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 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 H₂SO₄: H₂O₂) 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-Glycidoxypropytrimethoxysilane, 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.

Keywords:
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1. Introduction
Zirconia (ZrO₂) is an innovatively essential ceramic material. Technological importance of ZrO₂ is due to physical and mechanical properties. ZrO₂ has polymorphism properties, high dielectric constant and wide band gap.

(m-ZrO₂) → (t-ZrO₂) → (c-ZrO₂)
Monoclinic → tetragonal → cubic phases
(1370 °C) → (1900–2300 °C)

m-ZrO₂ is stable at temperatures below 1170 °C [1,2]. Amorph and crystalline ZrO₂ 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, C₆H₃O₃Si ≥98%), 3-aminopropyl-Triethoxysilane (3-APTES, H₂N(CH₂)₃Si(OC₂H₅)₃,
propylmethacrylate, (TMSPM, H₂C=C(CH₃)CO₂(CH₂)₃Si(OCH₃)₃), 2-propanol (IPA, (CH₃)₃COH, >99%), Sulfuric acid (H₂SO₄, 95-97%), and hydrogen peroxide (H₂O₂, 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.

To clean glasses surfaces, they were dipped to piranha solution. The piranha solution is a mixture of H₂SO₄:H₂O₂ (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.
Silane-based ZrO₂ 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 ZrO₂ coatings were proved hydrophobic structure. Optical band gaps of thin film were obtained as 3.68 and 3.62 eV for GLYMO-ZrO₂ and TMSPM-ZrO₂, 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.
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References

[1] Garcia J. C., Scolfaro L. M. R., Lino A. T., Freire V. N., Farias G. A., Silva C. C., Leite Alves H. W., Rodrigues S. C. P. and da Silva Jr E. F., “Structural, electronic, and optical properties of ZrO₂ from ab initio calculations” Journal of Applied Physics 100, 104103 (2006) Doi:10.1063/1.2386967
[2] Ciuparu D., Ensueque A., Shafeev G., Bozov-Verduraz F. “Synthesis and apparent bandgap of nanophase zirconia” Journal Of Materials Science Letters 19 (2000) 931– 933. Doi:10.1023/A:1006799701474
[3] Patel U.S., Patel K.H., Chauhan K.V., Chawla A.K., Rawal S.K. “Investigation of various properties for zirconium oxide films synthesized by sputtering” Procedia Technology 23 (2016) 336 – 343. Doi:10.1016/j.protcy.2016.03.035
[4] Adnan M. M., Dalod A. R. M., Balcı M.H., Gluma J. and Einarsrud M.A. “In Situ Synthesis of Hybrid Inorganic–Polymers Nanocomposites” Polymers 10 (2018) 1129. Doi:10.3390/polym1011129
[5] Yedikardes F.B. “Preparation And Characterization Of Anti Bacterial, Anti Scratch And Easy To Clean Multifunctional Coatings By Sol Gel Method”, M.Sc. Thesis, ITU, June 2016
[6] Bezir N. Çiçek, Evcin A., Kayali R., Özen M.K., Bałyacı G. “Comparison of Pure and Doped TiO₂ Thin Films Prepared by Sol-Gel Spin-Coating Method” ACTA PHYSICA POLONICA A, 132 (2017) page 620-624 Doi:10.12693/APhysPolA.132.620
[7] Adamczyk A., “The influence of ZrO₂ precursor type on the structure of ZrO₂-TiO₂-SiO₂ gels and selected thin films”, Journal of Molecular Structure 1171 (2018) 706-716 Doi:10.1016/j.molstruc.2018.06.068
[8] Halbus A.F., Horozov T.S. and Paunov V.N. “Self-grafting copper oxide nanoparticles show a strong enhancement of their anti-algal and anti-yeast action” Nanoscale Advances 1 (2019) 2323-2336 Doi:10.1039/c9na00099b

[9] Vengadaesvaran B., Arun N., Chanthiriga R., Bushroa A. R., Ramis Rau S., Ramesh K., Vikneswaran R., Alshabeeb G. H. E., Ramesh S. and Arof A. K., “Scratch resistance enhancement of 3-glycidoxypropyltrimethoxysilane coating incorporated with silver nanoparticles” Surface Engineering 30 (2014) 177-182 Doi:10.1179/1743294413Y.0000000238

[10] Lee M.H., Min B.K., Son J.S. and Kwon T.Y. “Influence of Different Post-Plasma Treatment Storage Conditions on the Shear Bond Strength of Veneering Porcelain to Zirconia” Materials 9:43 (2016) 2-12. Doi:10.3390/ma9010043

[11] Bezir N. Çiçek, Evcin A., Kayali R., Kaşikçi Özen M., Esen K., Cambaz E.B. “Characteristic Properties of Dy-Eu-Ce Co-Doped ZrO2 Nanofibers Fabricated via Electrospinning”, Acta Physica Polonica A, 130, 1 (2016) 300-303 Doi:10.12693/APhysPolA.130.300

[12] Hassamien A.S., Akl A.A. “Effect of Se addition on optical and electrical properties of chalcogenide CdSSe thin films” Superlattices and Microstructures 89 (2016)153-169 Doi:10.1016/j.spmi.2015.10.044