The Production of UV Absorber Amorphous Cerium Sulfide Thin Film

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This study investigates the production of cerium sulfide (CeS_x) amorphous thin films on substrates (commercial glass) by chemical bath deposition at different pH levels. The transmittance, absorption, optical band gap and refractive index of the films are measured by UV/VIS Spectrum. According to XRD analysis, the films show amorphous structure in the baths with pH: 1 to 5. It has been observed that the optical and structural properties of the films depend on pH value of the bath. The optical band gap (2.08 eV to 3.16 eV) of the films changes with the film thickness (23 nm to 1144 nm). We show that the refractive index has a positive relationship with the film thickness, where the values of 1.93, 1.45, 1.42, 2.60 and 1.39 are obtained for the former, and 34, 560, 509, 23 and 1144 nm (at 550 nm wavelength) for the latter. We compare the optical properties of amorphous and crystal form of CeS_x thin films. We show that the optical band gaps of the amorphous CeS_x are lower than that of crystal CeS_x.

Keywords: *CeS_x thin films, Chemical Bath Deposition, Thin film, UV absorber glass*

1. Introduction

As a lanthanide, cerium is strongly electropositive. It can easily transformed to oxides. The cerium salts such as hydroxide, carbonate, oxalate, phosphate, fluoride and sulfide are insoluble in the water. With the transitions between 4f and 5d electron configurations, cerium (III) compounds can absorb light in ultraviolet region outside the visible area. Cerium has many sulfide compounds, such as cerium (III) sulfide, Ce_2S_3, cerium mono sulfide, CeS, and tri cerium tetra sulfide, Ce_3S_4[1-3].

Cerium (III) sulfides are known as sesquisulfides. Cerium sesquisulfides exist in three different allotropic forms as α-Ce_2S_3, β-Ce_2S_3 and γ-Ce_2S_3. The structure and colors of these sulfides are as follows: black/brown or orange in orthorhombic form, burgundy in tetragonal form and dark red in cubic form. According to the literature, α-Ce_2S_3, β-Ce_2S_3 and γ-Ce_2S_3 are formed at high temperature, that is < 900 °C, > 900 °C and > 1200 °C, respectively. Cerium mono sulfides have also different thermal and electrical properties. Moreover, cerium oxides are used in a wide variety of technologic areas[2-3].

This paper aims to produce CeS_x thin films via chemical bath deposition, at different pH values, and to examine their structural and optical properties. With amorphous CeS_x form, we can obtain thin films with lower optic band gap and reflection index. The optical properties of CeS_x thin films can be controlled with the pH of the chemical bath. To our knowledge, there exists no study on the production of CeS_x thin films via chemical bath deposition for solar cells, sensors or detectors. The relation between pH of the bath and the structural and the optical properties of CeS_x film has not been studied so far, especially for the cerium sulfides films which are produced at the acidic area. Kariper[4] has produced crystalline cerium sulfide thin films at the pH values greater than 6. This study compares optical properties of crystalline and amorphous CeS_x thin films.

2. Experimental Method

The components of bath are concentrated ammonia solution, 0.1 M $(NH_4)_2Ce(NO_3)_6$ and 0.2 M thioacetamide. First, 10 ml 0.1 M $(NH_4)_2Ce(NO_3)_6$ and 10 ml 0.2 M thioacetamide are added in baker containing 20 ml deionized water. Concentrated ammonia solution is used to adjust the pH of the bath. 60 µl, 80 µl, 120 µl and 180 µl of concentrated ammonia solution (NH_3) are added to the prepared baths to adjust their pH values to 2, 3, 4 and 5. The pH values of the chemical baths are measured using a pH meter (Lenko mark 6230N). The original pH of the solution is 1.15 before adding ammonia to the baker. Chemical baths are hold at 50 °C for 12 hours.

The crystalline structure of CeS_x is confirmed by X-ray diffraction (XRD) with a $CuK\alpha_1$ radiation source (Rikagu RadB model, λ=1.5406 Å) over the range $10° < 2\theta < 90°$ at a speed of 3° min^{-1} with a step size of 0.02°. Optical measurements are performed at room temperature using Hach Lange 500 Spectrophotometer, by placing an uncoated identical commercial glass substrate to the reference beam. Optical spectrum of thin films is recorded at the wavelength range of 300-1100 nm.

3. Results and Discussion

Fig. 1 shows XRD patterns of various cerium sulfide thin films produced at different pH values by using chemical bath

deposition method (a: pH 1, b: pH 2, c: pH 3, d: pH 4, e: pH 5). XRD patterns of the films show amorphous structure form for CeS_x. Kariper[4] and Witz et al.[5] have obtained crystalline structures for CeS_x at pH > 6. They have also observed no relationship between thicknesses of the thin films and pH of the bath. In this study, film thicknesses are found to be 34, 560, 509, 23 and 1144 nm for pH 1, 2, 3, 4 and 5, respectively, as shown in Fig. 2.
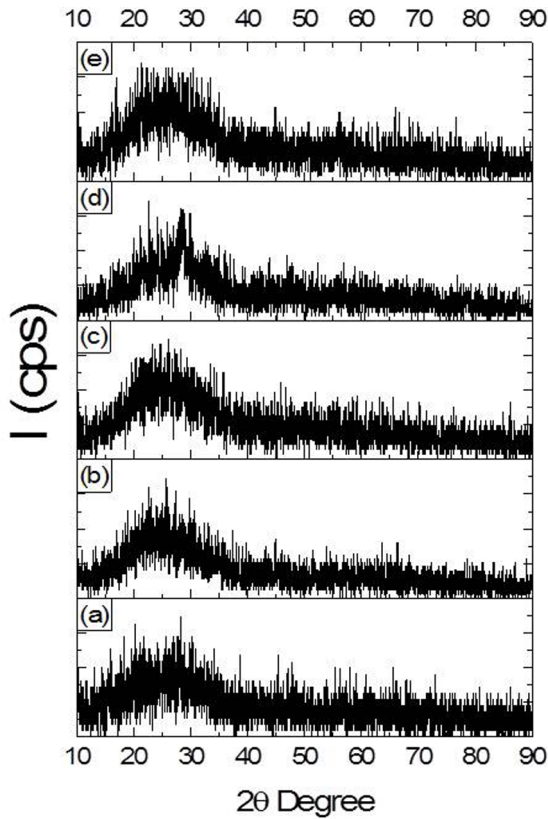

Figure 1. XRD spectrum of Cerium Sulfide thin films produced at different pHs (a) pH: 1, (b) pH: 2, (c) pH: 3, (d) pH: 4, (e) pH: 5.
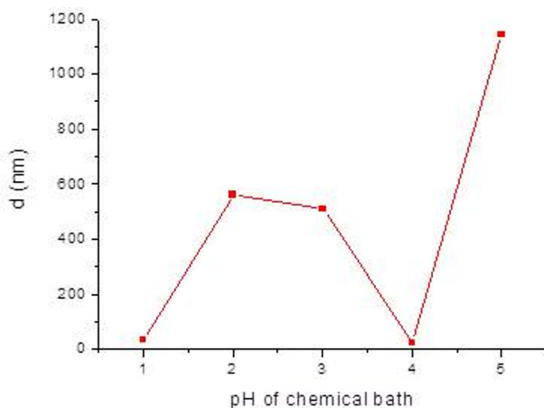

Figure 2. Film thickness of CeS_x thin films produced at different pH.

Optic band gap energy (Eg) is determined from the absorption spectra of the films using the following relation, where A is a constant, α is absorption coefficient, hν is the photon energy and n is a constant, equal to ½ for direct band gap semiconductor.

$$(\alpha h\nu) = (h\nu - Eg)^n \qquad (1)$$

Figure 3 shows the plot of $(\alpha h\nu)^2$ vs. hν for CeS_x films produced at different pH: (a) pH 1, (b) pH 2, (c) pH 3, (d) pH 4, (e) pH 5. Witz et al. have stated that direct band gap of pure single crystal cerium sulfides thin film (especially, sesquisulfides) is higher than 3.3 eV, because its dielectric constant is high[5]. We have calculated optical band gap of crystalline cerium sulfide thin films in the range of 2.86-3.23 eV. Urbach tail formed in amorphous structure allows the parabolic conductivity band to switch to a lower energy level, which is just below the conductivity band of the energy tail. Therefore, excited electrons are positioned at this energy level before switching to the conductivity band, which leads to an increase on conductivity. These results show that amorphous CeS_x thin films are very useful for solar cells[5].

Transmittance (T) of CeS_x thin film can be calculated by using reflectivity (R) and absorbance (A) spectra from the following expression:

$$T = (1-R)^2 e^{-A} \qquad (2)$$

Transmission measurements shown in figure 4 are performed at room temperature, in the range of 300-1100 nm. Transmission is calculated as 68, 88, 89, 45 and 90 % (at 550 nm wavelength), for film thickness 34, 560, 509, 23 and 1144 nm, respectively. In addition, reflectance values have been calculated and found to be 10.13, 3.38, 3.07, 19.75 and 2.76 % respectively (at 550 nm wavelength). According to literature, the reflectance of cerium sulfides is around 10% at 550 nm wavelength, however bulk cerium sulfides show higher reflectance over 700 nm wavelengths. It is known that reflectance is related to film thickness. Transmissions of the films are in line with film thicknesses. Cerium sulfides are known to be useful reflectors with high performance pigment[2].

Refractive index and extinction coefficient of the films are computed by the following formulas:

$$n = \frac{(1+R)}{(1-R)} + \sqrt{\frac{4R}{(1-R)^2} - k^2} \qquad (3)$$

$$k = \frac{\alpha\lambda}{4\Pi} \qquad (4)$$

Refractive index values of 1.93, 1.45, 1.42, 2.60 and 1.39 (at 550 nm wavelength), shown in figure 5, is in line with the film thickness, which is measured as 34, 560, 509, 23
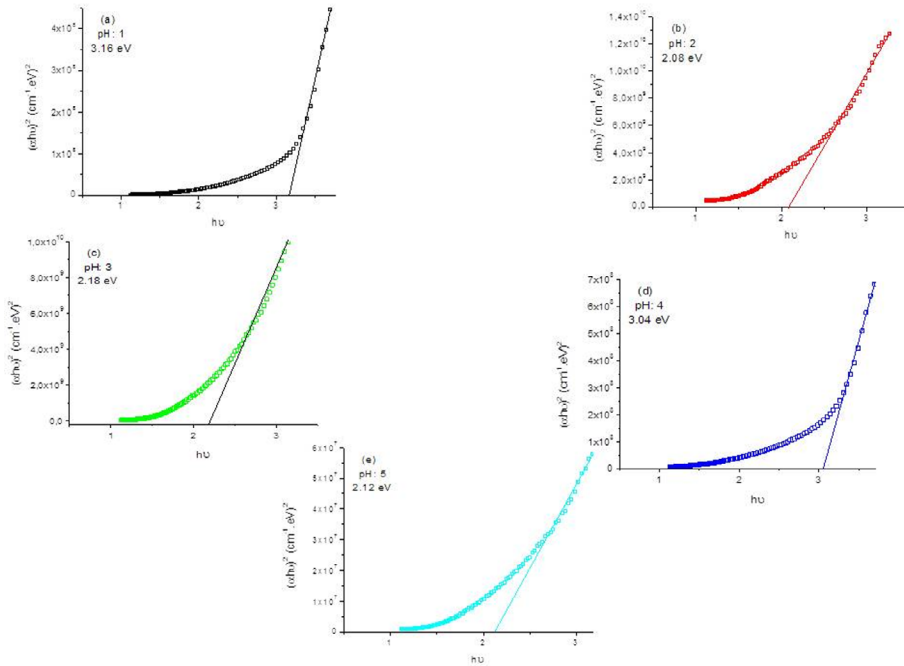
Figure 3. Plot of $(\alpha h\upsilon)^2$ vs. $h\upsilon$ for CeS$_x$ films produced at different pH: (a) pH 1, (b) pH 2, (c) pH 3, (d) pH 4, (e) pH 5.
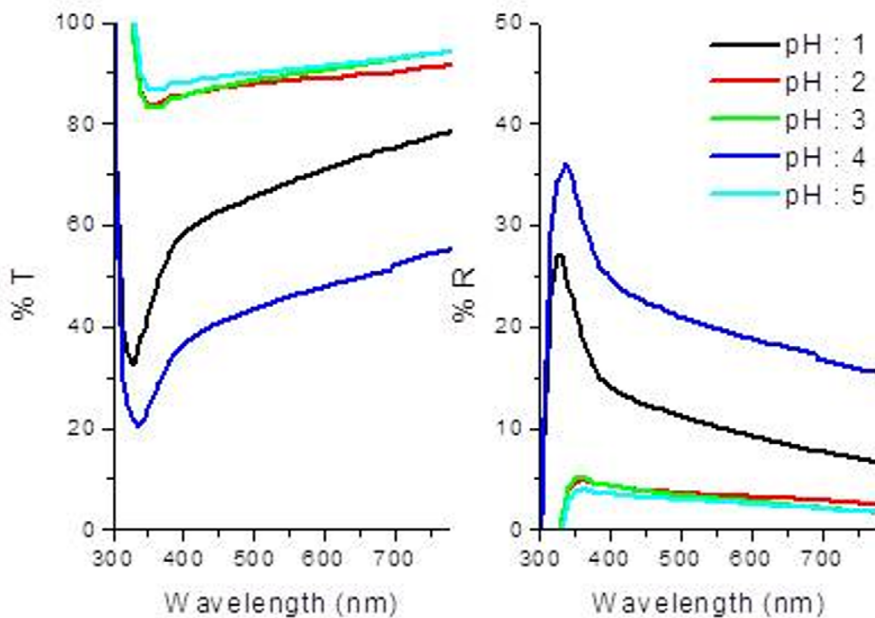

Figure 4. Transmittance (T) and reflectivity (R) of CeS$_x$ thin films produced at different pH.

and 1144 nm, respectively. Extinction coefficient, calculated as 0.011, 0,003, 0.003, 0.024 and 0.003, is also behaved as refractive index (at 550 nm wavelength). Refractive index of cerium sulfides (Ce$_2$S$_3$) is known to be 2.7[2]. Refractive index of bulk cerium sulfides is around 2.5-3 in visible region, and 3-3.5 in UV region. Similarly, extinction coefficient of bulk

cerium sulfides is around 0-0.5 in visible region, however it increases to 1.0 in UV region[2,6]. According to these results, thinner films that we have produced show better reflective properties than the thicker films in the literature. These results show that the optical properties of the films are in line with the film thicknesses. In the literature, UV absorbing materials
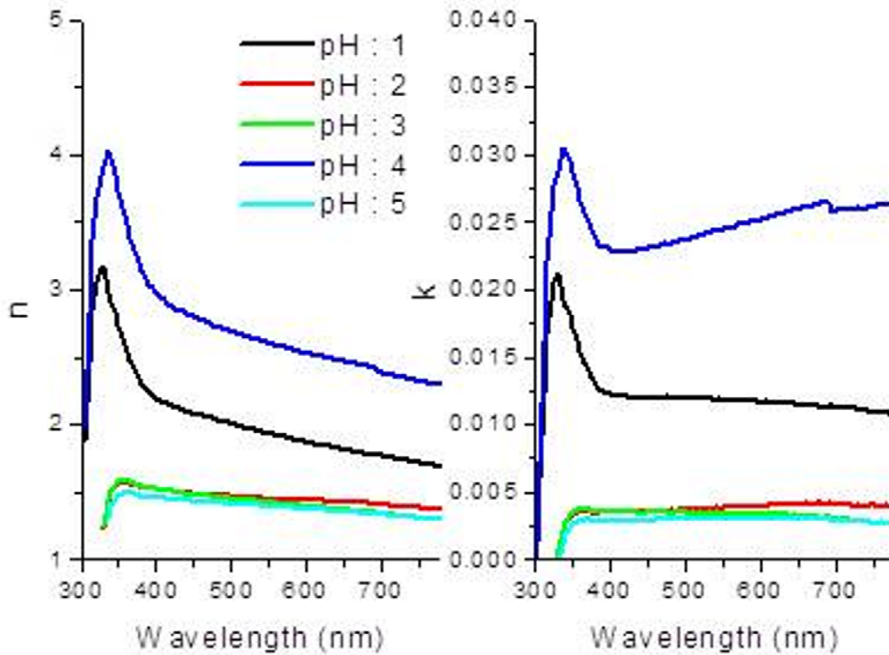
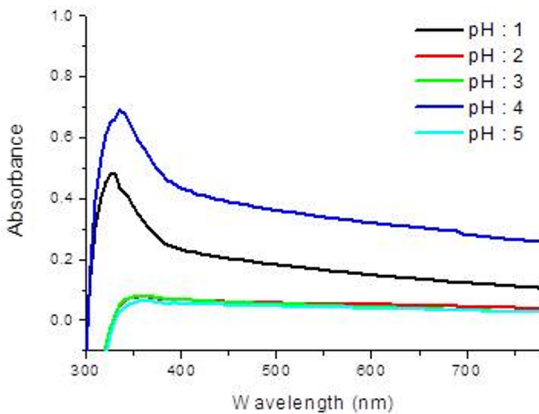**Figure 5.** Refractive index (n) and extinction coefficient (k) of CeS$_x$ thin films produced at different pH.

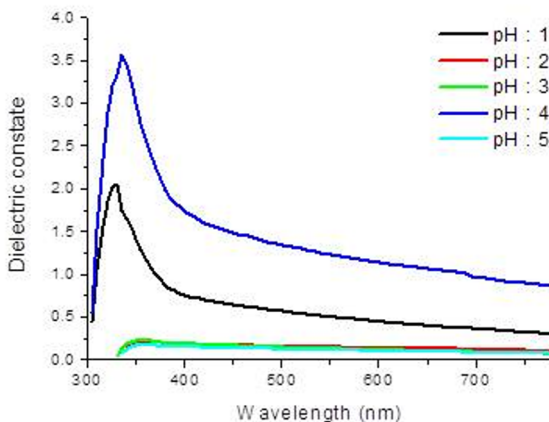**Figure 6.** Absorbance of CeS$_x$ thin films produced at different pH.

Figure 7. Dielectric constant of CeS$_x$ thin films produced at different pH.

start absorption over 450 nm wavelength. Therefore, an increase after that wavelength is observed on both reflective index and extinction coefficient and both increases parallel[6]. At the same time, reflective index may vary according to the thickness of the material. As the thickness of the film increases, the material absorbs more light, which leads to an increase on reflective index[7].

Figure 6 and 7 show absorbance and dielectric constant of CeS$_x$ thin films produced at different pH. The absorbance values of 0.164, 0.053, 0.048, 0.338 and 0.043, are in line with the film thickness (at 550 nm wavelength). Dielectric constant values of CeS$_x$ are found as 0.501, 0.145, 0.131, 1.226 and 0.116 (at 550 nm wavelength). Higher absorbance and dielectric constant values are observed at 330-335-360 nm wavelength. Cerium sulfides are known as UV absorber material. Perrin and Wimmer have reported that doping alkali to the film has caused an electron transition between 4f-5d orbitals. With the contribution of 3p valance band of sulfide, a conduction band has been formed in UV region[8]. Therefore, the electric area formed in the UV region has considerably affected dielectric constant. Moreover, thick film contains more particle, which leads to an increase on the absorption and some increases may be observed on the dielectric constant[9]. According to the literature, such a material with these optical properties is quite useful in semi-conductor technology[10].

4. Conclusion

In our previous study, we have produced crystalline cerium sulfide thin films. This paper is concerned with amorphous cerium thin films and their optical properties. We compare amorphous and crystalline thin films in terms of prominent optical properties in table 1.

Table 1. Compare of the some optical properties of the amorphous and crystalline thin films.

	pH	Optical Band Gap (eV)	Refractive index (550 nm)	Absorbance (550 nm)
Amorphous structures	1	3.16	1.93	0.164
	2	2.08	1.45	0.0053
	3	2.18	1.42	0.048
	4	3.04	2.60	0.338
	5	2.12	1.39	0.043
Crystalline and polycrystalline phases[5]	6	3.14	2.52	0.319
	7	2.99	2.79	0.388
	8	2.86	2.92	0.422
	9	2.92	2.19	0.231
	10	3.23	1.63	0.093

It is well-known that optical band gaps of the amorphous thin films are lower than crystalline ones. Selji et al. discuss this subject in their study[11]. Urbrach tails form a conductivity band over the valance bands. Excited electrons switch to upper bands with lower energy, thus refractive index and the absorbance of crystalline thin films are higher than those of the amorphous ones, assuming that film thickness and average grain size are same. Refractive index and absorbance of the films increase in thicker films, with the interaction of the light with more grains[12-13]. It should be noted that amorphous CeS thin film glasses are convenient for UV absorber and opto-electronic devices.

5. References

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