Dokuz Eylül Üniversitesi Mühendislik Fakültesi Fen ve Mühendislik Dergisi
Dokuz Eylul University Faculty of Engineering Journal of Science and Engineering

Basılı/Printed ISSN: 1302-9304. Elektronik/Online ISSN: 2547-958X

Investigation of SiO_2 Coatings Synthesized by Acid and Base Catalysis Sol-Gel Dip Coating Technique

Asit ve Baz Kataliz Sol-Jel Daldırmalı Kaplama Tekniği ile Üretilen SiO_2 Kaplamaların İncelenmesi

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Geliş Tarihi / Received: 09.10.2017 *Araştırma Makalesi/Research Article*
Kabul Tarihi / Accepted:27.06.2019 *DOI:10.21205/deufmd.2019216322*
Atıf şekli/ How to cite: TAVSANOGLU,T. (2019). Investigation of SiO2 Coatings Synthesized by Acid and Base Catalysis Sol-Gel Dip Coating Technique. DEUFMD, 21(63), 941-947.

Abstract

Present study deals with the effect of acid and base catalysis on SiO_2 coating properties that were synthesized by sol-gel dip coating technique. Microstructural properties of the coatings were characterized by SEM and EDS was used to determine the coating composition. Spectrophotometer has been used to measure the optical properties of the coatings. The results demonstrated that SiO_2 coatings deposited by both acid and base catalysis sol-gel dip coating technique were homogeneous and well-adherent. Acid catalyzed SiO_2 coatings resulted with dense and smooth surface morphologies whereas base catalyzed SiO_2 coatings had nanoporous structure with nanovoids ranging between 15-30 nm. According to the optical analyses, SiO_2 coatings have very high transmittance values demonstrating that they are highly transparent especially in the visible light range.

Keywords: *SiO_2 coatings, sol-gel dip coating, microstructural properties, nanoporous structure, optical properties*

Öz

Mevcut çalışma, asit ve baz kataliz şartlarının, sol-jel daldırmalı kaplama tekniği ile üretilen SiO_2 kaplama özelliklerine etkilerinin incelenmesi üzerinedir. Mikroyapısal özellikler SEM ile incelenmiş ve kaplama kompozisyonunu belirlemek için EDS kullanılmıştır. Kaplamaların optik özelliklerini ölçmek için spektrofotometre kullanılmıştır. Elde edilen sonuçlar, hem asit hem de baz kataliz sol-jel daldırmalı kaplama tekniği ile üretilen SiO_2 kaplamaların homojen yapıda olduğunu ve iyi yapışma özelliği gösterdiğini ortaya koymuştur. Asit kataliz ile üretilmiş SiO_2 kaplamalar yoğun ve pürüzsüz yüzey morfolojilerine sahipken baz kataliz ile üretilen SiO_2 kaplamalar, boyutları 15-30 nm arasında değişen nano boşluklar içeren nanoporoz yapıdadır. Optik analiz sonuçlarına göre, SiO_2 kaplamalar özellikle görünür ışık aralığında oldukça şeffaf olduklarını gösteren çok yüksek ışık geçirgenlik değerlerine sahiptirler.

Anahtar Kelimeler: *SiO_2 kaplamalar, sol-jel daldırmalı kaplama, mikroyapısal özellikler, nanoporöz yapı, optik özellikler*

1. Introduction

Due to the its unique properties such as adjustable refractive index, controllable microstructure, high laser damage threshold and good transmittance in the visible region, SiO_2 coatings are in high demand in many application areas such as microelectronics, optoelectronics, sensors, photo-catalysis, self-cleaning and solar energy technologies [1-4]. SiO_2 coatings are getting common for use in optical, magnetic and thermal applications such as anti-reflective coatings, high reflection and thermal insulations [5,6]. In addition, their dielectric properties make SiO_2 coatings interesting for different microelectronic structures [7].

Numerous techniques have been used to deposit SiO_2 coatings such as, sputtering, chemical vapor deposition, chemical etching and sol-gel process [8]. Recently, SiO_2 coating synthesis by sol-gel process has become a new alternative method because of its several advantages such as low equipment costs, large area deposition at room temperature, good homogeneity, ease of composition control and possibility of deposition on curved substrates [9,10].

The properties of silica coatings prepared by sol-gel process are closely related to the catalysis conditions [9]. With the base catalysis, the silica coating turns out to be a kind of nice optical material with low optical constant, while its scratch resistance is relatively low, in contrast, with acid catalysis silica coating has too dense to have porous structure [9]. The catalyzer type has very high importance for SiO_2 sol-gel production in the hydrolysis and condensation process and the type of the catalyzer determines the pH value of the solution [9-10]. From previous studies, it is known that SiO_2 coating microstructure has a dense network with enhanced hydrolysis process for pH value below 7, and above 7 exhibits a porous network with the improving condensation process [11-13]. According to the applications and desired properties, it is possible to adjust amount of reactants and pH value in sol-gel dip coating technique [14,15]. The important point is to adjust the rate and limit of the reaction of precursor and this can be controlled by amount and strength of catalysts [14,15]. Although the effect of the catalysis conditions on different properties of SiO_2 coatings synthesized by sol-gel process is previously studied, a thorough literature study shows that the relationship between the catalyzer types and structural, chemical and optical properties of the coatings has not been yet established in details [16-19]. For example, in a previous study we investigated the structural and optical properties of acid catalyzed SiO_2 coatings [16]. B. Gunduz et al. studied the optical constants and electrical conductivity properties of acid catalyzed SiO_2 coatings [17]. A. Shokuhfar et al. characterized the change in the optical transmittance values and surface morphologies of acid catalyzed SiO_2 coatings with different TEOS/Ethanol molar ratios [18]. W. Zhang et al. investigated the effect of Pluronic F-127 addition and the withdrawal rate on the optical transmittance and surface morphologies of base catalyzed SiO_2 coatings [19].

In this study, two different sols were prepared with different pH values (acid and base catalysis) and synthesized SiO_2 coatings were investigated on the basis of their microstructure, surface morphologies, chemical composition and optical properties. The novelty in this study is the attempt to reveal the relationship between the catalysis conditions (acid and base) and the microstructural, chemical and optical properties of SiO_2 coatings.

2. Material and Method

SiO_2 coatings were synthesized on glass and Si (100) substrates. Before each deposition, the substrates were cleaned in ultrasonic bath in acetone, ethanol and distilled water respectively. The solution used for the synthesis of SiO_2 coatings with acid catalysis consists of tetra ethyl ortho silicate (TEOS), ethanol, water and concentrated HCl. Molar ratios of 1:10:2 were used for TEOS:Ethanol:Water. The solution was stirred during 30 min with a magnetic stirrer, and then a few drops of HCl were added to adjust the pH between 2 and 3. Base catalyzed sol-gel solution was prepared by using TEOS, ethanol and NH_4OH with the ratio 1:45:2, respectively. The pH value of the mixture was measured as 9. The final solutions were stirred during 3 hours and aged for 7 days at ambient atmosphere. Dip coating technique was used to obtain SiO_2 coatings with an automated machine at 60 mm/min dipping-rising speed. Glass and Si (100) substrates were used in each deposition. 5 and 10 dipping-rising cycles were realized. Samples were dried during 10 min between each cycle at ambient atmosphere. All the depositions were realized at room temperature.

JEOL JSM-7600F model field-emission SEM/EDS were used for microstructural examination and chemical analyses. NKD 7000 model spectrophotometer (Aquila, UK) has been used to measure the optical properties over the spectral range from 300 to 1100 nm. Crystal structure of SiO_2 coatings was characterized by XRD studies. The analyses were made by a grazing incidence X-ray diffractometer with a thin film attachment (PANalytical X'Pert[3] Powder).

3. Results

Microstructural analyses of acid catalyzed SiO_2 coatings deposited on Si substrates for 5 and 10 dipping-rising cycles were realized on their cross-sections by SEM observations and the results are presented in Figure 1. As can be seen from the figure, well-adherent, homogenous and featureless (without any specific microstructural features such as columnar, granular etc.) SiO_2 coatings of about (a) 800±50 nm and (b) 1.8±0.1 μm were successfully deposited. The thickness increases with the increase in the dipping-rising cycles and according to SEM observations one cycle results about 160-180 nm coating thickness. EDS area scan analyses are performed on the cross-sections of the acid catalyzed SiO_2 coatings to prevent any substrate effect and the results are demonstrated in Table 1. According to EDS results, near stoichiometric SiO_2 coatings were obtained and the dipping-rising cycles do not have any effect on the chemical composition of the coatings.

Table 1. Elemental analyses of acid catalyzed SiO_2 coatings

Elements	Si at%	O at%
SiO_2 (5 cycles)	39.5	60.5
SiO_2 (10 cycles)	38.6	61.4

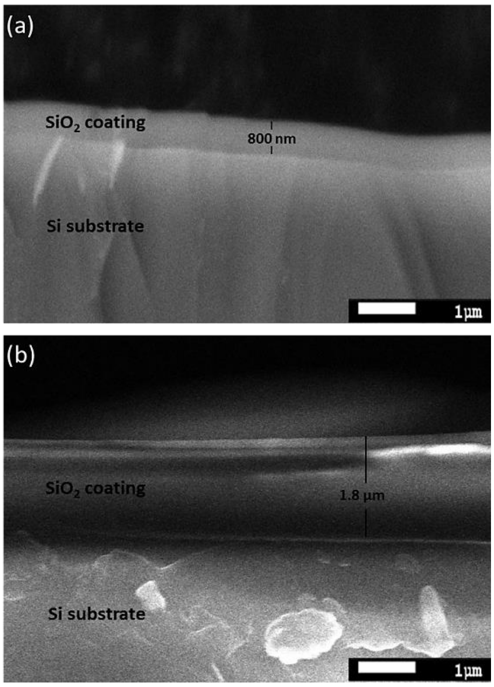

Figure 1. Microstructures of acid catalyzed SiO_2 coatings deposited with (a) 5 cycles and (b) 10 cycles

Figure 2 shows the cross-sectional microstructural analyses of base catalyzed SiO_2 coatings for 5 and 10 dipping-rising cycles respectively. As can be seen from the figure, well-adherent, homogenous SiO_2 coatings of about (a) 800±100 nm and (b) 1.8±0.1 μm were successfully deposited.

The chemical composition of base catalyzed SiO_2 coatings are given in Table 2. According to EDS results, near stoichiometric SiO_2 coatings were obtained and the dipping-rising cycles do not have any effect on the chemical composition of base catalyzed SiO_2 coatings.

Table 2. Elemental analyses of base catalyzed SiO_2 coatings

Elements	Si at%	O at%
SiO_2 (5 cycles)	37.2	62.8
SiO_2 (10 cycles)	38.1	61.9

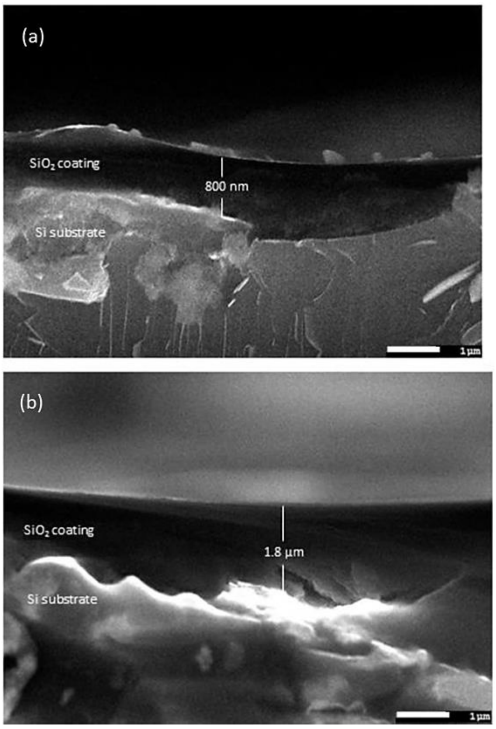

Figure 2. Microstructures of base catalyzed SiO_2 coatings deposited with (a) 5 cycles and (b) 10 cycles

Surface morphologies of SiO_2 coatings were also observed by high-resolution SEM analyses and the results are demonstrated in Figure 3, taken from 10 cycle acid catalyzed and 10 cycle base catalyzed coatings. As can be seen from the figure, acid catalyzed SiO_2 coating exhibit dense and smooth surface morphology (Figure 3a) whereas base catalyzed SiO_2 coating surface has nanoporous structure with nanovoids ranging between 15-30 nm (Figure 3b). The differences in the surface morphologies are consequences of the catalyzer, and resulting reaction processes.

The crystalline structure of the coatings deposited in this study was investigated by grazing incidence X-ray diffraction using Cu-Kα radiation over the 2θ range of 15–100°. The θ scan method with a fixed incidence angle of 1° was used.

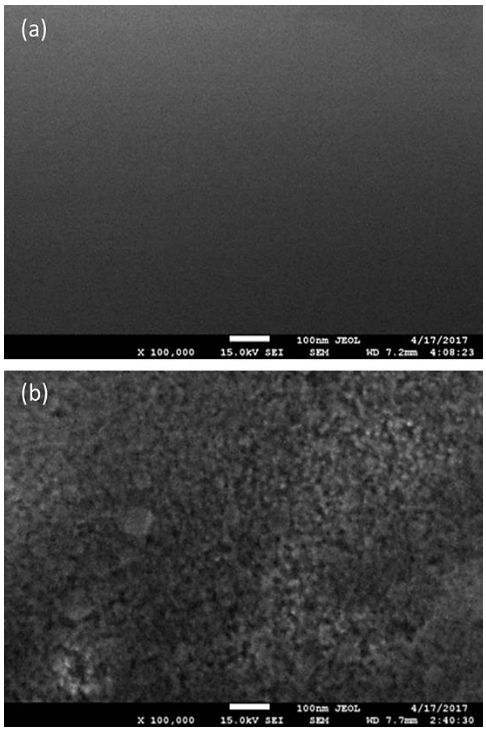

Figure 3. Surface morphologies of (a) acid catalyzed SiO_2 coating (b) base catalyzed SiO_2 coating

In Figure 4, a representative XRD pattern of SiO_2 coatings is given. As can be seen from the figure, the coatings showed no characteristic peaks for SiO_2, indicating that all the coatings deposited in this study were amorphous

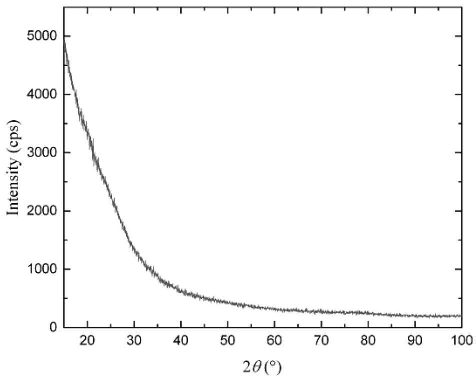

Figure 4. Representative XRD pattern of SiO_2 coatings

The optical properties of SiO_2 coatings deposited on glass substrates were measured by spectrophotometer analyses over the spectral range of 300-1100 nm and compared with uncoated glass sample. Results are shown in Figure 5.

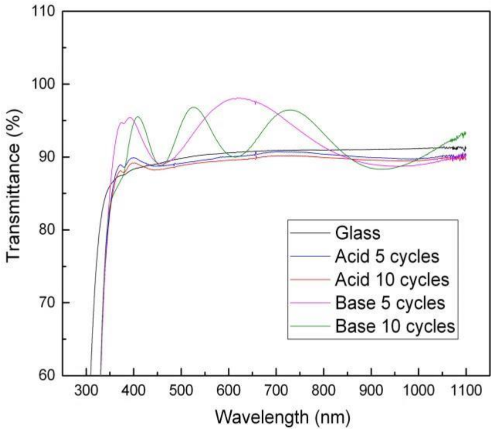

Figure 5. Transmittance values of uncoated glass, acid and base catalyzed SiO_2 coatings for 5 and 10 dipping-rising cycles

As can be seen from the figure, SiO_2 coatings have very high transmittance values demonstrating that they are highly transparent especially in the visible light range (390-700 nm) and the increase in the thicknesses do not have any considerable effects on the transmittance of the coatings. While acid catalyzed coatings exhibit a linear transmittance behavior and transmittance values near uncoated glass of about 90%, base catalyzed coatings exhibit even higher transmittance values compared to uncoated glass of about 97%, especially in the visible light range with a wavy behavior. It is believed that the nanoporous structure of the base catalyzed coatings caused the wavy transmission structure and the increase in the transmission by decreasing light reflection, because of the difference in the light scattering from the nanoporous and dense media [20].

According to the results, the structural properties of the coatings synthesized in our study both by acid and base catalysis are in good agreement with the literature data [11,21-23]. The transmittance values, especially for base catalyzed SiO_2 coatings are higher compared to the previous studies [3,10,13]. It is believed that the nanoporous structure is the reason for very high transmittance values when compared to SiO_2 coatings deposited with other techniques [3] and higher degrees of basicity when compared with sol-gel based deposition techniques [10]. It should also be noted that there is no chemical and/or elemental characterization data in the literature which could be compared with the present results.

4. Discussion and Conclusion

In this study, SiO_2 coatings were successfully deposited on glass and Si (100) substrates by sol-gel dip coating technique. Acid and base catalyzed two different solutions were used to observe the difference in the structural, chemical and optical properties of the coatings. Following conclusions were drawn from our study;

1. According to SEM cross-sectional analyses, homogenous, well-adherent and featureless SiO_2 coatings with thicknesses between 800±100 nm and 1.8±0.1 μm were synthesized using both acid and base catalyzed solutions.
2. According to EDS analyses, near stoichiometric SiO_2 coatings were obtained. The catalyzer type and the dipping-rising cycles do not have any effects on the chemical composition of the coatings.
3. Surface morphological analyses by high-resolution SEM demonstrated that acid catalyzed SiO_2 coatings exhibit dense and smooth surface structures whereas base catalyzed SiO_2 coatings have nanoporous structure with nanovoids ranging between 15-30 nm.
4. Grazing incidence XRD analyses demonstrated that the coatings showed no characteristic peaks for SiO_2 indicating that the coatings deposited in this study were amorphous.
5. According to the optical analyses, SiO_2 coatings have very high transmittance values demonstrating that they are highly transparent especially in the visible light range (390-700 nm) and the increase in the thicknesses do not have any considerable effects on the transmittance of the coatings.
6. Acid catalyzed coatings exhibit a linear transmittance behavior and transmittance values near the uncoated glass of about 90% whereas base catalyzed coatings exhibit even higher transmittance values than uncoated glass

of about 97% with a wavy behavior especially in the visible light range.

7. It is believed that the nanoporous structure of the base catalyzed coatings caused the increase in the transmission by decreasing light reflection.

Acknowledgement

This work has been granted by Mugla Sitki Kocman University Research Projects Coordination Office, Project Grant Number: 14/060, title "Synthesis and Characterization of SiO_2 Thin Films by Sol-Gel Technique" and Project Grant Number: 17/184, title "Synthesis and Characterization of Porous Silica Films by Base Catalysis Sol-Gel Dip Coating Technique".

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