

Sodium diffusion barrier coatings prepared by sol–gel method

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In the case of electrically conducting layers prepared on a glass substrate, sodium diffuses into the SnO₂ film and deteriorates their electric properties. Sodium barrier diffusion properties of thin layers based on SiO₂, and SiO₂ modified by various contents of Al₂O₃, TiO₂, ZrO₂, CeO₂, prepared by sol–gel, have been the subject of this study. Morphology and optical properties of the coatings have been analyzed. XPS technique has been used to evaluate the barrier properties of prepared coatings by measuring sodium 1s peak changes after thermal treatment of the coating. The best properties have been obtained for the coating based on SiO₂–Al₂O₃ system and containing 0.08 mol of Al. It has been found that blocking properties of the coating are mainly connected with its microstructure. The role of added modifiers lies in changing the microstructure of formed gel.

Keywords: sol–gel, barrier coatings, X-ray photoelectron spectroscopy (XPS), sodium diffusion.

1. Introduction

Electrically conducting transparent thin films based on tin or indium have found many applications, mostly in electronic devices. However, their electric parameters can deteriorate as a result of the diffusion of alkaline ions from a glass substrate. Silica and alumina thin films are widely used as blocking layers to prevent diffusion of sodium from glass into tin oxide layers. Alkaline ions present in commercial soda-lime glass diffuse from the interior to the surface when the glass is immersed in water or exposed to a high-humidity atmosphere with temperature around the dew point. At the surface, alkali dissolves in water or forms chemical compounds with substances from the surroundings. The primary driving force for the alkali transport is the concentration gradient. Quite high sodium losses are induced in soda-lime glass surfaces by Na₂SO₄ microcrystals which are formed when SO₂ gas is blown onto the hot surface during a draw up from the melt. When SnO₂ film is spray-deposited on a hot sheet glass, NaCl microcrystals are created by the interaction with the SnCl₄ solution [1]. These microcrystals can destroy or change the properties of SnO₂ film. Protective coating should therefore have barrier properties in both directions.

The presence of alkali ions in the coating has a negative influence on its electric properties. Alkali ions can lead to decreasing or even vanishing of electric conductivity of SnO₂ oxide [2]. Thin blocking layers prevent the corrosion of glass surfaces due to ambient moisture and the diffusion of alkali ions (Na, K, Li) from the glass substrate into the alkaline-sensitive coatings such as TiO₂, SnO₂ or tin-doped indium oxide (ITO) [1].

The high density of the barrier coatings is important to prevent the adsorption of water vapour from the ambient atmosphere and the diffusion of alkali ions from the glass. The density of thin films is determined by deposition conditions, *i.e.*, the deposition process and the parameters used. Thin layers with low densities, *e.g.*, films produced by sol–gel techniques or reactive evaporation, have also reduced blocking properties. The blocking capability of these layers can be drastically increased by a temperature treatment at 500 °C for one hour [1].

A sol–gel technique has many advantages and is often preferred over other more advanced techniques. Sol–gel deposition processes offer an inexpensive but efficient route to deposit such films. It is the only process to make glass and ceramic films at a relatively low cost. Sodium diffusion barrier coatings are usually fabricated by vacuum evaporation [3], sputtering [4] or electrolytic deposition processes [5]. The sol–gel process offers a different approach to the synthesis of these oxide coatings [6]. A thin film produced by the sol–gel method has very high homogeneity and large mechanical and chemical durability. Sol–gel also helps to control the microstructure of deposited films (*e.g.*, pore volume, pore size). SiO₂, TiO₂, and Al₂O₃ thin films are most often used as a barrier against the diffusion of alkali ions.

MIZUHASHI [7] have studied electric properties of SnO₂ film deposited on 100 nm SiO₂ barrier coating and concluded that they are similar to those of SnO₂ film obtained on pyrex glass. The application of SiO₂ and TiO₂ thin films prepared by sol–gel as barrier coatings has been considered by BACH [1] and FU GUANGHUI *et al.* [8]. SiO₂ film with a thickness of about 700 Å reduces the concentration of sodium ions in the ITO film from 1 µg/cm² to 0.2 µg/cm². The effect of the SiO₂ in preventing the sodium diffusion was more evident when the film thickness was higher or the film was treated at a higher temperature. SARAIE *at al.* [9] and SAWADA *at al.* [10] have confirmed that the Al₂O₃ amorphous coating can also prevent the sodium diffusion.

The aim of this paper was to prepare thin layers with different chemical composition by the sol–gel method and to examine their blocking properties.

2. Experimental procedure

Thin films were deposited from the TEOS (tetraethylorthosilicate) based sol by a spin coating method (1800 rpm). Soda-lime microscope glass slides (2×2 cm²) were used as a substrate. The following compounds were used to prepare sols: TEOS Si(OC₂H₅)₄ (Aldrich), MTMS CH₃Si(OCH₃)₃ (Aldrich), TEOT C₈H₂₀O₄Ti (Merck),

Table 1. Chemical composition of the sols.

Sample	TEOS [mol]	C ₂ H ₅ OH [mol]	Additive [mol]	H ₂ O [mol]	HCl [mol]	C ₃ H ₈ O [mol]
TM01	1	2.0	0.04 MTMS	4.35	0.05	—
TA01	1	4.0	0.08 Al(NO ₃) ₃ ·9H ₂ O	3.90	0.05	—
TA02	1	4.0	0.15 Al(NO ₃) ₃ ·9H ₂ O	4.50	0.05	—
TA03	1	4.0	0.20 Al(NO ₃) ₃ ·9H ₂ O	5.10	0.05	—
TT01	1	3.2	1.05 TEOT	2.30	0.04	9.8
TZr01	1	3.6	0.20 ZrCl ₄	3.20	0.05	—
TCe01	1	0.4	0.05 Ce(NO ₃) ₃ ·6H ₂ O	1.75	0.03	—

Al(NO₃)₃·9H₂O, ZrCl₄, C₂H₅OH (POCH SA), isopropyl alcohol C₃H₈O (POCH SA). Hydrochloric acid HCl (POCH SA) was used as a catalyst. The chemical composition of the sols is listed in Tab. 1. The sol preparation procedure is shown in Fig. 1.

After the preparation, the coatings were dried at 160 °C during 5 min and next they were subject to thermal treatment at a temperature of 450 °C for 5 min in air in order to achieve the stability of the quantity of sodium on the surface.

The transmittance of the thin films was measured by UV-VIS Konica Minolta CM-2600d/2500d spectrometer. SEM micrographs were performed using Nova Nano SEM 200 FEI Company microscope. X-ray photoelectron spectroscopy analyses were

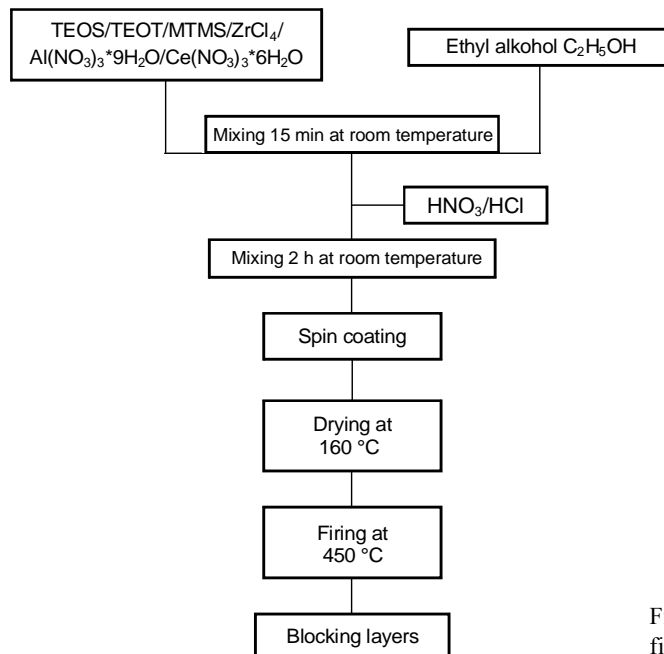


Fig. 1. Preparation procedure of thin films by sol-gel process.

performed on “as made” samples using VSW spectrometer with a hemispherical analysis. Spectra were obtained using Al K α radiation source operated at 200 W and 10 kV. An electron energy analyzer was set to FAT mode with the pass energy of 20 eV. The shift of the binding energy caused by the surface charging effect was calibrated by assuming the binding energy of C 1s to be always 284.6 eV [11]. The quantity analysis was carried out applying XPS sensitivity factors published by BRIGGS and SEAH [12].

T a b l e 2. XPS results for analyzed blocking layers. Results for a glass substrate are also shown.

	C 1s			O 1s		
TM01						
Max [eV]	284.6	287.0	286.2	532.3	530.7	533.9
FWHM [eV]	2	2.27	1.81	1.92	2.04	1.55
Area	3742.9	722.2	1508.4	63848.8	5807.3	4227.7
TA01						
Max [eV]	284.6	286.1	87.1	531.8	529.9	
FWHM [eV]	1.64	2.24	3.2	2.1	1.33	
Area	6433.7	4520.4	908.6	70407.5	2733.1	
TA02						
Max [eV]	284.5	286.2	287.6	532.1	530.4	
FWHM [eV]	1.77	1.49	2.03	2.11	1.54	
Area	5608.1	1716.1	354.6	69804.4	3955.1	
TA03						
Max [eV]	284.6	86.3	289.1	532.4	530.7	
FWHM [eV]	1.67	2.12	1.86	2.12	1.47	
Area	3698.2	3350.1	257.3	89182.5	5355.7	
TT01						
Max [eV]	284.6	286.1	287.8	530.1	531.9	
FWHM [eV]	1.8	1.65	1.01	1.91	2.07	
Area	6837.0	3472.8	214.4	37526.8	44894.1	
TZr01						
Max [eV]	284.6	284.2	286.7	532.2	530.3	
FWHM [eV]	1.81	1.92	3.13	2.09	1.77	
Area	5873.6	3631.6	778.5	90775.8	13056.9	
TCe01						
Max [eV]	284.6	286.1	288.0	532.3	530.8	533.7
FWHM [eV]	1.82	2.16	1.81	1.85	2.03	1.81
Area	8325.0	6441.4	442.8	88565.1	9179.2	8317.6
Glass substrate						
Max [eV]	284.7	287.7		531.8	535.6	
FWHM [eV]	2.0	2.8		2.8	2.3	
Area	8116.9	1317.6		40623.1	3365.4	

3. Results and discussion

3.1. Photoelectron spectroscopy – XPS

Photoelectron spectroscopy was used to evaluate blocking properties of prepared layers. The intensity of Na 1s line is proportional to atomic concentration of sodium on the surface. Assuming the continuity of the layer, a lower concentration of sodium is expected for the layer with better blocking properties. The results of XPS

Table 2. Continued.

	Si 2p		Additive			Na 1s
TM01			Si			
Max [eV]	102.8	103.4				1071.7
FWHM [eV]	1.99	2.8				2.47
Area	14712.3	3894.6				16111.4
TA01			Al			
Max [eV]	102.4		73.6			1072.4
FWHM [eV]	2.06		1.86			2.39
Area	14224.9		793.8			13266.1
TA02			Al			
Max [eV]	102.8		74.1	71.9		1072.0
FWHM [eV]	2.07		1.86	1.2		2.39
Area	10686.9		1742.9	99.4		26026.8
TA03			Al			
Max [eV]	102.9		74.3			1072.5
FWHM [eV]	2.09		1.91			2.34
Area	12590.7		2564.4			26231.8
TT01			Ti			
Max [eV]	102.4		458.6	464.4	459.5	1071.8
FWHM [eV]	2.14		1.75	2.52	4.38	2.16
Area	11748.7		46352.7	24376.8	6449.2	26381.3
TZr01			Zr			
Max [eV]	102.7		182.4	184.8		1071.8
FWHM [eV]	2.15		1.83	2.0		2.3
Area	21376.5		7617.8	5770.7		29792.3
TCe01			Ce			
Max [eV]	103.1					1071.7
FWHM [eV]	2.1					2.32
Area	24579.8					21899.8
Glass substrate						
Max [eV]	103					1071.5
FWHM [eV]	2.4					2.4
Area	3886.4					16785.3

studies obtained with the standard uncertainty of 10% were summarized in Tab. 2 while Tab. 3 presents the quantity analysis based on these studies. The lowest concentration of sodium (0.03%) was analyzed for a sample TA01 containing 0.08 M Al/1 M Si – Fig. 2. An increase in alumina content in the layer leads to a substantial increase of sodium peak – Tab. 3. This finding confirms the fact that blocking properties are connected with the microstructure of the layer and that the role of alumina is to change the microstructure. Alumina in low concentration leads to a higher polymerization degree of the layer with higher fractal factor as compared to pure Si layer. Most probably alumina substitutes silica in the 3-dimension network formation. A higher content of alumina leads however to its precipitation in the form of a separate phase. The Si phase is less polymerized with a tendency to particle formation. Such behaviour is based on much lower Si 2*p* binding energy observed for TA01 sample 102.4 eV. Such low binding energy is characteristic of fractal structures where silica has at least one unconnected bond or some part of silica is substituted by other atoms (Al, Ti). In this case, better blocking properties can be connected with the continuity of the layer. Any precipitation or phase separation leads to phase boundary formation, which is a path to rapid diffusion for sodium.

T a b l e 3. Quantity analysis based on XPS results.

Atomic concentration [%]	TM01	TA01	TA02	TA03	TT01	TZr01	TCe01	Glass substrate
C	11.28	21.47	15.11	11.96	16.15	13.85	18.89	29
O	52.86	50.14	54.96	58.62	47.92	52.98	49.89	52.8
Si	32.54	23.84	19.47	19.08	16.68	26.66	28.26	11.4
Additive	—	1.94 Al	4.89 Al	5.67 Al	14.83 Ti	2.15 Zr	—	—
Na	3.31	0.03	5.57	4.67	4.4	4.36	2.96	5.8

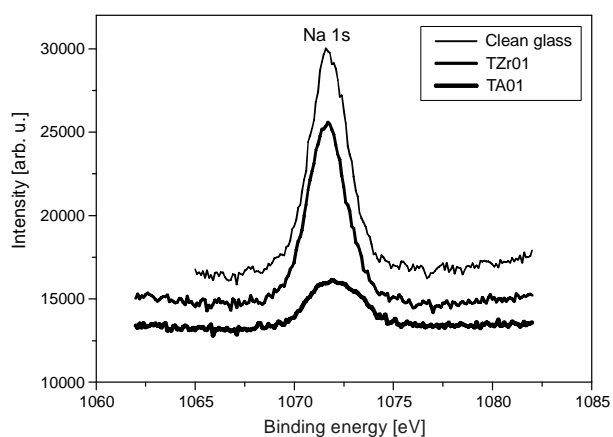


Fig. 2. XPS spectra – Na 1s region for clean glass (5.8%), TZr01 (4.36%) and TA01 (0.03%) samples.

3.2. Optical properties – UV-VIS

The reflectance curves of the layers are shown in Fig. 3. Characteristic interference peaks are observed. The reflectance measurements were used to calculate thickness of the layer, assuming the following relation [13]:

$$2nd = \left(\frac{1}{\lambda_1} - \frac{1}{\lambda_2} \right)^{-1}$$

where: λ_1, λ_2 – wavelength at the successive maxima, n – refractive index of the layer, d – thickness of the film. The results are shown in Tab. 4 including the refractive indexes of the layer were calculated on the basis of chemical composition of the layer. The thickness of the layer is a complicated function of the chemical composition of the sol. Even small changes in the composition influence the rate of condensation

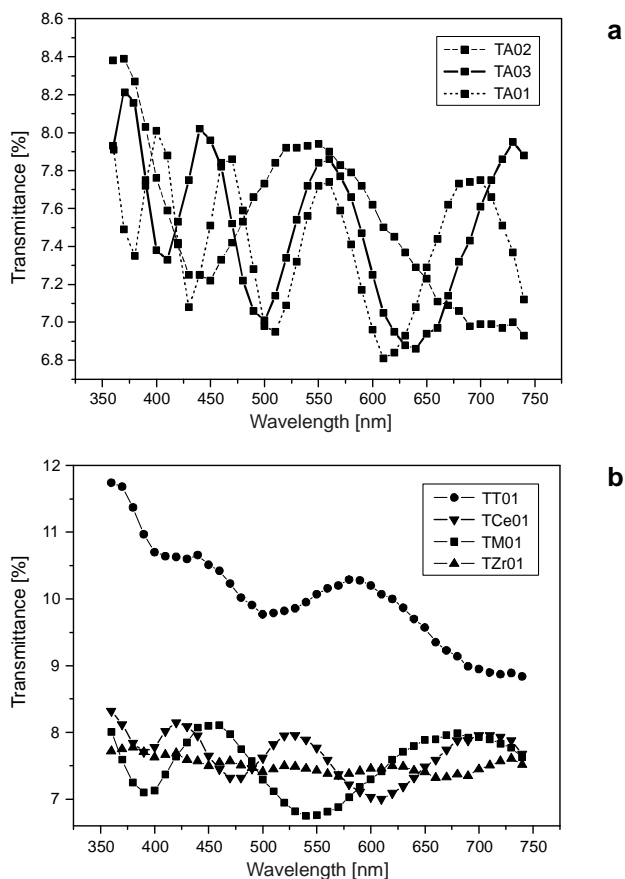
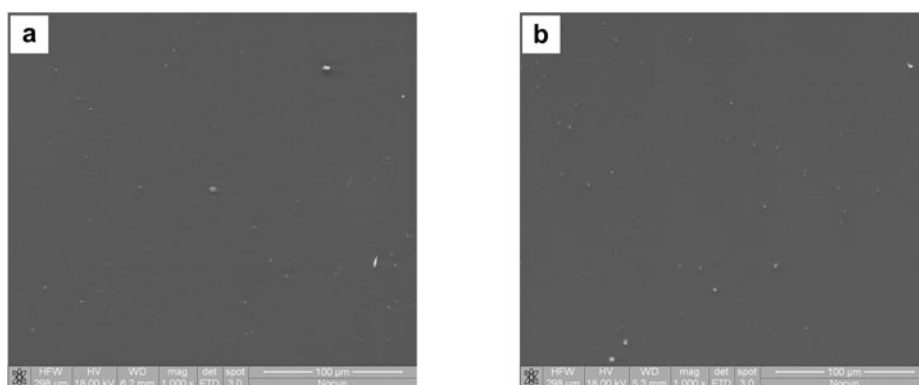


Fig. 3. Reflectance curves for prepared layers; **a** – results for alumina modified layers, **b** – titania, ceria, silica and zirconia modified layers, respectively.

T a b l e 4. Thickness of the layer estimated on the basis of reflectance measurements.

Name	Thickness [nm]	Refractive index
TM01	487	1.46
TA01	905	1.48
TA02	377	1.50
TA03	679	1.51
TT01	307	2.97
TZr01	1268	1.57
TCe01	679	1.49

Fig. 4. Scanning electron micrographs of sodium diffusion barrier coatings: **a** – TT01, **b** – TZr01 sample.

which leads to changes in a viscosity of the sol. Blocking properties of the layers are not however a linear function of the layer thickness. The best blocking properties are measured for TA01 sample, while the thickness of the sample TZr01 is much higher – Tab. 4.

3.3. Microstructure observations – SEM

The surface morphology of the blocking films fired at 400 °C were studied SEM and selected results are shown in Fig. 4. The layers are amorphous, continuous and crack-free. However, morphology details are not seen under the microscope used.

4. Conclusions

Sodium diffusion blocking properties of the layers prepared by the sol–gel method depend mainly on the microstructure of the layer. The best results can be obtained when the layer is continuous and crack-free with a high fractal index structure. In studied cases, the best results were obtained for a TEOS based layer modified

with 0.08 mol% of Al. Any precipitation or phase separation in the layer can lead to increase in sodium diffusion from the substrate to the top of the layer.

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