Spectroscopic properties of sol-gel prepared hafnia

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The aim of the studies carried out at beamline „I“ in Hasylab facility was to investigate the spectroscopic properties of sol-gel prepared nanocrystalline hafnia and hafnia-silica powders. The sol-gel route for preparation of composites mentioned inherently causes quite unexpected phase mixtures and defects to be present in otherwise known crystalline systems. In this situation the feedback from spectroscopic measurements is badly needed to understand the structure, defect content and their origin. In present study the emission bands of the samples were determined at different excitation energies as well as the excitation spectra of the most prominent emission band features. Additional temperature dependent changes in spectral features of the samples were recorded to investigate the fine structure of defect related emission.

Figure 1: The PL spectrum of HfO$_2$ and the corresponding excitation spectra for 2.4 eV and 4.0 eV emission bands.

Present study revealed the presence of quite known self trapped exciton emission at ~4.0 eV (slightly shifted to the red) in the sol-gel prepared hafnia (see figure 1). Additionally a broad oxygen vacancy related emission band was observed at ~2.4 eV. While the excitonic emission was expectedly most efficiently excited through band-to-band absorption (>5.8 eV), the defect related band revealed substantial excitation band at ~ 4.2 eV. Based on a comparison to a recent theoretical evaluation of oxygen vacancy species in monoclinic hafnia [1] it is proposed that the excitation band it due to optical transitions from valence band to singly-ionized vacancy (at 4.67 eV) or doubly-ionized vacancy (at 4.91 eV) leading to the 2.4 eV emission.
Additionally the 2.4 eV emission band showed unusual non-monotonic jump-like blue shift at around 140K indicating a temperature assisted change in surrounding of the emitting defect. It is proposed that the cause for jump-like behavior may be phase transition or configurational change in the emitting entity. Similar centre has also been found in sol-gel prepared zirconia meaning that it is common between the two oxides. The results of the work have been published [V. Kiisk et. al. Physica B, 2009, article in press].

References