5.2 HIGH NEUTRON DOSE IRRADIATION OF DIELECTRIC MIRRORS

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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

HfO_2/SiO_2 and Al_2O_3/SiO_2 dielectric mirrors show impressive resistance to neutron irradiation to 0.1 dpa. However, for the HfO_2/SiO_2 mirror the neutron dose causes crystallinity changes in the film layers of the mirrors and substrate resulting in decreases in reflectivity of the HfO_2/SiO_2 mirror following post irradiation annealing. Cooling following annealing resulted in delamination. Al_2O_3/SiO_2 mirrors appear to have added stability with little microstructural and optical property changes in samples irradiated up to 0.1 dpa and annealed to 673 K. However significant Si and Al interdiffusion cause compositional variation that will eventually result in the formation of aluminum-silicate structures on the layer interface, disrupting the optical properties.

Optical tests of samples irradiated to 1 and 4 dpa during the first half of 2013 confirmed that both the HfO_2/SiO_2 and Al_2O_3/SiO_2 do not survive exposure to 4 dpa, resulting in film delamination. Microstructural evaluations of the 4 dpa samples are now being performed to verify and build upon the low dose results.

PROGRESS AND STATUS

Introduction

The changes in the microstructure of film layers and their effect on optical properties of Al_2O_3/SiO_2 and HfO_2/SiO_2 mirrors will be presented at the 17th International Radiation Effects in Insulators (REI-17) conference held June 30 through July 5, in Helsinki, Finland. A journal paper is currently undergoing ORNL peer review prior to external submission to the Journal of Nuclear Materials. The following is a condensed description of that work.

Irradiation to 0.1 dpa

Dielectric mirrors of HfO_2/SiO_2 and Al_2O_3/SiO_2 designed for optimum reflectivity at 248 nm with 11 and 30 bi-layer coatings, respectively, survived irradiation to 0.1 dpa at 448 K without film cracking or delamination from their sapphire substrates. Subsequent post-irradiation annealing of only the 0.1 dpa samples resulted in a loss of reflectivity in the HfO_2/SiO_2 mirror, while the Al_2O_3/SiO_2 type remained unaffected. Microstructural changes that correlate to optical property changes of the mirror were investigated.

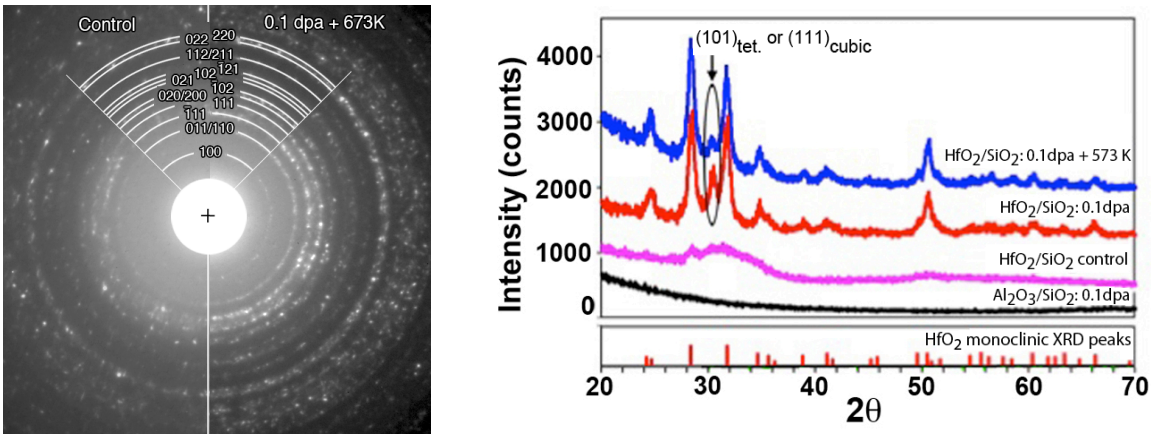
In the case of the Al_2O_3/SiO_2 mirror, no significant changes were measured in the optical properties under the varying exposure conditions, with only a few nanometer shifts to shorter

wavelengths of the mirror peak reflectivity. The film layers of the Al_2O_3/SiO_2 mirror remained amorphous over all exposure conditions tested. While fused silica bars also tested with the mirrors underwent up to ~2.25% densification [1], no changes could be measured in the SiO_2 layers of the Al_2O_3/SiO_2 mirror. Increasing irradiation dose and thermal annealing temperature (in either the unirradiated control or post-irradiated condition), the amount of interdiffusion between the Al_2O_3 and SiO_2 layers was measurably increased. Despite the composition changes observed across the film layers no secondary phases appear at the film interfaces.

The stability of the Al_2O_3/SiO_2 mirror to irradiation arises from the amorphous structure of the constituent layers that are more accepting of damage. Though point defect formation can still occur in the amorphous structures, the retained damage in the amorphous structure is much less than that of crystalline structures [2]. The amorphous structure of the films may be more accommodating to the Si/Al interdiffusion, providing with it an added level of stability to the mirror. The flexibility and variation in the Si-O-Si bond with little energy differences makes this material very stable against thermal degradation and crystallization.

The 0.1 dpa irradiated HfO_2/SiO_2 mirror showed the largest shift in the peak reflectivity range toward shorter wavelengths, the result of a substantial decrease in SiO_2 layer thickness. 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 detected between the constituent layers in the examined mirrors, irradiation densification of SiO_2 is suspected along with the removal film layer defects and irregularities related to the fabrication of the mirrors.

Changes in the crystalline structure of the HfO_2 layer in the HfO_2/SiO_2 mirrors was observed through electron and X-ray diffraction following irradiation and subsequent annealing treatments. The as-deposited mirrors displayed polycrystalline monoclinic structured grains with some retained amorphous regions between crystallites. The intensity of the diffracting grains of the as-deposited films is much less than that recorded in the annealed or irradiated diffraction patterns (Figure 1) in both X-ray and electron diffraction patterns. The amorphous regions disappeared on irradiation to 0.1 dpa or with thermal aging of the unirradiated control material. With irradiation, additional reflections from the HfO_2 film appear in the XRD spectrum. However, these reflected peaks are too few to positively distinguish between the tetragonal and cubic structures due to the dominance of the monoclinic reflections in the pattern. The appearance of non-monoclinic 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]. The amount appearing in the 0.1 dpa mirrors is relatively little, approximately 8% from XRD intensity calculations based on the technique of Benyagoub [5] for similar transformations in ZrO_2, and could not easily be positively identified through TEM. Based on ion irradiation studies in ZrO_2 [6], the structural transformation from the monoclinic phase in the low energy ion nuclear stopping dominated regime is the result of the imposing strain field associated with the oxygen deficiencies from irradiation. While experimental characterization of the transformation in ZrO_2 conclusively identified the transformed phase as tetragonal, clear confirmation in our work could not be made. The cubic/tetragonal intensities in the electron and X-ray diffraction patterns fade with subsequent annealing of the 0.1 dpa irradiated mirrors, presumably due to recovery of some of the irradiation-induced defects. In the irradiated and/or annealed conditions, an increase in the 100 reflections of the monoclinic HfO_2 grains is observed in the suggesting an increase in twinning in the HfO_2 possibly as the result of increased grain growth.



(a) (b)

Figure 1. Electron (a) and (b) X-ray diffraction (XRD) patterns of the HfO_2/SiO_2 mirrors following different exposure conditions. Both patterns show an increase in the crystallinity of the mirror following irradiation and annealing. The amorphous XRD spectra of the Al_2O_3/SiO_2 mirror following irradiation to 0.1 dpa is also shown for comparison.

Loss in reflectivity with annealing was only observed in post-irradiate annealing of the 0.1 dpa HfO_2/SiO_2 mirrors and not observed at lower doses or in the unirradiated plus annealed material. Irradiation to 0.1 dpa resulted in the formation of a semi-amorphous layer within the sapphire at the interface with the first deposited HfO_2 layer (Figure 2a). This observation is similar to that reported by Usov *et al* [7] in HfO_2/MgO multi-layer films on sapphire irradiated by 10 MeV Au ions between 90 and 800 K. In which irradiation temperatures <300 K promoted amorphization of the HfO_2 film layer in contact with the substrate, while higher irradiation temperatures favored amorphization in the sapphire. In our work, neutron irradiation at 448 K produced an amorphous boundary within the sapphire layer for the 0.1 dpa mirrors. In the 0.1 dpa HfO_2/SiO_2 mirror the amorphization of the sapphire in the near surface region may have been aided by the state of stress at the interface as well as the transfer of oxygen to the HfO_2 layer due to losses in the film layer.

Microstructural examination of the 0.1 dpa HfO_2/SiO_2 mirror annealed at 673 K revealed buckling of the first HfO_2 layer adjacent to the sapphire (Figure 2b,c). Under the detached regions an amorphous interlayer was present. This amorphous layer was identified as containing Al and O based on EDS examination. No Hf was detected in either the amorphous region or within the near surface layer of the substrate. In the locations where detachment of the HfO_2 layer has not occurred, strain in the sapphire is observed through the distortions in the lattice images and could be seen extending to 1.5 nm from surface.

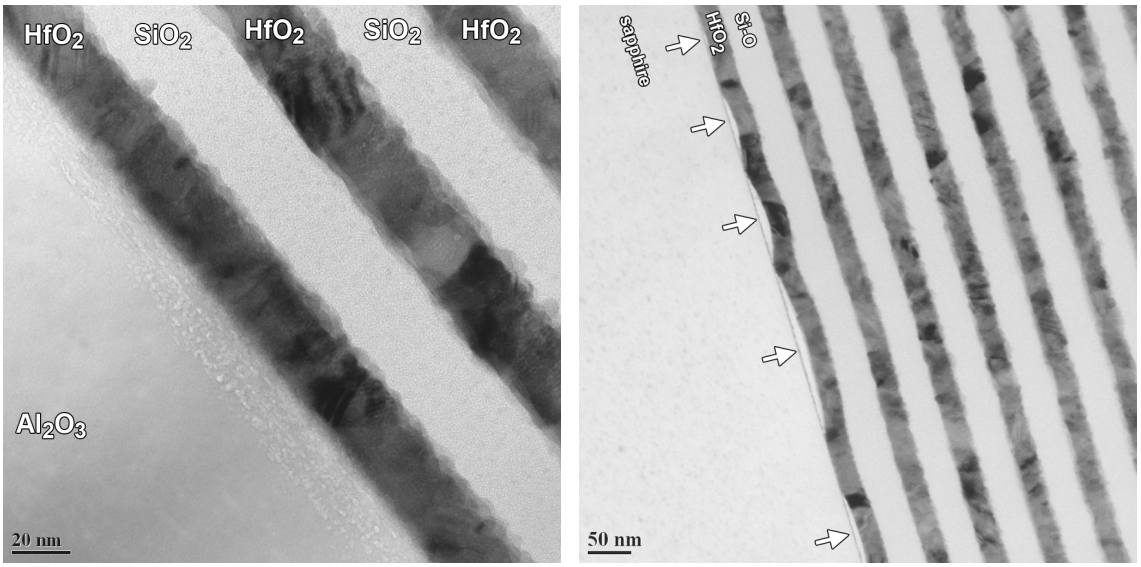
The compressive stress associated with the HfO_2 films likely has increased with irradiation or thermal exposure as indicated by the development of non-monoclinic HfO_2 polymorphs as well as the development of the larger columnar grain structures and the removal of the amorphous component of the as-deposited films. The annealing of the 0.1 dpa-irradiated materials appears to have facilitated the reduction of the stresses in the films through buckling and coalescence of the amorphous phase under the detached layers.

The detachments observed in the HfO_2 film layer at the substrate create little disruption in the subsequent film layers. The perturbations observed in the TEM sample alone would not be responsible for the substantial drop in reflectivity of the mirrors. Therefore, what is observed at the substrate in the TEM of the 0.1 dpa annealed material can be viewed as starting points for the cause of delamination. As the fractured film layers were no longer in-place on the mirrors, the samples extracted for TEM examination were taken from regions where film layers are still attached and had not progressed to the extremes of delamination. The HfO_2 film at the interface shows a buckle-type delamination mode of failure. While there are many locations along the substrate interface that show these buckles, with spacing between peaks in the bent locations averaged near 350 nm, the high stiffness of the substrate eliminates the possibility of other delamination modes such as wrinkling [8-10]. However, some measure of compliance may be afforded by the substrate through the amorphous Al-O that fills under the deviations in the film layer.

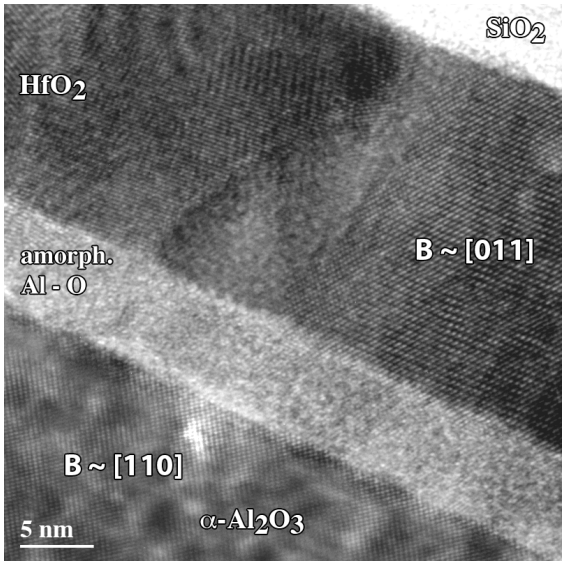
Following on work by Nowacki [11], Reichling *et al.* [12] showed that the stress produced by thermal changes imposed on a surface defect between the substrate and film can be calculated by equation 1. Damage through delamination of the mirror layers can be initiated when this stress needed to overcome film adhesion exceeds a critical value based on the size of the flaw with radius *b*, as described in terms of equation 2.

$$\sigma = \frac{(1-\nu)E}{(1-2\nu)(1-\nu)}\alpha T \qquad \text{(Eq. 1)}$$

$$\sigma_c = \left[\frac{\pi E \gamma_s}{2(1-\upsilon^2)b}\right]^{1/2} \qquad \text{(Eq. 2)}$$



(a) (b)



(c)

Figure 2. TEM micrographs of the 0.1 dpa irradiated HfO_2/SiO_2 (a) at the interface of the sapphire substrate showing a semi-amorphous boundary formed within the substrate. Post-irradiation annealed 1 hour at 673K showing (b) delamination of the HfO_2 layer at the interface of the sapphire substrate (indicated by arrows). Higher magnification image (d) at the interface showing a section of the buckled HfO_2 first layer with an amorphous aluminum oxide interlayer between it and the substrate.

Assuming the stress initiates through the thermal changes during annealing and is equal to that of the critical delamination stress, the critical flaw size can be solved for. This assumes that much of the damage is driven by the HfO_2/substrate interface, with a disc-shaped flaw. Taking available data for monoclinic HfO_2 of E = 220 GPa [13], n = 0.25 [0], a = $9x10^{-6}$ °C^{-1}, and that for the surface energy of HfO_2 (110) g_s = 2.2 J/m^2 [15], the critical flaw radius size is calculated at 370 nm. As expected, this is larger than the smaller surface deviations observed in the TEM from which the non-fractured portions of the film were examined.

The increase in reflectivity loss with annealing temperatures supports the premise that the thermal induced stresses associated with fracture are at play. Additionally, since only the 0.1 dpa irradiated HfO_2/SiO_2 mirror showed delamination failures following annealing, it is assumed that the amount of strain and amorphous volume formed within the substrate is less for the 0.001 and 0.01 dpa-irradiated samples.

CONCLUSIONS

Our experimental work to date on HfO_2/SiO_2 and Al_2O_3/SiO_2 dielectric mirrors indicate an impressive irradiation resistance relative to the previous studies and the expected exposure conditions expected for application in inertial confinement fusion devices. However, for the case of the HfO_2/SiO_2 mirror, increased neutron dose causes crystallinity changes in the film layers of the mirrors and substrate resulting in decreases in reflectivity of the HfO_2/SiO_2 mirror following post irradiation annealing. During annealing, stress relaxation created buckling in the first HfO_2 layer, which creates defects at the substrate/film interface. On thermal cooling from annealing these defects were sources of increased film stress resulting in delamination initiated from defects that have reached a critical size.

The amorphous layers of the Al_2O_3/SiO_2 mirrors appear to afford added stability under irradiation, where little microstructural and optical property changes occur in samples irradiated up to 0.1 dpa and in post-irradiated annealing to 673 K. However, significant Si and Al interdiffusion was measured across the interface of the constituent layers. This compositional variation will eventually reach a level in which the amorphous structure can no longer accommodate and will result in the possible formation of aluminum-silicate structure on the layer interface disrupting the optical properties.

CURRENT AND FUTURE WORK

Work has continued on the optical testing of the high neutron dose samples irradiated to 1 and 4 dpa during the first half of 2013. In brief, optical tests have confirmed that both the HfO_2/SiO_2 and Al_2O_3/SiO_2 do not survive exposure to 4 dpa, resulting in film delamination. The detailed microstructural examination performed in the low dose work as outlined in this semiannual has firmly established an understanding of the root causes of failure. Microstructural evaluations of the 4 dpa samples are now being performed to verify and build upon the low dose results.

Current work also includes the testing of absolute reflectivity of the mirror samples through the newly installed and tested NeCu deep UV laser system. Measurement of absolute reflectivity of the mirrors will complete the optical testing work.

Additional optical testing through ellipsometry of single layer SiO_2, Al_2O_3 and HfO_2 films on sapphire has also been performed for the 0.001, 0.01, 0.1, 1 and 4 dpa conditions. The results are now being analyzed.

Future work will include microstructural evaluation of the 1 dpa mirrors. The Al_2O_3/SiO_2 mirror shows differences compared to the lower dose samples in the photospectrometry data collected. In that the peak reflectivity range is contracted and shifted to longer wavelengths in the 1 dpa mirror, opposite of that observed at lower doses. It is suspected that interfacial compounds may be forming between the film layers. While the 1 dpa HfO_2/SiO_2 mirror has showed no change in its photospectrometry spectrum compared to the 0.1 dpa exposures, microstructural analysis will confirm the radiation-induced changes that led to failure at 4 dpa.

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