ESRF	**Experiment title:** **Crystallization in Er^{3+}-doped SiO_2-HfO_2 planar waveguides using GIXRD**	**Experiment number:** **HS3276**
Beamline: BM01	**Date of experiment:** from: 18-07-2007 to: 23-07-2007 and from: 1-10-2007 to: 2-10-2007	**Date of report:** 19-03-2008
Shifts: 15+3	**Local contact(s):** Ana Diaz, Till Metzger	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

*__N. D. Afify__**,** ***G. Dalba**, ***M. Mattarelli,**
Department of Physics, University of Trento, Via Sommarive 14, 38100 Povo (Trento), Italy

***F. Rocca**, **C. Armellini**,
IFN-CNR, Section "FBK-CeFSA" of Trento, Via alla Cascata 56/c, 38100 Povo (Trento), Italy

Report:

Aim of the experiment

The experiment aimed to follow crystallization in pure and Er^{3+}-doped SiO_2-HfO_2 planar waveguides, in order to study the influence of HfO_2 content, of doping with Er^{3+}, and of thermal treatment on their phase transformation, crystalline phase characteristics, and microstructure. In particular, we were interested in a precise refinement of crystallographic structure (e.g. lattice parameters) and microstructure (e.g. crystallite size, lattice distortion, and their spatial distribution) of HfO_2 nanoparticles produced by opportune thermal treatment.

Experimental

The samples were three series of silica-hafnia waveguides, with different compositions, produced by different synthesis tecniques (sol-gel and rf- sputtering), and deposited on v-SiO_2 or silicon substrates.

1) The first series comprises three sets of waveguides thermally treated only at 1000°C: pure and 1 mol % Er^{3+}-doped $80SiO_2$-$20HfO_2$ prepared by sol-gel and dip-coating; 0.35 mol % Er^{3+}-doped $87.5SiO_2$-$12.5HfO_2$ prepared by RF sputtering. Each sample in each set corresponds to a different annealing time, ranging from 30 minutes to 24 hours.

2) The second group of samples comprises two sets of waveguides thermally treated for short (30 minutes) or long (24 hours) duration: pure and 1 mol % Er^{3+}-doped $70SiO_2$-$30HfO_2$ prepared by sol-gel and dip-coating. In these two sets, each sample was thermally annealed at a single different temperature, ranging from 900°C to 1200 °C.

3) The third group comprises one set of waveguides prepared by RF sputtering with a composition 0.35 mol % Er^{3+}-doped 95 SiO_2-5 HfO_2. Each sample was thermally annealed at one temperature (ranging from 600°C to 1200°C) for short time (30 minutes). The peculiarity of this group is the low content of HfO_2.

As originally planned, grazing incidence XRD have been performed on all the samples, in the main station of ID01. The quality of data was very good and a Rietveld refinement of data was obtained for all the samples. An example is presented in Figure 1.

Moreover, we have also done GISAXS measurements, in the range 0.6 to 5 nm^{-1}, in two different geometries. For the in plane configuration, the incident angle was set to 0.5° , corresponding to a penetration depth of about 100 nm. For the out of plane configuration, the incident angle was changed in the range 0.1- 5°.

Main results

We have followed the nucleation of HfO_2 nanoparticles in silica-hafnia amorphous matrix, upon heat treatment (HT).

The GIXRD data were analyzed by Rietvield method. The fit allowed to determine size distribution of HfO_2 cristallites and the lattice constants of the doped and undoped nanocrystals.

Figure 1 shows experimental results and the fits for the undoped $80SiO_2$-$20HfO_2$ serie. Figure 2 shows the results obtained from the fit for the average size of crystallites in the first group of samples.

The GISAXS data were analyzed in the framework of LMA approximation. The fit allowed to determine the size distribution of the HfO_2 particles (whether amorphous or crystallized), the quantity of HfO_2 in the particles (filling factor) and the minimal distances between them. An example of SAXS data and fits are reported in figure 3. Figure 4 reports the values of particles size. The agreement with the XRD measurements is very good.

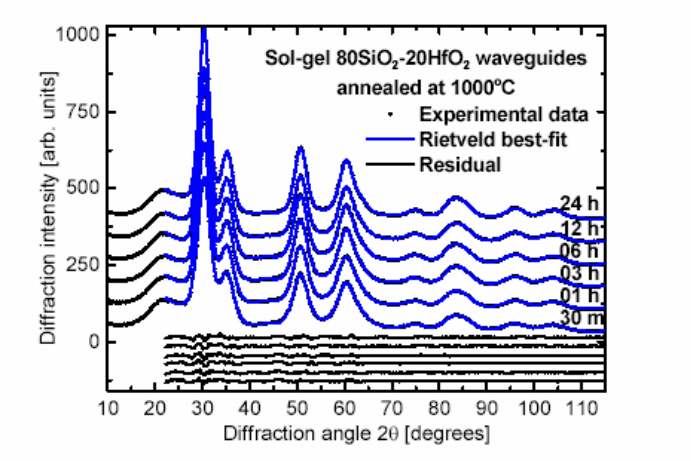

Figure 1

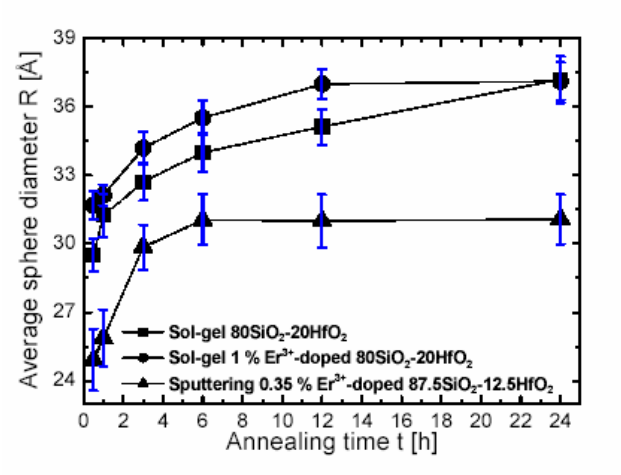

Figure 2

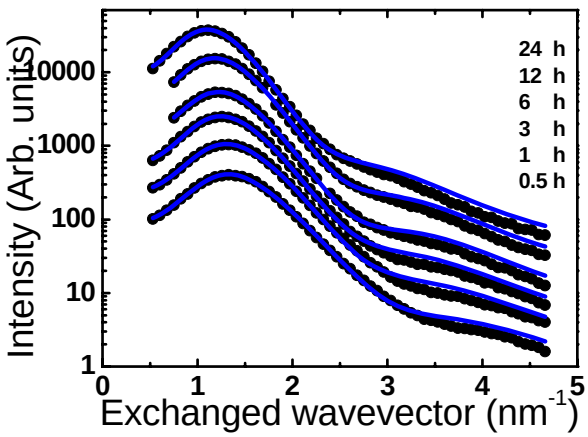

Figure 3

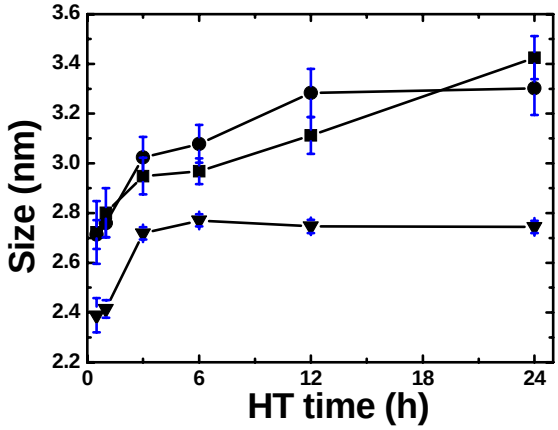

Figure 4

Conclusions and future work

The growth of HfO_2 nanocrystals is in agreement with other experimental data such as XRD, TEM and Raman. However, SAXS detects HfO_2 islands also before the formation of detectable nanocrystals (for example HT at 900°C for 30% HfO_2 samples, or at 1000°C for 5% HfO_2). These results are in agreement with EXAFS and photoluminescence measurements that showed the presence of pure HfO_2 regions around the erbium ions also in the glassy phase, but without being able to estimate their size.

After the crystallization, it appears that the sizes measured by SAXS and XRD are comparable, excluding the presence of amorphous HfO_2 regions around the nanocrystals.

The HfO_2 filling factor is practically independent on the heat treatment: 0.18 for the dip-coated films and 0.12 for the sputtered ones. In the series where the annealing temperature was changed, the evolution is more important.

In the 70-30 films, the average size of the particles ranges from 1 nm (HT at 900°C, still amorphous) up to 10-12 nm (HT at 1200 °C). The filling factor, which is about 5% at 900°C, increases with temperature and at 1100°C, all HfO_2 appears to be in the formed particles, in agreement with Raman spectroscopy and TEM microanalysis results. Also in the 95-5 serie, as measured by GISAXS, there is a continuous increase of the average size with temperature (ranging from 1.5 nm at 900°C up to 4 nm at 1200°C). There is no evolution in the filling factor (about 3%)

In general, the ratio between the distances between particles and their radii decreases with heat treatment. This could be related to the increased diffusion length of hafnium atoms, which allows the formation of (relatively) nearer particles.

The study of such relation, which has also important consequences on the material transparency, deserves further investigation. Performing SAXS measurements in a down extended q-region could allow determining with greater accuracy the correlation between diffusion and transparency [1].

[1]M. Mattarelli, M. Montagna, P. Verrocchio, "*Ultratransparent glass ceramics: The structure factor and the quenching of the Rayleigh scattering*" , Appl. Phys. Lett. 91, 061911 (2007).