heterojunction

In this work, was investigated with n-type ZnO/n-type, a single crystal Si heterostructures. N-type silicon wafers with a resistivity of (ρ = 0-30cm) were cut into pieces of the size of 0.4 cm^2. The used Si wafers were cleaned to reduce the contamination by using etching solution HF:H_2O =1:10 prior to each experiment. The wafers were cleaned and dried by the following block diagram:

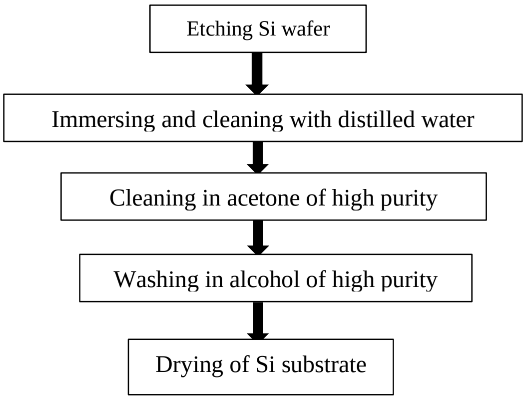


Fig. 1 Block diagram of preparing to growth on Si wafers

And then, zinc oxide powder was deposited on n-type Si substrates by thermal evaporation method. ZnO deposited on Si substrates were carried out with different annealing temperatures 700ºC, 800ºC, 900ºC for 90 min at each temperature to compare. Then, analysed characteristics of these concerning with various temperatures. The ZnO powder could not be deposited at low temperatures because it melts at 1800°C under normal pressure. After annealing, these were cleaned with HF:H_2O =1:10 solution and distilled water. Then, ZnO-Si heterojunction layers were achieved. Silicon wafers of n-type (100) was used in the present research. ZnO epitaxial layers grown on Si substrates by thermal evaporation method analysed by EDX, XRD and SEM were descried as follows. To enhance the achievement of higher efficiency, silver is widely used for doping to ZnO as an improvement of solar characteristics.

III. RESULLTS AND DISCUSSIONS

A. Energy Dispersive X-Rays Analysis

EDX analysis is used as a tool for studying the composite of elementary particles. Figure 2 shows the EDX analysis for ZnO grown on Si sample. From this pattern, Zn, Si and O peaks are deeply in combined with each other.

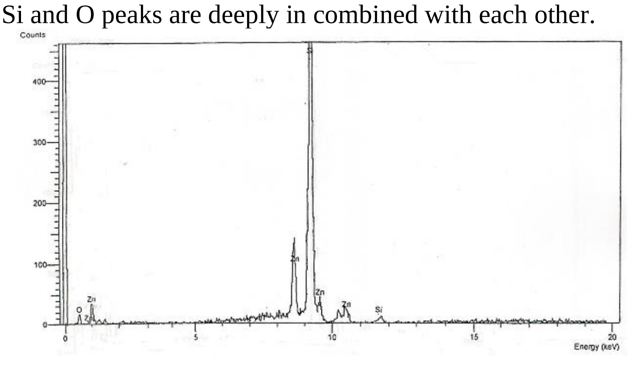


Fig 2. The Energy Dispersive X-ray (EDX) Analysis of ZnO-Si Sample

B. X-Ray Diffraction Analysis

XRD pattern is analysed for phase formation transformation, lattice parameters, and the preferred orientation of ZnO thin film. The ZnO-Si sample is also examined with a RIGAKU model RINT 2000 diffractometer. The XRD analysis of ZnO-Si specimen with applied 40 kV and 30mA, the k-alpha filter and Cu X-ray (λ= 1.54056 Aº) detection is done.

ZnO grown on Si substrate via thermal evaporation method is examined by XRD pattern shown in Figure 3. According to Bragg's Law, the condition for constructive reflection of the incident radiation is

$$2d \sin\theta = n \lambda \qquad \text{............ Equation 1}$$

Consider parallel lattice planes space d apart, an integral number n of wavelengths λ and θ is measured from the plane.

$$\frac{1}{d^2} = \frac{4}{3}\left[\frac{h^2+hk+k^2}{a^2}\right] + \frac{l^2}{c^2} \qquad \text{............ Equation 2 [12]}$$

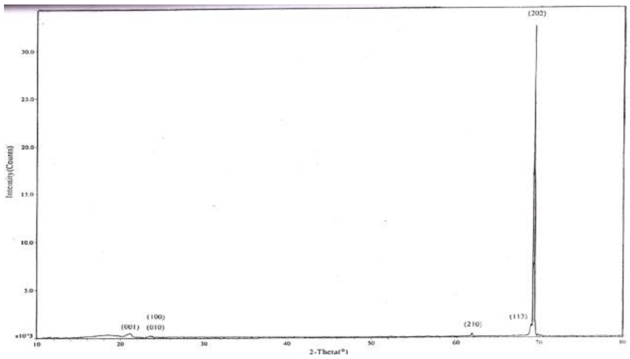
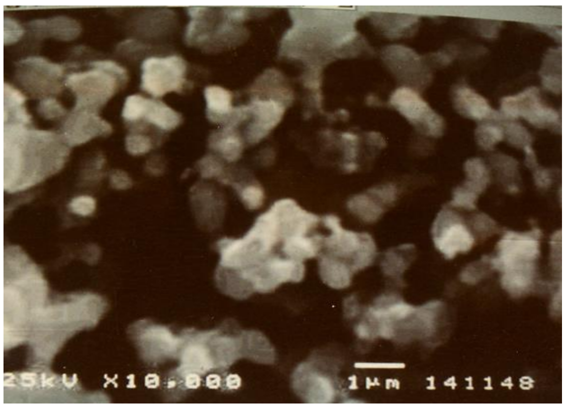


Fig 3. The XRD Pattern of ZnO-Si Sample at Annealing 800ºC

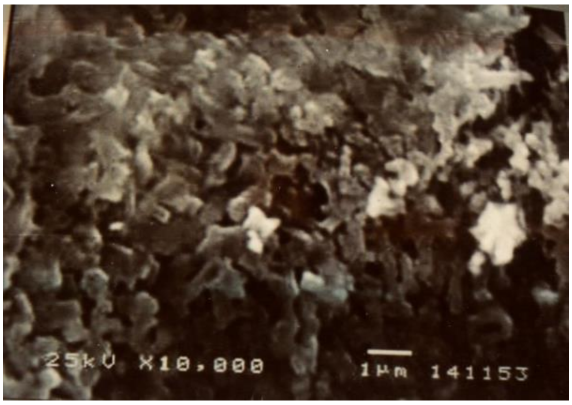
As the experimental results, the lattice constants are a= 3.212 Aº and c= 5.139Aº. The calculated ratio c/a is very closed to the theoretically accepted value 1.6 for hexagonal. So, it can be concluded that zinc oxide might be successfully diffused into the Si substrate.

C. *Scanning Electron Microscope (SEM) View on Zinc Oxide Films*

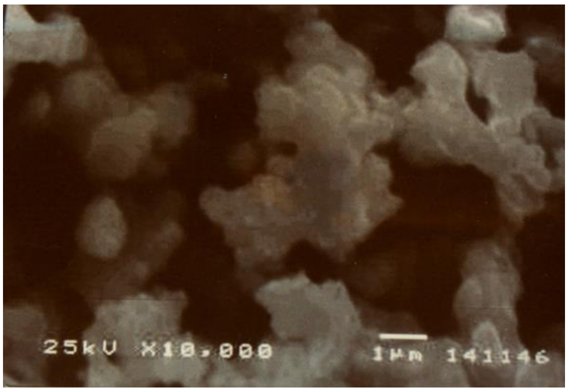
SEM analysis is measured for microstructural thin film semiconducting materials because of the physical properties of the specimen which give rise to contrast in the micrographs. The surface morphologies of studied ZnO- Si samples are using SEM. Figure 3 (a), (b) and (c) show the SEM photographs of the surface of the ZnO layer grown on Si substrates at different annealing temperatures. ZnO-Si sample at annealed temperatures 700ºC and 900ºC can be found that the quality of ZnO films are stacking and roughly thick films as seen in Figure 4(a) and 4(c). The film prepared at annealed temperature 900ºC are relatively thick and poorly transparent than annealed temperature 700ºC due to light scattering.



(a)



(b)



(c)

Fig 4. The SEM Photographs of ZnO Layer Grown on Si Substrate at Different Annealing Temperatures (a) 700°C (a) 800°C (b)900°C

Figure 4 (b) can be seen the SEM photograph of the surface of ZnO epitaxial layers grown on Si substrate for crystallographic orientation (100) at annealed temperature 800 ºC. They can be clearly described that the films prepared at different annealing temperatures have different physical properties of the specimens. They all are composed of small hexagonal formed particles. With increasing substrate temperature, the small ZnO particles aggregate are formed. However, too high a temperature (> 900ºC) was found to reduce the transparency of the ZnO thin film, and thus 800ºC annealed temperature is optimum temperature in this work. Thus, the substrate temperature is usually considered to have the most significant effect on the quality of the film.

D. Study on the Characteristics of ZnO- Si Fabricated Thin Film

Zinc Oxide, wide band gap semiconductor, has high excitation energy that makes an important material for conductive type devices. The wide spread applicability of this semiconducting oxide is related both to its range of conductive variability and to the fact that it responses to oxidize. In this research, n-type ZnO layer is operated as a solar cell device that grown on n- type silicon substrate that has band gap of 1.1 eV. The electrical characteristics

1) Photoelectric Properties

Firstly, the electrical characteristics of ZnO-Si heterojunction is investigated by measuring I-V plot under large bias region and low bias region. The current is predominantly by electrons and the continuity requirement for the total current density to be constant throughout those regions. It is of interest to consider the minority carriers (holes). The hole current in ZnO is greater than the n+ region in Si because of more amount of hole density in n region of ZnO. After that, TSC – temperature characteristics are also examined. According to the analysis, the ZnO- Si samples have photoelectric effect nature. The experimental illuminated I-V characteristics of ZnO-Si heterojunction at different annealed temperatures are as shown in Figure 5. From the experimental measurements, the optimum currents can be measured for quenching temperature 800°C.

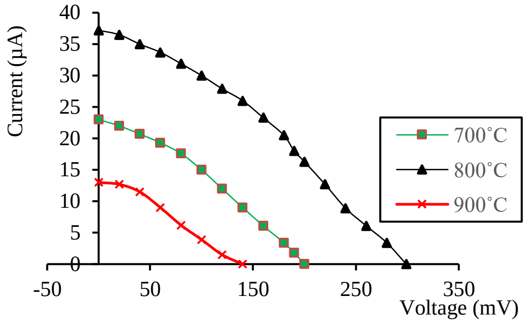


Fig 5. The Illuminated I-V Characteristics of ZnO-Si Heterojunctions at Different Annealing Temperatures

In order to clarify the polarity of I-V curve of ZnO-Si sample, the method of thermally simulated current (TSC) was applied. The effect of temperature applied biasing voltage on TSC curve (thermal sampling method) for ZnO-Si sample is shown in Figure 6. According to the result, the current due to the back electromotive force induced by applying dc voltage increases with an increase of ambient temperature, illustrates a maximum current, I_m and then decreases with a further increase of ambient temperature. From these results, the value of I_m is in close connection to the polarity of I-V curve, thus the larger polarity results in the higher value of I_m. The value of temperature is almost independent of the bias voltage. The sample is cooled to room temperature and the I-V curves are checked to be recovered to initial ones.

As the above mentioned, the origin of electromotive force and the deep trapping level may be responsible for the degradation of I-V curve in the view point of space charged polarization of trapped charge. Therefore, TSC observed in ZnO layer grown on Si substrate for playing in I-V curve. The Schottky-type barriers layer due to the difference of work function or the traps at surface state exists at the interface between ZnO layer and Si substrate. So, thermally observed in ZnO layer due to the recovery from electrical stress in Schottky-type barriers layers or the thermal release of electrons from traps.

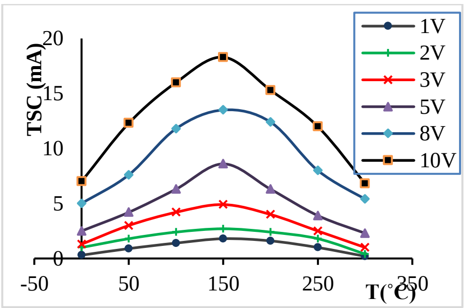


Fig 6. Effect of Biased Voltage on TSC Curves of ZnO-Si Thin Film

Figure 7 represents the dependence of photovoltage (V_{oc}) and photocurrent (I_{sc}) on the incident light intensity. They can be obviously seen that both the values of V_{oc} and I_{sc} are increasing with increasing of light intensity, agreeing with theoretical aspects.

The most important parameter for a comparison of solar cells is the efficiency (η) of light conversion. In this work, the efficiency of the solar cell is calculated by using the equation:

$$\eta = \frac{P_{max}}{P_{in}} \qquad \text{............ Equation 3}$$

The fill factor (FF) determines the maximum power from the photovoltaic cell. The fill factor can be expressed by the following equation:

$$FF = \frac{P_{m} I_{m}}{V_{oc} I_{sc}} \qquad \text{............ Equation 4}$$

where, V_m, I_m = cell voltage and cell current at the maximum power point of the I-V characteristics of photovoltaic cell

P_{max} = power maximum output power

P_{in} = power of the incident light source [13]

In the present work, although photo voltage achieved from the cell has fair values, photocurrents are a little poor. It is evident that the larger gap material produces the largest open-circuit voltage, while the lowest gap material which absorbs a greater portion of the incident spectrum, generates the largest short-circuit current. On the other hand, a large energy gap can give a higher photo voltage and a lower photocurrent. This is also one fact that the efficiency is lower.

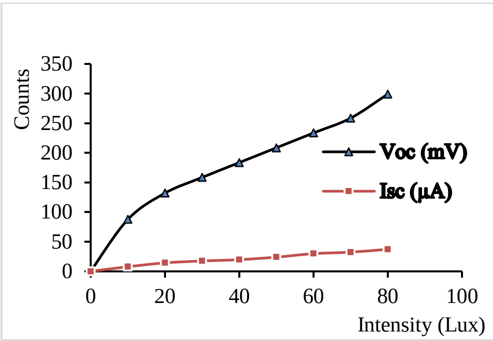


Fig 7. Dependence of V_{oc} and I_{sc} on the Illuminated Intensity

The calculated cell parameters of ZnO-Si hetero-junction are described in Table1.

TABLE 1
PROPERTIES OF ZnO-Si SOLAR CELLS PREPARED AT DIFFERENT ANNEALING TEMPERATURES

Substrate Orientation	**Annealing Tempera-ture (°C)**	**V_{oc} (mV)**	**I_{sc} (µA)**	**P_m (µW)**	**η (%)**	**FF (%)**
Si(100)	700	200	23.1	1.60	1.48	34.52
	800	299	37.2	4.14	3.83	37.22
	900	130	12.6	0.51	0.47	31.20

Figure 8 depicts that the calibration of intensity vs. wavelength plot for 5W electric bulbs under visible wavelength region. From this condition, the orange light has optimum intensity.

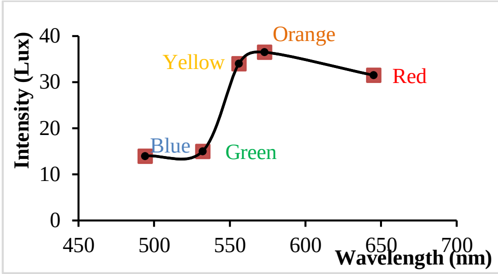


Fig 8. Calibration of Intensity Vs Wavelength Graph

The I-V characteristics of ZnO-Si solar cells are also measured with various light intensities (using 5W electric bulbs) under different wavelengths in the visible range are illustrated in Figure 9.

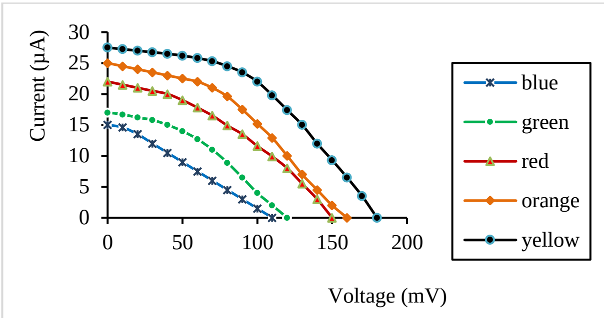


Fig 9. I-V Characteristics of ZnO-Si Cell under Different Wavelengths in Visible Region

As seen in figure, the current-voltage characteristics of various light intensities under different wavelengths in the visible range are illustrated. From the experimental result, ZnO-Si sample under yellow light is more sensitive than under other visible light regions.

The orange light has optimum intensity (λ~573nm) but the best photocell characteristics are achieved under yellow light (λ~556nm). This is because of the window effect. The corresponding emission wavelength can be calculated from the following equation.

$$\Delta E_g = hc/\lambda \qquad \text{................ Equation 4}$$

Where, $\Delta E_g = E_{g1} - E_{g2}$

The calculated corresponding emission wavelength is approximately 561 nm.

E. Investigation of Silver Contact on ZnO-Si Solar Cell

Many solar cell configurations have been proposed for achieving higher conversion efficiency. The cell parameters may vary widely depend on the structural defects of the material and the nature and amount of chemical impurities. In this work, the silver is contacted on ZnO-Si cells at quenching temperature 450ºC for 1 hr intended to achieve higher efficiency. Figure 10 shows the compared results under illuminated I-V characteristics for ZnO-Si solar cells at annealing temperature 800°C for 90 min with silver contact on ZnO-Si solar cell. Photo doping of a cell characteristic phenomenon in ZnO-Si junction is occurring when certain Ag is deposited on the film diffuse into the film by light irradiation.

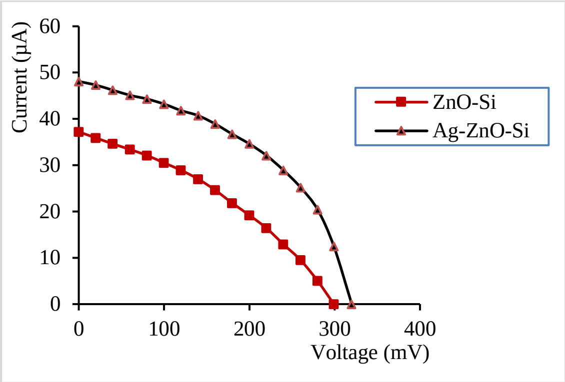


Fig 10. Comparison for the Illuminated I-V Characteristics of ZnO-Si and Ag-ZnO-Si Photo Cells

The compared cell parameters for ZnO-Si and Ag-ZnO-Si can be obviously seen in Table 2. From the experimental results, the open-circuit voltage, the short-circuit current, the fill-factor, the maximum output power (P_m) and the efficiency (η) of Ag-ZnO-Si cells are better than ZnO-Si solar cells. Therefore, Ag-doped ZnO thin film can greately improve the absorption of the cells. Compare to pure ZnO, solar cell's energy conversion efficiency improvement of 2.79% is obtained with Ag doped ZnO thin film.the cell parameters may vary widely depend on the nature and structure of the material and the amount of chemical impurities.

TABLE 2
THE COMPARISON CELL PARAMETERS FOR ZnO-Si AND Ag-ZnO-Si PHOTOCELLS

Photocell	V_{oc} (mV)	I_{sc} (μA)	P_m (μW)	η (%)	FF (%)
ZnO-Si	299	37.2	4.14	3.83	37.22
Ag-ZnO-Si	320	48.1	7.15	6.62	46.45

IV. CONCLUSIONS

Single crystalline silicon is more expensive, but higher efficiency than other crystal structures. ZnO exhibits a variety of interesting properties such as high electrochemical coupling, great stability of hexagonal phase, and a wide bandgap of 3.37 eV. Moreover, ZnO can also be considered an excellent material for optical method because it has strong (sharp) lattice absorption band.

In this research, the ZnO- Si thin film at annealing temperatures has been studied in EDX, XRD and SEM analyses for surface morphologies, elementary composition and film's structural properties. Then, the electrical and optical characteristics are studied by illuminated I-V curve, TSC- T (˚C) and I- V examined under different wavelength in the visible region. From the experimental result, the optimum ZnO-Si solar cell characteristic is annealing temperature 800 ˚C for 90 min. Then the silver contact on ZnO-Si solar cells are purposed to achieve for higher conversion efficiency. Their respective photo conversion efficiencies are 3.83 % and 6.62%. Therefore, silver is a suitable contact material for solar cell application to achieve higher efficiencies.

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