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INFLUENCE OF DOPANTS AND DEPOSITION TEMPERATURE ON THE OPTICAL AND SOLID STATE PROPERTIES OF DYE-SENSITIZED NOVEL NANOHYBRID $Zn_xSn_yO_z$ THIN FILMS DEPOSITED USING SPRAY PYROLYSIS

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Dye-sensitized Novel Nanohybrid $Zn_xSn_yO_z$ thin films were prepared on glass substrates using spray pyrolysis technique. The dye used is extract from the leaves of *tectona grandis.* A 0.1M of Zn^{2+} and 1% was used respectively. Depositions were done at different substrate temperature of 50^{o}C, 100^{o}C, and 150^{o}C. The effect Zn^{2+} ion and dye extract from *tectona grandis* leaves on optical and solid state properties of the films were examined and analysed. The result showed that the absorbance of the undoped SnO thin films at various substrate temperatures vary from about 0.1-0.7. The absorbance generally increased with deposition/ substrate temperature exhibiting a maximum for films deposited at 150^{o}C. The average transmittance of both un-doped and Zn^{2+} doped SnO thin films at 350nm is above 90% regardless of the film thickness. The dye doped samples showed an improvement in optical transmission at 625nm. The reflectance spectra of all films exhibited a similar trend. Peak reflectance was observed at 350nm for un-doped and Zn^{2+} doped samples of SnO thin films while peak reflectance can be observed at 625nm for dye doped samples. It is also observed that the band gaps of the dye doped samples are lower: 1.55eV- 1.83eV than those of the Zn^{2+} doped samples: 1.60eV – 2.20eV. This showed that the incorporation of the dye shifted the fundamental absorption edge of the un-doped SnO thin films thus providing tuning effect of the band gap for device applications.

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Keywords: Spray pyrolysis, Optical properties, Dopants and temperature

1. Introduction

Dye-sensitized solar cell has a number of attractive features; it provides flexible solar modules, it can be fabricated using conventional roll-printing techniques that are less expensive than the conventional method. The novel in solar cell technology is that portable electronic devices could be re-charged using a low light level potentials and partial shading like solar panels [6]. Dye-sensitized cells are very strong absorbents of light as they harness larger amounts of sunlight more than silicon based solar cells. [10]. Transparent conductive oxide (TCO) films are widely used in many fields including optoelectronic devices. Indium tin oxide is the best transparent conductive oxide (TCO) films that are known for its excellent optical and electrical properties. However, Indium used in indium tin oxide is a scarce resources and expensive. [16] and [8]. Doping with selective elements help to enhance and control the structural, electrical and optical properties of SnO thin films. In addition, doping improves the number of charge carriers and the conductivity of SnO films, for potential application in optoelectronic devices especially in solar cells. Hence, alternative dopants were sorted using Zn^{2+} and dye extract from the leaves of *tectona grandis* dye extract on SnO thin films. Tin oxide (SnO) and tin-doped indium oxide (ITO) layers, are widely used as transparent conductive oxide (TCO) layers in solar cells due to their superior electrical and optical properties. Generally, SnO is a wide band gap semiconductor with an energy gap of 2.5eV and 3eV. [13], [4].

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In this study SnO, doping is achieved by adding Zn^{2+} atom and dye extract from the leaves of *tectona grandis* into the compound using simple, vacuum free and cost effective spray pyrolysis method in order to tune the optical properties of SnO. The optical properties of the grown layers were examined and analysed.

2. Experimental details and characterization

Aqueous solution of 0.1M of Tin (II) chloride ($SnCl_2$) was prepared by dissolving 19gram of the salt in 100ml of distilled water as a source of SnO. Also, aqueous solution of 0.1M Zinc Chloride was prepared by dissolving 1.36g in 100ml of distilled water as a source of Zn^{2+} (dopants), Sodium hydroxide was used as source of OH^- and dye extract of *Tectona grandis* as dopants

The microscopic glass slide used as the substrates has a surface area of 26mm X 76mm, thickness – 1.0mm and refractive index – 1.52. The substrates were wiped with acetone and cotton to remove visible contamination such as dust. Then the substrates were immersed in ethanol solution for 5 hours followed by washing with distilled water in order to remove surface oxides and precipitation. The substrates were finally ultrasonically cleansed and oven dried.

To obtain SnO thin films 40ml of 0.1M aqueous solution of Tin (II) chloride and 4 drops of aqueous ammonia was measured into 50ml glass beaker. The mixture was stirred under high speed technique for about 5minutes using magnetic stirrer in order to obtain uniform solution. After the stirring 10ml of the solution was measured out using pump syringe into spray pyrolysis sample bottle which was fastened on valve rod of air brush and sprayed for 60seconds on heated substrate at the temperature of 50^{o}C using the compressor with the air brush at pressure of 22 Pa. These were repeated for 2 different 10ml of the solution at 100^{o}C and 150^{o}C respectively at deposition angle of 28^o, height of 36m, distance and time of 60seconds.

The dopants or impurities are normally 10% of chosen volume of the solution in conventional chemical experiment. To obtain SnO:Zn, 1ml of 0.1M of $ZnCl_2$ was mixed with 18ml of 0.1M of $SnCl_2$ and to the mixture was added 1ml of NaOH. Similarly, to obtain SnO:dye, 1 % of the dye was added to a mixture of 1ml of 0.1M of $ZnCl_2$ and 18ml of 0.1M of $SnCl_2$ The mixture was stirred using a magnetic stirrer for 30 minutes in order to obtain homogenous solution. After the stirring, 10ml of the resulting mixture was measured into sample bottle that was fixed on nozzle valve and sprayed on heated substrate temperatures of 50^{o}C, 100^{o}C and 150^{o}C.

2.1. Characterization

Optical properties of the as-grown films were measured using Thermo scientific GENESYS 10S model UV-VIS spectrophotometer. Other optical and solid state parameters were deduced from the transmittance and reflectance spectra.

3. Results and discussion

The films grown were milky white in appearance which gradually turned to brown colour with the increase of temperature. All the deposited films are pore free, uniform and strongly adherent to the substrate surface

The average transmittance of both un-doped and Zn^{2+} doped SnO thin films at 350 nm is above 90 % regardless of the film thickness (Fig. 1-2), which is in good agreement with reported values [14],[15], [5]. The dye doped sample showed an improvement in optical transmission at 625 nm (Fig. 3). In our view, the transmittance increases could be attributed to the organic content of the dyes. Generally, the required transmittance of transparent conductive thin film solar cells is over 85 % and as such these results indicate that SnO thin films are a good candidate to be used as a window layer in solar cells [5]. The average transmittance of some of the layers both Zn^{2+} and dye doped SnO thin films deposited in this work is above 50 % in the visible region. Human eye is sensitive only to the range 400-700 nm and is peaked at 500 nm [2]. This is an important factor in

window coatings and is met in some of the samples deposited in this work. The infrared region is the heat portion of electromagnetic spectrum and some samples of our films showed appreciable transmission in this region, which placed them as suitable materials for the construction of poultry houses for the purpose of admitting heat into the building for warming young chicks that has not developed protective feathers. This has the potential of reducing the cost energy consumption associated with electric bulbs, stoves, etc. These findings are corroborated by the work of other researchers [2], [7], [1]. In the Literature, the transmittance of thin films can be greatly modified by different deposition variables.

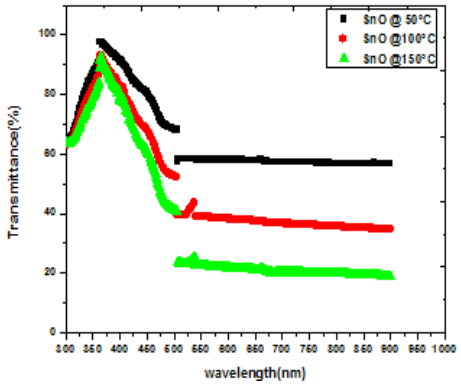

Fig. 1. Transmittance Vs Wavelength for SnO (undoped).

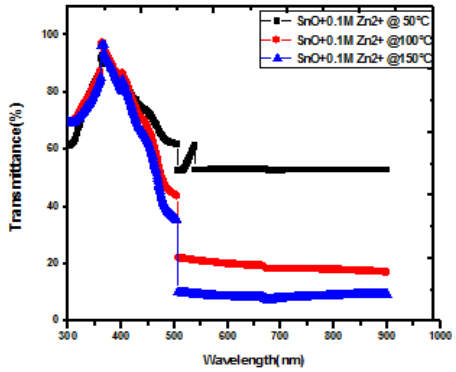

Fig. 2. Transmittance Vs Wavelength for SnO+0.1M of Zn^{2+} (doped).

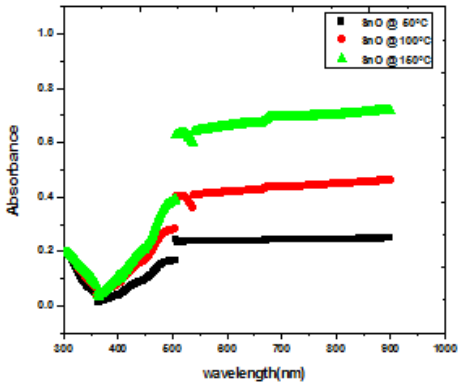

Fig. 3. Transmittance Vs Wavelength for SnO + dye (1%) (doped).

The absorbance of the un-doped SnO thin films at various bath temperatures vary from about 0.1-0.7 (Fig. 4). These ranges of values are within the limit stipulated by Lambert-Beer's law. Our values agree with those of Saeideh *et al*. (2011) for SnO thin films but at variance with values obtained by Suresh and Jiban (2015) for SnO_2 thin films all deposited by chemical bath method. The absorbance generally increases with bath temperature exhibiting a maximum for films deposited at 150^{o}C. The infrared region absorbed better compared to other regions, which is not in agreement with higher absorbance in the UV region reported by Onyia and Nnabuchi (2015), and Florian *et al*. (2019) for chemically deposited SnO thin films subjected to different annealing temperatures. The observed optical behaviour could be attributed to the deposition conditions. The absorbance spectra for 0.1M Zn^{2+} doped SnO thin films showed similar trend (Fig. 5) but differed in terms of magnitude of absorption and behaviour of the curves. This clear optical behaviour showed that we can tune the optical properties to suit a specific application by varying growth parameters. When natural dye extract from tectona grandis were introduced as dopants, a different behaviour was observed in terms of the absorbance curves and range of values (Fig.6). In our view, the abrupt optical behaviour as a consequence of incorporation of dyes into SnO thin films matrix may be associated with the organic content of the dyes.

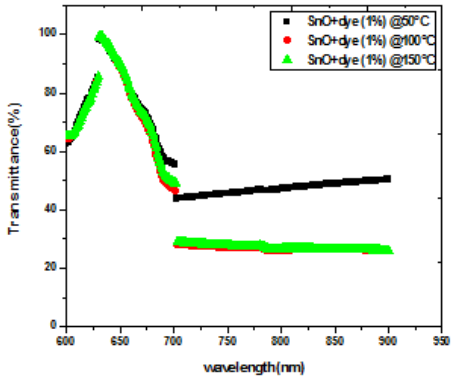

Fig. 4. Absorbance Vs Wavelength for SnO (undoped).

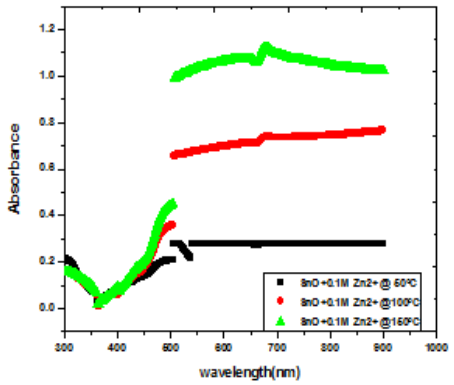

Fig. 5. Absorbance Vs Wavelength for SnO+0.1M of Zn^{2+} (doped).

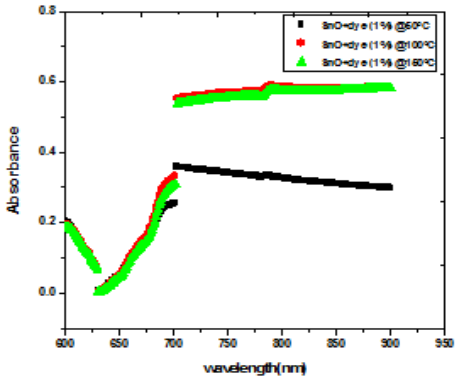

Fig. 6. Absorbance Vs Wavelength for SnO+ 1% dye (doped).

The reflectance spectra of all films exhibited a similar trajectory, fluctuating between maxima and minima (Figs.7-9). Peak reflectance can be observed at 350 nm for un-doped and Zn^{2+} doped samples of SnO thin films while peak reflectance was observed at 625 nm for dye decorated samples. It can be inferred that the incorporation of Zn^{2+} concentrations into SnO matrix did not significantly affect the reflectance. The same trend was observed when the dyes were introduced into SnO films except for 5% dye sample which showed significant increase in optical reflectance. For the Zn^{2+} doped SnO films, the lowest reflectance is about 5 % and 25 % for dye decorated layers. This suggests that these films layers can be used as anti-reflective surfaces.

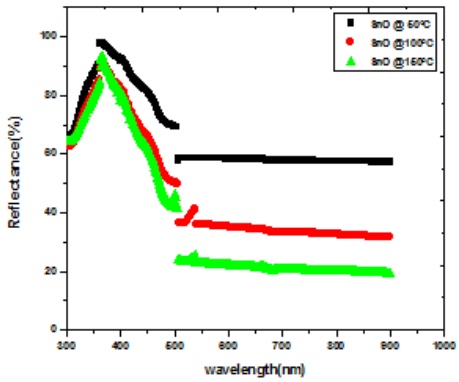

Fig. 7. Reflectance (%) Vs Wavelength for SnO (undoped).

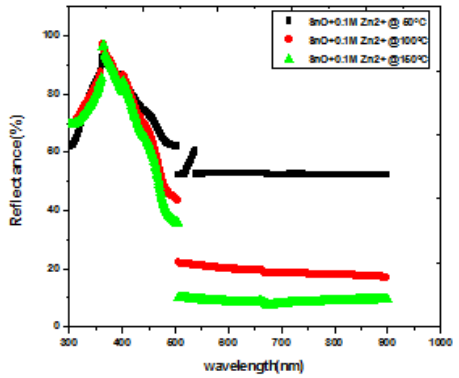

Fig. 8. Reflectance (%) Vs Wavelength for SnO+ 0.1of Zn^{2+} (doped).

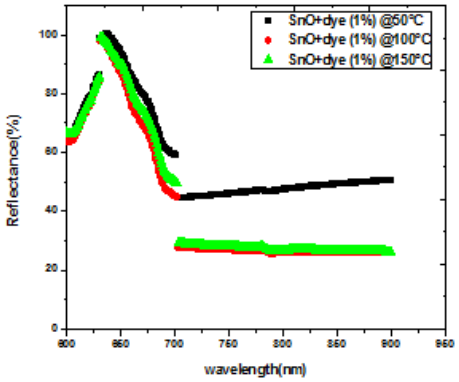

Fig. 9. Reflectance Vs Wavelength for SnO+ dye (1%) dye (doped).

The direct band gap was extracted by linear extrapolation of α^2 versus hv plot to zero on the energy axis (Fig. 10-12) shows that the band gap of un-doped SnO films at 50^{o}C, 100^{o}C and 150^{o}C bath temperatures are 2.00 eV, 2.10 eV and 2.20 eV respectively. The band gap for 0.1M Zn^{2+} doped layers are 1.60 eV, 1.80 eV and 2.00 eV at bath temperatures of 50^{o}C, 100^{o}C and 150^{o}C respectively. In the configurations, 0.1M of Zn^{2+} doped sample showed clear trend with substrate temperature variations. When the dopant was changed to natural dye extracts from *tectona grand* the band gap was greatly adjusted. The band gap for 1 % doped dye samples at 50^{o}C, 100^{o}C and 150^{o}C bath temperatures are 1.55 eV, 1.58 eV and 1.60 eV respectively.

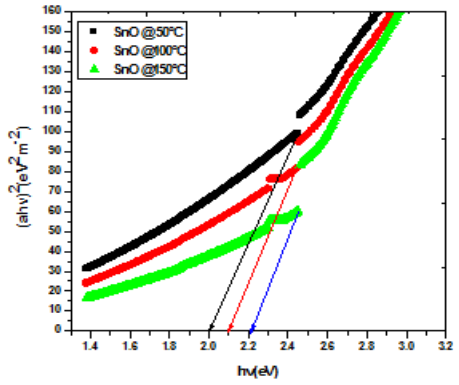

Fig. 10. $(\alpha hv)^2$ (eV^2m^{-2}) Vs hv(eV) for SnO (undoped).

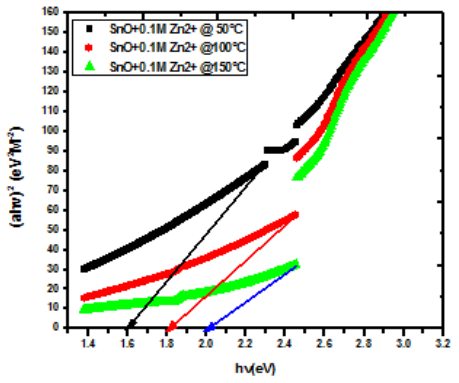

Fig. 11. $(\alpha hv)^2$ (eV^2m^{-2}) Vs hv(eV) for SnO+0.1M of Zn^{2+}(doped).

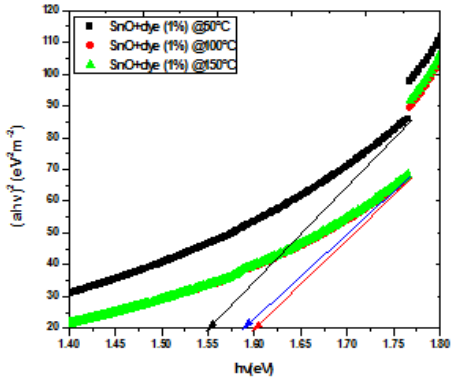

Fig. 12. $(\alpha h\nu)^2$ (eV^2m^{-2}) Vs hν(eV) for SnO+dye (1%) (doped).

It can be observed that the band gap of the dye doped sample is lower than those of the Zn^{2+} doped sample. The narrowing of the band gap may be a consequence of the organic content of the dyes which were incorporated into SnO_2 films matrix. The incorporation of the dyes shifted the fundamental absorption edge of the un-doped SnO thin films thus providing tuning effect of the band gap for specific applications. Generally, the wide direct band gap energy exhibited by these films make them ideal for use as window layer in hetero-junction solar cells.

4. Conclusion

In this study, the effect Zn^{2+} and dye extract from leaves of *tectona grandis* on optical properties of the films were examined and analysed. The result showed that the absorbance of the undoped SnO thin films at various bath temperatures vary from about 0.1 – 0.7. The absorbance generally increased with bath temperature exhibiting a maximum for films deposited at 150^{o}C.

The average transmittance of both un-doped and Zn^{2+} doped SnO thin films at 350nm is above 90% regardless of the film thickness. The dye doped samples showed an improvement in optical transmission at 625nm. The transmittance increase could be attributed to the organic content of dyes. The average transmittance of some of the layers both Zn^{2+} and dye doped SnO thin films deposited in this work is above 50% in the visible region.

The reflectance spectra of all films exhibited a similar trend. Peak reflectance was observed at 350nm for un-doped and Zn^{2+} doped samples of SnO thin films while peak reflectance can be observed at 625nm for dye decorated samples. It is observed that the incorporation of Zn^{2+} concentrations into SnO matrix did not significantly affect the reflectance. It was also observed that the band gap of the dye doped sample is lower: 1.55 – 1.88eV than the Zn^{2+} doped sample, 1.60 – 2.22eV. The incorporation of the dyes shifted the fundamental absorption edge of the un-doped SnO thin films thus providing tuning effect of the band gap for solar cells application. The evaluated band gap showed a red shift upon doping with the energy band gap decreased from 1.60 – 2.22eV to 1.55 – 1.88eV for the investigated doping concentration ranges.

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