The role of heat treatment in improving photoluminescence and optically stimulated luminescence of HfO₂

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Abstract. HfO₂ is a metal oxide from the IV-B family whose properties have been widely applied in electronics and which displays an important blue emission. Despite this fact, few studies have been dedicated to understanding the role of heat treatment on its luminescence properties. Therefore, this study aimed to investigate the Photoluminescence (PL) and Optically Stimulated Luminescence (OSL) of HfO₂ powder synthesized by the precipitation method and the influence of calcination on its luminescence. PL spectra results showed a broad emission band at about 2.6 eV, which was related to absorption at 4.1 eV. Green and blue stimulated luminescence spectra depicted emission bands in a similar region, varying between 2.44 up to 2.71 eV. The increase in the heat treatment temperature promoted signal enhancement, which could be associated with higher oxygen vacancy concentrations. OSL dose-response curves for the sample calcined at 1600 °C are linear up to 0.6 Gy and a good signal reproducibility is observed, which makes the material suitable for OSL dosimetry.

1 Introduction

Hafnium Oxide (HfO₂) is a dielectric material that has been increasingly used in the microelectronic area since it shows properties such as high thermal stability, a large bandgap of about 5.6-5.8 eV, and chemical stability [1-2]. It can be synthesized in different ways, allowing it to obtain distinct properties and/or crystallographic phases [2]. Due to the presence of several defects in the material, mainly oxygen vacancies, which explains the possibility of charge transport on it, the material displays important electronic and luminescence properties [1]. Applying high-temperature treatment is an option to increase the defect concentrations and improve its luminescence. In our previous study, it was already pointed out that a calcination treatment at 1600 °C intensified the Thermoluminescence (TL) and Optically Stimulated Luminescence (OSL) emissions [3].

While the noticeable luminescence from this crystal, mostly in the blue region, has already been reported [1], the effect of heat treatment on Photoluminescence (PL) and OSL spectra was not in-depth performed. Therefore, this work aimed to contribute to the luminescent characterization of HfO₂ using PL and OSL spectral measurements and to evaluate the use in OSL dosimetry.

2 Methodology

HfO₂ nanoparticles were synthesized using the precipitation method [3,4], with hafnium tetrachloride (HfCl₄) and potassium hydroxide (KOH) as precursors. Obtained powders were calcined for 2 hours at different temperatures of 1000, 1200, 1400, and 1600 °C.

PL was analysed using a Horiba Fluorolog fluorimeter, which has a 450-W Xenon arc lamp, coupled with a bifurcated fiber-optic probe, composed of illumination and collecting cables and with a numerical aperture of 0.22. OSL spectra and decay curves were obtained using a Lexsyg research TL/OSL reader, with a built-in β source (dose rate of 0.02 Gy/s), and an Andor Technology iDus 420 Series CCD camera coupled to a Shamrock 163 spectrometer. A Schott-BG 39 filter 3 mm was used for IR stimulated luminescence (IRSL) spectra, and a combination of BG39 and an Edmund Optics 525 nm OD4 short pass filter for green stimulated luminescence (GSL) spectra. For Continuous-wave OSL (CW-OSL), a Hoya-U340 7.5 mm was used for blue stimulated luminescence (BSL), different short pass filters centered at 330, 365, and 410 nm for GSL, and for IRSL, the same as used in the spectrum. X-ray irradiation was performed in an Xstrahl chamber model RS225.

3 Results and discussion

Figure 1 depicts the emission and excitation spectra for HfO₂. When the sample is stimulated in the UV region (300 nm), a broad emission band can be noticed in the blue region. The increase in the heat treatment temperature leads to an increase in signal intensity, which may be associated with a higher concentration of defects.
The excitation spectrum shows that the absorption band is centered at about 300 nm, which coincides with the excitation wavelength used for measuring the emission spectrum.

This blue emission has been previously associated with oxygen vacancies and characterized by an absorption band at 5.2 eV [1]. Here, the emission occurs in a similar energy region, whereas the absorption band has a lower energy value. The Chromaticity Diagram from PL data (Fig. 2) presents that besides the signal increase observed, the emission is slightly shifted to a darker blue region.

The heat treatment was also effective in improving the OSL properties, increasing the intensity for both IRSL and GSL spectra. Figure 3 illustrates the case for IRSL measurements. The emission occurs in the same region as for the PL spectra, which indicates that the same defects could be responsible for both luminescence types.

OSL spectra and PL curves fitted with Gaussians equations indicated central energies that vary between 2.44 to 2.71 eV, depending on the type of stimulation and heat treatment (Table 1). IRSL emission bands have energy values slightly lower than those from GSL, which could be related to the higher stimulation wavelength.

For HfO$_2$ calcined at 1600 °C, CW-OSL dose-response curves showed a linear behavior up to 0.6 Gy for green, blue, and IR stimulation. A reproducibility study with 8 cycles demonstrated a variation lower than 10 %.

4 Conclusions

HfO$_2$ crystals display a notable blue emission, related to oxygen vacancies, which can be improved by heat treatment. OSL properties indicate that the material has the potential to be applied as a dosimeter.

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