



Structural investigation of photonic materials at the nanolevel using XPS

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ABSTRACT

This work deals with X-ray photoemitted spectra (XPS) from materials which are of interest for photonic applications. In particular $x\text{HfO}_2 - (100 - x)\text{SiO}_2$ ($x = 10, 20, 30$ mol%) glass–ceramics planar waveguides and silver ion-exchanged (0.5, 1.5, 5 mol%) sodalime glasses are investigated. The aim of the work is to explore the material structural changes occurring at the nanometric scale which are produced during the fabrication process in order to enlighten the formation of the nanostructures. The results show that XPS is sufficiently sensitive to detect the formation of nanostructures in the analyzed materials providing at the same time also chemical information. Both these inputs are important to tune the production processes to increase the efficiency of the optical devices.

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1. Introduction

Glass–ceramic materials and silver ion-exchanged sodalime containing rare earth ions have been of particular interest in the recent period thanks to the peculiar properties they show due to the formation of crystalline nanostructures dispersed in the amorphous glassy network. In the case of silica–hafnia waveguides it is possible to change the rare-earth environment from amorphous to crystalline by applying a thermal annealing. This opens interesting opportunities in photonics since these materials combine the advantages of glass optics with the effects of a crystalline matrix on the rare earth ion emission [1]. The formation of nanocrystalline structures is the effect of a spinodal decomposition occurring in the glassy matrix due to the intrinsic instability of the silica–hafnia system. As demonstrated by Kim and McIntyre [2] under specific conditions, the system separates in its silica and hafnia components with a net gain in energy [2,3]. The second system is a silver-exchanged sodalime glass usually employed in integrated optics [5]. As for hafnia, also silver is highly disruptive of the silica network. An increase of the silver concentration in the glassy network falls into a silver condensation in nanoparticles with a reconstruction of the silica network and an increase of the system stability [4]. Both silica–hafnia and sodalime systems were investi-

gated using XPS with the aim to correlate the spectral modifications with the occurrence of structural changes. The optimization of the device efficiency requires the study of the chemical and structural changes in relation to the composition and production processes. In this work we will use XPS to obtain information concerning the electronic configuration of the atoms composing the glassy network of our samples. This made possible to follow both chemical and structural changes allowing a refinement of the fabrication conditions which can be tuned to increase the optical efficiency.

2. Experimental

Two series of silica–hafnia planar waveguides activated by 0.3 mol% Er^{3+} ions were prepared using the sol–gel method as described elsewhere [1]. Erbium-activated $\text{SiO}_2\text{–HfO}_2$ films were deposited on $\nu\text{-SiO}_2$ substrates by dip coating, with a dipping rate of 40 mm/min. Before further coating, each layer was annealed in air for 50 s at 900 °C. Final films, resulting from 30 to 35 coatings, were stabilized by a last treatment in air at 900 °C. Three waveguides containing Si/Hf molar ratio of 70/30, 80/20 and 90/10 (samples SH10, SH20, SH30) were produced. In order to nucleate nanocrystals inside the planar waveguides a final annealing at 1000 °C for 30 min was performed (samples ASH10, ASH20 and ASH30). Concerning sodalime glasses the molar composition of the Er/Yb-activated glass is: 67 SiO_2 , 14.4 Na_2O , 9.1 CaO , 1.9

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Al_2O_3 , 0.9 P_2O_5 , 0.9 K_2O , 1.9 Er_2O_3 , 3.9 Yb_2O_3 (mol%). Four samples were produced cutting the glasses in plates, which were thinned down to 200 μm and optically polished. The samples were Ag^+ ion exchanged by keeping them for 67 h at 390 °C in a molten salt bath of NaNO_3 containing a variable molar concentration (0.5%, 1.5%, and 5%) of AgNO_3 . These ion-exchanged plates will be referred to as $\text{SAg}0.5$, $\text{SAg}1.5$, and $\text{SAg}5.0$, (more details are given in [6]). XPS core lines were acquired using a Scienta ESCA 200 (monochromatized $\text{AlK}\alpha$ X-ray source) with an energy resolution of 0.35 eV considering the charge compensation. For both the series of samples the core lines were fitted using Gaussian components.

3. Results

In Fig. 1(A) it is shown the O1s oxygen core line from the SH30 and ASH30 samples. As it can be observed the O1s lineshape strongly changes as a function of the HfO_2 concentration. The O1s core line was fitted using three Gaussian components as shown in the inset of Fig. 1(A). The first component at higher BE describes the SiO_2 chemical bond, the component at lower BE corresponds to oxygen bonded to hafnium while the intermediate component was associated to hafnium silicate. In Fig. 1(B) is reported the trend of the relative abundances of oxygen in these three different chemical states as estimated in the three ASH samples. Similarly to the previous example, Fig. 2(A) shows how an increase of the Ag concentration strongly influences the O1s line-shapes. These last were deconvolved in three Gaussian components (see the inset of Fig. 2A). The component at higher BE was associated to the Si–O bridging oxygen atoms (BO). At intermediate BE the Gaussian component describes the various oxides of the sodalime glass. Finally the component at lower BE is relative O–Na or O–Ag non bridging oxygen atoms (NBO). Fig. 2B shows how the change in the silver concentration influences the abundance of the BO and NBO. As it can be observed increasing the silver concentration an increase of the integral intensity of the BO component is observed. To this increase corresponds a specular trend of the NBO. The extent of the Na-to-Ag ion exchange is then expected to strongly influence the structure of the glassy matrix.

4. Discussion

The XPS spectra shown in Fig. 1(A) indicate that the O1s peak positions depend on the HfO_2 concentration. Let us refer to the inset of Fig. 1(A). At the lowest Hf concentration, the system is pre-

valently composed by a SiO_2 network. The O1s core line reflects this situation with a spectrum dominated by the component 1 placed at ~ 532.6 eV typical of silicon oxide. Increasing the Hf concentration, increases the intensity of the component 2 falling at ~ 531.5 eV. This component at lower BE with respect to that of pure silica is associated to hafnium silicate. This is in agreement with the lower electronegativity of Hf atoms in comparison to Si atoms. In fact, the formation of the Si–O–Hf bonds causes a charge transfer from hafnium to oxygen atoms lowering their BE. Fig. 1(A) shows also marked differences between samples SH30 and ASH30. The absence of component 3 on the low BE tail makes the O1s lineshape of SH30 more symmetric with respect to ASH30. In other words, the formation of hafnium silicate persists only for Hf concentrations <30% [7] and in absence of thermal treatments. Hafnium silicate is, in fact, a metastable system which at 1000 °C experiences a phase decomposition with the formation of hafnium oxide. This is shown by Fig. 1(A) where the O1s core line of ASH30 samples shows a non negligible component 3 at ~ 530.4 eV associated to HfO_2 . In agreement with theoretical diagrams [8], our experiments show that at 1000 °C increasing the Hf concentration we fall into the miscibility gap [2] and the system undergoes a spinodal decomposition. As a matter of fact here we demonstrate that the XPS analysis of the O1s and the Si2p (not shown here) core lines [7] are able to detect the occurrence of this phase decomposition. Moreover, the two silica and hafnia phases lead to different structures. Differently from silica that requires a high energy to condensate in a crystalline phase, the amorphous hafnia system can reduce its free energy organizing in a crystalline form [8]. This was demonstrated for our ASH sample using TEM which was able to detect the formation of HfO_2 nanocrystals [1]. The evolution of the Si, O, and Hf XP-core lines enable us to obtain both chemical information and the structural rearrangements induced by thermal treatments and/or modification of the sample composition. The ability of XPS to provide information concerning the formation of nanostructures embedded in an amorphous glassy matrix is confirmed also considering the sodalime glasses. There is a wide literature concerning the effects of quantum confinement on the XP-core lines ([9–11] and references therein). Here we present the results of a complex analysis which accounts both for chemical and structural effects. In fact, the modulation of the oxygen core lines accompanied by the changes of that of Ag, testify the presence of condensation of silver in nanoparticles. This, on its turn, brings about a structural rearrangement of the glassy matrix. The BO, NBO trend can be explained by a reduction of the ionic interaction between silver and oxygen due to the formation of silver nanoparticles. The Ag clusters possess a metallic character because only

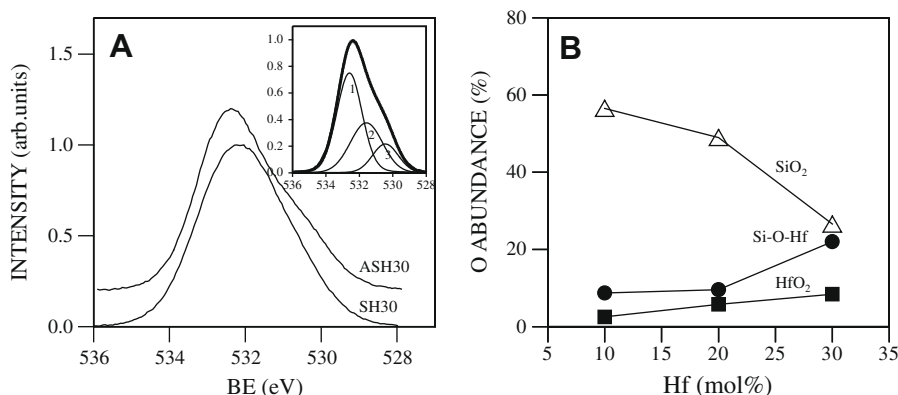


Fig. 1. (A) Lineshape change of the oxygen 1s core line as a function of the heat treatment applied. The inset shows an example of the peak fitting performed on the ASH30 sample. (B) Trend of the SiO_2 , Si–O–Hf and HfO_2 abundances as a function of the hafnia concentration in the samples.

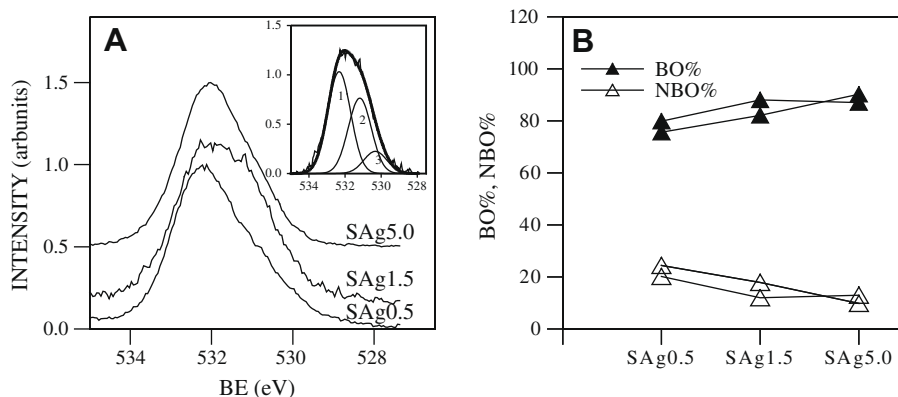


Fig. 2. (A) XPS O1s core-level spectra for the ion-exchanged sodalime glasses (SAG). An example of peak fitting is shown in the inset for the sample SAg1.5. (B) Trend of the BO, NBO percentual abundance as estimated from the O1s peak fitting from two series of spectra.

few atoms on the nanoparticle surface may interact with the glassy matrix. So the migration of Ag into the cluster leads the parent oxygen free to rearrange into the glassy network. This view is in agreement with the model proposed by Wang [4]. In this model, at given silver concentration and temperature, silver migrate and aggregates in nanoparticles as it happens in our case. The unsaturated ionic bonds left by silver, transform in more stable covalent Si–O–Si bonds with a partial reconstruction of the silica matrix. Let us refer to the O1s fit shown in the inset of Fig. 2(A) and (B) and in particular to components 1 and 3 of the fit (component 2 at ~ 531.2 eV is associated to the sodalime oxides not affected by the modulation of the Ag content). Following the Wang's model, at very low silver concentration we have mainly silver–oxygen ionic interactions. They are mirrored by the component 3 of the O1s core line fit at ~ 530.5 eV leading to a high NBO% value. A different situation occurs at the highest Ag concentration. Here silver is mainly condensed in nanoclusters and the most part of oxygen is accounted by the component 1 at ~ 532.3 eV. This component is associated to SiO_2 bonds and to high BO% values. Note that a comparison among the O1s fit components 1 and 3 requires a normalization for the Ag atomic abundance. Finally, at the intermediate silver content, the high contribution of both BO and NBO bonds described by components 1 and 3 leads to a prominent O1s broadening.

So also in this case a careful analysis of the XP spectra put in evidence structural changes which occur in sodalime glasses at the nanometric scale. This interpretation is reflected by the strong changes in the optical spectra. It is well known that the ion Ag exchange leads to an increase of the glass absorbance. This is related to the presence of the broad band associated to the surface plasmon resonance at ~ 400 nm which forms when silver condensates in nanoparticles. In our sodalime glasses we observe that the photoluminescence (PL) intensity of optically active erbium ions positioned in close proximity of anisotropic Ag nanoparticles is significantly enhanced if the nanoparticles support plasmon modes that are resonant with the erbium emission [12,13]. In other words an energy transfer between Ag nanoparticles and Er ions occurs.

5. Conclusions

XPS analysis of silica–hafnia waveguides and silver ion-exchanged sodalime glasses provide information concerning the nanostructural modifications induced in these materials by changing their composition (hafnium% and silver%, respectively). In the case of silica–hafnia system the relation between O1s BE, chemical bonding modification, and phase separation was demonstrated. In Ag-exchanged sodalime glasses the relative abundance of BO and NBO is discussed in relation with the formation of silver nanoparticles.

In both the systems these structural changes directly influence the optical spectra and in particular the emission from Er^{3+} ions. For this reason the information obtained from XPS are of paramount importance for tuning the fabrication procedure to increase the optical efficiency of these materials.

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