

SYNTHESIS AND CHARACTERIZATION OF TERNARY CuSbS_2 THIN FILMS: EFFECT OF DEPOSITION TIME

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Thin films of CuSbS_2 have been grown on glass substrate using the chemical bath deposition (CBD) technique at room temperature. The chemical bath for the deposition of CuSbS_2 is made up of antimony chloride (SbCl_3), sodium thiosulphate ($\text{Na}_2\text{S}_2\text{O}_3$) and copper chloride (CuCl_2). In this present work, these films were deposited at different dip time and characterized for the structural, morphological and optical properties. These properties were studied by means of X-ray diffraction (XRD), optical microscope and optical spectrophotometer for their potential application in solar energy devices. The optical properties revealed the presence of direct band gaps with energies in the 1.30 to 2.30eV range. The result shows that deposition time influences both the optical properties and band-gap energy of the films.

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1. Introduction

The properties of ternary and binary thin films prepared by various techniques such as spray pyrolysis, molecular beam epitaxy, electrodeposition, chemical bath deposition and chemical vapour deposition have been reported [1-3]. The metal-metal chalcogenides are increasingly studied in the search for new semiconductor materials for efficient solar energy conversion through photo-electrochemical solar cells [4-5]. Large area thin film semiconductor materials have been found useful generally in the areas of optics, optoelectronics, microelectronics, thermal devices, surface engineering, integrated circuits, etc [6-8].

Chemical bath deposition of semiconductor thin films is by now recognized as a versatile low-cost method to produce thin films of I-VI, II-VI, III-V, IV-VI and V-VI compounds. This technique is the most cost saving, convenient and simple, which is highly reproducible. It makes use of the fact that films can be deposited on substrates whether metallic or not by dipping them into suitable solution baths containing metal salts without applying any external field. This technique has been employed extensively by various authors to synthesis thin films of antimony sulphide in the form of binary [6, 9-13], ternary [14] or as a stack of two binary compounds [15-18]. Most of the reported ternary thin films involving antimony sulphide have been achieved through annealing of chemically deposited stack of two binary compounds [15-17].

In this present work, chemical bath deposition was employed to deposit directly ternary thin films of CuSbS_2 at different deposition time (different dip time). The effect of dip time on the optical properties and band gap energy of the deposited films were then studied for possible photovoltaic application.

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2. Experimental details

Glass microscope slides were cleaned by degreasing them in concentrated hydrochloric acid for 24 hours, washed in detergent solution, rinsed in distilled water and dried in oven at 30°C above room temperature. The bath constituents for deposition of CuSbS_2 thin films were antimony trichloride (SbCl_3), acetone, sodium thiosulphate ($\text{Na}_2\text{S}_2\text{O}_3$) and copper II chloride (CuCl_2).

In a typical deposition set-up, the chemical bath was composed of 1.3g of SbCl_3 dissolved in 5ml of acetone, 25ml of 1M $\text{Na}_2\text{S}_2\text{O}_3$, 5ml of 0.1M CuCl_2 and 15ml of H_2O put in that order into 50ml beaker. Four experimental set-up were made with each containing clean microslide, inserted vertically through synthetic foam. The deposition was allowed to proceed at room temperature for different dip time after which the coated substrates were removed, washed well with distilled water and allowed to dry. The deposited films were labelled based on the dip time: A(1.0 hour), B(1.5 hours), C (3.0 hours) and D(3.5 hours).

The thin films on glass substrate were characterized by optical microscope (at magnification of 200x) for the surface morphology. The X-ray diffraction (XRD) analysis was carried out using Philips PW 1500 X-ray diffractometer of $\text{CuK}\alpha$ wavelength (1.5408Å). The composition of the films were also determined by using energy dispersive x-ray fluorescence (ED XRF). Optical properties of chemical bath deposited CuSbS_2 thin films were measured at room temperature by using Unico-UV-2102PC spectrophotometer with glass substrate as a reference in the wavelength range of 200–1000 nm.

3. Results and discussion

3.1. Thickness variation

Fig. 1 shows the thickness of the CuSbS_2 thin films obtained at different dip time. The figure shows a gradual increase in the thickness of the films as deposition time increased, an indication of homogeneous precipitation process taking place with time.

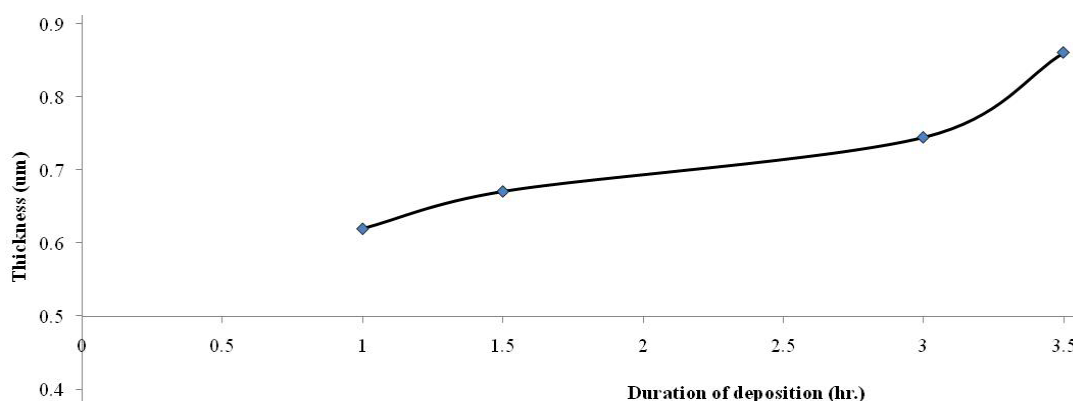
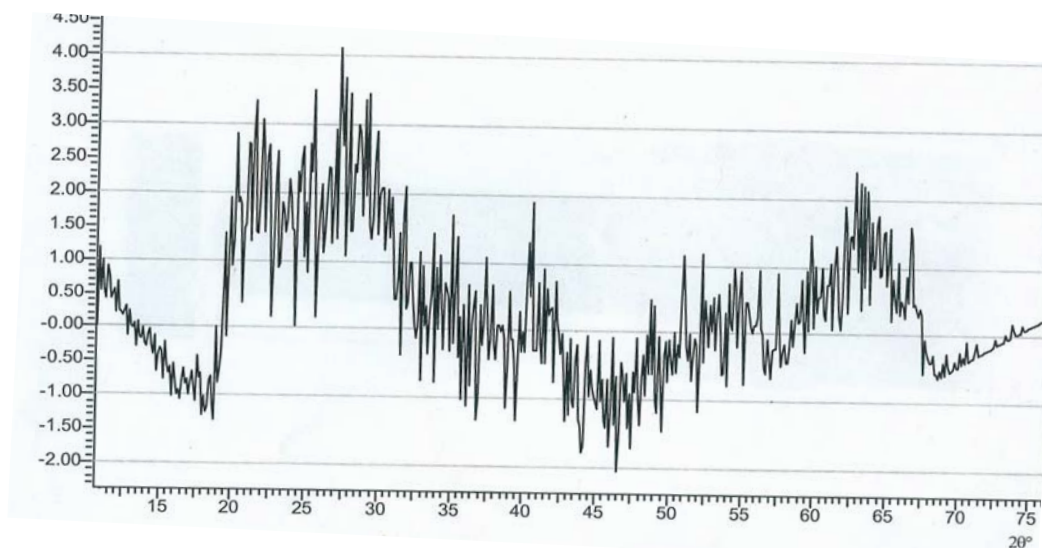


Fig. 1. Thickness vs. deposition time for CuSbS_2 thin films.

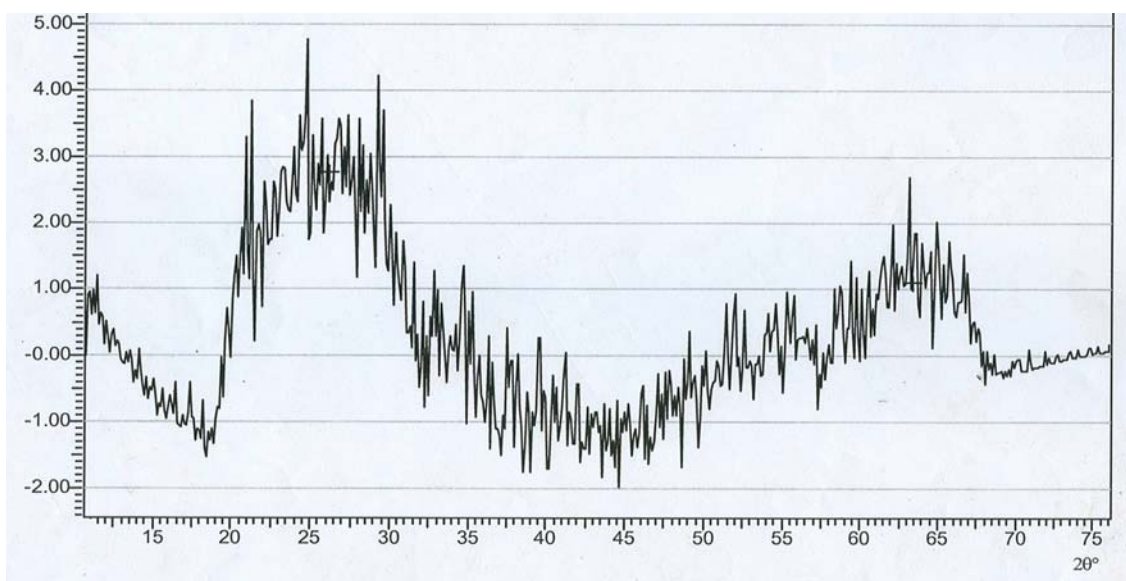
3.2. X-ray diffraction study

Fig. 2 shows the XRD patterns of CuSbS_2 thin films deposited in this work at different dip time. Peak broadening has been observed in recorded diffraction patterns, which shows the formation of crystalline thin films. A close examination of the two diffractograms show an

improvement in the crystallinity of the films as deposition time increases. A comparison between the spectra of the two films in (a) and (b) show that there is more crystallization and more orientation of the crystal growth in the case of the film deposited at 3.0 hrs dip time. The lines became more stronger with slight preferential orientation ($2\theta = 24.42^\circ$) which corresponds to (400) plane (JCPDS 44-1417).



a. Film grown at 1.0 hour dip time



b. Film grown at 3.0 hours dip time

Fig. 2. XRD pattern for CuSbS_2 thin films.

The crystalline grain size was calculated using the Scherrer formula on the (400) peak. From the Scherrer formula, the grain diameter,

$$D = 0.89 \lambda / \beta \cos \theta, \quad (1)$$

where D is the average crystallite size, λ is the wavelength of the incident X-ray, β is the full width at half maximum of X-ray diffraction and θ is the Bragg's angle. The crystallite size for the thin film of CuSbS_2 was found to be 19.54 nm.

3.3. Surface morphology

The surface microstructure of the films were obtained by taking the photomicrograph of the films coated on the transparent glass slide with wide KPL-W10x/18 Zeiss Standard 14 photomicroscope with M₃₅ 4760+2-9901 camera at a magnification of X200. The photomicrographs of the films are displayed in figure 3. A close observation of the optical micrographs of SbCuS_2 thin films show a decrease in grain size as dip time increases. This resulted to increase in crystallinity of the film as is evidence in the XRD displayed in figure 2. However, there is evidence of the presence of pin holes in the samples which became less pronounced as deposition progressed. The figure also shows greater copper population in the deposited thin films as dip time increased from 1 hour (micrograph not shown here) to 3.5 hours.

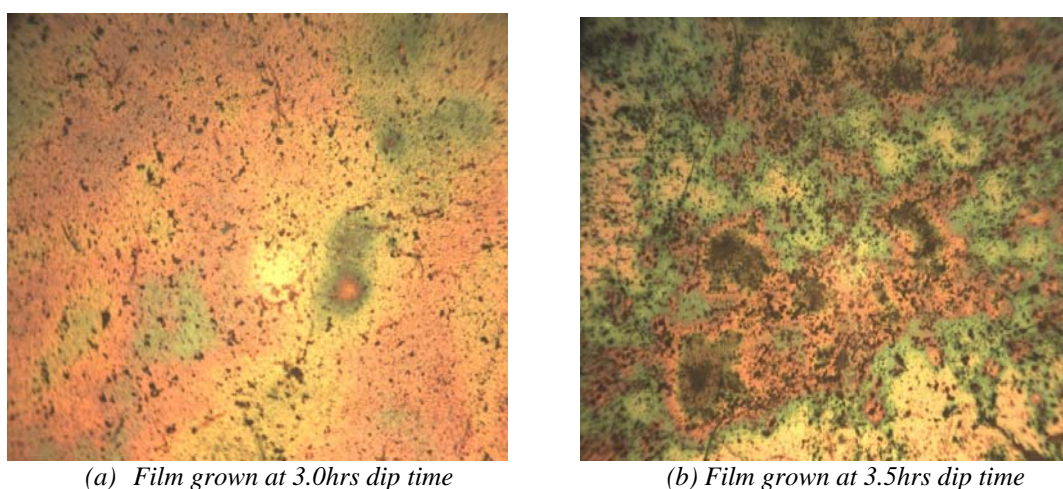


Fig. 3. Optical micrographs of CuSbS_2 thin films at different dip time.

3.4. Composition study

The elemental composition and chemical states of the films under study was analyzed by Energy dispersive x-ray fluorescence (EDXRF). The EDXRF of CuSbS_2 thin films deposited at different dip time are shown in Table 1. The concentration of Sb and Cu can be seen in table 1a and 1b. The presence of sulphur can not be detected by the instrument used for this analysis. Other elements present in the table may have come from the glass slide used for the deposition of the films.

Table 1a: CuSbS_2 thin film grown at 1.0hr dip time.

Analysed elements:

El	counts	compound	conc	
K Ka	2894 ± 72	K	1.779 ± 0.654	%w
Ca Ka	29239 ± 334	Ca	5.412 ± 1.896	%w
Ti Ka	799 ± 42	Ti	279.292 ± 110.189	ppm
Mn Ka	365 ± 53	Mn	46.279 ± 17.513	ppm
Fe Ka	10969 ± 120	Fe	1343.252 ± 470.119	ppm
Ni Ka	778 ± 66	Ni	121.753 ± 45.118	ppm

Cu Ka	2690 ± 83	Cu	531.831 ± 186.763 ppm
Zn Ka	548 ± 68	Zn	142.820 ± 53.322 ppm
Sr Ka	532 ± 59	Sr	362.200 ± 136.808 ppm
Cd La	1879 ± 110	Cd	8781.506 ± 1221.718 ppm
Sb La	2844 ± 165	Sb	7371.695 ± 771.016 ppm

Table 1b. CuSbS_2 thin film grown at 3.5hr dip time.

Analysed elements:

El	counts	compound	conc
K Ka	3055 ± 75	K	1.878 ± 0.687 %w
Ca Ka	31265 ± 352	Ca	5.787 ± 2.029 %w
Ti Ka	825 ± 44	Ti	288.381 ± 118.656 ppm
Cr Ka	138 ± 47	Cr	<21.733
Mn Ka	564 ± 56	Mn	71.510 ± 26.856 ppm
Fe Ka	11657 ± 123	Fe	1427.504 ± 500.395 ppm
Ni Ka	1305 ± 71	Ni	204.225 ± 73.730 ppm
Cu Ka	4171 ± 95	Cu	824.634 ± 290.261 ppm
Zn Ka	920 ± 73	Zn	239.771 ± 88.789 ppm
Sr Ka	349 ± 65	Sr	237.609 ± 94.093 ppm
Cd La	1641 ± 121	Cd	8781.506 ± 1221.718 ppm
Sb La	4809 ± 176	Sb	1.247 ± 0.082 %w

3.5 Optical Studies and band gap analysis

Absorbance and transmittance spectra data of the deposited thin films are displayed in figures 4 and 5 respectively. The absorbance and transmittance depend on the deposition time and the wavelength.

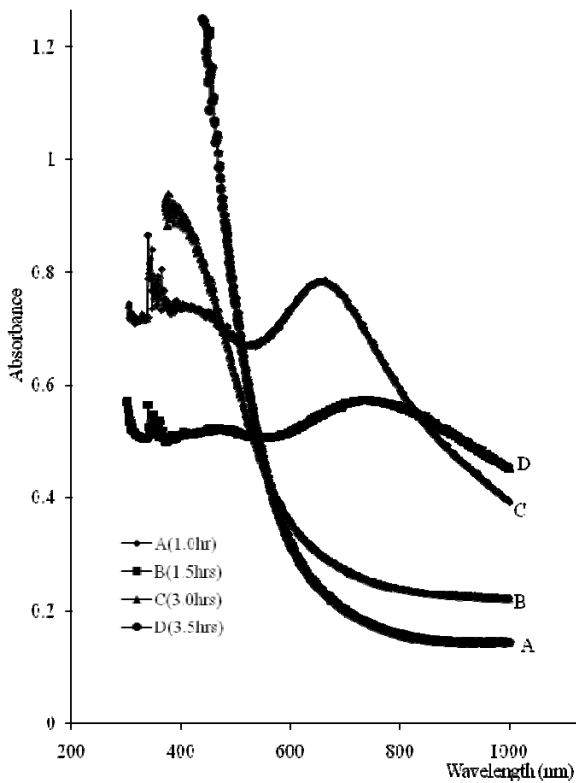


Fig.4. Absorbance vs. wavelength for CuSbS_2 thin films at various dip time

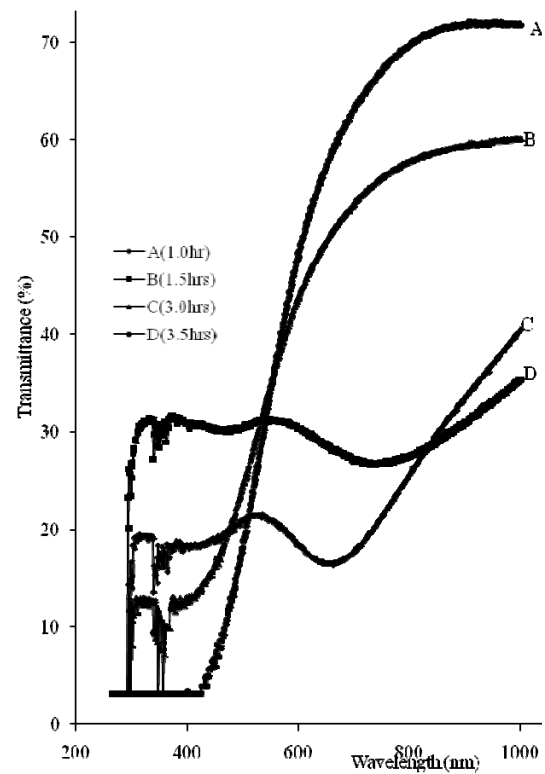


Fig.5: Transmittance vs. wavelength for CuSbS_2 thin films at various dip time.

From Fig. 4, we observe strong absorption of incident radiation in the visible portion of solar spectrum. The figure reveals a twist in the trend of the films' absorbance as the dip time increases. At wavelength of between 300 – 500nm, films deposited at lower dip time have the highest absorbance but as we approach the NIR regime, the reverse becomes the case. This indicates easy control of application area by simply choosing appropriate deposition time during the film growth. Thin films with high absorption coefficient in the visible portion of the solar radiation and a direct allowed band gap of about 1.9eV or less has been regarded as a promising absorber for thin film photovoltaic applications [19]. A close observation of figure 5 shows that transmittance generally increases with wavelength and decreases with dip time. This implies that the transmittance is higher if the dip time is low. It has been observed that the thickness of thin solid films in which the film formation and kinetics takes place ion by ion condensation has a linear relationship with deposition time [20, 21]. Hence, the observed differences in transmission are only due to difference in thickness but also to fundamental differences in film absorption. Figure 5 also shows that the films deposited below two hours have high transmittance of above 50% in the NIR region of the solar spectrum. The property of high transmittance in the NIR exhibited by the films therefore makes them good materials for the construction of poultry roofs and walls. This will allow maximum infrared radiation to warm the chicks during the day thereby reducing the high cost on energy required in poultry houses.

Fig. 6 shows typical curves of the energy versus the squared absorption coefficient for thin films of CuSbS_2 . The fundamental absorption which corresponds to the electron excitation from the valence band to the conduction band can be used to determine the nature and value of the optical band gap. The relation between the absorption coefficient (α) and the incident photon energy ($h\nu$) can be written as [22]

$$(\alpha h\nu)^{1/n} = A(h\nu - E_g) \quad (2)$$

where A is a constant, E_g is the band gap of the material and the exponent n depends on the type of transition. The values of n for direct allowed, indirect allowed and direct forbidden transition are $n = 1/2, 2, 3/2$ respectively. The direct band gap of the films were obtained from the linear portion of $(\alpha h\nu)^2$ versus $h\nu$ plot as shown in Fig. 6.

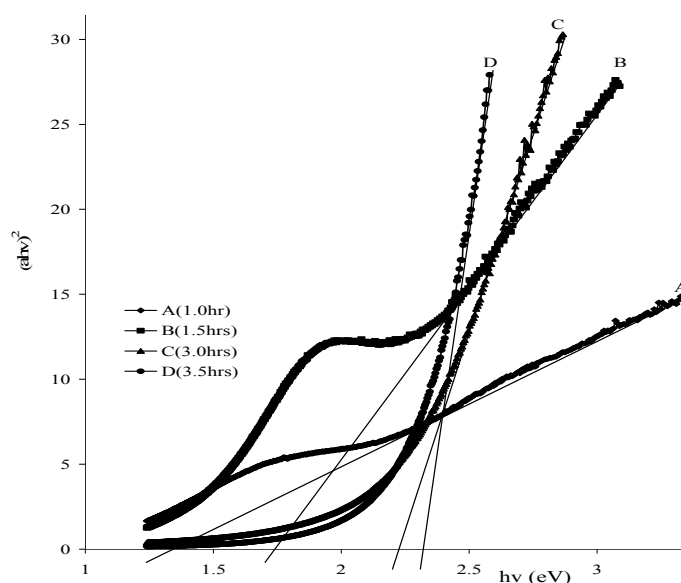


Fig. 6. Plot of $(\alpha h\nu)^2$ vs. $h\nu$ for CuSbS_2 thin films at various dip time.

The values obtained for the thin films lie in the range of 1.30 – 2.30eV. We can deduce from Fig. 6 that as dip time increases, the thickness of the films increase as well and this leads to decrease in band edge sharpness and an increase in energy gap. This is in agreement with the report [23] that optical band gap depends on film thickness, deposition and annealing temperature. For CuSbS₂, the values obtained here are in close agreement with the values reported by other authors for ternary CuSbS₂ thin films obtained by annealing stack of Sb₂S₃-CuS thin films[15,17]. A close observation of the values of the band gap energy displayed in figure 6 shows that films deposited at 1.0hour and 1.5hours dip time have band gap values in the range of the values reported for Sb₂S₃ thin films [11,13,16]. Interestingly, at a higher deposition time, the band gap energy changes and become closer to the values reported for CuS thin films[24].

We now propose a high efficiency photovoltaic cell based on the CuSbS₂ thin film absorber layer. By way of double deposition of the films, first at lower dip time followed by a second deposition at a higher dip time a solar absorber layer would emerge with the potential to convert most of the photon energy incident on it. There are two basic sources of energy loss in the photovoltaic conversion process: (1) Non- absorption of photon with energy $E_{ph} < E_g$, and (2) dissipation of excess energy ($E_{ph} - E_g$) of the absorbed photons. The former loss increases with E_g while the latter decreases with E_g . Clearly, there must be an optimal band gap, E_g where the energy conversion efficiency will be maximum. A lowered band-gap would reduce the photon energy threshold for absorption. It is our view that by employing the technique reported here for the fabrication of solar absorber layer, the energy loss as mentioned above would be taken care of, and a cell with high conversion efficiency would emerge. Other research geared towards reducing/eliminating the above losses is based on the formation of an intermediate band (IB) within the semiconductor bandgap that enables the absorption of sub-bandgap photons to excite electrons from the valence band to the IB followed by the absorption of a second sub-bandgap photon to excite the electrons in the IB to the conduction band [25].

4. Conclusions

This study focuses on direct deposition of ternary thin films of CuSbS₂ at room temperature without high temperature annealing. The films were deposited at varying dip time. XRD study reveals better crystallization of the films at a relatively higher deposition time. XRD pattern shows that the CuSbS₂ thin films have a preferred orientation in the (400) plane. Optical studies and band gap analysis show that dip time has significant effect on these properties. From the varied band gap energy exhibited by this films, the CuSbS₂ thin films deposited in this work could be used as a solar absorber layer in the fabrication of photovoltaic cell. Due to their low transmittance in the VIS, the films could also be applied as anti-dazzling coatings in car windscreen and driving mirrors to reduce the dazzling effect of light at night.

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