

Erbium doped sol-gel materials for optical applications

Anette Berni, Martin Mennig, Helmut Schmidt

Institut für Neue Materialien (INM), Im Stadtwald, Geb. 43, 66123 Saarbrücken, Germany

ABSTRACT

A new chemical nanotechnological route for the preparation of fully densified doped SiO₂ coatings with thicknesses in the low μm -range on Si- and SiO₂-wafers has been developed. Beside pure SiO₂ coatings, that might be useful as a buffer layer on silicon, silicate layers with increased refractive index are needed for planar waveguide application. Therefore, a synthesis for the preparation of nano particulate sols was developed, thus allowing the incorporation of dopands like Al₂O₃, PbO and Er₂O₃ for passive and active layers. Alumina was incorporated for the improvement of the Erbium solubility in active components. The coating sols consist of an organic binder, dissolved in a suspension of nanoscaled silica particles (10 nm in diameter) and dopands and were applied on Si- and SiO₂-wafers by spin coating. After removal of the binder at 500 °C, investigated by IR-spectroscopy, highly porous ($n_D = 1.23$) but transparent doped silica layers were obtained. The densification of the layers was examined by measuring the refractive index by ellipsometry as a function of the densification temperature. Completely densified layers with thicknesses between 1.7 μm (doped SiO₂) and 6.5 μm (doped SiO₂) were obtained at temperatures between 1000 °C (doped SiO₂) and 1100 °C (pure SiO₂). The layer thickness and unevenness was determined by interferometric measurements. The optical loss of Al₂O₃ and PbO doped layers was measured by prism coupling, the Er₂O₃ doped layers with Er³⁺ concentrations of up to 2.5 mole % show fluorescence around 1500 nm with a fluorescence lifetime of about 3.6 ms.

Key words: waveguide, sol-gel, Erbium-doped.

1. INTRODUCTION AND STATE OF THE ART

The rapid development of local and world wide optical networks leads to a strong demand in low cost basic components. Optical communication systems will then reach levels where cost is a critical factor for the spreading of this technology. The potential for achieving high performance at reduced cost through integration remains a major driver for the development of integrated components. Another important cost factor is the fabrication technology of the components themselves. State of the art techniques to fabricate such components are flame hydrolysis [1], physical vapour deposition [2,3] or ion exchange techniques [4,5,6]. Ion exchange and flame hydrolysis are established technologies. Both suffer from high costs especially for the micropatterning. In addition there are technical problems to fabricate active components by ion exchange, because the active sites cannot be ion-exchanged and are therefore present in the cladding. One disadvantage of the flame hydrolysis technique is the difficulty to cover etched micropatterns with narrow gaps completely by the cladding material and the control of mechanical stress.

Therefore it is interesting to investigate wet chemical technologies. However, state of the art sol-gel-derived SiO₂ layers on Si wafers are prepared from tetraethoxysilane (TEOS) based sols by a multilayer spin-coating technique (thickness of 0.1 μm for every single layer, e.g. 100 coating steps for a total thickness of 10 μm) and thermal densification by

Rapid Thermal Processing (RTP) using a flash annealer [7]. It has been shown, that flash annealing allows to control the stress formation during the densification of the SiO₂ xerogel according to shrinkage of the layer and different thermal expansion behaviour of substrate and layer by overheating the substrate using high heating and cooling rates of about 2000 K/min. But this multilayer processing is expensive and the probability for the inclusion of dust particles or other defects is increasing with every processing step. Using nanocomposite SiO₂ sols synthesised from tetraethoxysilane and colloidal silica sols, the maximum thickness of a single spin coated SiO₂ layer on a 4" wafer could be increased to 1 µm after RTP at 1000 °C [8]. Higher layer thicknesses with the demanded homogeneity could only be obtained by multistep processing due to too low viscosity of the sols. Waveguiding layers were obtained by doping with Er₂O₃, Al₂O₃, P₂O₅ or TiO₂ [7]. These results show that the incorporation of SiO₂ nanoparticles could significantly increase the critical thicknesses of a single layer. However, the formation of a rigid SiO₂ gel network by the used alkoxide components always leads to the well known problems of shrinkage and stress formation during drying and sintering [9]. Therefore, a completely new approach was used. The coating sol was synthesised only from SiO₂ nanoparticles and an organic binder, but without any alkoxides to avoid the formation of a rigid SiO₂ xerogel backbone. PVA was chosen as organic binder because of its high OH-content that should allow a very good wetting with the colloidal silica particles. Due to the good wetting behaviour, agglomeration of the SiO₂ nanoparticles and thus the formation of large pores should be avoided. This was assumed to be the most important prerequisite for a high viscous sintering process, which is necessary to prevent from crystallisation process in doped silica layers.

2. EXPERIMENTAL

2.1 Synthesis of the SiO₂ coating sol [10]

For the preparation of SiO₂ coating sols 78,2 g ultrapure tetraethoxysilane (99.999 %, Fluka) was dissolved in 195 g ethanole and 124 g water (including 6.7 g NH₃ 1 mole / l) was added. The solution was heated up to 70 °C for 70 h. Under these conditions, spontaneous nucleation and growth takes place. A nanoparticulate SiO₂ sol with particle sizes of around 10 nm in diameter was obtained. To 100 g of this nanoparticulate SiO₂ sol, 19 g of a 10 wt% solution of polyvinylalcohol (Mowiol 18-188, Hoechst) in water was added. The solid content was adjusted to 25 wt % SiO₂ by removing the solvents.

2.2 Synthesis of the doped SiO₂ sols [11]

For the synthesis of Al₂O₃ and PbO doped SiO₂ coating sols, 35 g HNO₃ 1 mole / l was added dropwise to 100 g of the nanoparticulate SiO₂ sol. 2.1 g aluminiumisopropylate and 0,8 g leadnitrate was dissolved in this solution. Then 23 g of a 10 wt% solution of polyvinylalcohol in water is added. The solid content was adjusted to 10 wt % by removing the solvents.

For the synthesis of Al₂O₃ and Er₂O₃ doped SiO₂ coating sols, 35 g HNO₃ 1 mole / l was added dropwise to 100 g of the nanoparticulate SiO₂ sol. 2.1 g aluminiumisopropylate and 2,2 g erbiumnitratepentahydrate was dissolved in this solution. Then, 23 g of a 10 wt% solution of polyvinylalcohol in water was added. The solid content is adjusted to 10 wt % by removing the solvents.

2.3 Primer layer

A primer layer (the primer layer is only used to achieve a better adhesion of the SiO₂ coating on silicon wafers) was synthesized by mixing 30 g ethanol, 69.5 g water and 0.5 g n-aminopropylaminoethyltriethoxysilane and stirring for 1 h at room temperature.

2.4 Layer preparation

The nanoparticulate sols described in chapter 2.1 and 2.2. were applied to 4" silicon wafers (SiO₂ sols) and on 4" silica wafers (doped sols) using the spin-coating technique. A spin coater working in closed atmosphere (Süss) was used under cleanroom conditions in order to avoid a rapid evaporation of the solvents. An adapted spinning technique was developed due to the optimisation of the sol composition and the spinning parameters. This technique allows the application of single layers and double layers and is shown in the following scheme.

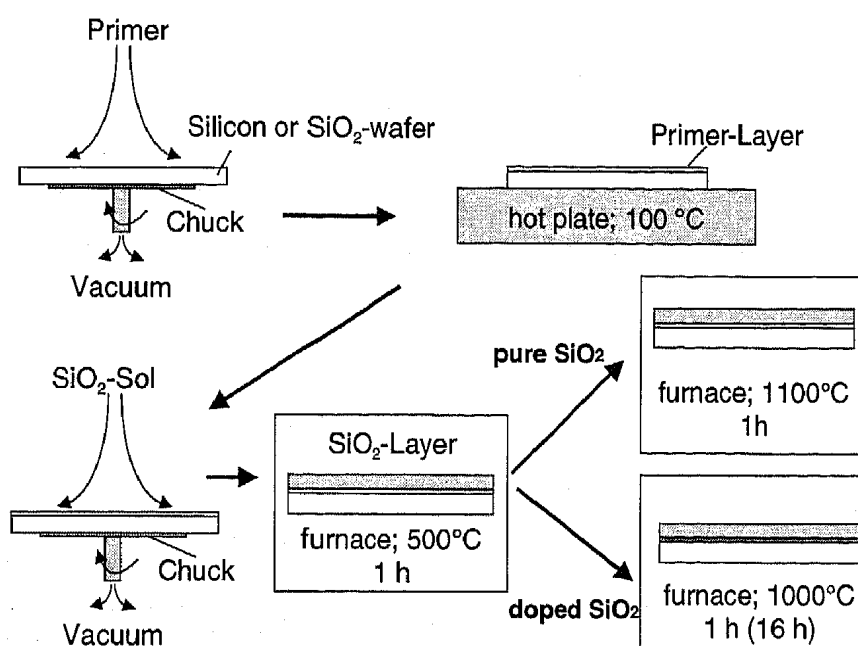


Figure 1: Scheme of single and double layer application by spin coating using the nano particulate sols developed

The pure SiO₂-sols were applied on silicon wafers, the doped sols were coated on SiO₂-wafers. To achieve a better adhesion between the pure SiO₂-sols, an primer layer, consisting in an hydrolysed aminosilane (see chapter 2.3) was applied on the silicon wafers. The primer layer was heated on a hot plate at 100 °C for 5 minutes. The SiO₂-sol was applied on the primer layer. The doped sols were applied on SiO₂-wafers without any primer layer. The layers were pre heated at 500 °C for 1 h and afterwards densified in a muffle furnace according to a temperature program, described in chapter 3.2. A more detailed description is given in [11,12].

2.5 Characterisation

To determine the particle size of the nanoparticulate SiO₂ sols, transmission electron microscopy was performed in a high resolution transmission electron microscop, Philips, Type CM200FEG. The differential thermal analysis of the

gel to determine the temperature profile of the densification was performed in a DTA/TG , Bähr, Type STA 500. Before the measurement, the gels were dried at 100 °C, using Al₂O₃ as reference. Infrared measurements of the layers were performed in a IR-spectrometer, Bruker, Type FTIR-ISF-66v with a evacuable sample room and optics. Refractive indices were measured by a ellipsometer, SPORA, Type ESGV. Layer thicknesses and layer homogeneity were determined by interferometric measurement with an interferometer , Sentec, Type FTP 500.

3. RESULTS AND DISCUSSION

3.1 Synthesis of a nanoparticulate SiO₂ sol and SiO₂ coatings on silicon wafers

Preliminary tests with commercially available colloidal silica sols (Levasil 300-30 from Bayer) lead to crystallisation during firing the layers at temperatures above 1000 °C. It was assumed that this was due to Na⁺ impurities in the technical product. Therefore, colloidal silica sols were prepared according to [10], by a modified Stoeber-process, using ultrapure TEOS and ammonia water instead alkaline compounds as basic catalyst in order to minimise the content of impurities, as described in chapter 2.1.

A TEM micrograph of the so prepared colloidal silica sol is shown in fig. 2

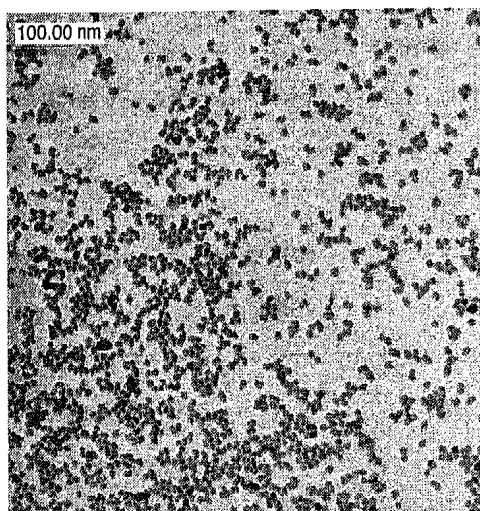


Figure 2: TEM micrograph of the SiO₂ particles prepared from ultra pure TEOS under basic catalysis

By adding PVA as organic binder, homogenous, water based SiO₂ coating sols were obtained which were stable for more than 3 weeks at room temperature. By systematic variations of the PVA : SiO₂ ratio and the solid content of the sol it was found [12], that a solid content of about 25 wt.% and the binder content of about 35 wt.% related to SiO₂ in the particulate sol in combination with the use of an aminosilane as a substrate primer allowed the preparation of homogeneous gel films with thicknesses of 8 μm ± 0.1 μm on 4'' silicon wafers by spin-coating.

3.2 Synthesis of doped SiO₂ sols and doped coatings on SiO₂ substrates

Beside pure SiO₂ coatings, that might be useful as a buffer layer on silicon, silicate layers with increased refractive index are needed for waveguiding. Therefore, a synthesis for the preparation of nano particulate sols in the SiO₂-Al₂O₃ system was developed, allowing the incorporation of Er₂O₃ and PbO. For passive waveguide applications, the system SiO₂-Al₂O₃-PbO was pointed out to be promising. Sols were synthesised for layers with the final molar composition of 92.5 SiO₂-5.0 Al₂O₃-2.5 PbO. Alumina was incorporated for the improvement of erbium solubility in active components. PbO was introduced in order to obtain a refractive index increase of about 0.005, which is assumed to be usefull for monomode waveguiding at 1550 nm wavelength on SiO₂ wafer substrates. As a model system for such type of coatings a molar composition of 92.5 SiO₂-5.0 Al₂O₃-2.5 Er₂O₃ (corresponding to 1.2·10²¹ Er³⁺·cm⁻³ assuming silica density) was chosen. During the corresponding investigations it was proven that the incorporation of these components is impossible using basic silica sols because of precipitation of the corresponding alkoxides [12]. Since basic catalysis is needed for the preparation of nanoparticulate SiO₂ sols [13] the pH of this sol was changed from pH = 11 to pH = 4 by rapid adding HNO₃. It could be proven by electron microscopy and ξ -potential measurements, that the SiO₂ nanoparticles only change their surface charge without agglomeration or dissolution [10]. After that, the dopands and the binder could be added as described in chapter 2.1 and 2.2. Using these coating sols, homogeneous gel layers with thicknesses of 10 μ m + 0.1 μ m could be obtained in a single coating step [12].

3.1 Development of the thermal densification

During the thermal densification of the gel layers, first all organic compounds have to be burned off without crack formation and second, a complete densification has to be obtained by high viscous sintering at temperatures around T_g in order to avoid crystallisation. In order to find a suitable temperature-time program for the removal of the organic compounds, a DTA / TG measurement of the basic catalysed SiO₂-sol was performed. The result is shown in fig. 3.

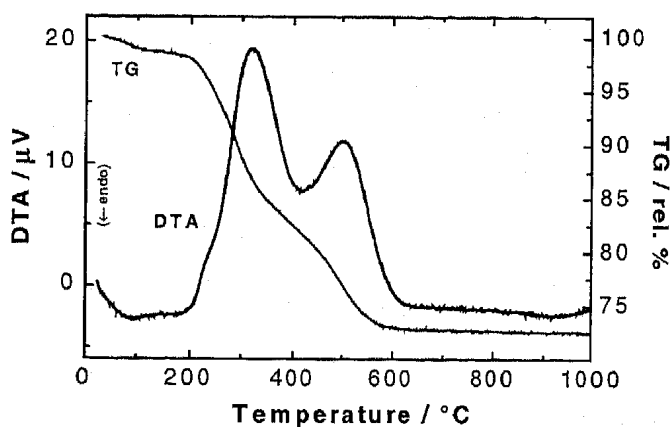


Figure 3: Thermal analysis of coatings on the basis of nano particulate sols and PVA as a binder

Fig. 3 clearly shows two exothermic peaks at 320 °C and 530 °C with a total weight loss of about 75 % which corresponds very well to the chosen solid content of 25 % (see chapter 2.1), if one assumes that this is due to the burning off of the binder. Furthermore, the DTA / TG measurement indicates that at temperatures higher than 500 °C the corre-

sponding coatings should be free of residual organics. To prove this, infrared measurements of the layer, densified at different temperatures were performed. Figure 4 shows the result.

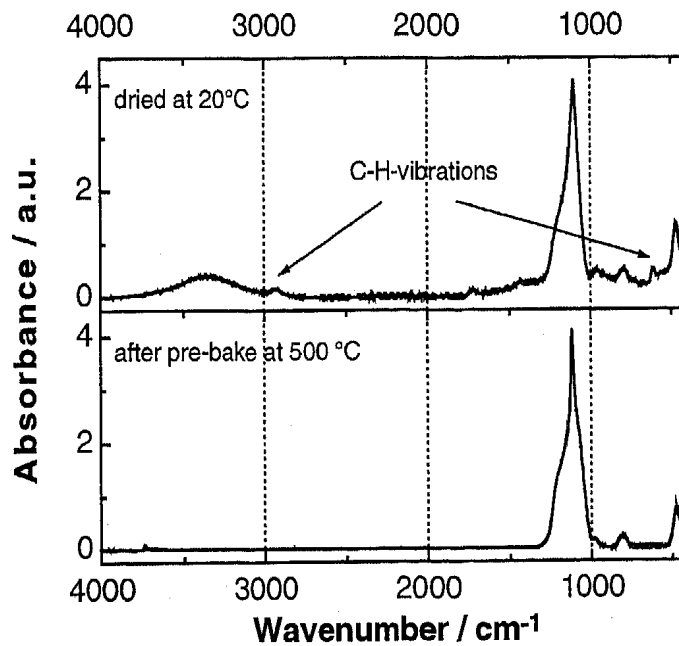


Figure 4: FTIR spectrum of a SiO₂ coating prepared from a nano particulate sol, see chapter 2.1 and PVA as a binder after drying at room temperature and after pre-bake at 500 °C

Figure 4 clearly shows, that after drying at 20 °C, there is a remarkable organic content, which is completely removed after baking at 500 °C for 1 h. From these results, a temperature-time program with heating ramps of 2 K / min and 2 h plateaus at 250 °C and 500 °C was chosen. After this treatment, clear, colourless and crack-free coatings were obtained.

3.2 Determination of the refractive index

The next question was to find suitable conditions for the complete densification of the layer at a minimum temperature around T_g . The densification process was monitored by ellipsometric refractive index measurements. This was possible, because the coatings were fully transparent without any scattering in all states of thermal densification from room temperature up to 1100 °C [12]. The primer layer could not be detected by ellipsometry [12], indicating a thickness < 2 nm [14]. Therefore, the influence of the primer on the densification of the SiO₂ layers and on the refractive index measurements can be neglected. The result is presented in fig. 5.

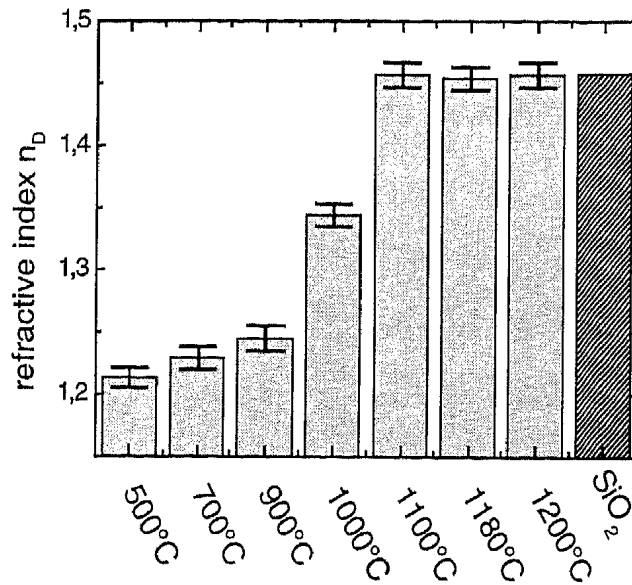


Figure 5: Ellipsometric measurement of the refractive index n_D of SiO₂-coatings (see chapter 2.1) on Si-wafers sintered at different temperatures

The results are summarised in the figure 5. After the prebake at 500 °C, a refractive index of about 1.213 is obtained, which corresponds to a porosity of about 54 vol %, assuming a refractive index of 1.46 of the SiO₂ skeleton in the nanoporous layer. This fits very well to the chosen PVA : SiO₂ ratio of 35 : 100 taking into account a density of the dry PVA of about 0.6 g/cm³ [15]. The measurement indicates an increase of the refractive index n_D from 1.213 for a layer sintered at 500°C for 1 h to 1.457 for a layer sintered at 1100°C for 1 h, which is within the errors of measurement equal to the refractive index n_D of pure SiO₂ (1.458). Therefore the SiO₂ layers described above were densified under these conditions. This result is of very high importance, because the complete sintering at temperatures below T_g allows shape retaining in the densification of micropatterns in xerogels and also avoids phase separation in doped systems. The latter might be especially important for Er³⁺ doped systems.

In densification experiments of the Er-doped layers at a temperature of 1100 °C for 1 h phase separation for the Erbium-doped layers was obtained, as determined in FEG-SEM investigations [12]. The approach for avoiding these phase separation was a decrease of densification temperature (down to 1000 °C) in combination with an increase of densification time (up to 16 h). To determine the grade of densification, refractive index measurements related to the densification temperature of the layers were performed. Fig 6 shows the result of the refractive index measurements.

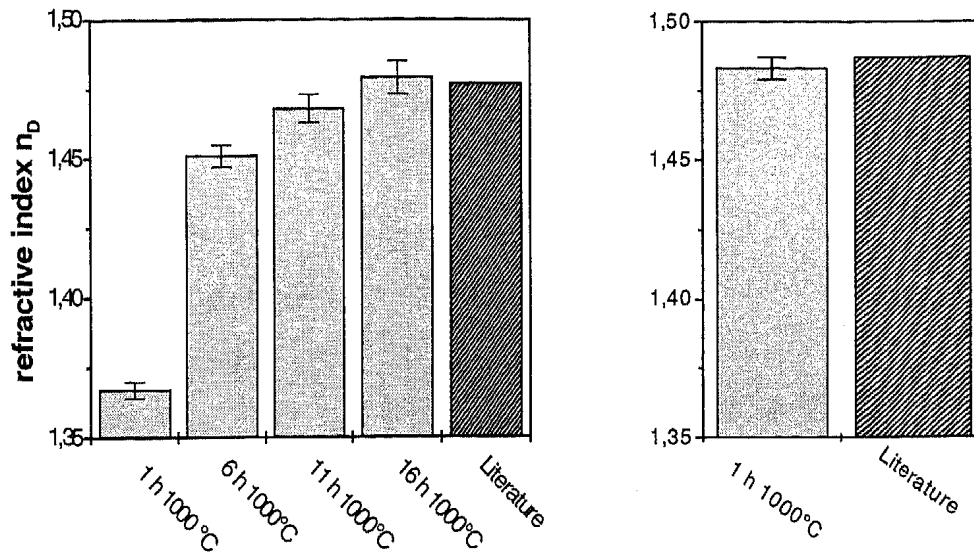


Figure 6: Ellipsometric measurements of the refractive index n_D of Erbium doped coatings (molar composition 92.5 SiO₂-5.0 Al₂O₃-2.5 Er₂O₃) (left) and PbO doped coatings (molar composition 92.5 SiO₂-5.0 Al₂O₃-2.5 PbO) (right) densified at 1000 °C in dependence upon densification time

From fig. 6 (left diagram) one can see, that the refractive index of the Er³⁺ doped layers becomes equal to the value, calculated with the Appen factors from [16] after firing for 16 h at 1000 °C. The right diagram of fig. 6 shows the result of the refractive index measurements for an Er³⁺- free layer doped with 5 mole % Al₂O₃ and 2.5 mole PbO, dedicated for passive waveguide applications. The ellipsometric measurement clearly shows, that a complete densification is obtained after firing for 1 h only at 1000 °C. Comparing this result with the one for pure SiO₂ (see fig.5) one can see clearly the T_g -decreasing effect of the PbO doping, as expected. The good agreement between the refractive index of the densified layers with the calculated index for glasses with the same composition [16] also indicates, that there is no loss of PbO, Er₂O₃ or Al₂O₃ during the synthesis and densification of the layers.

3.3 Layer thickness and homogeneity

The next question was about the homogeneity of thick SiO₂ layers on wafer scale. This was investigated for SiO₂ layers on Si-wafers because the homogeneity can easily be monitored by interferometric mapping in this case due to the high difference in refractive index of substrate and layer. The result is given in fig. 7.

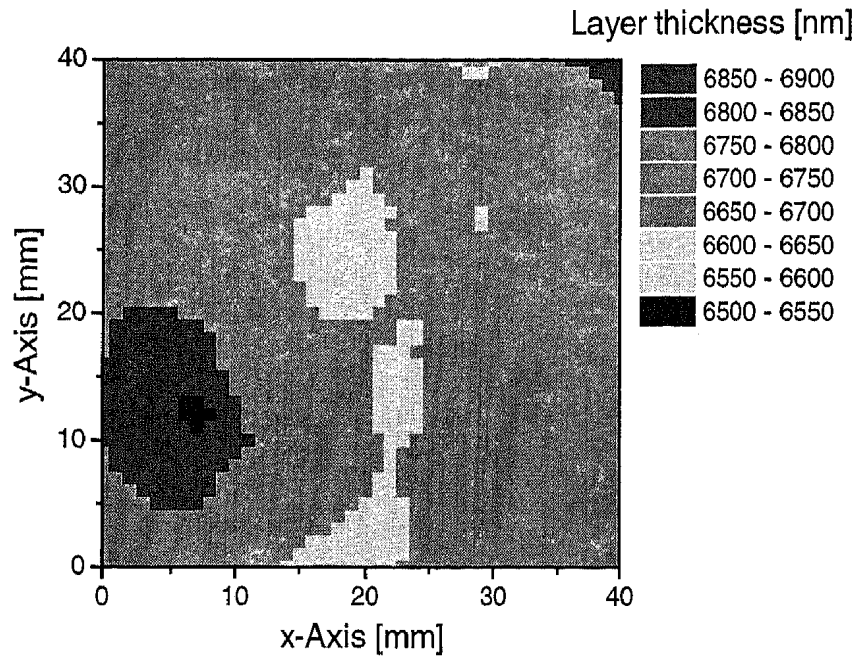


Figure 7: Interferometric measured thickness of a SiO₂-double layer after densification at 1100 °C applied by spin coating using a nano particulate sol

Fig. 7 shows an average thickness of the double layer of $6.7 \pm 0.1 \mu\text{m}$ after densification at 1100 °C for 1 h. This is a significant improvement of the state-of-the art. Fig. 7 also indicates that the homogeneity has to improved by further investigations including alternative coating techniques.

3.4 Optical properties

Optical loss measurements were performed by prism-coupling. The optical loss at 633 nm of a 1.7 μm thick PbO-doped double layer applied on SiO₂ by dip-coating and densified at 1000 °C for 1 h was determined to be $0.9 \text{ dB}\cdot\text{cm}^{-1}$, as one can see from fig.8.

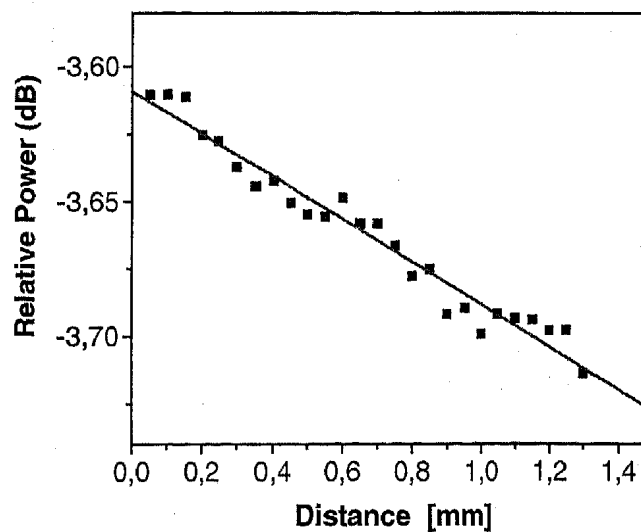


Figure 8: Optical loss measurement by prism-coupling of a 1.7 μm thick PbO-doped layer on SiO₂

The low optical loss of 0.9 dB/cm at 633 nm in the layer with a thickness which is too thin for optimum wave propagation, indicates very low scattering losses, which might have been assumed to be critical for particulate coating sols.

The next interesting question in this content was to investigate, whether the particulate character of the SiO₂ sol would lead to clustering of Er³⁺ ions and therefore have an influence on the fluorescence behaviour of the Er³⁺ dopands.

The following figures show the fluorescence spectrum and the fluorescence lifetime measurement of a 1.5 μm thick SiO₂-Al₂O₃-Er₂O₃ (92.5-5.0-2.5 mole %) layer on a silica slide. The layer was densified at 1000°C for 16 h.

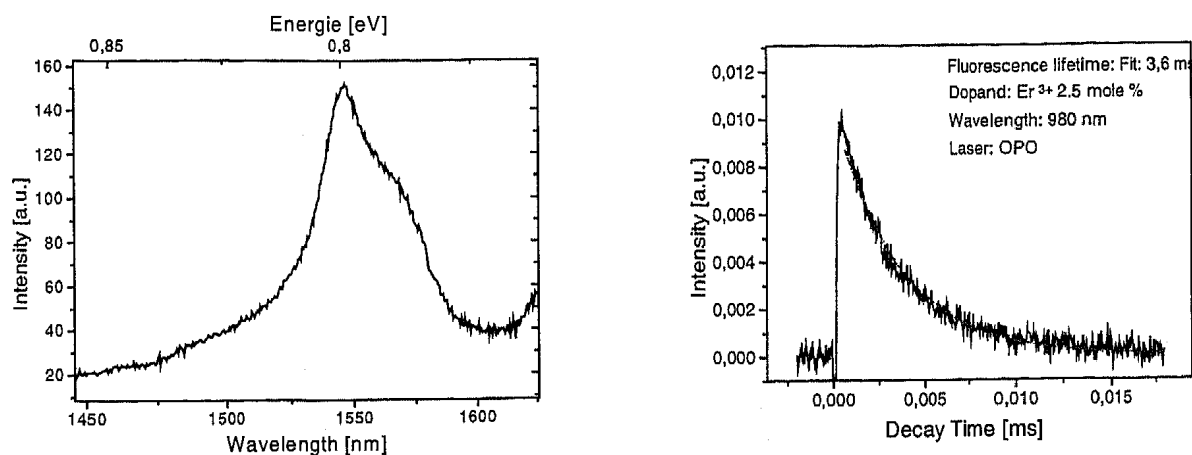


Figure 9: Er-fluorescence spectrum (left) and fluorescence decay curve (right) for a thick oxide film on silica doped with 2.5 mole % of Er densified at 1000 °C for 16 h

The fluorescence maximum was determined to be about 1545 nm, whereas the corresponding fluorescence lifetime was 3.6 ms. This is a remarkably long lifetime with respect to the high Er³⁺ concentration. This value is in good agreement with lifetimes measured in lead silica glasses, doped with Er³⁺ in comparably high concentrations [17], so that concentration quenching can occur. Future optimisation of the Er³⁺ concentration and investigation of other possible quenching sources (OH, impurities) will have to be prepared in the future.

4 CONCLUSION

The results reported here lead to the following conclusion. Coating sols, prepared from nanosized SiO₂ particles with high purity and PVA as organic binder are very useful for the preparation of μm-thick gel and glass layers on Si and SiO₂ substrates. During the wet stage of the layer formation, the PVA molecules must act as a perfect surface modifier for the SiO₂ nanoparticles, because not any kind of agglomeration occurs during the drying step. This is very important for a complete densification at temperatures around T_g. The case of Er³⁺ doped layers has proven, that this really necessary to avoid crystallisation.

Therefore, this new nanotechnological approach to wet chemically derived thick doped and undoped SiO₂ layers can be assumed to be a very useful basis for future technology development for passive and active planar waveguide components.

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