Morphological features and optical properties of nanosized ZrO₂ films prepared by sol-gel spin coating

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Abstract. Homogeneous thin ZrO₂ films were prepared by spin coating. The X-ray diffraction (XRD) analysis revealed the presence of a mixture of monoclinic and tetragonal ZrO₂ polycrystalline phases with nanosized crystallites. The samples were smooth and crack-free with a ganglia-like microstructure and had transmittance of about 80% in the UV-visible range. We established that adding polyethylene glycol (PEG) to the precursor affects the phase composition, morphology and optical properties of the films. The photoluminescence (PL) spectra of the samples revealed a broad violet emission. Some of the PEG-modified films exhibited about twice as intense PL emission as the non-modified films. Their emission bands were more complex, consisting of several additional peaks after deconvolution.

1. Introduction

In the recent decades, the thin ZrO₂ films have attracted special interest among other semiconductor metal oxides due to their advantageous physico-chemical properties. Moreover, they possess excellent optical properties, such as high refractive index, large optical band gap, low optical loss and high transparency in the visible and near infrared region [1]. This makes them an essential material in the optical field, including broadband interference filters, active electro-optical devices (including light emitting diodes), scintillators, tunable lasers, etc. [2]. Various deposition methods, such as RF sputtering, pulsed laser deposition, plasma spraying, electrochemical deposition, chemical vapor deposition (CVD), spray pyrolysis and sol-gel are being applied [3-9]. Among them, the sol-gel method has proven to be one of the most appropriate low-cost technologies for preparation of homogeneous, uniform and high-quality ZrO₂ films. Furthermore, the sol-gel process leads to the existence of large number of surface defects (oxygen/Zr vacancies or interstitials) in the ZrO₂ films, which improves their photoluminescence properties [10]. In order to reduce the solvent evaporation rate, the formation of cracks and crystal defects and to suppress the grains growth and aggregation, various low-volatility organic agents are added to the sol-gel precursors: polyethylene glycol (PEG), polyvinyl alcohol (PVA), polyvinyl-pyrrolidone (PVP), hydroxypropyl cellulose (HPC) [11]. It is also known that PEG is often used in sol-gel synthesis as a 1-D structure-directing template [12]. In the

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available literature, however, there is little information about the effect of the addition of PEG ($M_w = 400$) on the morphological features and optical properties of the ZrO$_2$ sol-gel films, which is the focus of the present study.

2. Experimental part

Three types of precursor solutions were prepared using zirconyl chloride octahydrate (ZrOCl$_2$·8H$_2$O, Sigma-Aldrich). In order to reduce the surface tension, a mixture of ethanol and butanol was used as a solvent, which was added to the Zr precursor under vigorous stirring for 30 min. A small amount of a catalyst – nitric acid (HNO$_3$), was also added (molar ratio ZrOCl$_2$:HNO$_3$ = 3:1); this solution was marked as S-1. In the second solution (S-2), acetyl acetone (AcAc) was added as a complexing agent (molar ratio ZrOCl$_2$:HNO$_3$:AcAc = 3:1:1). The final solution (S-3) was prepared by addition of a small quantity of PEG to solution S-2 in order to investigate the effect of the polymer on the morphology and optical properties of the films (molar ratio ZrOCl$_2$:PEG = 100:5:6). Two types of substrates were used: microscope glass and Si wafers, which were cleaned preliminarily in ethanol. Commercial spin coating apparatus (WS-650 Laurell Technologies) was used for obtaining homogeneous thin films on the desired substrates. The selected spin-coating program consisted of two steps of spinning with different duration and speed (rpm): first step – 500 rpm for 1 second; second step – 1200 rpm for 30 seconds. The drying of every layer was carried out at 150 °C for 10 min in air. The deposition-drying cycles were repeated in order to obtain thin films with the desired thickness. Finally, the samples were heated at two different annealing temperatures – 600 °C and 800 °C for 1 hour in air.

The phase composition of the samples was studied by X-ray diffraction with CuKα-radiation (Philips PW 1050 apparatus). The size of crystallites was calculated using Sherrer’s formula. A scanning electron microscope (SEM) JEOL JEM-200CX was used for morphology observation of the films. The transmittance and reflectance spectra of the samples were measured using a Cary 5E (Varian) UV-VIS-NIR spectrophotometer in the spectral ranges 200-900 nm and 320-800 nm, respectively. The optical constants ($n$ and $k$) and the films thickness were determined from the reflectance spectra using a calculating procedure developed previously [13]. The photoluminescence measurements were performed at room temperature at an excitation wavelength of 230 nm by a FluoroLog3-22 Spectrofluorometer (Horiba Jobin Yvon).

3. Results and discussion

3.1. Phase structure and composition

The XRD analyses revealed that the films possessed a mixture of monoclinic and tetragonal ZrO$_2$ crystallographic phases (figure 1). Similar results were reported by Berlin et al. for thin films obtained from ZrOCl$_2$·8H$_2$O [14]. The diffractograms of the films prepared without a PEG addition revealed a well-crystallized baddeleyite monoclinic phase, which was predominant in the S-1 sample (figure 1a). Furthermore, the amount of tetragonal phase increased in the samples with the addition of acetyl acetone (figure 1b) and became the predominant phase type in the S-3 sample, where PEG was introduced (figure 1c). This could be explained with the dual effects of carbon atoms: i) the amorphous carbon suppresses the growth of tetragonal ZrO$_2$ crystallites within the size-dependent limit for tetragonal ZrO$_2$ phase (8-16 nm) [15]; ii) the carbon atoms may enter the zirconia lattice and act as a stabilizer by producing excess oxygen vacancies [16].

![Figure 1. XRD patterns of S-1 (a), S-2 (b) and S-3 (c) ZrO$_2$ films, annealed at 600 °C.](image-url)
Table 1 presents the crystallites size of the films determined according to the respective peaks of the tetragonal and monoclinic phases. The treatment at higher temperature also affected the size of crystallites, which is to be expected.

**Table 1.** Size of crystallites, $D$ (nm) for the different crystallographic phases of the films.

| $T_{ann}$ | $D$: Tetragonal (101) peak | $D$: Monoclinic (111) peak |
|----------|-----------------|-----------------|
| 600 °C   | S-1: 24,6        | S-1: 29,1        |
|          | S-2: 20,5        | S-2: 30,2        |
|          | S-3: 14,5        | S-3: 13,2        |
| 800 °C   | S-1: 23,9        | S-1: 30,4        |
|          | S-2: 12,3        | S-2: 20,8        |
|          | S-3: 11,3        | S-3: 18,6        |

3.2. Surface morphology

The morphology of the thin films deposited on Si substrates was studied by scanning electron microscopy. It was observed that at low magnifications all samples were similar with a very densely-packed, smooth and crack-free surface. A closer look at a higher magnification, however, revealed some differences. As seen in figure 2, the addition of acetyl acetone alone did not change the microstructure of the films, but when PEG was introduced, a dense ganglia-like film structure was formed. Similar microstructure was reported by Lin et al. for PVA-modified ZrO$_2$ films [17]. It was also observed that the different annealing temperatures applied did not affect the films morphology.

![Figure 2](image.png)

**Figure 2.** SEM images of the different ZrO$_2$ films annealed at 800 °C.

3.3. Optical properties

The optical transmittance ($T$) and reflectance ($R$) were measured for the samples deposited on glass substrates and annealed at 600 °C. Figure 3 shows that in the visible spectral range all films possessed high transmittance with values of about 80%, which indicates a good overall optical quality. The calculated absorption values $A = 100 - T - R$ at a wavelength of 600 nm are 3.7%, 2.7% and 5.7% for samples S-1, S-2 and S-3, respectively. This means that the addition of PEG slightly increases the optical losses in the films. The data for the optical constants ($n$ and $k$) of all samples, as well as their thickness ($d$) are summarized in table 2.

![Figure 3](image.png)

**Figure 3.** Transmittance and reflectance spectra of the different ZrO$_2$ films annealed at 600 °C.

3.4. Photoluminescence

Three general explanations for the ZrO$_2$ luminescence emission have been proposed: i) from an impurity; ii) intrinsic self-trapped excitons and iii) from intrinsic defects (F and F+ centers, Zr$^{3+}$).
Table 2. Thickness, \( d \) (nm), refractive index, \( n \) and extinction coefficient, \( k \).

|     | \( 600^\circ C \) | \( 800^\circ C \) | \( 600^\circ C \) | \( 800^\circ C \) | \( 600^\circ C \) | \( 800^\circ C \) |
|-----|------------------|------------------|------------------|------------------|------------------|------------------|
| \( d \) (nm) | 49               | 57               | 46               | 48               | 41               | 50               |
| \( n \)       | 1,82             | 1,89             | 1,45             | 1,58             | 1,59             | 1,59             |
| \( k \)       | 0,027            | 0,018            | 0,041            | 0,034            | 0,041            | 0,035            |

Currently, the latter (ii and iii) luminescence mechanisms are generally accepted [10]. Figure 4a displays the excitation spectrum of the S-2 sample, annealed at \( 800^\circ C \). The maximum excitation wavelength of all films was found to be 230 nm, which corresponds to 4,9 eV and was used to obtain high-intensity PL emission. This value is near the band gap of tetragonal \( \text{ZrO}_2 \) (~5,1 eV) [18]. In the PL spectra of all samples, a broad emission band at around 403 nm appeared, which corresponds to violet emission (figure 4b). These bands can be assigned to singly-ionized oxygen vacancies in \( \text{ZrO}_2 \) nanomaterials, where the emission results from the radiative recombination of a photo-generated hole with an electron occupying an oxygen vacancy (F and F\(^+\) centers). Similar values of PL peaks were reported by Kumari et al. for \( \text{ZrO}_2 \) nanostructures prepared from an inorganic zirconium precursor [19]. In general, according to the available literature data, the PL intensity of \( \text{ZrO}_2 \) films increases with the rise of the annealing temperature. In our experiment, however, the samples treated at temperatures of \( 600^\circ C \) showed a higher PL intensity than those treated at \( 800^\circ C \). This result correlates very well with the results obtained by Wang et al. [20] for \( \text{ZrO}_2 \) nano-powders and could be explained with the faster decrease of the concentration of singly-ionized associated oxygen vacancy defects (AOD\(^+\) centers) as compared to that of F\(^+\) centers. This tendency was more pronounced for the S-3 films – it was seen that the PEG sample annealed at \( 800^\circ C \) exhibited a significant decrease in the PL intensity. According to the literature, in the temperature interval 600-800\(^\circ C\) a gradual degradation of the PEG occurs via two consecutive processes: pyrolysis at 654\(^\circ C\) and combustion at 734\(^\circ C\) [12]. As a result of these processes, the bonds between ether groups (\( -\text{O}- \)) in the PEG structure with the zirconium precursor are destroyed, thus decreasing the amount of surface defects responsible for the PL emission.

![Figure 4](image_url)  
Figure 4. PL spectra of excitation (a), emission (b) and deconvolution of PL emission peak (c).

Two main differences can be noted in the PL emission spectra of the films obtained from PEG containing solution: i) the sample annealed at \( 600^\circ C \) exhibit about twice as high PL intensity as the films without polymer; ii) the PL spectra of S-3 samples possess a more complex shape consisting of three peaks after deconvolution (figure 4c). The additional peak registered at lower wavelengths (346 nm) could be associated with surface defects. A similar effect of polymer addition on the PL peak area and intensity was reported for ZnO powders by Marković et al. [21]. According to this research group, an increase of the surface-to-bulk defect ratio may induce an overall increase of the violet-blue
emission, which was also evident in our case. The observed short-wavelength PL emission of our samples makes them suitable candidates for application in light emitting devices.

4. Conclusions
Thin nanosized ZrO$_2$ films were deposited successfully by sol-gel spin coating using precursors with and without PEG additive and annealed at 600 °C and 800 °C. The films crystallized in a mixture of monoclinic and tetragonal ZrO$_2$ phases with small crystallites. It was established that the PEG addition promotes the stabilization of the tetragonal phase. The surface morphology of all samples was smooth, dense and without cracks. The PEG-modified sample had a more uniform and finer structure than the non-modified samples. The thin films had a good optical quality with transmittance values of about 80%. The photoluminescence spectra showed broad emission bands at about 403 nm corresponding to violet emission. It was also observed that the PEG-modified films annealed at 600 °C exhibited about twice as high PL intensity as those without PEG. Their emission bands were more complex, consisting of several additional peaks after deconvolution which could be explained by surface defects. The ZrO$_2$ thin films thus obtained could find application in photonic devices due to their luminescence properties in the short wavelengths range.

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