Journal of Nuclear Materials 482 (2016) 175–186

Contents lists available at ScienceDirect

Journal of Nuclear Materials

journal homepage: www.elsevier.com/locate/jnucmat

The radiation response of mesoporous nanocrystalline zirconia thin films

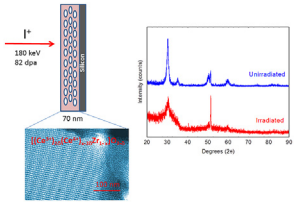
Ayelén M. Manzini [a], Martin A. Alurralde [a], Gustavo Giménez [b], Vittorio Luca [a, *]

[a] Comisión Nacional de Energía Atómica, Centro Atómico Constituyentes, Av. General Paz 1499, 1650 San Martin, Provincia de Buenos Aires, Argentina
[b] Instituto Nacional de Tecnología Industrial - CMNB, Av. General Paz 5445, 1650 San Martín, Provincia de Buenos Aires, Argentina

HIGHLIGHTS

- Radiation response mesoporous and nanocrystalline $Ce_xZr_{1-x}O_2$ thin films measured.
- Radiation response evaluated using X-ray scattering methods XRR and GIXRD.
- Irradiation resulted in film shrinkage and elimination of the monoclinic phase.
- In unstabilized films the tetragonal ZrO_2 phase was stable up to 82 dpa.
- Very little grain growth occurred even at the highest doses.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 28 April 2016
Received in revised form
5 October 2016
Accepted 6 October 2016
Available online 12 October 2016

Keywords:
Irradiation
Zirconia
ZrO_2
Mesoporous
Radiation damage
Thin films

ABSTRACT

The next generation of nuclear systems will require materials capable of withstanding hostile chemical, physical and radiation environments over long time-frames. Aside from its chemical and physical stability, crystalline zirconia is one of the most radiation tolerant materials known. Here we report the first ever study of the radiation response of nanocrystalline and mesoporous zirconia and Ce^{3+}-stabilized nanocrystalline zirconia ($Ce_{0.1}Zr_{0.9}O_2$) thin films supported on silicon wafers. Zirconia films prepared using the block copolymer Brij-58 as the template had a thickness of around 60–80 nm. In the absence of a stabilizing trivalent cation they consisted of monoclinic and tetragonal zirconia nanocrystals with diameters in the range 8–10 nm. Films stabilized with Ce^{3+} contained only the tetragonal phase. The thin films were irradiated with iodine ions of energies of 70 MeV and 132 keV at low fluences (10^{13} - 10^{14} cm^{-2}) corresponding to doses of 0.002 and 1.73 dpa respectively, and at 180 keV and high fluences (2×10^{16} cm^{-2}) corresponding to 82.4 dpa. The influence of heavy ion irradiation on the nanocrystalline structure was monitored through Rietveld analysis of grazing incidence X-ray diffraction (GIXRD) patterns recorded at angles close to the critical angle to ensure minimum contribution to the diffraction pattern from the substrate. Irradiation of the mesoporous nanocrystalline zirconia thin films with 70 MeV iodine ions, for which electronic energy loss is dominant, resulted in slight changes in phase composition and virtually no change in crystallographic parameters as determined by Rietveld analysis. Iodine ion bombardment in the nuclear energy loss regime (132–180 keV) at low fluences did not provoke significant changes in phase composition or crystallographic parameters. However, at 180 keV and high fluences the monoclinic phase was totally eliminated from the GIXRD pattern of films prepared at both 350 and 500 °C implying either a monoclinic-to-tetragonal or a monoclinic-to-amorphous transition. This irradiation at very high doses resulted in film shrinkage and a loss of mesopore ordering but little or no degradation of the crystallinity of the tetragonal phase. A small increase in the

* Corresponding author.
E-mail address: vluca@cnea.gov.ar (V. Luca).

http://dx.doi.org/10.1016/j.jnucmat.2016.10.019

crystalline domain size of the $tZrO_2$ phase was noted in these films. In contrast, single-phase Ce^{3+}-stabilized tetragonal nanocrystalline zirconia mesoporous films prepared at 350 °C suffered considerable loss of crystalline order when irradiated at 82 dpa. This loss of crystallinity was less pronounced in films heated to 500 °C. The loss of crystallinity of the tetragonal phase in the Ce-stabilized tetragonal zirconia thin films w.r.t. the tetragonal phase in the unstabilized films was attributed to the oxygen vacancies introduced in the latter due to the need for charge compensation.

1. Introduction

In the fusion and fission nuclear systems of the future there will be a need for materials that can tolerate extreme conditions of temperature and pressure as well as extremely intense radiation fields [1,2]. In the case of advanced fission energy systems, radiation tolerance is important both in terms of the endurance of structural materials and as inert matrix fuels for the burning of minor actinides. The stability of the matrix is also of paramount importance when contemplating materials for direct immobilization of actinides and fission products present in PUREX raffinates where self-irradiation is important [3]. Considerable effort has gone into developing glasses, ceramics and glass-ceramic waste forms that are chemically durable and radiation tolerant over very long time frames [4].

Although many decades of intense research have gone into understanding the radiation response of a wide range of materials in the context of all of the above applications, many questions remain as to what really determines the radiation response of different materials including ceramics [5].

Most studies of the radiation response of ceramics have focused on bulk microcrystalline oxides. However, it is well appreciated that the properties of materials at the nanoscale can be markedly different from those of their bulk microcrystalline counterparts. The literature is replete with descriptions of nanomaterials that show dramatic differences in physical, chemical, electronic, catalytic, magnetic and mechanical properties with respect to their bulk properties. Therefore, there is little expectation that nanocrystalline materials should behave similarly to microcrystalline materials in their response to radiation.

In fact relatively few studies have so far been published aimed at understanding the differences in the radiation response between nanostructured and bulk materials. Although common wisdom suggests nanocrystalline materials with higher surface-to-volume ratios and therefore a higher proportion of defect sinks should possess greater radiation resistance [6,7], it has been well noted [8,9] that this is not always the case.

Bulk crystalline zirconium oxides are reputedly among the most radiation tolerant materials known. It has been reported that microcrystalline cubic ZrO_2 can tolerate swift heavy ion irradiation up to whopping doses of 200 [10] and 680 dpa [11] without becoming amorphous. In contrast, it has been reported that nanocrystalline ZrO_2 with particle size of 3 nm can be easily amorphized using 1 MeV Xe^{2+} at a flux of 6.25×10^{11} cm^{-2} s^{-1} corresponding to doses only about 1 dpa [12]. This is a highly surprising result given that some studies indicate that reduction into the nanometer size regime results in a great improvement in radiation tolerance owing to defect annihilation at surfaces [6]. More recent studies on relatively dense nanocrystalline ZrO_2 films hundreds of nanometers in thickness and comprising nanoparticles of tens of nanometers have shown marked grain growth but no amorphization [13–15].

These studies highlight the differences in radiation response of ZrO_2 at the micro and nano scale regimes. Uberuaga et al. [16] have thrown into sharp relief the importance of grain boundary structure on sink efficiency.

Mesoporous metal oxides prepared by supra-molecular templating constitute a relatively new class of materials and they can have very high surface areas and therefore an abundance of grain boundaries far beyond those observed in the abovementioned materials. They can be prepared with an enormous range of pore architectures and compositions and having different physical forms including xerogels, monoliths and thin films. Aside from variability in pore architecture it is also possible to prepare many mesoporous metal oxides that not only possess ordered pores but in which the pore walls are made up of tiny nanocrystals. Mesoporous silicates are not in this category since they generally display high degrees of pore ordering but never any crystallinity in the pore walls. On the other hand group IV mesoporous oxides such as TiO_2 and ZrO_2 can be prepared that show both pore ordering and nanocrystalline walls. Although methods for the preparation of mesoporous zirconia and titania thin films with nanocrystalline walls were described some time ago, these showed collapse of porous structure at relatively low temperatures [17]. Recently the preparation of highly thermally stable mesoporous nanocrystalline zirconia thin films has been reported [18]. It is well appreciated that transport and other properties of oxide films depend critically on the porosity of the architecture of thin films [19]. It should be fairly obvious that by far the largest contribution to porosity and the density of exposed nanocrystal interfaces is attributed to the pore surfaces rather than the film surfaces themselves. Many intriguing questions could therefore be posed as to how such interesting materials respond to radiation.

For the abovementioned class of mesostructured materials the radiation response has only very recently begun to be addressed. Dourdain et al. [20] reported the first study of the radiation response of hexagonal mesoporous silicate thin films with non-crystalline pore walls using swift heavy ion irradiation (Xe, $E = 92$ MeV at 10^{14} cm^{-2}). For such films it was demonstrated that the impact of heavy ion irradiation on pore ordering was subtly dependent on the crystallographic symmetry of pore ordering. It was observed that a 3D hexagonal ($P6/mmc$) SiO_2 film comprising spherical pores of about 2.5 nm in diameter were rendered completely X-ray amorphous while a 2D hexagonal ($P6m$) film comprising cylindrical pores having a diameter of 5.3 nm maintained order after comparable irradiations. No hypothesis for why the film with smaller pores was more easily damaged was ventured. In contrast there are no reports of the radiation response of mesoporous and nanocrystalline metal oxide thin films.

The objective of the present study was to measure and understand the radiation response of mesoporous and nanocrystalline ZrO_2 thin films (60–80 nm) supported on silicon wafers and to compare with films stabilized in the tetragonal phase using Ce^{3+}. Given that such materials are extremely porous and possess abundant free interfaces they should be quite radiation resistant compared to bulk materials. Iodine ions in two energy regimes