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Surface and morphological features of ZrO_2 sol-gel coatings obtained by polymer modified solution

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Motivation overview

Why ZrO_2 coatings?

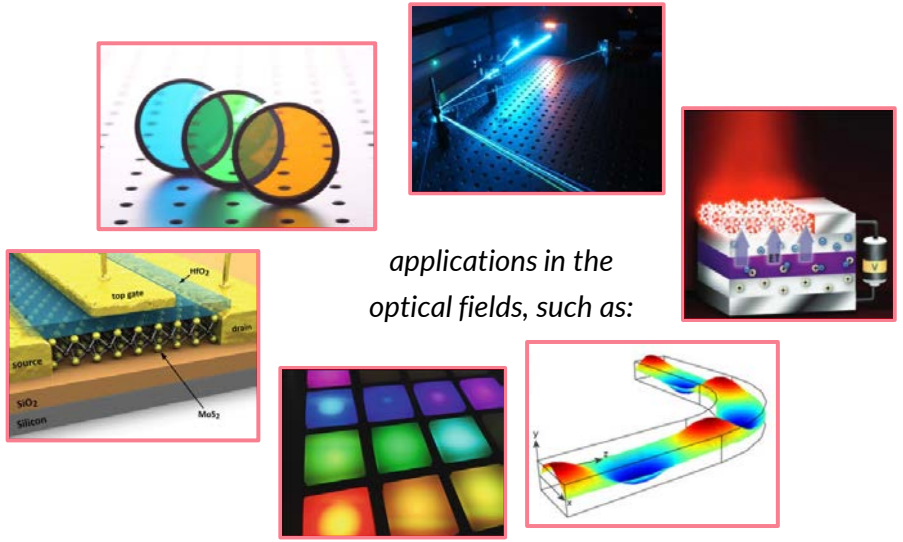
- high refractive index
- large optical band gap
- low optical loss
- high transparency in the visible and near infrared region

Why sol-gel deposition?

- easy, low cost technique
- homogeneous, uniform films

Why polyethylene glycol (PEG) incorporation?

- to reduce the solvent evaporation rate
- to suppress the grains growth and aggregation
- PEG is used as 1-D structure-directing template



applications in the optical fields, such as:

- broadband interference filters
- active electro-optical devices (including light emitting diodes)
- scintillators
- tunable lasers

PEG modified ZrO_2 precursor solutions

Base **0.08 M** zirconium precursor solution:

$ZrOCl_2.8H_2O$ + HNO_3 + Acetyl Acetone (*3:1:1 molar ratio*)

in a mixture of ethanol and butanol

+

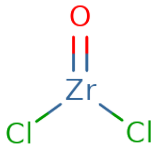
different amount of polymer

0.2 ml PEG
(*PEG:Zr=3.7:100*)

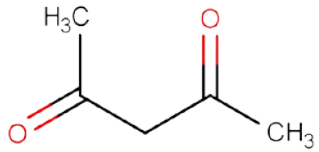
0.3 ml PEG
(*PEG:Zr=5.6:100*)

0.4 ml PEG
(*PEG:Zr=7.5:100*)

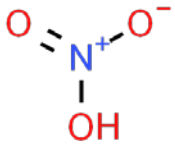
Roles of the ingredients:



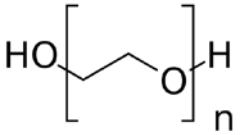
$ZrOCl_2$
(*Zr source*)



Acetyl Acetone
(*complexing agent*)



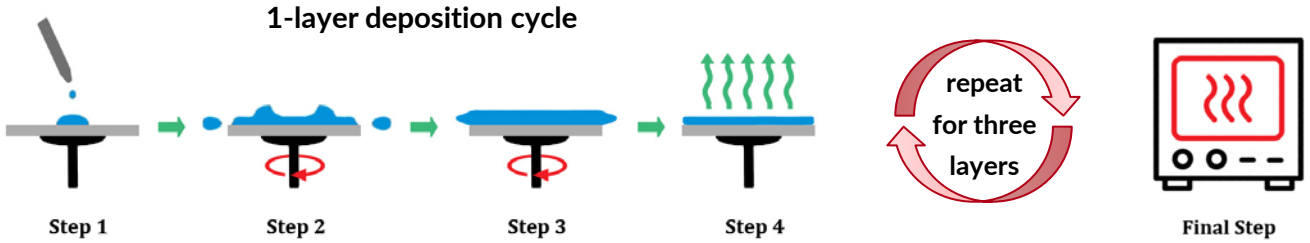
HNO_3
(*catalyst*)



PEG (Mw = 400)
(*polymer addition*)

the ethanol and butanol solution reduces the surface tension and improves the wettability

Spin coating deposition parameters

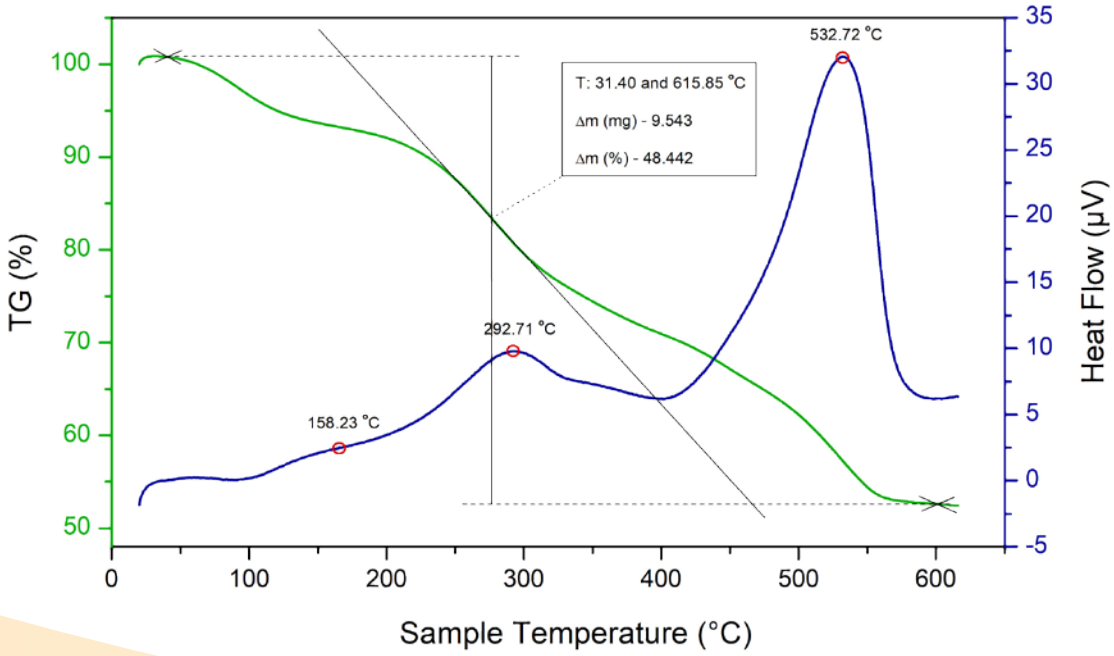


The sol-gel (spin coating) deposition takes the following steps:

- apply a 0.22 ml droplet of the precursor solution on a Si wafer substrate
- spin at 500 rpm for 1 sec to achieve better wetting of the entire substrate
- spin at 1200 rpm for 30 sec to form a thin, homogenous film
- evaporate the solvent at 150 ^{o}C for 10 min in air
- repeat the first 4 steps 3 times to achieve the desired film thickness
- heat the coatings at 600 ^{o}C for 1 hour in air for better crystallization of the ZrO_2

commercial spin coater used:
WS-650 Laurell Technologies

Thermal behavior of precursor solution



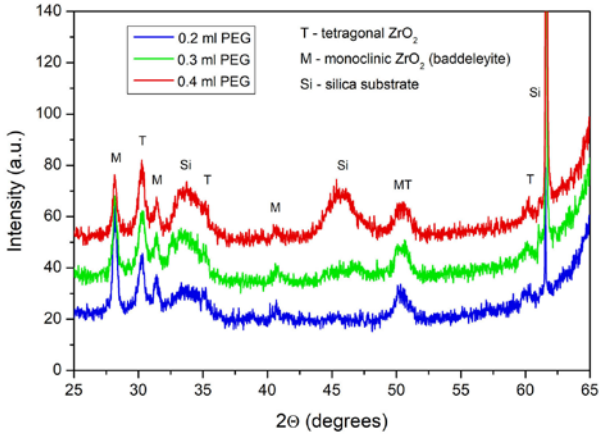
TG-DTA profile of the precursor containing 0.3 ml PEG and dried at 150 °C

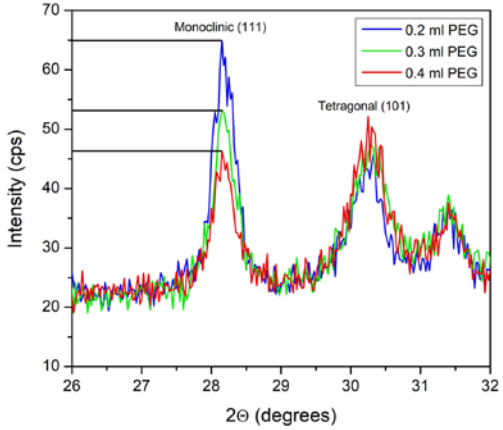
The TG-DTA analyses revealed:

- two stages of thermal decomposition with exothermic effects and 48 wt % weight loss
- the process is rather complex – two or three steps may occur consecutively or partially simultaneously
- the peaks correspond to the degradation of the polymer and zirconium precursor, the oxidation of the decomposition products and the crystallization of ZrO_2
- these processes end completely at about 590 °C – for this reason we have chosen the final treatment temperature of our coatings to be 600 °C

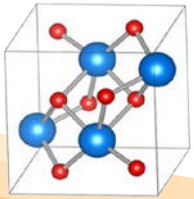
Phase structure and composition study

- according to the XRD study, all films possess a mixture of monoclinic and tetragonal ZrO_2 crystallographic phases
- with the increase of the PEG amount, the intensity of the main monoclinic peak (111) decreases
- the carbon atoms suppress the grains growth under the 30 nm threshold and thus facilitate the formation of the compepative tetragonal ZrO_2 phase

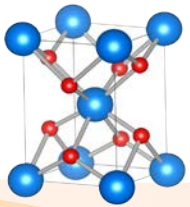




XRD patterns of the coatings & comparison of the intensity of the main monoclinic peak



monoclinic ZrO_2



tetragonal ZrO_2

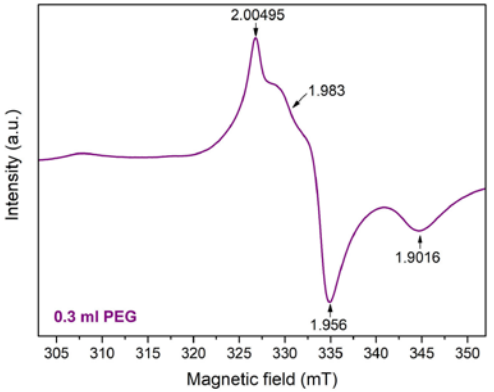
Size of crystallites, determined from the respective main crystallographic peaks

samples	*monoclinic (111) peak*	*tetragonal (101) peak*
0.2 ml PEG	*23 nm*	*15 nm*
0.3 ml PEG	*24 nm*	*13 nm*
0.4 ml PEG	*24 nm*	*14 nm*

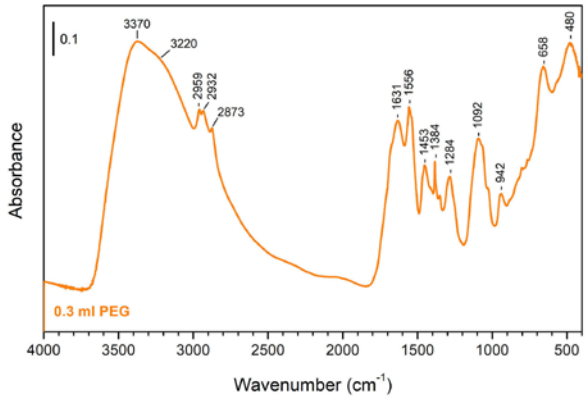
Phase structure and composition study

The EPR spectrum reveals a superposition of few lines, which may correspond to two types of paramagnetic species:

- the first type is probably assigned to Zr^{3+} ions, which are located in the bulk ($g_{\perp}$ = *1.983* and $g_{//}$ = *1.956*) and on the surface of the material ($g_{//}$ = *1.9016*)
- the line of the second type of particles (the signal with g = *2.00495*) is overlapped and accounts for either free radicals (most probably oxygen) or some carbon related impurities from the PEG addition



EPR spectrum of dried precursor with 0.3 ml PEG

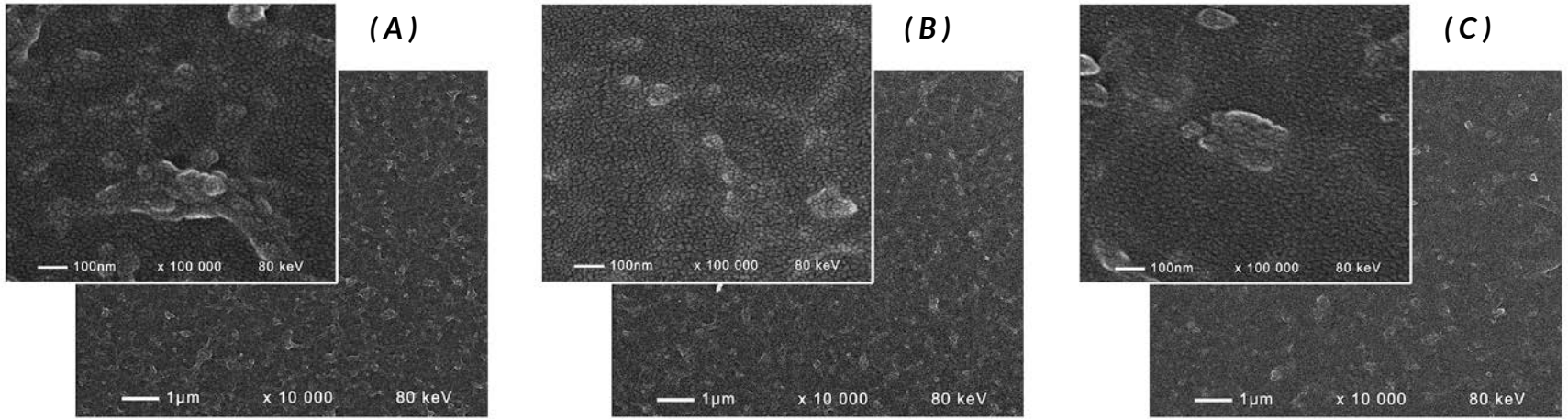


FT-IR spectrum of dried precursor with 0.3 ml PEG

The FT-IR spectrum presents:

- broad peaks in the region of 3200 - 3400 cm^{-1} which are due to –OH vibrations, their shape and position suggesting the presence of hydrogen-bonded solvent molecules (H_2O) and hydrogen-bonded –OH groups attached to the Zr atom
- peaks ranging from 1530 - 1650 cm^{-1} which indicate the formation of bidentante complex with keto-enoic equilibrium behaviour, denoting evident ring formation and coordination of the Zr with acetyl acetone carbonyl groups
- typical PEG methylene C–H symmetric and C–C streching bands, located at 2932 and 942 cm^{-1} respectively

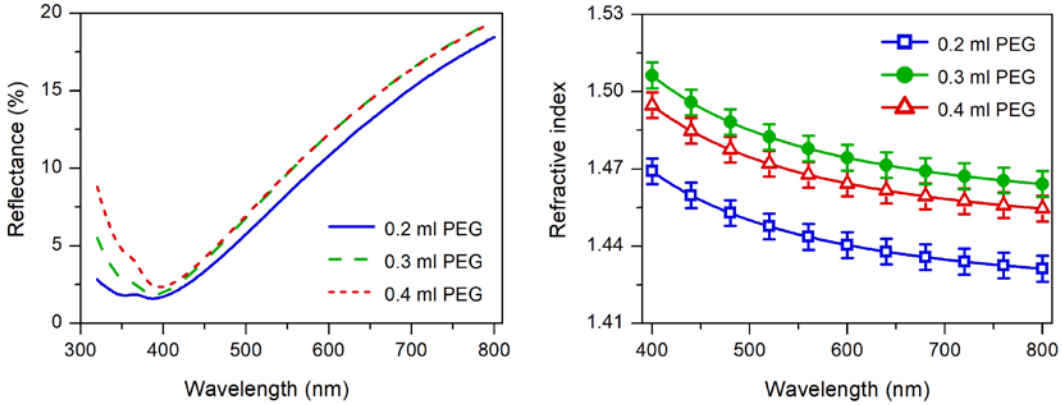
Surface morphology of the coatings



*SEM images at 10 000 and 100 000 times magnification of samples with 0.2 ml **(a)**, 0.3 ml **(b)** and 0.4 ml PEG **(c)***

- the thin films are dense and crack free with uniform morphology and secondary particles with sizes of about 100 nm formed on the coatings surface
- the increase of PEG amount in the precursor has some smoothening effect on the films: less secondary particles are observed, but their individual size is getting bigger in the sample, obtained from the solution with the highest amount of polymer
- the 0.3 ml PEG coating is both smooth, has small surface particles and also the ganglia-like nanostructure of the thin film is best revealed in that sample

Optical properties and free volume investigation



Reflectance spectra and refractive index with respective errors as vertical bars

Thickness (nm), refractive index, extinction coefficient and free volume (%) of the samples

samples	*thickness (nm)*	*refractive index*	*extinction coefficient*	*Free volume (%)*
0.2 ml PEG	*81 ± 1*	*1.440 ± 0.005*	*0.080 ± 0.005*	*21 ± 1*
0.3 ml PEG	*79 ± 1*	*1.474 ± 0.005*	*0.075 ± 0.005*	*15 ± 1*
0.4 ml PEG	*80 ± 1*	*1.464 ± 0.005*	*0.074 ± 0.005*	*16 ± 1*

- the reflectance values of the 0.2 ml PEG sample are smaller compared to the other samples with stronger deviation at shorter wavelengths
- all samples exhibit normal dispersion of the refractive index which means that *n* decreases with wavelength
- the annealing at 600 °C leads to the complete degradation of added PEG and the introduction of free volume in the films (calculated using the effective medium approximation of Bruggeman)
- the increase of PEG amount from 0.2 ml to 0.3 ml causes the films to shrink more during the annealing, which leads to a decrease of free volume from 21 % to 15 %
- this also leads to an increase of density and consequent increase of *n* with 0.034

Summary

- nanosized layers of ZrO_2 were successfully deposited by spin coating sol-gel technique from inorganic zirconium precursor modified with different amounts of PEG
- all samples crystallize in a mixture of monoclinic and tetragonal ZrO_2 phase with small crystallites (< 25 nm)
- it was established that with increasing the amount of PEG in the precursor, the degree of crystallinity of the monoclinic phase decreases
- the surface morphology of the coatings was found to be uniform, dense and crack free with secondary particles over the film
- the EPR analyses detected the presence of Zr^{3+} ions as well as some carbon impurities, probably left from the polymer addition
- the modifying of the precursor with structure directing agent PEG, resulted in the introduction of free volume in the thin films within 15 % to 21 %
- it was observed that the sample obtained from the solution with 0.3 ml PEG showed a decrease in free volume, probably due to shrinkage during the high temperature annealing, which consequently led to an increase of the refractive index to 1.47

Thank you for reading!

For more details on the study, please download our full paper!