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Hybrid zirconium sol-gel thin films with high refractive index.

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ABSTRACT

We describe the synthesis of optical quality thin film materials with high refractive index, employing zirconium based hybrid sol-gel precursors. As the zirconium propoxide precursor is unstable in the presence of a strong nucleophilic agent such as water, two synthesis routes have been performed employing a chelating agent and an organosilane precursor to avoid the formation of any undesired ZrO_2 agglomerates, leading to organo-zirconate complexes and silicato-zirconate copolymers, respectively. The prepared hybrid sol-gel materials were deposited by spin-coating to form a transparent thin film on silicon substrates, and heat treated at 100 °C for the final stabilisation of the layer.

The effect of the two synthesis routes on the optical properties of zirconium based hybrid sol-gel material is discussed. It was found that the nature and concentration of the organosilane precursor can significantly affect the structural properties of the deposited films. A correlation was also demonstrated between the concentration of the organosilane precursor and the refractive index of the material. By reducing the concentration of organosilane precursor, high refractive index materials were obtained. Similar behaviour was observed for the materials synthesised via chelating agent. The synthesis employing an organosilane precursor produces films with higher refractive index. A maximum refractive index of 1.746 was measured at 635nm for the deposited thin films.

Keywords: zirconium, sol-gel hybrid, optical material, high refractive index

1. INTRODUCTION

In the last decade high refractive index optical thin films made from sol-gel syntheses have attracted considerable interest because of the possibility to easily fabricate low cost optical waveguide sensors with high sensitivity in the visible and near infrared range. Indeed in optical waveguides, when the light propagates within a high refractive index medium; total internal reflection occurs and produces an evanescent field that decays exponentially in the surrounding medium. This evanescent field (typically below 500 nm) can be used in fluorescence based sensors to differentiate the surface bound biomolecules from other fluorescent molecules contained in the bulk solutions which are outside the evanescent field. This greatly enhances efficiency compared to classical fluorescence detection configurations [1].

In recent years, two types of configurations have been developed for the fabrication of evanescent wave sensor. The first configuration employs a single-mode waveguide with a high refractive index as a guiding layer (Figure 1a). It has been demonstrated that when operating with single-mode waveguides, a higher refractive index contrast provides a more intense evanescent field [2]. The optimum thickness for the waveguide is usually between 50 and 300 nm, depending on the refractive index value. These nanometric waveguides requires good optical performance with low roughness and good transparency. In the second configuration, a high refractive index thin film layer is deposited on top of a standard slot waveguide, typically of micrometre dimension [2-3]. The light is coupled directly into the waveguide by aligning the fibre with the slot waveguide facet. The purpose of the high refractive index top layer is to enhance the evanescent field (Figure 1b and 1c). The optimum thickness for the high refractive index top layer depends on the refractive index value and is usually between 30 and 150 nm.

Hence, evanescent field optical sensors require the use of a high refractive index layer with nanometric thickness. The optical quality of this layer is critical to avoid any propagation losses and to obtain a strong evanescent field. In addition to good optical properties, the material often needs to be deposited at low temperature (100°C) to facilitate the integration of the different optical components on glass or plastic substrate [4-5-6]. However, most high refractive index materials used in evanescent field sensors are deposited through classical sputtering deposition. With decreasing the

thickness of the waveguide film, the propagation losses increase due to the light scattering caused by the surface roughness [7].

Hybrid materials have been recently proposed as an alternative to conventional materials. They are composed of both organic and inorganic moieties, which can be covalently bounded or stabilised within the same matrix via the presence of electrostatic interactions [8]. Due to the possibility of precisely controlling the content of each moiety, it has been possible to develop new materials exhibiting intermediary mechanical, optical and thermal properties. Hybrid organic-inorganic materials are promising candidates for the fabrication of high refractive index materials with good optical quality because they offer the possibility to combine the high refractive index of bulk metal oxide with the low temperature sol-gel process of organic compounds. Recent work on the development of hybrid organic-inorganic coatings of metal oxides such as TiO_2 [9-10] and ZrO_2 [11-12], have reported an increase in the refractive index of hybrid sol-gel materials. Metal oxides are particularly interesting because of the high refractive index of the bulk material (in the range of 2.13 and 2.2 for zirconium oxide). These metal oxides are often transparent in the visible range which makes them advantageous for optical devices requiring high refractive index and high transparency.

A sol-gel process incorporating zirconium alkoxide has been recently proposed for the preparation of ZrO_2 thin films [12-13]. However most of the ZrO_2 thin films were obtained at high temperature ($> 400^\circ\text{C}$) [12-13]. In our previous investigation [14], organically modified silicon based polymers have been prepared from a formulation employing a chelating agent and organosilane precursors. The refractive index of these resulting films never exceeded 1.56. In this work, we describe the synthesis and refractive index characterisation of different materials employing chelating agent and organosilane precursors with the addition of zirconium propoxide to increase the refractive index. The optical properties of zirconium based hybrid material are compared according to the concentration and type of precursors. The process temperature never exceeded 100°C .

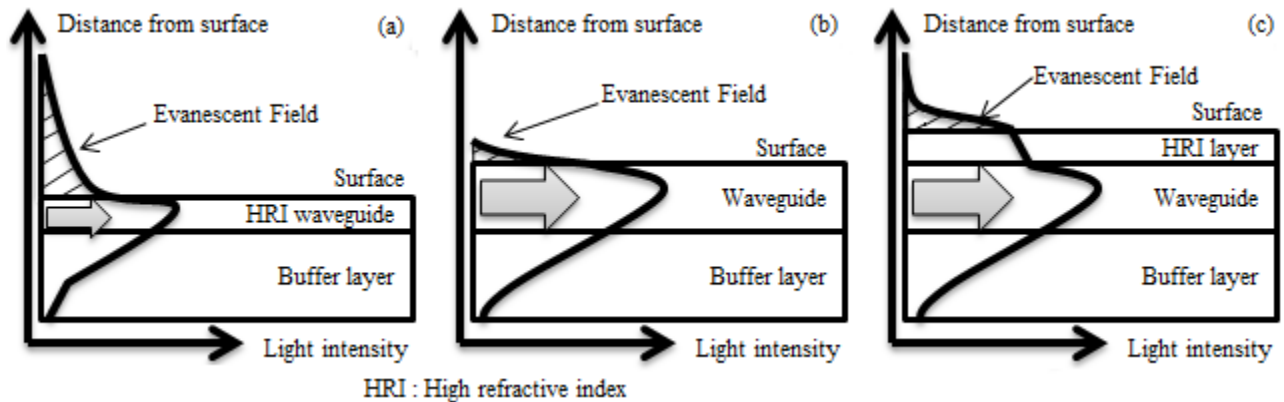


Figure 1. (a) high refractive index planar waveguide, (b) slot waveguide without high refractive layer on top, (c) slot waveguide with high refractive layer on top.

2. EXPERIMENTAL

2.1 Sol preparation

As sketched in Figure 3a, two strategies have been employed to synthesise transparent and homogeneous hybrid zirconium solutions. The first involved a two step process, employing a pre-hydrolysed Ormosil precursor, MAPTMS, PHTES or DHPDES (Figure 2). Firstly, the organosilane precursor was pre-hydrolysed under a vigorous stirring for 45 minutes using an $\text{HCl } 5.10^{-3} \text{ N}$ aqueous solution with a hydrolysis rate of 25% against the reactive methoxide groups. This allowed the formation of silanol groups (Si-OH) and initiates the formation of the siloxane (Si-O-Si) backbone. The solution was then diluted 20 times using 2-propanol (IPA) and left stirring for another 45 minutes prior to the second hydrolysis. As demonstrated before [15], the introduction of zirconium propoxide (ZPO) within a pre-hydrolysed organosilane system involves catalysis of the formation of the siloxanes bonds by attraction of the OH groups located on the silane network. This results in an indirect and slow hydrolysis of the ZPO precursor, leading to stable and transparent solutions. The second step involved a dropwise hydrolysis of the whole system employing a pH 7 aqueous solution, leading to 50 mol.% hydrolysis compared to the total number of reactive alkoxide groups.

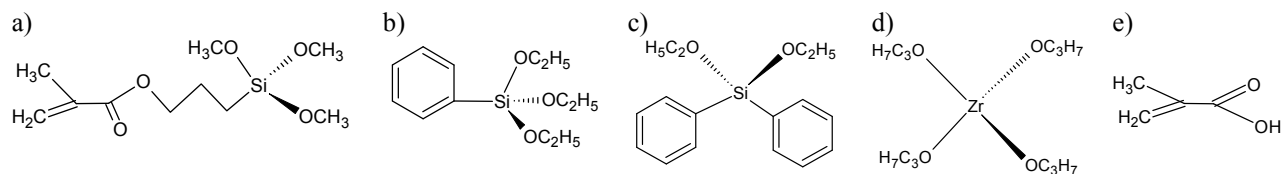


Figure 2. Chemical structures of the precursors employed in the sol-gel syntheses. a) zirconium propoxide (ZPO), b) methacryloyloxypropyltrimethoxysilane (MAPTMS), c) phenyltriethoxysilane (PHTES), d) diphenyldiethoxysilane (DPHDES) and e) methacrylic acid (MAAH)

The second route utilised a chelating agent to decrease the reactivity of the ZPO precursor in the presence of a strong nucleophilic groups, such as water (Figure 3b and 3c). Indeed, the addition of methacrylic acid (MAAH) to ZPO caused the formation of a zirconate complex, in which the number of reactive alkoxide groups is decreased, thereby making this precursor less reactive to hydrolysis. Furthermore, the dilution with IPA (400 times) contributed to further inhibit the condensation kinetics during the hydrolysis step, allowing the development of fully stable solutions.

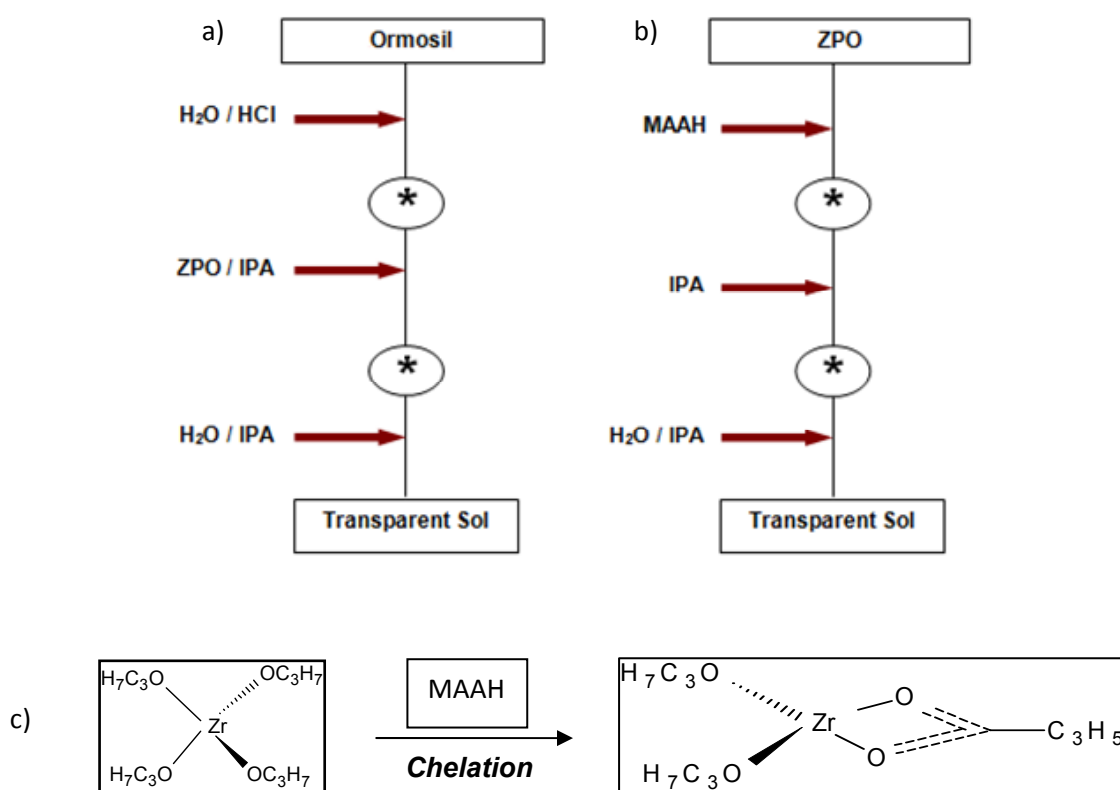


Figure 3. Schematic diagram of the a) ormosil and b) chelation routes employed in the sol-gel syntheses of ZrO_2 thin films and c) the chemical scheme of the zirconium chelation by the methacrylic acid.

2.2 Characterisation techniques

Zirconium based hybrid sol-gel was deposited by spin-coating on silicon substrate to form transparent thin films, and heat treated at 100 °C for the final stabilisation of the layer. Optical measurements and physical characterisations were made in order to determine the performance of this material with ellipsometry, profilometry and absorption measurements. Thickness and refractive index of the films were calculated using the Tauc-Lorentz model from the ellipsometry measurements. For both series of materials, the thickness of the thin films was measured to be between 80 and 150 nm. The roughness measurements were performed with a non-destructive optical profilometer (Veeco Wyko NT1100). The Veeco Wyko NT1100 is an optical profiler providing three-dimensional surface profile measurements without contact. The measurements were carried out in PSI (Phase Shift Interference) mode.

3. RESULTS AND DISCUSSION

3.1 Effect of the nature of the organosilane precursor on the refractive index value

The materials prepared using the three different type of organosilane precursors (MAPTMS, PHTES and DPHDES) have been optically characterised. To compare and discuss the influence of the nature of the organosilane precursor on the final refractive index value, the concentration of each precursors was kept at 10 mol.% against the ZPO precursor. The refractive index values were measured to be 1.692, 1.710 and 1.711 at 635 nm for the films containing MAPTMS, PHTES and DPHDES, respectively.

The progressive increase of the refractive index can be primarily explained by the molecular structure of the employed precursor. Indeed, PHTES and DPHDES contain one and two phenyl groups, respectively (Figure 2) compared to MAPTMS which does not contain phenyl groups. Such aromatic groups exhibit higher polarisabilities than linear aliphatic groups, the result of which is a significant increase of the refractive index. The electron cloud in the π aromatic-bonds is easily distorted, inducing a high electric field. In fact, this property results from the mesomeric effect generated by the permanent circulation of the π electrons contained in the conjugated bonds of the cyclic groups. Furthermore, the high sterical hindrance of the aromatic group can also contribute to the increase in the average size of oligomers, then leading to higher refractive index values. Following these results, we have decided to focus our work on employing the DPHDES as the main organosilane network modifier in order to investigate the effect of its concentration on the optical properties of the ZPO precursor.

3.2 Effect of the DPHDES molar concentration on the refractive index value

Figure 4 shows the variation of the refractive index of the material as a function of DPHDES concentration at three different wavelengths (475, 635 and 830 nm). One can observe that for any selected wavelength, the refractive index exhibits the same tendency, within two distinct domains from 0 to 1 mol.% and from 1 to 10 mol.% of DPHDES. At 635 nm, the progressive decrease of the DPHDES concentration from 10 to 1 mol.% results in a regular increase of the refractive index from 1.71 to 1.746. However, for concentration of DPHDES below 1 mol.%, the refractive index decreases down to 1.739. In general, the refractive index of thin film materials is intimately related to the morphological and structural characteristics. The morphology is mainly associated with the porosity and the roughness of the films; although the structure relates more to the composition of the employed materials. Following these considerations, we can propose that for concentration of DPHDES above 1 mol.%, the refractive index follows the law of composition of mixtures where the refractive index value is mainly determined by the overall molar refraction. This suggests that in this range of concentrations, the developed materials exhibit almost identical densities. However, below 1 mol.% of DHPDES, the morphological aspect seems to predominate over the structural considerations, as a decrease of the refractive index is observed, which is attributed to formation of pores in the inorganic network thus decreasing its density.

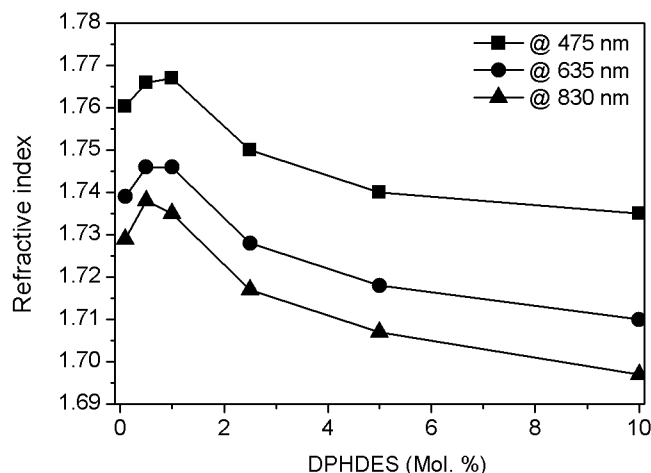


Figure 4. Refractive index as a function of DPHDES molar concentration at selected wavelengths (475 nm, 635 nm and 830 nm)

3.3 Effect of the chelating agent on the refractive index value

Figure 5 shows the wavelength dependant refractive index of hybrid zirconium materials as a function of the chelation degree employing MAAH. One can observe that a progressive decrease of the MAAH content in the range 0.01-1 mol.% (while keeping the ZPO concentration constant) causes a quasi-linear increase of the refractive index values from 1.587 to 1.716, which is a proof of the high homogeneity of the developed materials. Unlike the DPHDES, for any selected wavelength, no decrease of the refractive index can be observed for the lowest concentration of MAAH, which demonstrates that the optical properties are strictly dependant on the molar refraction of the materials. However, the exact explanation of the morphological differences could be explained by the structures of the inorganic network created by both organic modifiers, which is at this stage still not fully identified and is not the main scope of this paper. Further investigations are currently taking place in our group and will be the subject of a future report.

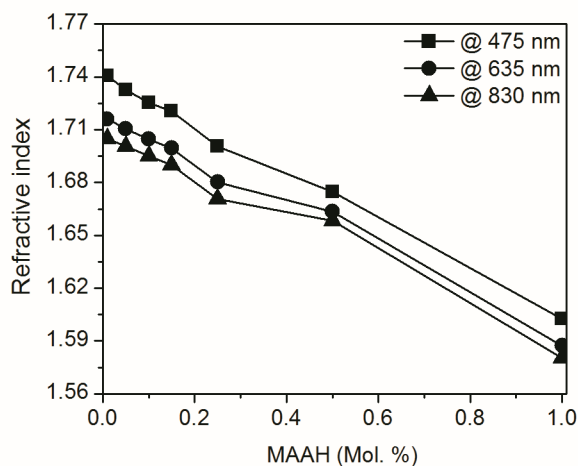


Figure 5. Refractive index as a function of MAAH molar concentration at selected wavelengths (475 nm, 635 nm and 830 nm)

3.4 Optical quality

The optical performance of the material that gave the highest refractive index for both strategies was determined through visible absorption spectroscopy and roughness measurements. Figure 6 shows the absorbance spectra of the two optimised sol-gels: a) 1 mol.% of DPHDES and b) 0.01 mol.% of MAAH. The absorption for the sol-gel containing 1

mol.% of DPHDES was higher than for the one containing 0.01 mol.% of MAAH. This can be explained by the presence of aromatic compounds in the DPHDES which are known to present stronger absorption in the UV range [16].

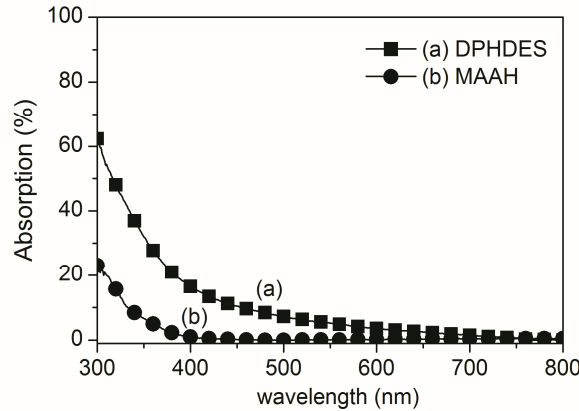


Figure 6. Absorbance spectra of hybrid zirconia sol-gel containing (a) 1 mol.% DPHDES and (b) 0.01 mol.% MAAH

The roughness of the thin films, as measured by an optical profilometer, revealed that on average the materials composed of DPHDES exhibit surface inhomogeneities approximately two times higher, compared to the MAAH based materials, as shown in figure 7 and 8. Indeed, one can observe that DPHDES based materials tend to form regular inhomogeneities with an average roughness of 3.14 nm, although the inhomogeneities seems to be more dispersed in the MAAH based thin films, resulting in a decrease of the average roughness.

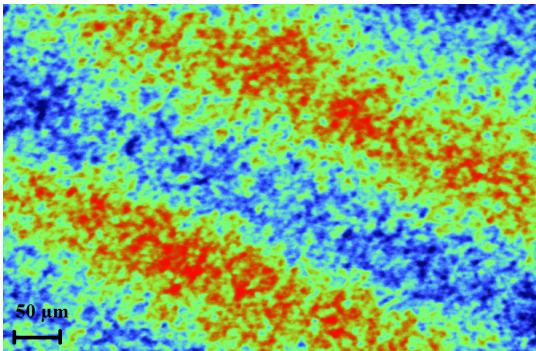


Figure 7. Roughness of 3.14 nm measured for sample containing 1 mol.% of DPHDES

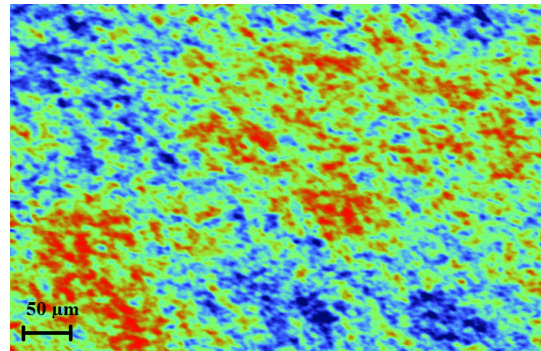


Figure 8. Roughness of 1.73 nm measured for sample containing 0.01 mol.% of MAAH

From these results we conclude that the material composed of 0.01 mol.% of MAAH is the most suitable and promising material for optical sensor applications requiring high refractive index and excellent optical performances.

4. CONCLUSION

High refractive index materials have been prepared using two original syntheses strategies at ambient temperature. The first strategy employed organosilane precursor while the second one employed chelating agent. The correlation between the refractive index and the material composition is discussed and it is proposed that the effect of the molar refraction and the morphology of the thin film materials are the main factors influencing the refractive index values. The maximum refractive indexes obtained were 1.746 for the material containing 1 mol.% of DPHDES and 1.716 for the material containing 0.01 mol.% of MAAH. However the material containing 0.01 mol.% of MAAH showed lower roughness and better optical absorption compared to the material containing 1 mol.% of DPHDES, hence making it as an excellent candidate for the development of optical sensors requiring high refractive index and low propagation loss in the visible range.

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