OPTICAL AND STRUCTURAL PROPERTIES OF CrSe THIN FILM WITH CHEMICAL BATH DEPOSITION

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Chromium selenide (CrSe) crystalline thin film produced with chemical bath deposition on substrates (commercial glass). Transmittance, absorption, optical band gap and refractive index investigated UV/VIS. Spectrum. The hexagonal form observed of structural properties in XRD. The structural and optical of CrSe thin films were analyzed at different pH. SEM and EDX analysis studied for surface analysis and elemental ratio in films. Some properties of films changed with pH and these properties investigated change of pH. The pH values were scanned at 4-9. The optical band gap changed with pH between 3.70 to 3.86 eV. Also, the film thickness changed with pH at 761 nm to 889 nm. The transmission was coherent with the film thickness 82.41, 88.30, 92.47 and 79.06 % (550 nm wavelength) which were at 865, 761, 785 and 889 nm, respectively. Refractive index changed with the film thicknesses at 1.59, 1.45, 1.34 and 1.67 (550 nm wavelength) which were at 865, 761, 785 and 889 nm, respectively.

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1. Introduction

Many methods are using producing of thin films such as dc magnetron sputtering [1], excimer laser metal organic deposition [2], thermal evaporation [3], RF magnetron sputtering [4], electron beam evaporation [5]. Chemical bath deposition is very useful and inexpensive method for the researchers rather than these methods. The researchers produced metal chalgogenides with chemical bath deposition method.

The metal selenides were produced first time by Kutscher in 1960s' as producing PbSe with chemical bath deposition [6-7]. After the Kutscher, the researchers synthesized the other metal selenides. This was important that which was reactive of chemical bath? Some one used thioselenourea or N,N-dimethylselenourea, the others used $NaSeSO_3$ for selenium sources [8-11]. The sodium seleno sulphide was commonly used by the researchers. Although many selenides produced sodium seleno sulphide, chromium selenides was not studied with this method by the researchers. A few researchers studied chromium selenide for properties of magnetism and structural [12-17].

The aim of this paper was produced CrSe thin film with chemical bath deposition and investigated its structural, optical properties. The crystal structure and optical properties of CrSe could be controlled with pH of chemical bath. CrSe thin film is produced many times with chemical bath deposition for the solar cell substrates or magnetic materials. Chromium selenides exhibit interesting structural, magnetic and electrical properties.

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2. Method

The selenium source was prepared with reflux. 1:1 mol ratios of sodium selenium sulphide were added in reflux and 100 mL distillated water. The reaction temperature was 80°C and the reaction time was 4.5 hours. The residual is filtered end of the reaction.

The components of baths were NH_3 2 %, 10 mL 2.5×10^{-3} M cadmium nitrate and 10 mL prepared Se source solution. Firstly, 10 ml 2.5×10^{-3} M cadmium nitrate and 10 ml Se source solution added in baker which was filled 30 ml deionized water. The NH_3 2 % was used adjust the pH of bath. In order to adjust the pH value of the solution to 10, 9 and 8; 0.5, 1.0 and 2.5 mL of NH_3 2 %, respectively, was added to the solutions. The main solution pH was 7. The pH values of the chemical baths were determined using a pH meter (Lenko mark 6230N). The chemical baths were waited 12 hours at room temperature (21 °C).

The X-ray diffractogram (XRD) were recorded using a Rikagu RadB model diffractometer with $CuK\alpha_1$ (λ=1.5406 Å) radiation in the different range 2θ angle 10-90°. Surface morphology was studied by EVO40-LEO scanning electron microscopy (SEM) operating at an accelerating voltage of 20 kV. Chemical analysis by EDX was performed with an EDX spectrometer attached to the SEM. The optical absorption measurement was carried out in the wavelength range from 300 to 1100 nm by using a Hach Lange 500 Spectrophotometer. The film-coated glass substrate was placed across the sample radiation pathway while the uncoated glass substrate was put across the reference path. The absorption data were manipulated for the determination of the band gap energy.

3. Results and Discussion

XRD patterns of the CrSe films deposited by CBD at different pH values are shown in Figure 1 (a: pH 4, b: pH 5, c: pH 6, d: pH 9) and XRD data's of films compared with ASTM values in table 1. The higher intensity peaks can be select in XRD patterns. The monoclinic structure of Cr_7Se_8 was dominant structure at pH: 4 and 5. At pH: 5, CrSe peak located in the structure. Also, monoclinic structure of Cr_3Se_4 designated at pH: 6. Nevertheless, the monoclinic structure of Cr_7Se_8 was dominant character in the acidic area. At the basic area, the monoclinic structure Cr_3Se_4 was overwhelming phase at pH: 9. The pH of chemical bath was very effective on the structure. The researchers also observed same things. Cr_2Se_3 and Cr_7Se_8, Cr_3Se_4 crystallizes were neighboring phases in the monoclinic crystal system [18-19, 13-14]. They thought that the structure of chromium selenide was changed with annealing temperature. So this method is very useful for producing chromium selenide at different phases of chromium selenides. The properties of these phases also were benefit from magnetic properties.

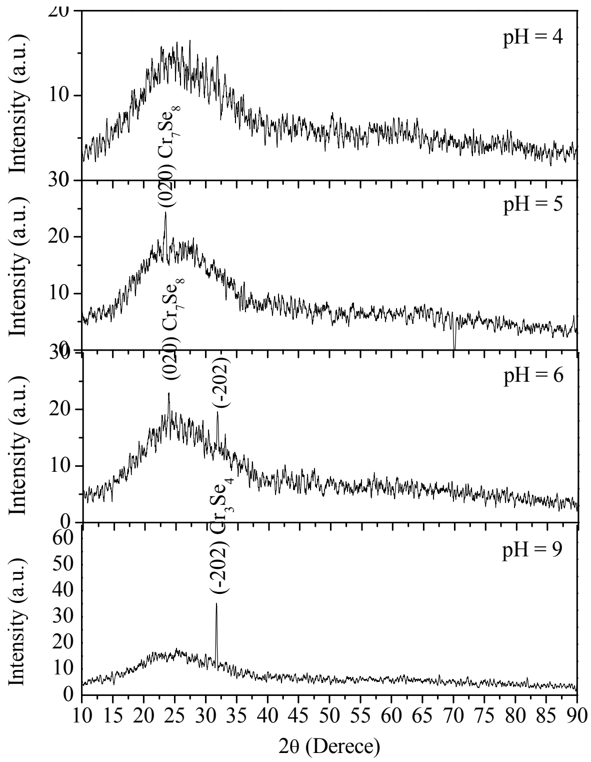

Fig. 1. X-ray patterns of CrSe films deposited in a bath solution at: (a) pH : 4, (b) pH : 5, (c) pH : 6 and (d) pH : 9.

Table 1. XRD datas of ASTM values versus films

pH	ASTM Data File	ASTM Value	Observed Value	Miller İndice
4	74-1242	31.90	31.88	Cr_7Se_8 (222)
	74-1242	24.13	23.47	Cr_7Se_8 (020)
5	73-2235	27.74	27.72	CrSe (100)
	74-1242	24.13	23.88	Cr_7Se_8 (020)
6	74-1241	31.78	31.78	Cr_3Se_4 (-202)
9	74-1241	31.78	31.78	Cr_3Se_4 (-202)

The structural parameters such as grain size (D), dislocation density (δ), for all films were evaluated by XRD patterns and presented in Table 2. The grain size of the thin films was calculated by XRD patterns using Debye Scherrer's formula [20],

$$D = \frac{0.9\lambda}{B\cos\theta} \tag{1}$$

where D is the grain size, λ is the X-ray wavelength used, β is the angular line width at half-maximum intensity in radians and θ is Bragg's angle. The grain size and dislocation density of the films is calculated using the FWHM of (222), (020), (020) and (-202) peaks obtained through the Scherrer's method. The dislocation density (δ) given more information on the amount of defects in the films was given by the formula [20],

$$\delta = \frac{1}{D^2} \tag{2}$$

Higher δ values indicate lower crystallinity levels for the films and indicate the amount defects in the structure. For the films larger D, smaller δ values indicate better crystallization of the films [20].

$$N = \frac{t}{D^3} \tag{3}$$

where N is the number of crystallites per unit area. The higher N value indicates abundance of crystallization.

Table 2. The grain size (D), dislocation density (δ), film thickness (d), optical band gap and the number of crystallites per unit area (N) values of CdSe thin films at pH: 4, 5, 6 and 9.

pH	d (nm)	D (nm)	Eg (eV)	$\delta\times10^{-4}$ (lines/m^2)	$N\times10^{-4}$ (1/m^2)
4	865	47	3.70	4.43	4.10
5	761	39	3.73	6.48	8.26
6	785	34	3.80	8.53	10.97
9	889	20	3.86	24.69	54.00

Table 2 is shown the grain size (D), dislocation density (δ) and the number of crystallites per unit area (N) values of CdSe thin films at pH: 4, 5, 6 and 9. The structure changed with pH while the grain size decreased with pH at 47, 39, 34 and 20 nm, respectively. Although, the film thickness drawn parabolic curve at 865, 761, 785 and 889 nm, respectively with pH, shown in figure 2. The film thickness was not correlated with the grain size. The dislocation density of films increased with pH at 4.43, 6.48, 8.53 and 24.69 $\times10^{-4}$ lines/m^2. The dislocation density of films increased with get smaller grain size. The highest value of the number of crystallites per unit area was at pH: 9 which was 54×10^{-4} m^{-2}. It behaved as the dislocation density, but the number of crystallites per unit area increased faster than the dislocation density. This result is agreeable to XRD patterns. The highest intensity of peak is at pH: 9 with monoclinic structure of Cr_3Se_4. The single crystalline phase may be producing while the different deposition temperature of growth on the different substrates, especially, not amorphous substrates.

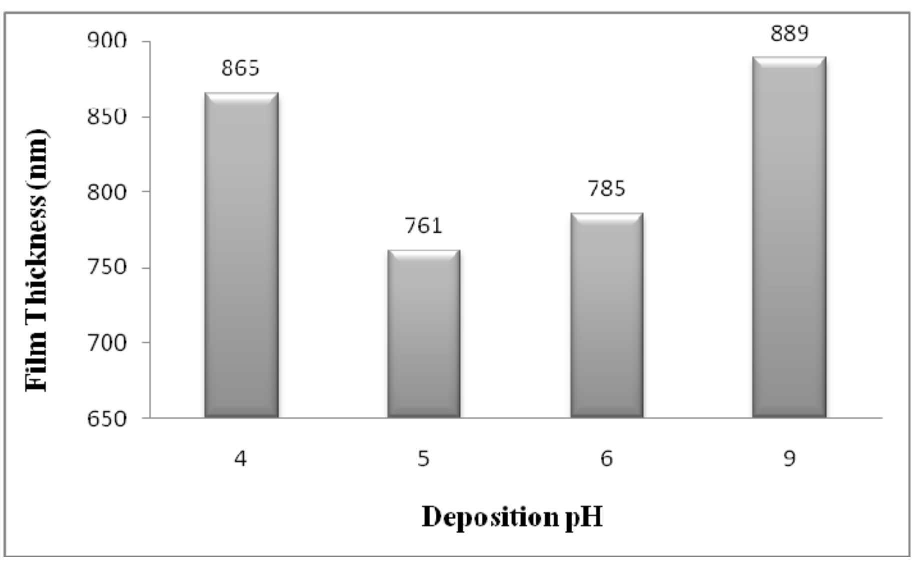

Fig. 2. The film thickness of CrSe thin films

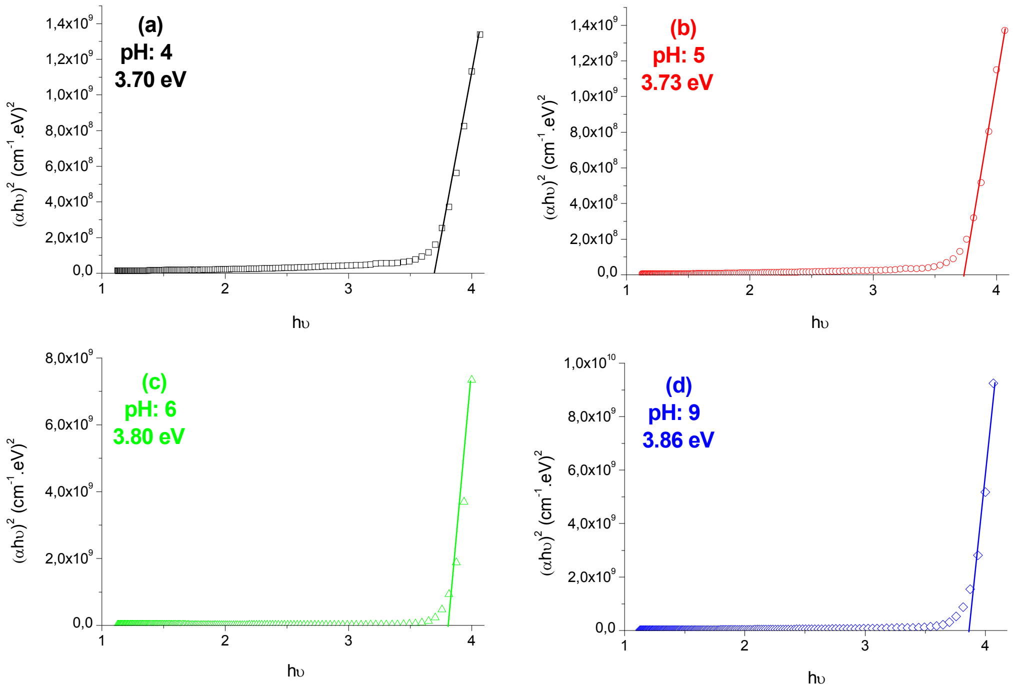

Fig. 3. Plot of $(\alpha h\upsilon)^2$ vs. hυ for CrSe films at different pH: (a) pH 4, (b) pH 5, (c) pH 6, (d) pH 9.

The optic band gap energy (Eg) was determined from the absorption spectra of the films using the following relation [21-22]:

$$(\alpha h\nu) = A(h\nu - Eg)^n \tag{4}$$

The plot of $(\alpha h\upsilon)^2$ vs. hυ for CrSe films at different pH is shown in figure 3. The optic band gap of CrSe thin films aroused at 3.70, 3.73, 3.80 and 3.86 eV at pH: 4, 5, 6 and 9. The optic band gap of the structure of crystalline Cr_3Se_4 at pH: 6 and 9 was higher than the structure of crystalline Cr_7Se_8 at pH: 4 and 5. The grain size affected the the optic band gap. The quantum size affected the optic band gap at different pH [20], this is a well-known reality [23, 11].

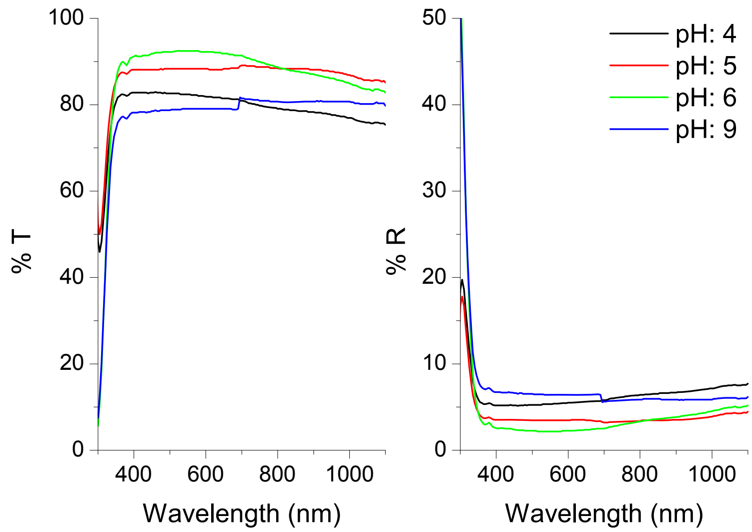

Fig. 4. Transmittance and reflectance of CrSe thin films obtained from baths with different pH of baths

Transmittance and reflectance of CrSe thin films are obvious from figure 4. The transmission was coherent with the film thickness 82.41, 88.30, 92.47 and 79.06 % (550 nm wavelength) which were at 865, 761, 785 and 889 nm, respectively. The reflectance also changed with the film thickness at 5.32, 3.45, 2.18 and 6.42 (550 nm wavelength), respectively. This result is good according to film thickness, although transmittance and reflectance is not congruent with the thickness.

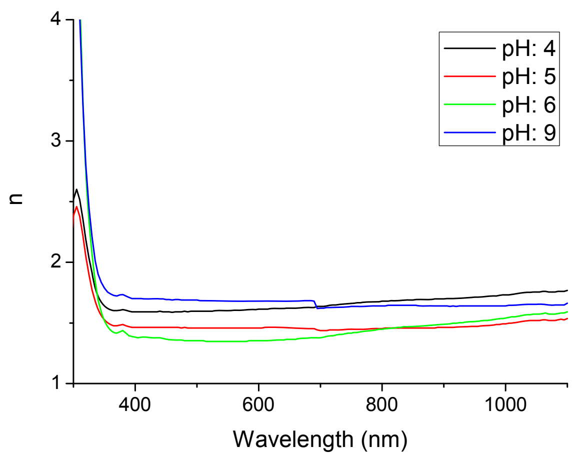

Fig. 5. Refractive index of CrSe thin films obtained from baths with different pH of baths

Fig. 5 is shown refractive index of CrSe thin films with different pH. The refractive index behaved as transmission. It changed with the film thicknesses at 1.59, 1.45, 1.34 and 1.67 (550 nm wavelength) which were at 865, 761, 785 and 889 nm, respectively. The refractive index increased with the film thickness get thicker. According to literature, the refractive index is increased with the film thickness [20, 24]. The light is interact further grains in structure when the film thickness is increasing.

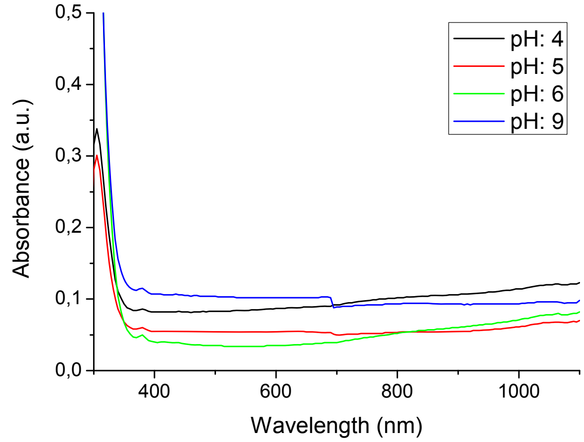

Fig. 6. Absorbance of CrSe thin films at different pH

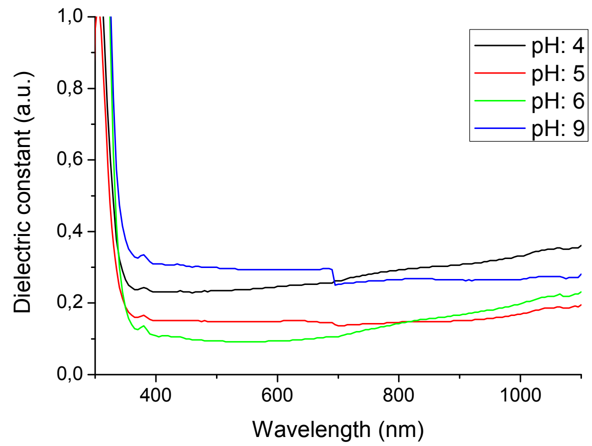

Fig. 7. Dielectric constant of CrSe thin films at different pH

Fig. 6 and 7 are shown absorbance and dielectric constant of CrSe thin films at different pH. Absorbance also imposed the film thickness at 0.084, 0.054, 0.034 and 0.102, respectively. The highest value of absorbance was calculated at pH: 9, which was 0.102. The dielectric constant also behaved absorbance at 0.237, 0.148, 0.091 and 0.293, respectively. This result is show that the Cr_3Se_4 crystalline phase was affected very much in electrical area. These results are in agreement with the literature. XRD patterns are match with ASTM values. The relation of the grain size and the optic band gap [20]. Transmission is inversely correlated with the film thickness [24].

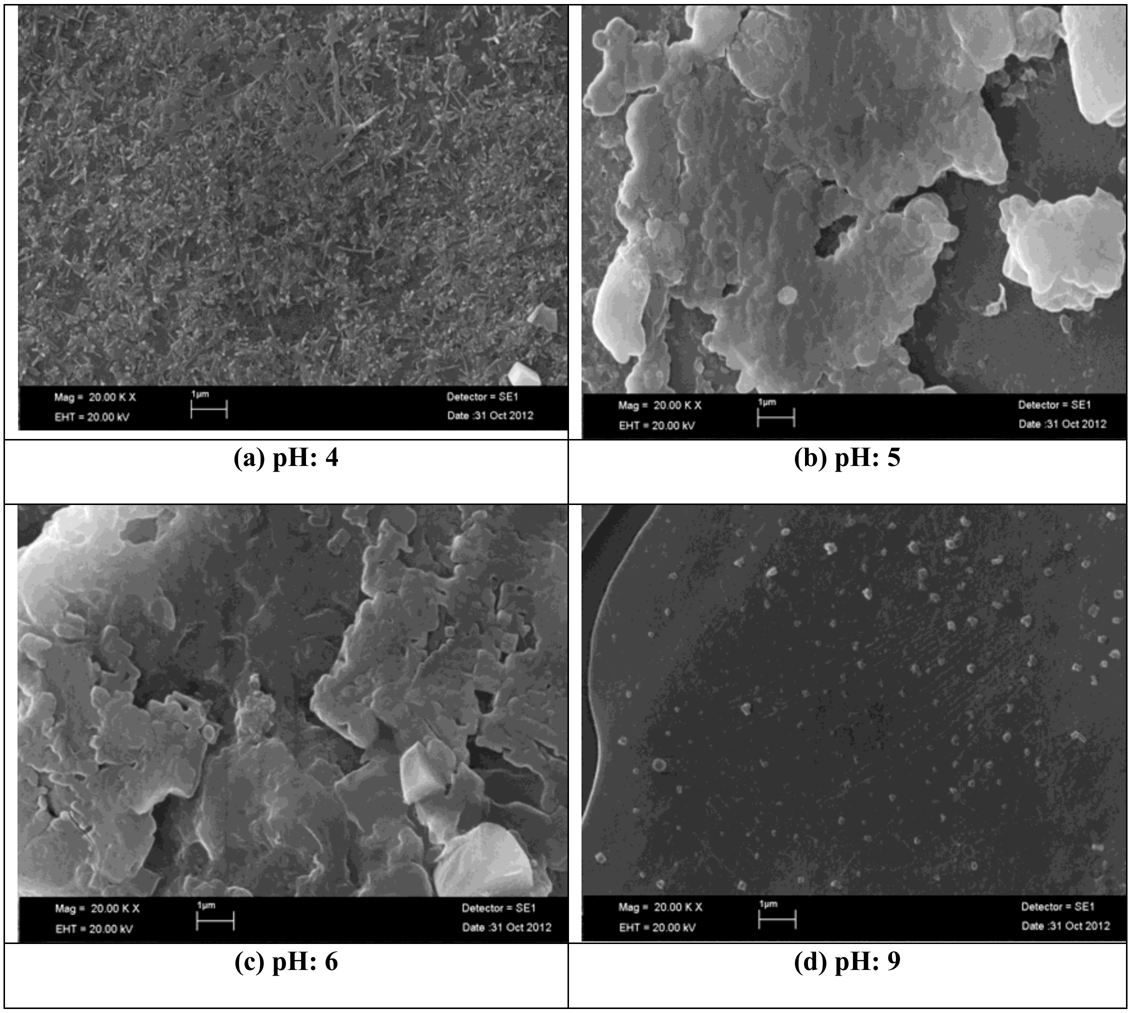

Fig. 8. SEM images of CrSe thin film at different pH (1µm), (a) pH: 4, (b) pH: 5, (c) pH: 6, (d) pH: 9.

The SEM images are shown in figure 8. The mixed phase of pH: 5 and 6 was clearly observed in figure 8b and 8c. The single phase of pH: 4 and 9 was distinguished very easy. The structure of Cr_7Se_8 showed styliform grains at pH: 4, when the structure of Cr_3Se_4 showed dotty grains on a layer. The grains of the mixed phase at pH: 5 and 6 were bigger than the grains of single phase at pH: 4 and 9. The structure converted to Cr_3Se_4 at pH: 4 in acidic media, when the structure of film converted to Cr_7Se_8 at pH: 9 in basic media. But mixed phases were observed in or near the neutral media.

4. Conclusion

The CrSe thin films produced at different pH. The film structure chanced with pH affect. The structure converted to Cr_3Se_4 at pH: 4 in acidic media, when the structure of film converted to Cr_7Se_8 at pH: 9 in basic media. But mixed phases were observed in or near the neutral media. So, some properties of the films changed with pH, actually, with changing different phases as transmission, refractive index, optical band gap. I think that produced these films can be useful in optical and electrical applications.

References

[1] MTS Nair, PK Nair, Semicond. Sci. Technol., **4**, 191 (1989).
[2] S Wang, W Wang, Z Lu, Mater. Sci. Eng. B, **103,** 184 (2003).
[3] S Couve, L Gouskov, L Szepessy, Thin Solid Films, **15,** 223 (1973)
[4] MTS Nair, PK Nair, Semicond. Sci. Technol. 1989, **4:** 599-602
[5] PK Nair, VM Garcia, AM Fernandez, HS Ruiz, MTS Nair, J. Phys. D: Appl. Phys., **24**, 441 (1991).
[6] RH Bube, Photoconductivity of Solids. New York, (Wiley, 1960)
[7] DE Bode, In: Physics of Thin Films, Vol. 3. (Academic Press, 1966), New York and London, p 275
[8] VM García, MTS Nair, PK Nair, RA Zingaro, Semicond. Sci. Technol., **11,** 427 (1996).
[9] PU Asogwa, Journal of Non-Oxide Glasses, **2,** 183 (2010).
[10] AS Khomane, PP Hankare, J. Alloy Comp., **489,** 605 (2010).
[11] VR Shinde, CD Lokhande, RS Mane, SH Han, Appl. Surf. Sci., **245,** 407 (2005).
[12] A Maurer, GJ Collin, Solid State Chem., **34,** 23 (1980).
[13] T Ohtani, R Fujimoto, H Yoshinaga, M Nakahira, Y Ueda, J. Solid State Chem., **48,** 161 (1983).
[14] VA Ivanova, Sh. D Abdinov, GM Aliev, Phys. Status Solidi, , **24,** K145 (1967).
[15] D Babot, M Chevreton, JL Buevoz, R Langnier, B Lambert-Andron, M Winterberger, Solid State Commun., **30,** 253 (1979).
[16] M Winterberger, G Andre, J Hammann, J Magn. Magn. Mater., **147,** 167 (1995).
[17] J Dijkstra, CF van Bruggen, C Haas, RA deGroot, J. Phys. Condens. Matter, **1,** 9163 (1989)
[18] M Chevreton, M Murat, C Eyraud, J. Phys. (Paris), **24**: 443 (1963).
[19] A Maurer, G Collin, J. Solid State Chem., **34:** 23 (1980).
[20] A Ateş, MA Yıldırım, M Kundakcı, A Astam, Semicond. Process., **10,** 281 (2007)
[21] N Benramdane, WA Murad, RH Misho, M Ziane, Z Kebbab, Mater. Chem. Phys., **48,** 119 (1997).
[22] B Pejova, I Grozdanov, A Tanusevski, Mater. Chem. Phys., **83,** 245 (2004).
[23] L Xu, X Li, Y Chen, F Xu, Appl. Surf. Sci., **257,** 4031 (2011).
[24] HE Esparza-Ponce, J Hernández-Borja, A Reyes-Rojas, M Cervantes-Sáncheza, YV Vorobiev, R Ramírez-Bon, JF Pérez-Robles, J González-Hernández, Mat. Chem. Phys., **113,** 824 (2009).