Narrow Band Gap Ternary Absorber Layer for Solar Cell for Small Business Enterprises in Equatorial Africa

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ABSTRACT

According to recent studies, on the Daily nation newspaper, in Kenya of 6th January 2017 featured the story, the number of people doing the same thing in surrounding villages was so high that many of them had to leave their phones behind at the charging centre (for up to three days) before returning to pick them. To fight darkness, up to 80 percent of Africans depend on personal generators, candles and kerosene (paraffin) lamps to provide basic lighting. Let's not even talk about all the other things we desperately need electricity for – iron clothes, pump water, charge mobile phones etc. In this article, we shall focus on the types of solar cell materials that can be used to fabricate solar cell to be installed on roof tops to generate electricity used by individuals and households. Photovoltaic devices are used to convert solar radiation energy into electrical forms of energy for various uses. Current research is geared towards using thin films with wide band gaps to allow optimum penetration of radiation within the VIS - NIR region. Inorganic wide band gap, $Cd_xZn_{1-x}S$ thin films and narrow band gap, PbS thin films were optimized through chemical solution technique in this study. Wide band gap thin films of $Cd_xZn_{1-x}S$ were grown at about 82^0C while those of narrow band gap thin films of PbS were grown at room temperature utilizing aqueous conditions. Their optical constants were investigated and found to be suitable for solar cells applications.

Key words

Solar cell, small business enterprise, energy demand, CdxZn1-xS, Band gap, resistivity, Open Voltage, VIS - NIR region

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INTRODUCTION

It's important that entrepreneurs get right factors that drive the demand for solar energy in Africa. Many village markets in Africa are so remote and it would take decades for electricity to come by. African governments do not consider a priority to connect small towns and villages though they have a huge demand for electricity. Mobile phones, which have been widely successful in Africa, have changed the profile of power consumption in Africa. The mobile phone connectivity is forcing millions of poor Africans to look elsewhere for power to charge their phones. It's now clear that more people in African now depend on mobile phones to contact relatives, obtain information about farm product prices, and make/receive small money transfers. What African small entrepreneurs and especially those in rural areas, villages and towns needs now is an alternative that is *cheap, easy to deploy, decentralized* and *effective* enough to provide electricity to millions of people in the shortest possible time. The cheapest available source is the solar power. It has a potential to satisfy all these requirements. Since most parts of Africa sits on or at or along the earth's equator, the sun's radiation reaches many parts of the continent including the remotest parts – villages, mountain tops, anywhere and everywhere, solar cell technology forms a core priority to solving the energy demand that Africa requires. Despite all the good things said about solar power, it has not spread as fast as expected because of its cost but also due to unprecedented research into alternative solar cell materials. The high upfront cost of solar equipment has made it difficult to compete against other sources of power has motivated the investigation of new materials to design portable solar cells for local use. Investing in solar energy may have a lot of benefits and save lots of money in the long term, but many African families can simply not afford the high initial capital.

Inorganic thin films intended for applications photovoltaic devices are rare. This is because of their structure, inter-band transitions and other optical properties are difficult to maximize when intended for solar radiation harvesting so as to provide enough energy. These thin films have activities that take place when electrons transit between energy bands (Chapin, and Pearson, 1954) that are difficult to modify for harvesting solar radiation. Thin film nanotechnology for solar cell has made several attempts to fabricate cheap photovoltaic cells so as to produce power for homes, small commercial uses or electric current (Schroder, 1998) with little success. They all work on the concept that a solar cell absorbs photons from the sun and convert them directly or indirectly into electricity. This means that they must have an absorber layer which has a majority hole carriers and a window layer that has a majority electron carriers and allow maximum radiation to penetrate it. Many researchers have devoted their efforts to solution technique because it is a non-expensive method for thin film preparation. Doping CdS thin films to produce ternary thin film derivatives using inorganic elemental dopants like boron (Khallaf *et al.,* 2009), indium (Shadia *et al.,* 2008), zinc (mosiori *et al.,* 2014) arsenide and chlorine (Amanullah *et al.,* 2005) has produced thin films properties suitable for use as window layers. Out of all these attempts, doping using elemental zinc ions is gaining prominence as a good candidate for wide band gap materials for solar cells.

THEORY

Optical Properties

It is generally agreed that the refractive index (n) of a thin film can be calculated using the equation proposed by Ravindra *et al.* (2006) as;

$$n = [(1+R^{1/2})/\ (1-R^{1/2})] \tag{1}$$

while optical refractive index (n) and energy band gap (E_g) related as;

$$n = 4.08 - 0.62E_g \tag{2}$$

Dielectric constants are used to describe any losses caused by optical conductivity (σ) in thin films where real and imaginary parts of the dielectric constant are given by;

$\varepsilon_c = \varepsilon_r + \varepsilon_i$ (3)

and they were estimated using the relations;

$\varepsilon_1 = n^2 - k^2$ (4)

$\varepsilon_2 = 2nk$ (5)

The absorption coefficient (α) can be calculated using the equation;

$\alpha = 2.303A/d$ (6)

where α is the absorbance coefficient value at a particular wavelength (λ) and is the thickness(*d)* of the semiconductor film. Extinction coefficient is calculated using the relation;

$k = \alpha\lambda/4\pi$ (7)

Electrical Properties

One of the techniques used for measuring resistivity is the Four- Point Probe. Current is passed thought the outer two probes and the potential developed across the inner two probes and it is measured through any of the other five combinations of current and voltage probes can in principle be used to give resistivity as:

$$\rho = \frac{2\pi SI}{V} = \frac{E}{J} = \frac{1}{\sigma} = R\frac{A}{l} \qquad (8)$$

where *S* is the probe spacing in centimeters end $S_1 = S_2 = S_3$ where the SI unit is ohm meter. Electrical resistivity, ρ, is a measure of how strongly a material opposes the flow of electric current while e lectrical conductivity, σ, or specific conductance is the reciprocal quantity, and measures a material's ability to conduct an electric current with SI unit of siemens per meter ($S{\cdot}m^{-1}$). Many resistors, semiconductors and conductors have a uniform cross section with a uniform flow of electric current and are made of one material. The resistance of a given sample will increase with the length, but decrease with greater cross-sectional area. Resistance is measured in ohms.

Solar Cell Properties

Solar cells are known to absorb photons randomly to generate electron-hole pairs which form the source of dark current (Collavini, et al., 2015). The resulting current density, j_e can be expressed as;

$$j_e(V) = J_o[\exp(\frac{qV}{k_B T}) - 1] \qquad (9)$$

where k_B = Boltzmann constant and T = Kelvin temperature. Under thermal equilibrium condition, the dark current, J_o can be formulated as;

$$J_o = q\int_o^\alpha a(\lambda, W)\frac{\Gamma_0(\lambda)\lambda}{hc_0}\,\partial\lambda \qquad (10)$$

where the sun spectrum **Γ** is replaced by the black-body emission spectrum of solar cell, $\mathbf{\Gamma_o}$. For perovskite solar cells, the Shockley-Read-Hall recombination (Filipič, et al., 2015) gives a non-radiative current, J_t as;

$$J_t(V) = q\gamma\eta_i W \exp(\frac{0.5qV}{k_B T}) \qquad (11)$$

where, γ = monomolecular recombination rate, η_i = intrinsic carrier density, W = cell thickness.

EXPERIMENTAL DETAILS

Preparation of substrates

Microscope research glass slides were used as substrates. They were degreased in hydrochloric acid, washed with detergent, rinsed in distilled water and dried in air.

Chemicals and Reagents

Cadmium nitrate, ammonium nitrate, thiuorea, de-ionized water, NH_4OH (29.4%) and other required chemicals were purchased. Some were used as they were bought while others were prepared a few minutes before use to have minimum decomposition taking place. Solutions were prepared from analytical grade chemicals.

Growth Procedures

Growth of Wide Band gap thin film layer: Cadimium zinc sulphide thin films were chosen as a wide band gap layer. Precursor solutions of concentrations of 0.038 M cadmium nitrate, 0.076 M ammonium nitrate, and 0.076 M thiuorea were prepared in de-ionized water. Small amounts of 25 ml of the each solution was taken into a separate beaker and topped up to 100 ml using de-ionized water, heated to about 82^o C and by using a burette, dilute NH_4OH was added drop-wise to maintain a pH of about 9. Varying concentrations of zinc nitrate solutions so as to vary zinc ions from 1.0 - 0.6 according the chemical formula, $Cd_xZn_{1-x}S$. Glass slide substrates were inserted suspended vertically from synthetic foam which covered the beakers containing the bath solution for about 25 minutes, taken out, cleaned and kept for characterization.

Growth of Narrow Band gap thin film layer: Lead sulphide thin films were chosen as a narrow band gap layer. Growth was done by sequential additions of solution of 5 ml of 0.5 M lead nitrate as a source of Pb^{+2} ions, 5 ml of 2 M sodium hydroxide as source of alkaline medium, 6 ml of 1 M thiourea as source of S^{-2} and 2 ml of 1 M tri-ethanolamine as a complexing agent. Lead ions of varying concentration from 0.3M to 0.7M at intervals of 0.1M were prepared to optimize the thin films in which 5ml of lead nitrate poured into a 100ml beaker followed by 5ml of 2M sodium hydroxide and the mixture was thoroughly stirred using an electric stirrer to obtain a milky solution. This was followed by adding 6ml of 1M thiourea followed immediately by 2ml of 1M tri-ethanolamine while stirring and a substrate was inserted vertically at room temperature for 120 minutes.

Fabrication of the Solar Cell: An optimized wideband layer with a band gap of 2.72 eV and having the highest transmittance with lowest refractive index, lowest absorption and extinction coefficient was chosen. An optimized narrow band gap thin film with lowest refractive index, lowest transmittance and high absorption and extinction coefficients was equally chosen. Silver paste was used as the ohmic contact.

Characterization of thin films layers

Optical properties: The resultant PbS thin films were homogeneous, well adhered to the substrate and specularly reflecting. $Cd_xZn_{1-x}S$ films were smooth, uniform, adherent, bright yellow orange in colour where the yellowness decreased with increasing zinc content. Reflection and transmission spectra were measured at room temperature in the spectral range of 260–2000 nm (4.54 –1.08 eV) using NIR-VIS IR spectrophotometer DUC 3700 instrument at ambient temperature.

Electrical properties: Electrical properties were studied using a four point probe connected to Kethley 2400 source meter interfaced with a computer using Labview program at ambient temperature.

Characterization of the Solar Cell

A solar simulator in the VIS-NIR region was used to measure the solar cell's I-V characteristics.

RESULTS AND DISCUSSIONS

Growth Mechanisms

Many nano-chemical researchers in thin films suggest that the reaction mechanism for the formation of CdS through this growth method is as shown in eq. 12 to eq. 15. Cadmium salts in the presence of ammonium hydroxide solution form the complex compounds in the steps shown by eq. 12 - 15.

$$NH_{3(aq)} + H_2O_{(l)} \Rightarrow NH_4{}^{+} + OH^{-} \quad (12)$$

$$Cd(NO_4)_2 + 4(NH_3) \Rightarrow Cd(NH_3)_4[NO_3]_2 \quad (13a)$$

$$Zn(NO_4)_2 + 4(NH_3) \Rightarrow [Zn(NH_3)_4[NO_3]_2] \quad (13b)$$

$$Cd(NH_3)_4{}^{2+} \Rightarrow Cd^{2+} + 4NH_3 \quad (14a)$$

$$Zn(NH_3)_4{}^{2+} \Rightarrow Zn^{2+} + 4NH_3 \quad (14b)$$

$$Cd(OH)_2 \Rightarrow Cd^{2+} + 2OH^{-} \quad (15a)$$

$$Zn(OH)_2 \Rightarrow Zn^{2+} + 2(OH)^{-} \quad (15b)$$

Thiourea is a sulphide-ion source in an alkaline medium where the sulphide ions are released slowly as shown in eq. 16 and eq. 17;

$$(NH_2)_2CS + 3OH \Rightarrow NH_3 + CO_3{}^{-2} + S \quad (16)$$

$$SH^{-} + OH^{-} \Rightarrow S^{-2} + H_2O \quad (17)$$

$$xCd^{+2} + (1-x)Zn^{+2} + S^{-2} \Rightarrow Cd_xZn_{(1-x)}S \quad (18)$$

Hence the cadmium ions (Cd^{+2}) react with sulphide (S^{-2}) ions and zinc ions (Zn^{+2}) to form $Cd_xZn_{1-x}S$ precipitate which in turn produces the thin film under slow reaction mechanism as shown in equations eq. 3, eq. 4 and eq. 6. Therefore, the reactions expressed by eq. 12 to eq. 18 are interrelated in which ammonium ions affects cadmium ions Cd^{+2}, the precipitation of cadmium hydroxide [$Cd(OH)_2$], forming tetra-ammine-cadmium complex ions [$Cd(NH_3)_2{}^{+2}$].

Electrical Properties of Narrow Band Gap layer

The resistivity of PbS was 9.171 × 10^3 Ω-cm and decreased to 6.78 ×10^3 Ω-cm but thereafter increased almost linear to 1.26 × 10^4 Ω-cm at 0.7M PbS which translates to an electrical conductivity range of 1.09 - 0.79 × 10^{-5} S-cm^{-1} as shown in figure 1. This observation was attributed to the large levels of scattering centres due to amorphous nature of the films as lead concentration increases (Kumar and Sankaranayanan, (2009); Kasim *et al.* 2008),. Amorphous thin films have higher concentration of scattering centres (Saliha, (2009); Vidhya, and Velumeni, (2009).

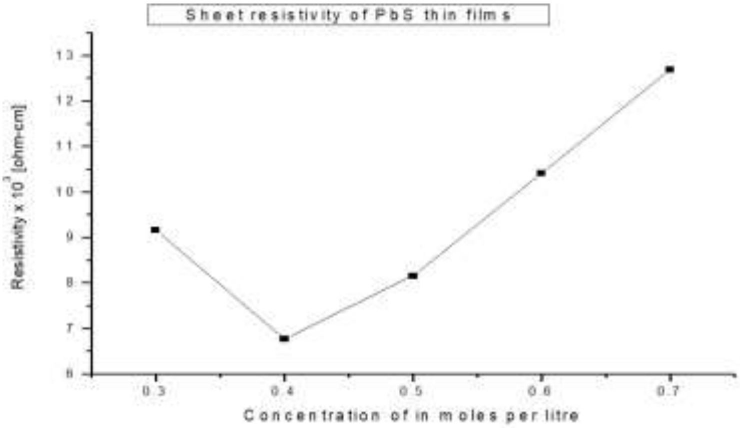

Figure 1: Graph of resistivity against concentration of PbS films

Electrical Properties of Narrow Band Gap layer

The electrical resistivity of $Cd_xZn_{1-x}S$ increased with increase of Zn ions from 1.09 × 10^2 Ω-cm to 1.36 × 10^2 Ω-cm shown in figure 2. Zn impurities caused more scattering centres. This caused a reduced the mean free path and this was attributed to increase in scattering at the grain boundaries in addition to the normal bulk scattering centres present.

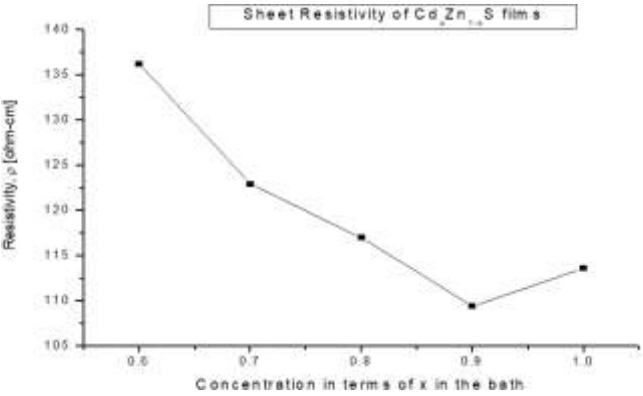

Figure 2: Optical properties of $Cd_xZn_{1-x}S$

Therefore the motion of charge carriers through the thin film grains suffer extra scattering at the grain boundaries. The Zn impurity dopant caused the tuning of the electrical properties. This observation was similar to those observed by Vidhya and Velumani, (2009) and by Song *et al.* 2006.

Optical Properties of Wide Band Gap layer

Zn impurities were observed to reduce reflectance and absorbance and increase transmittance within the visible and infrared range. This decrease in refractive index decreased was attributed to the colour of the films observed that varied with change in concentration. Its band gap can be tailored to vary from 2.43 eV to 3.32 eV depending on its constituents and preparation techniques. However, these films formed high quality wide bandgap layer properties (Kumar and Sankaranayanan, (2009), Kasim *et al.* (2008), Saliha, (2009), Vidhya and Velumeni, (2009) with transmittances of 90%, 80%, 79% and 65% respectively in the wavelength range of 300 – 1200 nm.

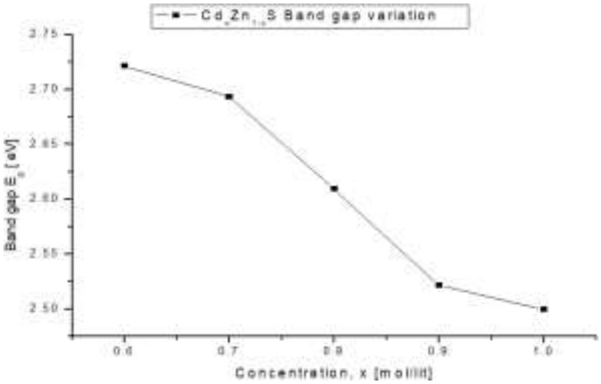

Figure 3: Band gap variation for $Cd_xZn_{1-x}S$

Optical Properties of Narrow Band Gap layer

Lead sulphide thin films had their energy gap consistently at 0.41 eV. That band gap is below the optimum theoretical band gap for maximum absorber material of about 1.5 eV (Popa *et al.*, 2006), used to fabricate solar cells.

Wide Band gap Layer/ Narrow Band Gap Absorber layer Solar cell

The addition of Zn onto CdS was intended to enhance open-circuit voltage (V_{oc}) and short-circuits current (I_{sc}) in hetero-junction devices by widening the band gap.

Table 2: Variation of current against voltage in Band Gap/Narrow band gap layer as measured by solar simulator.

Voltage [V]	Current [A]	Power [w]
0.00	0.031	0.0
0.05	0.031	0.00155
0.10	0.031	0.0031
0.15	0.031	0.00465
0.20	0.030	0.006
0.25	0.028	0.007
0.27	0.027	0.00729
0.29	0.026	0.00754
0.31	0.023	0.00713
0.33	0.020	0.0066
0.35	0.015	0.00525
0.36	0.010	0.0036
0.37	0.001	0.00037

The result was a decrease in window absorption losses due to an enhanced wide band gap. Solar simulator was used to determine the cell's I-V characteristics. The experimental I-V characteristics results were tabulated in table 2 and figure 3, figure 4 and figure 5 illustrates current/or and power variation with voltage while table 3 displays of the solar cell parameters. As observed (from table 3 and figures 3, 4 and 5), the solar cell fabricated had a short circuit current, I_{sc} = 0.031 A, open voltage, V_{oc} = 0.37V, a fill factor, ff = 0.66 or 66 % and an efficiency, η = 0.9. since fill factor of a solar cell is a measure of the quality of a cell, a large fill factor of 1 is desirable and it corresponds to I-V sweep that is more square-like where typical fill factors ranges from 0.50 to 0.82 (50 % - 82%).

Table 3: Band Gap/Narrow band gap layer solar cell parameters

Cell parameters	Value of parameter/unit
I_{sc}	0.031 A
V_{oc}	0.37 V
V_{max}	0.29 V
I_{max}	0.026 A
P_{max}	0.00754 W
ff	0.66
η	0.9

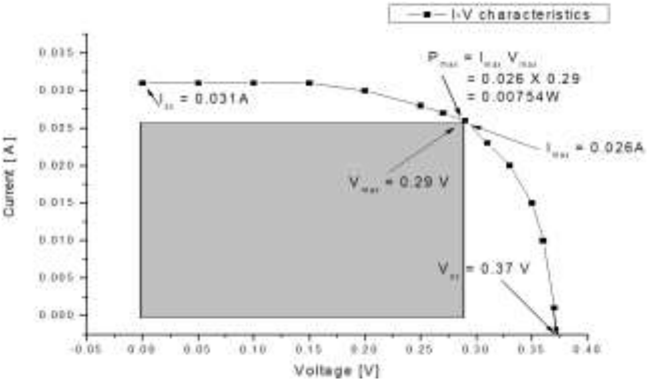

Figure 4: I-V curve characteristics of Band Gap/Narrow band gap layer solar cell

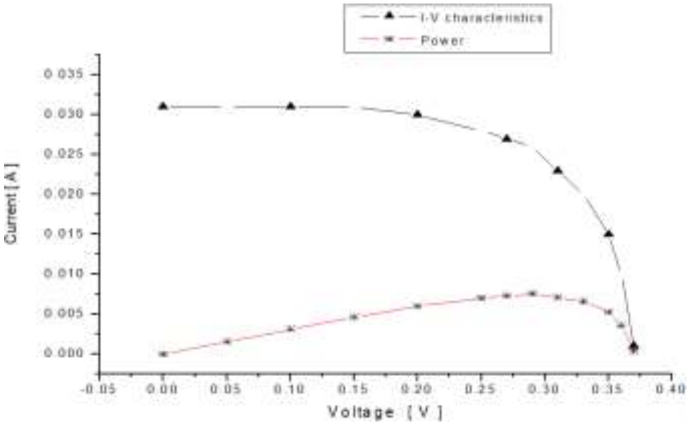

Figure 5: I-V curve and power-voltage characteristics of Band Gap/Narrow band gap layer solar cell

CONCLUSIONS

Small-scale solar energy can provide millions of people with a first step on the energy ladder. But it cannot in the medium term fill the energy void left by large-scale utilities. African governments must aim for an annual growth rate in power generation of 10% a year for the next two decades – about five times current levels. Countries such as Ethiopia, Kenya and Rwanda have demonstrated this is possible. Wide band gap and narrow band thin films were grown by chemical bath technique and characterized. They were successfully used to fabricate a solar cell with a short circuit current, I_{sc} = 0.031 A, open voltage, V_{oc} = 0.37 V, an efficiency, η = 0.9 and a fill factor, ff = 0.66 or 66 %. Considering the square-like nature of the I-V curve and a fill factor of 0.66, it was concluded that the cell formed a good *p-n* junction for solar cells.

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