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Full Length Research Paper

Optical Properties of Copper Selenide Thin Film

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Thin films of copper selenide (CuSe) were chemically deposited onto a glass substrate. We studied optical properties which include absorbance, reflectance, transmittance, refractive index, using a Janway 6405 UV/Visible spectrophotometer. Surface morphology of the films were carried out using an Olympus Optical microscope. A bandgap of 2.2eV and refractive index of 2.5 was obtained for CuSe thin film.

Keywords: Copper Selenide, Optical properties, chemical bath.

INTRODUCTION

Copper selenide is a metal chalcogenide semiconductor that comes in different stoichiometric composition such as CuSe, $\mathrm{Cu_2Se}$, $\mathrm{Cu_3}Se_2$,$\mathrm{Cu_5}Se_4$ and non-stoichiometric composition such as $\mathrm{Cu_{2-x}Se}$ (Dhanam et al., 2005). Copper selenide exists in different crystallographic forms even at room temperature. This includes orthorhombic, monoclinic, (Heyding and Murray, 1976), cubic, (Bhuse et al., 2001), tetragonal and hexagonal forms depending on the method of fabrication. It is a semiconductor with p-type conductivity due to copper vacancies, a property which is useful in the solar cell production. $\mathrm{Cu_{2-x}Se}$ is reported to possess a direct band gap of 2.2 eV and an indirect band gap of 1.4 eV for x = 0.2 (Hermann and Fabick, 1983). According to (Okereke and Ekpunobi, 2011), the direct band gap varies in the range of 2.0eV to 2.3eV as the thickness varies from $1.54\mu m - 1.67\mu m$ while the indirect band gap was found to vary from 0.4eV – 0.8eV and average grain size of 3.78Å. Also, a direct band gap ranged from 2.35eV – 2.38eV and indirect band gap of 1.20eV – 1.0eV was obtained by (Garcia et al., 1996). Band gap energy of 2.33eV from chemical bath deposited copper selenide film was reported by (Grozdanov , 1994). CuSe has various applications, $Cu_{2-x}Se$ has been used in several heterojunction systems: $Cu_{2-x}Se$ / $ZnSe$ for injection electroluminescence (Aven and Cusano, 1964), for photodiodes (Tell and Wiegand,1977), for solar cells (Haram and Santhanam, 1994). In the present investigation, we have described the growth of CuSe thin films on glass substrates using chemical bath technique. Film growth was optimized by varying the volume of complexing agent. Prepared films have been subjected to optical microscopy, optical properties of the deposited films is studied and the observed results are discussed in detail. The optical absorbance (in arbitrary units) of the deposited films was obtained using Janway 6405 UV/Visible spectrophotometer ranging from 300–1100nm of the electromagnetic spectrum. Optical microscopy of the deposited films were done using an Olumpus optical microscope. Other parameters like transmittance, reflectance and refractive index were calculated using theory.

MATERIALS AND METHOD

Copper selenide (CuSe) thin films were deposited on glass substrate by chemical bath deposition method. Deposition parameter such as concentration of complexing agent was optimized. The deposition of CuSe thin film by CBD was based on the reaction between $\mathrm{Copper\ (II)\,chloride\ dihydrate}$ $(\mathrm{Cu}Cl_2.2H_2O)$ which served as the source of copper ion, $\mathrm{Cu^{2+}}$ and sodium selenosulphate (Na_2SeSO_3) which served as the source of anion, $\mathrm{Se^{2-}}$. EDTA solution was used as a complexing agent. Five slides were grown, the concentration of Copper (II) chloride dehydrate, sodium selenosulphate, ammonia solution, temperature (300K) and deposition time were kept constant, while the

Table 1. Bath Constituents for the Dposition CuSe Thin Film

Reaction bath	Dip time (hr)	Temp. (K)	pH	$CuCl.2H_2O$		Na_2SeSO_3 Vol. (ml)	EDTA		H_2O Vol. (ml)	NH_4OH	
				Mol. (M)	Vol. (ml)		Mol. (M)	Vol. (ml)		Mol. (M)	Vol. (ml)
CS_1	24	301	10.1	0.5	10.0	5.0	0.1	2.0	60	14.0	10.0
CS_2	24	300	10.3	0.5	10.0	5.0	0.1	4.0	60	14.0	10.0
CS_3	24	301	10.2	0.5	10.0	5.0	0.1	6.0	60	14.0	10.0
CS_4	24	300	10.2	0.5	10.0	5.0	0.1	8.0	60	14.0	10.0
CS_5	24	300	10.3	0.5	10.0	5.0	0.1	10.0	60	14.0	10.0

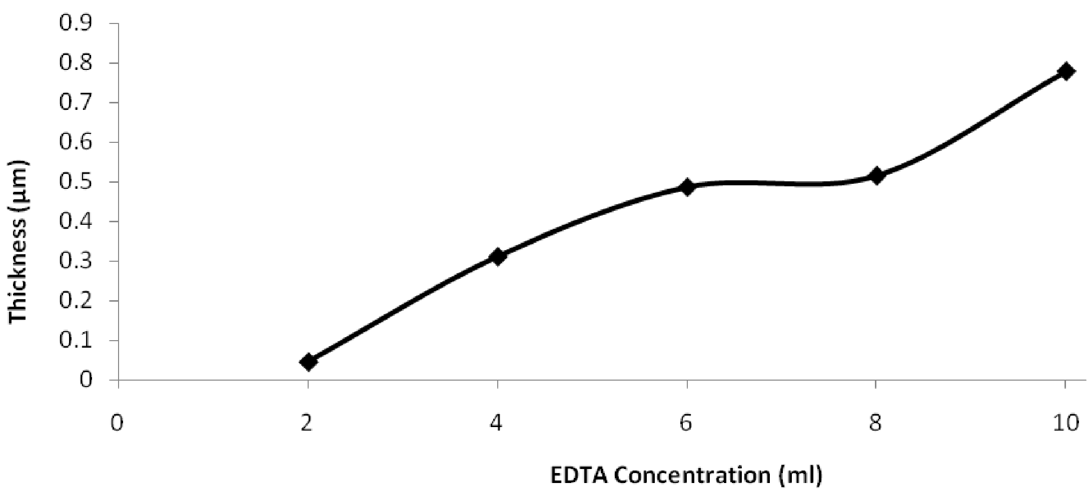

Figure 1. Variation of Thickness with Complexing Agent

concentration of EDTA was altered as shown in table 1 below. The Na_2SeSO_3 solution used in this experiment was prepared by mixing 5g selenium powder (99 % purity) with 25g anhydrous sodium sulphite in 250 ml of distilled water. The mixture was refluxed at a temperature of $100°C$ for 2hours, 30 minutes before being used in the experiments.The Na_2SeSO_3 so prepared was used immediately because of instability of the Na_2SeSO_3 compound. Ammonium solution was used to maintain the pH of the bath in an alkaline medium suitable for the deposition. The pH of the baths were obtained at values between 10.2 ± 0.1.

The reaction mechanism is of the form:

$$CuCl_2.2H_2O + \text{EDTA} \rightleftarrows \text{Cu[EDTA]}^{2+} + \text{Cl}^- + 2\text{H}_2\text{O}$$

$$Cu[EDTA]^{2+} \rightleftarrows Cu^{2+} + EDTA$$

$$Na_2SeSo_3 + 2OH^- \rightleftarrows Na_2SO_4 + Se^{2-} + \text{H}_2\text{O}$$

$$Cu^{2+} + Se^{2-} \rightleftarrows CuSe$$

RESULTS AND DISCUSSION

Figure 1 shows the variation of film thickness with complexing agent. A careful look at the graph indicates that thickness increased as volume of complexing agent

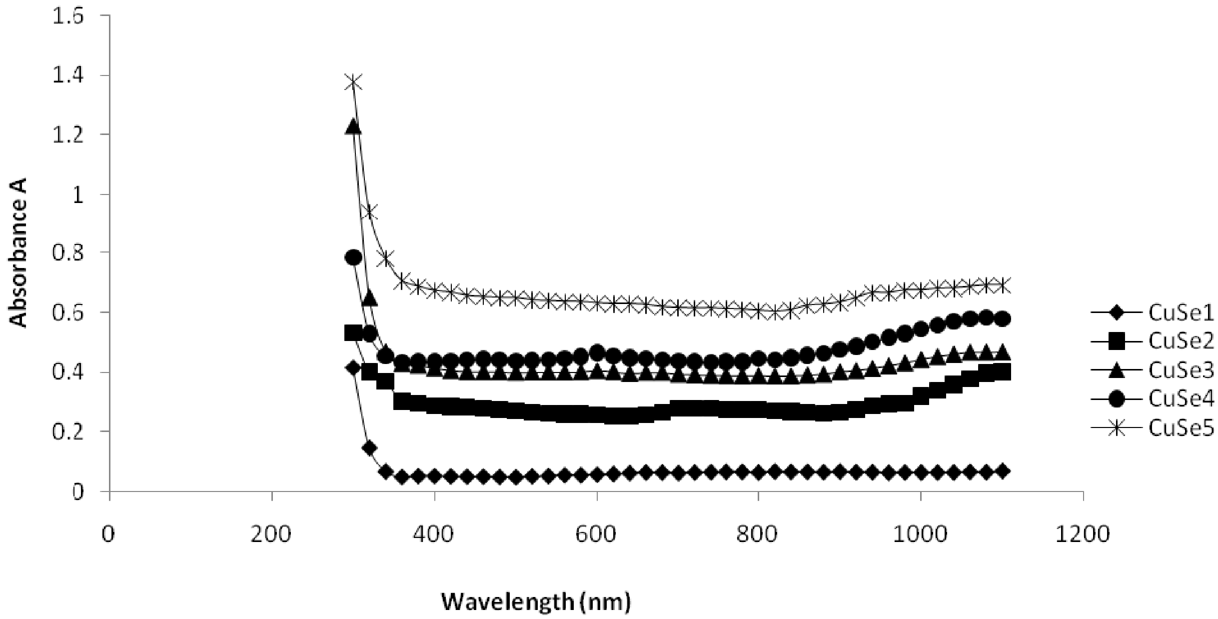

Figure 2. Absorbance Spectra of as grown CuSe

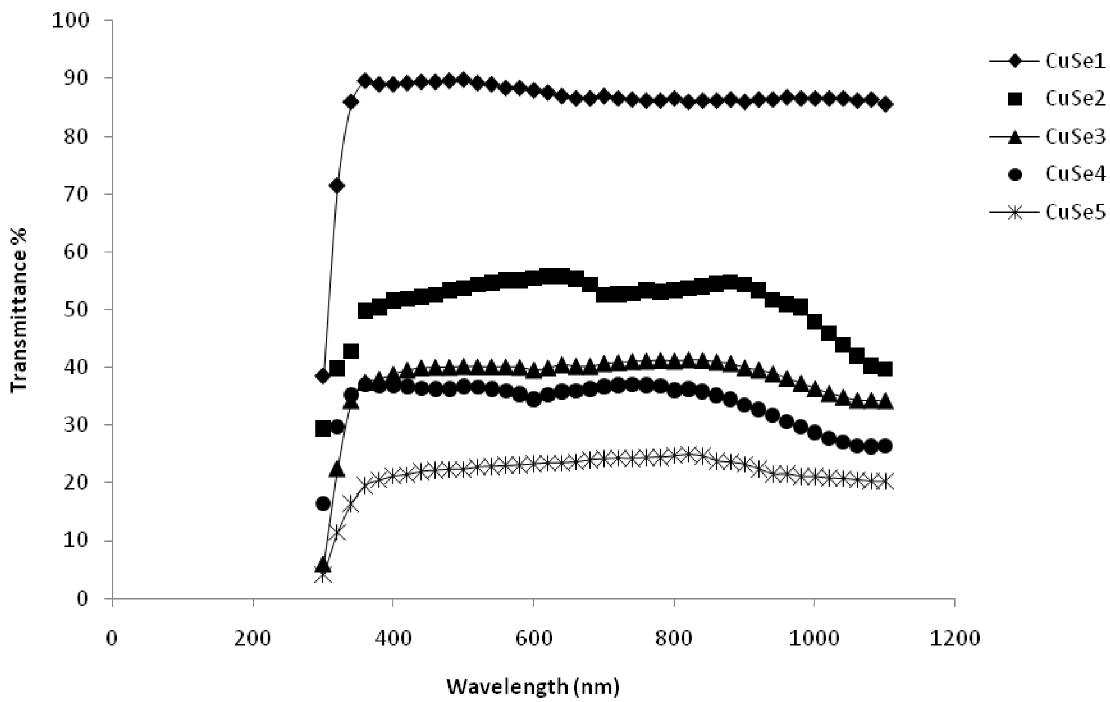

Figure 3.Transmittance Spectra of as grown CuSe

increased with an optimal film thickness of 0.8 at 10mls volume of complexing agent. One can therefore infer that there is a direct proportionality between the thickness of the grown film and the complexing agent. Figures 2,3 and 4 shows the absorbance, transmittance and reflectance spectra of the deposited copperselenide thin film respectively. Slide $CuSe_5$, which has the highest concentration of EDTA has the highest absorbance while slide $CuSe_1$, which has the lowest concentration of EDTA has the lowest absorbance. An absorbance of > 0.6 is observed for slide $CuSe_5$ throughout the UV/VIS/NIR region of the electromagnetic spectrum, while an

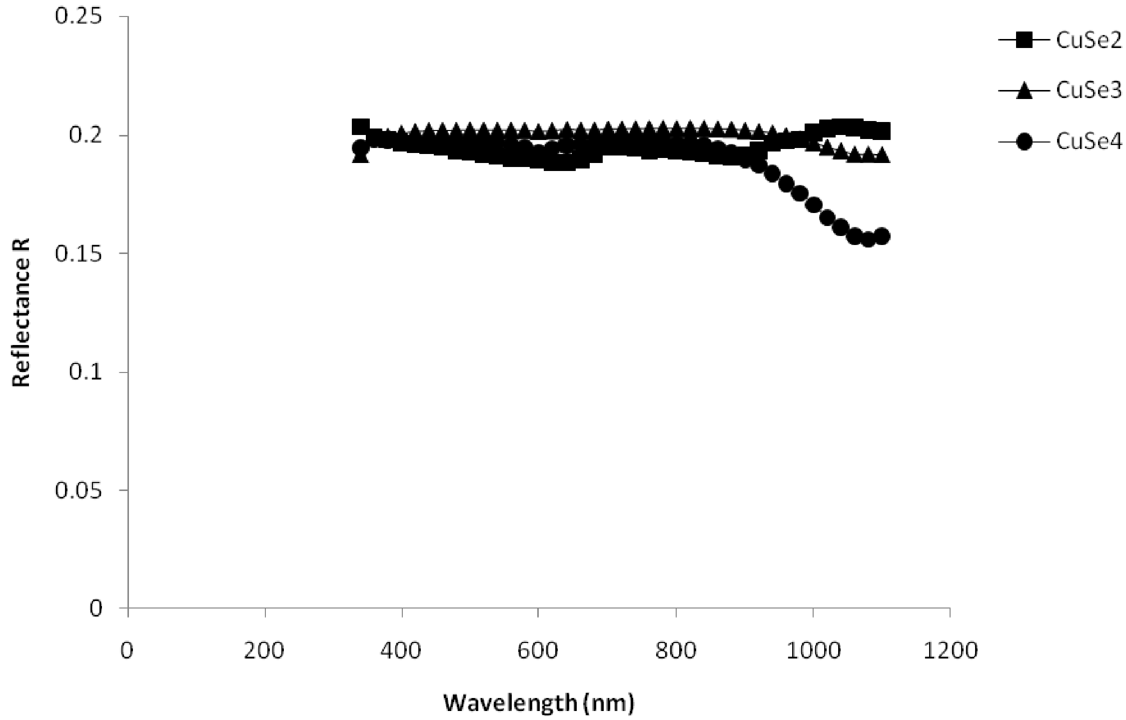

Figure 4. Reflectance Spectra of as grown CuSe

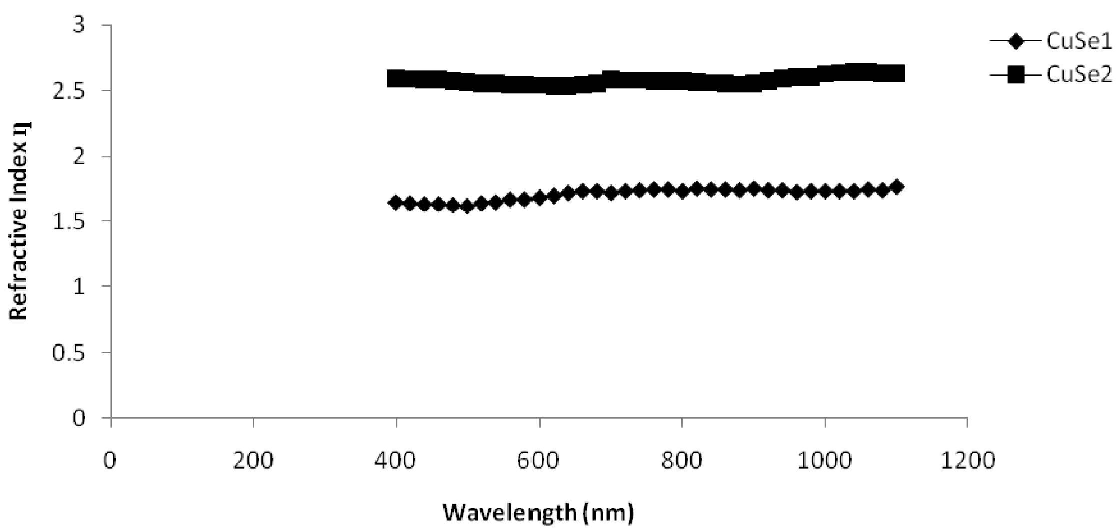

Figure 5. Variations of Refractive Index of as grown CuSe with wavelength

absorbance of < 0.1 is observed for slide $CuSe_1$ throughout the UV/VIS/NIR region of the electromagnetic spectrum. The same trend is also visible for $CuSe_2$, $CuSe_3$ and $CuSe_4$. Transmittance of approximately 90% is observed for slide $CuSe_1$ through out the UV/VIS/NIR region of the electromagnetic spectrum, while for slide $CuSe_5$, a transmittance of approximately 20% is observed. The same trend is also observed for slide $CuSe_2$, $CuSe_3$ and $CuSe_4$. Reflectance of approximately

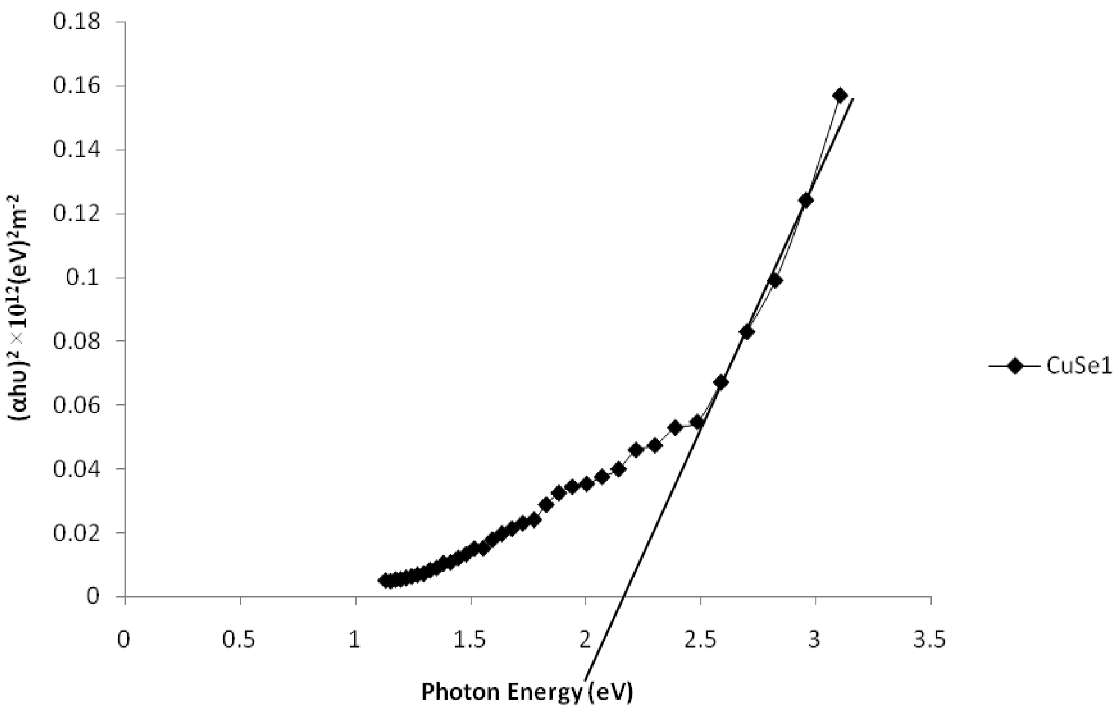

Figure 6. Plot of $(\alpha h\upsilon)^2$ versus photon energy for CuSe film (slide $CuSe_1$)

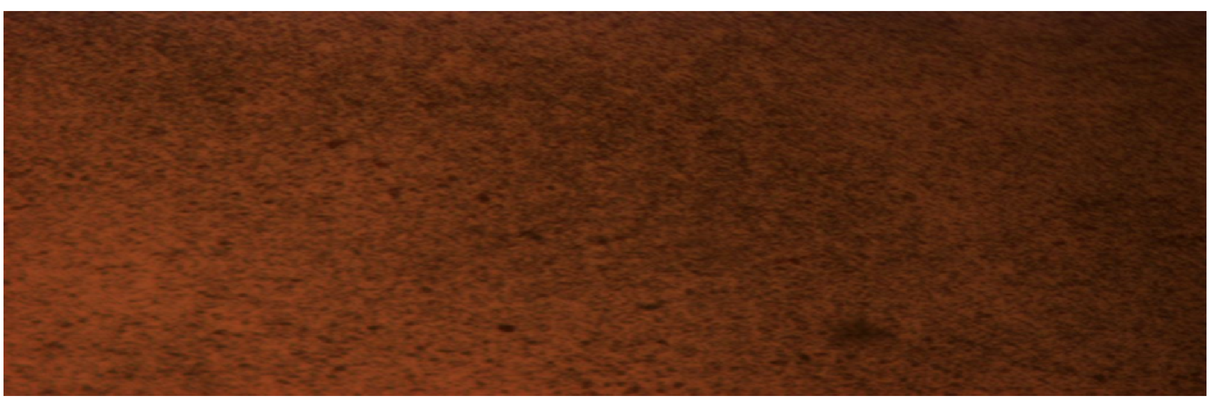

Figure 7. Optical Micrograph of CuSe thin film

0.2 at a wavelength range of (400 – 700)nm is observed for slide $CuSe_2$, $CuSe_3$ and $CuSe_4$. The reflectance is generally low, this makes CuSe thin film suitable for antireflection coating.

Fig. 5 shows the refractive index as a function of wavelength. A refractive index of approximately 2.5 is observed for slide $CuSe_1$ throughout the UV/VIS/NIR region of the electromagnetic spectrum. While for slide $CuSe_2$ approximately 1.5 is observed. Our result is also consistent with 1.7 – 2.6 obtained by (Offiah et al., 2012).This of refractive index for CuSe thin film makes it s uitable for use in optoelectronic devices.

The optical band gap (E_g) of the films were estimated from $(\alpha hv)^2$ versus hv curves shown in Fig. 6 for $CuSe_1$. The straight nature of the plot indicates the existence of direct transition. The band gap was determined by extrapolating the straight portion to the photon energy axis at $(\alpha hv)^2 = 0$. It was found to be $2.2eV$. Our value is consistent with those of (Lakshimi et al., 2000) with optical energy band gap of $2.20eV$. This value of energy band gap shows that CuSe films have wide band gap which make them suitable for window layers materials for photovoltaic cells.

Fig. 7 shows the optical micrograph of the deposited CuSe thin film. From the micrographs, it can be seen that the surface of the film is smooth and covers the glass substrate well. The grains are very small with equal size and shape.

CONCLUSION

We have demonstrated using chemical bath deposition technique, the synthesis of CuSe thin film. A bandgap of 2.2eV was obtained for CuSe thin film. Refractive index of approximately 2.5 was obtained for CuSe thin film throughout the UV/VIS/NIR region of the electromagnetic spectrum. The film with the highest concentration of EDTA (slide $CuSe_5$) has the highest absorbance with a value of > 0.6 and the lowest transmittance of approximately 20% throughout the UV/VIS/NIR region of the electromagnetic. The film with the lowest concentration of EDTA (slide $CuSe_1$) has the lowest absorbance, with a value of > 0.1 and the highest transmittance of approximately 90% throughout the UV/VIS/NIR region of the electromagnetic.

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