5.2 IRRADIATION EFFECTS ON MICROSTRUCTURE AND OPTICAL PERFORMANCE OF MULTILAYERED DIELECTRIC MIRRORS

N.A.P. Kiran Kumar, K.J. Leonard, G.E. Jellison and L.L. Snead (*Oak Ridge National Laboratory)*

OBJECTIVE

The goal of this work is to evaluate the upper neutron irradiation dose and thermal limits of two promising dielectric mirrors types, through an investigation of the radiation and thermally induced microstructural and optical property changes. While specifically of interest for use in laser control of inertial confinement fusion systems, the examination of the radiation induced structural changes in the films will be beneficial for the development of other thin-film based electronic components and sensors used in nuclear applications.

SUMMARY

Specifically engineered Al_2O_3/SiO_2 and HfO_2/SiO_2 dielectric mirrors grown on sapphire substrates and exposed to neutron doses of 1 and 4 dpa at 458±10 K in the High Flux Isotope Reactor (HFIR), resulted in reductions in optical reflectance, indicating a failure of the multilayer coating. HfO_2/SiO_2 mirrors failed completely when exposed to 1 dpa, whereas the reflectivity of Al_2O_3/SiO_2 mirror reduced to 50%, eventually failing at 4 dpa. Transmission electron microscopy (TEM) observation of the Al_2O_3/SiO_2 specimens showed defects increase in size with irradiation dose from 1 to 4 dpa. Heavy interdiffusion leading to formation of Al-Si rich phase and cracking of some of Al_2O_3 layers was observed across the Al_2O_3/SiO_2 mirrors; however the interdiffusion is less evident in HfO_2/SiO_2 mirrors. Delamination at the interface between the substrate and first layer was typically observed in both 1 and 4 dpa HfO_2/SiO_2 specimens, where buckling type delamination was a major observation at all doses.

PROGRESS

Introduction

Dielectric mirrors (also known as Bragg reflectors) are considered as one of the crucial components for both inertial and magnetic confinement fusion systems where they function as transmitters of electromagnetic energy with extremely low losses. These mirrors are made up of thin alternating layers of high and low refractive index dielectric material deposited on a substrate. The refracted light from these 1/4λ thick layers results in constructive interference producing high levels of reflectance. Changes to the number, type and thickness of layers allow mirror tuning to a specific wavelength and working range of peak reflectance [1]. While the as-irradiation performance is critical for fusion application, dielectric mirrors have historically performed poorly under irradiation due to their underlying constituents. High quality mirrors are required for diagnostic and remote handling applications in fusion reactors [2]. Any limitations in the mirrors would severely impact the efficiency of the mirror considered for fusion systems.

The present study was performed on Al_2O_3/SiO_2 and HfO_2/SiO_2 dielectric mirrors exposed to neutron doses of 1 and 4 dpa at 185±10°C in the High Flux Isotope Reactor (HFIR). This study is an extension of our previous study on the low dose irradiated dielectric mirrors where the Al_2O_3/SiO_2 mirror showed an impressive radiation resistance at 0.1 dpa and HfO_2/SiO_2 mirror showed loss in reflectivity following post irradiation annealing due to crystallinity changes [3, 4]. The objective of this work is to continue beyond the earlier low dose studies (0.1 dpa and less) to fully understand the failure mechanisms that were beginning to be observed in earlier studies. Understanding the origin of coating damage would not only provide important information for the development of future multilayer mirrors but also helps in producing coating with improved irradiation stability.

Experimental Procedure

The Al_2O_3/SiO_2 and HfO_2/SiO_2 mirrors were obtained from Spectrum Thin Films Inc. The mirrors were produced with ion-assisted electron beam vapor deposition. This deposition method has been the standard process for fabricating multilayer optical coatings due to its ability to scale-up to large substrate sizes and its flexibility for complex designs at relatively low cost. Sapphire was used as a substrate for both the mirrors and all the mirrors used in the present study were designed for an optimum reflectivity at 248 nm. Al_2O_3/SiO_2 mirror consist of 30 bi-layers and HfO_2/SiO_2 consist of 11 bi-layers with the high index layers such as Al_2O_3 and HfO_2 being the first and last layers of the respective mirrors. The sapphire substrates are of 6 mm in diameter and 2 mm in thickness with a surface roughness <10A°.

Earlier studies on the samples involved the neutron irradiation of the mirrors samples to 0.001, 0.01 and 0.1 dpa at 448±10 K. The current work involves the irradiation of a second set of samples to higher doses followed by analysis of the optical and microstructural changes to the mirrors. Irradiations to $1x10^{26}$ and $4x10^{26}$ n/m^2 (E>0.1 MeV) at 458±10 K, corresponding to approximately 1 and 4 dpa, were completed in the peripheral hydraulic tube at the HFIR. The samples are encapsulated in specialized 1100 grade Al holders to eliminate damage to the mirror surfaces, while targeting the appropriate irradiation temperature. The sample holders were unloaded in the LAMDA lab to ensure proper handling of the mirrors.

Optical examination of the samples included measuring changes in the relative spectral reflectance versus wavelength and the absolute reflectivity at 248 nm for the irradiated and post-irradiated annealed specimens. The optical changes are correlated to microstructural changes in the films examined through transmission electron microscopy (TEM) and compared to the unirradiated controls in order to elucidate strain effects at the film/substrate interface.

Results and Discussions

Microstructure of As-received Dielectric Mirrors

Figure 1 shows the cross-sectional bright-field images with the layered structure of the as-received Al_2O_3/SiO_2 and HfO_2/SiO_2 mirrors. Al_2O_3/SiO_2 mirrors consist of 30 bi-layers and HfO_2/SiO_2 mirrors consist of 11 bi-layers. Each layer of Al_2O_3/SiO_2 mirrors showed amorphous structure and the average layer thicknesses of the Al_2O_3 and SiO_2 films in the TEM images are 33 nm and 40 nm, respectively. The as-deposited bi-layers of HfO_2/SiO_2 mirror comprise of polycrystalline HfO_2 layers, showing monoclinic structure with some amorphous regions between the grains, and amorphous SiO_2 layers with average layer thicknesses of 26 nm and 40nm, respectively. The average crystallite size of polycrystalline HfO_2 layers is 13 nm. The films show clear and smooth layers with no intermixing. The high resolution TEM micrograph in Figure 1 (d) shows the grain orientations of polycrystalline HfO_2 layer. HfO_2 grains showed no orientation preference within the HfO_2 layers.

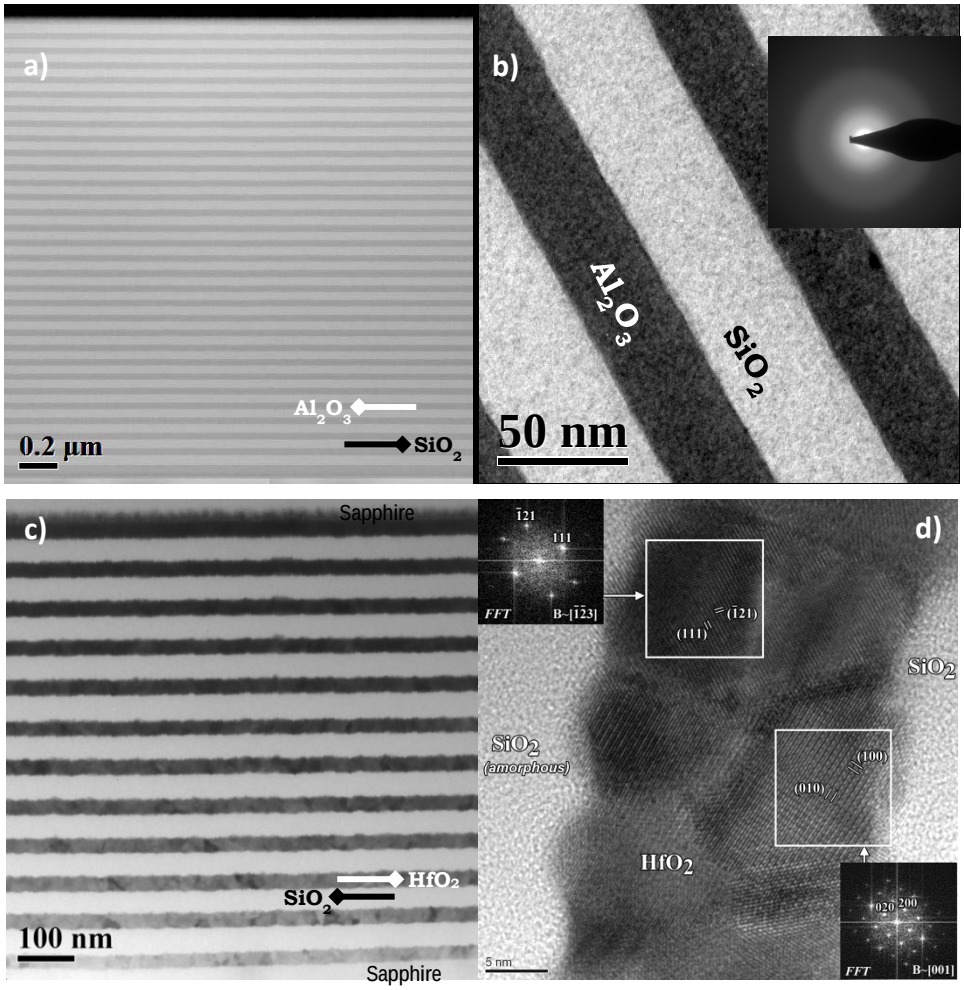


Figure 1. Cross-section TEM micrographs of a) Al_2O_3/SiO_2 mirror showing layered structure, b) High resolution image of Al_2O_3/SiO_2 mirror with an embedded diffraction pattern confirming the amorphous structure of the layers c) HfO_2/SiO_2 mirror showing layered structure d) High resolution image of HfO_2/SiO_2 mirror showing the grain orientation (Insert is the fast Fourier-transformation (FFT) showing the crystal orientation).

Optical Properties of the Irradiated Dielectric Mirrors

Both Al_2O_3/SiO_2 and HfO_2/SiO_2 mirrors were specifically designed to exhibit maximum reflectivity at wavelength of 248 nm. Figure 2 shows the measured reflectance spectrum of two types of mirrors exposed to different irradiation doses. The measurements performed with a spectrophotometer has been normalized to the absolute reflectivity of each sample measured specifically using a NeCu laser (Photon Systems, deep UV NeCu laser, 248.6 nm wavelength). Minimal or no noticeable change in reflectivity was observed following neutron irradiation to 0.1 dpa. Detailed study on optical behavior of low dose irradiation mirrors can be found elsewhere [4]. A drastic drop in reflectance was observed in the specimens subjected to 1 dpa and 4 dpa. HfO_2/SiO_2 mirrors failed completely when exposed to 1 dpa, whereas the reflectivity of Al_2O_3/SiO_2 mirror reduced to 50% at 1 dpa and the mirror failed at 4 dpa. The loss in optical reflectivity indicates the failure of multilayer coating at higher doses. Generally, the optical reflectivity of the dielectric mirrors depends on several factors such as interface roughness and non-uniform layer thickness. In addition, preferential swelling in the layers, leading to flaking off of the film

layers could also impact the reflectivity of the multilayers [5]. However, visual inspection of the mirrors after higher dose irradiations showed no signs of crazing or large scale pealing of the mirror layers, but did show localized speckling indication that the drop in reflectance of high dose irradiated mirrors is more due to local microstructural changes rather than broad scale changes related to substrate / film strain influences.

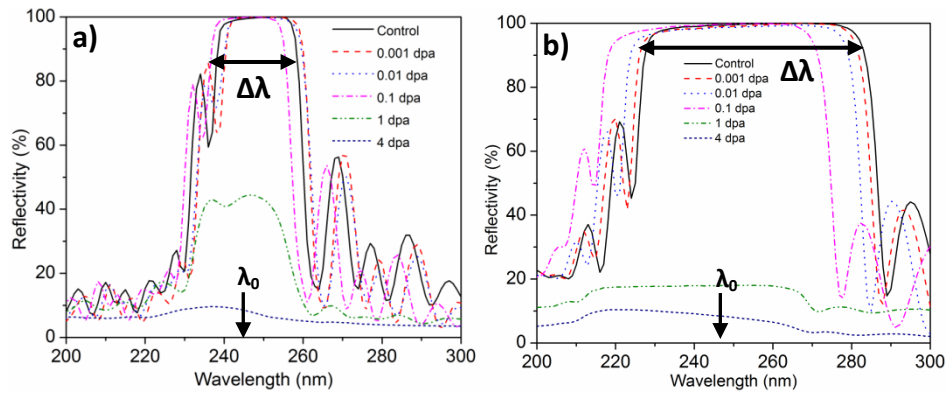


Figure 2. Reflectance of the mirrors compared with low dose results a) Al_2O_3/SiO_2 mirrors b) HfO_2/SiO_2 mirrors

<u>Microstructural Changes in Irradiated Al_2O_3/SiO_2 Mirrors</u>

TEM observation of the irradiated Al_2O_3/SiO_2 specimens showed partial crystallization of Al_2O_3 layers. Selected area electron diffraction pattern revealed a pattern indicative of crystalline structure which could be indexed as cubic γ-Al_2O_3. Figure 3 shows the layered structure and diffraction pattern of the Al_2O_3/SiO_2 mirror exposed to 1 dpa. The γ-Al_2O_3 is described as a defect spinel structure with several cation site vacancies. The amorphous Al_2O_3 (α-Al_2O_3) transform to crystalline γ-Al_2O_3 at elevated temperatures [6, 7]. Furthermore, radiation induced structural transformation of thermodynamically stable α-Al_2O_3 into metastable polymorphs such as κ-, γ-, δ-,θ-Al_2O_3 has also been well established [8, 9]. In contrast, limited studies have been performed to investigate the structural changes in α-Al_2O_3 after irradiation with particles such as ion, neutron and electron. Few studies showed the transformation of α-Al_2O_3 to γ-Al_2O_3 occur under electron irradiation by breaking and rearrangement of unstable Al-O bonds [10-12]. Similar phase transformation was also observed after high energy ion irradiations on α-Al_2O_3 films [13, 14]. The metastable nature of the γ-Al_2O_3 equally promotes reverse transformation of γ-Al_2O_3 to α-Al_2O_3 under irradiation [14]. Therefore, additives such as Si increase the stability of γ-Al_2O_3 [15, 16] where, Si cations occupy the vacancies in γ-Al_2O_3 leading to formation of strong and short Si-O bonds consequently stabilized the γ-Al_2O_3 phase. Although, the overall mechanism leading α-Al_2O_3 to γ-Al_2O_3 structural change under irradiation is still not clear. In the current study it was believed that the atomic rearrangement during irradiation lead to transformation of α-Al_2O_3 to γ-Al_2O_3, where the latter phase is stabilized by diffusion of Si atoms.

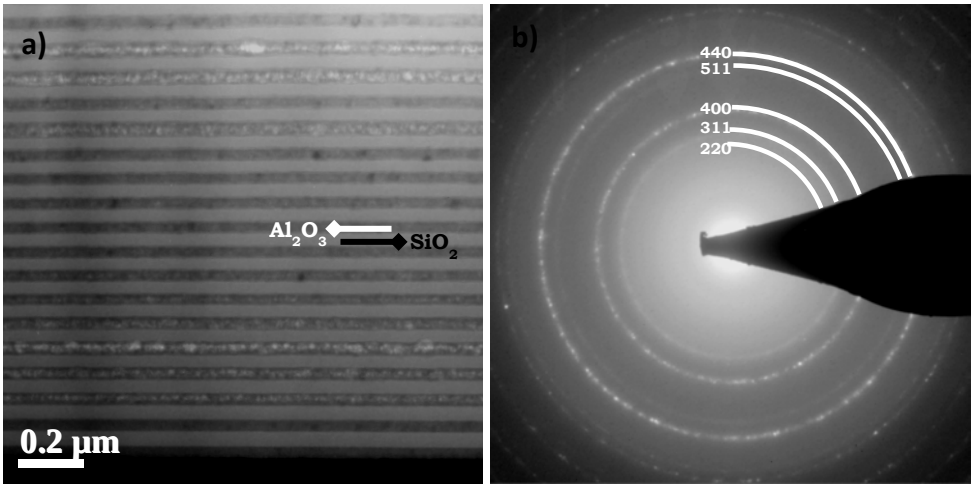


Figure 3. Al_2O_3/SiO_2 mirror after 1 dpa exposure. a) Layered structure b) Diffraction pattern

<u>Al_2O_3 and SiO_2 interdiffusion</u>

Low temperature solid state diffusion is a typical phenomenon observed in irradiated materials. The diffusion rates of Al and Si atoms differ significantly and several factors such as irradiation temperature and irradiation dose influence the diffusion process [17]. Severe interdiffusion was observed in Al_2O_3/SiO_2 mirrors after irradiations (see Figure 4 and 5). The formation of Al-Si rich regions on the Al_2O_3 layers was typically observed at both doses. However, uniformity in the second phase formation was not observed. Only few Al_2O_3 layers were found to have Al-Si rich regions, whereas in the other Al_2O_3 layers less segregation was observed. In addition, SiO_2 layers adjacent to Al-Si rich Al_2O_3 layers shrunk more than other SiO_2 layer in the specimen lead to non-uniform layer thickness of the SiO_2 layers.

The partial crystallization of α-Al_2O_3 to γ-Al_2O_3 could be the reason for this complex behavior of the Al_2O_3/SiO_2 mirrors under high dose irradiations. In general, the energy required to displace an atom from the lattice site of any material depends on factors such as bonding strength and the ability of the material to accommodate an interstitial atom in the structure. The aluminum and oxygen ions in Al_2O_3 have threshold displacement energies of 20 and 65 eV whereas silicon and oxygen atoms in SiO_2 have displacement energies of 20 and 10 eV, respectively [18,19]. In addition, the ionic material such as Al_2O_3 show higher binding energy than covalent bonded SiO_2. Accordingly irradiation would introduce nonstoichiometric numbers of Si, O and Al atoms and also due to weak bonding structure of SiO_2, more Si and O atoms will be displaced than Al atoms. Therefore, during irradiation gradual transformation of α-Al_2O_3 to γ-Al_2O_3 occurs by inward diffusion of excess oxygen atoms produced from SiO_2 layers. Further, the transformed γ-Al_2O_3, with a defect structure and cation vacancies, would act as precursor for the diffusion of silicon atoms, where the enhanced diffusion leading to formation of Al-Si rich phase was observed. The segregation at the other sites where the Al_2O_3 still shows amorphous structure is much less.

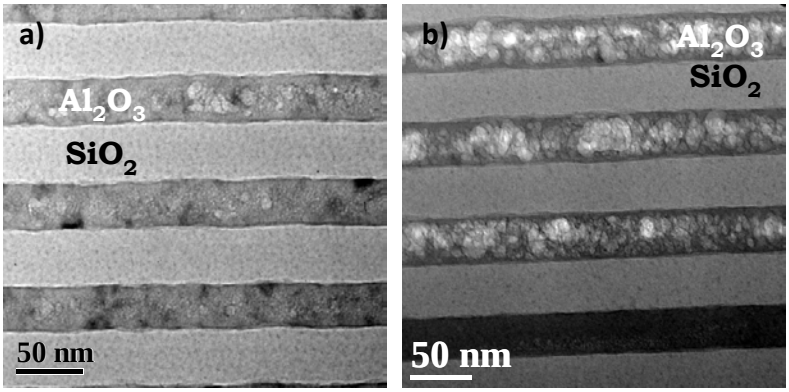


Figure 4. Al_2O_3/SiO_2 mirror exposed to 1 dpa showing non-uniform second phase formation on Al_2O_3 layers a) Less segregation b) Heavy segregation

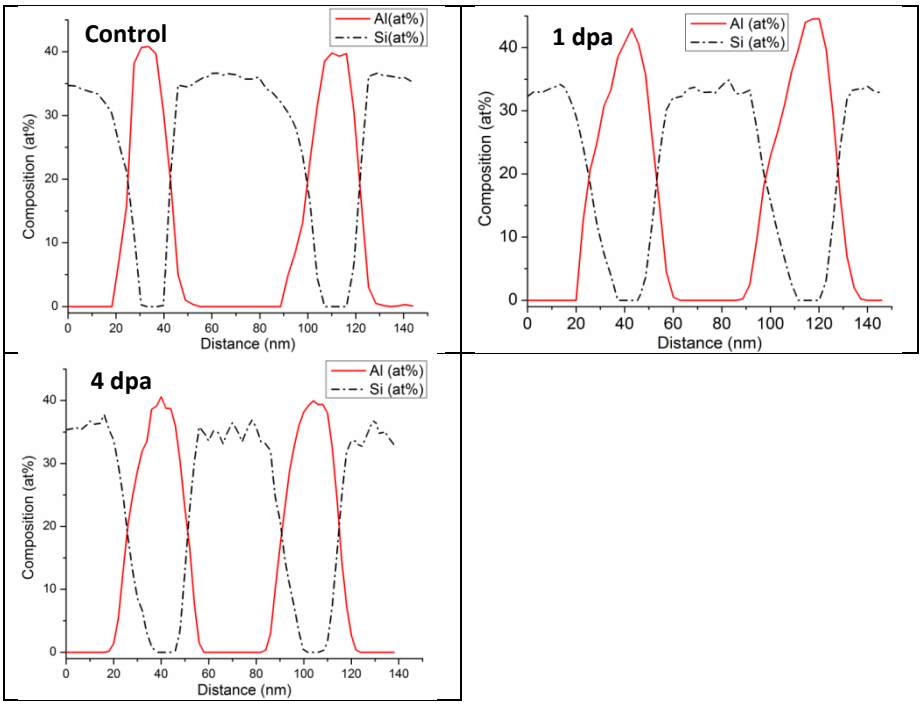


Figure 5. Energy dispersive spectrometry plots of constituent layers of the Al_2O_3/SiO_2 showing interdiffusion with the increase in irradiation dose.

Swelling defects

Apart from the Al/Si interdiffusion, new types of swelling defects were observed in SiO_2 layers of irradiated Al_2O_3/SiO_2 mirrors (see Figure 6). The typical size of each defect was ≈8 nm in 1 dpa and ≈ 42 nm in 4 dpa specimens. The defects in 1 dpa specimen were observed at the Al_2O_3/SiO_2 layer interface and with the increase in irradiation dose further growth of swelling defects occur in the SiO_2 layer. Energy dispersive spectrometry measurements along the SiO_2 layers did not yield any conclusive results due to its weak signal strength at the swelling region. The increase in the size of swelling defects with the irradiated dose suggests that the Al/Si interdiffusion plays a vital role at higher doses in Al_2O_3/SiO_2

mirrors. In addition, an increase in thickness of SiO_2 layer at the swelling region creates a small deviation in the subsequent Al_2O_3 layers. In general, increase in thickness of SiO_2 layer would produce a shift in the working range to slightly longer wavelengths. This is difficult to see based on the misshapen reflectance curves in Figure 1a as compared to the control. The irregularity in the 1 and 4 dpa reflectance curves are likely due to the observed features in the SiO_2 layers. Further work on understanding the swelling defects and the influence of these defects on the optical reflectivity is planned.

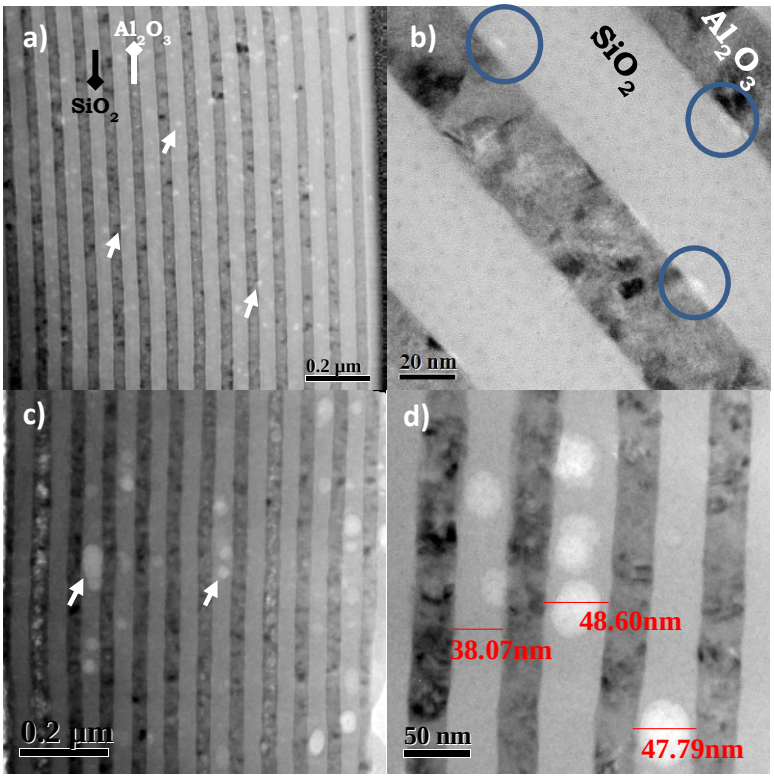


Figure 6. TEM micrographs showing the swelling defects in Al_2O_3/SiO_2 mirror, a), b) low and high magnification TEM micrographs in mirrors after 1 dpa dose, c), d) low and high magnification TEM micrographs showing swelling defects in mirrors after 4 dpa dose.

<u>Microstructural Changes in Irradiated HfO_2/SiO_2 mirrors</u>

Drastic drop in reflectivity was observed in the HfO_2/SiO_2 mirrors exposed to doses of 1 and 4 dpa. The loss in reflectance is attributed to the change in microstructure of the mirrors under high dose irradiations. Figure 7 shows the TEM micrographs of irradiated HfO_2/SiO_2 mirrors. Complete crystallization of the HfO_2 layer with the disappearance of amorphous regions was observed on irradiation to 1 and 4 dpa. The dominance of monoclinic reflections was still observed in HfO_2 layers. An increase in average grain size of HfO_2 layers to 20 nm at 4 dpa from 13 nm in a control sample was observed. The grain growth in metallic oxides is usually not expected in the low-temperature regime of <0.1 T_m (T_{irr}=185±10°C). However, previous work has shown that in nanocrystalline metallic systems at low temperatures the grain growth is driven solely by the reduction in grain boundary area by thermal spikes during displacement cascade [20]. In addition, other studies on ceramic materials have presented similar observations [21, 22]. This suggest that even in HfO_2 films irradiation-induced grain growth is believed to be the dominating mechanism behind the enormous increase in grain size under irradiation at T_{irr}=185°C.

Mirrors after irradiation showed more columnar morphology that extends through the film thickness. In addition, formations of twins were also observed in the HfO_2 layers. In the present case, the formation of

nanotwins can be ascribed to the growth encounter during irradiation-induced grain growth, which is restricted to one direction by the thickness of the film layer.

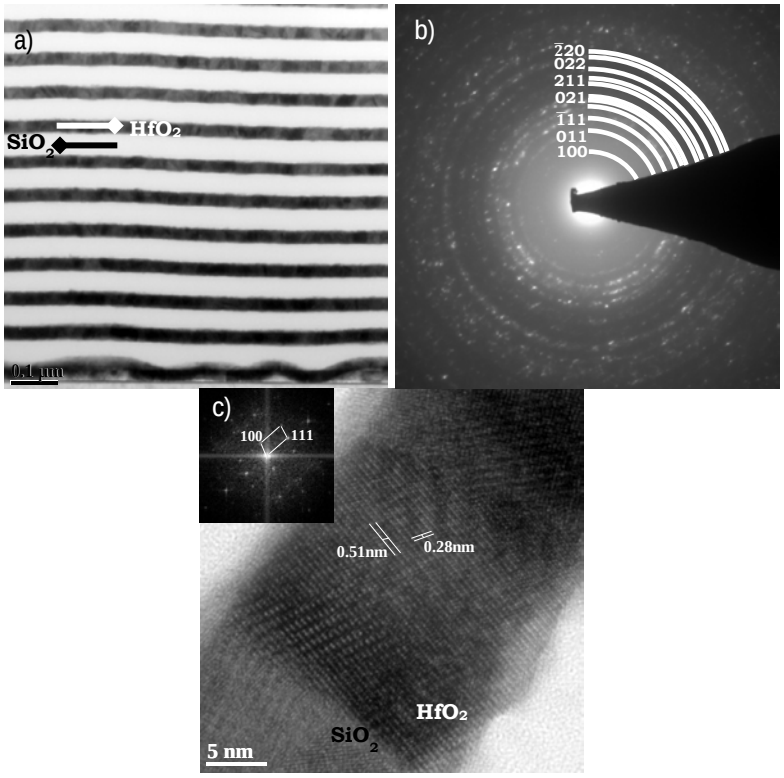
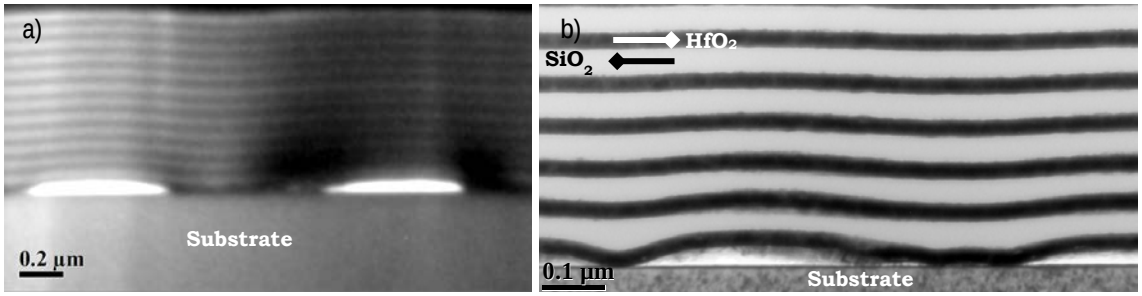


Figure 7. Cross-section TEM micrographs a) layers of HfO_2/SiO_2 mirror Irradiated to 1 dpa b) diffraction pattern showing monoclinic structure of HfO_2 films c) columnar grain structure of HfO_2 layer.

Delamination

Figure 8a is a low magnification TEM micrograph showing all the layers of HfO_2/SiO_2 mirror exposed to a dose of 4 dpa. Buckling type delamination and wrinkling of the HfO_2/SiO_2 bilayers was observed. In addition, non-uniform SiO_2 layer thickness was observed close to the interface layer and is attributed to the release of stresses at the detached region (see Figure 8b). Usually the grain geometry, average grain size and the grain size distribution have a strong influence on the mechanical properties of the polycrystalline thin films. In the case of HfO_2 films, the enormous grain growth during high dose irradiations lead to redistribution of grain boundaries and will produce differences in strain at the boundary compared to the initial fabricated condition. While the densification of SiO_2 films with the irradiation dose (approx. 2.7% volume contraction after exposures above 0.1 dpa (see Figure 9)) could introduce compressive stresses within the SiO_2 films. An imbalance between compressive stresses in SiO_2 layers and grain growth tensile stresses in HfO_2 layers coupled with weak film/substrate interface bonding could possibly lead to a buckle-type delamination and the disruption in the subsequent layers above the delaminated interface layer could lead to wrinkling of the multilayers.



(a)

Figure 8. a) Low magnification TEM micrograph showing the buckle-type delamination at the substrate layer interface and wrinkling of the subsequent film layers, b) High magnification showing the disruption in subsequent layers.

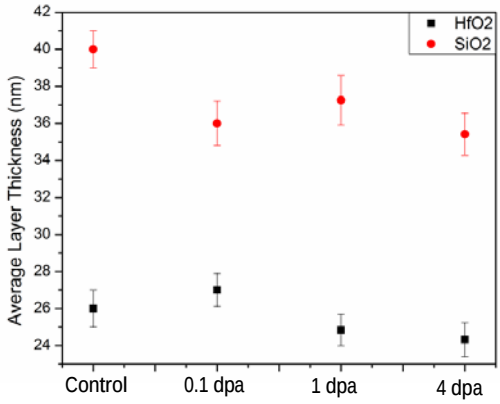


Figure 9. The average thickness of the constituent film layer in the HfO_2/SiO_2 mirrors at different irradiation doses (Densification of SiO_2 under irradiation was observed and the amount of densification reached a saturation limit at 0.1 dpa)

FUTURE WORK

Further analysis using Electron Energy Loss Spectroscopy (EELS) is being performed on the film layers to map the swelling defects observed in Al_2O_3/SiO_2 mirrors in order to understand the possible mechanism behind the defect formation. TEM examination of high dose irradiated mirrors is ongoing. A publication titled "Irradiation Effects on Microstructure and Optical Performance of Multilayered Dielectric Mirrors" is under preparation and the results will be presented at the ANS winter conference- 21st Topical Meeting on the Technology of Fusion Energy (TOFE).

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