5.2. High Neutron Dose Irradiations of Dielectric Mirrors — K. J. Leonard, G. E. Jellison, Jr., L. L. Snead (Oak Ridge National Laboratory), and A. P. K. K. Nimishakavi (University of Tennessee)

OBJECTIVE

The goal of this work is to evaluate the upper neutron irradiation dose and thermal limits of two promising dielectric mirror 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

Our experimental work to date on HfO_2/SiO_2 and Al_2O_3/SiO_2 dielectric mirrors indicate an impressive irradiation resistance. However, with increasing dose, chemistry and crystallinity changes in the film layers of the mirrors result in decreases in reflectivity of the HfO_2/SiO_2 mirror following post irradiation annealing. This contribution discusses the recent microscopy work on the 0.1 dpa-irradiated mirrors to assess the causes in optical property changes. Further work has been initiated this year for higher irradiation dose experiments to determine the upper neutron irradiation dose and thermal limits of the HfO_2/SiO_2 and Al_2O_3/SiO_2 mirrors. At the time of this writing, irradiation capsules have completed $1x10^{21}$ and $4x10^{21}$ n/cm^2 (E>0.1 MeV) exposures at 448 K, corresponding to approximately 1 and 4 displacements per atom (dpa). Post irradiation examination of the high dose mirrors will begin at the start of 2013.

PROGRESS

Introduction

The stability of the film layers in dielectric mirrors under combined thermal and neutron radiation environments were an early concern for applications in beam control and diagnostic systems of inertial confinement fusion energy systems. Improvements in deposition methods, quality of films, refinement of the number of bi-layers and choice of more radiation resistant substrates all provide an increase in radiation stability. Recent work by the authors on HfO_2/SiO_2 and Al_2O_3/SiO_2 mirror types has demonstrated radiation stability to displacement doses to 0.1 dpa [**Error! Reference source not found.**]. However, the upper thermal and radiation limits, as well as the structural changes in mirrors causing degraded optical properties are not well known. This work expands the neutron irradiation examination of two dielectric mirror systems based on alternating Al_2O_3/SiO_2 and HfO_2/SiO_2 films on single crystal sapphire substrates tuned for maximum reflectivity at 248 nm. New data on the 0.1 dpa samples examined this past quarter are discussed in the results section, while details on the irradiation testing to 4 dpa are presented in the experimental procedure section. The irradiation exposures to 4 dpa have just completed their time in the reactor, with post irradiation testing about to begin.

Experimental Procedure

Spectrum Thin Films Inc. manufactured the HfO_2/SiO_2 and Al_2O_3/SiO_2 mirrors tuned for maximum reflectivity at 248 nm examined in this study. The repeating bi-layer films were

deposited by electron-beam deposition with ion-assist on alpha-Al_2O_3 (sapphire) substrates. Substrate size was 6 mm diameter by 2 mm thick. In addition to the mirrors, monolayer films of Al_2O_3, SiO_2 and HfO_2 were also deposited on the substrates and included in the same exposure testing as the mirrors. Film layer thicknesses were 26, 32 and 40 nm for the HfO_2, Al_2O_3 and SiO_2 layers, respectively. To achieve peak reflectivity at 248 nm, the HfO_2/SiO_2 mirror consisted of 11 bi-layers of the 1/4l films and 30 bi-layers for the Al_2O_3/SiO_2 mirror.

Previous work on these samples have involved the neutron irradiation of the mirrors and monolayer samples to 0.001, 0.01 and 0.1 dpa at 448 K. The current work involves the irradiation of a second set of samples to higher doses followed by similar post irradiation examination (PIE) of the optical and microstructural changes to the mirrors. Irradiations to $1x10^{21}$ and $4x10^{21}$ n/cm^2 (E>0.1 MeV) at 448 K, corresponding to approximately 1 and 4 displacements per atom (dpa), were completed in the peripheral hydraulic tube at the High Flux Isotope Reactor (HFIR) on November 3, 2012. 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 will be unloaded at the LAMDA lab to ensure proper handling of the mirrors, this is to begin at the start of 2013.

Testing of the 1 and 4 dpa samples will include 1 hour post-irradiation thermal anneals of the mirrors with peak thermal annealing temperatures of 573 K for the HfO_2/SiO_2 mirror and at 673 K for the Al_2O_3/SiO_2 mirror to be considered based on earlier research work. Annealing studies of the unirradiated controls have already been performed.

Optical examination of the samples will include 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 will be correlated to microstructural changes in the films examined through transmission electron microscopy (TEM). Ellipsometry will be performed on the irradiated HfO_2 and Al_2O_3 monolayer films deposited on the sapphire substrates for select conditions and compared to the unirradiated controls in order to elucidate strain effects at the film/substrate interface.

RESULTS

It was found in earlier work that irradiation to 0.1 dpa showed no change in absolute reflectivity of either the HfO_2/SiO_2 or Al_2O_3/SiO_2 mirrors and that no further decrease in optical properties of the Al_2O_3/SiO_2 mirrors was found after 1 hour annealing in vacuum up to 673 K. Examples of the reflectivity versus wavelength normalized to the measured absolute reflectivity are presented in Figure 1. The changes in the working range, the peak reflectivity range in the wavelength spectrum, with irradiation and thermal annealing is the result of changes in film thickness layers of the mirrors. The change in working range for the Al_2O_3/SiO_2 mirror is small and correlates to the nearly insignificant change in average film thickness (Figure 2a) for the different exposure conditions. The measured data range for the Al_2O_3/SiO_2 mirror layer thicknesses for the different exposure conditions are within the statistical measurement of error to that of the control. This was not the case for the HfO_2/SiO_2 mirror, as the changes in working range were greater as was the measured decrease in SiO_2 layer thickness (Figure 2b) in both the irradiated and thermal annealing conditions. The cause for the difference in behavior of the SiO_2 layers in the two mirrors may be related to both compaction of the SiO2 layer, but to the overall changes occurring in the other film layers in the mirrors. With increasing irradiation dose and thermal annealing temperature, the amount of interdiffusion between the Al_2O_3 and SiO_2 layers increases (Figure 3a). However, despite the measureable amount of composition

change, no significant change in film thickness occurs and no interlayer appears in the Al_2O_3/SiO_2 mirrors (Figure 4). The stability of the Al_2O_3/SiO_2 mirror to irradiation and thermal heat treatment arises from the amorphous structure of the constituent layers that are more accepting of damage. Furthermore, the amorphous structure may be more accommodating to the Si/Al interdiffusion, which may also provide an added level of stability to the mirror. Increased stability to laser damage initiation threshold (LDIT) was reported in amorphous TiO_2/SiO_2 mirrors that incorporate 17% SiO_2 into the TiO_2 layer [1]. The modified mirrors showed an increase in thermal stability of the films with no degradation in LDIT measured at annealing temperatures 75% higher than that limiting the unmodified mirrors, which indicated signs of crystallization of the TiO_2 layer.

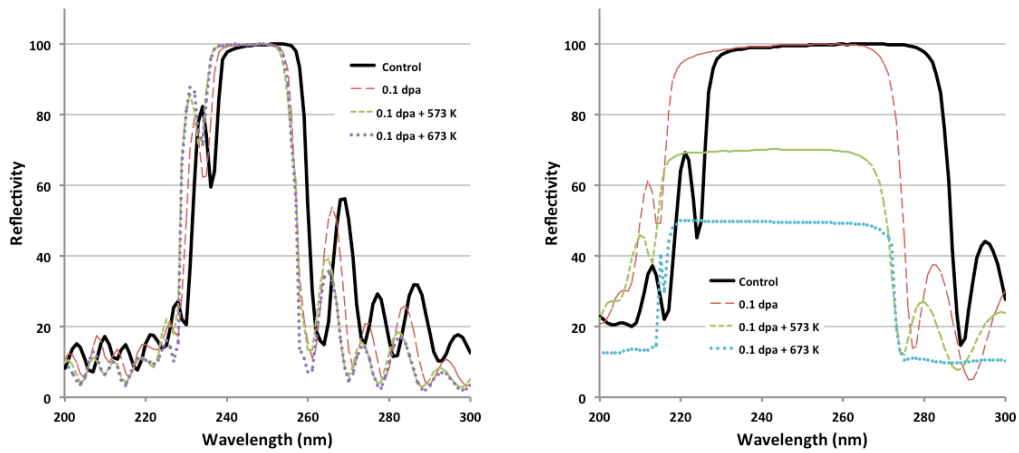


Figure 1. Changes in the working range of the mirrors measured through specular reflectance normalized to the absolute reflectivity measured by excimer laser measurements at 248 nm. (a) The Al_2O_3/SiO_2 mirrors showing stability up to 0.1 dpa and in post irradiation thermal treatments to 673 K. (b) The HfO_2/SiO_2 mirror showing loss of reflectivity with post irradiation annealing of the 0.1 dpa irradiated samples.

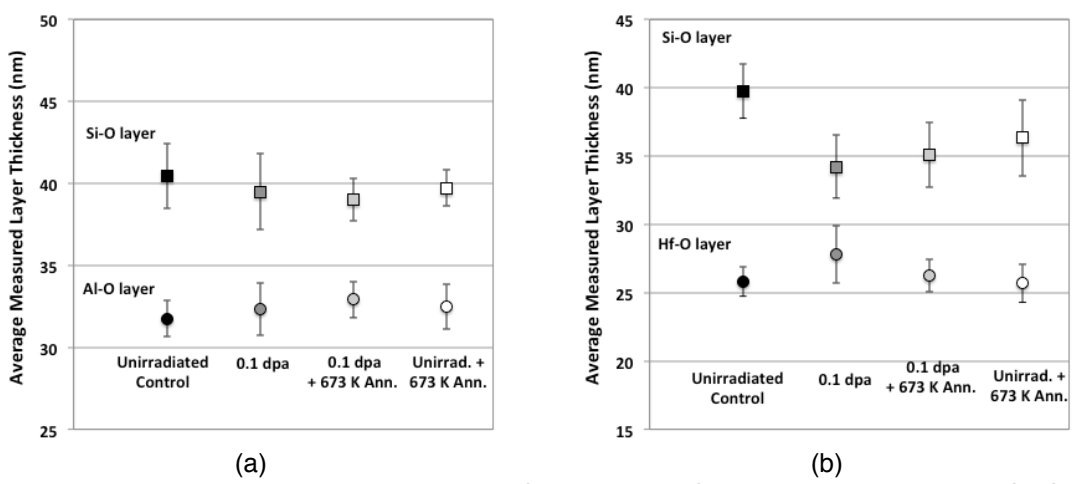
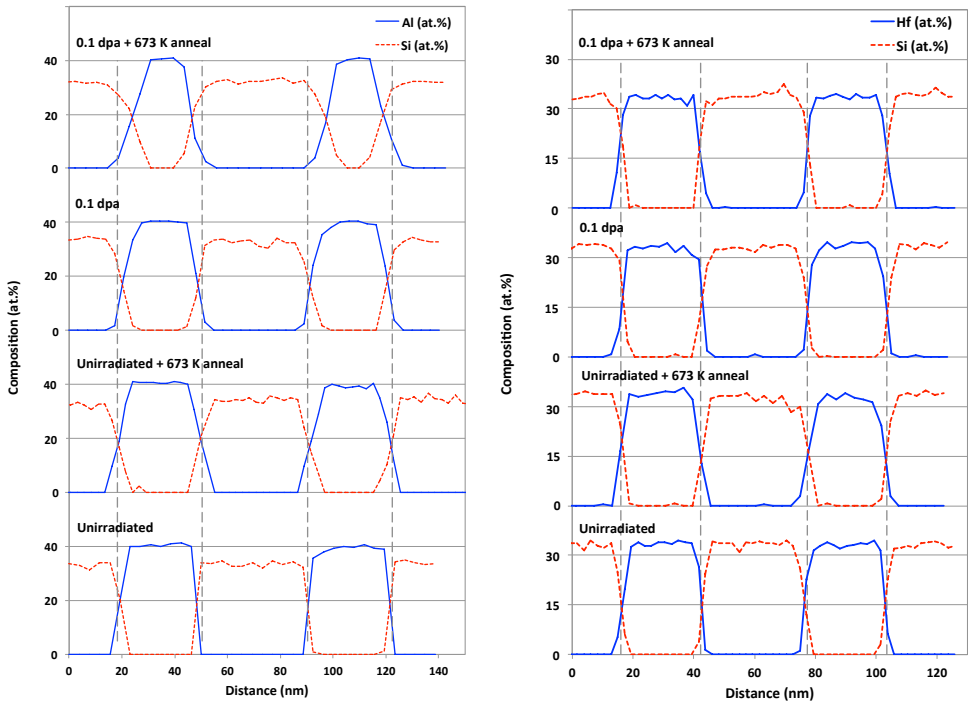
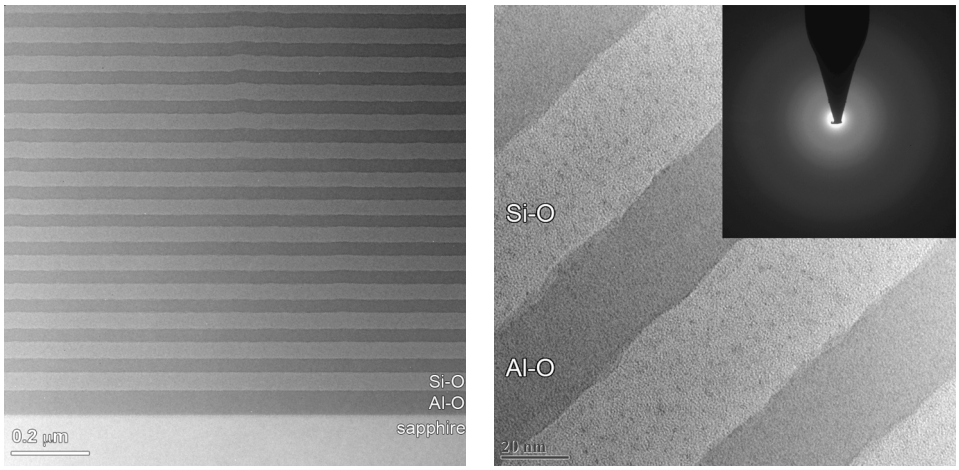


Figure 2. The average measured thickness of constituent film layers in the (a) Al_2O_3/SiO_2 and (b) HfO_2/SiO_2 mirrors. Error bars represent the standard deviation in the data with each data point representing over 30 measurements of at least 5 different film layers, with the exclusion of the base layer at the sapphire substrate that is intentionally thicker than the subsequent layers.



(a) (b)

Figure 3. The calculated compositions of the constituent layers measured through energy dispersive spectroscopy of the (a) Al_2O_3/SiO_2 and (b) HfO_2/SiO_2 mirrors. Showing the interdiffusion between the Al/Si bearing layers with increasing irradiation dose and thermal annealing for the Al_2O_3/SiO_2 mirror and the lack of interdiffusion in the HfO_2/SiO_2 mirrors.

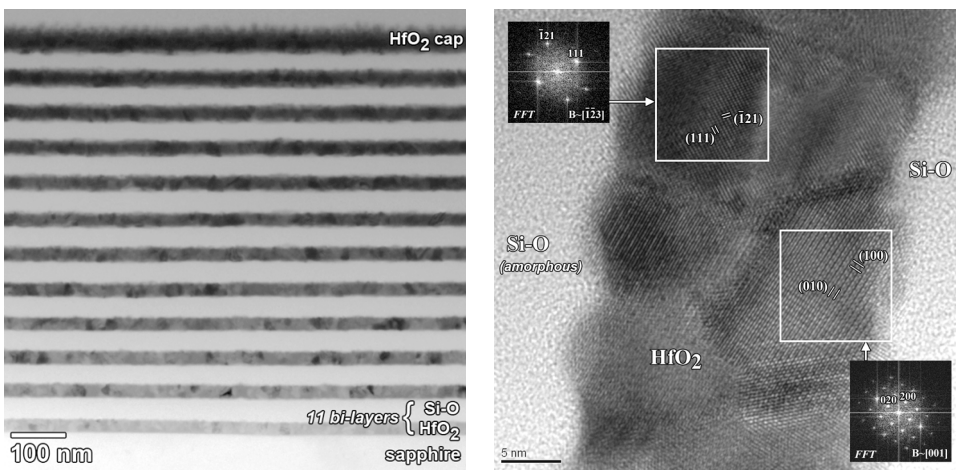


(a) (b)

Figure 4. TEM micrographs of the Al_2O_3/SiO_2 mirror irradiated to 0.1 dpa and annealed 1 hour at 673 K. (a) Low magnification image showing relatively smooth layers with limited perturbations that create repeating deviations in subsequently deposited layers. (b) Higher magnification image taken in a defocused condition showing some black spot defects in the amorphous layers and no interphase formations. Disturbances at the film interfaces are due to localized film roughness, the thickness of the sample at that location and the defocused conditions used.

Decreases in reflectivity of the HfO_2/SiO_2 mirror irradiated to 0.1 dpa with increasing annealing temperature (Figure 1b) was observed and attributed to changes in the crystallinity of the HfO_2 layer and the corresponding changes state of strain at the HfO_2 / sapphire interface. The 0.1 dpa irradiated HfO_2/SiO_2 mirror showed the largest shift in working range toward lower wavelengths, the result of substantial decrease in SiO_2 layer thickness (Figure 2b). This was also the case for the 673 K annealed control where a reduction in the SiO_2 layer was measured. As no significant interdiffusion of Hf and Si were measured between the constituent layers in the examined mirrors, Figure 3b, densification of SiO_2 is suspected.

Changes in the crystalline structure of the HfO_2 layer in the HfO_2/SiO_2 mirrors were observed through electron and X-ray diffraction following irradiation and subsequent annealing treatments. The as-deposited mirrors displayed polycrystalline monoclinic structured grains in the HfO_2 layers with an average grain size of 13 nm (Figure 5). However, the as-deposited HfO_2 layers showed some amorphous structuring around the crystalline grains when viewed under high-resolution imaging. The amorphous regions disappeared on irradiation to 0.1 dpa or with thermal aging of the unirradiated control material. With irradiation to 0.1 dpa, cubic or tetragonal HfO_2 reflections appear in electron and X-ray diffraction patterns (reflected peaks are too few to positively distinguish which of the two polymorphs are present), but fade away with subsequent annealing. The appearance of cubic structured grains in irradiated HfO_2 films have been observed in ion-irradiated films in both the electronic as well as nuclear stopping dominating conditions [3,4].

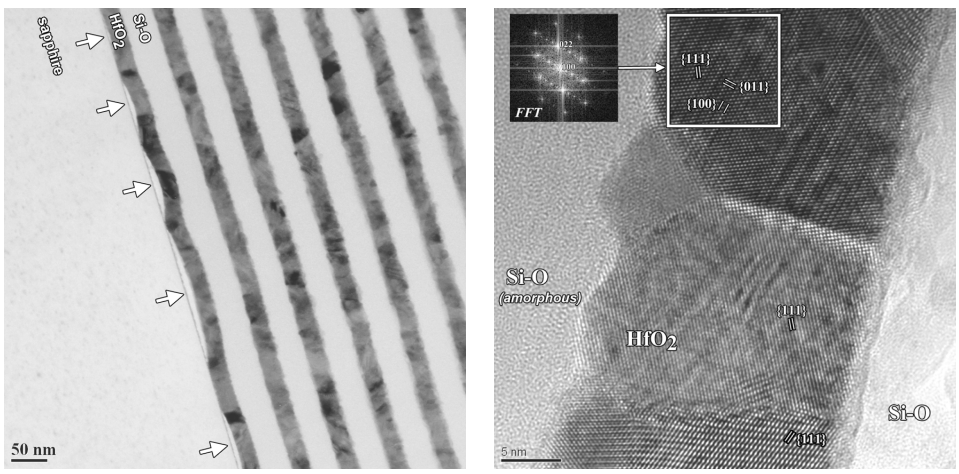


(a) (b)

Figure 5. Low (a) and (b) high magnification TEM micrographs of the unirradiated HfO_2/SiO_2 mirror, showing the polycrystalline grain structure of the HfO_2 and amorphous SiO_2 layers.

The loss in reflectivity with annealing was only observed in samples irradiated to 0.1 dpa and not observed in the unirradiated plus annealed material. The loss in reflectivity was linked to a delamination of the first HfO_2 layer at the sapphire substrate as observed in TEM examinations (Figure 6). The amount of delamination is approximately equal to the percent loss associated with the reflectivity. The precise cause for the delamination is difficult to identify, as no secondary phase or defects were observed at or near the delamination locations in either the HfO_2 layer or in the substrate. The cause is believed to be an effect of strain conditions at the interface, but the reason for appearing in the 0.1 dpa + annealed samples and not in the unirradiated control is not clear. Though an increase in average grain size to 16 nm was

measured for the 0.1 dpa-irradiated sample (no further increase measured on annealing to 673 K), a similar grain size was measured for the 673 K annealed unirradiated control. However, the grain structure of the irradiated sample showed a more columnar grain structure that has more grains spanning the thickness of the film layer (compare Figure 5b and Figure 6b). However, there does not appear to be any common alignment of the grains to a particular direction, which could possible increase the strain condition on the adjacent substrate interface. Electron diffraction images taken of the polycrystalline HfO_2 layers in the 0.1 dpa + 673 K annealed and unirradiated plus annealed conditions shows well defined intensities with no diffuse amorphous or non-monoclinic intensities appearing and are indistinguishable from each other. The high-resolution images taken of the HfO_2/sapphire interface are being reviewed further to identify any changes in the orientation of the HfO_2 grains in the first layer with irradiation as compared to the control samples. A further analysis of the strain state between the HfO_2 layer and substrate through ellipsometry of the monolayer films irradiated at the same time are considered for the next stage of work. The monolayer films will allow for cleaner analysis of the ellipsometry data than the multi-layer mirrors.



(a) (b)

Figure 6. TEM micrographs of the 0.1 dpa HfO_2/SiO_2 mirror post irradiation annealed 1 hour at 673 K. (a) Delamination of the HfO2 at the interface of the sapphire substrate (indicated by arrows). (b) High magnification image showing the polycrystalline grain structure of the HfO_2 and amorphous SiO_2 layers.

FUTURE WORK

The mirror and monolayer samples irradiated to 1 and 4 dpa have completed their exposures at HFIR and will undergo capsule disassembly at the start of 2013. The samples on unloading will be examined for any crazing, cracks or delamination through visual inspection. The mirrors will then undergo spectrometry analysis of the specular reflectivity followed by absolute reflectivity measurements performed using a 248 nm wavelength excimer laser. Examination of ellipsometry data for the higher dose irradiated monolayer films of HfO_2 and Al_2O_3 in comparison to unirradiated control material will be used to elucidate strain effects at the substrate film interfaces. Following optical testing, TEM examination of select specimens will be performed to determine structural changes in the films causing the observed optical changes.

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