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Deposition and Bandgap Tailoring Of SnO Nano Thin Films by Coating with Zn, Cr and Dye of *Tectona Grandis* Leaf

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Abstract
Tin oxide (SnO) thin films are one of the most extremely studied due to its usefulness in UV-detector. SnO is known for wide bandgap of 3.6eV which makes it a good candidate for window layers in heterjunction solar cells. Transition metal chalcogenides (TMCs): Zinc (II) Sulphide (ZnS), Chromium (II) Sulphide (CrS), and dye-extracts exhibits unique properties such as high conversion efficiency, good absorption coefficient and good bandgap energy. These properties make their thin films versatile as coating materials. Spray pyrolysis Master Airbrush Brand-model G25, G255-SET and G266-SET have been used to deposit SnO, SnO:Zn-ion, SnO:Cr-ion, and SnO:dye of tectona grandis at 0.1M and 1% concentration respectively. The deposition was done at different substrate temperature of 50^{o}C, 100^{o}C, 150^{o}C and 200^{o}C. The dye used is extract from the leaves of tectona grandis. The effect of substrate temperature on the optical properties of the SnO (core) and SnO/TMCs (biphasic) films were examined and analysed vis-a-vis the bandgap. The result showed that the optical transmittance decreased with increase in substrate temperature for SnO (core). The bandgap energy for SnO is 2.00eV, 2.10eV, and 2.20eV at 50^{o}C, 100^{o}C, and 150^{o}C substrate temperature respectively. The energy band gap increased with substrate temperature indicating a blue shift. The result showed that for biphasic films under study the bandgap in all samples were in neighbourhood of 1.7eV-3.90eV for the different substrate temperature. All the energy band gap of the biphasic films is slightly lower than those of the core. 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. The results reveals 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.

Key Words: *Bandgap, Dopants (Zn^{2+} & Cr^{2-}), Dye of tectona grandis, and Substrate temperature*

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I. Introduction

Tin oxide (SnO) thin film has been one of the most extremely studied oxides because of its usefulness as a UV detector. As important group (II-VI) semiconductor with wide bandgap of 3.6eV, its thin film has versatile character. This film possesses wide applications in various technological fields, such as low electrical resistance with high optical transparency in the visible range, electrode materials in solar cells, flat display window layers, photo sensors among other applications including opto-electronic devices [8]. Many researchers had focused on the development of biphasic nanostructured materials on a nanometer scale, due to their device applications in several areas. According to Manoj, *et al* (2015), biphasic nanostructured composites are type of biphasic materials which have an inner structure of one material and outer structure of another material made of different components. These components have been the interest, as they can exhibit unique properties arising from the combination of the core and coating materials in their geometric or designed form. It is an alternative means of blending the best properties of the both for optimum enhancement.

Biphasic nanostructure materials have been designed so that the coating material can improve the reactivity of the surface, thermal stability, or oxidation stability of the core structured material. TMC coating materials with different constituents show enhanced properties that differ from their corresponding non-functionalized uncoated bulk. [7]. The coating materials are important because they can influence the charge, functionality, and as well as improve the dispersive nature of core structured material. SnO has recently received much attention because of its unique properties, especially as an absorber layer in thin film solar cells. This is because the constituent elements tin and sulphur have emerged as simple, non-toxic and affordable materials for thin films solar cells since a decade [6, 9]. The compound has direct energy bandgap of 1.35eV for photovoltaic solar energy conversion [6].

Further, the electrical and optical properties of Tin oxide can be easily tailored by modifying the growth conditions as a coating material to a suitable metallic oxide without disturbing its crystal structure [9]. The unique properties of Tin Suphide (SnS) could has the possible applications such as opto-electronics solar cell devices batteries, biomedical sciences and as well as sensors [6]. SnS also, exhibits stable low-symmetric doubled layer orthorhombic crystal structure.

Dye-sensitized thin films fabrication has continued to gain more attention among researchers in thin film technology across the globe due to the fascinating synergetic properties or complimentary behaviours offered by the composite nanostructures.

The enormous growth of interest in solar energy is the consequence of the need to produce a cleaner energy that is inexpensive and less pollutant to the environment. The solar energy is the most abundant and environmentally friendly renewable energy resource. Photovoltaic's offers an alternative means of producing essential electrical power without further endangering the delicate balance of our fragile ecosystems. It is the direct means of conversion of solar energy to electricity.

Presently, Silicon base solar cells/panel dominates photovoltaic industries. It is known fact that silicon is an abundant element on earth crust but its high cost of production has hindered wide used of silicon material for commercial production of electricity. This is because silicon is indirect band gap material and the cost of processing it is very high. To minimize the high cost of silicon based solar cell, thin film technology solar cells is gaining recognition. Literature is filled with researches on thin film deposition using different techniques. Many publications on binary, ternary and core-shell thin film [4], [1], and [2] exist. Although there are many publications of dye sensitized solar cells. However in this work, thin films of the form SnO:Zn, SnO:Cr and SnO:dye was prepared using the spray pyrolysis technique.

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), A 0.1M, of Cr was equally prepared by dissolving 0.5g of Cr salt in 100ml of distilled water to obtain Cr-ion, 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^oC using the compressor with the air brush at pressure of 22 Pa. These were repeated for 2 different 10ml of the solution at 100^oC and 150^oC 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^oC, 100^oC and 150^oC.

II. 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

Optical properties of the as-grown films were measured using Thermo scientific GENESYS 10S model UV-VIS spectrophotometer. The values of the bandgap were deduced from the transmittance and reflectance spectra.

Bandgap Studies

Figures 1-5 shows the plot of $(\alpha hv)^2$ (eV^2m^{-2}) against hv(eV) for SnO (core), SnO+ 0.1M Zn^{2+}, SnO/ZnS, SnO/CrS and, SnO /dye (1%) deposited at different substrate temperatures of 50°C, 100°C, 150°C and 200°C respectively.

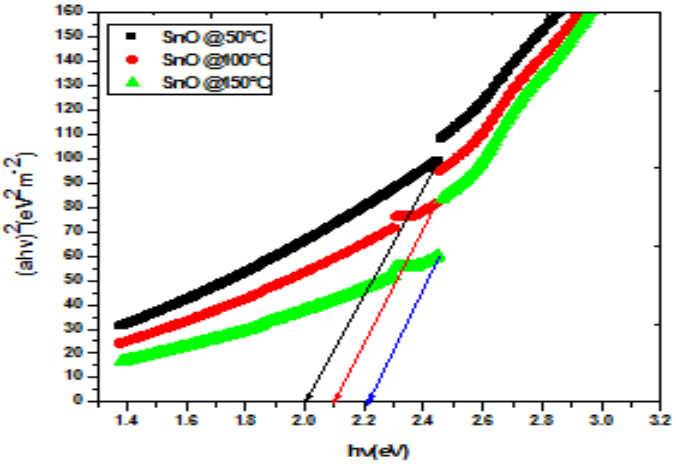

Fig.1: $(\alpha hv)^2$ (eV^2m^{-2}) Vs hv(eV) for SnO (undoped)@ 50°C, 100°,& 150°C

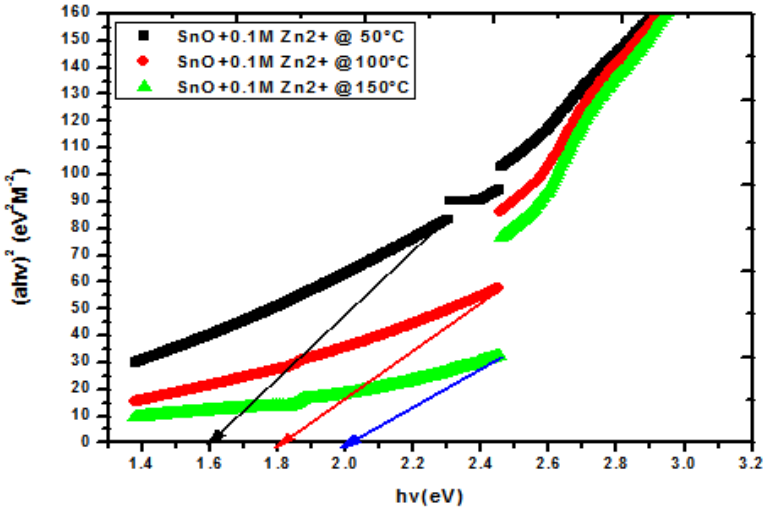

Fig.2: $(\alpha hv)^2$ (eV^2m^{-2}) Vs hv(eV) for SnO+ 0.1M Zn^{2+} (doped) @ 50°C, 100°,& 150°C

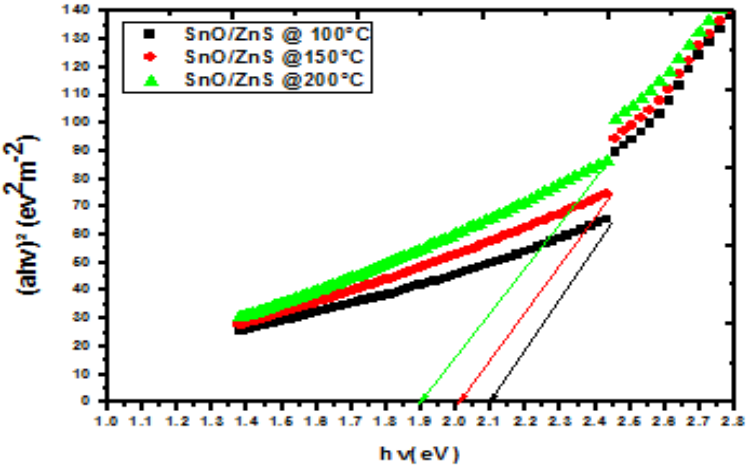

Fig.3. $(\alpha hv)^2$ (eV^2m^{-2}) Vs hv(eV) for SnO/ZnS @ 100°C, 150°C & 200°C

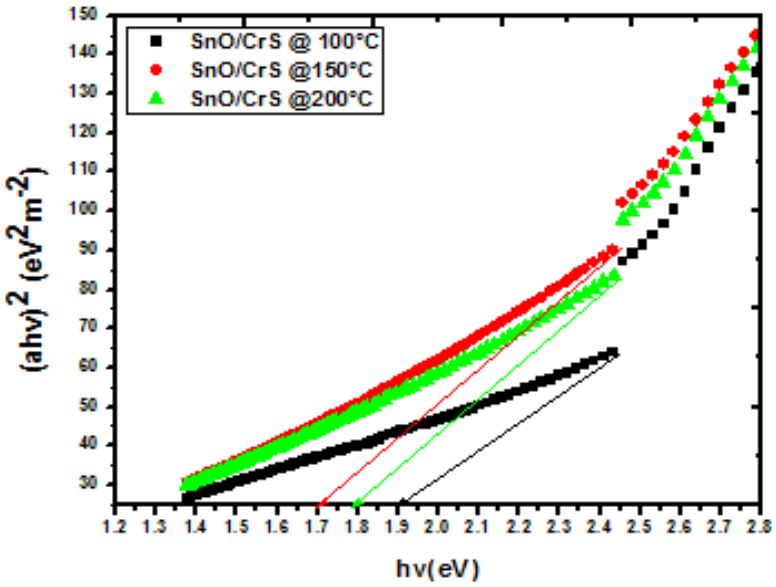

Fig.4: $(\alpha hv)^2$ (eV^2m^{-2}) Vs hv(eV) for SnO/CrS @ 100^OC, 150^OC & 200^oC

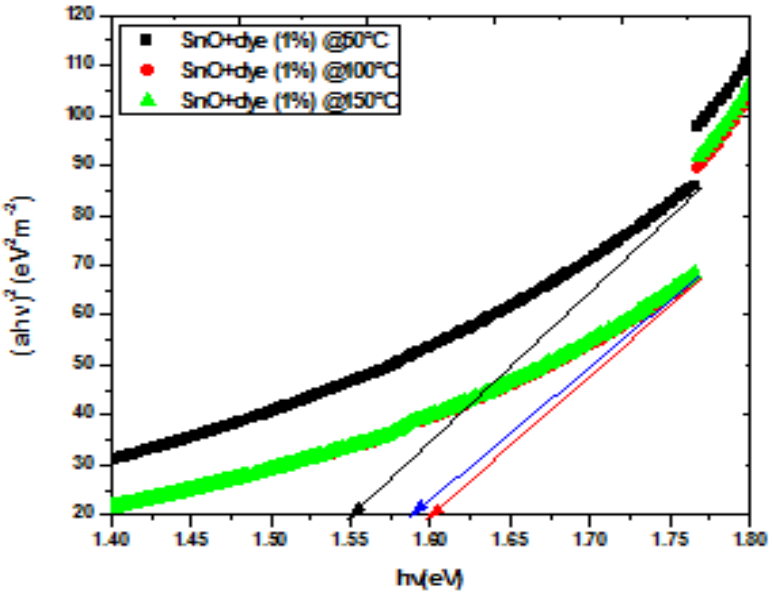

Fig.5: $(\alpha hv)^2$ (eV^2m^{-2}) Vs hv(eV) for SnO /dye (1%) (doped)@ 50^oC, 100^oC & 150^oC

III. Discussion

The direct band gap was extracted by linear extrapolation of α^2 versus hv plot to zero on the energy axis as shown in figures 1-5. The band gap of un-doped SnO films at 50^oC, 100^oC and 150^oC substrate 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 substrate temperatures of 50^oC, 100^oC and 150^oC respectively. The values for Zn^{2+} doped samples showed clear trend with bath temperature variations. When the dopant was changed to natural dye extracts from the leaf of *tectona grandis* at various proportions, the band gap was greatly adjusted. The band gap for 1% doped dye samples at 50^oC, 100^oC and 150^oC bath temperatures are 1.55 eV, 1.58 eV and 1.60 eV respectively. It can be observed that the band gaps of the dye doped samples are lower than those of the Zn^{2+} doped samples. 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. The use of wide band gap materials as window layers in solar cell fabrications is to minimize the recombination loss prevalent in direct band gap semiconductors thereby admitting a maximum amount of light to the junction region and the absorber layer [3]. CdS thin films are widely used as window layer in CIGS solar cells. However, there are great concern about the toxicity of Cd in this architecture [5] and so; several alternative window layers are currently being investigated to replace CdS. In our view, SnO doped Zn^{2+} and dye of leaf of *tectona grandis* deposited in this work stand high for possible incorporation in CIGS solar cell. The evaluated band gap showed a red shift upon doping with the energy band gap decreasing from 1.55 – 1.88eV to 1.60 – 2.22eV for the investigated doping concentration range. Our results when compared with a related study by Srinivasulu *et al* , 2017. Synthesis and characterization of Fe-doped ZnO thin films deposited by chemical spray pyrolysis. The films with lower Fe-doping concentration (≤ 2 at.%) showed wide band gap than the pure and highly Fe-doped ZnO films. The evaluated band gap showed a red shift upon doping with the energy band gap decreased from 3.24 eV to 3.01 eV for the investigated doping concentration range. The above finding agrees with our reported results.

IV. Conclusion

The bandgap energy for SnO is 2.00eV, 2.10eV, and 2.20eV at 50^oC, 100^oC, and 150^oC substrate temperature. The energy band gap increased with substrate temperature indicating a blue shift. The result showed that for biphasic films the bandgap was found in all samples in the neighbourhood of 1.7eV-3.90eV for the different substrate temperature. All the energy band gap of the biphasic films is slightly lower than those of the core. 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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