# Ion-assisted deposition of moisture-stable hafnium oxide films for ultraviolet applications

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A design-of-experiments statistical approach was taken to determine the optimum ion gun operating parameters for the deposition of moisture-stable, low-absorbing hafnium oxide films by ion-assisted electron-beam evaporation. Factors identified as affecting the quality of hafnia films were chamber pressure, deposition rate, ion gun source gas composition, and ion gun current. Both oxygen and argon were used as source gases. High and low levels of the factors were chosen on the basis of our experience with the operating range of the system, and we made a series of 24 runs with all possible combinations of these factors. From a statistical analysis of the data, we find that the best films are obtained with a 1:1 mixture of argon and oxygen, 3–3.5 $\times$ $10^{-4}$ Torr chamber pressure, 0.3-nm/s deposition rate, and 0.5-A ion gun current. X-ray diffraction measurements show that the ion-assisted films exhibit a partial monoclinic crystalline structure, whereas the unassisted films are amorphous. © 2002 Optical Society of America

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## 1. Introduction

Hafnium oxide is an excellent material for use in the UV spectral range because of its low-absorption cutoff edge and high index of refraction.[1,2] However, to utilize hafnia as the high-index material in the production of steep UV edge filters, a structural problem of the film must be addressed.[3] Hafnia films deposited by electron-beam evaporation exhibit a columnar microstructure that allows entry of water vapor and air into the pores of the film.[4] Such films display a spectral shift upon exposure to moisture in the atmosphere, which condenses in the voids of the film and changes the film's effective refractive index.

It is well known that the density of hafnia films can be increased significantly when the growing film is subjected to ion bombardment.[5–9] Lehan *et al.* found that hafnia films evaporated by a reactive ion assist process when argon is used as the source gas, and an oxygen backfill exhibited no measurable moisture shift.[5] Furthermore, they found that the refractive index of the films increases as the ion momentum per arriving atom increases. Alvisi *et al.* related the structural properties of ion-beam-assisted hafnium oxide films to the ion momentum and found that the density of the film increases with increasing ion momentum.[8] An improvement in the refractive index of hafnia from 2.00 to 2.11 at 350 nm with ion assist was reported by McNally *et al.*[9]

The goal in this study is to explore how the parameters of ion gun current, source gas composition, deposition rate, and chamber pressure affect the moisture stability and UV transmission of hafnium oxide films. We apply design-of-experiments and statistical analysis methods to extract the most information from the fewest number of experimental runs.

## 2. Experimental Procedure

Hafnium oxide films were deposited in a retrofitted 1-$m^3$ box coater equipped with a Sloan Multihearth 270° electron-beam gun and a Denton Vacuum Model CC-105 cold cathode ion gun. The geometry of the deposition system is shown in Fig. 1. Hafnia was deposited from the oxide state onto rotating fused-silica substrates (50 mm $\times$ 50 mm, 1-mm thickness). The substrate temperature was kept constant at 130°C during the deposition with a quartz heater. The optical thickness of each film was 16 quarter-waves of material measured at 250 nm in transmission mode through the center substrate.

The ion gun source gases were oxygen and argon administered by two mass flow controllers (MKS Instruments, Model 1179A). No additional gases were introduced in the chamber except through the ion

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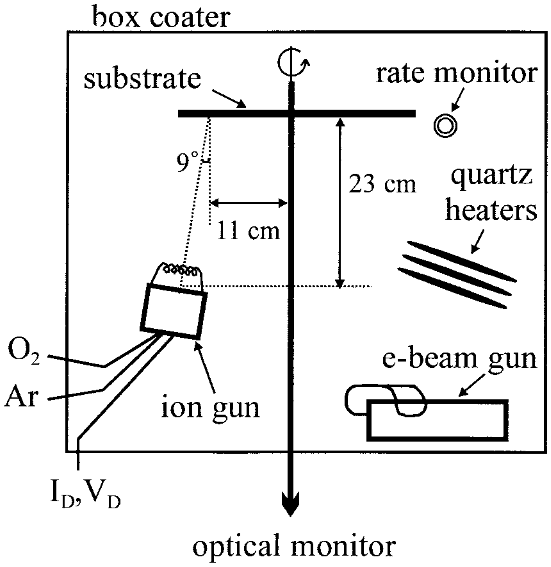


Fig. 1. Configuration of the experimental setup.

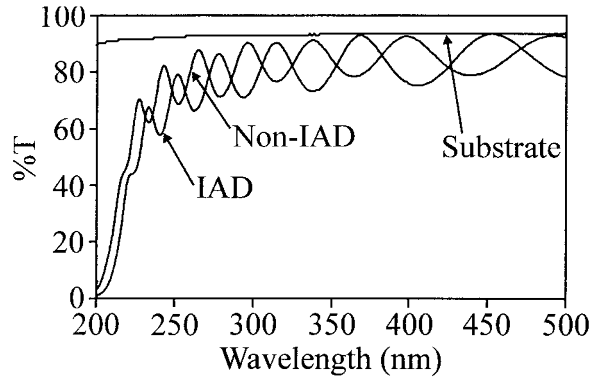


Fig. 2. Transmission of hafnia films deposited with and without ion assist compared with a bare substrate. Ion assist parameters correspond to run 3 in Table 1. IAD, ion-assisted deposition.

gun. The $O_2$ pumping speed of the chamber was approximately 2500 l/s. The ion gun was operated under constant current mode. We made no measurement of the energy or flux of the ions impinging on the substrate. However, Zabeida *et al.*[10] have measured the ion energy distribution functions for a Denton Vacuum CC-105 ion gun installed in their system. On the basis of their measurements at similar pressure and ion gun drive current, we can estimate that our mean ion energies are of the order of 100 eV.

We identified four experimental variables that would possibly affect the moisture stability and UV absorption of the hafnium oxide films: chamber pressure, deposition rate, ion gun current, and ion gun source gas mixture. On the basis of our knowledge of the stable operating range of the system, we chose relevant high and low values for each variable. The chamber pressure during each run was kept constant between either 3–3.5 $\times$ $10^{-4}$ or 4–4.5 $\times$ $10^{-4}$ Torr. The ion gun current was either 0.5 or 0.85 A. The source gas mixture was chosen to be all oxygen, all argon, or an equal mixture of the two. The deposition rate was either 0.3 or 0.6 nm/s and was monitored with a quartz-crystal microbalance (Leybold Inficon, Model XTC-2). The deposition rate is determined from the change of mass of the film on the crystal per deposition time. The relationship of the mass of the film to its thickness depends on the packing density, which is related to the chamber pressure and ion gun parameters. Therefore the deposition rate is not an entirely independent variable. We carried out a designed experiment in which hafnium oxide films were made using all possible combinations of chamber pressure, deposition rate, ion gun current, and ion gun source gas mixture. In this scheme there are a total of 24 runs ($2^5$–$2^3$) because the conditions with no source gas flow are not possible. Statistical analysis of the data was performed with the JMP 4.0 software package by the SAS Institute (Cary, North Carolina).

Films were evaluated for moisture stability and absorption at 250 nm. We measured the moisture stability of the films at constant room temperature using a dry nitrogen purge in the chamber of a Cary 50 UV–Visible spectrophotometer (Varian Inc.). Samples were first soaked in water for several minutes, and after removal the transmission was measured in ambient conditions. The sample chamber of the spectrometer was then purged with industrial-grade nitrogen gas (water-vapor content <5 parts per million) until no further shift was seen in the transmission spectrum. Typically, approximately 10 min was sufficient to stabilize the wavelength shift of the films. Shift was defined as $(\lambda_{wet} - \lambda_{dry})/\lambda_{dry} \times 100\%$, where $\lambda_{wet}$ and $\lambda_{dry}$ are the wet and dry wavelength values of an interference fringe located near 300 nm. The limit of moisture shift detection on our instrument was approximately 0.016% (0.05 nm at 300 nm). As a simple estimate of UV absorption of the films, we used the upper transmission envelope value at 250 nm (Fig. 2).

X-ray diffraction measurements were carried out by CAMET Research, Inc. (Goleta, California). Films sent for X-ray diffraction measurements were deposited onto [110]-cut sapphire substrates. Measurements were performed on a Bragg–Brentano diffractometer with CuK$\alpha$ radiation with a diffracted beam monochromator.

## 3. Results and Discussion

### A. Ion Gun Operation for UV Films

Before beginning the series of experiments, we noticed that the ion gun itself was causing the substrate to become more absorbing in the UV. During ion gun operation, with no hafnia deposition taking place, the transmission of the substrate at 250 nm decreased linearly as a function of ion gun operation time. We attributed the primary source of this contamination to the bottom liner of the ion gun.

To investigate this contamination problem, we operated the ion gun for 15 min under constant condi-

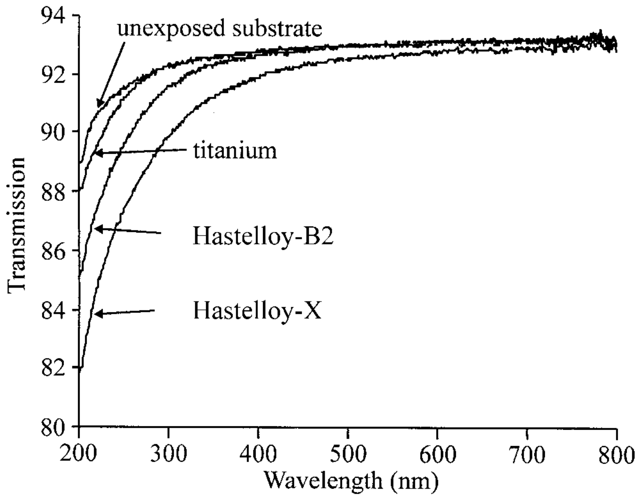


Fig. 3. Transmission of fused-silica substrates after 15-min exposure to the ion gun with various bottom liner materials. In each case, chamber pressure was 3–3.5 $\times$ $10^{-4}$ Torr, ion gun current was 0.85 A (gun voltage was 150 V), and a 1:5 $O_2$:Ar source gas ratio was used.

tions (ion gun current, 0.85 A; voltage, 150 V; chamber pressure, $3 \times 10^{-4}$ Torr; source gas mixture, 5:1 Ar:$O_2$) with various bottom liner materials. The transmission of an exposed substrate was compared with an unexposed substrate (see Fig. 3). The original bottom liner material was Hastelloy-X, an alloy of primarily Ni, Cr, Fe, and Mo. At 250 nm, the transmission of the exposed substrate was 4% points less than the unexposed substrate. Hastelloy-B2, a material composed primarily of Ni and Mo, was tested next under the same conditions. It was found that transmission at 250 nm improved by approximately 2%. Last, we tried titanium as a bottom liner material and found that the transmission improved another 2% and was similar to the transmission of the unexposed substrate. We attribute this to a lower sputtering rate for the titanium material.[11] All the results presented in this paper were produced by use of a titanium bottom liner. Lehan *et al.*[5] also found that hafnia films deposited with ion assist exhibited a larger extinction coefficient ($k$ = 3–5 $\times$ $10^{-4}$ at 300 nm) than films produced without ion assist. They attributed this absorption to ion gun contamination consisting of trace amounts of nickel and tungsten from the ion gun grids and filament.

### B. Ion Gun Optimization for Hafnia Films

Table 1 presents moisture shift and UV transmission results for the 24 experimental runs. Also listed is the ion gun voltage during each run, which varies according to pressure and ion gun current and is not directly controlled. The voltage is given as a range because it always fluctuates somewhat during ion gun operation. Typically the voltage varies by approximately 5%; however, under certain conditions the voltage fluctuation is much higher. Some of the runs with low pressure and high current were not attainable because of ion gun instability under those conditions; these runs are marked with a dash in the

**Table 1. List of Experimental Run Settings with Measured Results[a]**

| Run Number | Pressure ($\times 10^{-4}$ Torr) | Rate (nm/s) | Current I (A) | Ar:$O_2$ Ratio | V (volts) | % Shift | % $T$ at 250 nm |
|---|---|---|---|---|---|---|---|
| 1 | 3–3.5 | 3 | 0.5 | 0:1 | 315–322 | 2.6 | 78 |
| 2 | 3–3.5 | 3 | 0.5 | 1:0 | 171–325 | 0.02 | 53 |
| 3 | 3–3.5 | 3 | 0.5 | 1:1 | 300–400 | 0.02 | 74 |
| 4 | 3–3.5 | 3 | 0.85 | 0:1 | 283–292 | 0.84 | 70 |
| 5 | 3–3.5 | 3 | 0.85 | 1:0 | —[a] | — | — |
| 6 | 3–3.5 | 3 | 0.85 | 1:1 | — | — | — |
| 7 | 3–3.5 | 6 | 0.5 | 0:1 | 285–290 | 2.6 | 83 |
| 8 | 3–3.5 | 6 | 0.5 | 1:0 | 250–270 | 0.115 | 52 |
| 9 | 3–3.5 | 6 | 0.5 | 1:1 | 220–350 | 0.7 | 73 |
| 10 | 3–3.5 | 6 | 0.85 | 0:1 | — | — | — |
| 11 | 3–3.5 | 6 | 0.85 | 1:0 | — | — | — |
| 12 | 3–3.5 | 6 | 0.85 | 1:1 | — | — | — |
| 13 | 4–4.5 | 3 | 0.5 | 0:1 | 269–285 | 3.1 | 80 |
| 13b | 4–4.5 | 3 | 0.5 | 0:1 | 254–286 | 2.9 | 77 |
| 14 | 4–4.5 | 3 | 0.5 | 1:0 | 138–148 | 1.2 | 76 |
| 15 | 4–4.5 | 3 | 0.5 | 1:1 | 231–247 | 0.6 | 77 |
| 16 | 4–4.5 | 3 | 0.85 | 0:1 | 293–306 | 3.4 | 79 |
| 17 | 4–4.5 | 3 | 0.85 | 1:0 | 147–181 | 0.02 | 31 |
| 18 | 4–4.5 | 3 | 0.85 | 1:1 | 235–242 | 0.17 | 71 |
| 19 | 4–4.5 | 6 | 0.5 | 0:1 | 340–355 | 3.1 | 80 |
| 20 | 4–4.5 | 6 | 0.5 | 1:0 | 138–147 | 1.6 | 80 |
| 21 | 4–4.5 | 6 | 0.5 | 1:1 | 215–243 | 1.8 | 83 |
| 22 | 4–4.5 | 6 | 0.85 | 0:1 | 260–400 | 1.6 | 75 |
| 23 | 4–4.5 | 6 | 0.85 | 1:0 | 135–169 | 0.02 | 37 |
| 24 | 4–4.5 | 6 | 0.85 | 1:1 | 247–257 | 1.12 | 81 |

[a]Dash indicates that runs were not attainable because of ion gun instability under those conditions.

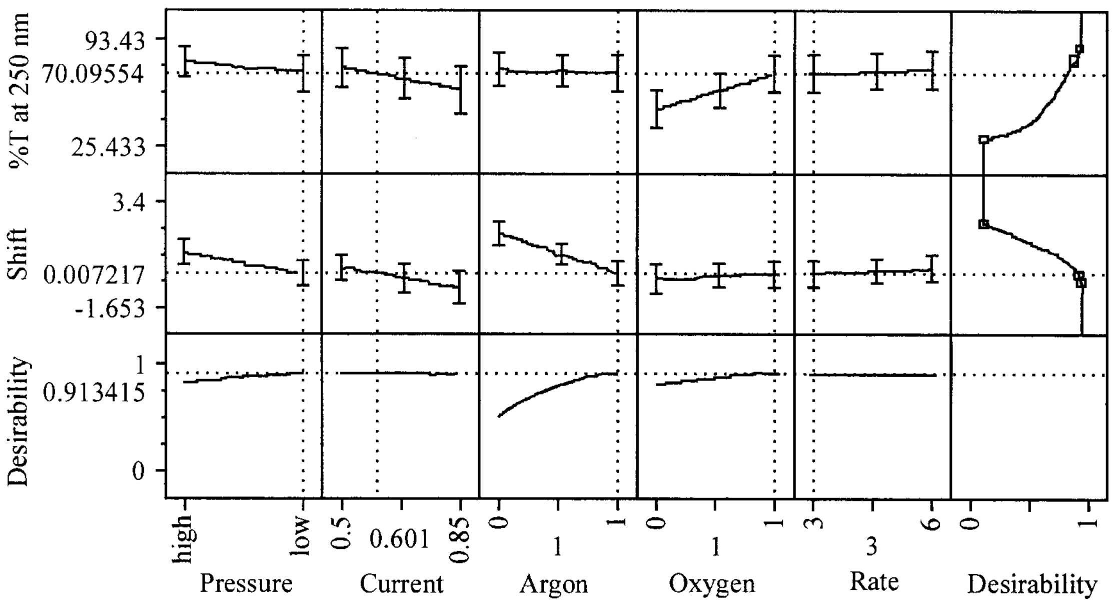


Fig. 4. Prediction plots derived by JMP software showing the effect of each of the five factors on the moisture shift and UV transmission. The desirability was maximized, and the dotted lines show the optimal settings for minimum moisture shift and maximum UV transmission.

ion gun voltage, moisture shift, and UV transmission columns of Table 1. The runs were performed in random order to prevent any systematic effects of run order from biasing the results.

These results (set of four factors and two responses) were input to the JMP software, and a least-squares analysis was performed with the two-way interactions considered. Figure 4 shows a prediction plot derived by JMP. The desirability functions are set to maximize transmission at 250 nm and minimize moisture shift. The dotted vertical lines indicate the optimal values of each of the factors, and the dotted horizontal lines show the resulting values of the responses. The importance of each factor to each response is indicated by the slope of its response curve. We find that argon flow has a large effect on moisture stability and not much effect on UV transmission. Conversely, oxygen flow affects UV transmission greatly but has little effect on moisture shift. It appears that deposition rate has minimal effect on either response. Chamber pressure affects both moisture shift and UV transmission, but it affects the moisture shift more than the UV transmission. Ion gun current has a considerable and nearly equal effect on both responses.

Because no center runs were performed, we cannot say that the response lines are actually linear. However, we can say that one set of optimal parameters within the parameter space that we explored is 3–3.5 $\times 10^{-4}$ Torr chamber pressure, an equal mixture of argon and oxygen, 0.3-nm/s deposition rate, and 0.5-A ion gun current. If the response lines are indeed linear, we should find that slightly increasing the ion gun current to a value near 0.6 A represents a nice balance between minimum moisture shift and maximum UV transmission.

The moisture shift and UV transmission of non-ion-assisted hafnia films at 130°C and 300°C are given in Table 2 and are compared with the values for ion-assisted films under optimal and nonoptimal conditions. A film produced with no ion assist at 130°C exhibits a 2.3% moisture shift. When the temperature is increased to 300°C, this shift is decreased by approximately an order of magnitude. When ion assist is incorporated under the optimal conditions and at 130°C, the moisture shift decreases by another order of magnitude. It is interesting to note that, under nonoptimum ion assist conditions, namely, high pressure, low ion current, all-$O_2$ source gas, and either high or low deposition rate, the moisture shift is actually higher than that for an unassisted film at the same temperature.

The refractive indices of the films produced with optimal condition ion assist and with no ion assist are plotted as a function of wavelength in Fig. 5. There is an average improvement of approximately 0.1 in the refractive index for the ion-assisted film over the wavelength range 250–500 nm. At 250 nm, the re-

**Table 2. Moisture Shift and UV Transmission of Hafnia Films Produced under Different Process Conditions**

| Process | Temperature (°C) | Moisture Shift (%) | % $T$ at 250 nm |
|---|---|---|---|
| No IAD[a] | 130 | 2.3 | 89 |
| No IAD | 300 | 0.2 | 88 |
| IAD[b] | 130 | $<0.02$ | 74 |
| IAD[c] | 130 | 3.1 | 80 |

[a]Ion-assisted deposition.
[b]Low-pressure, low-rate, low-current, equal-mix $O_2$ and Ar.
[c]High-pressure, high-rate, low-current, all $O_2$.

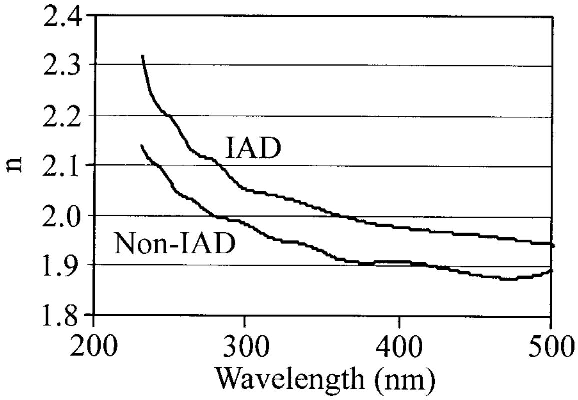


Fig. 5. Refractive index $n$ of ion-assisted and non-ion-assisted hafnia films deposited at 130°C as a function of wavelength. Ion-assisted film was deposited with optimal parameters. IAD, ion-assisted deposition.

fractive index is 2.19 for the ion-assisted and 2.06 for the non-ion-assisted film. Values of the absorption coefficient are 0.006 and 0.003 for an ion-assisted and unassisted film, respectively. We can compare this with the $n$ and $k$ values achieved for a hafnia film produced with the advanced plasma source by Leybold Systems. Götzelmann *et al.* measured a refractive index of 2.21 and an absorption coefficient of 0.002 at 250 nm.[7] Although the refractive-index values are similar, our absorption coefficient is three times larger. A more extensive investigation of the ion gun parameter phase space involving center points may lead to a film that exhibits less loss.

### C. X-Ray Diffraction Measurements

The x-ray diffraction pattern of a film deposited without ion assist is shown in Fig. 6(a). The broad peak

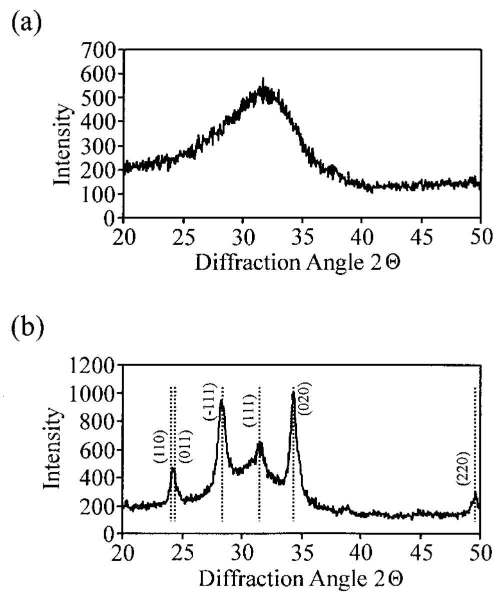


Fig. 6. X-ray diffraction patterns of hafnia films. (a) Non-ion-assisted film deposited at 130°C. (b) Ion-assisted film deposited at 130°C with optimal parameters.

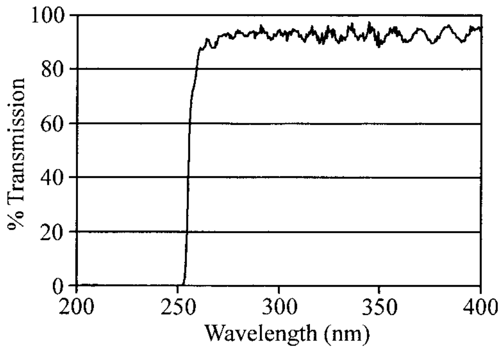


Fig. 7. High-phase-thickness hafnia silica edge filter stack deposited under optimal hafnia ion assist conditions. The filter exhibits no measurable moisture shift.

is indicative of an amorphous structure. In Fig. 6(b), the diffraction pattern of an ion-assisted hafnia film is shown. Here we find several sharp peaks superimposed on a broad background. The peak positions are indicative of a monoclinic structure. The fraction of crystalline hafnium oxide is estimated to be between 10 and 30%, and the width of the diffraction lines indicates an onset of crystallization. The crystallite size is unknown at this time.

### D. Application

We applied this research with hafnia to the production of high-phase-thickness hafnia silica stack edge filters (see Fig. 7). The optimal ion gun parameters found for hafnium oxide were applied to both materials during the entire deposition. The total thickness of the coating is approximately 3 μm, and it exhibits no measurable moisture shift. The 50% transmission cut-on edge of this particular filter is at 256 nm, and the transmission in the passband averages above 90% from 260 to 1200 nm. It is interesting that the ion gun parameters that are optimum for moisture-stable, high-transmitting hafnia films also give rise to a moisture-stable, high-transmitting hafnia silica stack coating.

## 4. Conclusion

There is a sensitive balance between moisture stability and UV transmission in ion-assisted hafnium oxide films. We have achieved acceptable results only with a mixture of argon and oxygen used as the ion gun working gas. Films deposited with oxygen exhibit large moisture shifts, and films deposited with argon exhibit unacceptably low UV transmission. It may be that films deposited with only argon as a source gas are not fully oxygenated. Argon ions are more massive than oxygen ions, and the higher energy may cause preferential sputtering of oxygen from the growing film. Use of oxygen alone as the source gas may not provide high enough energy ions to produce a dense, more crystalline film.

Using statistical methods of data analysis, we can conclude that the best quality films result from low chamber pressure ($3–3.5 \times 10^{-4}$ Torr), low rate (0.3 nm/s), an equal mixture of Ar and $O_2$, and some intermediate value of ion gun current (between 0.5 and 0.85 A). X-ray diffraction measurements indicate that unassisted films are amorphous in structure, and the effect of an optimized ion assist process is to induce a monoclinic crystal structure that is denser and moisture stable. Such films are excellent high-index layers for optical filter applications in the UV spectral region.

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