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Evidence of an ion-beam induced crystalline-to-crystalline phase transformation in hafnia

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Abstract. Samples of monoclinic hafnia were irradiated with increasing fluences of 800 and 300 MeV Kr ions giving rise to a slowing down essentially caused by high electronic excitations. Their structural evolution was monitored *in situ* by the X-ray diffraction technique. The results indicate, for the first time to our knowledge, the occurrence in monoclinic hafnia of an ion-beam induced crystalline-to-crystalline phase transition. The new formed phase is very likely tetragonal and appears with an effective threshold in the deposited electronic energy loss which is around 20 keV nm^{-1}. In addition, the evolution of the amount of the produced phase with the ion fluence exhibits a sigmoidal shape suggesting a mechanism for phase transformation which needs two ion impacts. Some features of this phase transition are compared with those obtained in the case of zirconia, a well-known isomorphic material with hafnia.

PACS. 61.80.Jh Ion radiation effects – 61.82.Ms Insulators – 64.70.Kb Solid-solid transitions

1 Introduction

It is generally admitted that the irradiation of crystalline oxides with high energy heavy ions, where the slowing down is mainly due to the electronic energy loss, often leads to the formation of highly defective or amorphous tracks along the ion trajectories. However, recent results demonstrate that in certain circumstances crystalline-to-crystalline phase transitions can also occur. This is well illustrated with the case of pure zirconia (ZrO_2) which can undergo a transformation from the monoclinic to the tetragonal phase [1-5]. Since ion-beam induced crystalline-to-crystalline phase transition appears to be a relatively uncommon phenomenon, it came out highly desirable to extend these studies to other materials in order to comprehend the underlying mechanisms of this transformation.

For this purpose, hafnia (HfO_2) seems to be a good candidate. The reason for that comes from the fact that hafnium and zirconium are known to present remarkable resemblance in their metallic state as well as in their compounds. This likeness is most important than in any group of two elements. This is not only due to their electronic structure but also comes from the quasi-identity of their atomic (1.6 Å for Zr and 1.67 Å for Hf) and ionic radii (0.8 Å for Zr and 0.81 Å for Hf). Accordingly, hafnium dioxide (HfO_2) has chemical, structural, and physical properties which present many similarities with those of zirconium dioxide (ZrO_2). For example, under normal pressure and temperature conditions, both oxides have a monoclinic structure. For zirconia, the lattice parameters are such that: $a = 5.150$ Å, $b = 5.211$ Å, $c = 5.317$ Å and $\beta = 99.23°$; while for hafnia, the elementary cell is just slightly modified: $a = 5.1170$ Å, $b = 5.1754$ Å, $c = 5.2915$ Å and $\beta = 99.21°$. In addition, during heat treatment, both zirconium dioxide and hafnium dioxide are known to undergo a first transition to the tetragonal phase followed by a second transition to the cubic phase. For instance, the tetragonal phase appears at ~ 1100 °C for zirconia and at ~ 1800 °C for hafnia.

Therefore, owing to these various chemical, physical, and thermodynamical similarities, it appears quite attractive to explore the possibility of ion-beam induced phase transition in HfO_2.

2 Experimental

The raw material comes from a commercial hafnia powder having a purity of 99.9 %, a grain size around 5 μm, and consisting of monoclinic hafnia. The samples were prepared in the form of pellets having a diameter of 12 mm and a thickness ~ 1 mm obtained by compaction at room temperature and under a pressure of 330 MPa. They were heated at 900 °C for 6 hours in order to improve their toughness allowing then an easy handling. The samples were irradiated with Kr ions of 800 and 300 MeV at the medium energy line of the Ganil accelerator in Caen. Both irradiations were performed at room temperature with an ion flux limited to 3×10^8 ion cm^{-2} s^{-1} in order to minimize target heating and charge effects. The samples

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were characterized *in situ* by X-ray diffraction analyses using a diffractometer equipped with a copper anticathode and a curved position sensitive detector covering an angular domain of 120°. The X-ray incident angle was fixed at 12° in order to have a probed depth limited to $\sim 1\,\mu$m, significantly lower than the ion projected ranges and within a thickness where the electronic and nuclear energy losses of the irradiating ions remain nearly constant. As a matter of fact, according to the TRIM code [6], the ion projected ranges of 800 and 300 MeV Kr ions in monoclinic hafnia (assuming a density of $9.68\ \mathrm{g\,cm^{-3}}$) are $\sim 42.4\,\mu$m and $\sim 17.5\,\mu$m, respectively. In the thickness probed by the analyzing X-rays (*i.e.*, $\sim 1\,\mu$m), the electronic and nuclear stopping powers of these ions are practically constant and respectively equal to $\sim 18.3\,\mathrm{keV\,nm^{-1}}$ and $\sim 13.7\,\mathrm{eV\,nm^{-1}}$ in the case of 800 MeV Kr, and $\sim 21.9\,\mathrm{keV\,nm^{-1}}$ and $\sim 31.7\,\mathrm{eV\,nm^{-1}}$ for the irradiation with 300 MeV Kr ions.

3 Results and discussion

Similarly to the case of zirconia, the three allotropic phases of hafnia are very close to each other from the crystallographic point of view. Therefore, a lot of their characteristic X-ray diffraction peaks arise nearly at the same angle [7]. However, the most intense lines which arise at $2\theta \sim 30°$ are almost well resolved: the (101)/(111) line of the tetragonal/cubic phase is located between the well separated $(11\bar{1})$ and (111) peaks of the monoclinic phase. Consequently, for the identification of a phase transition in this material (monoclinic ↔ tetragonal/cubic), only the region of the X-ray spectra located between $2\theta \sim 27°$ and $2\theta \sim 33°$ is of great interest. Accordingly, Figure 1a presents, within this angular domain, the evolution with the ion fluence of the X-ray spectra recorded on a monoclinic hafnia sample before and after irradiation with 800 MeV Kr ions. It appears that these spectra do not exhibit any significant change with the ion irradiation. The lines $(11\bar{1})$ and (111) characteristic of the monoclinic phase remain present and there is no evidence for an appearance of an additional peak. Therefore, one can deduce from these results that there is no ion-beam induced phase transition with 800 MeV Kr ions up to a total fluence of $1.3\times10^{13}\ \mathrm{Kr\,cm^{-2}}$. In addition, Figure 1b also shows the evolution with the ion fluence of the X-ray spectra recorded on a hafnia pellet before and after irradiation with 300 MeV Kr ions. In contrast to Figure 1a, these spectra clearly exhibit the appearance of a new peak at $2\theta \sim 30°$ as well as a reduction of the intensity of the lines $(11\bar{1})$ and (111) belonging to the monoclinic phase. These changes start to appear at $\sim 6\times10^{12}\,\mathrm{Kr\,cm^{-2}}$ and they increase with the ion fluence up to $\sim 2.5\times10^{13}\,\mathrm{Kr\,cm^{-2}}$ where they seem to saturate. The fact that the peaks $(11\bar{1})$ and (111) of the monoclinic phase are still present even at very high fluences indicates that a significant fraction of monoclinic hafnia still remains in the irradiated sample. The peak which appears at $2\theta \sim 30°$ can be ascribed either to the line (101) of the tetragonal phase or to the line (111) of the cubic structure, or to a possible mixture of these two phases. This peak is thus the proof of the occurrence of a phase transformation from the monoclinic to the tetragonal and/or the cubic phase. It is worth mentioning that a similar situation was previously observed in zirconia; however, additional Raman analyses permitted to reveal that the final state of the phase transition is mainly tetragonal and certainly not cubic [1]. Therefore, owing to the strong isomorphism between $\mathrm{HfO_2}$ and $\mathrm{ZrO_2}$, one can reasonably assume that in the case of hafnia the new formed phase is also tetragonal. Nevertheless, so as to definitely ascertain the exact nature of the formed phase and to especially collect some details about the atomic movements leading to this structural transformation, the recourse to other microstructural characterization techniques is planned in the near future.

Furthermore, in order to identify the driving force of this phase transformation, an additional experiment [8] was performed by irradiating other hafnia pellets with 5 MeV Br ions. These samples were also analyzed by X-ray diffraction with an incident angle of 2° in order to probe a depth $\sim 0.25\,\mu$m, well below the ion-projected range $\mathrm{R}_p \sim 1.22\,\mu$m. Within the depth probed by the X-rays, the estimated average electronic and nuclear energy losses are $\sim 3.3\,\mathrm{keV\,nm^{-1}}$ and $\sim 689\,\mathrm{eV\,nm^{-1}}$, respectively. It is worth to mention that no phase transformation was detected up to a total fluence of $10^{16}\,\mathrm{Br\,cm^{-2}}$. Consequently, the phase transition induced by 300 MeV Kr ions cannot be ascribed to the nuclear energy loss but to the electronic energy loss instead. Moreover, since 800 MeV Kr ions do not induce any phase transformation up to $1.3\times10^{13}\,\mathrm{Kr\,cm^{-2}}$, one can deduce that there is an apparent threshold in the electronic energy loss which is located between 18 and $22\,\mathrm{keV\,nm^{-1}}$.

Owing to the fact that hafnia exhibits X-ray diffraction patterns quite similar to those of zirconia [7] (due to the strong isomorphism between the two materials), the quantitative analysis of the X-ray spectra can also follow the method proposed by Garvie and Nicholson [9]. According to this method, the concentration C of the tetragonal phase is directly given by:

$$C = \frac{I(101)}{I(11\bar{1}) + I(111) + I(101)} \tag{1}$$

where $I(11\bar{1})$, $I(111)$, and $I(101)$ are the peak integrals of the corresponding lines $(11\bar{1})$, (111), and (101) of the monoclinic and tetragonal phases. The results obtained by such analysis are presented in Figure 2 which describes the evolution of the tetragonal phase produced by 300 MeV Kr ions in function of the ion fluence. It clearly appears that the kinetics of the phase transition has a sigmoidal shape like in zirconia [2–4]. It is well-known that such a behavior is a signature for the necessity of track overlapping before phase transition can develop. Therefore, in the same way to the case of zirconia, it is possible to reproduce the experimental data with the following expression [10–12]:

$$\Delta C(\Phi) = \Delta C(\infty)\left(1 - \sum_{k=0}^{n-1} \frac{(\sigma\Phi)^k}{k!}\exp(-\sigma\Phi)\right) \tag{2}$$

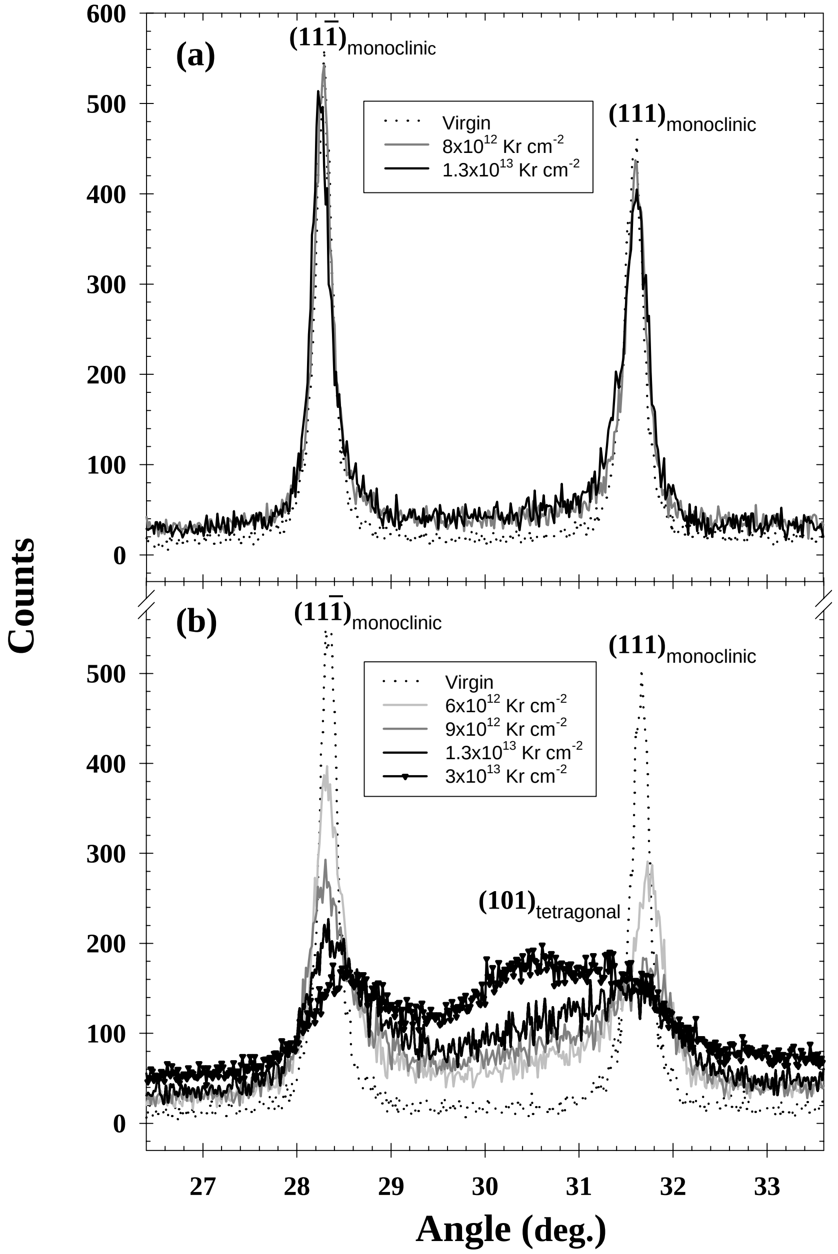

Fig. 1. X-ray spectra recorded on hafnia samples before and after irradiation with different fluences of 800 MeV (a) and 300 MeV (b) Kr ions. For the sake of clarity, only the angular domain delimited by the diffraction peaks (11$\bar{1}$) and (111) of the monoclinic phase is shown.

where $\Delta C(\Phi)$ is the increase of the concentration of the tetragonal phase with the ion fluence Φ, $\Delta C(\infty)$ the total increase of this concentration at saturation, σ the cross section of the cylinder around the ion trajectory where matter undergoes transformation, and n the minimum number of ion impacts necessary to reach the final state. The fit of equation (2) to the experimental data is represented by a solid line in Figure 2 and provides the following values: $\Delta C(\infty) = 0.42$, $\sigma = 1.6 \times 10^{-13}$ cm^2, and $n = 2$.

The fact that the concentration of the tetragonal phase reaches a saturation value of 0.42 at very high fluences indicates that the ion-beam induced monoclinic to tetragonal phase transition is far from being entirely completed. Such a result confirms more significantly the previous indications obtained in zirconia where the saturation value was found to be around 0.85 [2–4]. The difference between the two saturation values may express that the monoclinic to tetragonal transition is more difficult to develop in hafnia than in zirconia. Such a behavior deviates from the various well-known similar chemical and physical properties shared by these materials. Nevertheless, it is worth mentioning that other saturating partial transformations

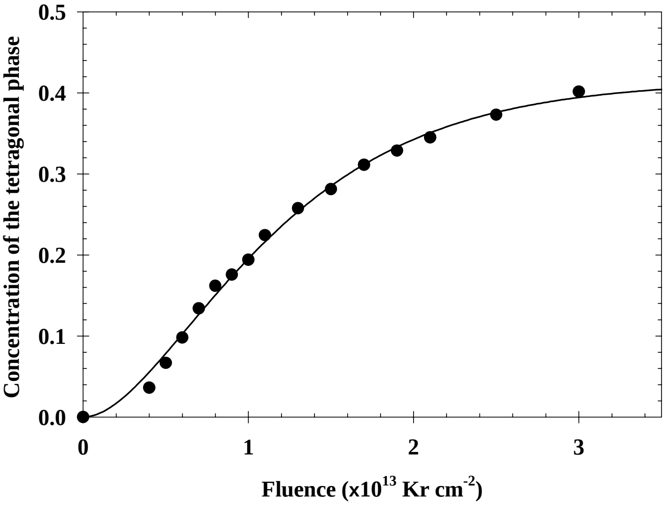

Fig. 2. Evolution with the ion fluence of the concentration of the tetragonal phase in the case of the irradiation with 300 MeV Kr ions.

also exist in other processes involving ion irradiation like amorphization of alumina at low energy [13] and disordering of calcium fluoride at high energy [14].

The fit of the experimental data clearly indicates that the minimum number of ion impacts necessary to reach the final transformed state (which is a mixture of the tetragonal and monoclinic phases) is equal to 2. This is exactly what was observed in zirconia within a wide range of the deposited electronic energy loss obtained by varying the nature and the energy of the irradiating ions [2–4]. Therefore, it appears that in both materials, the kinetics of the phase transition requires a double ion impact mechanism suggesting that the latter is most likely a constant feature of this phase transformation. The role of the first ion impact is probably to create enough radiation-induced defects mostly oxygen vacancies which seem to be necessary to assist the transition from the monoclinic to the tetragonal phase by allowing for the expansion of the interatomic distances and the increase of the cation coordination number [15,16].

The obtained value of the average cross section ($\sigma = 1.6 \times 10^{-13}$ cm^2) of the cylinder where matter undergoes transformation when the deposited electronic energy loss ($21.9\,\mathrm{keV\,nm^{-1}}$) is just above the threshold is quite comparable to that obtained in similar conditions in zirconia ($\sigma = 1.8 \times 10^{-13}$ cm^2 for $\frac{\mathrm{d}E}{\mathrm{d}x} = 14.2\,\mathrm{keV\,nm^{-1}}$). This result also corroborates the fact that the same mechanism is responsible for phase transformation in both materials.

The present experiments also allowed to deduce an effective threshold in the electronic energy loss for the monoclinic to tetragonal phase transition in hafnia which is about 20 $\mathrm{keV\,nm^{-1}}$ quite above the corresponding value ($\sim$ 13 $\mathrm{keV\,nm^{-1}}$) obtained in the case of zirconia. It is worth mentioning that these threshold values evolve in the same direction as the corresponding transition temperatures at equilibrium, namely ~ 1400 K for zirconia and ~ 2100 K for hafnia. Such a result certainly deserves further investigations.

4 Conclusion

The experiments reported in the present paper reveal for the first time that ion irradiation of monoclinic hafnia can induce a transition to another crystalline phase. The latter is very likely tetragonal. This result gives additional evidence that swift heavy ion irradiations of crystalline materials are not limited –as usually assumed– to damage creation giving rise either to defect formation within the original structure or sometimes to crystalline to amorphous phase transition. Moreover, it appears that this crystalline-to-crystalline phase transition is not fully complete and that its kinetics obeys a double impact mechanism. Finally, it was found that the threshold in the electronic energy loss for inducing the phase transition in hafnia ($\sim 20\,\mathrm{keV\,nm^{-1}}$) is quite higher than that determined previously for zirconia ($\sim 13\,\mathrm{keV\,nm^{-1}}$) in agreement with the corresponding transition temperatures at equilibrium.

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