Optical and Solid State Characterization of Optimized Manganese Sulphide Thin Films and Their Possible Applications in Solar Energy

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ABSTRACT

The solution growth technique was used to deposit six thin film of manganese sulphide on micro-slides at different bath parameters, which include temperature, molarity of solution, volume of solution and water, time of deposition and pH, from bath compositions of: Manganese chloride ($MnCl_2.4H_2O$), sodium thiosulphate ($Na_2S_2O_3$), distilled water, and ethylene diamine tetra acetic acid (EDTA) which served as the complexing agent.

A spectrophotometer was used to measure the absorbance, while percentage transmittances of the films were measured with Fourier Transform Infrared (FTIR) spectroscopy and a spectrophotometer. Energy Dispersive X-ray Fluorescence (EDXRF) was used to determine the elemental compositions of the films.

The optical and solid state characteristics revealed that films of manganese sulphide (MnS) have low absorbance ~ 0.033 – 0.40, high transmittance ~ 4 – 99%, and low reflectance ~ 0 – 20% throughout the ultraviolet, visible, and infrared regions. Other results are ranges of thickness, t ~ 1.96 – 2.69μm, refractive index, n~1.39 – 1.74 and energy band gap, Eg ~ 2.60 – 3.90eV. The above results show that MnS could be coated on solar collectors to enhance solar energy collection. It could also be used as anti-reflection coatings.

(Key words: solar coating, thin film deposition, chemical deposition, optical properties, solid state characteristics, photovoltaic, MnS).

INTRODUCTION

Solar energy is a source of free, natural, and non-polluting energy that man can harness for useful applications. Currently, there are many solar energy conversion methods such as photochemical (PC), photo-electrochemical (PEC), and photovoltaic (PV) (Udeajah 1996). With appropriate conversion method, solar energy could be used for lighting, desalination, refrigeration, drying industrial processes, and water heating. (Unaogu and Okeke, 1990).

When thin films are coated on substrates and characterized, the results will show their areas of application is solar energy. Thin film is a thin material formed from the process of atom–by-atom, molecule–by–molecule, ion–by–ion, or cluster of species–by–cluster of species condensation (Okujagu and Okeke, 1997). The techniques for the deposition of thin films include thermal evaporation, electron beam evaporation, activated reactive evaporation, epitaxy, and ion plating (Campbell, 1967 and Dutta, 1985). Others are chemical vapour deposition (Chopra & Das, 1983), spray pyrolysis (Onyia & Okeke, 1989), electrochemical deposition, anodization, and solution growth technique (Ndukwe, 1993, Ezema 2005).

In this paper, the solution growth technique method was used to deposit manganese sulphide on glass slides, at different bath parameters. They were characterized to determine their solid state and optical properties, elemental compositions and thicknesses. The areas of application of the films were determined based on the results of the characterization.

EXPERIMENTAL DETAIL

Manganese sulphide was deposited by the reaction of solutions of manganese chloride ($MnCl_2.4H_2O$), sodium thiosulphate ($Na_2S_2O_3.5H_3O$), distilled water, and EDTA, which served as the complexing agent. The reaction equations are given below:

$MnCl_2.4H_2O + EDTA \longleftrightarrow [Mn(EDTA)]^{2+} + 2Cl^- + 4H_2O$

$[Mn(EDTA)]^{2+} \longleftrightarrow Mn^{2+} + EDTA$

$Na_2S_2O_3.5H_2O \longleftrightarrow Na_2O_3 + 5H_2O + S^{2-}$

$Mn^{2+} + S^{2-} \longleftrightarrow MnS \downarrow$

The six manganese sulphide films were deposited at different bath parameters as presented in Table 1.

After the deposition, a PYE-UNICAM® SP8-100 model of the spectrophotometer was used to measure the absorbance of the films. The percentage transmittances in the infrared region were measured directly with Fourier Transform Infrared (FTIR) spectrophotometers. Other optical and solid state properties like transmittance, reflectance, absorption coefficient, energy bandgap, refractive index, extinction coefficient, optical conductivity, real and imaginary dielectric constants were calculated. The thicknesses of the films grown were calculated using optical methods while the structural characterization was done with a microscope (HUND WETZLAR® H600) and camera (RICOH® 35mm SLR, XR – X300). The Energy Dispersive X–ray Fluorescence method was employed to determine the elemental compositions of the thin films.

THEORETICAL CONSIDERATION AND CALCULATIONS

The optical and solid state properties of the films were obtained through the following equations:

Absorbance, A obtained from the common logarithm of the reciprocal transmittance.

$$\text{Transmittance, } T = I/I_o$$

where I is the transmitted flux and I_o is the incident flux (Lothion, 1958).

$$\text{Reflectance, } R = 1 - A - T$$

Absorption coefficient,

$$\alpha = \frac{In\left(\frac{1}{T}\right)}{t} = In\left(\frac{1}{T}\right) \times 10^6 m^{-1}.$$

$$\text{Bandgap, } E_g = h\nu - \alpha^2.$$

where h is Plank constant and ν is the frequency.

$$\text{Refractive index, } n = \frac{1 + R^{1/2}}{1 - R^{1/2}}$$

Extinction coefficient, $K = \frac{\alpha\lambda}{4\pi}$ (Pankove, 1971)

$$\text{Dielectric constant, } \varepsilon_r + \varepsilon_I = (n + ik)^2.$$

where ε_r is called the real dielectric constant and ε_1 is called the imaginary dielectric constant.

$$\text{Optical conductivity, } \sigma_{op} = \frac{\alpha n c}{4\pi}.$$

where c represents velocity of light.

RESULTS, ANALYSIS, AND DISCUSSION

The spectral absorbance of manganese sulphide films grown under varying conditions at 300K for 3 samples are displayed in Figure 1.

Figure 2 is the transmittance curve for films A_3, A_5, and A_8 while Figure 3 is the reflectance curve for the three samples.

The results revealed that the films have low absorbance and high transmittance of range 40–99% throughout the ultraviolet, visible, and infrared regions of the electromagnetic spectrum. They also recorded very low reflectance within the same range as shown in Figure 3.

Figure 4 and Figure 5 are infrared transmittance curves for plain slides and A_{11} film. It revealed that transmittance is reduced at high temperature radiation.

The range of bandgap is from 2.6eV to 3.4eV as shown in Figure 6.

Table 1: Preparation of Manganese Sulphide (MnS) Thin Films.

Reaction bath	Dip time (hr)	Temp (°C)	pH	$MnCl_2.4H_2O$		$Na_2S_2O_3.5H_2O$		EDTA		H_2O
				Mol (M)	Vol. (ml)	Mol (M)	Vol. (ml)	Mol (M)	Vol. (ml)	Vol. (ml)
A_3	48	Room	3.5	1.0	5	0.5	2	0.10	2	31
A_5	48	Room	4.5	0.5	2	1.0	2	0.10	2	34
A_8	30	Room	4.5	0.5	2	0.5	2	0.01	5	31
A_{10}	30	Room	4.8	1.0	5	1.0	5	0.01	5	25
A_{11}	27	Room	4.5	0.5	4	0.5	4	0.01	10	12
A_{12}	4	55	6.0	1.0	2	1.0	2	0.01	2	24

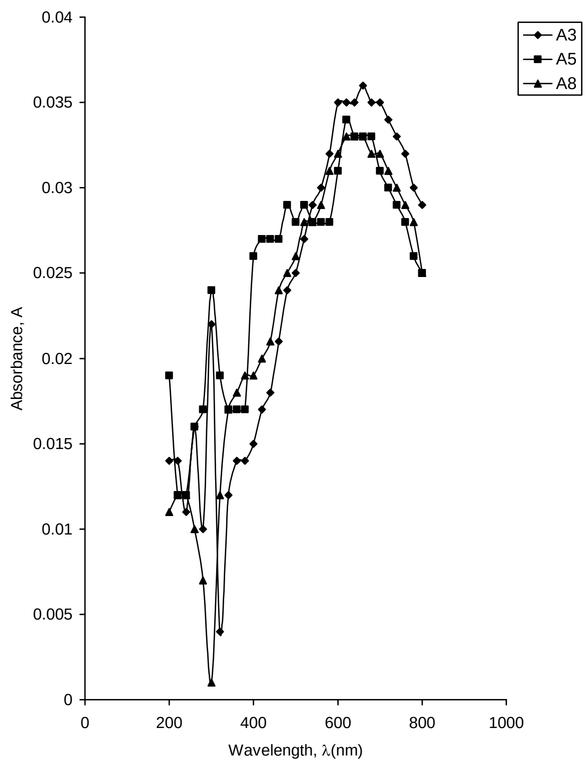

Figure 1: Spectral Absorbance of Manganese Sulphide (MnS) – A_3, A_5, and A_8.

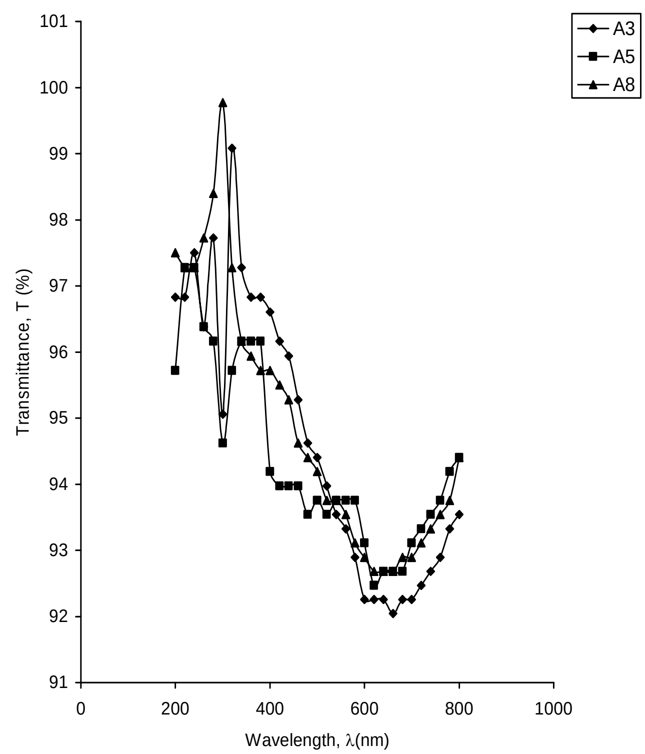

Figure 2: Spectral Transmittance of Manganese Sulphide (MnS) – A_3, A_5, and A_8.

The plots of extinction coefficient vs. photon energy for films A_5 and A_8 are shown in Figure 7 while Figure 8 shows the plot of refractive index against photon energy. It is observed that the range of refractive index is ~ 1.2 – 1.5 for films A_3, A_5, and A_8. The peak value of the refractive index was recorded at the photon energy of 4eV.

Figure 9 shows the plot of real and imaginary parts of dielectric constant vs. photon energy for film A_3. Between the photon energy of 1.6eV and 6.2eV, the real part of the dielectric constant, ε_R decreases sharply as the photon energy increases having a minimum value of –20 corresponding to a photon energy of 6.2eV. The imaginary part also decreases sharply within the same range of photon energy but in opposite direction.

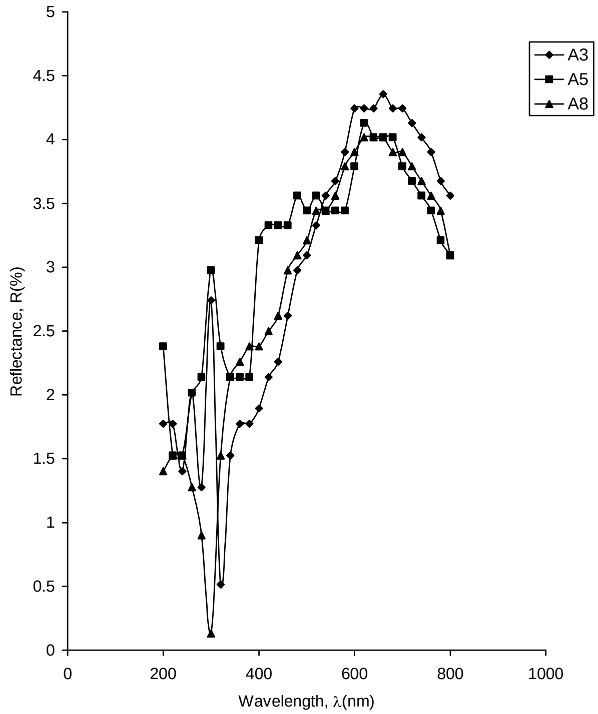

Figure 3: Spectral Reflectance Manganese Sulphide (MnS) – A_3, A_5, and A_8.

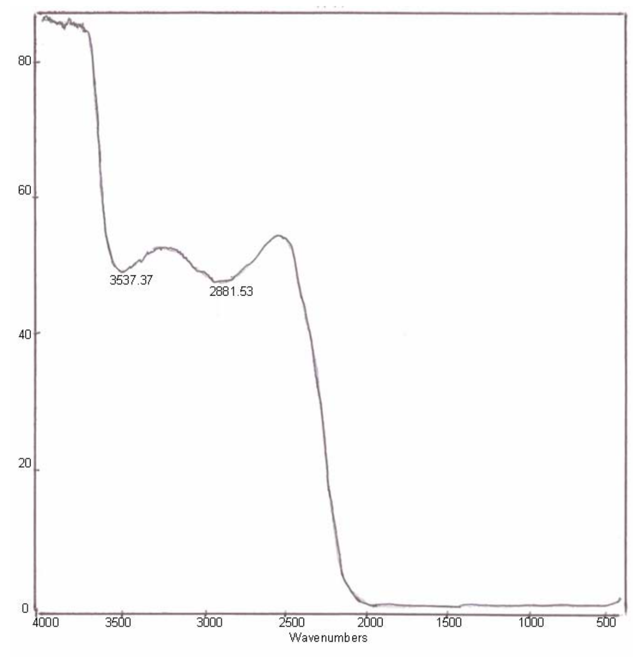

Figure 5: Infrared Transmittance Curve of Manganese Sulphide (MnS) – A_{11}.

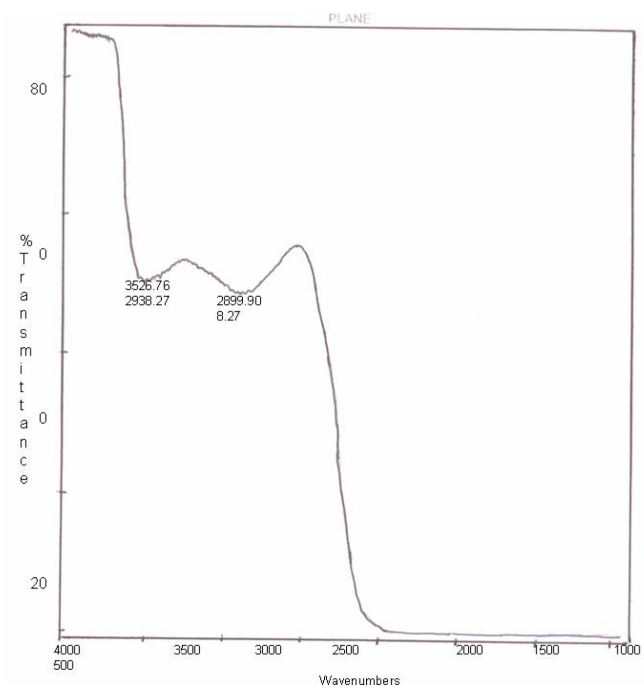

Figure 4: Infrared Transmittance Curve of Plane Slide.

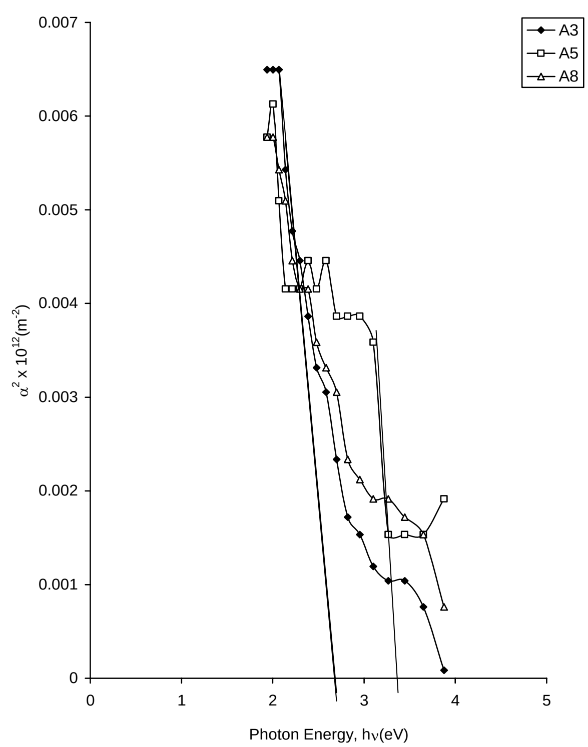

Figure 6: Location of Energy Gap for Manganese Sulphide (MnS) – A_3, A_5, and A_8.

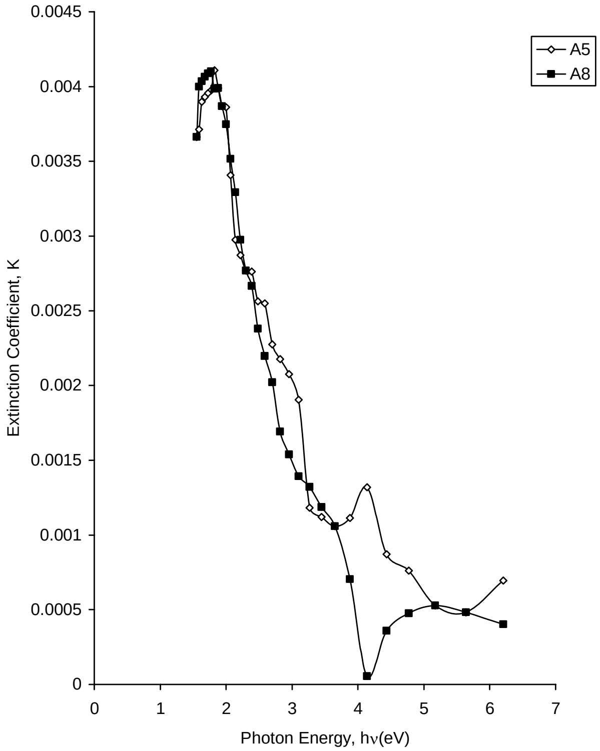

Figure 7: Plot of Extinction Coefficient vs. Photon Energy for Manganese Sulphide (MnS) – A_5 and A_8.

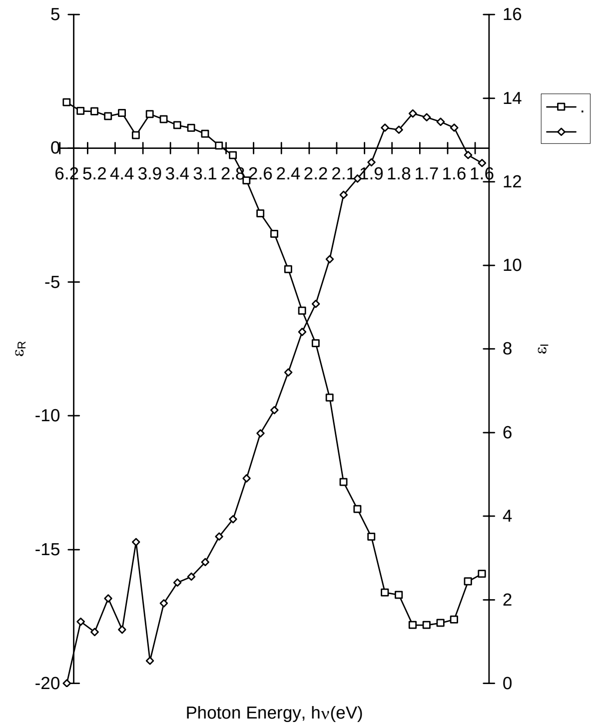

Figure 9: Plot of Real (ε_r) and Imaginary (ε_i) parts of the Dielectric Constant vs. Photon Energy for Manganese Sulphide (MnS) – A_3.

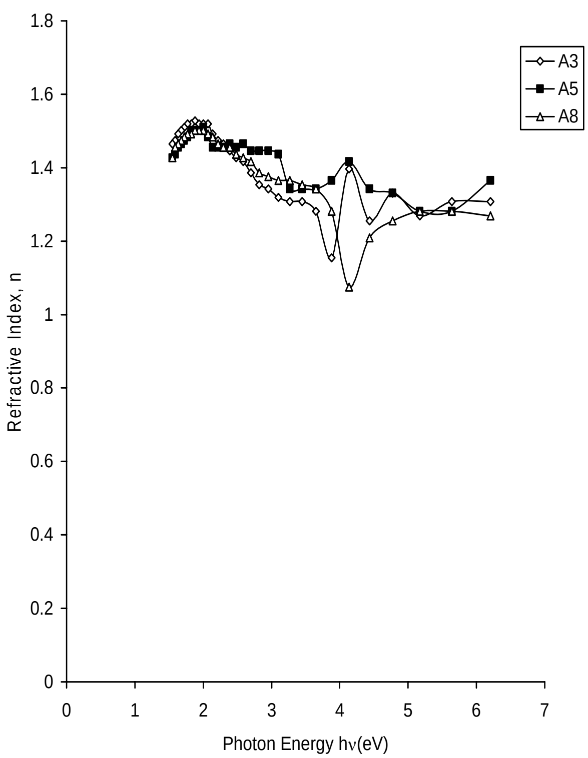

Figure 8: Plot of Refractive Index vs. Photon Energy for Manganese Sulphide (MnS) – A_3, A_5, and A_8.

The plots of optical conductivity vs. photon energy for A_3, A_5, and A_8 are presented in Figure 10.

The average values of the optical, solid state properties, and thicknesses of manganese sulphide films grown under varying conditions are tabulated in Tables 2 and 3 below.

From Table 2, excluding films A_3 and A_5, it is observed that as dip time and thickness decrease, refractive index, n, extinction coefficient, K, optical conductivity, σ_{op}, real dielectric constant, ε_R and absorption coefficient, α increase.

The Energy Dispersive X-ray Fluorescence method was employed to determine the elemental compositions of the thin films grown. Results for a plane glass slide (blank) and those for the A_3 films are presented in Tables 4 and 5, respectively.

Table 2: Optical Properties and Thicknesses of MnS Films Grown under Varying Conditions at 300k.

Reaction bath	Dip time (hr)	Average n	Average K x 10^{-3}	Average σ_{op} x 10^{12}(S^{-1})	Average α x 10^6(m^{-1})	Average thickness, t (μm)
A_3	48	1.41	2.432	1.89	0.05	2.67
A_5	48	1.43	0.002	1.99	0.06	2.59
A_8	30	1.40	0.002	1.80	0.05	2.69
A_{10}	30	1.44	0.003	2.40	0.06	2.63
A_{11}	27	1.49	0.003	4.12	0.09	2.54
A_{12}	4	1.74	0.006	9.37	0.18	1.96

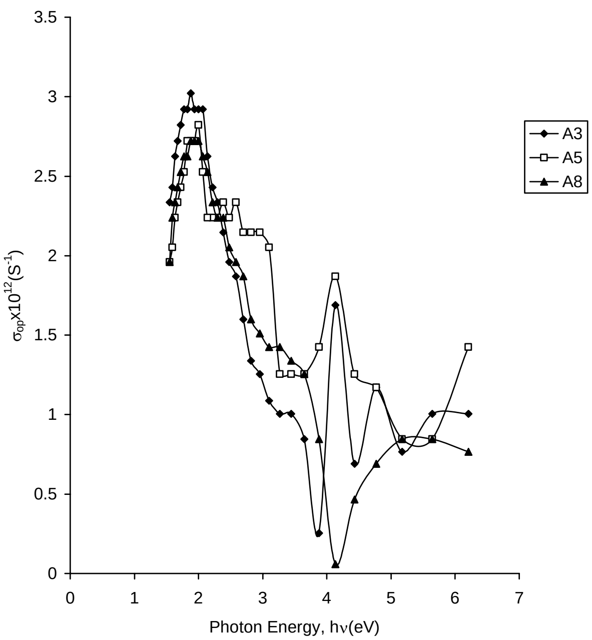

Figure 10: Plot of Optical Conductivity vs. Photon Energy for Manganese Sulphide (MnS) – A_3, A_5, and A_8.

CONCLUSION

It is possible to deposit manganese sulphide films at varying conditions by the solution growth technique. The characterization of these films has revealed their suitability in solar energy applications. The low reflectance and high transmittance throughout the ultraviolet, visible, and infrared regions of the electromagnetic spectrum by A_{12} film make it suitable for solar energy collection. Therefore, if it is coated on the surface of a solar collector, the film will reduce the reflection of solar radiation and transmit radiation to the collector fluid. Films like A_{10}, A_{11}, and A_{12}, which transmit highly at λ ~ 0.35–0.75μm could be used as photosynthetic coatings. This is because they are likely to exhibit selective transmittance of Photosynthetic Active Radiation (PAR).

Table 3: Solid State Properties of MnS Films Grown Under Varying Conditions at 300k.

Reaction bath	Dip time (hr)	Bandgap (eV)	Avg. (ε_R)	Avg. (ε_I)
A_3	48	2.6	-6.40	7.14
A_5	48	3.4	2.04	0.01
A_8	30	2.6	1.94	0.01
A_{10}	30	3.8	2.09	0.01
A_{11}	27	3.9	2.29	0.01
A_{12}	4	3.5	2.36	0.02

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Table 4: EDXRF Analysis Results of Blank Slide.

EL	E[KEV]	INT[C/S]	S	T	CONC [FRAC]	ERROR
K	3.312	0.052	1.65E+03	0.0025	1.18E-02	-LOD-
CA	3.690	0.518	1.96E+03	0.0033	8.06E-02	3.68E-03
TI	4.508	0.056	4.50E+03	0.0042	2.91E-03	-LOD-
BA	4.450	0.057	2.09E+03	0.0041	6.59E-03	-LOD-
V	4.949	0.039	6.74E+03	0.0054	1.04E-03	-LOD-
CR	5.411	0.042	8.76E+03	0.0067	7.03E-04	-LOD-
MN	5.895	0.050	1.11E+04	0.0083	5.26E.04	-LOD-
FE	6.400	0.222	1.38E+04	0.0103	1.53E-03	1.23E-04
CO	6.925	0.041	1.71E+04	0.0126	1.88E-04	-LOD-
NI	7.472	0.033	2.14E+04	0.0153	9.78E-05	-LOD-
CU	8.041	0.034	2.51E+04	0.0185	7.21E-05	-LOD-
ZN	8.631	0.042	3.01E+04	0.0221	6.21E-05	-LOD-
AS	10.532	0.055	4.27E+04	0.0361	3.50E-05	-LOD-
PB	10.540	0.047	2.50E+04	0.0361	5.05E-05	-LOD-
BR	11.907	0.037	5.93E+04	0.0480	1.28E-05	-LOD-
RB	13.375	0.07	6.46E+04	0.0619	1.72E-05	4.32E-06
SR	14.142	0.337	7.03E+04	0.0695	6.75E-05	4.37E-06
Y	14.933	0.043	7.60E+04	0.0775	7.09E-04	-LOD-
ZR	15.746	1.213	9.77E+04	0.0858	1.42E-04	3.86E-06
NB	16.584	0.047	1.06E+05	0.0942	4.63E-06	-LOD-
MO	17.443	0.064	1.15E+05	0.1029	5.27E-06	-LOD-
S	2.307	0.024	1.85E+03	0.0009	1.46E-02	2.43E-03

SAMPLE: IS5728 MATRIX: [AO(RES) = 11000] WEIGHT (g/cm^2): 0942 Blank

Table 5: Analysis results of Manganese Sulphide (A_3).

EL	E[KEV]	INT[C/S]	S	T	CONC [FRAC]	ERROR
K	3.312	0.046	1.59E+03	0.0025	1.08E-02	-LOD-
CA	3.690	0.536	1.89E+03	0.0033	8.58E-02	4.05E-03
TI	4.508	0.052	4.35E+03	0.0042	2.82E-03	-LOD-
BA	4.450	0.046	2.02E+03	0.0040	5.49E-03	-LOD-
V	4.949	0.054	6.52E+03	0.0054	1.51E-03	-LOD-
CR	5.411	0.047	8.46E+03	0.0067	8.15E-04	-LOD-
MN	5.895	0.0038	1.08E+04	0.0083	4.21E.02	1.49E-03
FE	6.400	0.222	1.33E+04	0.0102	1.60E-03	1.39E-04
CO	6.925	0.041	1.65E+04	0.0125	1.92E-04	-LOD-
NI	7.472	0.037	2.06E+04	0.0152	1.17E-04	-LOD-
CU	8.041	0.036	2.43E+04	0.0183	7.85E-05	-LOD-
ZN	8.631	0.035	2.91E+04	0.0220	5.34E-05	-LOD-
AS	10.532	0.063	4.12E+04	0.0358	4.17E-05	-LOD-
PB	10.540	0.053	2.41E+04	0.0359	6.04E-05	-LOD-
BR	11.907	0.043	5.73E+04	0.0477	1.56E-05	-LOD-
RB	13.375	0.068	6.24E+04	0.0615	1.74E-05	4.45E-06
SR	14.142	0.380	6.79E+04	0.0690	7.93E-05	4.73E-06
Y	14.933	0.056	7.34E+04	0.0770	9.68E-06	3.21E-06
ZR	15.746	1.185	9.44E+04	0.0852	1.44E-04	4.10E-06
NB	16.584	0.050	1.02E+05	0.0939	5.08E-06	-LOD-
MO	17.443	0.056	1.11E+05	0.1022	4.88E-06	-LOD-
S	2.307	0.033	1.85E+03	0.0009	3.03E-02	2.01E-04

SAMPLE: IS5728 MATRIX: [AO(RES) = 11000] WEIGHT (g/cm^2): 0942 A_3

Further characterization in the far infrared region was done at National Research Institute for Chemical Technology (NARICT), Zaria with the assistance of S.T. Diete Spiff.

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