The variations of hydrophilic self-cleaning properties and refractive index dependence in the ZrO$_2$ thin films by Gamma Irradiation

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ABSTRACT

ZrO$_2$ thin film samples were produced by the sol-gel dip coating method. Four different absorbed dose levels (such as ~ 0.4, 0.7, 1.2 and 2.7 Gray-Gy) were applied to ZrO$_2$ thin films. Hence, the absorbed dose of ZrO$_2$ thin film was examined as physical dose quantity representing the mean energy imparted to the thin film per unit mass by gamma radiation. Modification of the grain size was performed sensitively by the application of the absorbed dose to the ZrO$_2$ thin film. Therefore the grain size reached from ~50 nm to 87 nm at the irradiated ZrO$_2$ thin film. The relationship of the grain size, the contact angle, and the refractive index of the irradiated ZrO$_2$ thin film was investigated as being an important technical concern. The irradiation process was performed in a hot cell by using a certified solid gamma ray source with 0.018021 Ci as an alternative technique to minimize the utilization of extra toxicological chemical solution. Antireflection and hydrophilic properties of the irradiated ZrO$_2$ thin film were slightly improved by the modification of the grain size. The details on the optical and structural properties of the ZrO$_2$ thin film were examined to obtain the optimum high refractive index, self-cleaning and anti-reflective properties.

Keywords: Absorbed Dose; Irradiation; Optical Properties; Thin Film; Zirconium Oxide

1. Introduction

Thin films of zirconium oxide (ZrO$_2$) have attracted attention due to their advantageous properties for future thin layers technology. Zirconium oxide (ZrO$_2$) possesses good dielectric, optical, mechanical and chemical properties. Additionally, it exhibits high refraction index, very good transparency, great chemical stability and direct wide gap, with an optical band gap in the range of 0.0–5.85 eV$^{[1,2]}$. Hence, ZrO$_2$ can be used in a wide range of applications such as optical filters, laser mirrors, barrier layers, buffer layers for super-conducting ceramics, as a biomaterial for prostheses, gas sensor, optical storage elements, scintillators and luminescent oxygen-sensors etc.$^{[1,3]}$. Pure or doped ZrO$_2$ thin film continues to present sufficiently high thermoluminescence (TL) yield after irradiation with ionizing or ultraviolet (UV) radiation$^{[3]}$.

ZrO$_2$ thin films with different morphologies are prepared by several methods such as chemical vapor deposition (CVD), spray pyrolysis, reactive RF sputtering, polylol route, hydrothermal method bio-template method, ultra-sound assisted precipitation method, room temperature precipitation method, solution combustion method and sol–gel method$^{[4,5]}$. Among these techniques, the sol–gel method can be used in the production of the thin films for electronics and optics. The sol-gel...
method is of particular interest because of several advantages such as its simplicity, low processing temperature, stoichiometry control and its ability to produce uniform, chemically homogenous films and the formation of multi and mixed layers\cite{1,2}. The sol–gel process involves the preparation of a “sol” (mostly colloidal), the transformation of the sol into a solid “gel” phase and crystallization by heating at increased temperatures (calcination). The first and second stages determine a chemical composition and the calcination stage controls the phase evolution of ZrO$_2$ from amorphous to nanocrystalline and crystalline phase transformation (monoclinic to tetragonal, etc.)\cite{3}. The sol–gel process also allows the deposition of films and coatings with variable thickness from nm to micrometer, in an easy and fast way, by the use of either dip-, spin- or spray-coating procedures\cite{6}. The ZrO$_2$ thin film can be produced with refractive indices $n$ ranging from 1.35 to 2.50 and film thicknesses $d$ from 150 to 1500 nm. The ZrO$_2$ thin film is hard, durable, and laser-damage-resistant thin films with high refractive index and it is widely used to produce multilayered coatings, also for the UV spectral range\cite{7}.

Generation of energy by using clean and environmental-friendly technologies is one of the major aims in industrial and scientific areas. Among the various coating techniques, the coating performed with sol–gel method is one of today’s environment-protective methods. The sol–gel coating of ZrO$_2$ attracts attention since it is an environmental-friendly coating method\cite{8}. As the ZrOCl$_2$·8H$_2$O is low toxicity of zirconium salts low toxicity of ZrOCl$_2$·8H$_2$O makes the use of ZrOCl$_2$·8H$_2$O attractive at the production of solution in this study. Hence it was possible to avoid the use of high level chemical toxicity by minimizing the production of hazardous chemical solution waste. Besides, more economical and environmentally friendly technologies are researched to adopt more eco-friendly thin film production methods in industrial and scientific areas. The utilization of irradiation treatment at several production steps can be preferred as a practical and rapid process to obtain the efficient performance in the devices containing thin film\cite{9}. In this study, the ionizing radiation effect on structural and optical properties was used in the ZrO$_2$ thin film. Therefore, the improvements in the structural and optical properties were obtained, avoiding the production of extra hazardous chemical solution waste. The irradiation treatment by using the gamma radiation was a key parameter to manage the optical constants and the grain sizes of the ZrO$_2$ thin film to use them as protective and biomimetic layers. The agglomeration tendency of the irradiated grains at 0.7 Gy has resulted with high refractive index and more hydrophilic properties. There was a relation between the refractive index and hydrophilic properties with the rise of the grain size of the irradiated ZrO$_2$ thin film.

2. Experimental part

The sol–gel dip coating method at the production of the ZrO$_2$ thin film seems a candidate as more ecolabel coating method than other ZrO$_2$ thin film coating methods in the advance future economic coating technology for the industry\cite{8}.

ZrOCl$_2$·8H$_2$O is an attractive material in several procedures due to its low toxicity\cite{10}. ZrOCl$_2$·8H$_2$O can be used for the environmentally friendly methods\cite{11}.

Hence, zirconium oxychloride octahydrate (ZrOCl$_2$·8H$_2$O) inorganic precursor solution (Sigma Aldrich puriss grade, ≥99.0\%) was used for the production of ZrO$_2$ thin films. All the substrates were cleaned with ethyl alcohol and rinsed with deionized water and they were sterilized with water vapour in an auto clave furnace (Nuve OT 012 Bench Top Steam Sterilizer) then dried at 100°C in drying oven (Binder ED 53). The solvent was determined as a mixture of 2-butanol and ethanol (in the ratio 1:1). Homogeneous solution including zirconium oxychloride octahydrate (2 wt.%) was produced by mixing 1 mol of zirconium oxychloride octahydrate in 1/3 of the total volume of mixed 2-butanol and ethanol. The solution was stirred for 45 minutes by use of a magnetic stirrer (Heidolph MR 3001K). Water for hydrolysis and nitric acid for oxidation (water: HNO$_3$: acetylacetone = 20: 0.4: 3) were added to the salt–alcohol solution. The stirring was continued for another 90 minutes to obtain
clear and transparent solution. The precursor solution prepared at 60°C deposited on cleaned soda-lime silicate glass substrates. Dip coater (KSV dip coater LMX2) with computer controlled was used and the dip coating parameters were chosen as 10 cm/min lifting speed and 90° vertical lifting. The dip coated films were dried at room conditions and pre-fired at 150°C. This process of coating and drying was repeated for 9 times in a heater. ZrO₂ film samples were annealed at 500°C for 1 h in air similar with the literature[12]. After the coating process, the remaining solution was stored in a dark glass bottle to prevent the degeneration of solution and used within 60 days at the refrigerator.

A certified Co-60 radioisotope was used as a gamma ray source emitting the photons with two different energies (1.17 MeV and 1.33 MeV) to examine the rise of the absorbed dose effect on the optical properties. Hence, the provided gamma ray beam was assumed as a monochromatic beam at ~ 1.25 MeV. The used Co-60 radioisotope had an activity level of 0.018021 Ci and it was determined as an appropriate irradiation source to evaluate the changes in the structural and optical properties of the ZrO₂ film samples. The absorbed dose level of the ZrO₂ thin film was the important parameter as the cumulative dose for the thin film samples at the irradiation area. The properties of the used Co-60 radioisotope were presented at the irradiation process of ZrO₂ thin film samples in Table 1.

| Radioisotope | Kγ(R m²/Ci h) | A (Ci) | T1/2(y) | Eγ (MeV) |
|--------------|---------------|--------|---------|----------|
| Co-60        | 1.32          | 0.018021 | 5.27    | 1.17 and 1.33 |

In this study, the ZrO₂ thin film samples were placed around the gamma irradiation source panoramically (in Figure 1). The cumulative dose level of the sample was considered as the total dose resulting from the repeated exposures of the ionising radiation. Because radiation fields can varies with several irradiation conditions (geometry or time) for a period of time[9]. Hence, four different absorbed dose levels were obtained such as ~ 0.4, 0.7, 1.2 and 2.7 Gy to examine the details of the changes in the optical and structural properties. All of the irradiation tests were conducted at room temperature.

The thicknesses of the ZrO₂ thin film samples were determined by using Veeco Dektak 6M Stylus surface profilometer after the optical properties of ZrO₂ thin films prepared by sol-gel method were determined employing transmittance and reflectance spectrophotometry in UV and VIS range between 190–1100 nm by using PG Instruments T80 UV-VIS spectrophotometer. Thickness measurement was obtained from the coated to the uncoated part of the glass. Therefore, the thickness of the thin film was determined as ~ 80 nm[13]. The use of the ionizing radiation was a key parameter to limit the chemical solution toxicity without the generation of the extra hazardous chemical solutions at the environment.

3. Results and discussion

The surface morphology of the film was examined using 2D Scanning Electron Microscope (SEM). There were voids between the grains in some areas of surface as depicted in Figure 2(a)-(d). The surface of the irradiated ZrO₂ thin film at 0.4 Gy was composed of the equiaxial grains (~50 nm) in Figure 2(a). The dimension of grains in which induced by gamma irradiation at 0.7 Gy had ~ 87.3 nm in Figure 2(b) and their dimension was the highest one with respect to the dimension of grains in other ones. The dimension of the grains was ~ 74.5 nm and decrease on the surface of the film at

Figure 1. Irradiation settlement of the ZrO₂ thin film samples.

The thicknesses of the ZrO₂ thin film samples were...
1.2 Gy in Figure 2(c) and the dimension of grains is ~64.8 nm of the film at 2.7 Gy in Figure 2(d). While the grains separated to more small grains due to the absorbed dose of the film, they started to gather and piled up at several places on the surface of the films at 1.2 Gy and 2.7 Gy. The changes of beta transmission of the ZrO$_2$ thin films supported the variation of the grain size in our previous study\cite{13}.

The properties of the surface started to change obviously at 0.7 Gy. The absorbed dose of 0.7 Gy was important to investigate the optical constants of the thin film. It was interesting to note that when the absorbed dose of the specimen reached to 1.2 Gy, the dimension of the grains decreased again. Moreover, the gathering of the grains in the induced film took place more obviously at the certain places on the surface of the films in Figure 2(c-d). The gathering of the grains at the surface of the film increased when the absorbed dose increased. But it was determined that there was the combination of grains with each other on the surfaces of irradiated specimens. The change of the valance state of impurity atoms in the irradiated thin film can be explained with the formation of new electronic order in defect centers as the result of the new configuration of the ions while the gathering of small grains with the rise of the absorbed dose in the thin film structure.

The changes in transmittance (in Figure 3) and reflectance (Figure 4) of the irradiated ZrO$_2$ thin film samples were examined with the rise of the absorbed dose. The colour of the irradiated ZrO$_2$ thin film samples changed to darker colour tones with rise of the absorbed dose. The transmittance of the irradiated ZrO$_2$ thin films decreased with the rise of the grain size. Besides, the transmittance shifted towards the higher wavelength (red shift) in UV range as the absorbed dose increased. This behaviour is compatible with the decrease in transparency of the irradiated ZrO$_2$ thin films depending on the improvement of the optical absorbance. The red shift of the irradiated ZrO$_2$ thin film at 0.7 Gy (in Figure 3) distinguished clearly with the improvement of the optical absorbance (in Figure 5) as the irradiated thin film (at 0.7 Gy ) reached maximum grain size from ~50 nm to ~87 nm. However, there is not considerable information on the details of the changes in optical constants of the irradiated ZrO$_2$ thin film by gamma radiation in previous studies\cite{14}. The rise of the grain size resulted with the decrease of the optical transmittance of the irradiated thin film (at 0.7 Gy). The rise of the grain size resulted with the decrease of the reflectance of the ZrO$_2$ thin film. The minimum reflectance of the thin film irradiated at 0.7 Gy was determined at the film with maximum grain size reached from ~50 nm to ~87 nm. The reason of this was the decrease of the grain boundaries around the course grains. The changes in refractive index of the ZrO$_2$ thin film samples irradiated at different absorbed dose levels were determined from the transmittance according to Swanepoel’s envelope method in this study. The details on the determination of the refractive index were presented in the previous studies\cite{15}. The interference fringes shifted towards the higher wavelength (red shift) region. Swanepoel’s envelope method stated the minimum and maximum envelops of transmittance spectrum in the weak and medium absorption regions; extrapolating the graph of the refractive index at the strong absorption region in the literature\cite{16}. The optical constants of ZrO$_2$ thin films were affected by the gamma irradiation. It was possible to determine the changes in optical constants such as the refractive in-
dex (n) (in Figure 6), extinction coefficient (k) (in Figure 7) and absorption coefficient (α) (in Figure 8) with the rise of the grain size in this study. There were the increases in n, k and α values of the irradiated ZrO₂ thin film as the result of the increase in grain size (in Figure 2). The rises of n, k and α were related with the enhancement of optical absorption as the result of the controlling of the absorbed dose. The increase of the optical constants of the irradiated films was related with the gathering of the grains at the surface of the film with the controlling of the absorbed dose according to the SEM images (in Figure 2). Photoluminescence (PL) studies provide information about the electronic band transitions, structure, defects and chemical composition of the optical materials[2]. The exciton luminescence and intrinsic defects related luminescence are known in a number of oxides. For ZrO₂, the photoluminescence is of much interest for both theoretical and experimental investigations. There are some references to make an evaluation between the results of this study and results in literature by using different irradiation sources. A broad PL emission is observed at ~ 480 nm for ZrO₂ structures after the samples are induced by UV irradiation in the literature[2]. The refractive index increases with the reduction of the transmittance of the films as the absorption region of the transmittance spectra rises towards higher wavelength region, in the previous study of Berlin et al.[5]. In this study, it was determined that there were the dramatic changes in optical constants at ~ 480 nm. The photoluminescence effect at ~ 480 nm supported the rise of the optical transmittance and decrease of the optical absorbance slightly depending on the increase of the scattered photons. Besides, the decrease of the optical absorbance has led the decrease of the optical constants over ~ 480 nm. It was thought that the improvement of the grain sizes in irradiated ZrO₂ thin film at 0.7 Gy indicated the enhancement of the photoluminescence effect dominantly at the coarse grains with 87 nm.

Figure 3. (a) The changes in transmittance of the irradiated ZrO₂ thin film; (b) the details on the changes in the transmittance.

Figure 4. (a) The changes in reflectance of the irradiated ZrO₂ thin film; (b) the details on the changes in the reflectance.
The surface contact angle of the ZrO₂ thin film was determined by using a contact angle measurement instrument. The contact angle values of the thin film decreased slightly and a minimum value of around 24.62° was obtained with the increase of the grain size when the absorbed dose was set to 0.7 Gy. The rise of the grain size led to increase the surface roughness and the decrease of contact angle values of the thin film resulted with the improvement of the hydrophilic properties. Hence, the contact angle was decreased by irradiation and wettability of hydrophilic nanostructured ZrO₂ surface was modified slightly with increasing surface roughness. The nanoscale roughness having coarse grains (~87 nm) has influenced the surface wettability slightly at 0.7 Gy. The ZrO₂ thin film derived on soda-lime glasses has presented a relation between the refractive index and hydrophilic properties as the result of the change in the size of the grains.
4. Conclusions

The ZrO$_2$ thin film was derived from ZrO-Cl$_2$·8H$_2$O (which is low toxicity of zirconium salts) by using sol-gel dip coating method as it is a green friendly alternative coating method. The irradiation treatment has played a role in the enhancement of the optical constants (such as refractive index, the extinction coefficient and absorption coefficient) of the ZrO$_2$ thin film. The improvement in the irradiated grain size supported to rise the refractive index by minimizing the production of hazardous chemical solutions. The rise of the grain size of the irradiated ZrO$_2$ thin film improved the optical constants. There was a relation between the induced optical constants and the gathering of the irradiated grains by gamma radiation. The red shift in UV range by using gamma irradiation was enhanced with the rise of the grain size. It was possible to control the dimension of grains with the applied absorbed dose. The agglomeration tendency of the irradiated grains has enhanced slightly the refractive index and hydrophilic properties of the ZrO$_2$ thin film. The grain size reached a maximum value from ~50 nm to 87 nm when the absorbed dose of ZrO$_2$ thin film attained to 0.7 Gy.

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