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PREPARATION OF $CdS_{1-x}Se_x$ THIN FILMS BY A CHEMICAL DEPOSITION METHOD, AND EXAMINATION OF SOME OPTICAL AND PHOTOELECTRICAL PROPERTIES

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A b s t r a c t: The method of chemical deposition of $CdS_{1-x}Se_x$ is based on the chemical reaction between the hydroxy-citric complex of the cadmium, with sulfide and selenide ions, produced by the chemical decomposition of thiourea and sodium selenosulfate, in alkali media. Sodium silicate glass was used for substrates.

The composition of the thin films was verified by X-ray analyses. From the optical spectra, as well as from the spectral sensitivity of the photoconductivity, the values of the band gaps (E_g) were evaluated for a set of 10 samples of $CdS_{1-x}Se_x$, where x varies from 0 to 1. It was found that the E_g value decreases with the increase of x.

Introduction

The preparation and examination of the physical properties of the semiconductive materials are problems of great importance in modern science. Nowadays, the composite semiconductor thin films are subject to very extensive studies, which is due to their potential applicability for photovoltaic cells, LED, gas sensors and other electrooptical devices.

Semiconductor thin films can be prepared by different methods such as vacuum evaporation, spray-pyrolysis, electrolysis, molecular beam epitaxy magnetron spattering, chemical deposition (electroless method) [1], etc. One of the most promising and cheapest methods with respect to the equipment and energy consumption, is the method of chemical deposition. A wide range of thin films with a high quality, such as CdS [2], CdSe [3], PbS [4], PbSe [5], SnS [6], Ag_2S [7], and many others, were prepared by this method on different substrates: insulators, semiconductors, and metals. Mixtures and especially solid solutions of semiconductor compounds, such as $CdS_{1-x}Se_x$ [8], $CuInSe_2$ [9], $CdSe_{1-x}Te_x$ [10], etc., are of special interest, due to the possibility of variation of the band gap E_g.

The mechanism of deposition of thin $CdS_{1-x}Se_x$ films is studied in this work. The system contains a water solution of hydroxy-citric complex of cadmium, sodium selenosulfate and thiourea in an alkaline medium.

The X-ray analyses showed that under the reaction conditions (pH > 10.5), thin films of a solid $CdS_{1-x}Se_x$ solution, with a dominant hexagonal crystal structure, were obtained. Ten samples of $CdS_{1-x}Se_x$ films, where x varies from 0 to 1, prepared by the method of chemical deposition, under conditions of heterogeneous nucleation, are presented in this paper. The values of the E_g, were calculated from the data of optical spectra, and from the spectral sensitivity of the photoconductivity.

Experimental part

The sodium-silicate glass substrates were initially degreased by chromsulphuric acid, and after rinsing with distilled water in an ultrasonic bath, were activated by a solution of tin (II) chloride and thiourea [11]. The substrates were further deeped in a reactive solution (100 mL) which contained:

0.40 mol/dm^3 $CdCl_2$ – 10 mL
1.00 mol/dm^3 $Na_3(CH_2)_2C(OH)(COO)_3$ – 10 mL
[note: The $(CH_2)_2C(OH)(COO)_3^{-3}$ will further on be denoted as Cit]
Na_2SeSO_3 and
$(NH_2)_2CS$ – thiourea.

The total mole portion of the Na_2SeSO_3 and thiourea was equal to 0.05. The alkalinity of the environment was set to pH = 11, by the addition of 0.1 mol/dm^3 of NaOH to the solution. The deposition of the thin $CdS_{1-x}Se_x$ films occurs according to the following chemical reactions:

$$Na_2Cd(CitOH) + (NH_2)_2CS + NaOH = CdS + Na_3Cit + (NH_2)_2CO + H_2O$$

$$Na_2Cd(CitOH) + Na_2SeSO_3 + NaOH = CdSe + Na_3Cit + Na_2SO_4 + H_2O$$

The formation of the thin films was initiated by dipping the substrates into the reaction solution, followed by constant mixing with 10 rotations per minute, at a constant temperature of 80°C. When the deposition process was completed (after some 40–50 minutes), the samples were rinsed and kept in distilled water for several hours. After drying, the samples were thermally treated at a temperature of 300°C in air, for 3 hours. The thickness of the films varied from 0.3 to 0.4 μm, depending on the preparation conditions.

The composition and the crystal structure of the thin films were verified by X-ray diffraction analyses using a JEOL DX-GO-F type diffractometer, with Ni-filtered radiation of Cu-anticathode.

The quantitative analyses were made by several methods, including atomic absorption spectrometry, polarography and ionometric analyses. The mole fraction of Se was determined by cathodic stripping analysis.

The optical spectra of the above described set of 10 samples of $CdS_{1-x}Se_x$ films, where x varies from 0 to 1, were recorded on a HEWLETH PACKARD spectrophotometer 8452A. The photosensitivity spectra were measured by the constant field method [12.]. A monochromator Univerzal XM-2, of Russian production, was used as a light source.

Results and discussion

From polarographic measurements it was found that cadmium ion forms a complex of Cd-citric anion in a neutral environment, with a stability constant $K = 1.6\ 10^4$ dm^3/mol [13]. Fig. 1 shows the UV spectra with the corresponding λ_{max} and the molar absorption coefficient (ε), of the water solutions of $CdCl_2$ (λ_{max} = 192 nm, $\log\{\varepsilon\}$ = 2.89), and Na_3Cit (λ_{max} = 196 nm, $\log\{\varepsilon\}$ = 3.10) and the spectrum of the product of their chemical reaction (λ_{max} = 196 nm, $\log\{\varepsilon\}$ = 3.09. Note that the brackets indicate that the numerical value is to be used; not the physical quantity.)

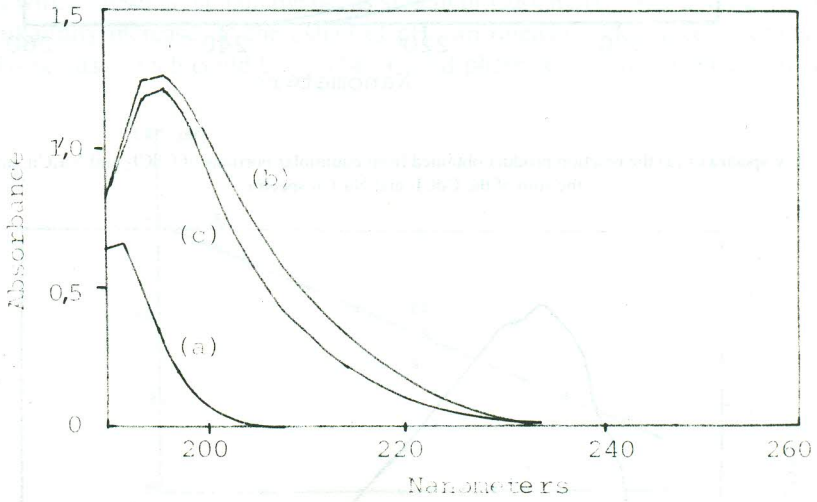

Fig. 1 - UV spectra of (a) $CdCl_2$, b) Na_3Cit, and (c) reaction product

There are appreciable differences in the position of the maxima and the molar absorption coefficient, between the spectrum of the product of the chemical reaction, and the arithmetic sum of the spectra of the starting chemicals $CdCl_2$ and Na_3Cit (λ_{max} = 194 nm, $\log\{\varepsilon\}$ = 3.23), as seen in Fig. 2, which is a qualitative proof of the existence of a complex of the Cd-anion with a citric ligand, which is in accordance with the existing knowledge from polarographic studies. If a strong base (such as NaOH for instance) is added. a hydroxy-citric anion of cadmium, with a stability constant $K = 2.0$

10^9 dm^3/mol [13], will be formed. The spectrum of such a hydroxy-citric complex of cadmium, for a mole ratio:

metal : ligand : base = 1 : 1 : 1

is presented in Fig. 3, where λ_{max} = 208 nm, and $\log\{\varepsilon\}$ = 3.14.

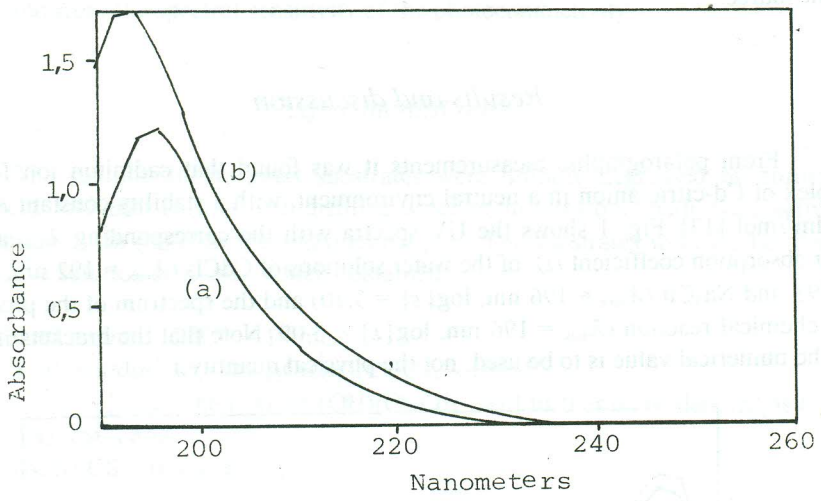

Fig. 2 – UV spectra of (a) the reaction product obtained from equimolar portions of $CdCl_2$ and Na_3Cit, and (b) the sum of the $CdCl_2$ and Na_3Cit spectra

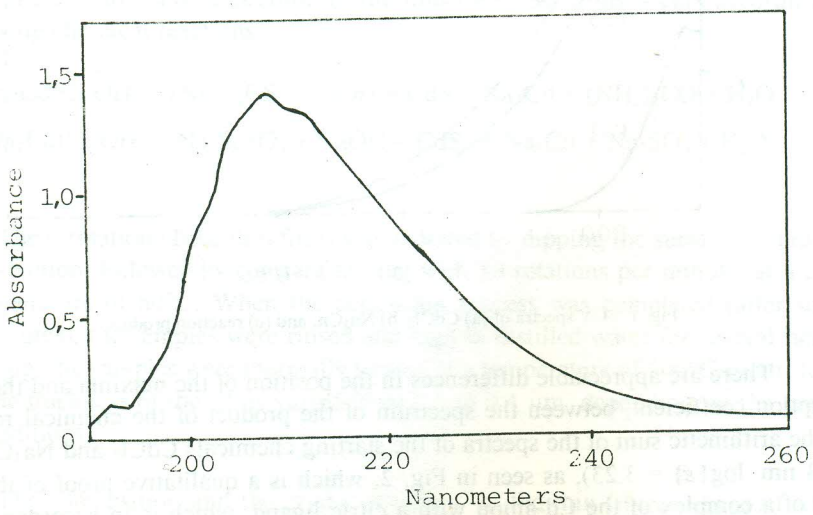

Fig. 3 – UV spectrum of $Na_2CdOHCit$ dissolved in water

The reaction system which contains the citric complex of cadmium[1], sodium selenosulfate, and selenourea is insufficiently alkaline to provide a spontaneous generation of S^{2-} and Se^{2-} anions which would enable the deposition of the $CdS_{1-x}Se_x$ thin films. By further addition of alkaline solution to the system, an intensive decomposition and precipitation occurs, which could possibly be followed by a simultaneous precipitation of cadmium hydroxide. In that case the deposition will take place according to the mechanism of heterogeneous nucleation, i.e. a thin layer of $Cd(OH)_2$ will be formed on the surface of the substrate. This layer will assist the $CdS_{1-x}Se_x$ thin film deposition. Analogously as in Ref. [4], the theoretical critical value for the alkalinity (pH_c) needed for the $Cd(OH)_2$ precipitation to commence was found to be

$$pH = \log\{C_{cit}\} - \log\{K_w C_{comp}/K K_{sp}\} \quad (1)$$

where

C_{cit} – is the concentration of the citric ion,

C_{comp} – is the concentration of the hidroxy-citric complex of cadmium,

K_w – is the ionic product of the H_2O,

K_{sp} – is the solubility product constant of $Cd(OH)_2$, (a value of $2.2\ 10^{-14}$ mol^3/dm^9 [13] was used in this work)

K – is the stability constant of the hydroxycitric Cd-complex.

A graphical interpretation of Eq. 1 is given in Fig. 4. A straight line marked with A illustrates the equilibrium between the $Cd(CitOH)^{2-}$ and $Cd(OH)_2$. The region marked with I presents the homogeneous system of $Cd(CitOH)^{2-}$ and extra Cit^{3-} anions. If the alkalinity increases to the extent of pH_c, an intensive spontaneous formation of $Cd(OH)_2$ occurs, which could be seen as a solid phase region, designated as II in Fig. 4.

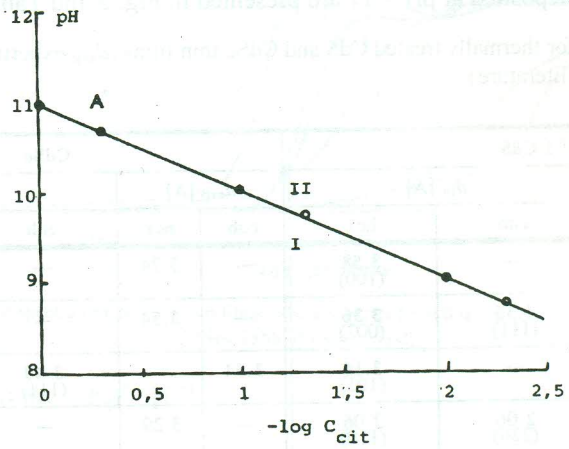

Fig. 4 – Graphical presentation of Equ. 1

Eq. 1 is valid only for room temperature conditions, at which the deposition of the thin $CdS_{1-x}Se_x$ films, especially under homogeneous nucleation conditions, is sufficiently slow.

[1] For other metal versus ligand ratios, other complexes may also exist [14].

It was empirically found that, when the deposition rate is sufficiently fast (at a temperature of ~ 80°C, and for a given concentration of the reaction chemicals), the optimal pH value required for the creation of active $Cd(OH)_2$ deposition centers varies between 10.5 and 11.5. If the alkalinity is increased above pH = 12, the obtained samples are of a rather bad quality. The study of their X-ray diffractograms shows the presence of CdO which simultaneously precipitates as a hydroxide, under the above-described conditions, together with the $CdS_{1-x}Se_x$. These thin films are mixtures, and do not show photoconductivity.

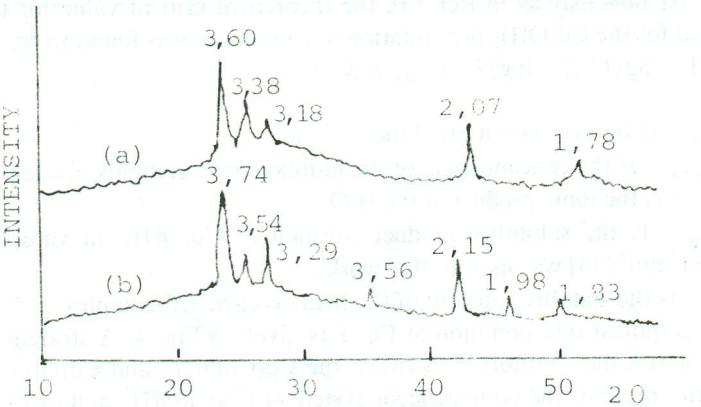

Fig. 5 – X–ray diffraction spectra of thermally treated thin films prepared at pH = 11: (a) CdS and (b) CdSe

The data obtained from the X-ray diffractograms of the pure samples (those for x = 0 and 1), deposited at pH = 11 are presented in Fig. 5 and Table I.

Table I – *d*-values for thermally treated CdS and CdSe thin films (d_{exp}-experimental values; d_{lit}-values from the literature)

CdS				CdSe			
d_{exp} [A]		d_{lit} [A]		d_{exp} [A]		d_{lit} [A]	
cub	hex	cub	hex	cub	hex	cub	hex
—	3.60	—	3.58 (100)	—	3.74	—	3.72 (100)
3.36	3.36	3.36 (111)	3.36 (002)	—	3.54	—	3.53 (002)
—	3.18	—	3.16 (101)	3.54	—	3.49 (111)	—
2.07	2.07	2.06 (220)	2.06 (110)	—	3.29	—	3.29 (101)
1.76	1.76	1.75 (311)	1.76 (112)	—	2.56	—	2.55 (102)
				2.15	2.15	2.14 (220)	2.15 (110)
				—	1.98	—	1.98 (103)
				—	1.83	—	1.83 (112)

One can easily see that the corresponding thin films contain hexagonal and cubic crystal phases. The analyses of the relative intensities I/I_0 [15] showed that the hexagonal phase is dominant. The films obtained under the condition of homogeneous nucleation exhibited cubic structure. On the other hand, for the films with hexagonal structure (for which $0 < x < 1$), none of the calculated d-values belonged to the pure structures (i.e. for which $x = 0$ and $x = 1$), shown in Table I, which strongly indicates that the thin films formed are solid solutions of $CdS_{1-x}Se_x$ type [16].

The mole ratio of selenium in the solution and in the film is not equal and may be presented by the following least-squares-best-fit linear equation:

$$x(\mathrm{Se})_{\mathrm{film}} = a\,x(\mathrm{Se})_{\mathrm{sol}} + b$$

where $a = 1.061$; $b = 0.048$ and correlation coefficient r equals 0.983.

The optical spectra of the thermally treated samples at a temperature of 300°C presented in Fig. 6 reveal a qualitative picture for the red shift of the absorption edge with the increase of x. Other information obtained from the transmission spectra analyses are the values of the $E_{g(\mathrm{tr})}$ of the $CdS_{1-x}Se_x$ thin films. Using the relation

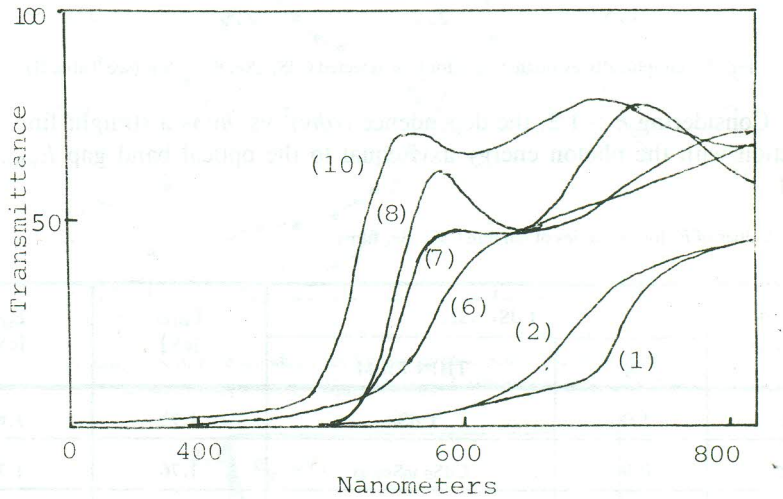

Fig. 6. Optical spectra of $CdS_{1-x}S_x$ thin films, where x varies from 0 to 1, thermally trated at 300^0 C (See Table II for a legend)

$$\alpha h\nu = B\,(h\nu - E_g)^n \quad [17],$$

where

α – is the absorption coefficient,
$h\nu$ – is the photon energy,
E_g – the band gap energy,
B – a constant,
n – a number that depends on the zone to zone electron transition. In our case, its value was found to be close to 1/2 which corresponds to direct electron transition.

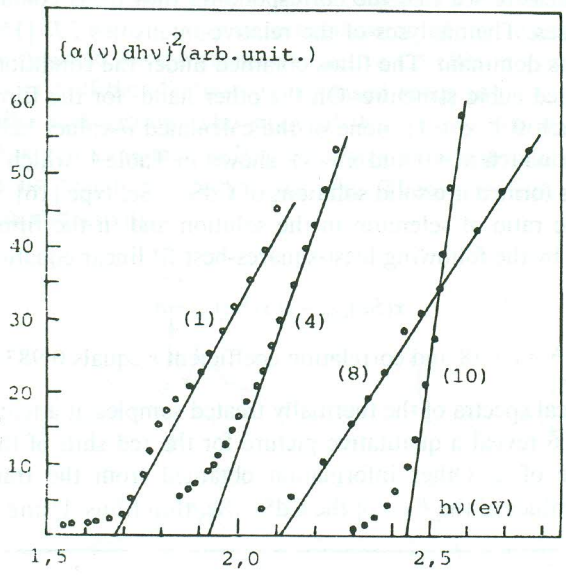

Fig. 7 – Graphically evaluated $E_{g(tr)}$ for four selected $CdS_{1-x}Se_x$ thin films (see Table II)

Considering $n = 1/2$, the dependence $(\alpha h\nu)^2$ vs. $h\nu$ is a straight line, with an intersection with the photon energy axis equal to the optical band gap $E_{g(tr)}$, Fig. 7, Table II.

Table II – Values of E_g for one series of ten thin $CdS_{1-x}Se_x$ films

Serial Number	$CdS_{1-x}Se_x$		$E_{g(ph)}$ [eV]	$E_{g(tr)}$ [eV]
	X	THIN FILM		
1	1.00	CdSe	1.72	1.68
2	0.90	$CdS_{0.10}Se_{0.90}$	1.76	1.70
3	0.78	$CdS_{0.22}Se_{0.78}$	1.88	1.80
4	0.75	$CdS_{0.25}Se_{0.75}$	1.95	1.92
5	0.65	$CdS_{0.35}Se_{0.65}$	1.99	1.94
6	0.59	$CdS_{0.41}Se_{0.59}$	2.03	1.96
7	0.26	$CdS_{0.74}Se_{0.26}$	2.18	2.03
8	0.12	$CdS_{0.88}Se_{0.12}$	2.26	2.12
9	0.05	$CdS_{0.95}Se_{0.05}$	2.36	2.17
10	0.00	CdS	2.53	2.44

The values of the optical band gap were also evaluated from the spectral sensitivity of the photoconductivity, $E_{g(ph)}$. Fig. 8 shows the dependence of the photoconductivity on the photon energy, for four samples, while for the other six, only the maxima that correspond to the $E_{g(ph)}$ are tagged [18]. It is obvious that the results for E_g, evaluated by two different methods, show good agreement. Besides, there is also a good agreement between the results for $E_{g(tr)}$ (cf. Table II) and $E_{g(ph)}$, on one hand, and those from the available literature data [19], on the other. The shift of $E_{g(ph)}$ due to the variation of x is shown in Fig. 9.

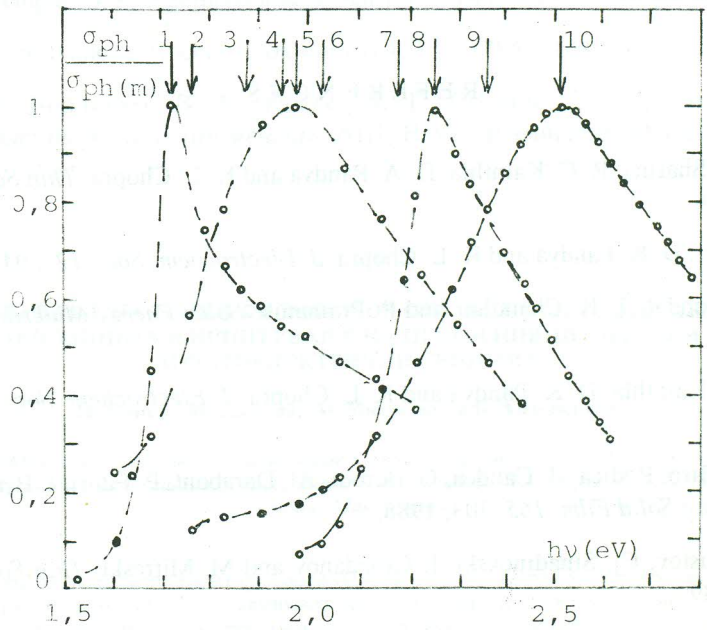

Fig. 8 – Spectral sensitivity of photoconductivity for one series of $CdS_{1-x}Se_x$ thin films. The peak photoconductivities coresponding to $E_{g(ph)}$ are tagged with arrows (see Table II))

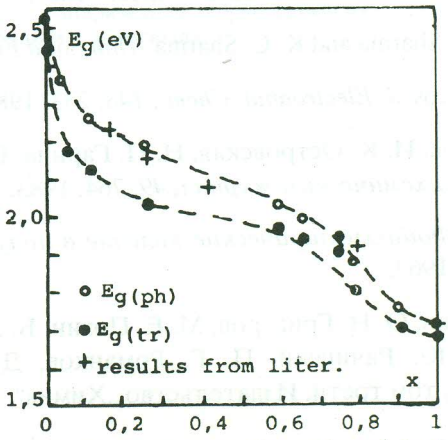

Fig. 9 – Dependence of E_g of the thin $CdS_{1-x}Se_x$ films on the mole fraction of selenium (x)

Conclusion

The thin $CdS_{1-x}Se_x$ films obtained by the chemical deposition method present solid solutions of CdS and CdSe. They exhibit very high photoconductivity. The ratio between the conductivity of the thin films, when illuminated with white light (60 mW/cm^2), and their dark conductivity, is of the order of magnitude 10^5. This gives an opportunity for these materials to find their application as photosensors in various electrooptical devices.

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Резиме

ПРИГОТВУВАЊЕ НА ТЕНКИ ФИЛМОВИ ОД $CdS_{1-x}Se_x$ ПО МЕТОД НА ХЕМИСКА ДЕПОЗИЦИЈА И ИСПИТУВАЊЕ НА НЕКОИ НИВНИ ОПТИЧКИ И ФОТОЕЛЕКТРИЧНИ СВОЈСТВА

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Методот за депозиција на филмови од CdS_{1-x} Se_x е базиран на хемиска реакција меѓу хидроксоцитратен комплекс на кадмиумот со сулфидни и селенидни јони, добиени со разложување на таложните реагенси тиоуреа и натриум селеносулфат, во алкална средина. Користени се супстрати од натриум силикатно стакло. Составот на препаратите е верифициран со рендгенска дифракциона анализа. Врз база на податоците од оптичките спектри и спектралната сензитивност на фотоспроводливоста, определени се ширините на забранетата зона за десет филма со различен состав. Ширините на забранетата зона опаѓаат со пораст на молскиот удел на селен во полуспроводливите материјали.