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Research Paper

Effect of Black Velvet Tamarind Doping on the Optical and Structural Properties of Sol-Gel Grown ZnS Thin Film Crystals

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Abstract—In this work black velvet tamarind doped ZnS thin films were grown using sol-gel method. Sodium silicate, tartaric acid, zinc nitrate (Zn source) and thiourea (S source) were the main starting materials, while solution drops of locally prepared grounded black velvet tamarind shell was used as dopant. The grown thin film crystals of ZnS and VT-doped ZnS were characterized for their optical and structural properties to determine their possible area of opto-electronic applications. The results of the characterizations showed that the grown thin films have high value of absorbance and percentage reflectance in the VIS and NIR regions. The refractive index of the films was also found to be high, in the range of 12.0-20.0, while the percentage transmittance is low but increased with an increase in wavelength. The bandgap energy of the films decreased as the number of VT drops increased. The values obtained from Tauc plots are 3.0, 2.93, 2.81 and 2.70 eV for un-doped ZnS, 1 drop VT/ZnS, 2 drops VT/ZnS and 3 drops VT/ZnS films respectively. The films have crystalline structures and the crystallite size, dislocation density and micro-strain are influenced by VT doping. The EDS results indicated that the target elements Zn and S in addition to O are present in the samples. These properties possessed by the deposited thin films made them good for opto-electronic applications such as photovoltaic cell, LEDs, waveguide, solar collector, fiber-optics etc.

Keywords—Sol-Gel, Velvet Tamarind, Zinc Sulfide, Bandgap, Photovoltaic Cells

1. Introduction

The vast potential applications of zinc sulfide (ZnS) materials have spurred researches into the exploitation of the material for many fields of electronic and opto-electronic applications. Researches have shown that the ZnS has been utilized for fabrications of many devices including Lasers, flat panel display devices, solar cells (buffer layers), electroluminescence, light emitting diodes (LEDs), sensors and detectors, blue light emitting diodes, electroluminescent devices, photovoltaic cells etc., [1-6]. The material has been known to belong to group II-VI compound semiconductors with a direct electronic transition and wide bandgap energy to the tune of at least 3.0 eV depending on the processing conditions, [7-9]. The range of the bandgap energy of ZnS strategically position the material for the overall applications adduced to it. For instance, as a wide bandgap material, ZnS and any related materials can transmit virtually all wavelengths of the solar spectrum, thereby overcoming optical absorption losses at shorter wavelengths and hence quantum efficiency is enhanced, [10]. Among other II-VI semiconductors such as cadmium sulfide, ZnS is highly favored for many applications because of its abundance in nature hence very cheap, non-toxic and thus environmentally friendly, [11]. These attributes have positioned ZnS base materials to taking giant stride to replacing CdS in many application devices. Research has equally shown that ZnS thin film materials exhibit high refractive index value, effective dielectric constant and transmittance in visible region and as such can be utilized as a filter, reflector and planar wave guide device applications, [12]. Two distinct crystal phases of cubic zinc blende (sphalerite) space group F43mc and hexagonal (wurtzite) structures of space group $P6_3mc$ are known to exist for ZnS and these phases have contributed to the diverse application potential of thin film structures of the material, [13]. To advance the device applications of ZnS materials, the thin film structures of the material have been fabricated using several processes. In addition, doping the material using different dopant and depositing the material under different conditions have equally been utilized to advancing the potential use of ZnS for different device applications. To further advance the use of ZnS, here we aimed at using the locally grounded prepared black velvet tamarind shell as dopant to dope the ZnS thin films to determine their effect on the properties of the material using sol-gel method. The choice of the material used as dopant (black velvet tamarind) stemmed from the various properties it possessed, [14, 15].

2. Related Work

In the efforts to advance the device applications of ZnS materials through doping processes using many different preparation methods, the photo-luminescence properties of ZnS and metal (Mn, Cu)-doped-ZnS ceramic powder deposited by wet chemical synthetic route has been reported by [16]. It was found that by incorporating Mn and Cu, ZnS can emits light in the entire visible window. This suggest that the luminescent centers of the host material were transferred to the ions of Mn and Cu. [17] reported chromium doped ZnS crystalline thin films synthesized by pulsed laser deposition by controlling the concentration of dopant and concluded through spectroscopic study that Cr^{2+}/ZnS thin films are promising for middle infrared lasing applications. Properties of Cr-doped ZnS thin films deposited by vapor deposition method with concentration ranging from 10^{18}-10^{20} dopants/cm^3 have also been reported by [18]. They discovered based on their study that low Cr concentration films with uniform composition are of sufficient quality in which short pathlength amplification devices may be possibly fabricated in the near future. Mn-doped ZnS nanocrystals thin film prepared by spin coating have been reported by [19]. The authors found that through PL spectra display blue and orange emission and absorption edge appears at around 250 nm. The films have the direct band gap values which fall within the range 4.43 eV–4.60 eV. They concluded that the spin coating is a simple and very useful method for synthesizing high quality ZnS:Mn nanocrystals thin films and thus a promising low-cost alternative to other high technology methods in the future. [20] used electron beam evaporation method to deposit copper-doped zinc sulfide thin film and studied their Photocatalytic, optical and electrical properties. The transmittance of the deposited films was found by the authors to decreased as a result of Cu doping and energy bandgap decreased from 3.45 to 3.20 eV as the Cu content increased. The film deposited with 3% Cu doping was found to display the best photocatalytic activities and the electrical resistivity decreased from 3.59×10^4 to 7.96×10^{-1} Ωcm with increasing Cu content from x = 3 to 9 at%. Effect of dopant concentration on structural and optical properties Mn doped ZnS films prepared by CBD method has been reported by [21]. The authors declared that doping ZnS improved the optical properties of the thin films by 30 % in the visible region and the best value of transmittance is obtained for ZnS:Mn with 5% Mn in the visible is 83 % while the band gap values are in the range 3.75 to 3.43 eV. [22] used the low-cost nebulizer spray pyrolysis (NSP) method to fabricate zinc sulfide thin films doped with neodymium (Nd/ZnS) on glass substrates at 450 °C and studied their structural, morphological and opto-electrical characteristics. The authors inferred that the Nd/ZnS exhibited polycrystalline hexagonal structure with preferential orientation along (102) plane, have high transmittance of 86% and band gap energy value tuned from 3.51 to 3.60 eV. A high sensitive ZnS thin film doped samarium element for photo-detector applications also deposited using nebulizer spray pyrolysis (NSP) method has equally been reported by [23]. They discovered that the bandgap values of pure ZnS was tuned from 3.48 eV to 3.63 eV for 1.5% Sm doped ZnS thin films. Cobalt-doped ZnS thin films deposited using pulsed laser deposition to study their properties have been reported by [24]. The authors reported that luminescence was observed in the green and red range which were attributed to the native defects or impurities. [25] used chemical bath method to La-doped ZnS thin films and observed that optical transmittance increased up to more than 80% for wavelength above 360 nm in La-doped ZnS thin films. The bandgap energy was found to decreased and flat-band potential shifted to quasi-metal for the La-doped ZnS and concluded based on their results that La-doped ZnS thin films could be valuable material to be adopted as transparent electrodes. The properties of tin-doped ZnS thin films deposited using the chemical bath deposition method and investigated by [26]. The crystallinity and optical transmittance of the films was found to improve while optical bandgap rise from 3.34 eV to 3.90 eV as Sn content increased.

3. Theory/Calculation

In studying various properties of the deposited thin film crystals of velvet tamarind doped zinc sulfide (VT/ZnS) the following properties and others were studied via their theoretical relations

Transmittance: this property of thin films is calculated based on the absorbance values obtained experimentally using the Beer-Lambert relation as given by [27, 28].

$$T = 10^{-A} \quad (1)$$

Where A is the absorbance.

Reflectance: this property is evaluated using the relation as given by [29].

$$R = 1 - \left(\frac{e}{10}\right)^{A/2} \quad (2)$$

Absorption coefficient and extinction coefficient: these properties are calculated using the equations as given by [30, 31].

$$\alpha = \frac{A}{\lambda} \quad (3)$$

$$k = \frac{\alpha\lambda}{4\pi} \quad (4)$$

Refractive index: the refractive index of thin film material is calculated using the relation as given by [32].

$$n = \frac{1+R}{1-R} + \sqrt{\frac{4R}{(1-R)^2} - k^2} \quad (5)$$

Bandgap energy: this other property is a very important property of thin film material and can be estimated from the plot of Tauc relation according to [33].

$$(\alpha h v)^2 = A(hv - E_g) \quad (6)$$

Crystallite size, dislocation density and micro-strain: these properties of material can be evaluated using the modified Scherrer relation and Wilson relation as shown in [34-38].

$$ln\beta = \ln\left(\frac{1}{cos\theta}\right) + \ln\left(\frac{k\lambda}{D}\right) \quad (7)$$

$$\delta = \frac{1}{D^2} \quad (8)$$

$$\varepsilon = \frac{\beta}{4Tan\theta} \quad (9)$$

Where β, θ, λ and k are full weight at half maximum, diffraction angle, wavelength of cu-kα x-ray radiation and shape factor (of constant value 0.9) respectively. The plot of lnβ as a function $\ln(\frac{1}{cos\theta})$ will give intercept (C) as ln(kλ/D). So that D can be estimated as follows, [39].

$$D = \frac{k\lambda}{Exp(C)} \quad (10)$$

4. Materials and Method

The materials used included; Digital weighing balance, 100 ml Glass beakers, 5 ml Measuring cylinder, Magnetic stirrer with hot plate and magnetic bead, Electric oven and Whatman filter paper (110 mm) thick. The reagents used include; zinc nitrate ($Zn(NO_3)_2$), thiourea, sodium silicate, tartaric acid [HOOC $(CHOH)_2$COOH] and locally prepared black velvet tamarind (VT).

The method employed in the fabrication the crystal film samples is Sol-gel method.

4.1 Experimental details

In preparation of undoped ZnS sample, 25 ml of freshly prepared sodium silicate ($NaSiO_3$) solution of pH more than 11.0 was measured into a 100 ml beaker and stirred using magnetic stirrer and then titrated with some quantities of 1 M tartaric acid [$HOOC(CHOH)_2COOH$]. The solution mixture formed gel and its pH indicated about 8.0. 20 ml of zinc nitrate ($Zn(NO_3)_2$ solution was added to the set gel to give zinc-tartanate as follows;

$$Zn(NO_3)_2 + H_6C_4O_6 \rightarrow ZnH_4C_4O_6 + 2HNO_3$$

The zinc-tartanate was generated in the gel as a white column ring system of gradually increasing thickness and the precipitation completed within fortnight. 20ml of freshly prepared thiourea was added to the set gel and covered to obtain ZnS according to the reaction;

$$ZnH_4C_4O_6 + CH_4N_2S \rightarrow ZnS + H_6C_4O_6 + CH_2N_2$$

In preparing the velvet tamarind doped ZnS samples, the above procedure was repeated and pipette drops of freshly prepared solution of smoothly grounded local black velvet tamarind were together added with 10 ml of thiourea unto the zinc-tartanate ($ZnH_4C_4O_6$) and covered for 24 hours to obtain the velvet tamarind doped ZnS (VT/ZnS) crystal films. The doping process were done for one pipette drop, two pipette drops and three pipette drops of the solutions of locally prepared black velvet tamarind (VT) as dopant to obtain 1 drop VT/ZnS, 2 drops VT/ZnS and 3 drops VT/ZnS samples respectively with the details of quantities of tartaric acid and zinc nitrate at which gels were formed as shown in Table 1.

Table 1. Concentration, pH and amount of the precursors used for the growth of ZnS and VT/ZnS crystal.

Samples	Quant. of Na_2SiO_3 (ml)	Quant. of tartaric acid (ml)	Quant. $Zn(NO_3)_2$ (ml)	Quant. of thiourea $CS(NH_2)_2$ (ml)	Quant. of black velvet
A	25.0	10.5	20	10	Zero
B	25.0	11.5	25	10	1 drop
C	25.0	13.5	30	10	2 drops
D	25.0	14.5	35	10	3 drops

The grown sample was first treated with all glass distilled water to avoid impurities and made slurry before, it was introduced into a Buckner funnel covered with filter paper, then attached to a suction flask connected to a vacuum pump through its nozzle. When the pump was put on, it created a vacuum that allowed for the absorption of H_2O from the sample. The filter in the Buckner funnel prevented the solid from being sucked. The sample was then taken to the oven at temperature of 104 ^{O}C for 30 minutes. After which, it was placed inside the desiccators to maintain dryness. $CaCl_2$ was used as a desiccant.

The grown films were subsequently characterized for their optical, structural, morphological and compositional properties using UV-VIS spectrometer, X-ray diffractometer and SEM/EDS machines respectively.

5. Results and Discussion

5.1 Optical properties of the deposited ZnS and VT/ZnS thin films

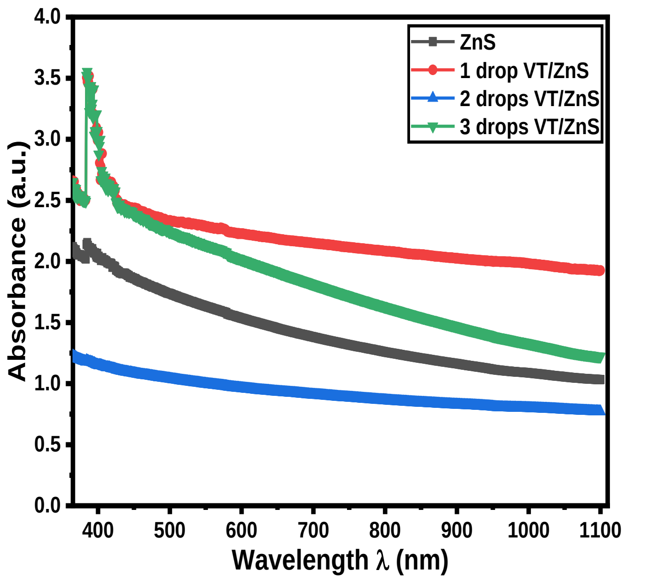

Figure 1. Graph of absorbance against wavelength for deposited ZnS and VT/ZnS thin films

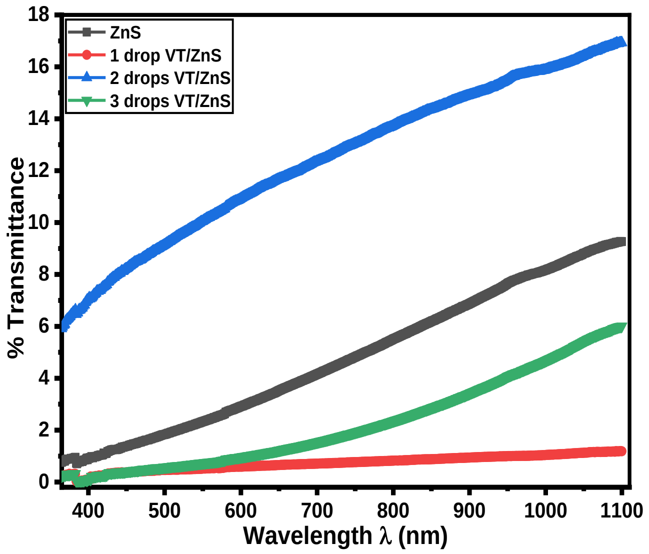

Figure 2. Graph of % transmittance against wavelength for deposited ZnS and VT/ZnS thin films

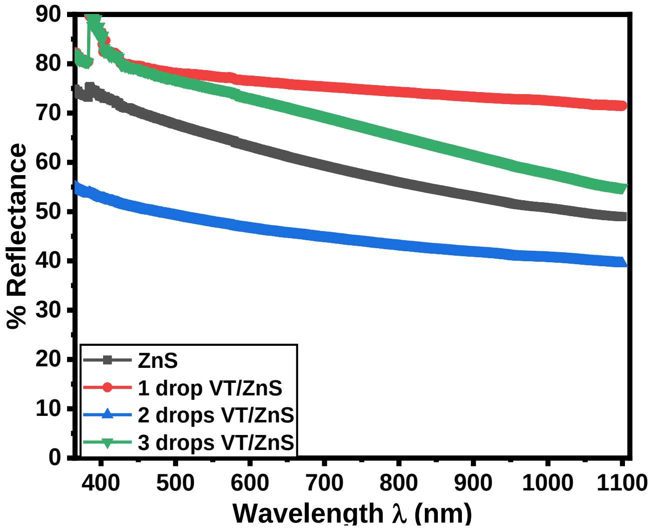

Figure 3: Graph of % reflectance against wavelength for deposited ZnS and VT/ZnS thin films

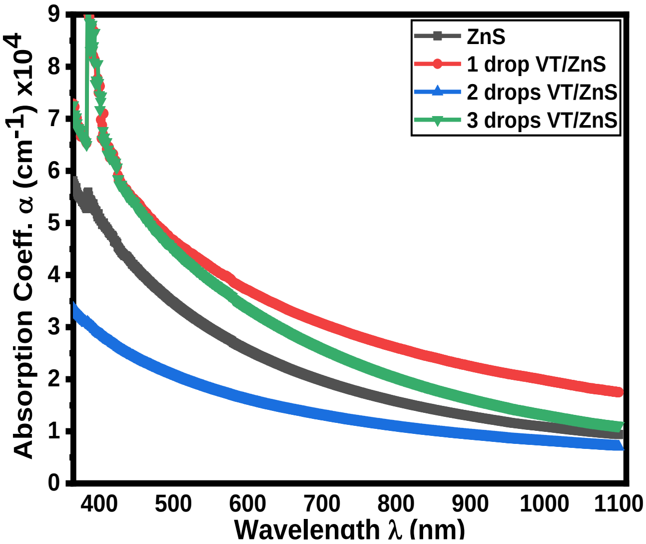

Figure 4. Graph of absorption coefficient against wavelength for deposited ZnS and VT/ZnS thin films

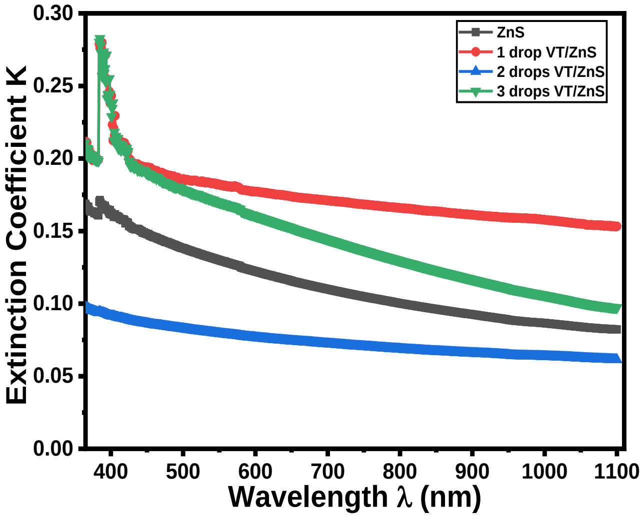

Figure 5. Graph of extinction coefficient against wavelength for deposited ZnS and VT/ZnS thin films

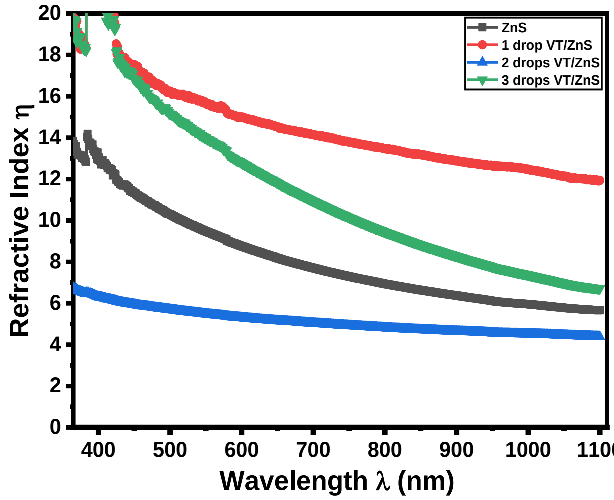

Figure.6. Graph of refractive index against wavelength for deposited ZnS and VT/ZnS thin films

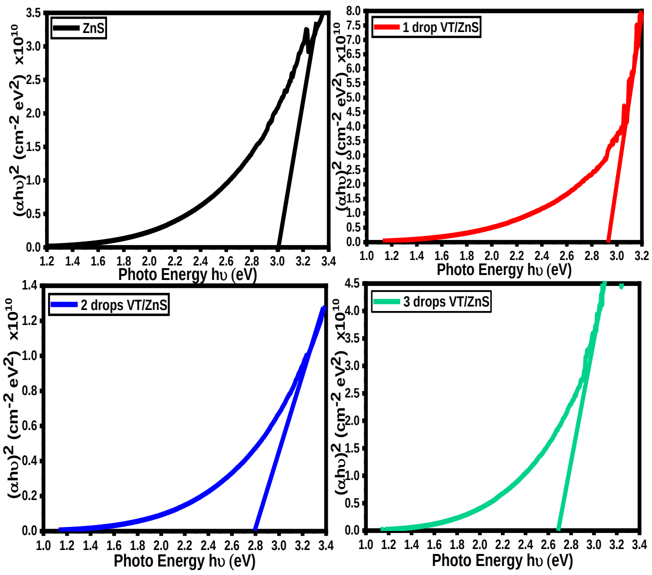

Figure 7. Plots $(\alpha h\upsilon)^2$ against photon energy for deposited ZnS and VT/ZnS thin films

5.2 Structural properties of the deposited ZnS and VT/ZnS thin films

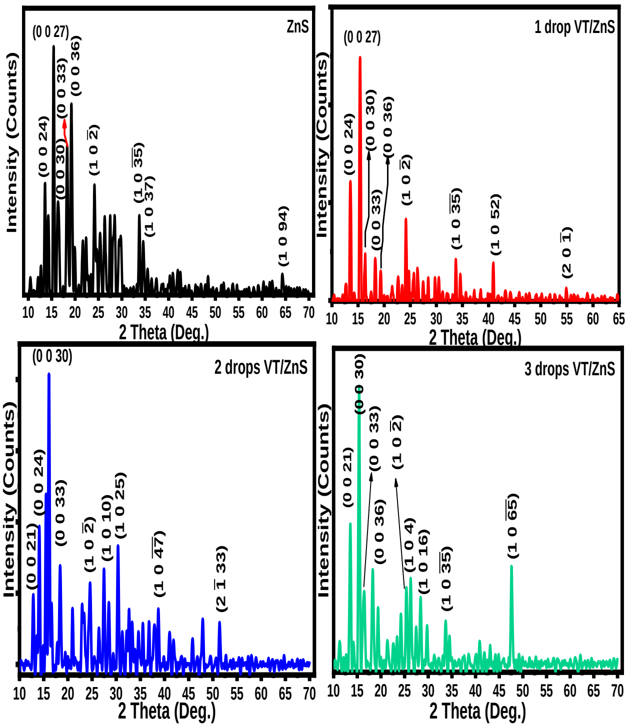

Figure 8. Plots of XRD patterns for deposited ZnS and VT/ZnS thin films

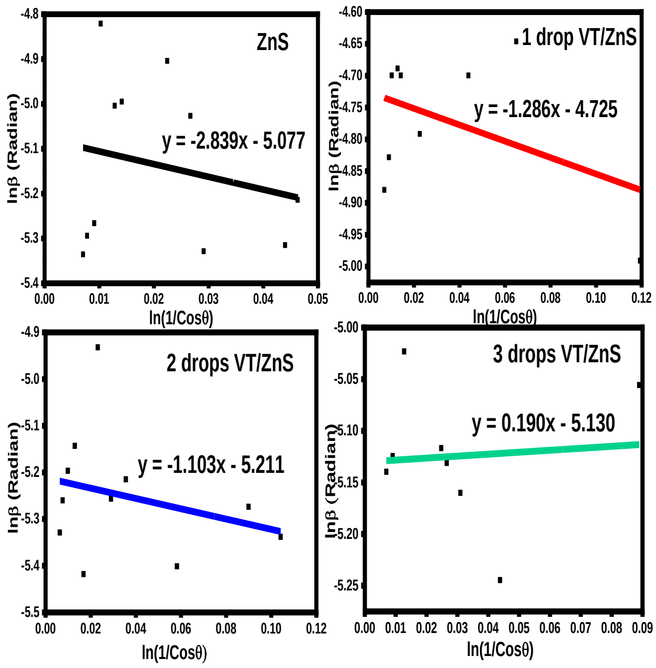

Figure 9. Modified Scherrer plots of the deposited ZnS and VT/ZnS thin films

5.3 Morphological properties of the deposited ZnS and VT/ZnS thin films

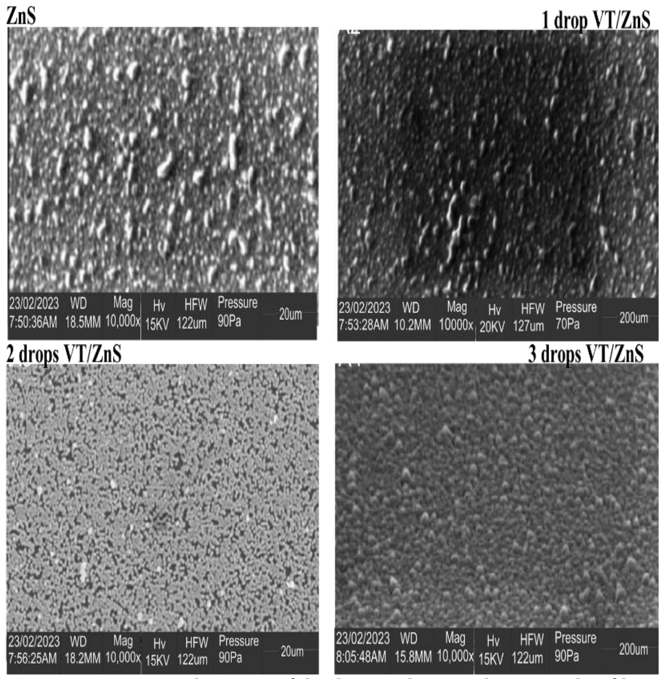

Figure 10. Micrograph images of the deposited ZnS and VT/ZnS thin film crystals

5.4 Compositional properties of the deposited ZnS and VT/ZnS thin films

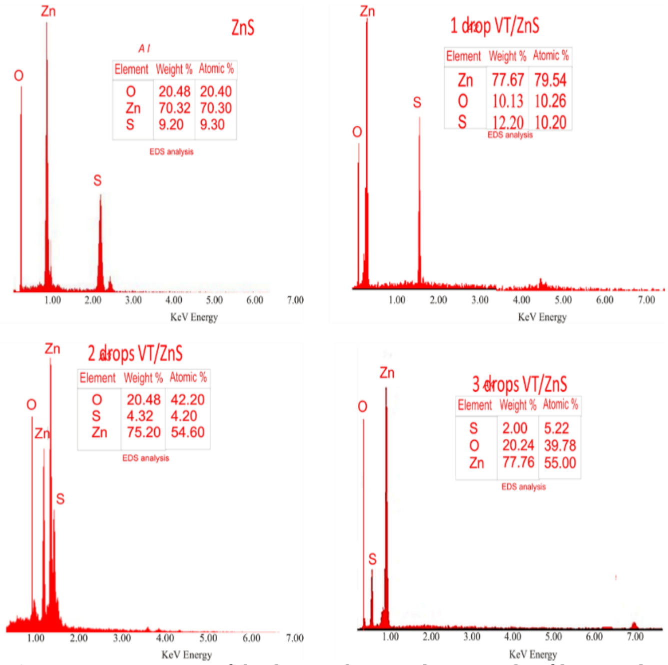

Figure 11. EDS spectra of the deposited ZnS and VT/ZnS thin film crystals

Discussion

Figure 1 is the graph of absorbance as a function of wavelength for the grown crystal films of ZnS and velvet tamarind doped (VT/ZnS). From the figure it was observed that the grown films have high absorbance generally but the absorbance decreases as the wavelength increased. The absorbance of the sample grown with one drop of velvet tamarind is the highest with value in the range of 2.0 to 3.5. This was followed by the sample grown with 3 drops of VT with absorbance in the range of 1.5 to 3.5 while the sample grown with 2 drops VT has the lowest absorbance value in the range 0.75 – 1.2 all throughout the visible and near infrared (VIS/NIR) regions of electromagnetic spectrum. The high absorbance film of this nature for Sn doped ZnS has been reported by [40] and the use of VT as dopant to dope ZnS material can improve its absorbance and the obtained films are suitable for solar collector device applications. Figure 2 is a plot of percentage transmittance as a function of wavelength. The transmittance of the films is very low as indicated in the figure with highest percentage in the range of 6 – 17 % exhibited by the sample 2 drops VT/ZnS. The sample grown with one drop VT (1 drop VT/ZnS) has the lowest transmittance percent in the range (0.5-2%). The transmittance however increased with an increase in the wavelength. The graph of percentage reflectance of the films against wavelength is shown in figure 3. The graph showed that the films have high reflectance but it decreases with an increase in the wavelength. The reflectance of the ZnS films initially increased to the reflectance range of 70 – 90 % with 1 drop VT and then decreased to reflectance in the range 40 – 55 % with 2 drops VT before increasing further to the range of 55 – 90 % with 3 drops VT. The high reflectance positions the deposited films for optical coating applications. Figure 4 is the graph of absorption coefficient against wavelength for the deposited thin films of ZnS and VT doped ZnS. The figure showed that absorption coefficient of the films is generally in the order of 10^4 cm^{-1} and decreased with an increase in wavelength. The absorption coefficient of ZnS films initially increased as a result of doping with one drop of VT and then decreased to lowest value in the range $1x10^3$ to $3.25x10^3 cm^{-4}$ in the VIS/NIR regions with 2 drops VT doping and thereafter increased again to higher value with 3 drops VT doping. The values of absorption coefficient exhibited by the deposited thin films of ZnS and VT/ZnS are in the range for semiconductor materials, [41]. Figure 5 is the plot of extinction coefficient as a function of wavelength. The graph showed that the extinction coefficient of the films is higher in the VIS region compared with the values in the NIR region of electromagnetic spectrum. The film deposited with 1 drop VT has the highest value in the range of 0.17 to 0.29 throughout the VIS/NIR regions while the film 2 drop VT/ZnS has the lowest value among the deposited films. The graph of refractive index against wavelength is shown in figure 6 for the deposited thin films of ZnS and VT/ZnS. The graph showed that the deposited films have high refractive index values in the range of 5.0 to 20.0 but decreased with an increase in the wavelength. The film deposited with 1 drop VT has the highest value in the range of 12.0 – 20.0 while the film (2 drops VT/ZnS) deposited with 2 drops of VT has the lowest value in the range of 5.0 – 6.0 throughout the VIS and NIR regions of electromagnetic spectrum. The high value of refractive index exhibited by the films position them for optical waveguide application since the speed of light in the materials will be greatly lowered. Figure 7 is the plots of $(\alpha h\nu)^2$ against photon energy of the grown crystal films of ZnS and VT/ZnS for determination of bandgap energy. In the figure the bandgap energy of the fabricate film crystals were obtained by extrapolating the straight-line portion of the curves on the photon energy axis at $(\alpha h\nu)^2$ equals to zero. This bandgap energy values obtained are 3.0 eV, 2.93 eV, 2.81 eV and 2.70 eV for 1 drop, 2 drops and 3 drops of VT doping respectively. Similar report for silver doped ZnS that has decreasing bandgap energy values has been reported by [42]. They are high band gap materials and as such can be used in high temperature, and high-power materials, [43,44]. The pattern of the results of XRD analysis carried on the deposited thin films of ZnS and VT/ZnS are displayed in figure 8. The figure indicated that the deposited films are crystalline as there exists various sharp peaks in the patterns. The XRD pattern for un-doped ZnS and all the VT doped ZnS films matched with the standard (JCPDS NO: 00-231-0813) for ZnS with space group (R 3 m:H) and crystal system trigonal (hexagonal axes). The corresponding crystal planes at different two theta Brag angles are as depicted in the XRD patterns of the films. The crystallite sizes of the films at different peak positions were estimated from plots of modified Debye-Scherrer relation (figure 9) and obtained values are 22.23 nm, 15.64 nm, 25.43 nm and 23.43 nm for un-doped ZnS, 1 drop VT/ZnS, 2 drops VT/ZnS and 3 drops VT/ZnS respectively. The values of dislocation density are $2.02x10^{-3}$ nm^{-2}, $4.08x10^{-3}$ nm^{-2}, $1.54x10^{-3}$ nm^{-2} and $1.82x10^{-3}$ nm^{-2} nm for un-doped ZnS, 1 drop VT/ZnS, 2 drops VT/ZnS and 3 drops VT/ZnS respectively. Their corresponding average values of micro-strain obtained are $8.46x10^{-3}$, $1.12x10^{-2}$, $6.66x10^{-3}$ and $7.52x10^{-3}$ for un-doped ZnS, 1 drop VT/ZnS, 2 drops VT/ZnS and 3 drops VT/ZnS respectively.

The SEM micrograph images of the deposited ZnS and VT/ZnS films is shown in figure 10. From the figure, it was observed that the un-doped ZnS film composed of small particle sizes that are densely packed together without pores or hollows in between them. The film also contains some micro rods which were evenly distributed on its surface thereby making it to be rough. The 1 drop VT/ZnS film also contain small particles that are densely packed together without pores in between them. There are also series of micro-rods that were distributed on the surface of the film thereby making its surface to be rough. SEM image of the film 2 drops VT/ZnS contain very tiny particles that were very closely packed together with very small gaps in between them. The surface of the film is however smooth as particles are quite indistinguishable. The film 3 drops VT/ZnS composed of particles that are spherical in shapes and closely packed together without pores in between them. All the films deposited are densely packed together and thus revealing the crystalline nature of the films.

The EDS spectra analysis of the deposited thin films of un-doped ZnS and VT doped ZnS are displayed in figure 11. The figure showed that the target elements Zinc (Zn) and Sulfur (S) in addition to Oxygen (O) were detected in the deposited films. The figure also showed that the weight % of Zn is highest among the elements in all the samples. The atomic % of Zn in the un-ZnS is 70.30 %, 79.54 % for 1 drop VT/ZnS, 54.60 % for 2 drops VT/ZnS and 55.0 % for the 3 drops VT/ZnS film. The atomic % of S in the samples were 9.20%, 10.20%, 4.20% and 5.22% for ZnS, 1 drop VT/ZnS, 2 drops VT/ZnS, 3 drops VT/ZnS films respectively.

6. Conclusion and Future Scope

Black velvet tamarind (VT) doped ZnS crystal thin films have been successfully grown using sol-gel method and characterized in this work to determine the effect of the VT as dopant on the optical and structural properties for possible opto-electronic device applications. The characterization results showed that the optical properties such as absorbance is very high and influenced by the VT doping. The transmittance of the films is low but increased in the NIR region of electromagnetic spectrum. The reflectance of the films increased up to the high percentage range of 70 – 90% for 1 drop VT doping and hence highly favoured for optical coating applications. The grown films have high refractive index values thus positioning them for optical waveguide application since the speed of light in the materials will be greatly lowered. The films have low extinction coefficient which decreased with an increase in wavelength suggesting higher values in VIS region. The optical bandgap energy of the films estimated from Tauc plots are 3.0 eV, 2.93 eV, 2.81 eV and 2.70 eV for the samples un-doped ZnS, 1 drop VT/ZnS, 2 drops VT/ZnS and 3 drops VT/ZnS respectively. These values decreased to the range of bandgap values in the visible range suitable for solar cell/photovoltaic cell device application. The results of structural analysis showed that the grown films are crystalline and the crystallites size, dislocation density and micro-strains of the films are influenced as a result of the VT doping. Our analysis indicates that the film 2 drops VT/ZnS is highly strained with highest micro-strain of 1.12×10^{-2}, dislocation density of 4.08×10^{-3} nm^{-2} and lowest crystallite size of 15.64 nm among the grown films. The SEM results showed that the films contain small particles that are densely packed together without pores in between them and the films 1 drop and 2 drops VT/ZnS contain series of micro-rods that were distributed on their surface thereby making its surface to be rough. The EDS analysis showed that the target elements Zn and S in addition to O were detected in the deposited films with Zn and S having the highest atomic % of 79.54% and 10.20% respectively in 1 drop VT/ZnS. These properties exhibited by the grown films of this nature position them for many opto-electronic devices such as solar cells, optical waveguide coating, LEDs, solar collector device etc.

Drawback

Limited source of fund was one of the major setbacks to the research work. We recommend that other properties like electrical (I-V characteristic), and magnetic, be investigated to determine other suitable areas of applications of the films.

Conflict of Interest

Authors declare that they do not have any conflict of interest.

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Authors' Contributions

The author Uchechukwu A. Kalu performed the experiment for the preparation of the samples subject to their characterisations and subsequent analysis. The authors Okpala U.V. and Okereke N. A. supervised the experimental preceding and subsequently examined the whole work to completion. The author Nwori A.N. did the data analysis, the literature review and wrote the first draft of the manuscript subject to review by the authors Okpala U.V and Okereke N.A. All authors reviewed and edited the manuscript and approved the final version of the manuscript as per the journal template.

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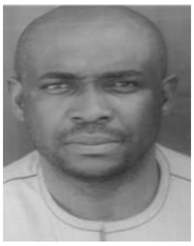

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