SiO$_2$-P$_2$O$_5$ films doped with CdSe have been prepared and investigated for temperature sensors applications. The films have been synthesized by sol-gel method, spin coating technique, the deposition being made on glass substrates. The sols have been prepared from tetraethylorthosilicate (TEOS) and phosphoric acid as precursors for SiO$_2$ and P$_2$O$_5$, respectively, together with ethanol and water as reaction environment and a hydrolysis reagent, respectively. The films have been deposited at three rotation rates: 1000 rpm, 2000 rpm and 3000 rpm, starting on the first day after the sol preparation moment and going on, four days consecutively, and then on the eighth day. We have analyzed the influence of the rotation rate and the time elapsed since the sol preparation till the deposition moment on the structural properties of the doped films. The films deposited at each rotation rate have been annealed at 200°C, 300°C, 350°C, 400°C, and 550°C in order to investigate the structural modifications noticed during the formation process of silicophosphate network.

**Keywords:** FTIR spectroscopy, Raman spectroscopy, sol-gel method, CdSe.

**INTRODUCTION**

CdSe quantum dots are extensively investigated due to their quantum confinement effect and size-dependent photoemission characteristics [1, 2].

The cadmium selenide films prepared by the sol-gel method were studied due to the their good chemical and physical properties, that results in their successful application in many areas, for instance, in gas sensors, photo-detectors, light amplifiers, laser micro cavities, solar cell, optoelectronic devices, temperature sensors, etc [3–5].

Starting from a solution, a further evolution into a gel requires successive reactions, which would ensure bonds between particles in a controlled way, similarly to the hydrolysis/condensation reactions in the silica polymerization.

The sol-gel process and the colloidal chemistry offer good opportunities for the synthesis of transparent materials embedding semiconductor nanocrystals. The work in this field has been carried out on group II-VI semiconductors, especially on CdSe for which the quantum size effect is well understood and the colloidal synthesis well controlled [6–8].

The sol-gel method offers certain advantages in comparison to classical solid-state synthetic routes, such as mild synthetic conditions, versatility, high homogeneity and purity of the final material, which are fundamental for the development of new advanced materials [9].

In the present paper, structural properties of CdSe-doped silicophosphate bulk gel material and films were investigated. The influence of the rotation rate and the time elapsed since the sol preparation till the deposition moment as well as the structural modifications that occurred after annealing at different temperatures were studied.

**EXPERIMENTAL**

Thin films with CdSe nanoparticles embedded in silicophosphate matrix were prepared by the sol-gel method, spin coating technique. As reagents we used tetraethylorthosilicate [(C$_2$H$_5$O)$_4$Si, 98 wt. %], phosphoric acid [H$_3$PO$_4$, 85 wt. %], distilled water, ethanol [C$_2$H$_5$OH, 98 wt. %] as reaction environment, and cadmium selenide [CdSe, 1 wt. %] as dopant powder. The molar ratio of precursors were TEOS/H$_3$PO$_4 = 5/1$; TEOS/C$_2$H$_5$OH = 1/2; TEOS/H$_2$O = 1/5. All reagents were used without any previous purification. Phosphoric acid was added to water and, separately, tetraethylorthosilicate [(C$_2$H$_5$O)$_4$Si was mixed with ethanol, then the two resulted solution were mixed together. After checking the pH of the solution, CdSe was added followed by mechanical stirring to improve the homogeneity of the precursor mixture [10, 12].

In the following, some chemical reactions of hydrolysis and condensation of the reagents are presented:

\[
\begin{align*}
(C_2H_5O)_4Si + H_2O & \rightarrow SiOH (OC_2H_5)_3 + C_2H_5OH \\
SiOH(C_2H_5)_3 + H_2O & \rightarrow Si(OH)_2(OC_2H_5)_2 + C_2H_5OH \\
Si(OH)_2(OC_2H_5)_2 + H_2O & \rightarrow Si(OH)_3(OC_2H_5) + C_2H_5OH \\
Si(OH)_3(OC_2H_5) + H_2O & \rightarrow Si(OH)_4 + C_2H_5OH
\end{align*}
\]
SiOH(OC\textsubscript{3}H\textsubscript{3})\textsubscript{3} + SiOH(OC\textsubscript{3}H\textsubscript{3})\textsubscript{3} → (OC\textsubscript{3}H\textsubscript{3})\textsubscript{2}Si-O-Si(OC\textsubscript{3}H\textsubscript{3})\textsubscript{2} + H\textsubscript{2}O

(\text{C}_{2}\text{H}_{5}O)\text{Si} + (\text{OH})\text{OP} → (\text{OC}\textsubscript{2}\text{H}\textsubscript{5})\textsubscript{3}\text{Si} \text{OP(OH)}\textsubscript{2} + \text{C}_{2}\text{H}_{5}\text{OH}

The CdSe – doped silicofosphate solution was kept at room temperature, the deposition being made on clean glass substrates, at three rotation rates: 1000 rpm, 2000 rpm and 3000 rpm, starting since the first day after the sol preparation moment and going on for four days consecutively and also on the eighth day. The gelification occurred on the ninth day. The layers were deposited, dried at room temperature in air and then thermally treated at different temperatures: 200°C, 300°C, 350°C, 400°C, 550°C, for 2 h.

The deposited films were characterized by Fourier Transform Infrared (FTIR) and Raman spectroscopy, fast, non-destructive and reproducible techniques which allow detecting and quantifying the changes that occur in the structure of those films.

The FTIR spectra were recorded with a Perkin Elmer Spectrophotometer-Spectrum 100, provided with a UATR accessory (Universal Attenuated Total Reflectance) in the range 550–4000 cm\textsuperscript{-1}. The measurement error was ± 0.1% and the number of scans 32.

Raman spectra were collected by means of the LabRAM HR 800 UV–VIS-NIR Horiba Jobin-Yvon system at room temperature. The samples were excited with the 514.5 nm line of an ion laser, focused on the surface sample with a confocal microscope, using an objective magnification X100, 1 \mu m\textsuperscript{2} laser spot size, laser power on the surface sample 2.6 mW, 0.5 to 1 cm\textsuperscript{-1} resolution with a 1800g/mm grating.

The X-ray diffraction (XRD) spectra were collected from 10° up to 70° (2θ) at room temperature, with a step size of 0.02° and a counting rate of 2s/step in a Brucker-AXS type D8 ADVANCE diffractometer.

RESULTS AND DISCUSSIONS

The evolution of the FTIR spectra of the films deposited within days 1, 2, 3, 4 and 8, with the treatment temperature, is presented in Table.

The FTIR spectra of the films deposited on the first day (Fig. 1a) of sol preparation show the absorption bands at ~ 787, 907, 1051, 1446, 1639, 3200 cm\textsuperscript{-1}, corresponding to the vibration modes as presented in Table 1. The intensities of the absorption bands situated at ~ 787, 907, 1051 cm\textsuperscript{-1} decrease with the increase of temperature, due to the break of some Si-O- and P-O- linkages during the evaporation of water and volatile organic compounds. The intensities of bands at 1446, 1639 and 3200 cm\textsuperscript{-1} characteristic for \delta (H\textsubscript{2}O) and \nu (OH) decrease with the increase of the treatment temperature and disappear after 350°C, indicating the loss of water. An interesting feature is the emergence of an absorption band at 575 cm\textsuperscript{-1}, attributed to 4-fold rings of SiO\textsubscript{2} that were formed at 550°C by breaking the chains Si-O-Si. The intensity of the band at 787 cm\textsuperscript{-1} attributed to \delta (Si–O–Si) decreases with the increase of temperature and splits into two bands, 732 and 783 cm\textsuperscript{-1}, confirming the broken linkages of Si-O-Si and the formation of P-O-P structures at the treatment temperature of 550°C. Weak Si-OH bands were noticed at about 2920 cm\textsuperscript{-1} starting from the thermal treatment at 300°C.

Analyzing the FTIR spectra of the films deposited on the second day (Table 1) and thermally treated at 200°, 300°, 350°, 400° and 550°C, it is necessary to specify that the absorption bands positions and intensities do not differ very much from the spectra recorded on the first day, except for the band at 2925 cm\textsuperscript{-1}. This is possibly due to Si-OH groups that disappear when the temperature is raised because of the condensation between Si-OH and P-OH units.

The films spin coated on the 3rd and 4th days exhibit spectra with noticeable different features as compared with first two days after sol preparation (Table 1). The shift to a higher energy of the absorption bands corresponding to \nu (Si-O) and \nu (P-O-P), respectively. The intensities of the bands around 800, 960 and 1051 cm\textsuperscript{-1} corresponding to Si-O and P-O linkages in different compounds do not decrease at elevated temperatures meaning that OH linked by Si-OH cannot be broken by evaporation of water and ethanol. The weak Si-OH band at ~ 2965 cm\textsuperscript{-1} present in the spectra of 800, 960 and 1051 cm\textsuperscript{-1} corresponding to Si-O and P-O linkages in different compounds do not decrease with the increase of the treatment temperature as a consequence of stronger bonds that cannot be broken by evaporation of water and ethanol. The weak Si-OH band at ~ 2965 cm\textsuperscript{-1} present in the spectra of days 3 and 4 at all treatment temperatures give evidence for the Si-OH groups formed during the hydrolysis phase of the sol-gel process that are entrapped in the film pores. The intensity of the stretch vibration of OH groups from the adsorbed H\textsubscript{2}O (1450 cm\textsuperscript{-1}), of deformation modes of OH groups and \delta (H\textsubscript{2}O) (3200 cm\textsuperscript{-1}) decreases with the increase of the treatment temperature. These bands do not disappear at elevated temperatures meaning that OH linked by different compounds was entrapped in the pores of the film.

On day 8 of the deposition (Fig. 1b), the absorption bands at 800 and 850 cm\textsuperscript{-1} attributed to \delta (Si–O–Si), \nu (PO\textsubscript{4}\textsuperscript{3-}), Si-O-P and \nu (POP) were present at all the treatment temperatures with no noticeable modifications in intensities. The intensity of the band at about 1039 cm\textsuperscript{-1} attributed to \nu (Si–O–Si)
Table 1. Bands assignment in FTIR spectra of CdSe – doped silicophosphate films

<table>
<thead>
<tr>
<th>Annealing temperature 200°C</th>
<th>Annealing temperature 300°C</th>
<th>Annealing temperature 350°C</th>
<th>Annealing temperature 400°C</th>
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<tbody>
<tr>
<td>Day since sol preparation</td>
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<td>1  2  3  4  8</td>
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<tr>
<td>787 787 795 799</td>
<td>802, 849</td>
<td>803 804 851 849</td>
<td>797 795 804 852, 851 850 850</td>
<td>791 787 803, 852, 800 850 850</td>
</tr>
<tr>
<td>907 903 931 943</td>
<td>948 907 903 943</td>
<td>951 951 951 951</td>
<td>907 907 955 951 951</td>
<td>904, 985 904, 959 956 952</td>
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<td>1051 1048 1051 1051</td>
<td>1035 1048 1047 1051</td>
<td>1051 1051 1036</td>
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<td>1446 1440 1443 1446</td>
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<td>1446 – 1453 1450 1446</td>
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<td>1639 1642 1639 1639</td>
<td>1633 1639 1635 1635</td>
<td>1635 1632 1646 1642 1635 1635 1635 1635 1632</td>
<td>1635 1646 1635 1635 1635 1632</td>
<td>1620 1643 1635 1635 1632</td>
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<td>2200</td>
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<td>2400</td>
<td>2965 2966 2968 2966</td>
<td>– 2968 2966 2970 2968 2966</td>
<td>2966 2925 – 2967 2966</td>
<td>2966 weak Si-OH band [15]</td>
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<tr>
<td>3200 3200 3200 3200</td>
<td>3200 3200 3200 3200</td>
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</tr>
</tbody>
</table>

δ = bending vibration mode  
ν = stretching vibration mode
was not modified with the increase of temperature. At all temperatures the bands at 1446, 1632, 2966 and 3200 cm\(^{-1}\), corresponding to stretch vibration of OH from the adsorbed H\(_2\)O, deformation modes of OH groups, \(\delta\) adsorbed H\(_2\)O, the weak Si-OH band and \(\delta\) (H\(_2\)O) were present. Since the water could not be evaporated at temperatures above 200\(^{\circ}\)C, we concluded that the water was entrapped in the pores of the films.

The FTIR spectra of the films deposited on different days and treated at 550\(^{\circ}\)C (Fig. 1d) exhibit the bands corresponding to \(\nu_{\text{sym}}\) (P-O-P) and \(\delta\) (Si–O–Si) shifted to higher wave numbers due to the formation of stronger bonds P-O-P and Si–O–Si. The intensities of adsorption bands at 1051 cm\(^{-1}\) increase on days 3 and 4 and decrease on day 8. Also on day 8, a shift towards lower wave numbers (energies) was noticed giving evidence of weaker Si-O-Si bonds in long chains. The bands corresponding to OH, Si-OH and H\(_2\)O vibration modes at 1446, 1632, 2966 and 3200 cm\(^{-1}\) were present only in the FTIR spectra of the films deposited on days 3, 4 and 8. To conclude, it is necessary to say that during the first two days the hydrolysis phase of the process was more pregnant, and due to the condensation process Si-O-Si, Si-O-P and P-O-P compounds were formed in smaller quantities. When the treatment temperature increased, the Si-OH and P-OH and H\(_2\)O bonds are broken and completely evaporated from the films, thus providing new Si-O-P bonds. Further, on days 3 and 4, the condensation process became pregnant and the increase of temperature allowed to OH groups to be entrapped in the pores of the films. As the gelification process is running, especially from the 3\(^{\text{rd}}\) day of the film deposition, at 300\(^{\circ}\)C and higher treatment temperatures, a band around 800 cm\(^{-1}\) is observed, assigned to bending/stretching modes of P-O-P, Si-O-P and O-P-O units. Thus, we can say that the structure of the deposited layers consists of a mixed framework built of [SiO\(_4\)] and [PO\(_4\)] tetrahedra.

Structural changes appeared as a result of the gelification process and the influence of the thermal treatment temperatures and different rotation rates on the hydrolysis/condensation process was investigated by Raman spectroscopy.

The gelification process was found to be performed, to a great extent, on day 8, taking into account that after this moment the gel could not be deposited on the glass substrate due to the incre-
ase of viscosity.

Figure 2a displays Raman spectra of bulk gel and films deposited on days 1 and 8, annealed at 200°C and 550°C.

**Fig. 2.** Raman spectra of CdSe-doped silicophosphate films: (a) Day 1 and Day 8, annealing at 200°C and 550°C; (b) Day 8, annealing at 200°C, different rotation rates; (c) Day 8, annealing at 550°C, different rotation rates.

The presence of the following main peaks was noticed at 475, 555, 800, 925, 980 and 1098 cm⁻¹. Thus, we attributed, in agreement with the literature data [14, 20, 21], the peak placed at 478 cm⁻¹ to the transverse-optical (TO) Raman vibration mode of Si-O-Si bonds, the peak at 555 cm⁻¹ to longitudinal optic (LO) rocking vibration mode of Si-O-Si, and the peak located around 1098 cm⁻¹ to stretching asymmetric vibration mode for Si-O-Si. The peak attributed to Si-OH, located at 925 cm⁻¹ in bulk gel, was shifted to 980 cm⁻¹ in films. The peak at about 800 cm⁻¹ is assigned to P-O-Si vibration mode.

The films deposited on days 2, 3 and 4 show similar Raman behavior and therefore we chose to present only films deposited on days 1 and 8 (see Fig. 2a).

The vibration modes specific to Si-OH (980 cm⁻¹) and H-O-H (2900 cm⁻¹) were noticed for the bulk gel and film at 200°C and their intensity decreased with the increase of annealing temperature, as expected.

A thorough analysis of the Raman spectra shows that the positions of the Si–O–Si (475, 555, 1098 cm⁻¹) and Si-O-P bands (800 cm⁻¹) remain invariable, irrespective of the heat treatment temperature.

The spectra of the films deposited on day 8 and annealed at 200°C at 3 different rotation speeds (Fig. 2b) are dominated by the peaks 475, 555, 800, 1098 cm⁻¹ without any significant modification with the rotation speed (thickness of the film). The peak at 980 cm⁻¹ corresponding to the vibration mode of Si-OH was noticed, only for 1000 and 2000 rpm. We suppose that at 3000 rpm (reduced thickness of the film) Si-OH groups are easily decomposed even at 200°C.

The spectra of films deposited in the 8th day annealed at 550°C at 3 different rotation speeds (Fig. 2c) reveal the same peaks as in Fig. 2b. No significant changes with the rotation speed were noticed.

The Raman characteristic band of CdSe could not be noticed in any samples due to small dimensions of the embedded microcrystals [22].

As it can be seen from Fig. 3, XRD pattern for CdSe 99,999% purity powder used as a dopant in silicophosphate films exhibits sharp lines characteristic for the semiconductor crystalline compound. The XRD lines are in accordance with data presented in [23, 24].

**Fig. 3.** XRD spectra of: (a) CdSe-doped silicophosphate film, deposited on Day 8, annealing at 550°C; (b) CdSe powder used as dopant.

As concerns the XRD pattern for the CdSe-doped silicophosphate film, day 8, annealed at 550°C for 2 h, (see Fig. 3), the non-crystalline feature of the graph is observed, which is due to the major vitreous silicophosphate network. It is to be taken into consideration that CdSe dopant lines do not appear due to a low concentration, bellow 5 wt. %, being under the detection limit of the measurement device and possibly due to the much reduced dimensions of the dopant particles.

**CONCLUSIONS**

The FTIR absorption spectra (550–4000 cm⁻¹) as well as the Raman spectra (150–3500 cm⁻¹), taken
by 514.5 nm laser excitation), revealed structural units specific to the silicophosphate matrix. These features revealed the role of vitreous network formers of SiO$_2$ and P$_2$O$_5$.

The time elapsed since the sol preparation till the deposition moment, as well as the thermal treatment at different temperatures, brought about changes of the structural peculiarities of the deposited films.

Different rotation speeds of the substrates used in the deposition process did not influence significantly the structure of the films.

The low concentration of CdSe dopant embedded in a predominant vitreous silicophosphate network did not allow giving evidence for the crystalline degree of semiconductor particles.

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