

White Light Using Phosphor Structure of ZrO_2 Films with RE Prepared by Atomic Layer Deposition and Spin Coating

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Phosphor-conversion white light structures were obtained using an original approach of deposition zirconium oxide (ZrO_2) layers by the atomic layer deposition method and doping these layers with rare-earth (RE) ions by the spin-coating technique. Crystalline atomic layer deposition films in tetragonal phase were deposited at relatively low temperature (well below 250 °C). $ZrO_2:RE$ multilayer structure was tested as an active layer, which can convert short wavelength emission (UV emission) to light in the visible spectral range. This can be an effective method to achieve the white-light emission.

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1. Introduction

Zirconium oxide (ZrO_2) material is extensively studied for its fireproof performance, low thermal conductivity, advantageous dielectric properties [1], and high refractive index. A good transparency from visible to near-infrared [2], high chemical stability, and high threshold of resistance to laser radiation are also important. All these properties have led to a large number of applications such as optical filters, laser mirrors [3], or heat barriers [4]. ZrO_2 layers were used as plug films for superconducting ceramics [5, 6], as biomaterials for prostheses [7, 8], as dosimeters [9], as gas sensors [10], and as components in fuel cells [11].

For above mentioned applications ZrO_2 thin films have been obtained using different growth methods like chemical vapor deposition (CVD), pulse laser deposition (PLD), physical vapor deposition (PVD) and sputtering. Unfortunately, these methods have some disadvantages, like relatively high deposition temperature (usually greater than 300 °C) in CVD method. These methods do not uniformly cover the films over high-aspect-ratio structures and does not ensure thickness control as is the case in PVD and sputtering methods [12].

There are several advantages of the atomic layer deposition (ALD) method used in the present study. First of all ALD is a self-limiting process which ensures nanometre level thickness control. Moreover, ALD is a low temperature process (deposition even at room temperature) which guarantees growth of amorphous or crystalline films. The ALD method is successfully used by several microelectronic manufacturers due to very good thickness control, uniformity, quality and material properties [13, 14]. These properties are highly advantageous since highly conformal insulating films, with high

dielectric constant, are desired for capacitor applications [15]. In all these cases, the ALD films are deposited by a repetitive process of a single monolayer (or less than a monolayer) deposition sequences [16]. Despite the fact that the ALD offers the ultimate control over film thickness and uniformity, its wider use is limited by difficulties in films doping, as we discussed in detail in several publications [17, 18]. Excellent conformity of the films grown by the ALD, and developed recently by us method of uniform doping, motivated the present study. Deposition of ZrO_2 by the ALD was investigated, checking possibility of their use in optoelectronic devices. The films doped with selected rare-earth (RE) ions were checked for application as active layers converting UV light to a visible.

The ZrO_2 layers are characterized by rather large energy gap and low phonon frequencies and thus are expected to be suitable hosts for rare-earth activators [19]. Consequently, RE doped oxide materials have been attractive for researchers because of their potential as light converters in optical devices such as detectors, temperature sensors, solid-state lasers, light-emitting diodes, displays, and photovoltaic cells [20, 21].

RE (europium, cerium, and terbium ions) doped ZrO_2 materials and phenomena of down-conversion mechanism were investigated. These multilayer structures were tested as active layers, which can convert short wavelength emission to light in the visible spectral range. For these phosphor applications we test in the present work an original approach of zirconium oxide depositing via the ALD method and doping these layers with RE ions by the spin-coating technique. ALD films were obtained at a relatively low temperature (well below 250 °C). We reported the growth and properties of ZrO_2 thin films doped with RE ions at concentration ranging from 4% to 5%. We concluded that this can be an effective means to achieve the white-light emission and to improve on this way light conversion efficiency, by an extension of absorbed spectral range by a solar cell material.

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2. Experimental

In the first phase of this work, ALD process parameters for ZrO_2 layers were optimized. The growth parameters were selected to allow doping with RE ions. In the ALD process tetrakis(dimethylamido) zirconium(IV) was used as a zirconium precursor and deionized water as an oxygen precursor. The oxide films were obtained in reaction chamber by double-exchange chemical reactions at sequential pulses of metal and oxygen precursors separated from each other by pulse of neutral gas (as a neutral gas nitrogen was used). In this way, the duration of the complete ALD cycle was approximately 20 s. Such optimum growth parameters provide self-limiting, homogeneous and conformal deposition of ZrO_2 layers on the whole surface of the samples tested. ZrO_2 thin films were prepared in the ALD processes at 240 °C using a Savannah 100 ALD system from Cambridge Nanotech Company.

In the next stage, RE ions were introduced into the structure of ZrO_2 layers. As a source of RE ions there was used a chemical solution of precursor dissolved in ethanol. Two different methods were used for applying a chemical solution to the surface of ZrO_2 layers made in the ALD processes. This resulted in two types of the ALD structure as shown in Fig. 1. Consequently, different phosphor structures were obtained by solution droplets distributed using the spin coating technique which provided uniform distribution of solution on the substrate. In the study these two preparation methods of phosphor structures were used followed by two modifications of the ALD processes. Structure A included two ZrO_2 layers separated by a thick layer of chemical compound containing RE forming the $\text{ZrO}_2/\text{RE}/\text{ZrO}_2$ with a thickness of approximately 220/80/220 nm. Structure B was the multilayers ($\text{ZrO}_2/\text{RE}/\text{ZrO}_2/\text{RE}/\text{ZrO}_2$ — 240/5/70/5/240 nm) for which there were received the best structural and optical results.

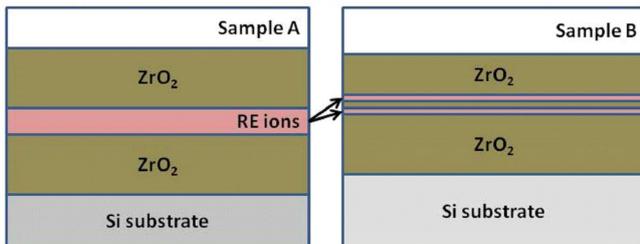


Fig. 1. Schematic diagram of the $\text{ZrO}_2/\text{RE}/\text{ZrO}_2$ phosphor structures with a thickness of approximately 220/80/220 nm (structure A) and $\text{ZrO}_2/\text{RE}/\text{ZrO}_2/\text{RE}/\text{ZrO}_2$ with a thickness of approximately 140/5/70/5/220 nm (structure B) prepared on silicon substrates.

The chemicals used in the experiment to introduce Eu, Tb and Ce, respectively, were as follows:

- europium(III) nitrate pentahydrate ($\text{Eu}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$),

- terbium(III) nitrate hexahydrate ($\text{Tb}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$),
- cerium(III) nitrate hexahydrate ($\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$).

Various molar concentrations (0.07, 0.05, and 0.02 mol/dm³) of the RE solutions were tested. The highest intensity of visible photoluminescence spectrum (before and after annealing of the structures) was obtained for structures with a molar solution of 0.05 mol/dm³. Introducing about 4% rare-earth ions to the crystalline structures of the ZrO_2 layers allowed efficient light emission in a wide spectral range.

The efficient ZrO_2 (Eu, Tb, Ce) white light emitters were achieved by annealing the starting material at a temperature of 800 °C under a neutral gas (argon in this case). Annealing at different temperatures (400, 600, and 800 °C) was also intended to improve crystalline quality of ZrO_2 films. These treatments facilitated also diffusion and homogeneous RE ions distribution in the layers. The obtained nanocrystalline structures (composed of crystalline grains) exhibited stronger luminescence, longer lifetime, reduced dispersion and a more homogeneous distribution of dopants as also reported in Ref. [22]. The crystalline structure of these materials can integrate large concentrations of active ions. This led to larger efficiency of such phosphors.

The investigated structures were characterized at a room temperature using a range of experimental methods. The structural characterization was performed by XRD, using the X'Pert Materials Research Diffractometer equipped with an X-ray mirror and a two-bounce monochromator at the incident beam. The diffracted beam was measured with a 2-dimensional solid-state X-ray detector (PIXcel). The layers thicknesses were measured by the spectroscopic reflectometer (Nanocalc 2000). The surface morphology was investigated by atomic force microscopy (AFM, Bruker Dimension Icon) using the PeakForce Tapping and silicon nitride probes with sharp tips (tip radius — 2 nm). The surface roughness was determined by a root mean square (RMS) roughness of the AFM height measurements from images taken from a 10 × 10 μm² region. Optical spectra of photoluminescence (PL) analysed structures have been characterized by the Solar CM2203 spectrophotometer with a xenon lamp.

3. Results and discussions

The matrix for doping with rare-earth ions was a layer of ZrO_2 obtained by the ALD method on silicon substrate. These ZrO_2 films deposited at 240 °C were polycrystalline. These layers had a tendency to crystallize in the tetragonal phase in the form of grains with a size larger than 10 nm even at relatively low temperature of the preparation, even below 300 °C. It is worth noting that the ALD process performed at temperatures below 150 °C produces amorphous layers of ZrO_2 , as discussed in detail in publications [23, 24].

Accordingly, the higher growth temperature has resulted in polycrystalline layers with a better crystalline quality, which is critical when introducing RE ions into the structure. Furthermore, the ALD process typically have led to pinhole free and smooth films having a high film density and precise stoichiometry [25, 26].

In the present study, ZrO_2 layers grown by ALD were characterized by a thickness of 200–240 nm and a small surface roughness of 5 nm. Additionally, chemical analysis (described in our previous papers [24, 27]) showed the expected oxygen-to-metal stoichiometric ratio of atomic concentrations in the ALD films, in this case Zr/O ratio was 0.56. The area density per ALD cycle was determined to be 5.68 g/cm^3 . ZrO_2 were low-energy phonon materials (lower than 700 cm^{-1} in tetragonal phase [28]) with large energy gap (in our case 6.6 eV as discussed in our publications [24]), and high chemical and thermal stability [1] which make its suitable host for rare-earth activator [19].

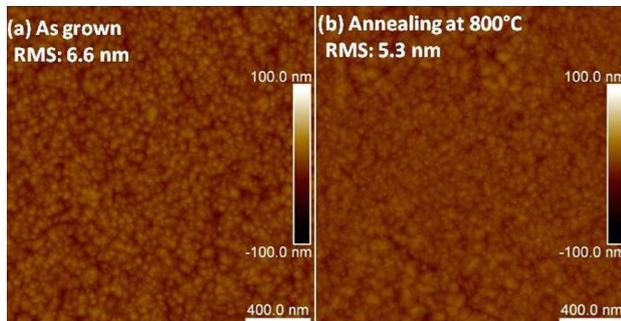


Fig. 2. AFM images of $2 \times 2 \mu\text{m}^2$ surface of $\text{ZrO}_2:(\text{Eu}, \text{Tb}, \text{Ce})$ samples demonstrated (a) as grown with RMS surface roughness equal to 6.6 nm and (b) annealing at 800°C with RMS surface roughness equal to 5.3 nm.

Combination of the ALD method (to obtain zirconium oxide matrix) and the spin coating technique (to introduce RE ions into the matrix) turned out to be an effective method to achieve phosphor, converting UV to white light. The obtained structures have a relatively small surface roughness of 6.6 nm which decreased to 5.3 nm after annealing the structures, as presented in Fig. 2. The photoluminescence spectra of structures with three RE dopants (cerium, europium and terbium) inserted to zirconium oxide matrix were shown in Fig. 3. Each of the RE ions generated three different colour line in visible spectrum — blue, red, and green. The photoluminescence spectra (excitation wavelengths: 271, 300, 380, or 400 nm) with Gaussian adjustment for $\text{ZrO}_2:\text{RE}$ structures included the following peaks with maxima in the visible wavelengths:

- for $\text{ZrO}_2:\text{Eu}$ (red emission) — 584, 613, 617, 626 nm;
- for $\text{ZrO}_2:\text{Tb}$ (green emission) — 476, 509, 559 nm;
- for $\text{ZrO}_2:\text{Ce}$ (blue emission) — 392, 436, 445 nm;
- for $\text{ZrO}_2:(\text{Eu}, \text{Tb}, \text{Ce})$ (white emission) — 438, 481, 536, and 654 nm.

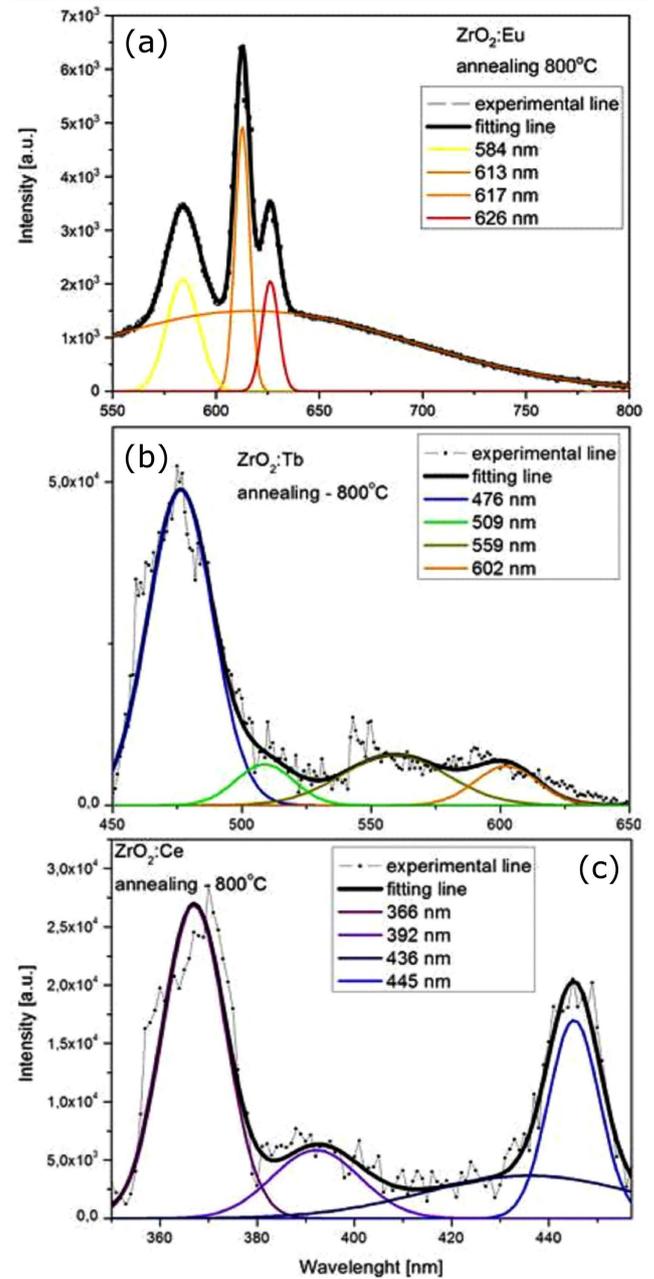


Fig. 3. Photoluminescence spectra of ZrO_2 doped (a) europium, (b) terbium, and (c) cerium ions with Gaussian multi-fit.

Annealed thin layers of $\text{ZrO}_2:\text{Eu}$ showed the strongest luminescence emission in a visible range of 550–650 nm (Fig. 3a). We observed three characteristic lines of Eu^{3+} ions — luminescence at 584, 613, and 626 nm due to $4f-4f$ transitions $^5D_0 \rightarrow ^7F_1$, $^5D_0 \rightarrow ^7F_2$ and $^5D_0 \rightarrow ^7F_3$, respectively [29]. After annealing thin layers of $\text{ZrO}_2:\text{Tb}$ presented strong luminescence emission in a visible range of 450–650 nm (Fig. 3b). We noticed four PL lines from trivalent terbium ions at 476, 509, 559, and 602 nm, which correspond to $4f-4f$ transitions $^5D_4 \rightarrow ^7F_6$, $^5D_4 \rightarrow ^7F_5$, $^5D_4 \rightarrow ^7F_4$ and $^5D_4 \rightarrow ^7F_3$,

respectively [29]. In Fig. 3c there was exhibited the photoluminescence of $\text{ZrO}_2\text{:Ce}$ doped phosphor annealed at 800°C temperature. $\text{ZrO}_2\text{:Ce}$ revealed a broad emission in 350–450 ultraviolet to visible light range. The maximum in visible range is at 445 nm, which is attributed to the electron transition from the $5d$ energy level of Ce^{3+} corresponding to the $4f\ ^2F_{5/2}$ state [29].

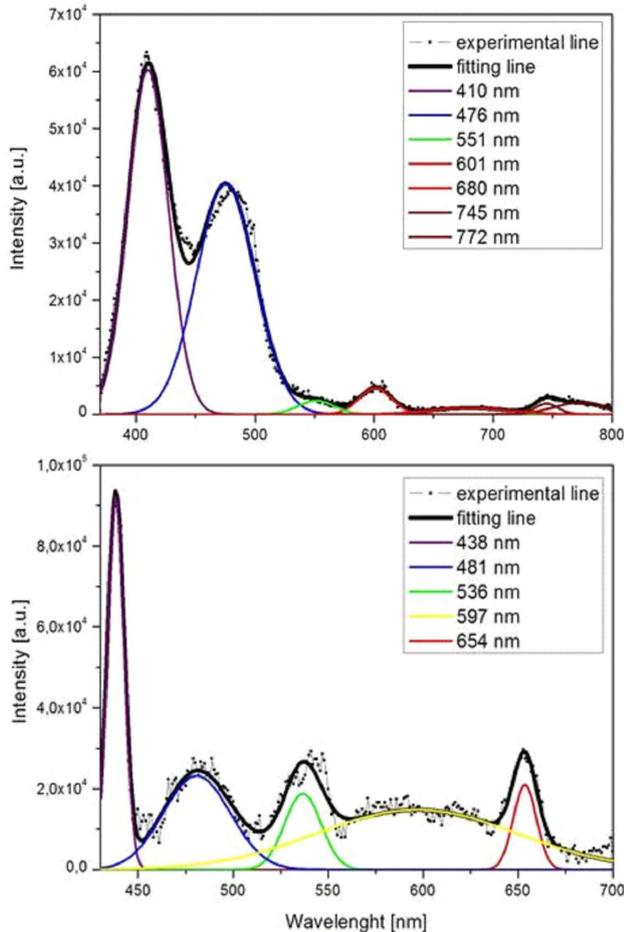


Fig. 4. Photoluminescence spectra of $\text{ZrO}_2\text{:}(\text{Eu}, \text{Tb}, \text{Ce})$ structures with 400 nm excitation for (a) as grown sample and (b) annealing sample with Gaussian multi-fit.

Figure 4a shows the photoluminescence spectra for three dopants inserted together into zirconium dioxide matrices before annealing. PL spectrum exhibited several emission lines with the strongest located at violet-blue region of visible light, with maximum around 410 and 476 nm. We noticed several additional PL lines with maximum 551, 601, 680, 745, 772 nm, which correspond to $4f\text{--}4f$ transitions of europium and terbium dopants. After annealing at 800°C (Fig. 4b) the photoluminescence spectrum was dramatically changed. The low energy region contained three sharp lines at 481, 536, and 654 nm, which correspond to blue, green, and red colours, respectively. These lines were attributed to three Ce, Tb, and Eu dopants. The resulting colour mixture gave

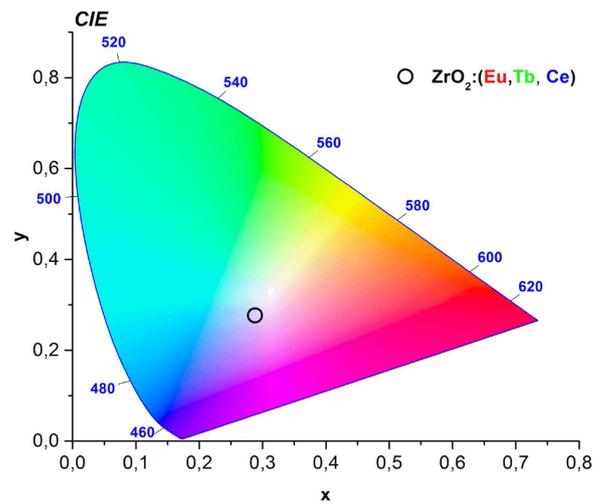


Fig. 5. CIE chromaticity diagram with light emitted by $\text{ZrO}_2\text{:}(\text{Eu}, \text{Tb}, \text{Ce})$ structure.

white light emission. For this parametrization of emitted colour there was calculated chromaticity diagram (CIE) as shown in Fig. 5. Therefore, we concluded that Ce, Tb, and Eu doped ZrO_2 phosphor, which exhibited white emission, has promising properties applications in white lighting. Thus, in this work we successfully developed the technology of active layers — $\text{ZrO}_2\text{:}(\text{Eu}, \text{Tb}, \text{Ce})$ converting shortwave emission to a visible light.

4. Summary

It has shown that the ZrO_2 films with Eu, Tb, Ce ions can be efficient phosphor-conversion white light structures. ZrO_2 thin film deposition technology has been developed using a low temperature ALD (below 300°C). The optimization of preparation processes was done for the introduction of rare-earth ions into the crystalline ZrO_2 matrix in tetragonal phase (identified via the XRD analysis not presented in the present work). The RE emission, observed using PL at room temperature, was found to be due to multiple RE optical centres in the zirconium oxide host. The PL spectra reveal $4f\text{--}4f$ transitions of the type $^5D_0 \rightarrow ^7F_1$ (584 nm), $^5D_0 \rightarrow ^7F_2$ (613 nm), $^5D_0 \rightarrow ^7F_3$ (626 nm) from Eu^{3+} , $^5D_4 \rightarrow ^7F_6$ (476 nm), $^5D_4 \rightarrow ^7F_5$ (509 nm), $^5D_4 \rightarrow ^7F_4$ (559 nm) and $^5D_4 \rightarrow ^7F_3$ (602 nm) from Tb^{3+} and from the $5d$ energy level to the $^2F_{5/2}$ $4f$ levels (445 nm) for Ce^{3+} . In addition, according to the CIE chromaticity diagram, the CIE coordinates, calculated for $\text{ZrO}_2\text{:}(\text{Eu}, \text{Tb}, \text{Ce})$, correspond to a point that lies in the white spectral region. The results of this work suggest that the materials prepared in the present work have significant potential for use in the field of phosphor applications.

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