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Electrical and optical characterization of $Cd_xZn_{1-x}s$ thin films deposited by chemical bath deposition in alkaline conditions

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Research Paper

***Mosiori Cliff Orori, Njoroge Walter N. and Okumu John**

Department of Physics, Kenyatta University,Nairobi, Kenya.

*Corresponding Author E-mail: cliffmosiori@gmail.com

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In this work ternary CdZnS thin films were prepared by chemical bath deposition by doping CdS with different concentrations of Zn ions. The chemical bath comprised of cadmium nitrate [$Cd(NO_3)_2$], as a source of $Cd^{2+,}$ zinc nitrate [$ZnNO_3)_2$]as source of Zn^{2+}, thiourea [$(NH2)_2CS$] as a source of sulphide ions [S^{2-}]in the presence of ammonia [NH_3] as a complexing agent. The competition mechanisms of Cd^{2+} and Zn^{+2} with the complexing agent [NH_3] to form complex ions usually plays a critical role in the formation of $Cd_xZn_{1-x}S$ thin films and therefore the influence of Zn^{2+} on the formation mechanisms of the $Cd_xZn_{1-x}S$ was discussed. Optical and electrical properties of these samples were analysed. Parameters like band gap (E_g), extinction coefficient (k), absorption coefficient (α), dielectric constant (ε), refractive index, (n)and resistivity (ρ) were calculated using the data obtained from different measurements. Optical band gap tunability of the deposited films for various Zn^{2+} concentrations was successfully demonstrated by UV-VIS-NIR spectroscopy. Transmittance in$Cd_xZn_{1-x}S$was found to be above 80%, optical band gap of 2.47-2.72 eV, refractive index of 2.58 – 2.39, and sheet resistivity of 1.09– 1.36 × 10^2 Ω-cm for *x* = 1.0 – 0.6.

KEY WORDS: Chemical bath deposition, $Cd_xZn_{1-x}S$, ZnS, CdS, electrical and optical properties, refractive index, transmittance.

INTRODUCTION

The growth of ternary semiconductor thin films has been studied extensively in recent years. These films offer a higher performance prospects in semiconductor devices like photovoltaic cells and photo-conducting devices. Cadmium and zinc compounds are direct band gap semiconductor materials suif for photovoltaic applications. Cadmium zinc sulphide ($Cd_xZn_{1-x}S$) has been investigated as an important candidate for a wide band gap material. The replacement of CdS with a higher energy gap ternary $Cd_xZn_{1-x}S$ has led to a decrease in window absorption loss (Oztas and Bedir, (2005) and lattice mismatching with the Cu in GaSe and Cd Techalcopyrite semiconductors. While the band gap of binary compounds can be tuned by changing the particle size, that of ternary semiconductor films can be tuned by changing the percentage composition of its contents. Various techniques have been adopted for the preparation of CdZnS, such as spray pyrolysis, sputtering, vacuum evaporation, metal organic chemical vapour deposition and chemical bath deposition (Saliha, 2009).Among these techniques, chemical bath deposition (CBD) is the most attractive because of its advantageous features over other deposition techniques because it is simple, gives high quality films at low temperatures, requires slow evaporation temperatures and easily coats very large surfaces. CBD deposition of cadmium zinc sulphide is based on a controlled release of the metal ions of Cd^{2+}, Zn^{2+} and sulphide ions (S^{2-}) from thiourea in an aqueous alkaline bath. It is agreed that metal ions and sulphide ions are slowly released owing to the control of the complexing agent to form a thin film on the substrate. Only a few investigations have focused on the influence of growth parameters on the optical and electrical properties of the thin films prepared by CBD for photovoltaic cells. Song et al.,(2005) showed that the grain size of CdZnS films increase with increasing Zn content in the solution and thus influence the optical properties of films. Gaewdang *et al.*(2004) investigated the effects of a mixture ration x ($x = [Zn^{2+}]/[Cd^{2+}+Zn^{2+}]$) on the surface morphology, structure and transmission properties and found it to produce a decrease in the grain size with the increase in mixture ratio. The above investigations suggested that the concentration of Zn ions is an important factor influencing electrical and optical properties of thin films during the CBD process. In this paper, $Cd_xZn_{1-x}S$ films were prepared by chemical doping of CdS with different concentrations of Zn ions where the concentration of Cd^{2+} was fixed while that of Zn^{2+} was varied in the chemical bath. Optical and electrical properties of the samples prepared by CBD were analysed. This study shows how Zn influences these optical and electrical properties of $Cd_xZn_{1-x}S$ thin films.

METHODOLOGY

The chemical bath constituents for the deposition of cadmium zinc sulphide included cadmium nitrate as source of Cd^{2+}, ammonium nitrate, zinc nitrate as source of $Zn^{2+}$and thiourea as source of S^{2}. The bath was composed of 0.038 M cadmium nitrate, 0.076 M ammonium nitrate, and 0.076 M thiuorea in de-ionised water. A 25 ml of the each solution was taken into a separate beaker and de-ionised water added to top up to 100 ml, then heated to about 82° C. Using a burette, NH_4OH (29.4%) was added drop-wise to the mixture to maintain a pH of 9. Glass substrates were inserted at of about 82° C for a deposition time of 25 min. Varying concentrations of zinc nitrate [$Zn(NO_3)_2$] solutions were added to the 100 ml beaker solution to vary zinc ions. The value of x($x = Zn^{2+}/[Cd^{2+} + Zn^{2+}]$) was varied from 1.0 - 0.6 where Zn varied from 0.0-0.4 according to the equation $Cd_xZn_{1-x}S$. A reaction mechanism for the formation of CdS was suggested as below;

$$NH_3 + H_2O \longrightarrow NH_4^+ + OH^- \qquad (1)$$

(a) Cadmium salts in the ammonium hydroxide solution form the complex compounds as:

$$Cd(NO_4)_2 + 4(NH_3)Cd \longrightarrow (NH_3)_4[NO_3]_2$$

$$Zn(NO_4)_2 + 4(NH_3) \longrightarrow (Zn(NH_3)_4)[NO_3]_2 \qquad (2)$$

$$Cd(NH_3)_4^{2+} \longrightarrow Cd^{2+} + 4NH_3 \qquad (3)$$

$$Cd(OH)_2 \longrightarrow Cd^{2+} + 2(OH)^-$$

$$Zn(OH)_2 \longrightarrow Zn^{2+} + 2(OH)^- \qquad (4)$$

(b) From thiourea as a sulphide-ion source in an alkaline medium, the sulphide ions are to be released slowly as follows:

$$(NH_2)_2CS + 3OH^- \longrightarrow 2NH_3 + CO_3^{-2} + S \qquad (5)$$

$$SH^- + OH^- \longrightarrow S^{-2} + H_2O \qquad (6)$$

(c) Cadmium ions will then react with Sulphide and zinc ions to form $Cd_xZn_{1-x}S$ from equations (3),(4), and (6):

$$x\,Cd^{+2} + (1-x)Zn^{2+} + S^{-2}\ Cd_x \longrightarrow Zn1\text{-}xS \qquad (7)$$

Reactions in eq.1 to 7 are interrelated and indeed the ammonia concentration present affects the concentration of cadmium ions Cd^{+2}, the precipitation of cadmium hydroxide [$Cd(OH)_2$], the concentration of the tetra-ammine-cadmium complex ion [$Cd(NH_3)_2^{+2}$], and the concentration of hydroxide ions [OH^-]. Electrical properties were studied using a four point probe connected to Kethley 2400 source meter interfaced with a computer using Labviewprogram while optical transmittance was measured using UV-VIS-NIR spectrophotometer 3700.

RESULTS

Optical properties

Films obtained by this method were smooth, uniform, adherent, bright yellow orange in colour where the yellowness decreased with increasing zinc content. CdS films had the highest reflectance and least transmittance below 24% and 75% respectively. $Cd_{06}Zn_{04}S$ films had the least reflectance in the visible range (figure 1a,b,c and d). Doping the films using Zn reduced reflectance and absorbance but increased transmittance within the visible and infrared range. Refractive index (n) was calculated using the equation proposed by Ravindra *et al.,* (2005) as

$$n = [(1+R^{1/2})/(1-R^{1/2})] \qquad (8)$$

and one that relate optical refractive index (n) and energy band gap (E_g) as;

$$n = 4.08 - 0.62E_g \qquad (9)$$

to give values shown in Table 1. It was observed that refractive index decreased with increase in Zn concentration and this explains why the colour of the films faded as concentration increased. Dielectric constants are used to describe any losses caused by

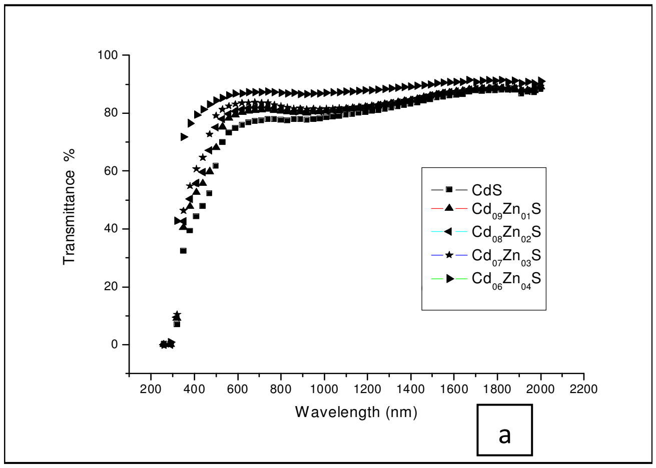

Figure 1a Optical properties of $Cd_xZn_{1-x}S$ (x = 1.0 to 0.6).

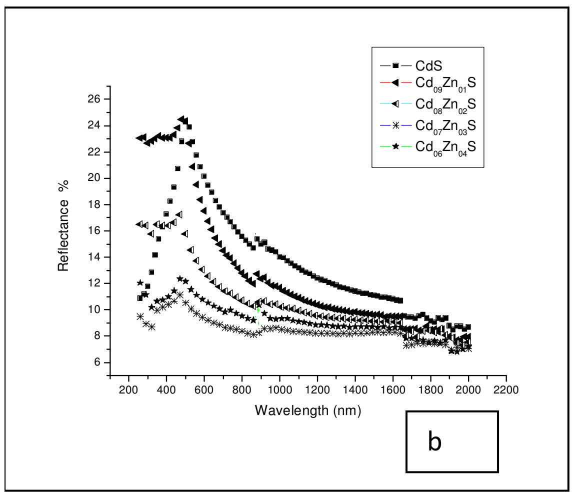

Figure 1b. Optical properties of $Cd_xZn_{1-x}S$ (x = 1.0 to 0.6).

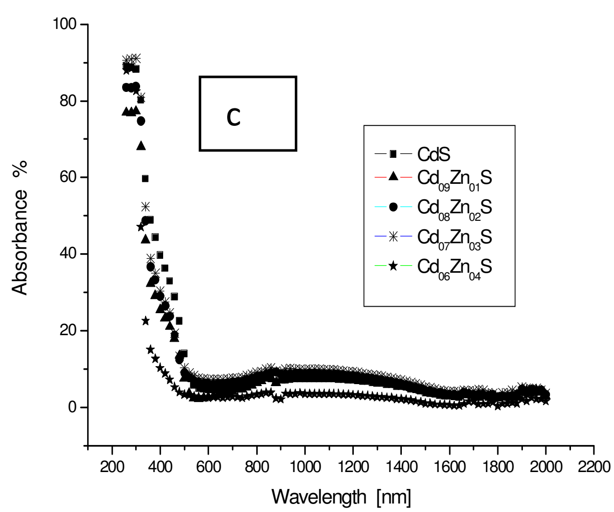

Figure 1c. Optical properties of $Cd_xZn_{1-x}S$ (x = 1.0 to 0.6).

Table 1. Optical and electrical properties of $Cd_xZn_{1-x}S$.

Film	Conc. of *Zn*	(n)	E_g[eV]	ρ[Ω-m]
$Cd_{06}Zn_{04}S$	0.4	2.39	2.72	136.19
$Cd_{07}Zn_{03}S$	0.3	2.41	2.69	122.91
$Cd_{08}Zn_{02}S$	0.2	2.46	2.60	116.98
$Cd_{09}Zn_{01}S$	0.1	2.51	2.52	109.37
CdS	0.0	2.53	2.47	113.56

State the meaning for n and if it has a unit indicate it.

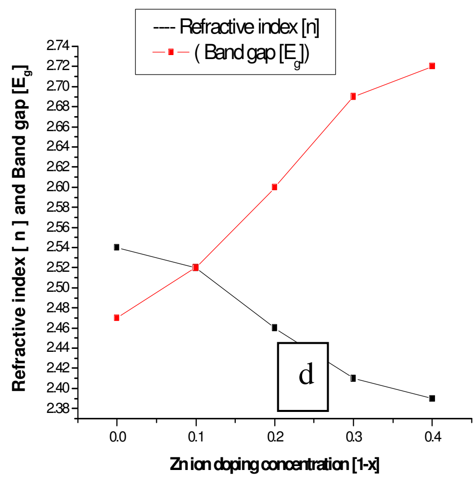

Figure 1d. Optical properties of $Cd_xZn_{1-x}S$ (x = 1.0 to 0.6).

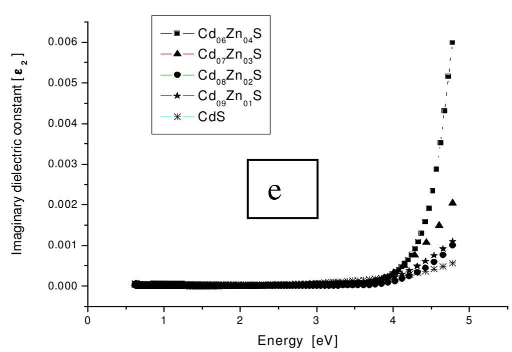

Figure 1e. Optical properties of $Cd_xZn_{1-x}S$ (x = 1.0 to 0.6).

optical conductivity (σ) in thin films where real and imaginary parts of the dielectric constant are given by;

$$\varepsilon_c = \varepsilon_r + \varepsilon_i \quad (10)$$

and they were estimated using the relations;

$$\varepsilon_1 = n^2 - k^2 \quad (11)$$

$$\varepsilon_2 = 2nk \quad (12)$$

The dielectric constant (ε) reduced as wave length increased at a constant Zn concentration and it explains why there are high optical conductivity loses at longer

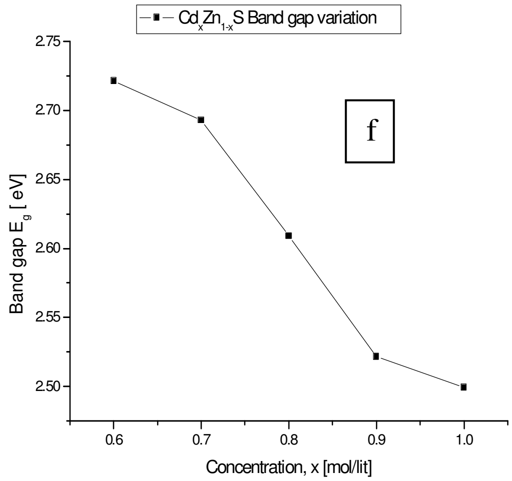

Figure 1f. Optical properties of $Cd_xZn_{1-x}S$ (x = 1.0 to 0.6).

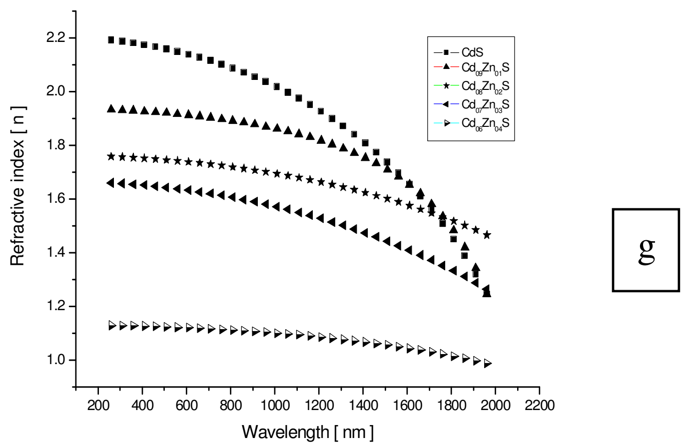

Figure 1g. Optical properties of $Cd_xZn_{1-x}S$ (x = 1.0 to 0.6).

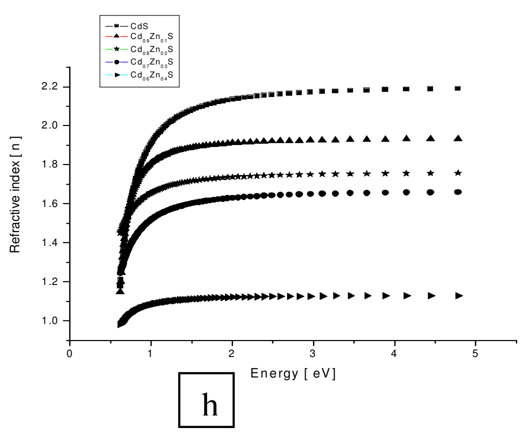

Figure 1h. Optical properties of $Cd_xZn_{1-x}S$ (x = 1.0 to 0.6).

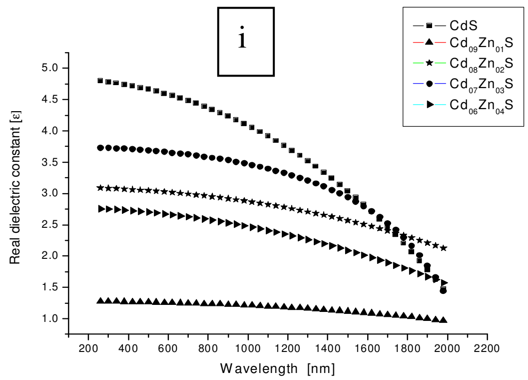

Figure 1i. Optical properties of $Cd_xZn_{1-x}S$ (x = 1.0 to 0.6).

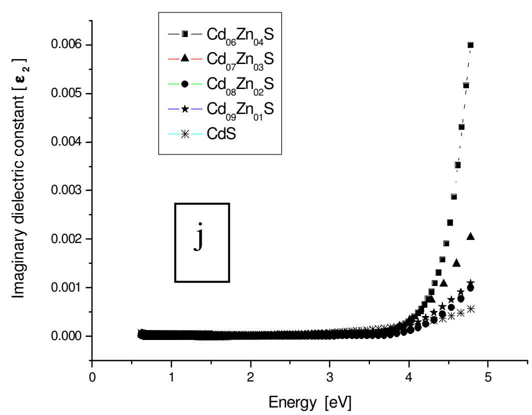

Figure 1j. Optical properties of $Cd_xZn_{1-x}S$ (x = 1.0 to 0.6).

wavelengths (figure 1 f and g).The absorption coefficient (α) was calculated using the equation;

$$\alpha = 2.303A/d \quad (13)$$

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

$$k = \alpha\lambda/4\pi \quad (14)$$

The both coefficients were very small over a wide range of wavelengths (figure 1 h, i and j) and as such very low photon energy absorption losses are experienced and thus form high quality window layer materials. Similar transmittance results have been reported (Kumar and,(2009), Kasim *et al.* (2008), Saliha, (2009),Vidhya and Velumeni, (2009) as 90%, 80%, 79% and 65% respectively in the wave length range of 300 – 1200 nm. Band gap was determined by drawing a graph of $(\alpha hu)^2$ versus the photon energy (*hu*) plot.The intercept of the curve with the photon energy (*hu*) axis gave a direct band gap by the Ugwu and Onah, (2007) relation:

$$\alpha = (hv - E_g)^{1/2} / hv \quad (15)$$

where *h* is Planck's constant and *hv* is the photon energy. They were obtained by extrapolating their linear portions of the plots $(\alpha hv)^2$ versus *hv* to α= 0. They were compared those obtained by modelling the Vergard's equation; $E_g = [2.42 + 0.69x + 0.62x^2]$ eV (16).

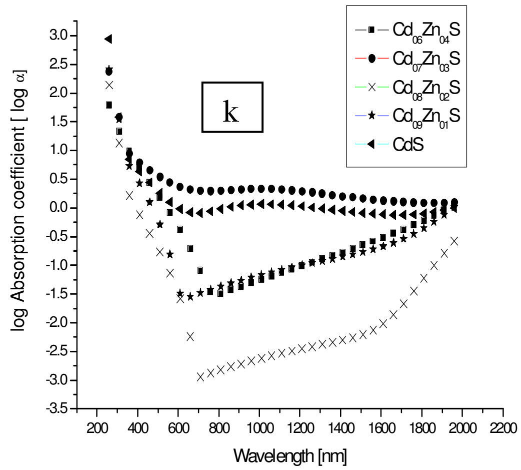

Figure 1k. Optical properties of $Cd_xZn_{1-x}S$ (x = 1.0 to 0.6).

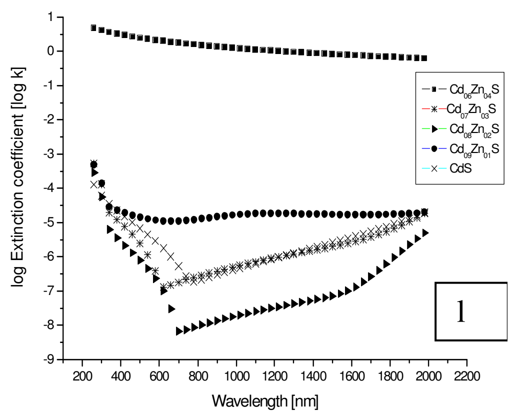

Figure 1l. Optical properties of $Cd_xZn_{1-x}S$ (x = 1.0 to 0.6).

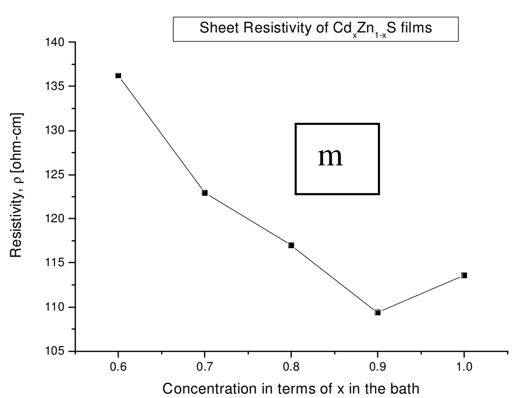

Figure 1m. Optical properties of $Cd_xZn_{1-x}S$ (x = 1.0 to 0.6).

where the value of *x* was modified from the 'x' to '(1-*x*)' such that equation (12) appeared as eq. (13)

$$E_g=[2.42 +0.69(1-x) +0.62(1-x)^2]eV \quad (17)$$

The shift of absorption edge toward shorter wave lengths was due to increasing Zn giving rise to an increase in energy gap (Figure 1 k, l and m). The presence of the energy gap for pure CdS phase of about 2.43 eV seems to be independent of the Zn ratio (*x*) and conversely, $Cd_xZn_{1-x}S$ phase presents the variation of energy gap from 2.50 to 2.72 eV when Zn ratio increases from 0.1 to 0.4. Table I shows that doped films had higher band gaps than pure CdS films. $Cd_{06}Zn_{04}S$ had the greatest band gap of 2.72 eV while CdS had the least value of 2.47 eV (figure 1e). This values agreed with Dzhafarov *et al.* (2006)'s value of 2.64 eV for heavily doped $Cd_xZn_{1-x}S$ films and Kasim*et al.* (2008) with an optimized value of 2.49 eV. Wider band gaps have been reported by Kumur and Sankaranayanan, (2009), Bacaksiz, (2006), (Vidhya and Velumini, 2009) and (Saliha, 2009) as 2.92 eV - 3.26 eV, 3.1 eV - 3.9 eV, 2.50 eV - 2.67 eV and 2.47 eV - 3.04 eV respectively.

CONCLUSION

$Cd_xZn_{1-x}S$ films were successfully prepared by solution doping of CdS with different concentration of Zn ions. The concentration of Cd^{2+} remained fixed which rendered it possible to understand the effect of Zn ion concentration on the growth mechanism of the CdZnS film. The low processing temperature used in $Cd_xZn_{1-x}S$ proposes that $Cd_xZn_{1-x}S$ as window material could be used to fabricate devices at low temperatures. Increase in transmittance was due increase in Zn ions in the bath resulting to band gaps of 2.47-2.72 eV. Refractive index decreased with Zn increase in the bath. Resistivity of the films increased with the increase in Zn concentration. The films were suitableas window layers for solar cells and opto-electronic devices.

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