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Influence of the phosphorous precursors on the structure and properties of the SiO_2-P_2O_5 sol-gel films

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Thin films in the SiO_2-P_2O_5 system are intensely studied due to their applications in microelectronics, sensing, nano-photonics, optoelectronics and as ionic conductors. Sol-gel is the most used method for preparation of such films. Previous studies established the very low reactivity of the phosphorous alkoxides and the high tendency of the phosphorous oxide to volatilise at thermal treatment. In order to identify the most appropriate precursor for obtaining layers with desired composition and properties a systematic study of the sol-gel film preparation using different phosphorous precursors was carried out. The films were deposited on ITO/SiO_2 coated glass substrates at room temperature. To check the influence of the type of precursors on the layers thermal stability and properties a post deposition annealing was performed at temperatures of 150 and 200^{0}C. The film characterization was carried out using various techniques as Spectroscopic Ellipsometry (SE), X-ray Photoelectron Spectroscopy (XPS), Fourier Transform Infrared Spectroscopy (FTIR).

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1. Introduction

Research of the silicophosphate system has been undertaken due to the similitude of P and Si coordinance. The simple oxide system SiO_2-P_2O_5 is the initial component for the synthesis of multicomponent glasses with applications in many fields.

Thin films in the SiO_2-P_2O_5 system are intensely studied due to their applications in microelectronics [1], nano-photonics [2], optoelectronics [3] and as ionic conductors [4-6].

The sol-gel process is a method by which inorganic oxides can be prepared at low temperatures by hydrolysis and polycondensation of the precursors in solution. This method avoids high temperature and is favourable for working with compounds with high phosphorus content, because of the high volatility of the phosphorus oxide. For this reason, sol-gel is the most used method for the preparation of the films mentioned above.

Previous studies established the very low reactivity of the phosphorous alkoxides and the high tendency of the phosphorous oxide to volatilise at thermal treatment [7, 8].

In order to identify the most appropriate precursor for obtaining layers with desired composition and properties, a systematic study of the sol-gel film preparation using different phosphorous precursors was carried out.

2. Experimental

2.1. Preparation SiO_2-P_2O_5 films by sol-gel technique

To achieve the purpose of the paper, studying the influence of the phosphorus precursor on the structure and properties of the films, the work solutions were prepared from a single SiO_2 source, tetraethoxyorthosilane (TEOS) and three different P_2O_5 precursors: triethylphosphate (TEP), triethylphosphite (TEPI) or phosphoric acid (H_3PO_4).

The molar percent ratio of the precursors were selected as to lead to a SiO_2-P_2O_5 oxid compostion of 90-10%. The molar ratio ethanol/sum of oxide precursors was 4 in the systems that used phosphorus alkoxides and was increased to 10 when the phosphorus precursor was phosphoric acid, due to the high gelation tendency of this system. The water was added in a molar ratio of 2 mols H_2O to the sum of oxide precursors. The hydrochloric acid was added to the system in molar ratio of 0.001 to the amount of all precursors.

The initial composition of the starting solutions and the experimental conditions used are presented in Table 1. First a solution of TEOS in ethanol was prepared to which the water containing HCl as catalyst and then the approppriate amount of P_2O_5 precursor (TEP, TEPI or H_3PO_4) was added. The solutions obtained starting with phosphorus alkoxides were stirred for 3 hours and were kept at room temperature for 24 h before deposition. The solution obtained with H_3PO_4 was stirred for only 30 minutes and was deposited immediately after preparation to avoid its gelation. The final solutions have a *pH* of about 3.

Films were deposited on ITO coated glass plates which were appropriately cleaned before the deposition. They were first dried at room temperature and then thermally treated at low temperatures (150 and 200 ^{o}C) for 15 minutes in order to avoid as much as possible the phosphorus loss from the films.

Table 1. Composition of starting solutions and experimental conditions for film preparation in the binary system 90% SiO_2-10%P_2O_5 (%mol).

Sample	Precursors	Molar ratio			pH of the mixture	Reaction conditions		Gelation time, days
		EtOH/ Σ precursor	H_2O/ Σ precursor	HCl/ Σ precursor		t,^{0}C	Time, h	
A	TEOS, TEP	4	2	0.001	3	20	3	30
B	TEOS, TEPI	4	2	0.001	3.5	20	3	60
C	TEOS, H_3PO_4	10	2	0.001	3	20	0.5	20

2.2. Characterization of the SiO_2-P_2O_5 films

Structural and optical characterization of the samples was carried out by Spectroscopic Ellipsometry (SE). The measurements were performed in air, in the 400-700 nm wavelength range at an angle of incidence of 70^0. The ellipsometric spectra have been fitted using a model (Fig. 1a) with three layers and five component (SiO_2, ITO, P_2O_5, TEP, TEPI and voids) based on Bruggemann's Effective Medium Approximation (B-EMA) [9]. The volume fractions of the components and the thickness of the layers were taken as fitting parameters. From the best fit one obtained the refractive index, n, the thickness of the films, d, and volume fractions of the components (Table 2). Dielectric constants taken from literature data bases have been used as reference (SiO_2 [10], SiO [10], P_2O_5 [11], TEP, TEPI were measured by a Pulfrich refractometer) in the ellipsometric program.

IR spectra were recorded on a Perkin Elmer SPECTRUM 100 spectrometer in the range 550-4000 cm^{-1}. All spectra were obtained using a UATR accessory with a resolution of 8 cm^{-1}, 32 scans and a CO_2/H_2O correction.

Chemical composition of the films was examined using X-ray photoelectron Spectroscopy (XPS). The spectra corresponding to the C(1s), O(1s) were recorded in a 20eV window, with 256 channels, and 200 msec dwell time. For the Si(2p) and P(2p), the spectra were recorded in a 50eV window, with 512 channels, and 200 msec dwell time. A VG ESCA 3 MkII-EUROSCAN Instr. Spectrometer was used in the following conditions:

- the X-ray source : an emission tube with an dual anode of Mg/Al; energy: 1486.7 eV (Al K_α);
- the pressure in the analysing room: 1.333×10^{-7} Pa;

4. Results and conclusions

Starting with the precursors mentioned above and in the experimental conditions presented in Table 1, continuous and adherent films to the substrate were obtained.

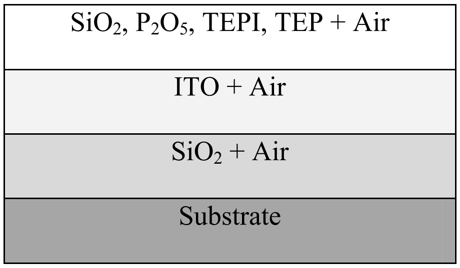
The ellipsometric data of as prepared and thermally treated films at 150 and 200 ^{o}C are presented in the Table 2.

From the SE analysis it was found that three different P_2O_5 precursors lead to three diferent samples thicknesses. As compared with the alkoxidic precursors, the thinner films have been obtained by using the phosphoric acid precursor. After thermal treatment at 150^{0}C the film densifies and the thickness decreases. By further thermal treatment a slightly decrease in the samples thickness can be noticed. The films obtained from TEP precursors (B-type coatings) exhibit a different behaviour, in which the thickness of he film increases by thermal treatment at 150^{0}C. This is an unusual conduct but could be correlated with the evolvement in the studied temperature range of the non-reacted P-precursor, leading to an important P loss from the films composition and consequently to an expanding of the film.

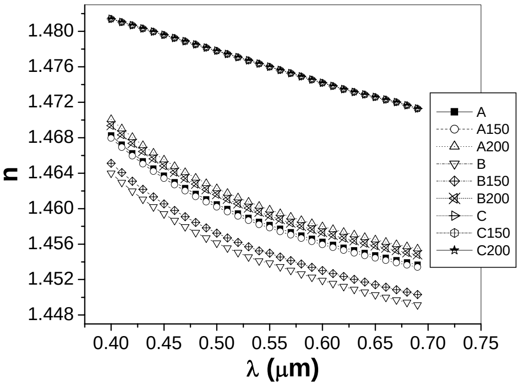
Further, from the best fit the refractive indexes for the A, B and C-type samples were obtained (Fig. 1b). As can be seen in Figure 1b, the lowest values were obtained for the B-type samples due to the evolution of the P-precursor from the film, that change its composition to a SiO_2 based one. For the films obtained from TEPI (A) slightly higher refractive indexes values were achieved while the highest values can be noticed for films prepared from H_3PO_4 precursors (C). The refractive index curves for the C, C150 and C200 samples are superimposed.

Table 2. Spectroellipsometric results of the sol-gel SiO_2-P_2O_5 films obtained from various precursors.

	Substrate						Coatings					
	SiO_2 layer			ITO layer								
Sample	**D(Å)**	**SiO_2 (%)**	**Air (%)**	**d(Å)**	**ITO (%)**	**Air (%)**	**d(Å)**	**SiO_2 (%)**	**P_2O_5 (%)**	**TEP (%)**	**TEPI (%)**	**Air (%)**
A	1640	99.83	0.17	1381	79.76	20.24	2377	92.32	-	-	7.03	0.65
A150	1710	99.22	0.78	1371	80.88	19.12	2127	93.73	-	-	5.74	0.53
A200	1660	99.64	0.36	1521	71.25	28.75	2057	99.79	-	-	0	0.21
B	1610	99.29	0.71	1741	59.54	40.46	2637	96.86	-	3.11	-	0.03
B150	1720	98.89	1.11	1771	58.95	41.05	2667	97.62	-	2.19	-	0.20
B200	1730	99.39	0.61	1781	58.47	41.53	2617	100	-	0	-	0
C	1170	99.82	0.18	1351	80.04	19.96	2120	90.90	8.95	-	-	0.15
C150	1520	99.82	0.18	1341	81.00	19.00	2090	90.90	8.94	-	-	0.16
C200	1460	99.42	0.58	1381	78.13	21.87	2080	90.90	8.94	-	-	0.16



a



b

Fig. 1 (a) Sketch of the model used for fitting the ellipsometric experimental spectra; (b) dispersion curves of the refractive index in the visible wavelengths range, obtained from the best SE fit, for the A (TEPI), B (TEP) and C (H_3PO_4) samples.

Fig. 2 presents the IR spectra of the films obtained with different phosphorous precursors as prepared and thermally treated at 200 °C, respectively. The bands corresponding to the stretching vibrations of Si-O-Si and P-O-P in the gels and in the Si and P-precursors overlap in all the analysed samples. However the different intensity of the bands in the 1000-1200 cm^{-1} wave number range, indicate a different structure of the as-prepared gels, as well as a different behaviour during the thermal treatment.

The different structure obtained after thermal treatment could be correlated in the case of H_3PO_4 precursor, to the film structural ordering, while in the case of P-alkoxides to their evolution from the system.

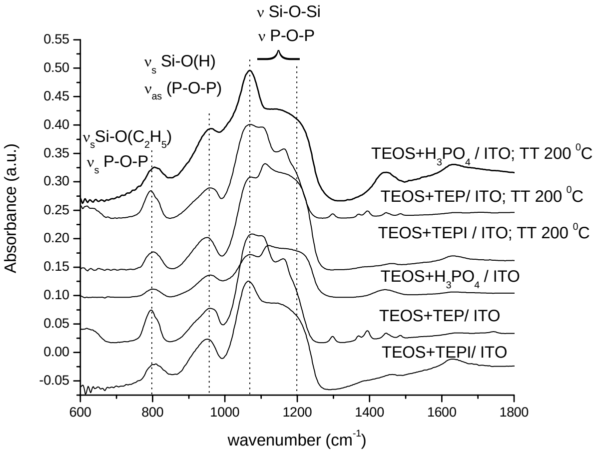
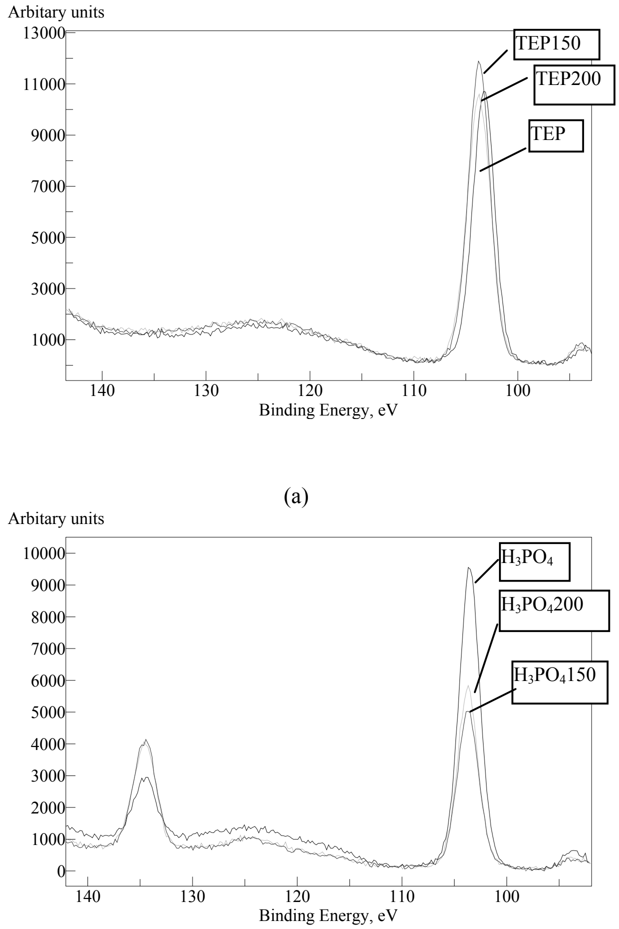


Fig. 2. IR spectra of the-as prepared and thermally treated films.

The evolution of the XPS spectra with temperature for the films obtained starting with TEP and H_3PO_4 is presented in the Fig. 3 a and b. In the case of the as-prepared films starting with TEP the presence of the P is not confirmed. This fact could be explained by the fact that the phosphorous component is not chemically bonded in the matrix, but only embedded and so, it can be easily evaporated from the film during the XPS analysis. This fact is under further investigation.



(a)

(b)

Fig. 3. XPS spectra evolution for the sample B prepared with TEP (a) and C prepared with H_3PO_4 (b). The bigger peak is Si and smaller peak is P.

5. Conclusions

The influence of the type of precursors on the layers thermal stability and properties by a post deposition annealing at temperatures of 150 and 200 °C was studied.

In the prepared films an importnat P loss was established, mainly when P-alkoxide was used as a P precursor. For film preparation in the SiO_2-P_2O_5 system, special care has to be taken in order to retain the P in the film composition.

After thermal treatment the films are generally densified, only the films obtained from TEP precursors exhibit a slightly different behaviour, in which the thickness of he film increases by thermal treatment at 150^0C, due to the P loss from film. The lowest refractive indexes are also for the B samples.

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