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Research Article

Sol-gel Preparation of Silane-based Zirconia Hybrid Thin Film

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Abstract:

The sol-gel process is an innovative advanced method, initially developed to synthesize glass and ceramics at low temperature. The sol-gel process can be used to synthesize materials with various of shapes, such as porous membranes, thin fibers, nano-size powders and thin films. In this study, epoxy and methacrylate-based silane coupling agents are used together with zirconium oxide to form a hybrid coating system on the glass surface. In the experimental study, an organic–inorganic molecular hybrid compound was prepared by the sol-gel method. Glasses were cleaned by traditional piranha solution (3:1 H_2SO_4: H_2O_2) to remove contaminants. Silanization was applied to increase the adhesion of hybrid coatings on glass substrates. Glass substrate was coated with this solution by a homemade dip-coater. (3-Glycidoxypropyltrimethoxysilane, GLYMO and 3-(trimethoxysilyl) propylmethacrylate, TMSPM) were chosen as a silane. Zirconia is an inorganic component of hybrid materials. 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

Zirconia (ZrO_2) is an innovatively essential ceramic material. Technological importance of ZrO_2 is due to physical and mechanical properties. ZrO_2 has polymorphism properties, high dielectric constant and wide band gap.

$$\underset{\text{Monoclinic}}{(m\text{-}ZrO_2)} \xrightarrow[(1370\ °C)]{} \underset{\text{tetragonal}}{(t\text{-}ZrO_2)} \xrightarrow[(1900\text{–}2300\ °C)]{} \underset{\text{cubic phases}}{(c\text{-}ZrO_2)}$$

m-ZrO_2 is stable at temperatures below 1170 °C [1,2]. Amorph and crystalline ZrO_2 are synthesized by different methods such as sol-gel, CVD, PVD, sputtering, anodization etc. [3]. A mixture of organic and inorganic polymer materials is defined as hybrid materials. They have been receiving considerable attention in many technological applications [4]. This combination in the same material creates new properties in terms of mechanical, electrical, physical or optical properties. They contribute to the increase of scratch resistance, UV resistance, durability, hydrophobicity or hydrophilicity, easy to clean property and flexibility of the coating surfaces [5]. Nowadays, there are numerous thin film coating methods. The sol-gel method is one of the most widely applied methods, since it is easy, cheap, and handy. The sol-gel method is an appropriate method for obtaining both inorganic and hybrid inorganic-organic polymers [6].

2. Materials and Method

3-Glycidoxypropyl-trimethoxysilane (GLYMO, $C_9H_{20}O_5Si$ >=98%), 3-aminopropyl-Triethoxysilane (3-APTES, $H_2N(CH_2)_3Si(OC_2H_5)_3$,

>=98%), and 3-(trimethoxysilyl) propylmethacrylate, (TMSPM, $H_2C{=}C(CH_3)CO_2(CH_2)_3Si(OCH_3)_3$) 2-propanol (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. Zirconium dioxide (Degussa P25, 21 nm) nano-particles were purchased Sigma-Aldrich. Chemical structure of silanes is shown in Fig. 1.

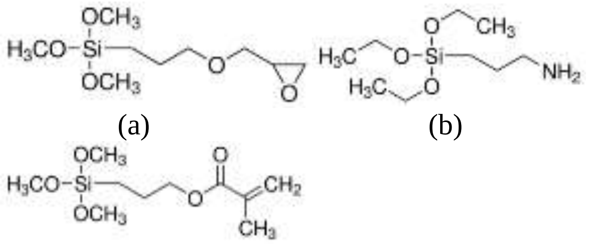

Figure 1. *Chemical structure of the a) 3-GLYMO, b) 3-APTES and c) TMSPM*

To clean glasses surfaces, they were dipped to piranha solution. The piranha solution is a mixture of H_2SO_4:H_2O_2 (5:1). Because it is a strong oxidant, it removes metals and organic contaminants from surfaces. Silanization solution was prepared by dissolving 0.5 g of 3-APTES in 50 mL isopropyl alcohol. GLYMO and TMSPM were mixed with deionized water and 2-propanol in two different beakers. Zirconium oxide nanoparticles were added and mixed the silane solutions for 1 hour. Then modified solution was coated on a glass sheet 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 the structure of silane based oxide coatings by using a Spectrophotometer (Shimadzu IR Prestige-21). As shown in Figure 2, the band at ~1050 cm^{-1} which is characteristic for –Si–O–C bond is observed. A characteristic band at 1460 cm^{-1}, which is for Zr-OH bonds vibrations [7]. Sharp bands, at 1510 cm^{-1} and 1560 $cm^{-1,}$ which are for –C=(O)–NH–.The two bands of OH groups appear at 3300 and 1650 cm^{-1} because of hydrolysis of the Si–O–Me groups [8 ,9].

3.2. SEM Analysis

The morphology and thickness of silane-based oxide coatings were determined from SEM (Leo 1430 VP) images of cross-section of coatings. As shown in Figure 3, SEM images look very similar, independently of the silane type.

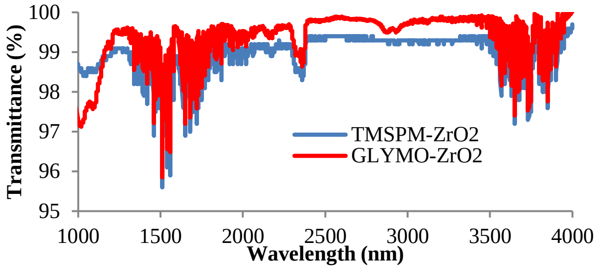

Figure 2. *FT-IR Analysis of silane-based zirconiumoxide coatings.*

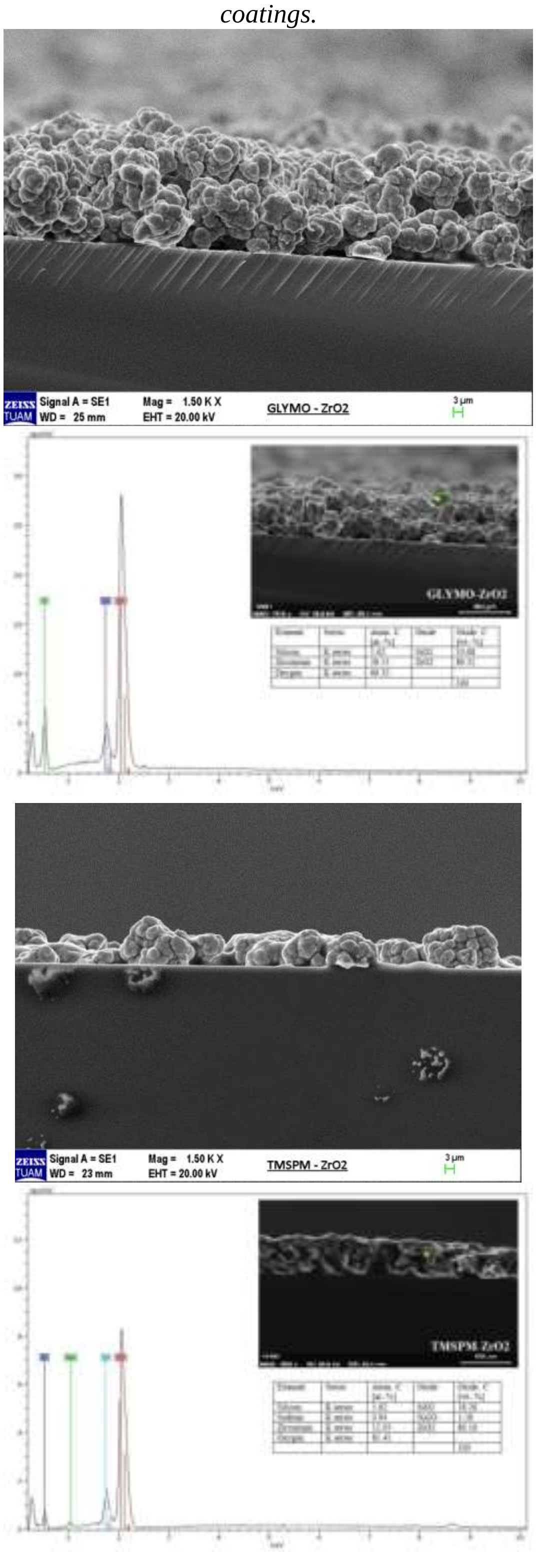

Figure 3. *SEM and EDX images of silane based oxide coatings.*

There are spherical crystallites on the surface [7]. SEM-EDX Analysis prove zirconium and oxygen element on the surface.

3.3. Contact Angles Measurements

Contact angle (CA) was utilized to determine the wettability of the silane-based zirconium oxide coatings. CA was determined by KSV Attention Theta Lite TL 101. As shown in Figure 4, CA results are 92° and 103° for GLYMO-ZrO_2 and TMSPM-ZrO_2, respectively. They have a hydrophobic character [3]. This indicates a stronger effect of the organic groups (CH_3, CH_2) on the CA values than the surface roughness of coatings [7, 10].

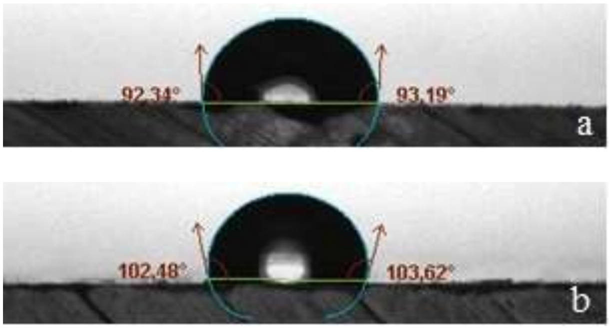

Figure 4. *Contact angles measurements of silane-based oxide coatings a) GLYMO-ZrO_2 and b) TMSPM-ZrO_2.*

3.4. Band Gap

The optical band gap of silane-based oxide coatings was calculated by Tauc's method. Experimentally, it was determined graphic of $(\alpha h\nu)^2$ versus the photon energy ($h\nu$). It shows that the plotting gives a straight slope in at a certain point [11,12]. The optical band gaps are given in table 1. Optical band gaps are lower than the values reported in the literaure (4.87-5.10 eV)[2].

Table 1. *The optic band gap of silane based oxide coatings.*

Silane type	**Band Gap eV**
GLYMO-ZrO_2	3.68
TMSPM-ZrO_2	3.62

4. Conclusion

Silane-based ZrO_2 thin films were successfully prepared at low temperature by the sol-gel process. Thin films thickness were between 10 and 15 µm. FT-IR results show that silane coupling agents were hydrolysed and attached to the surface. Surfaces of coating were smooth and homogenous. Contact angles of silane-based ZrO_2 coatings were proved hydrophobic structure. Optical band gaps of thin film were obtained as 3.68 and 3.62 eV for GLYMO-ZrO_2 and TMSPM-ZrO_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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