Manufacturing of SiO$_2$-ZnO materials with optical properties

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Abstract. Antireflection coatings have been widely used to increase the absorption of solar collectors and to reduce surface reflection. Many techniques have been explored to prepare thin coatings, such as sputtering, chemical etching, chemical vapour deposition, and sol-gel method. SiO$_2$-ZnO coatings were prepared on the surface of glass substrates via the sol-gel dip-coating process. The structural, morphological and optical properties of the coatings were characterized. The vitreous structure was identified by infrared spectroscopy (FTIR) and X-ray diffraction (XRD). Morphology of materials was observed by scanning electron microscopy (SEM). The reflectance spectra were investigated and the optical performance of the structure was determined.

1. Introduction

The wavelength of the light from sun that reaches the Earth’s surface conventionally ranges from 300 to 2500 nm. The human eye is sensitive to only a part of the electromagnetic spectrum. Antireflective coatings of glasses are used in many domains as buildings, solar cells, spectacles, etc. The purpose of reflective coatings is to keep objects cooler than they would be normally. The decrease of reflectance will be directly related to the increase of transmittance and the enhancement of conversion efficiency for solar cells [1-3]. Heat is a direct consequence of visible or infrared radiation incident on an object. The heat-producing region of the infrared radiation ranges from 700 to 1100 nm [1-3]. In order to prepare thin coatings, new techniques such as sputtering, chemical etching, chemical vapor deposition, and sol–gel method were used. Surface anti-reflection treatment can be categorized to 4 different techniques including surface texturing, single-layer interference coating, multi-layer coating and moth-eye structure forming [1,2]. Li [1] reported obtaining of bilayer porous coatings with refractive index of SiO$_2$ layer in the range from 1.10 to 1.45. The nanoporous ZnO/SiO$_2$ coatings preparation was made in two steps: 1) deposition of ZnO bottom layer and 2) deposition of SiO$_2$ top layer. Due to SiO$_2$ top layer, the coatings have nanoporous structure. Han [2] obtained the reflection lower to around 5.3% at the wavelength of 400 nm for moth-eye pattern.

In this paper, ZnO-SiO$_2$ coatings with antireflective properties were prepared on the surface of glass substrates using sol–gel dip-coating process. The structural, morphological and optical properties of single layer coatings were investigated. The influence of different molar ratio, pH, and thermal treatment on the optical properties was studied.
2. Experimental parts

The sol was synthesized using tetraethyl orthosilicate [Si(OC₂H₅)₄] (TEOS) and zinc acetate dehydrate [Zn(CH₃COO)₂ ∙ H₂O] as sol-gel precursors, HCl as catalyst and ethanol (C₂H₅OH) as solvent and distilled water for hydrolysis. All chemicals were reagent grade. Coatings with 10% ZnO and 90% SiO₂ were obtained by deposition of thin films on glass substrates by dip-coating at a controlled speed of 60 mm/min. Two precursor solutions with different molar ratio of were prepared as can be seen in table 1. The influence of water quantity on the properties of coatings was followed. The obtained coatings were noted S10ZA3 and S10ZA6. The coatings were consolidated at 200°C and then they were thermally treated at 500°C.

| Molar ratio TEOS:C₂H₅OH:H₂O | pH |
|-----------------------------|----|
| S10ZA3                     | 1 : 4 : 3 | 1 |
| S10ZA6                     | 1 : 4 : 6 | 1.5 |

Obtained coatings were characterized structural, morphological and optical. X-ray diffraction experiments were performed with Rigaku Ultima IV diffractometer in parallel beam geometry equipped with CuKα radiation (wavelength 1.5406 Å). The XRD patterns were collected in 2θ range between 10 to 70 with a speed of 5º/min and a step size of 0.02º. Structures of films were investigated by FT-IR Spectroscopy with a 6700 Nicolet FTIR Spectrometer in 400-1600 cm⁻¹ domain; with sensibility of 4 cm⁻¹. Morphology of coatings was observed with a scanning electron microscope (SEM) Quanta 250, produced by FEI Company. Samples preparation was minimal and consisted in immobilizing on a double-sided carbon tape, without coating. Diffuse reflectance UV-VIS spectra were recorded using a spectrophotometer Perkin Elmer Lambda 35. The certified reflectance standard has been used and the measurements were carried out in the range 900-200 nm.

3. Results and discussions

Figure 1 presents XRD patterns of the coatings after thermal treatment at 500°C. Both coatings have vitreous state, without crystallites. In order to see if vitreous state was a response of substrate - glass, or a response of coatings, we made X-ray diffraction measurements on coatings on glass substrate and two powders resulted from gels dried and thermally treated at 500°C. In all cases the materials have vitreous state.

Figure 2 presents the FTIR spectra of SiO₂-ZnO coatings after treatment at 200°C and Figure 3 presents FTIR spectra after thermal treatment at 500°C.

The wide bands in 850–1300 cm⁻¹ range, in 700–840 cm⁻¹ range, and below 600 cm⁻¹ were observed. The band with maximum at 1088 cm⁻¹ is attributed to ring or double chains of tetrahedra in silicates. In the spectra of S10ZA3-200°C and S10ZA6-200°C coatings two bands at 950 cm⁻¹ and 573 cm⁻¹ are presented. Both bands evolve as shoulders in S10ZA3-500°C and S10ZA6-500°C coatings. The band at 950 cm⁻¹ is assigned to Si-O vibration in chains of structural units. The bands at 573 cm⁻¹ and 788 cm⁻¹ can be assigned to Si-O-Zn or O-Zn-O bonds, in agreement to literature data [4].

The strong band at 458 cm⁻¹ is also characteristic of Si-O-Si bonds in agreement with literature data [4-7]. The shoulder at 448 cm⁻¹ present in spectrum of S10ZA6-200°C is characteristic to Si-O-Zn vibration. Fausta et all [8] reported vibration of Zn-O at 427 cm⁻¹ in 60TeO₂- (30-x) ZnO- 5Bi₂O₃- 5TiO₂- xB₂O₃ (where x = 0, 2.5, and 5 mol%). The bands at 482 cm⁻¹ assigned to the stretching vibrations of ZnO and at 735 cm⁻¹ due to the Zn–O bonding were observed by Slimani et al in ZnO films deposited on FTO glass substrate [9].
Figure 1. XRD patterns of SiO$_2$-ZnO coatings thermally treated at 500°C

Figure 2. Infrared spectra of SiO$_2$-ZnO coatings thermally treated at 200°C
The thermal treatment at 500°C leads to an ordering of the silica network as in silicates. From FTIR spectra can be concluded that the higher transmittance of coatings treated at 200°C is correlated with depolymerized silica network. In the coatings treated at 500°C the silica network is structured and structural units are more arranged. The bands below 600 cm\(^{-1}\) characteristic Zn-O vibrations are smaller due to strong bond energy of silica network.

Coatings treated at 500°C show high transmittance in infrared so they have good optical properties.

![Figure 3. Infrared spectra of SiO\(_2\)-ZnO coatings thermally treated at 500°C](image-url)
Figure 4 show morphology examined by SEM of SiO\textsubscript{2}-ZnO coatings after treatment at 500°C. The S10ZA3-500°C is uniform and homogeneous specific of vitreous coatings. The SEM image of the S10ZA6-500°C coating show small white separations. The observation is in agreement with FTIR results that show a network arrangement into coating.

![SEM images of SiO\textsubscript{2}-ZnO coatings: a) S10ZA3-500°C b)S10ZA6-500°C](image)

The reflectance spectra of the coatings were recorded and compared with the reflectance spectrum of the spectalon etalon. The results of the SiO\textsubscript{2}-ZnO coatings are shown in Figure 5.

In case of coatings consolidated at 200°C appear supplementary bands in UV zone at 272 nm and in Visible zone at 343 nm. ZnO thin film synthesized by sol-gel spin coating method shown a sharp decrease in UV-VIS absorption in the wavelength range of about 310 – 430 nm [10]. Motlan et all reported this absorption also in the visible light range and therefore suitable for optoelectronic application [10]. In the visible zone of the spectra, the baselines of diffuse reflectance curves exhibit an almost horizontal area below 10%.

The reflectance of the coatings after thermal treatment at 500°C increased in visible domain to 60% in case of S10ZA6-500°C and to 90% in case of S10ZA3-500°C.

In vitreous coatings the refraction index can be calculated with formula $n = \nu_0/\nu$ where $\nu_0$ in air and $\nu$ is wavelength in vitreous material. The refraction index in studied coatings is situated in blue zone and have value of $n=1.15$. 

**Figure 4.** SEM images of SiO\textsubscript{2}-ZnO coatings: a) S10ZA3-500°C b)S10ZA6-500°C
4. Conclusions
SiO$_2$-ZnO coatings present refractive properties in UV-Vis and infrared domains. Water content used in synthesis has influence on structure and morphology of the coating. Thermal treatment at 500°C leads to improvement of optical properties. The refraction index in studied coatings is situated in blue zone and have value of n=1.15. The studied materials can be used as protective and refractive coatings for glasses in applications as solar cell and in the optoelectronic devices.

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