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Impact of proton irradiation on photoluminescent properties of C-doped ZrO_2 films prepared by ALD

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ABSTRACT

Amorphous C-doped zirconia thin films grown by ALD technique on fused silica substrates have high transmittance and significant photoluminescence (PL) capacity suitable for application as a transparent material to convert high energy into lower energy photons as well as an optical sensor of radiation. Due to carbon doping, zirconia films present three main PL transitions: Transition I and II at $\lambda_{em} = 450$ nm ($\lambda_{exc} = 200$ and 270 nm), related to sp^3 and sp^2 C–C bonds, and Transition III at $\lambda_{em} = 450$ nm ($\lambda_{exc} = 300$ nm) that can be assigned to C═O bonds which introduce n levels in the π- π* gap. Protons with energy of 100 keV and two values of fluence ($1{\bullet}10^{12}$ p^+/cm^2 and $5{\bullet}10^{14}$ p^+/cm^2) were used to modify the film properties. The changes induced by the radiation in the chemical composition of the films have been monitored as a function of irradiation dose using in-depth resolved XPS analysis which evidenced modification of C–Zr, Zr–O, C–H, C–C/C═C and C═O bonds. We demonstrate that C–Zr bonds formed in the film depth are cleaved by protonation in favor of Zr–O, C–H and C═O bonds establishment. As a consequence, more defect levels are formed in the π- π* gap of carbon. Consequently, the emission due to Transitions III becomes more intense for high energy doses, getting intensity values close to Transitions I/II.

1. Introduction

Zirconium oxide (or zirconia, ZrO_2) manufactured using the atomic layer deposition (ALD) technique is a relatively uncommon thin film material for optical applications. ALD enables conformal coating of complicated surfaces and allows for atomic-scale engineering of materials and therefore, for an ideal process for engineering of the optical properties of coatings [1].

For many applications, zirconia may be implemented in the form of coatings, which may be a single film or a multilayer. Zirconia-based coatings are widely used for electric insulation in semiconductor devices [2], or as thermal barriers [3]. Zirconia thin films also represent a way to nanosize the material, which may result in an advantageous strategy for many demanding applications where traditionally bulk or powder materials have been used. The optical properties of thin films are known to be conditioned by their structure and microstructure, both dependent on the manufacturing method and the deposition conditions. Common ways to manufacture thin films of zirconia are (magnetron) sputtering [4] and electron-beam evaporation [5], although pulsed laser deposition [6] and sol-gel technique [7] may also be implemented.

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