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CdSe -DOPED PHOSPHATE GLASSY FILMS OBTAINED BY PLD ON SILICON SUBSTRATE♣

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Structural and morphological studies on Pulsed Laser Deposition (PLD) thin films based on phosphate glass doped with CdSe were performed. A KrF excimer laser was used to ablate thin films from CdSe target with oxide composition (wt. %): 70 P_2O_5-8 Al_2O_3- 19 Li_2O- 3 CdSe. The films were deposited on silicon wafers by varying two parameters (laser energy and the temperature of Si substrate): a) high vacuum and T_s=20 ^oC; b) high vacuum and T_s=200 ^oC; c) high vacuum and T_s=20 ^oC at lower laser energy and d) high vacuum and T_s=200 ^oC at lower laser energy. Micro-Raman and FTIR spectroscopy analysis were undertaken to investigate the structural properties of the deposited films. The chemical characterization and the morphology of the films were performed by Energy Dispersive X-ray spectroscopy (EDX), Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM). In order to perform a satisfactory reproducibility of the stoichiometry between the films and the vitreous target, the deposition parameters were modified appropriately. Analyzing the EDX spectra and the obtained SEM mapping images, a good elemental chemical uniformity of the PLD films were observed.

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1. Introduction

Pulsed laser deposition (PLD) technique is commonly used for epitaxial deposition of wide band gap semiconductor films, because of the simplicity and the low cost of such a technique with respect to other growth methods [1-3] and the good optical properties of the deposited films.

The feasibility of this approach is confirmed by the results obtained by the deposition of numerous materials. This technique has many advantages over more conventional methods namely the preservation of the stoichiometry and the higher mobility of the atoms on the substrate owing to the higher plasma temperature [4]. It has the particular potential of producing films with controlled morphology, density, crystalline phase and grain size, since it offers various possibility to control the size, chemistry and kinetic energy of the elementary 'building blocks' being

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deposited [5]. High deposition rates can be easily obtained and high substrate temperatures are not necessary [6].

Cadmium selenide was successfully deposited by pulsed laser deposition (PLD) [7-9]. In PLD the interaction of a focused laser beam with the target leads to the production of ions, molecules, clusters and high-quality films can be deposited by optimizing the laser fluence and other growth parameters.

CdSe is a binary II-VI semiconductor and it is considered as an important material for the development of different optoelectronic devices such as light emitting diodes, solar cells, photodetectors, electro photography, temperature sensors and lasers [10-12]. Semiconductor devices based on CdSe thin films strongly depend on the structural and optical properties of the films obtained from various experimental conditions. A direct band gap range of 1.65 eV-1.84 eV was reported for CdSe [12]. Several approaches have been developed to produce bulk materials doped with semiconductor compounds: melt-quenching glasses, sol–gel glasses, wet chemistry, etc. Different host networks like silicate glass, phosphate glass or polystyrene doped with semiconductor nanocrystals are of interest both for fundamental studies of quantum confinement phenomena and for applications in optoelectronics and optics [13, 14].

One of the most used doped matrix are phosphate glasses because they generally have higher thermal expansion coefficients, lower transition temperature, and higher electric conductivity than silicate and borate glasses [15-17].

In this work, thin films based on CdSe-doped phosphate glass were deposited by Pulsed Laser Deposition (PLD) technique on silicon substrates and their morphological and structural properties are presented and discussed.

2. Experimental (Theory, Modelling)

Ablation and deposition processes were performed in a stainless steel vacuum chamber. A pulsed KrF excimer laser (CompexPro 201 - Coherent) operating at 248 nm, with a repetition rate of 10 Hz and pulse width of 20 ns, was used as source for the ablation process. After having been reflected on two high-energy laser mirrors, the laser beam enters the stainless steel vacuum chamber through a quartz window and it is focused through a focal lens on a rotating target under an incidence angle of 60^{o}, providing a rectangular profile of the laser spot at the target impact. The substrate is positioned parallel to the target at a distance of 60 mm. The deposition chamber was pumped at a pressure of about 10^{-7} mbar before and after starting the deposition process. To obtain thin films, a CdSe target with oxide composition (wt. %): 70 P_2O_5-8 Al_2O_3- 19 Li_2O- 3 CdSe was used. The cadmium selenide doped phosphate glass target was prepared by melt-quenching method, using powder analytical grade reagents: $Li(PO_4)_3$, Al_2O_3 and CdSe [18].

The dried mixture was introduced in an alumina crucible and melted at 1200 ^{o}C, for 2 h followed by refining at 1250^{o}C for 1 h. After melting, the glass was cast in high purity graphite moulds and annealed at 400 ^{o}C for 2 h to release the internal strains.

The films were deposited on substrates of n-type Si wafers with dimensions of 10/10 mm previously cleaned in HF 10%, followed by distilled water and ethylic alcohol, quick-drying in air. In order to improve the morphology of the films we performed a study (see Table 1), varying two parameters (laser energy and the Si substrate temperature) as following: a) RT (room temperature) (Experiment 1); b) T_s=200 ^{o}C (Experiment 2); c) RT at lower laser energy (Experiment 3); d) T_s=200 ^{o}C at lower laser energy (Experiment 4).

FTIR spectra were recorded with a Perkin Elmer Spectrophotometer-Spectrum 100, provided with UATR accessory (Universal Attenuated Total Reflectance) in the range 550-1500 cm^{-1}. The measurement error is ± 0.1% and the number of scans 32.

Raman spectra were collected by means of LabRAM HR 800 UV–VIS-NIR Horiba Jobin-Yvon system, at room temperature. The samples were excited with the 633 nm line of He-Ne ion laser, focused on the surface sample with a confocal microscope, using an objective magnification X100, 1 μm^2 laser spot size, laser power on the surface sample 2.8 mW, 0.5 to 1 cm^{-1} resolution with an 1800g/mm grating.

UV-Vis absorbance spectrum was collected by using a Perkin Elmer Lambda 1050 spectrophotometer, in the range 300-650 nm.

Scanning Electron Microscopy (SEM) and Energy-dispersive X-ray spectroscopy (EDS) investigations were performed with a SEM Hitachi S-2600N instrument.

The surface structure of CdSe-doped phosphate glass was observed by atomic force microscopy AFM - XE 100 Park system.

Table 1.Used parameters in the pulsed laser deposition process for different experiments

Experiment no.	Substrat	Frequency/Pulse no.	Pressure (Torr)	Substrate temperature (^oC)	Laser energy (mJ)
1	Silicon	10 Hz/40.000	Vacuum x 10^{-6}	Room temperature	450
2	Silicon	10 Hz/40.000	Vacuum x 10^{-6}	200	450
3	Silicon	10 Hz/40.000	Vacuum x 10^{-6}	Room temperature	350
4	Silicon	10 Hz/40.000	Vacuum x 10^{-6}	200	350

3. Results and discussion

In the Fig.1, UV-Vis absorption spectrum of CdSe doped glass target is presented. The UV-Vis spectrum of the glass target doped with CdSe has a significant optical absorption bellow 350 nm, the slope of the curve indicating the dimensional range of the semiconductor dopant [19].

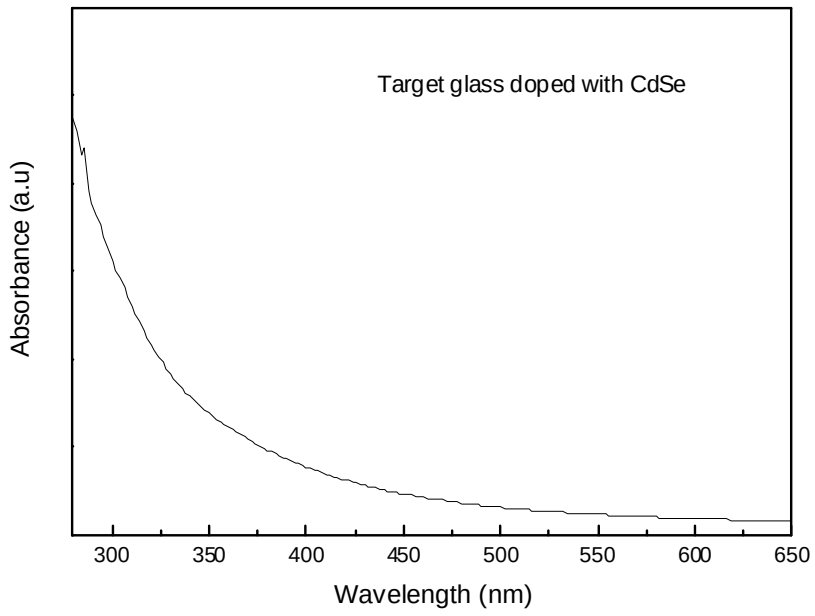

Fig. 1. UV-Vis absorbance spectrum of the glass target doped with CdSe powder.

Fig. 2 presents FTIR spectra of CdSe doped phosphate films prepared in the frame of the deposition experiments 1 to 4.

Optical phonons specific to phosphate vitreous network, in the range 500-1500 cm^{-1} are noticed. As seen from the Fig. 2, the frequencies of predominant absorption peaks are

characterized by an envelope covering two peaks near 726 and 783 cm^{-1}, an intense peak around 921 cm^{-1}, and a two broad peaks around 1110 and 1250 cm^{-1}.

According to literature data [20-22], it was found that the peaks around 726 and 783 cm^{-1} are due to the symmetric stretching vibration mode of ν_{sym} (P–O–P) bridges, the intense peak that appears at about 921 cm^{-1} is assigned to the symmetric stretching vibration mode of $(PO_4)^{3-}$ tetrahedral groups. The absorption band around 1110 cm^{-1} is assigned to asymmetric stretching of $(PO_3)^{2-}$ groups, characteristic of Q_1 structural units. The band at 1250 cm^{-1} has been attributed to the asymmetric stretching vibration mode of PO_2 groups, characteristic to Q_2 structural units. It is to be noticed that the increasing of the substrate temperature results in an increasing of the peaks intensity, possibly due to the densification of the film, as shown by the experiment 2 versus 1 as well as experiment 4 versus 3. The decreasing of the laser energy results in a decreasing of the peaks intensity due to the reduction of the films thickness, as presented in experiment 3 versus 1 as well as experiment 4 versus 2. It is to be observed that the deposited films exhibit similar vibration modes as in the glass target, revealing the reproducibility of the chemical composition in the ablation process.

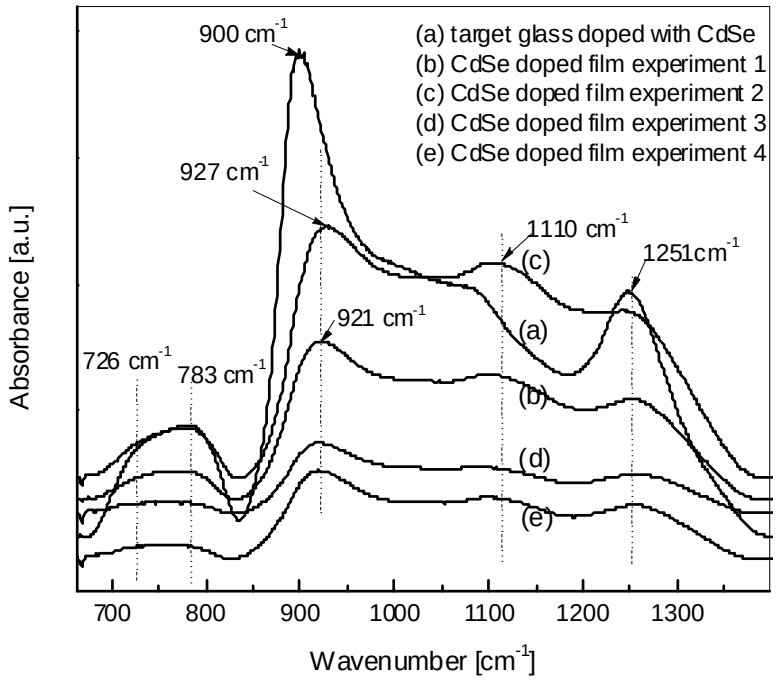

Fig.2. FTIR absorption spectra of: (b, c, d, e) - thin films based on phosphate glass doped with CdSe and (a)-glass target doped with CdSe

One of the main objectives of this work is to identify the presence of CdSe both in glass target and films. Since CdSe dopant is embedded in a majority phosphate vitreous network, it was difficult to identify Raman lines specific to the minority semiconductor phase because the collected spectra of the deposited films reveal also Raman pattern of the phosphate matrix. Consequently, the intensity of Raman peaks of CdSe dopant is weaker compared to the signals related to the vitreous matrix. Also, the small concentration of the dopant related to the amount of the phosphate matrix, influences the properties of the localized phonons and their interaction with excitation radiation, being difficult to detect specific vibration to CdSe (see Fig.3). Nevertheless, we successfully found specific lines to CdSe by searching the most appropriate excitation wavelength and using very high acquisition parameters (high number of measurement cycles and high acquisition time). Taking into consideration the absorbance spectrum of CdSe-doped glass

matrix (Fig. 1), 633 nm He-Ne laser excitation line was used, as the optical absorption at this wavelength is very much reduced and no luminescence of the dopant could be generated.

Fig.3. present the Raman spectra of CdSe powder use as dopant and the film deposited in experiment 1. In the CdSe doped film, experiment 1 following main peaks were noticed at 200, 300, 520, 708, and 1185 cm^{-1}. Thus, in agreement with literature data, we attributed the peak placed at 200 cm^{-1} to longitudinal optical (LO) Raman vibration mode of Cd-Se bonds [23, 24], the peaks at 300 cm^{-1}, 520 cm^{-1} and the broad band at 900-1050 cm^{-1} are specific to silicon substrate [25]. The peaks at about 708 cm^{-1} and 1185 cm^{-1} are assigned to P–O–P symmetrical stretching vibration mode and to PO_2 symmetrical stretching vibration mode, respectively [26, 27]. Raman spectrum of the powder semiconductor dopant (see Fig.1. b), collected in the range 150 – 450 cm^{-1} reveals the presence of two vibration modes specific to Cd-Se group. According to [23, 24], the presence of these two picks is related to the longitudinal optical (LO) phonon at about 200 cm^{-1} and its overtone (2LO) at 400 cm^{-1}.

We assume that the CdSe peak at about 400 cm^{-1} is overlapped by the glass matrix signal. It was observed that the films deposited in experiments 1, 2, 3 and 4 show similar Raman pattern. Therefore, we present only Raman spectrum for the film deposited in experiment 1.

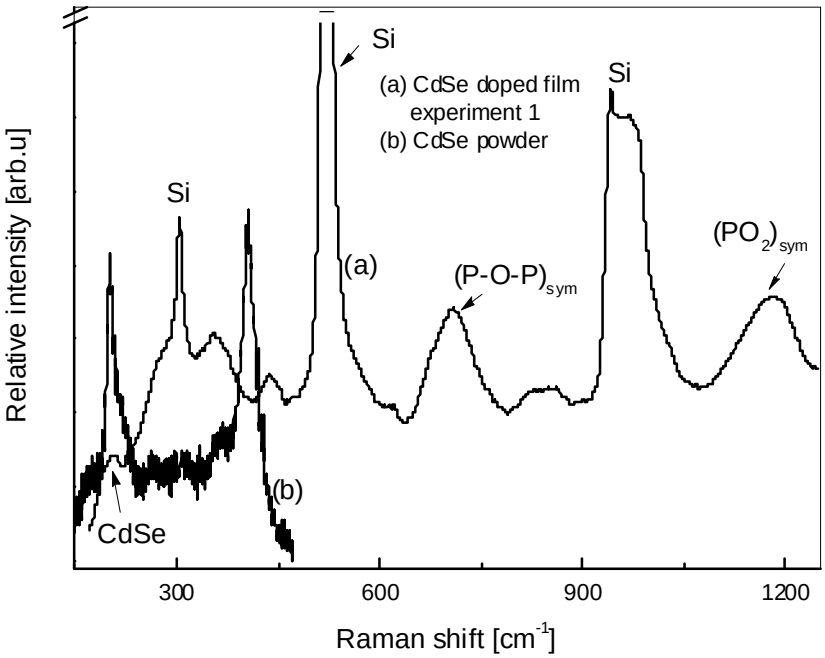

Fig. 3. Raman spectra of: (a) CdSe powder used as dopant of the glass target; (b) glass target doped with CdSe; (c) film based on phosphate glass doped with CdSe, from experiment 1.

In the Fig.4, SEM images of the films deposited in the frame of experiments 1 to 4 are presented. The SEM images of all four films deposited in the frame of experiments 1 to 4 show spherulite morphology as reported in [28, 29]. It is observed from the surface morphology that the films from experiment 1 and 2 are more homogenous and cover better the silicon substrate as compared with the films deposited in the frame of experiments 3 and 4.

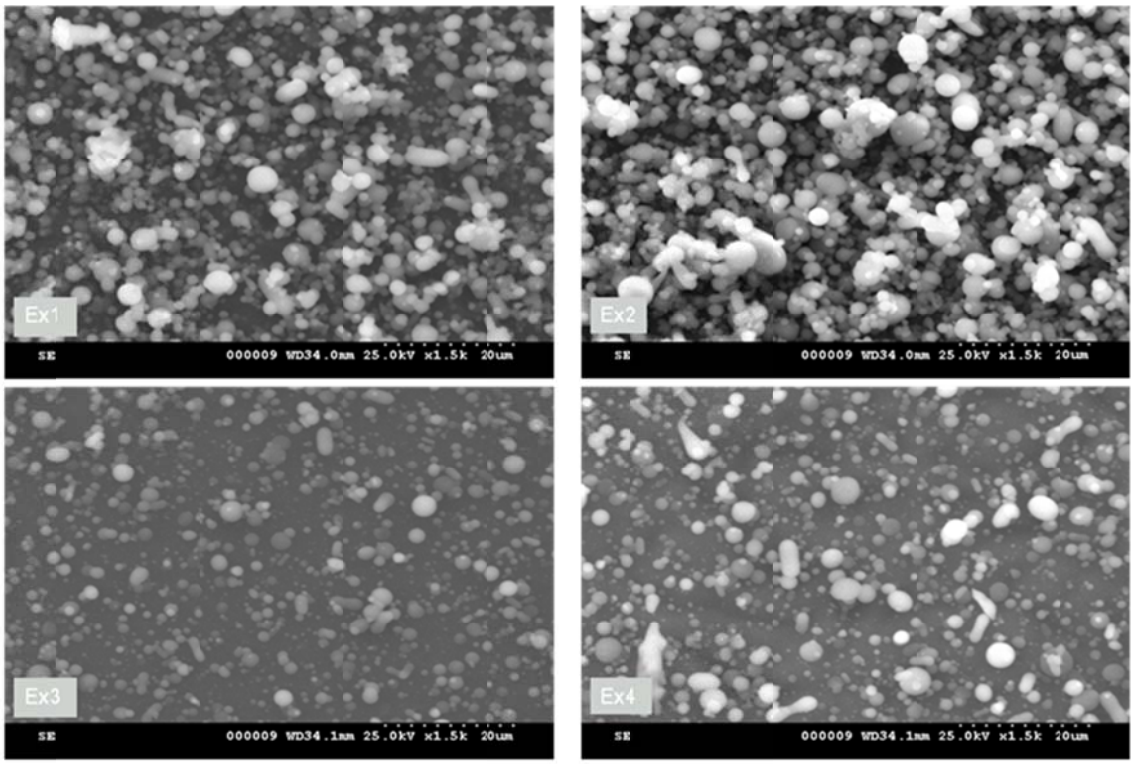

Fig.4 SEM image of CdSe thin film deposited in different condition: (a) experiment 1, (b) experiment 2, (c) experiment 3, (d) experiment 4, magnification x 1500.

The spherulites seem to slowly decrease in size in the experiments 3 and 4, possibly due to the decreasing of fluency in ablation process. This can suggest that for the same decreased laser fluency the increasing of the pulses should produce a smoother and continuous film.

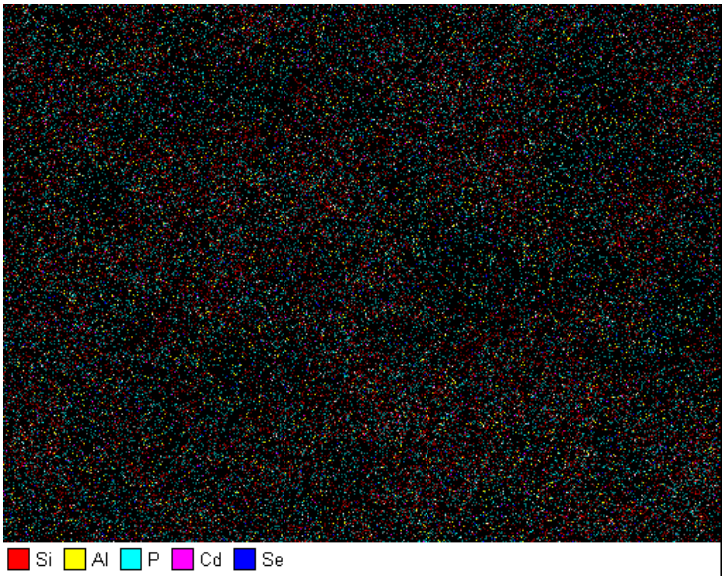

Fig.5. EDX mapping of CdSe-doped phosphate film from experiment 1.

In Fig. 5, EDX chemical mapping of CdSe-doped phosphate film from experiment 1 is shown. EDX mapping sustains the presence of cadmium selenide dopant and reveals that the constituent elements of the film are uniformly distributed on the layer surface.

EDX spectra (Fig. 6) show the presence of Si, P, Al, Cd and Se in the layer. As expected, a small amount of CdSe is found together with a significant amount of P from the vitreous network.

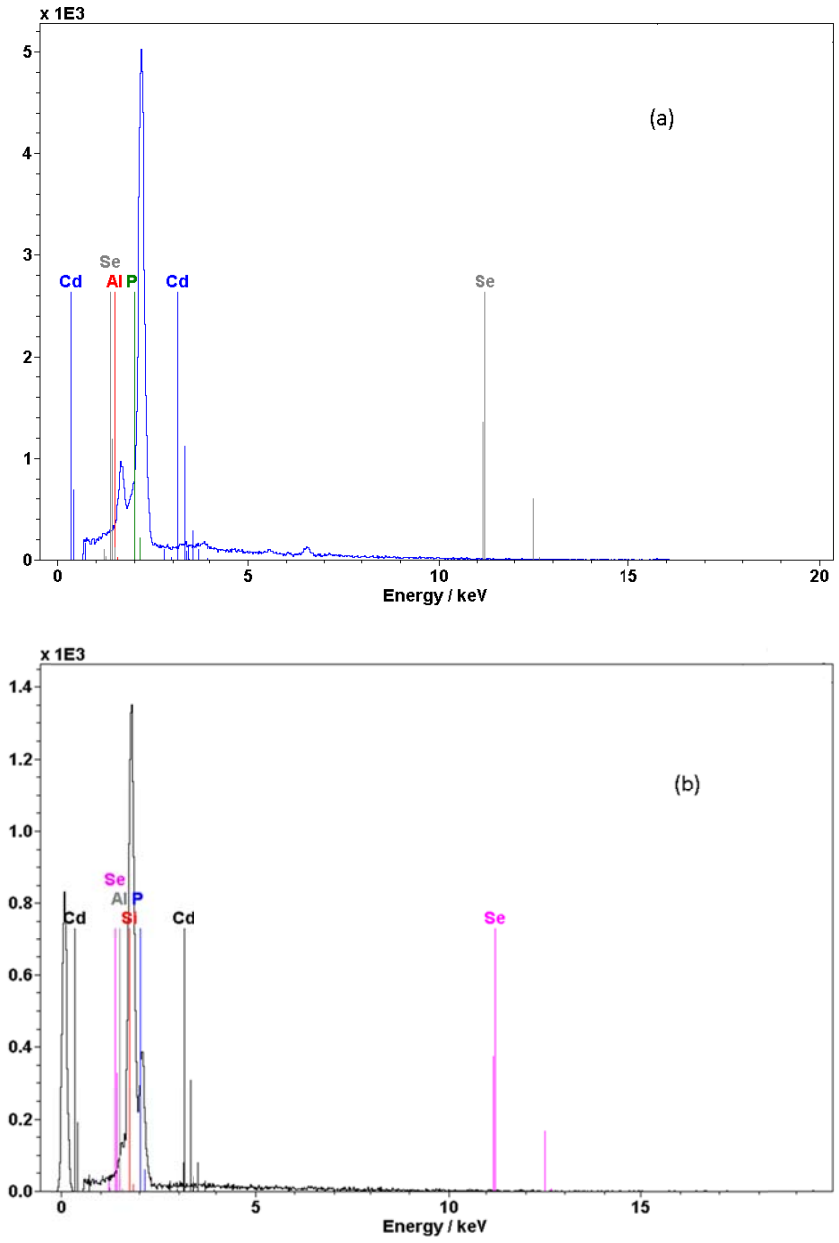

Fig.6. EDX Spectra of: (a) glass target doped with CdSe powder and (b) CdSe-doped film experiment 1.

Atomic force spectroscopy (AFM) image from the Fig.7 shows the morphology of the film prepared in the experiment 1. It is observed a high roughness of the deposited film, possibly due to the 248 nm operating wavelength.

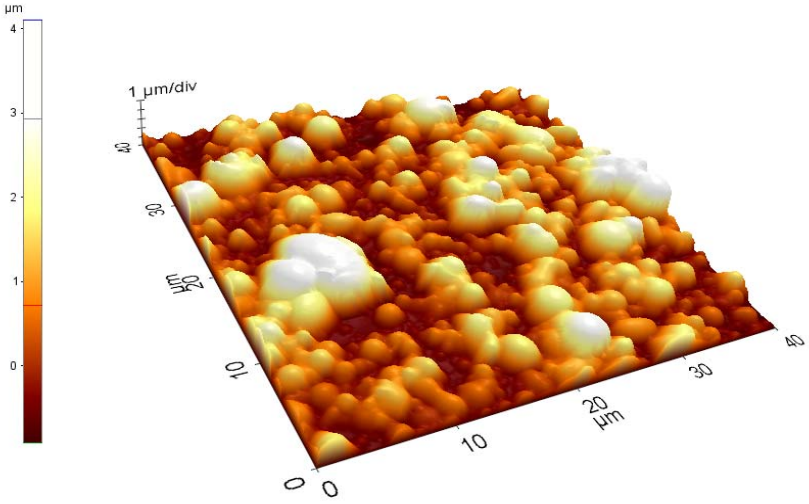

Fig.7. AFM image of CdSe-doped film from experiment 1

4. Conclusions

CdSe-doped phosphate films on silicon substrate have been deposited by PLD method. The influence of deposition parameters (substrate temperature and laser energy) on the structure and morphology of the doped films have been investigated.

FTIR spectroscopy revealed that the specific molecular vibrations of the target glass were successful reproduced in the deposited films whereas Raman spectra evidenced both lines specific to phosphate network and a specific line to CdSe dopant.

The morphology of the deposited films was investigated by SEM analysis that found an improvement of the homogeneity for the films prepared at higher laser energy and higher substrate temperature. EDX mapping revealed also an uniform elemental distribution in the deposited films. EDX spectra for the target and for the film certified the presence of the same chemical elements.

AFM image shows spherulitic units, as presented also in SEM images, specific to PLD deposition method.

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