

Growth technology, X-ray and optical properties of CdSe thin films

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Abstract

Cadmium selenium (CdSe) is a II–VI compound semiconductor material with suitable properties for applications in electronics and optoelectronics devices such as laser diodes, high-efficiency solar cells, nanosensors and biomedical imaging devices [1–3]. It has a direct band gap with high absorption coefficient near the band edge, which allows its use in thin films devices; it is especially interesting for application in solar hybrid systems [4]. The CdSe energy band gap is about 1.8 eV [5], which divides the solar spectrum in two parts, namely, the “thermal” part with $h\nu < E_g$ and the “optical” one with $h\nu > E_g$, both parts with practically equal radiation energy. Thus, CdSe layers can absorb the “optical” solar spectrum for photovoltaic energy conversion and transmit the “thermal” one to be employed in some other manner such as direct heating, heat engine or by another solar cell with narrower gap absorber in a tandem arrangement.

Introduction

CdSe films can be deposited by several techniques being the chemical bath deposition (CBD) method one of the most convenient. The CBD technique has been

used for many years to prepare thin films of chalcogenide semiconductors and other kind of materials, Nemec et al. [6], obtained films of closely packed nanocrystals of CdS by CBD using thiourea and an NTA complex of Cd in alkaline solutions, Gao et al. [7] prepared Zinc sulfide films by conversion of zinc oxide films in the presence of hydrogen sulfide. Sartale et al. [8] used a new route for the CBD that gives dense, compact and uniform ZnS thin film without ZnO even after annealing of the films. Nemec et al. [9], studied of properties of CdS nanocrystalline films prepared by CBD using thiourea and an NTA complex of Cd in alkaline solutions. Ortuño-López et al. [10] reported the properties of chemically deposited CdS films obtained by an ammonia-free method. Borges [11], realized the investigation of ZnS as a buffer layer in ZnO/ZnS/CuInS₂ devices. Nakada and collaborators [12], suggested a new doping technique for the manufacture of CuInGaSe₂ (CIGS) thin. Ennoui et al. [13], prepared Zn-compounds buffer layers as an alternative to the CdS for CuInGaSe₂ thin film solar cells. O'Brein et al. [14], prepared ZnS by chemical bath contained zinc ions, urea and thioacetamide but at modestly acid values of pH. Oladeji and Chow [15], obtained further insights into the CBD growth mechanisms of ZnS thin films using an aqueous medium containing a salt. At room temperature the optimum concentration of this salt has enabled to increase the thickness of the film by more 400%. Johnston et al. [16] produced ZnS polycrystalline thin film, nearly stoichiometric and uniformly thick by CBD using a novel complementary complexing agent, sodium citrate. Dona and Herrero [17] obtained ZnS thin films from NH₃/NH₂-NH₂/SC(NH₂)₂/ZnSO₄ solutions by CBD and studied the effect of various process parameters on the growth and the film quality. Mane and Lokhande

[18] prepared semiconducting NiS thin films deposited onto glass using successive ionic layer adsorption and reaction (SILAR) method. Thakoor et al. [19] used spray pyrolysis method to obtain coatings of chalcogenides of cadmium and their application to improved thin film solar cells. Lokhande et al. [20] reported deposition of cadmium selenide films over the pre-cleaned titanium, nickel, and ITO-coated glass substrates.

CBD is based on the controlled precipitation of a solid phase from their precursor ions in an aqueous solution. For the deposition of good quality thin films and well adherent to appropriated substrates the control of precipitants is a key factor. For this, a complexing agent is typically used, which traps the free metal ions in the solution to form a complex ion. The controlled release of the metal ions from the complex ions under the adequate conditions avoids fast precipitation of the solid phase and promotes the formation of a homogenous thin film on the substrate. The most common complexing agent for Cd ions employed in the chemical deposition of cadmium chalcogenides is ammonia. One of the drawbacks of ammonia is that its volatility modifies the pH and volume of the reaction solution during the deposition process making difficult the film reproducibility. However, the major problem with ammonia is connected with its high toxicity and environmental issues, which obviously become more serious for the case of large area deposition process. That is why in the last few years many research works have looked for ammonia-free CBD processes to obtain good quality cadmium chalcogenide films [20]. There are several feasible alternatives to ammonia as the complexing agent of Cd ions, being sodium citrate one of the most convenient. Sodium citrate is a cheap and harmless

organic compound, which has been used alone or in combination with ammonia for the chemical deposition of good quality CdS films [21–23].

In this paper we report an ammonia-free CBD process for the deposition of CdSe nanocrystalline thin films. The CBD process is based on the substitution of ammonia by sodium citrate as the complexing agent of Cd ions in the reaction solution. The chemically deposited CdSe films were studied by several techniques to determine their physical properties. The results show that this process provides CdSe thin films with high structural and optical characteristics, which are viable candidates for application in multi-stage solar energy conversion devices [4].

Experimental procedure

CdSe thin films were prepared by ammonia-free CBD on glass substrate. The substrates were cleaned with soap and deionized water in ultrasonic baths. The reactive materials used in the chemical bath were a cadmium chloride complexed with sodium citrate, and the sodium selenosulphate as the source of selenium ions. The preparation conditions such as solution concentration, pH value, deposition time, bath temperature and immersion cycles were optimized (see below) to get the nanocrystalline cadmium selenide films. Typically the thickness of 400–500 nm was obtained for a growing time of around 4 h in one cycle.

Four different starting chemical baths were prepared A, B, C and D. A (with 30 cm³ selenosulfate and 0.4 M CdCl₂), B (20 cm³ selenosulfate and 0.4 M CdCl₂), C (15 cm³ selenosulfate and 0.4 M CdCl₂) and D (30 cm³ selenosulfate and 0.5 M CdCl₂). First, the molar solutions of each ingredient were prepared. To prepare the different starting baths, the solution of CdCl₂ was first poured in a 100-ml beaker;

the other chemicals were added in the following sequence: sodium citrate 0.8 M, potassium hydroxide 0.8 M, a buffer solution with chemical grade of borate with pH 10 and finally sodium selenosulphate. All solutions were made using deionized water. The solution of sodium selenosulphate (0.12 M) was mixed by refluxing grey selenium powder with anhydrous sodium sulphite (99.8%) in 200 ml of water for 8 h. The four starting baths were prepared by mixing the molar solutions according to the volumes mentioned above. The pH was from 11.75 to 12.31. The beaker was introduced into a heated bath at 70 and 80 °C. Uniform films with good adhesion to the substrate were obtained at a pH of 11.75 and 80 °C.

The thin films were deposited from baths at room temperature and at the two indicated temperatures, for each temperature four different bath compositions A, B, C and D were used. The best samples for each temperature were obtained from solution A. Samples were deposited at three bath temperatures: room temperature

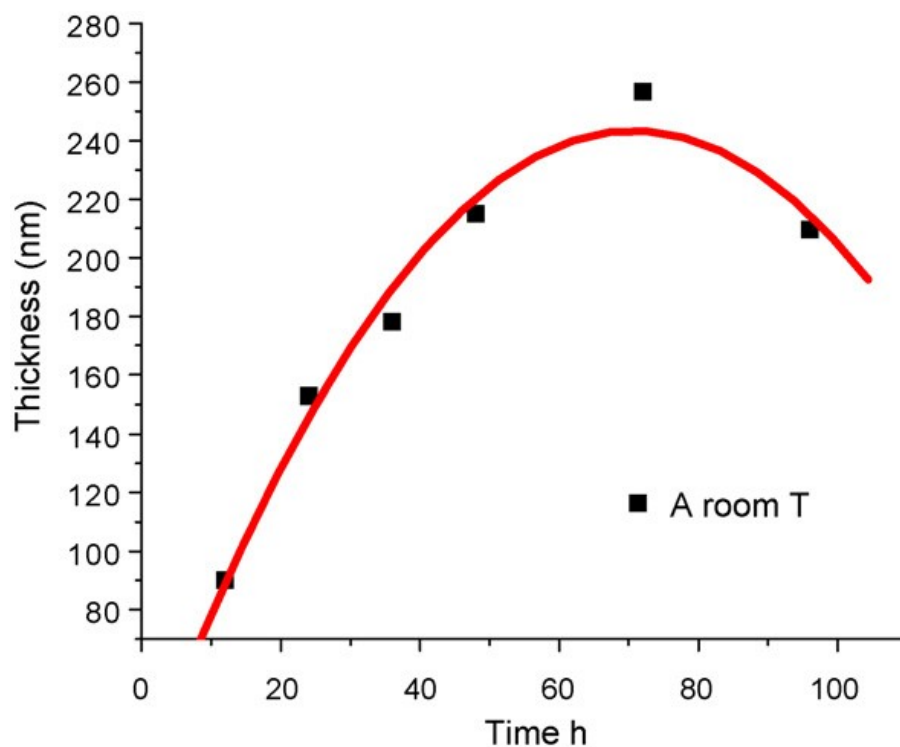


Fig. 1. Thickness vs. deposition time for CdSe thin films obtained from bath at room temperature for 12–96 h.

with immersion times of 12, 24, 36, 48, 72 and 96 h; 70 and 80 °C with depositions times of 2, 3, 4, 5 and 6 h.

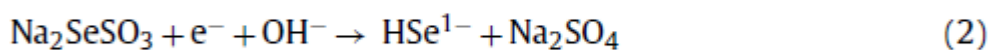
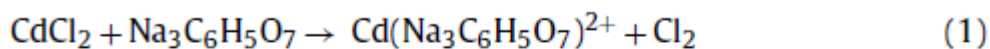
The films were characterized by optical absorption using a UV–vis spectrometer PerkinElmer Lambda2 in the wavelength range of 300–1100 nm. The chemical composition was obtained using energy dispersive X-ray analysis (EDX, DX Prime EDAX) coupled to a scanning electron microscope (JSM-5800LV JEOL). The structure was determined from X-ray data obtained from a RIGAKU diffractometer with Co Ka radiation, $\lambda = 1.78899 \text{ \AA}$ Ka1, Dmax of 2100, 30 kV and 16 mA in the range of 10–90°

in the 2 θ scale. The data were analyzed with the WinJade software by MDI. Sample thickness was measured using a Destak II version 2.3 Sloan profilometer.

Results and discussion

Chemical reactions and film thickness

Thin films of cadmium selenide were deposited on glass substrate by slow release of Cd²⁺ and Se²⁻ in the reactor, the pH was 11.75. Sodium citrate in cadmium chloride forms a complex, the growth mechanism of the CdSe film on glass substrates is speculated as follows:



The reduction of Na₂SeSO₃ to elemental Se and the liberation of Cd from

the complex were through the following reaction:



The behavior of thickness versus deposition time for films prepared with composition A from baths at room temperature and 80 °C are shown in Figs. 1 and 2, respectively. In both cases, film thickness increases with the immersion time, but after certain hours the growing process reaches the saturation and further only lower thickness values can be achieved. The maximum thicknesses obtained for the samples prepared from baths at room temperature and 80 °C were achieved in one immersion or deposition cycle; using two cycles it is possible to double film thickness values.

Deposition begins only when the chalcogenide concentration is high enough to allow nucleation to start, which occurs in the linear region of growth. As the limiting reactant is used up, growth will start to slow down and eventually stop due to depletion of the reactants [23].

The authors of Ref. [23] worked with nitrilotriacetic acid (NTA) as a complexant, reporting longer growth times than those for ammonia-based baths typically from a few days for film to achieve film thickness in the range of 100–300 nm.

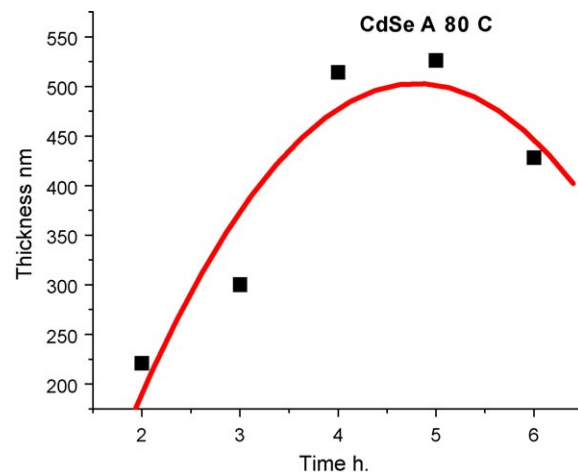


Fig. 2. Thickness vs. deposition time for CdSe thin films obtained from bath for solution A at 80 °C.

With the method used in this work, besides preventing the irreproducibility due to the vaporization of ammonia, only 4 h are needed to produce thin films with a thickness of about 500 nm.

Crystal structure

The X-ray diffraction data (Fig. 3) show that the majority of samples have one intense reflection peak at approximately 30° (2θ) and a much weaker one at about 54°. Samples obtained at lower temperatures (Fig. 3a and inset) have less defined crystalline structure (weaker and broader peaks), but again the main peak is around 30°, and there are smaller peaks at about 49°, 58° and 60°. Having compared these data with the references for cubic and hexagonal CdSe, we see that the main peak could belong to both structures (the (1 1 1) planes in case of cubic crystal and the (0 0 2) planes in hexagonal ones; the exact position is 29.5284° in both cases). However, the peak at 54° does not exist in cubic lattice. Therefore we conclude that the crystalline phase of the films deposited at high temperature is hexagonal (wurtzite) type, the main reflection is

caused by the (0 0 2) crystallographic planes normal to “c” axis, the interplanar distance “d” found from the Bragg law ($2d \sin \theta = n\lambda$, $n = 1$) is equal to

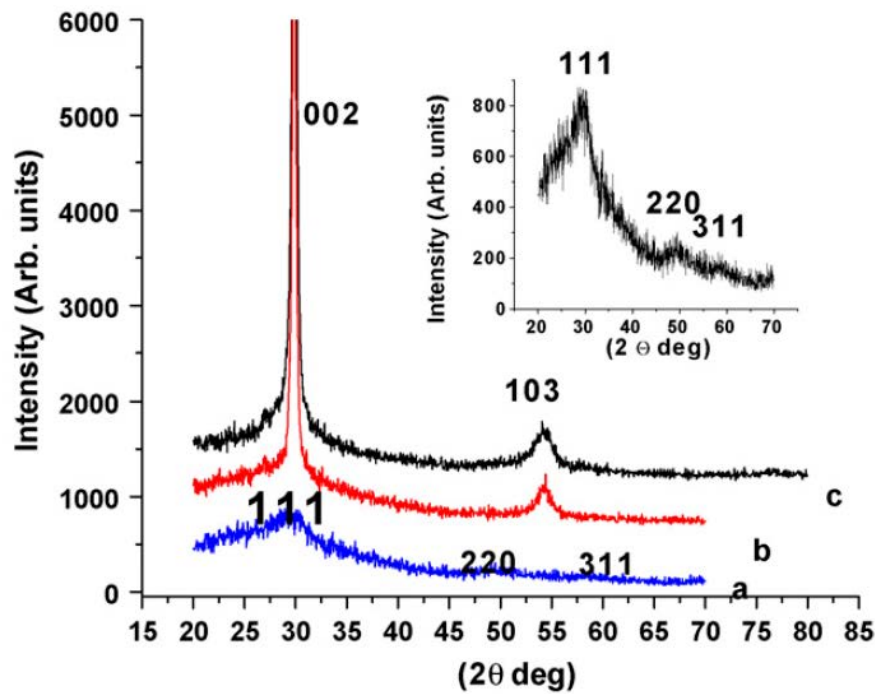
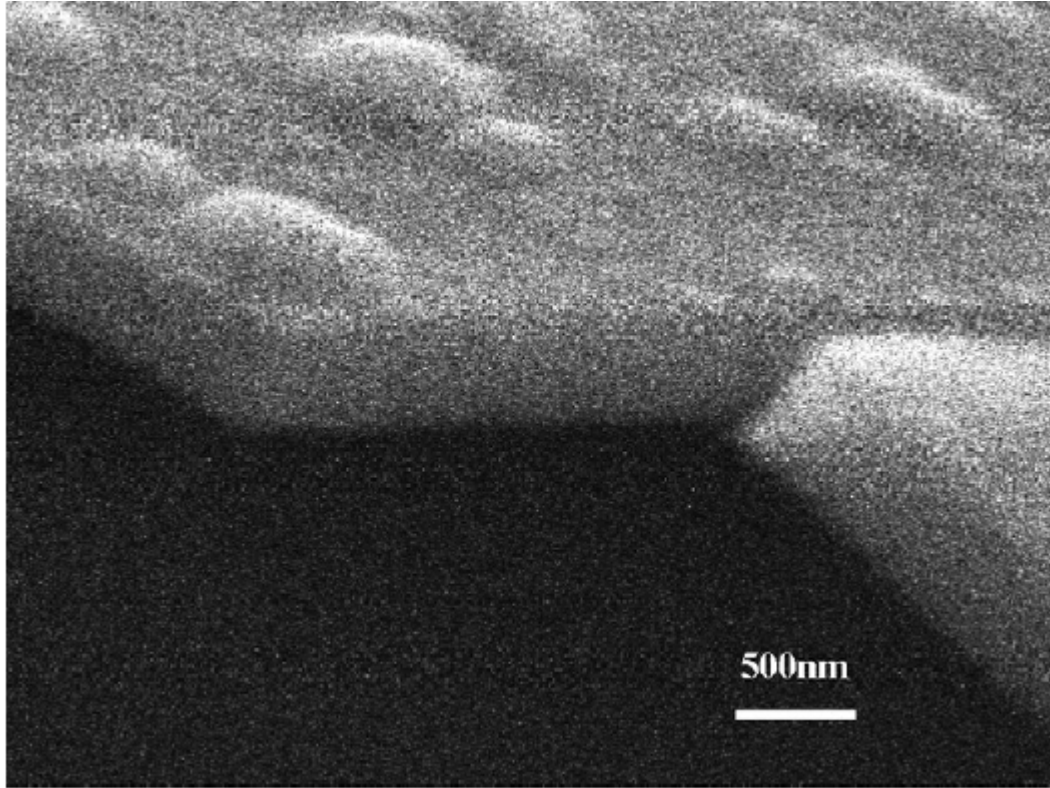


Fig. 3. X-ray patterns of CdSe films deposited in a bath solution A at: (a) room temperature, (b) 70 °C and (c) 80 °C.



4. Image illustrating the thickness of the film obtained in a single deposition cycle (magnification 30,000 \times).

$c/2 = 3.51 \text{ \AA}$ which means that the crystals are grown with the (0 0 2) planes parallel to the substrate. In this interpretation, the peaks at 54° should be ascribed to reflection from the (1 0 3) planes. The pattern from the low-temperature film (Fig. 3 inset) corresponds to the cubic lattice; here the main peak is caused by reflections from the (1 1 1) planes. The peaks observed at 49° and 59° correspond to reflections from (2 2 0) and the (3 1 1) planes, respectively; all the planes mentioned have a rather small index.

Crystal size of CdSe thin films was calculated by using Rigaku software WinJade by MDI V. 7.5. The average crystallite size was calculated by fitting the (0 0 2) for the hexagonal phase and the (1 1 1) peaks for the cubic phase

prepared at room temperature. The average crystal size was 22 ± 1 nm for samples prepared at 70 and 80 °C, respectively (this was confirmed by transmission electron microscopy). For the samples deposited at room temperature during 12 h, the crystal size varied from 3 to 5 nm (not shown in the image).

SEM and EDAX data

SEM study shows that film's surface is covered with uniformly distributed spherical grains from few nanometers up to clusters of 500 nm. Fig. 4 shows an example (film with composition A at 70 °C.) of the general morphology of the films; it was found that when the deposition time increases, the number of clusters increases too. In Fig. 4 it is seen that the thickness of films with composition A at 70 °C is approximately 500 nm, which corroborate the value obtained by profilometer. Fig. 5 shows the general elemental analysis of thin films with composition A and 70 °C, for; (a) one deposition cycle of 4 h and for (b) two deposition cycles 8 h, it is observed two main peaks corresponding to Cd and Se with a relation near to 1:1, the Cd atomic % was 49.20 and that of Se was 50.8 for one cycle (Fig. 5a). In the case of two cycles (Fig. 5b) the at % of Cd was 51.3 and that of Se was 48.70; the emission line of Silicon (from the substrate), in-between the Cd and Se lines, is now very small, indicating a thicker film of about 1 μ m. These results are consistent with the X-ray diffraction, which indicated the formation of CdSe.

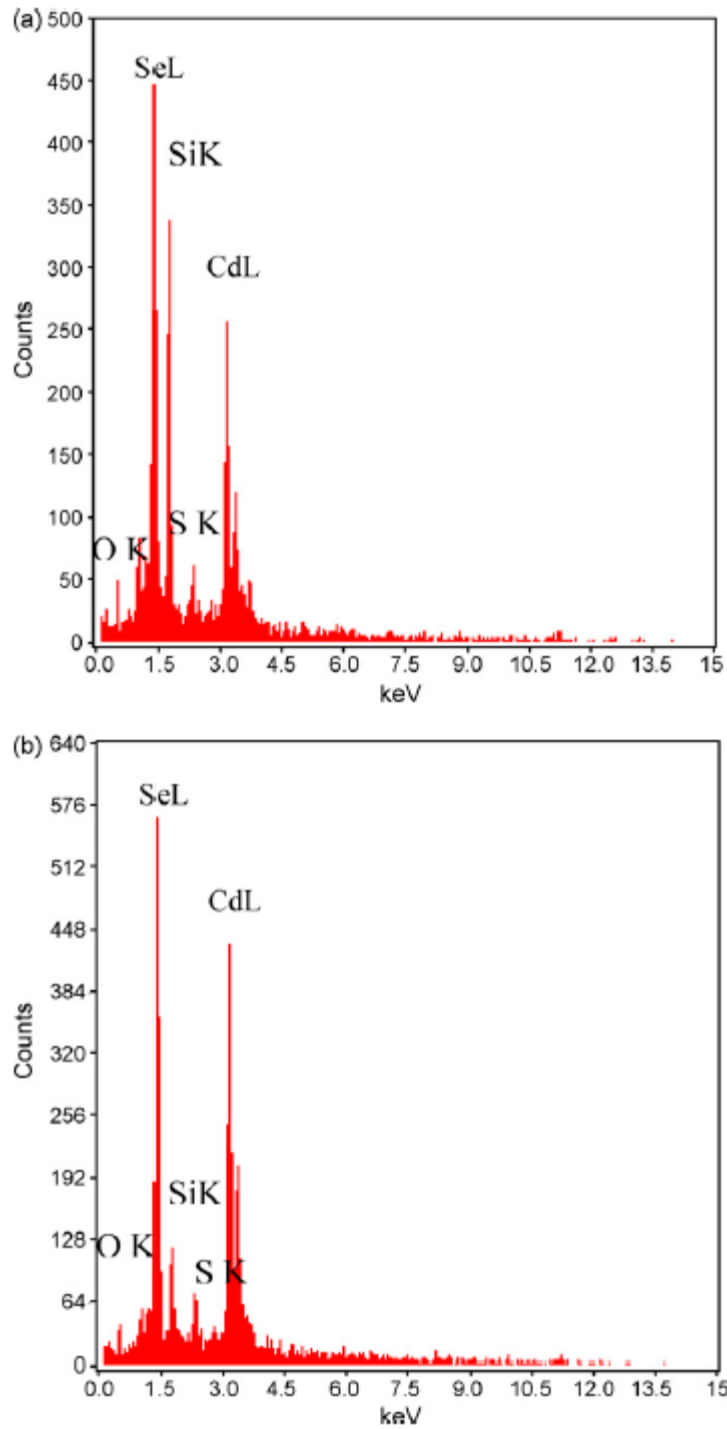


Fig. 5. X-ray energy dispersive spectrum of CdSe, composition A, (a) for one deposition cycle 4 h and (b) two deposition cycles 8 h. The peaks Si and O corresponded to elements of substrate. And the last picks at L alpha and beta lines of cadmium.

Optical properties

Fig. 6 presents the optical transmission (T, %) for 3 samples with a thickness of 0.2, 0.3 and 0.5 μm (high temperature deposition, different deposition time). All samples have high transparency at a wavelength region of $\lambda > 660 \text{ nm}$: from the figure one can see that the average light transmission here is 90%; taking into account that the measurements were using a reference glass sample which has a reflection from both surfaces of around 8%, we obtain the total reflection losses in the transparency region from our samples equal to 18%; this is exactly the expected value found from the Fresnel formula for a material with refractive index n equal to 2.49 [24]. The interference pattern observed in each case well agrees with this n value and the known sample thickness. From the data of Fig. 6 (corrected taking into account the reference sample), the absorption coefficient α for all three samples was found, using the well-known relation:

$$\alpha = \frac{1}{d} \ln \frac{1 - R}{T} \quad (5)$$

Fig. 7 shows the recalculated parts of the spectral curves in the region of the fundamental absorption edge. One can see that the dependence corresponds to direct transitions (approximately straight lines for the drawn quadratic curves, and the high value of the absorption coefficient near the absorption edge—around 10^4 to 10^5 cm^{-1}). The band gap obtained from Fig. 7 is around 1.88 eV, which exceeds the reported value for bulk CdSe (1.75–1.8 eV [20,21]). The small increase of the band gap in comparison with bulk material could be related with small grain size and/or to stress due to deformation of the film.

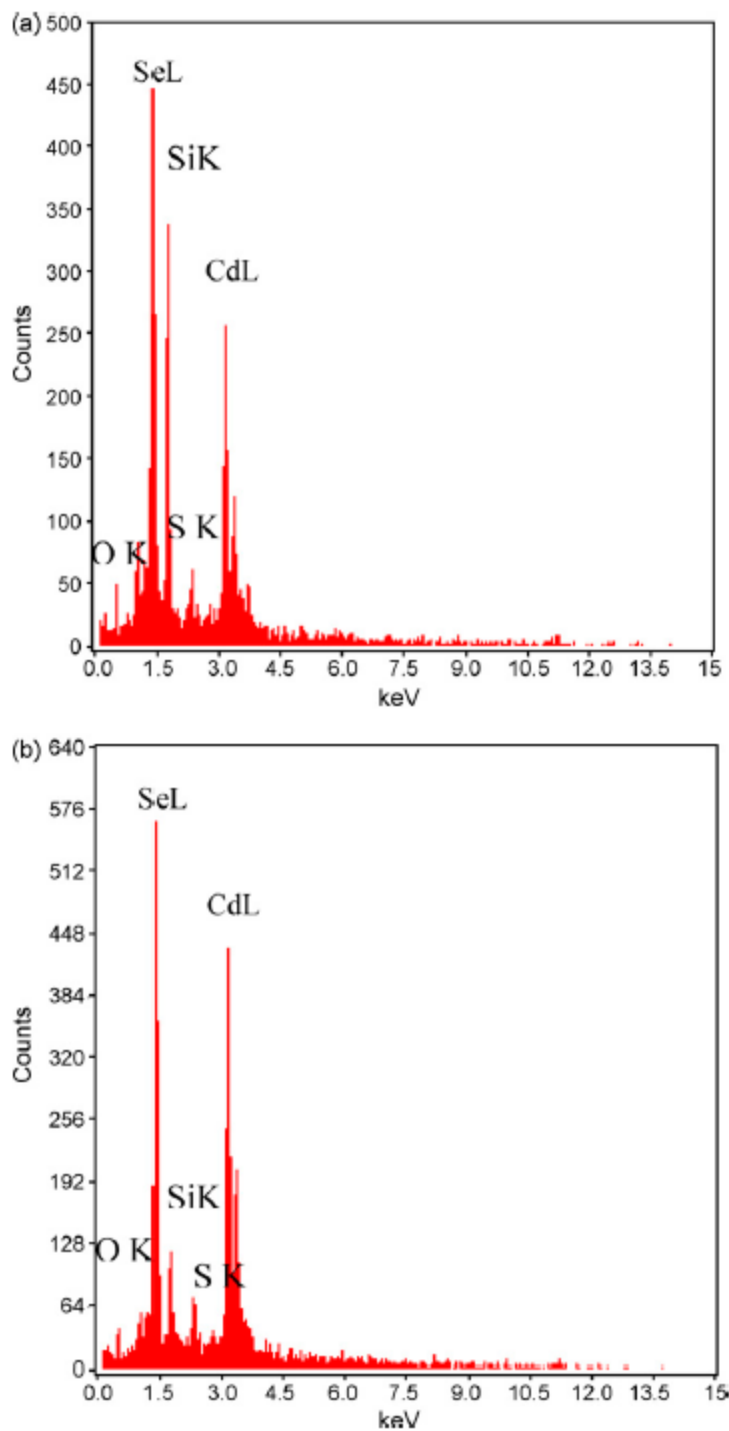


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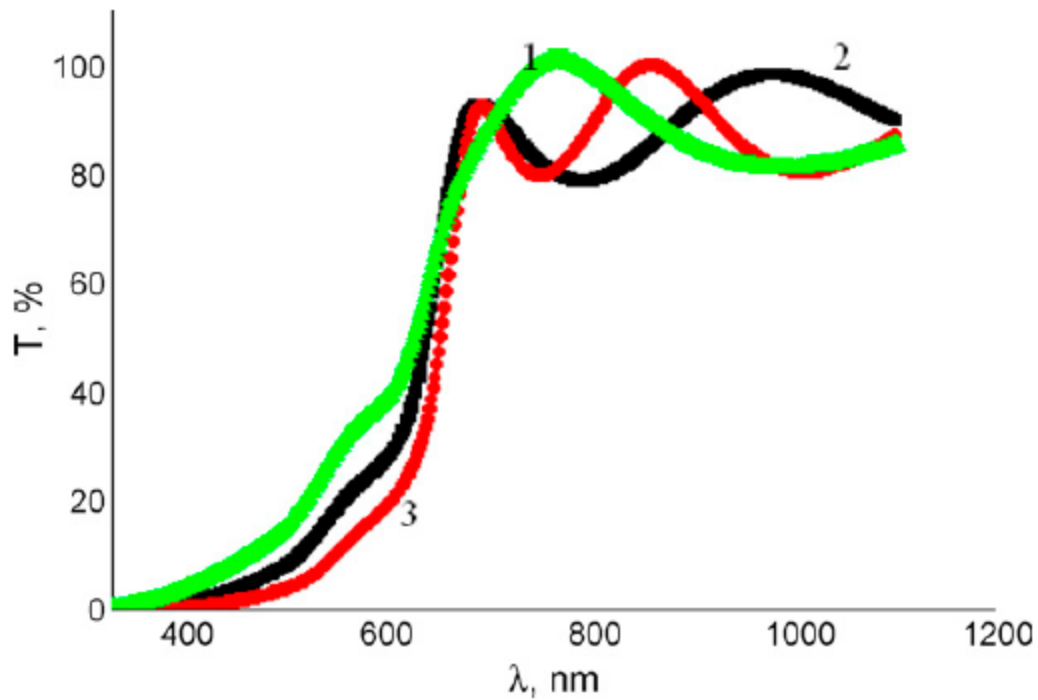


Fig. 6. Transmittance of CdSe thin films obtained from a bath at 80 °C with different deposition time: (1) 1 h, (2) 3 h and (3) 4 h in solution A.

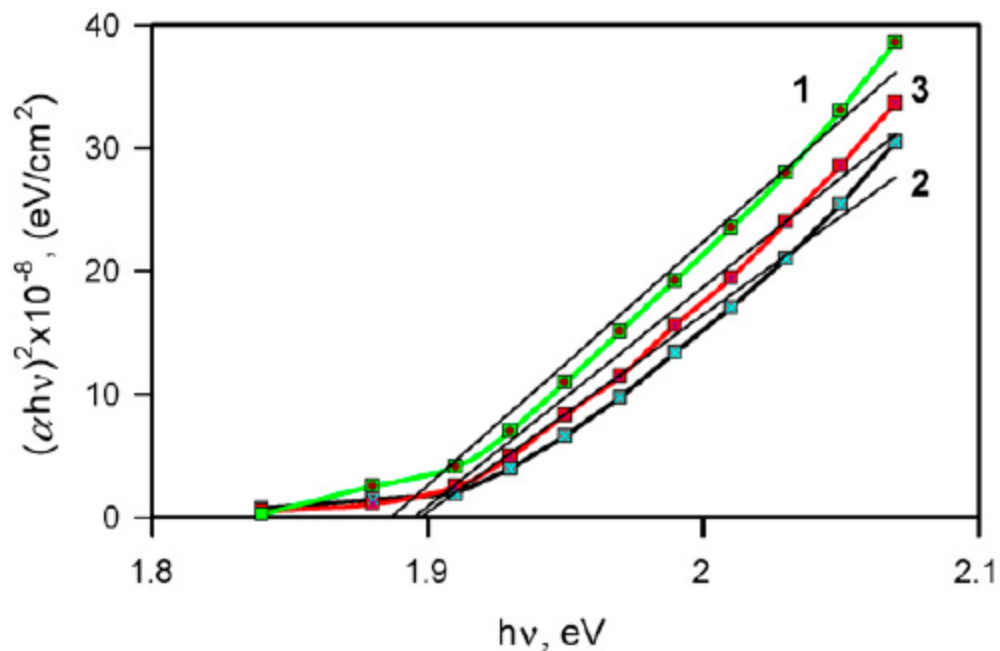


Fig. 7. Plot of $(\alpha h\nu)^2$ vs. $h\nu$ (derived from Fig. 6), (1) 1 h, (2) 3 h and (3) 4 h in solution A.

Conclusions

The best preparation conditions to produce homogeneous CdSe thin films from an ammonia-free chemical bath were obtained with the composition corresponding to solution A with a pH of 11.75, a bath temperature of 80 °C and an immersion time of 4 h. The films, with good adhesion to the glass substrates, were nanostructured with crystallites of around 20 nm, with an atomic Cd:Se ratio close to 1:1. Using these conditions, films with a thickness of 1 µm were obtained after two deposition cycles, this thickness is appropriate for apThe author would like to thank their colleagues, L.Ma.R. Avilés.

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