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Research Article

Sol-gel Preparation of Silane-based Titania Hybrid Composite Thin Film

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Abstract:

In this study, epoxy and methacrylate-based silane coupling agents are used together with titanium oxide to form a hybrid coating system on the glass surface. In the experimental study, an organic–inorganic molecular hybrid compound was prepared by sol-gel method. First glasses were cleaned by traditional piranha solution (3:1 H_2SO_4: H_2O_2) to remove contaminants. In order to improve the adhesion of hybrid coatings on glass substrates silanization treatment was applied. Silanization solution was prepared by dissolving 1 g 3-aminopropyl-Triethoxysilane (3-APTES) in 100 mL 2-propanol. Glass substrates were coated with this solution using a dip-coater. Silanes (3-Glycidoxypropyltrimethoxysilane, GLYMO and 3-(trimethoxysilyl) propylmethacrylate, TMSPM or MEMO) were mixed deionized water and 2-propanol. Titanium oxide was added and mixed the silane solutions for 1 hour. The resultant solution was coated on a glass sheet by dip coater with heater. After evaporation of solvents, coated samples were characterized by Fourier Transform Infrared Spectrophotometer (FTIR), Scanning Electron Microscope with Energy Dispersive X-ray Spectroscopy (SEM-EDX) and Contact Angle Goniometer.

1. Introduction

Functional hybrid composite coatings have many desirable properties for a wide range of technological and industrial applications [1,2]. Hybrid organic-inorganic composite coatings can be prepared by the sol-gel method and offer many excellent technical advantages [3]. The sol-gel process is a wet-chemical technique also known advanced coating method [4]. In hybrid coatings, silane compounds are used as an organic component [5]. TiO_2 thin films are important materials in nanotechnology [6].

2. Materials and Method

3-Glycidoxypropyl-trimethoxysilane (GLYMO, GPTMS, $C_9H_{20}O_5Si$ >=98%), 3-aminopropyl-Triethoxysilane (3-APTES, APTS, $H_2N(CH_2)_3Si(OC_2H_5)_3$, >=98%), and 3-(trimethoxysilyl) propylmethacrylate, (TMSPM, $H_2C{=}C(CH_3)CO_2(CH_2)_3Si(OCH_3)_3$) isopropyl alcohol (IPA, $(CH_3)_3COH$, >99%), Sulfuric acid (H_2SO_4, 95-97%), and hydrogen peroxide (H_2O_2, 30%) were purchased from Sigma-Aldrich and used directly, without further purification. Titaniumdioxide (21 nm, Sigma-Aldrich) nano-particles were used as inorganic compound in hybrid composite. Chemical structure of silanes is shown in figure. 1.

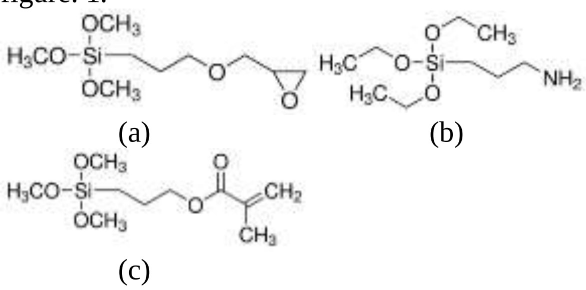

***Figure 1.** Chemical structure of the a) 3-GLYMO, b) 3-APTES and c) TMSPM*

Glass substrates were cleaned with piranha solution. The Piranha solution is a mixture of H_2SO_4:H_2O_2 (5:1). To enhance adhesion between coating and substrate, silanization was applied to glass surface. Silanization is the covering of a surface with the silane coupling agent. This solution was prepared by dissolving 3-APTES in isopropyl alcohol. Silane compounds (GLYMO and TMSPM) were separately mixed with deionized water and isopropyl alcohol in two different beakers. Titanium dioxide nanoparticles were added and mixed the silane solutions for 1 hour. The modified solution was then coated on a glass substrate by dip coater at 80 °C for four times.

3. Results and Discussion

3.1. FT-IR Analysis

FT-IR analysis was performed to identify structure of GLYMO and TMSPM based TiO_2 coatings by using Spectrophotometer (Shimadzu IR Prestige-21). Figure 2 show the difference in the FTIR spectra of GLYMO and TMSPM based TiO_2 coated glass substrate from 400 to 4000 cm-1. As shown in Figure 2, the peaks in between 500 cm^{-1} and 1000 cm^{-1} are assigned to the Ti-O vibration bond [7]. Asymmetric and symmetric CH_3 stretching vibrations at 2860 and 2900 cm^{-1} were observed. The two bands of OH groups appear at 3650 and 1650 cm^{-1} because of hydrolysis of the Si–O–Me groups. The band at 1510 cm-1 which is for –C=(O)–NH–. Also, a peak at 1050 cm^{-1} appears, which can be assigned to the formation of Si–O–Si bonds [8,9].

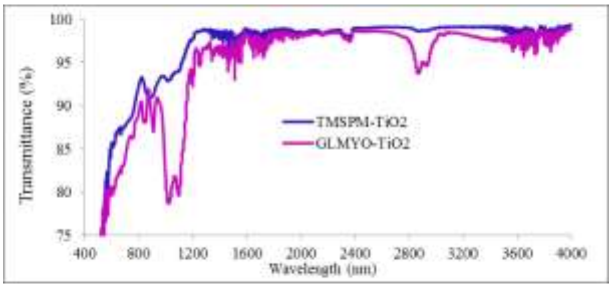

Figure 2. *FT-IR Analysis of silane-based oxide coatings.*

3.2. SEM Analysis

Scanning electron microscopy (SEM, Leo 1430 VP) was applied to examine the morphology of the samples. As shown in Figure 3, SEM images look very rough, independently of the silane type [10]. SEM-EDX Analysis prove titanium and oxygen element on surface.

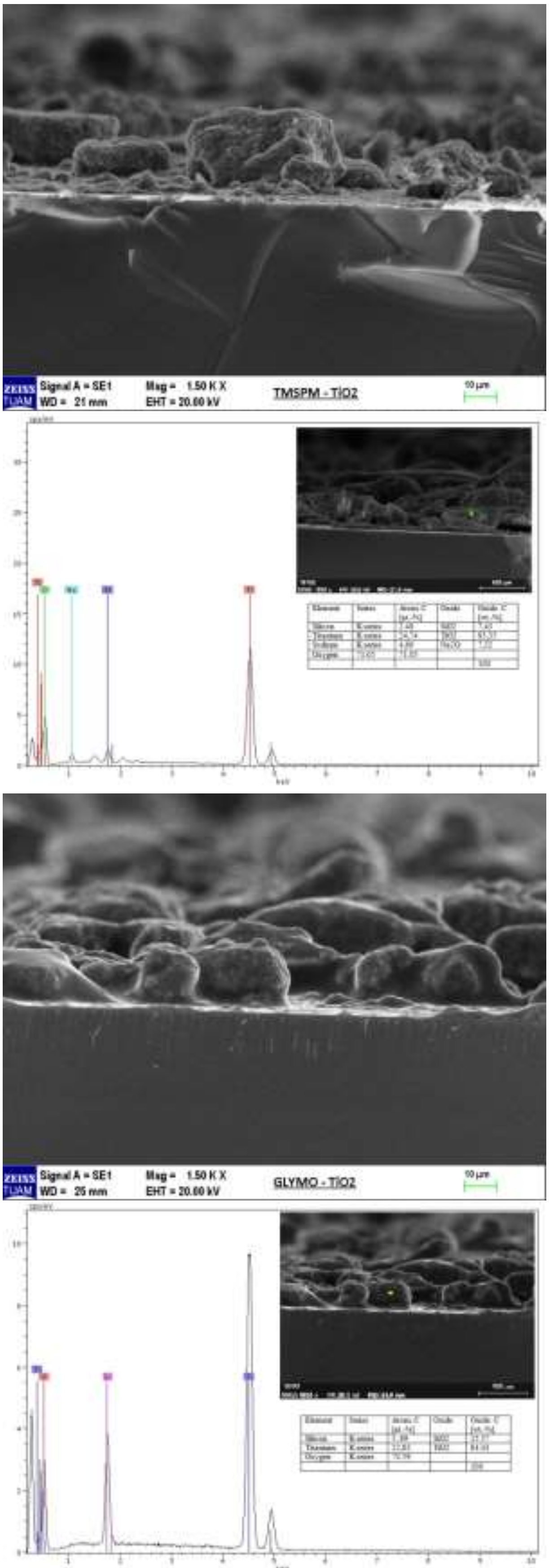

Figure 3. *SEM and EDX images of silane based oxide coatings.*

3.3. Contact Angles Measurements

Contact angle (CA) was utilized to determine the wettability of surfaces. CA of the silane-based titanium oxide coatings was determined by KSV Attension Theta Lite TL 101. As shown in Figure 4, CA results are 61° and 70° for GLYMO-TiO_2 and TMSPM-TiO_2, respectively. They have a hydrophilic character [11]. This indicates stronger effect of the hydroxyl groups on the CA values than the surface roughness of coatings [10, 12].

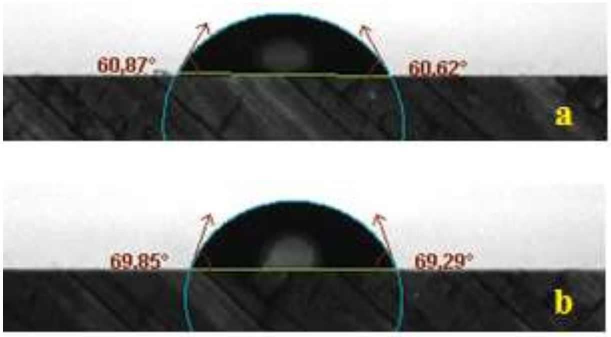

Figure 4. *Contact angles measurements of silane based oxide coatings a) GLYMO-TiO2 and b) TMSPM-TiO2.*

3.4. Band Gap

The energy band gap (Eg) of the silane-based TiO_2 films can be estimated by plotting $(\alpha h\nu)^2$ versus (hν). It was calculated by Tauc method. Figure 5 shows that the plotting gives a straight slope at a certain point [13, 14]. The optical band gap is found 3.58 and 3.46 eV for GLYMO-TiO_2 and TMSPM-TiO_2, respectively, near the value of 3.85 eV, found by H. Oh et al. [15].

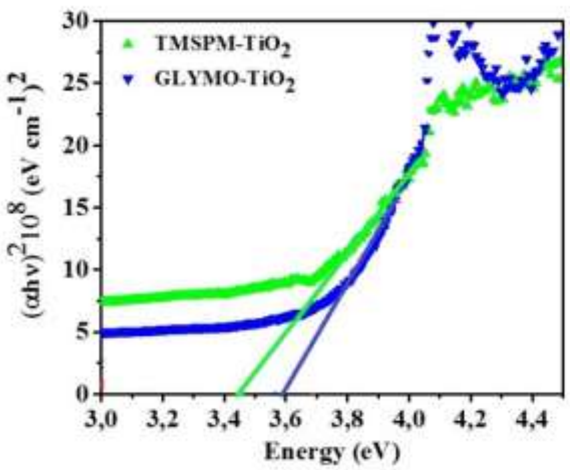

Figure 5. *Optic band gap of silane based oxide coatings.*

4. Conclusion

Silane-based TiO_2 thin films were successfully prepared at low temperature by sol-gel process. Thin films thickness were between 100 and 150 µm. FT-IR results show that silane coupling agents were hydrolysed and attached to the surface. Surfaces of the coating were smooth and homogenous. Contact angles of silane-based TiO_2 coatings were proved hydrophilic structure. Optical band gaps of thin-film were obtained as 3.58 and 3.46 eV for GLYMO-TiO_2, and TMSPM-TiO_2 respectively.

Author Statements:

- The authors declare that they have equal right on this paper.
- The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper
- The authors declare that they have no-one to acknowledge.

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