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Optical Properties and Moisture Stability of HfO_2 Thin Films Prepared by Ion Assisted Deposition for UV Applications

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الخصائص البصرية وثبات الاداء بوجود الرطوبة للاغشية الرقيقة لثنائي اوكسيد الهافنيوم المصنّعة بطريقة الطلاء الايوني المعزز للتطبيقات في نطاق ترددات المنطقة فوق البنفسجية

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الخلاصة

في هذا البحث تمت الاشارة الى التقدم الحاصل في طرائق التحكم في مواصفات المرشحات ذات النفاذية العالية وثبات الاداء في التطبيقات ضمن الظروف البيئية للمنطقة فوق البنفسجية. تمتاز هذه المرشحات بالانتقال من حالة النفاذية العالية للاطوال الموجية المحددة الى حالة القطع التام. ان المرشحات ذات السمك الطوري الاعلى التي تصنع تقليديا بترسيب ثنائي اوكسيد الهافنيوم تكون حافات الامرار فيها ذات ميل تدريجي . في هذا البحث تم تصنيع مرشح بطريقة الطلاء الأيوني المعزز لثنائي أوكسيد الهافنيوم لاستخدامه في التطبيقات في نطاق المنطقة فوق البنفسجية. عند اجراء المقارنة بين المرشح المصنع بطريقة الطلاء الايوني المعزز والمرشحات المصنعة بالطرق التقليدية اظهرت نتائج ثبات الاداء بوجود الرطوبة، وجود انحراف طفيف بمقدار (0.05%) بالنسبة للنوع الاول.

ABSTRACT

In this study the progress in the realization of environmentally stable, high phase thickness, long-pass edge filters for UV applications is reported. These filters are characterized by extremely sharp transitions from full transmittance to deep blocking. Such filters are manufactured via physical vapor deposition of Hafnia (HfO2). Filters with highest phase thickness exhibit the steepest edge slopes. In this work we produce two types of filters, the first one manufactured using Ion Assisted Deposition (IAD), and the second one prepared by Physical Vapor Deposition (PVD) technique. When comparing the results for moisture stability of edge filters produced by IAD and PVD, it is found that the filters produced with ion assist exhibit wet-dry shifts in edge wavelength location less than 0.05%.

Key Words: Ion-assisted deposition, HfO_2, Edge filter

1- INTRODUCTION

It is well known that Hafnium oxide which is also called Hafnia (HfO_2) has a high refractive index, good thermal and mechanical stabilities with relatively high laser damage threshold [1]. HfO_2 is a common material used for manufacturing of UV filters due to being transparent down about 250nm. Also, it exhibits less sensitivity to moisture stability than other thin film materials [2,3]. It is possible to make fully dense, moisture stable using IAD. Hafnium oxide was chosen for its high UV transparency and refractive index [4]. Using a new propriety monitoring technology we can deposit many layers. This allows for blocking and steeper edge slopes than that achieved before [5,6]. Refractory oxides deposited via conventional PVD (electron beam gun vapor source condensing onto substrates heated to 200-300^{0}C) exhibit a columnar microstructure that consists of solid columns of material oriented in the direction of film growth with interspersed voids throughout the thickness of the film [7-9]. This under-dense film displays a spectral shift upon exposure to moisture in the atmosphere, which condenses in the voids of the film and effectively changes the film refractive index. Films that are near bulk density are much less sensitive to change in relative humidity than films with significant columnar microstructure. Low void density is also correlated with increased film hardness and environmental durability. It is well established that the density of refractory oxide films can be increased significantly by subjecting the growing film to ion bombardment [10-12]. Ion-assisted deposition has been shown to increase the refractive index and improve moisture stability of Hafnia (HfO_2) films [13,14]. Lehan et al. [14] found that HfO_2 films evaporated using IAD exhibited no detectable moisture shift when argon was used as the ion source working gas and backfill of oxygen. In this study, two types of filters were manufactured. The first one manufactured using Ion Assisted Deposition (IAD), and the second one prepared by Physical Vapor Deposition (PVD) technique. The filters have high phase thickness multilayer coatings made with alternating layers of HfO_2.

2- EXPERIMENTAL

The dielectric stack oxide thin films were carried out in a coating system as shown in Figure 1. All films were deposited onto rotating fused silica substrates (50x50 mm squares, 1 mm thick). Substrates were heated to 300^0 C not utilizing to ion assist and to 120^0 C during IAD. The base pressure of the heated system was typically $5x10^{-5}$ mbar. The film optical thickness was monitored via direct optical monitoring of the geometrical center of the rotating substrate and the deposition rate was monitored using quartz crystal. Hafnia films were deposited at rate of 0.3 nm/sec, and silica films (SiO_2) were deposited at 0.7 nm/sec. An oxygen backfill of $5x10^{-4}$ mbar was used during the deposition without IAD. The ion gun source gas was either oxygen, argon, or a mixture via 2 mass flow controllers. The ion gun was regulated under constant current mode. Optimization was an iterative process in which multiple quarter waves of the material (16 quarter waves monitored at 250 nm) were deposited under a given set of conditions and resulting film was evaluated for UV transmission and moisture stability.

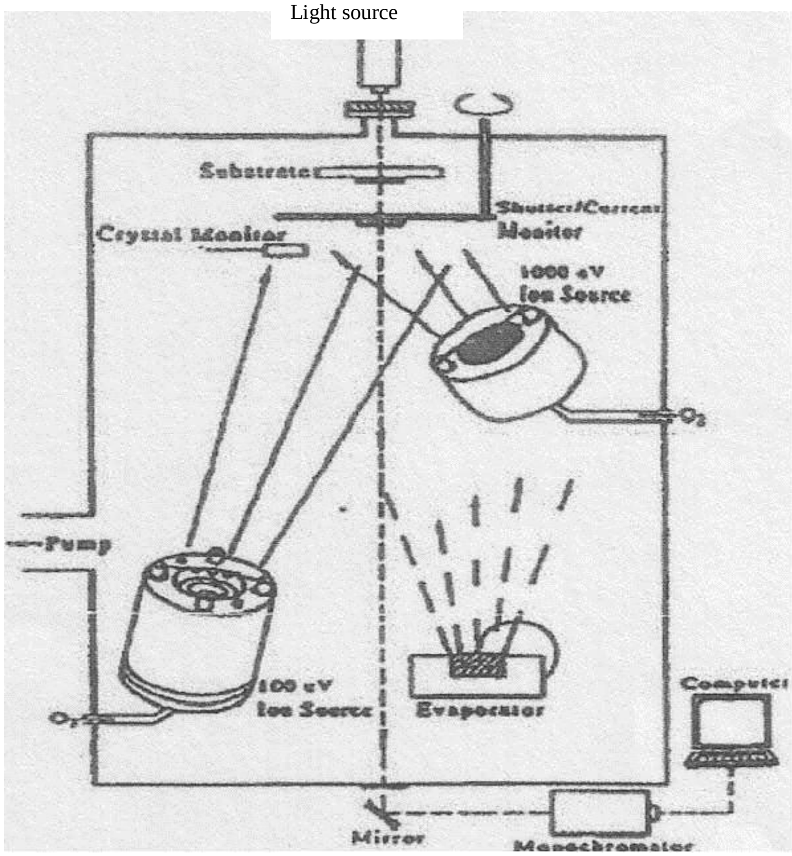

Figure 1. General equipment arrangement of the coating plant

The moisture stability of the dielectric stacks was measured at constant room temperature using a dry nitrogen purge in the chamber of a Cary 50 UV-VIS spectrophotometer. Samples were first soaked in water for 10 minutes, after removal, the location of 50% transmission cut-on wavelength of the edge slope was measured in ambient atmospheric conditions. The sample chamber was then purged with industrial grade N_2 gas (H_2O vapor content $\leq$ 5ppm) until the edge position stabilized. We found that 10 minutes was generally sufficient time to stabilize the wavelength shift of the films; the majority of the moisture shift would occur within the first 2 minutes of purging. The percent wavelength moisture shift was determined by:

$$\%Wavelength\ Shift = \frac{\lambda_{wet} - \lambda_{dry}}{\lambda_{wet}} \times 100$$

Where λ_{wet} and λ_{dry} are the wet and dry wavelength values of the 50% transmission cut-on edge. Optical density blocking curves were measured with the spectrophotometer under conditions of 32^0 C and approximately 30% relative humidity.

3- RESULTS AND DISCUSSION

First ion gun parameters were optimized for HfO_2 films via an iterative process in which the effect of the source gas composition and drive current (I_D) on the moisture stability and UV transmission of the films was measured. Figure 2 represents the moisture shift and UV transmission (extrapolated from the top envelope of the transmission curve at 250 nm) of the HfO_2 films as a function of gas ion drive current. The chamber was kept at $5x10^{-4}$ mbar during these runs in order to achieve higher ion currents. The gas ion energy was maintained at 300 eV. With oxygen ions, the percent wavelength moisture shift was higher than that for the film deposited without ion assisted (represented by dotted line) except at 1.0 amp drive current were identical. Furthermore there was a peak response at 0.5 amp caused maximal wavelength shift. Using argon ions, moisture shift decreases with increasing ion current. However, as ion current increases, UV transmission decreases significantly. This is due to the preferential sputtering of oxygen atoms from the growing film leading to poor in oxygen of the film stoichiometry [9].

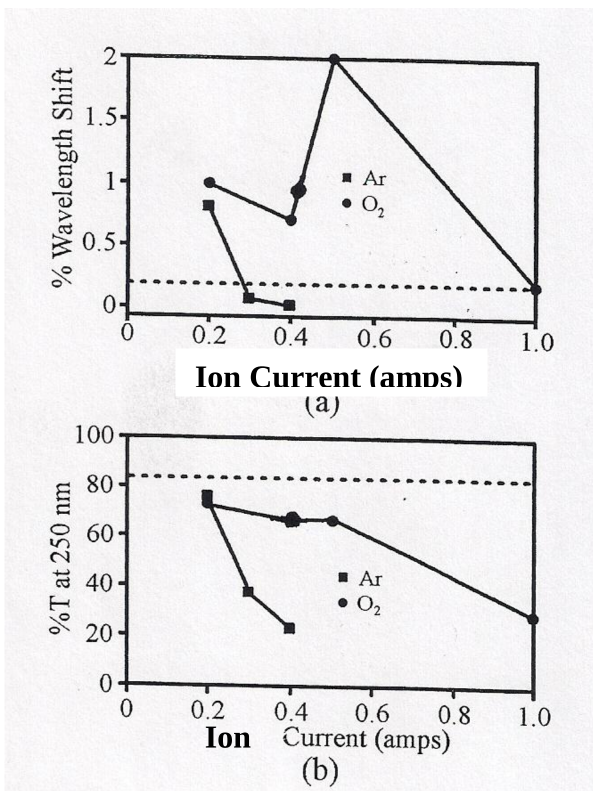

Figure 2 Optimization of the ion gas current for HfO_2 films a) maximum stability and b) transmission % at 250 nm wavelengths. The dotted line represent the values for films deposited without IAD.

Figure 3 represents the transmission and blocking curves for filters of different phase thickness deposited without IAD.

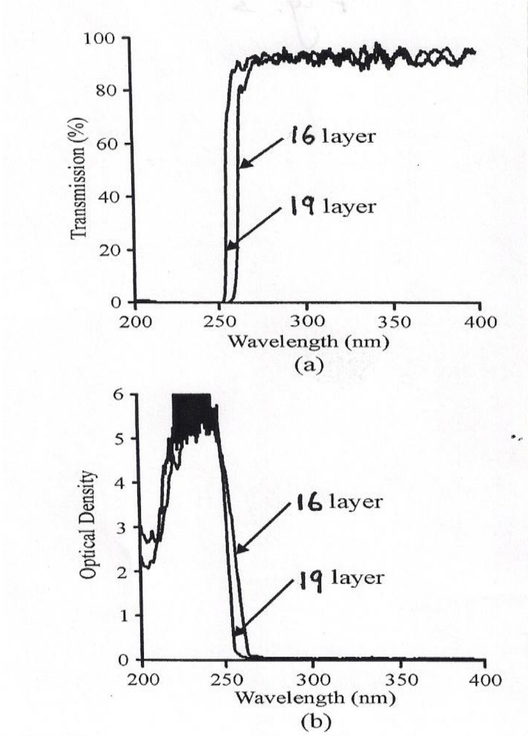

Figure 3 Spectral performance transmission %and Optical density for two long pass edge filter with 16 and 19 layers.

Two filters were compared; one composed of 16 layers, and the other one composed of 19 layers. Both filters transmitted 0.001% of the incident light at 248 nm (or equivalently, block with optical density equal 5). The 5-decade slope factor is defined according to the following equation:

$$\%\chi_5 = \frac{\lambda_{OD\ 0.3} - \lambda_{OD\ 5}}{\lambda_{OD\ 0.3}} \times 100$$

Where $\lambda_{OD\ 5}$ is the wavelength at which an optical density OD=5 is achieved, and similarly $\lambda_{OD\ 0.3}$ is the wavelength at OD=0.3, or 50% transmission, is achieved. This is a convenient description for UV edge filters in which OD=5 blocking of the Rayleigh scattering is typically required. Table 1 lists the wavelength of OD=5 and OD=0.3 blocking, and the resulting 5-decade slope factors for each filter.

Table I. Wavelength of OD=5 blocking & 50% transmission (OD=0.3) & corresponding slope factors for the two edge filters

Phase Thickness	$\lambda_{OD\ 5}$	$\lambda_{OD\ 0.3}$	χ_s Slope
16 layers	248 nm	262 nm	5.3%
19 layers	248 nm	256 nm	3.1%

The moisture stability of edge filters produced without IAD were compared to a 12 layer edge filters produced with IAD. The results of moisture shift of cut on edge wavelength position measured for films deposited with and without IAD are shown in figure 4. The results indicated that a conventionally deposited edge filter exhibits a moisture shift of about 2%. This corresponds to an approximately 4 nm shift in the cut-on edge wavelength. The edge filter produced with IAD showed a very small (≤0.05%) shifts, within the measurable error of the spectrophotometer.

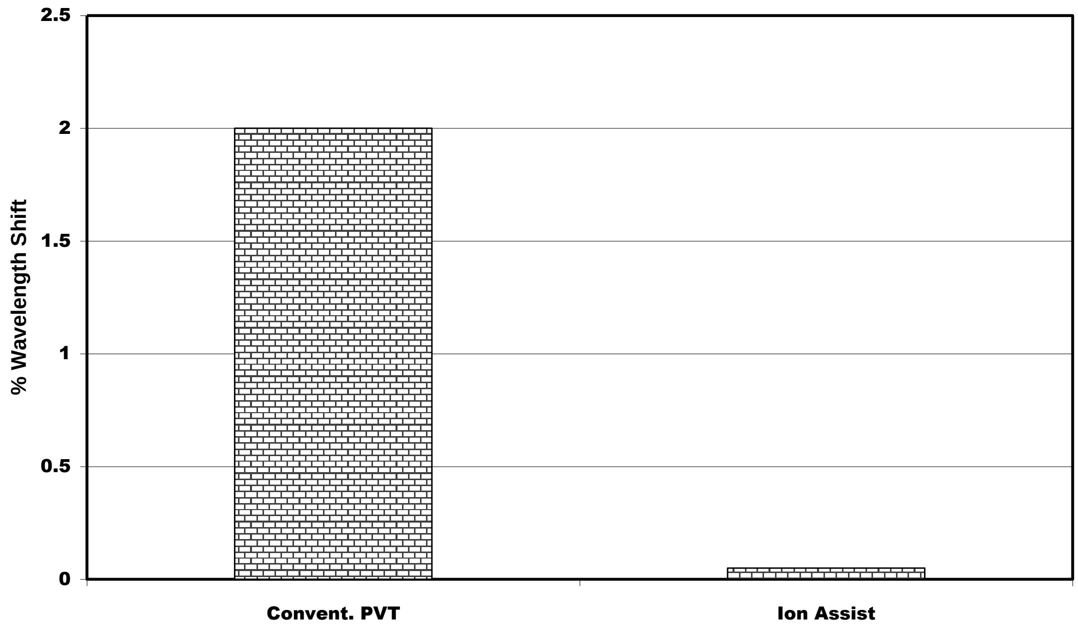

Figure 4 Moisture shift of cut on edge wavelength position measured for films deposited with and without IAD.

4 -Conclusions

We have made significant progress in developing a high phase thickness dielectric UV long-pass filter that has a greater than OD=5 blocking and steep edge slope. This film exhibited OD=5 blocking at 284 nm, and a 50% transmission cut-on edge at 256 nm. The transmission window extends to the glass substrate infrared cut-off, with low ripple and 90% average transmission. The results also showed that moisture stable films can be produced by ion bombardment during the deposition process. Moreover, edge filters produced with conventional PVD without IAD exhibited edge wavelength shifts when exposed to moisture of about 2%. Whereas the moisture shift measured for an edge filter produced with IAD was less than 0.05%.

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