ZnO sol-gel oxide coatings as materials for UV optical filters

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Abstract

Ultraviolet light influences materials structure causing the decomposition and degradation of organic compounds. One of the ideas to reduce the harmful effects of light is to protect materials by sol-gel coatings. ZnO sol-gel thin films on a glass substrate were obtained as optical filters. The filter effect of synthesized coatings stabilized in different temperatures were characterized by UV-Vis transmittance spectroscopy. The morphology and elemental composition of coating surface was determined by SEM and EDX. Scratch resistance and adhesion have been evaluated by scratch test. The coatings present high transparency in the visible region and absorption in the UV region (270-360 nm). The results suggest that the obtained materials have proper parameters for UV optical filters. Copyright © 2017 VBRI Press.

Keywords: Thin films, zinc oxide, UV absorbers, adhesion.

Introduction

The ultraviolet range of the light can decrease efficiency, stability and even damage materials during long exposition **[1]**. Natural or artificial UV radiation causes the decomposition and degradation of organic compounds because energy of UV photons is strong enough to break chemical bonds **[2]**. Natural UV radiation is the most damaging in the range of 290 nm – 350 nm, because it has the highest energy of the solar spectrum **[3]**. By controlling ingredients of the material, it is possible to create layers of various optical properties, e.g. blocking of a selected range of light. Thin films can be prepared by a variety of techniques including the sol-gel method which has emerged as one of the most promising processes. This method allowed to create homogeneous, transparent and multi component oxide layers of various compositions at low cost **[4**, **5]**.

Organic and inorganic UV absorbers have been widely studied as coatings used to protect materials against UV radiation **[6]**. Organic UV absorbers can be divided into two groups, those covering UVA (320 – 400 nm) and UVB range (290 – 320 nm). The application limits of organic absorbers result from their low effective lifetime because of self-photo-degradation polymer matrices and sensibility to heat **[7]**. An alternative to the organic UV absorbers is the usage of inorganic materials based on e.g. TiO_2, ZnO and CeO_2, which efficiently absorb the UV radiation and exhibit good heat resistance properties. The decreasing of the UV radiation in ZnO (and similar in other inorganic oxides TiO_2, CeO_2) is obtain by bandgap absorption and scattering of light. Inorganic absorbers, such as ZnO and TiO_2, are commonly used as sunscreen filters **[9]**. Unfortunately, inorganic absorbers also have some limitations. They have high light refraction caused by crystallized phase anisotropy and loose transparency in the visible region **[9]**.

ZnO films are characterised by a wide band-gap (3.3 eV), large exciton binding energy at a room temperature (60 meV) with optical transparency in the visible range **[10-13]**. ZnO films have been targeted such as solar cell windows **[14]**, gas-sensors **[13]**, transparent conductors **[9]**, transistors **[15]**, optical waveguides **[16]**, etc. UV absorber films based on the ZnO **[7, 17]** and hybrid composites, e.g. TiO_2-ZnO **[18]**, ZnO-CeO_2 **[7]**, TiO_2-SiO_2, TiO_2-CeO_2-SiO_2, CeO_2-SiO_2, TiO_2-ZnO **[9]** and ZrO_2-SiO_2 **[19]** can be obtained by the sol-gel method, which is efficient in producing thin, transparent, multi-component oxide layers on various substrates **[18]**. It was observed that the absorption of ZnO and other films in the UV was increased by the introduction of cerium **[7,9]**. Currently different metals such as Al, Mg, Mn have been studied as promising dopants for ZnO. Doping and combining ZnO with various metals leads to enhancing some of their properties, including the optical ones. Aluminium-doped zinc oxide coatings show higher transparency compared to ZnO coatings **[25]**. Recent papers focused on ZnO for UV light emitters, transparent electronics and UV photodetection **[23]**. The review of Y.W. Heo et al. suggests the future development of ZnO nanowires for transparent transistors, low-power signal processing, biodetection snd also gas and chemical sensing **[24]**.

The aim of this experiment was to synthesize transparent thin films based on inorganic ZnO absorber without any dopants, as a proper material for UV filters without losing the transparency in the visible region. Moreover, the obtained coatings had to have a good scratch resistance. ZnO samples were created with different numbers of layers and were analyzed in various conditions of thermal stabilization. In this paper the authors observed the influence of stabilisation temperature of ZnO coatings and the number of layers of coatings, on light absorption in the UV region. Moreover, the surface morphology and elemental analysis have been conducted and the scratch resistance has been evaluated.

Experimental

Coatings preparation

Thin ZnO films were synthesized according to the Ghodsi and Absalan procedure **[20]**. Zinc acetate dihydrate (97+% ZnAc, Alfa Aesar, USA) was used as a precursor, isopropanol (99.7% iPrOH, Avantor Performance Materials, Poland) and diethyloamine (98% DEA, Sigma Aldrich, Germany) were used as a solvent and a stabilizer, respectively. Zinc acetate dihydrate was added to isopropanol and the mixture was homogenized on a magnetic stirrer. After 30 minutes DEA stabilizer was added drop by drop to the mixture at a temperature of 60 °C and stirred for 1 hour. Reagents were added in the molar ratios as 1:60:8 (ZnAc:iPrOH:DEA, respectively). A stable and transparent hydrolysate was obtained. The films were deposited over a glass slide previously cleaned with ethanol. The transfer process onto a glass slide was carried out by the dip-coating technique at 100 mm/s with immersion times of 60 s. In such a way, the 1-layer and 2-, 3-, 4-, 5- layer coatings were obtained. The films were then annealed at a temperature of 200^{0}C for 10 min. The 5-layer coatings were additionally annealed at a temperature of 400 °C for 10 and 20 min.

Measurement methods

UV-Vis spectrophotometer

The transmittance spectra of the coatings were measured by UV-Vis spectrophotometer (UV-VIS Nicolet Evolution 100, Thermo Lab) in the Laboratory of Sol–Gel Materials and Nanotechnology at the Wrocław University of Science and Technology. The research was conducted in the measuring range of 190-900 nm. For each sample an added symbol depends on thickness: llc – one-layer-coating, 2lc – two-layer-coating, 3lc – three-layer-coating, 4lc – four-layer-coating and 5lc – five-layer-coating.

Scanning electron microscope (SEM)

Surface morphology, analysis of elements and determination of their distribution were performed using a scanning electron microscopy (SEM) HITACHI S-3400N and an X-ray microanalyzer (EDX, energy-dispersive X-ray) attached to the SEM in the Laboratory of Sol–Gel Materials and Nanotechnology at the Wrocław University of Science and Technology.

Scratch tester

The sample mechanic characterization was performed by a scratch tester (CSM Instruments, now Anton Paar) in the Multifunctional Amorphous and Crystalline Materials Laboratory at the Wrocław University of Science and Technology. Measurements were carried out with the diamond Rockwell indenter with a radius of 100 µm. The scratch test was conducted in the progressive mode, with a range of loading 0.03-10 N and speed load 1.5 mm/min.

Results and discussion

Optical properties

The tests of optical properties were carried out using a UV-Vis spectrophotometer to determine the activity of the obtained ZnO coatings for blocking light of a wavelength more than 260 nm (the wavelength up to 260 nm is blocked by a glass substrate). The results depend on the extent to which the ZnO band gap approximates 3.3 eV, which corresponds to the wavelength 366 nm [**10**]. The energy of the UV range is absorbed by atoms in the ZnO material and is powerful to excite electrons from the valence band to the conduction band **[1]**.

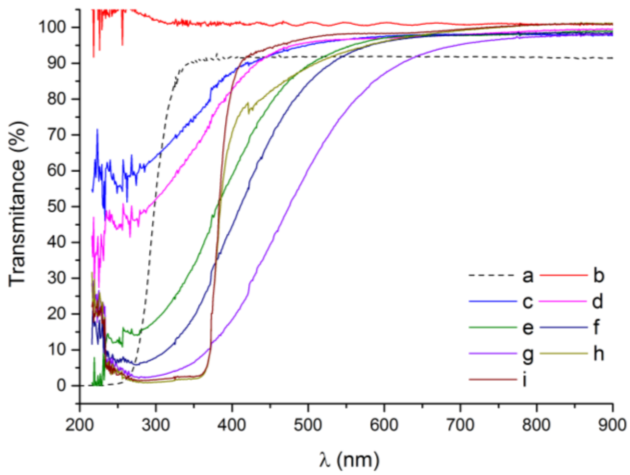

Fig. 1. UV-Vis spectra for ZnO coatings: (a) glass slide, (b) 1lc before thermal stabilization, (c) 1lc stabilized at 200^{0}C, (d) 2lc stabilized at 200^{0}C, (e) 3lc stabilized at 200^{0}C, (f) 4lc stabilized at 200^{0}C, (g) 5lc stabilized at 200^{0}C, (h) 5lc stabilized at 400^{0}C for 10 min, (i) 5lc stabilized at 400^{0}C for 20 min.

Fig. 1 shows the UV-Vis spectra in the wavelength range of 200-900 nm for multilayer coatings of ZnO. The films thermally treated at 200 ºC (1lc, 2lc, 3lc, 4lc, 5lc) show very low absorption in the UV region (260-400 nm) and weak transparency in the visible region (400-700 nm). This can be explained by the lack of crystal structure of zinc oxide at this temperature **[7]**. It was also observed that the absorption slowly increased with the thickness of the films obtained by the subsequent dip-coating process. Samples with 5 layers of ZnO (5lc) heated at 200 ºC show better absorption in the UV region (260-400 nm) than the same samples with a smaller number of ZnO layers (1lc, 2lc, 3lc and 4lc) annealed at the same temperature. The transmittance decreases near the ultraviolet region due to the band gap absorption of zinc oxide. High transmittance is observed in the sample with 5-layer-coating of ZnO annealed at 400 ºC for 20 minutes (line 'i' on **Fig. 1**). This sample shows good transparency (around 95%) in the region of 370-900 nm. This phenomenon was observed by other authors and are explained by the higher crystallinity of the ZnO phase **[7, 17]**.

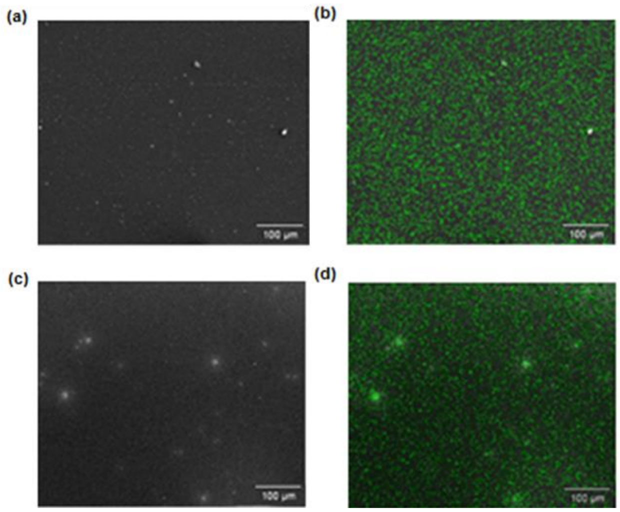

Fig. 2. SEM images and distribution of Zn atoms (green) of the ZnO thin films, (a, b) 1-layer coating, (c, d) 5-layer coatings. Magnification: 200x, scale bar: 100 µm.

Surface morphology and elemental composition

SEM-EDX images in **Fig. 2** show the morphological aspects on the ZnO thin films surfaces. The coatings are continuous and homogeneous (**Fig. 2a**, **c**) and simultaneously the distribution of zinc atoms is uniform in one-layer (**Fig. 2b**) and five-layer (**Fig. 2d**) ZnO coatings. The quantitative data from EDX analysis in **Fig. 3** showed that with the increase of the number of layers of ZnO sol-gel coating the amount of zinc grow and the amount of silicon drops. Due to the fact that the source of silicon is a glass substrate, the obtained results indicate higher thickness of five-layer-coating.

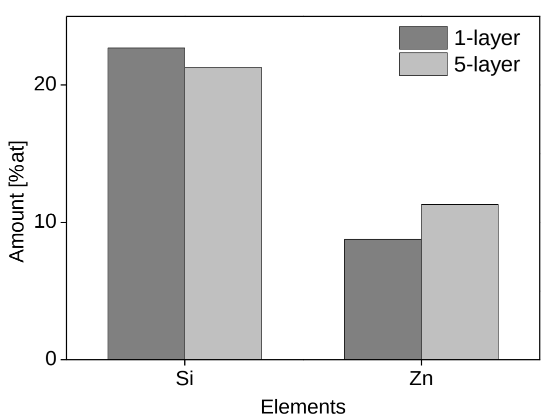

Fig. 3. The amounts [% at.] of Si and Zn in the 1-layer and 5-layer ZnO coatings covering the glass substrates.

Thin film scratch resistance

The adhesion and scratch resistance of ZnO five-layer-coating on glass substrates was examined by the scratch test. The scratch line was measured from 0 to 3 mm. At the point where the coating is broken, a scratch line has a length of 1.98 mm. Two specific points, understood as critical normal forces according to PN-EN 1071-3, were evaluated by visual examination of the scratch (**Fig. 4**). In this scratch test the critical load for film decohesion was determined as L_{c1} and for coating detachment as L_{c2}. The decohesion type is identified as a combination of a forward chevron tensile crack and an arc tensile crack. the empirical measure of the adhesive strength of the film was concluded by the load at which the detachment occurs, in this case at a load of 2.52 N. The obtained value is high in comparison to the results described in the literature, e.g. ZnO sol-gel coatings obtained by J. Lee et al. at a similar temperature (450 °C) on silica wafers were completely detached from the substrate at 15 mN **[21]**. Moreover, the literature analysis of different sol-gel coatings on glass shows that usually coating scratch resistance is similar to substrate (glass) scratch resistance **[22]**.

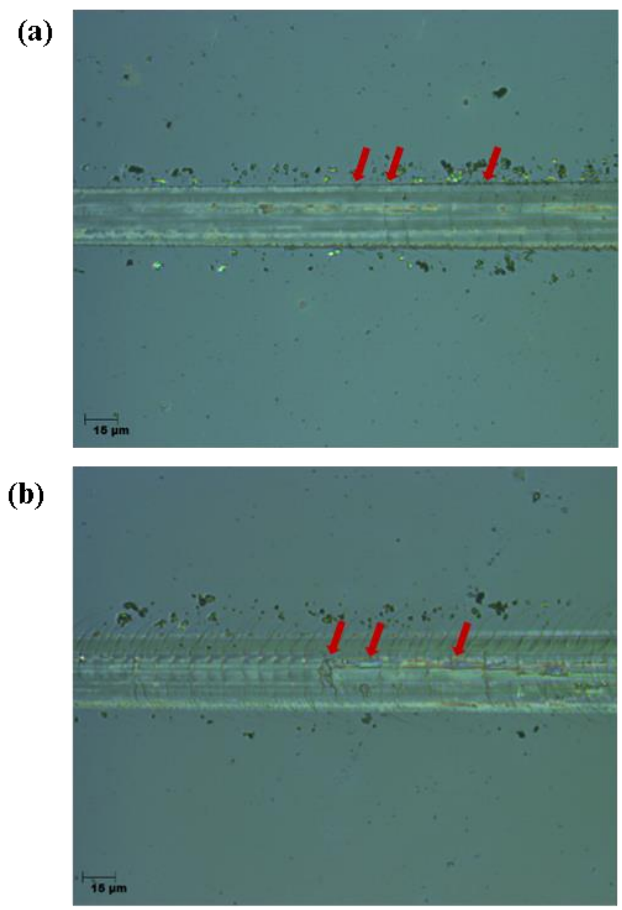

Fig. 4. Scratch test critical points for 5-layer ZnO coating (a – L_{c1}, b – L_{c2}). Scale bar: 15 µm.

Table 1. Value of critical load and lateral force of ZnO 5-layer coatings.

Sample	L_{c1}	L_{c2}
Substrate – glass slide	2,18 ± 0,14	-
ZnO 5-layer coating	0,69 ± 0,44	2,52 ± 0,54

Conclusion

ZnO coatings have been successfully prepared by the sol-gel method. In the synthesis process a stable colloidal hydrolysate was obtained and deposited on glass slides by dip-coating. ZnO thin films were homogenous on all measured areas and transparent in the visible range. The analysis of the UV-Vis spectra shows that 5-layer ZnO coatings stabilized at 400 °C for 20 min block wide UV region (from 260 to 370 nm) and they show high transparency (95%) in the range of 370 – 900 nm. The absorption of UV light by the ZnO coatings depends on their thickness and temperature of the stabilization. Its efficiency can be control through thickness of coatings and thermal condition of stabilization. The analyzed coatings exhibited good adhesion to glass substrate and the obtained value is high in comparison to the results described in the literature. The results suggest that the ZnO sol-gel coatings are a promising candidate to be used as optical filters or coatings for solar and eyeglass industry.

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