

Hafnium oxide thin films deposited by reactive middle-frequency dual-magnetron sputtering

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Abstract

Hafnium oxide thin films with a reactive dual-magnetron sputtering system were studied. They can be used for multilayer dielectric mirrors at wavelengths of 250 nm and longer. The regimes (and modes) at different electric powers and gas flows were studied and operational points were found. The power and oxygen-control (λ -control) techniques were applied to optimize the optical quality of the hafnium oxide film. The dispersion curves of the refractive index and extinction coefficient for different regimes were obtained. The reflectivity and transmission of $\text{HfO}_2/\text{SiO}_2$ stacks are demonstrated, with losses of $<0.1\%$ at the wavelength of 800 nm.

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1. Introduction

In the last two years the magnetron-sputtering (MS) technique applied to optical coatings has led to further progress in femtosecond optics and band filters [1–3]. MS has a stable deposition rate and therefore a multilayer mirror can be fabricated with time control only. This feature is important for such complex multilayer structures as chirped mirrors and band pass filters with broad transparency ranges [3]. Unfortunately, one of the disadvantages of the sputtering technique is the limited number of sputtering materials. For multilayer optical coatings it is usually sufficient to use two alternating materials of high and low refractive indices. Silicon dioxide (SiO_2) is usually used as low-index material due to its broad spectral transmission range. As high-index material, only niobium pentoxide, tantalum pentoxide, titanium oxide, aluminum oxide and zirconium oxide are known and can be used according to the application [4]. All of these have their advantages and disadvantages. Therefore, one can benefit from an increased number of useful materials. Hafnium oxide is an important material due to its high laser damage threshold [5] and broad

spectral range extending from 220 nm to 12 μm . The latter property made possible the realization of $\text{HfO}_2/\text{SiO}_2$ ultra-broadband chirped mirrors with a reflection spectral range extending from 300 nm to 900 nm [6]. The other materials mentioned above have absorption for wavelengths shorter than 350 nm and are unsuitable as high reflection index material for applications in the spectral range below 350 nm.

There has been no hafnium oxide films demonstrated with both good optical and good mechanical properties produced by reactive dual MS. The properties of hafnium oxide films are well known for electron beam evaporation [7–9], ion-assisted electron beam evaporation [10–12] and ion-beam sputtering [13] techniques. MS is just taking its first steps in the optical coating process and the optical properties of films are yet not well known in comparison with the film properties obtained with the technologies mentioned. There are many parameters in the MS process that can change the properties of a film, such as the cathode power, cathode gas flow (Ar and O_2 in our case), electric power of the plasma source and gas flow in the plasma source.

In this paper we report on the HfO_2 film properties produced with reactive MS. The films have low absorption, which gave us the possibility of producing two examples of high-quality $\text{HfO}_2/\text{SiO}_2$ stacks.

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2. Parameters of the MS process

All samples were produced with a Helios magnetron-sputtering machine (LeyboldOptics). Helios is equipped with two proprietary TwinMags magnetrons and a plasma source for plasma-ion assisted reactive middle-frequency dual-magnetron sputtering. Each magnetron contains two targets giving “dual” to the name of the process.

During the MS process the oxide and metallic modes were observed. The oxide mode is characterized by a low deposition rate and low absorption in films, whereas the metallic mode has both a higher deposition rate and higher absorption. In the metallic mode it is possible to make pure metallic films. By adding oxygen (see Fig. 1) the metallic mode transforms into the oxide mode. At some operational point rapid changes in the chamber pressure, voltage and current applied to the cathode and indications of the lambda sensor (sensor that detects oxygen in the chamber) were observed. These changes can be seen in Fig. 1. At oxygen flows higher than 21 sccm the cathode started to work in the oxide mode and the film grew very slowly at a rate of about 0.01 Å/s. When we then decreased the oxygen flow back to reach the metallic mode, hysteresis behavior of the parameters was observed: the voltage, current, pressure and lambda-sensor indicator showed other values for the same flow

of oxygen previously corresponding to the metallic mode. To return into the metallic mode, the oxygen flow must be decreased to a value much lower than 20 sccm. To have a high deposition rate, the working point should be chosen in the metallic mode. If the film has absorption, the working point has to be moved toward the oxide mode but without reaching it. There is a problem with stabilizing the process on the rather high operational curve slope between the metallic and oxide modes. For the MS process different operational regimes can be used: i) with constant cathode power and oxygen flow and ii) constant lambda-sensor indication value and oxygen flow. Lambda control usually guarantees a better film quality than power control, the reason being that the operational conditions of the target are shifted during its lifetime. In other words, the hysteresis operational curve drifts as a whole with time and the flow of oxygen or electric power applied must be varied to achieve the same operational point. When lambda control is applied, then the amount of oxygen is constant, whereas the cathode power is a variable parameter to provide the lambda sensor indication value constant. Each next point at curves in Fig. 1, 2 was measured after all the system parameters were stabilized.

The films obtained in this regime were of poor quality, with flakes. The films were flaked immediately after the coating chamber was vented. The transmission spectra of the films

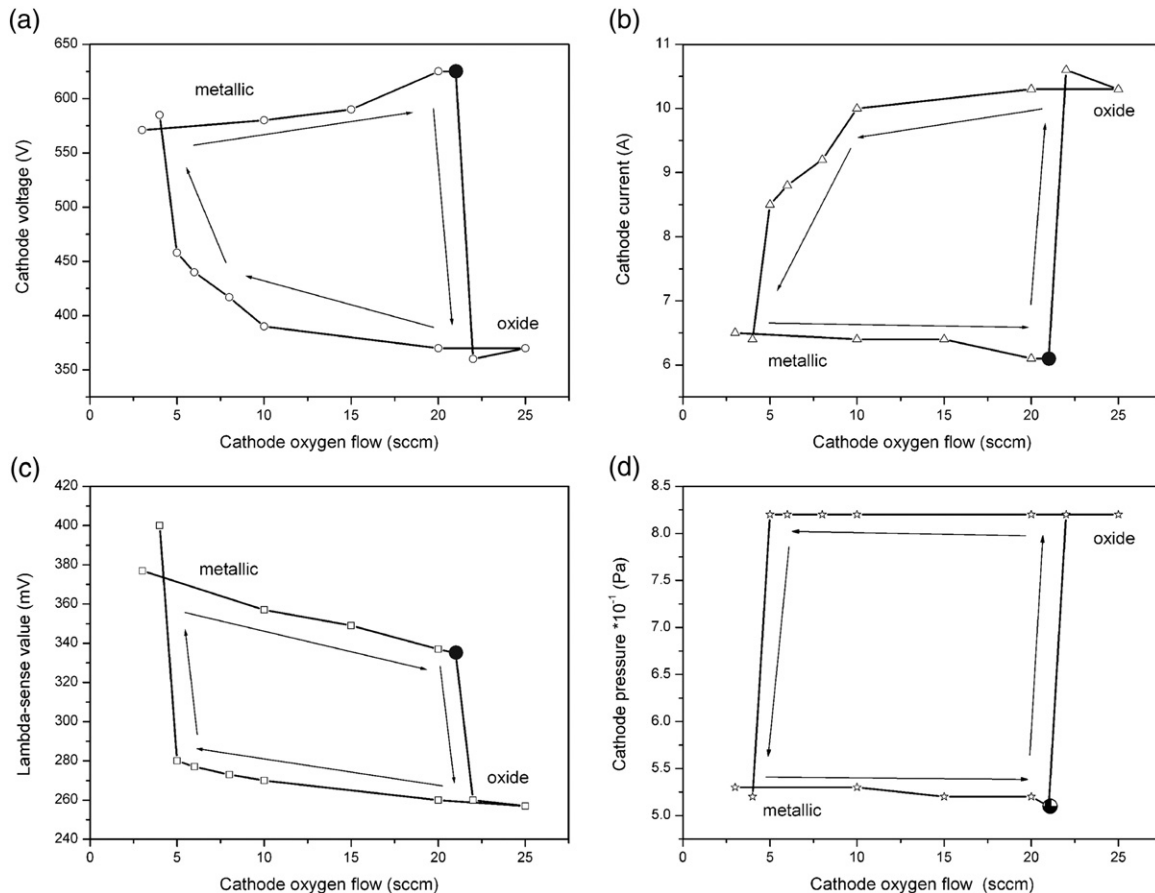


Fig. 1. The operational curves of the MS process. All curves were obtained for a constant cathode power of 3500 W and an argon flow of 40 sccm. The plasma source has a constant power of 1200 W and oxygen flow of 15 sccm. The cathode voltage behavior is shown in (a), the cathode current behavior in (b), the cathode lambda-sensor value in (c) and the pressure behavior in (d).

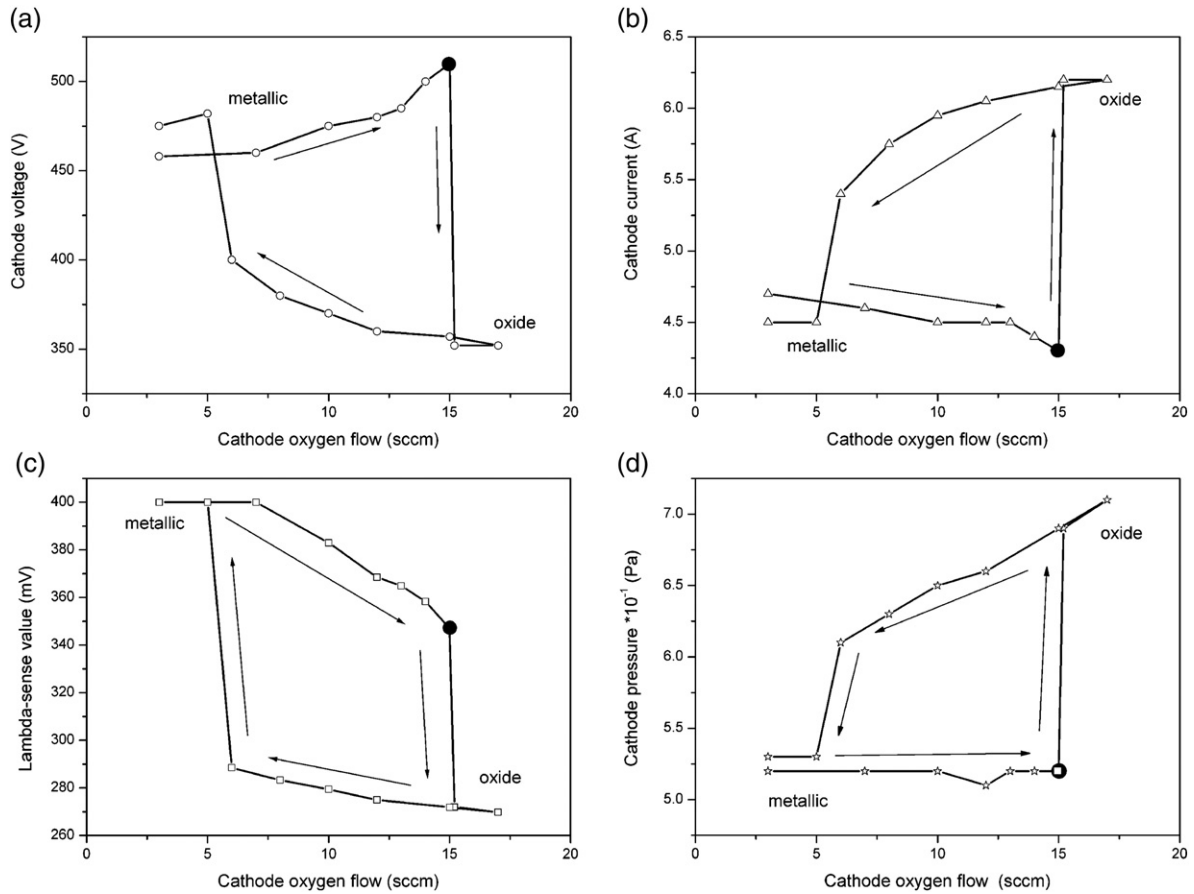


Fig. 2. Hysteresis curves of the MS process. All curves were obtained for a constant cathode power 2000 W and argon flow 40 sccm. The plasma source also has a constant power of 1200 W and oxygen flow of 15 sccm. The cathode voltage behavior is shown in (a), the cathode current behavior in (b), the cathode lambda-sensor value in (c) and the pressure behavior in (d).

prepared with these parameters are shown in Fig. 3. We concluded that the regime with a cathode power of 3500 W cannot be used, because high stress in the films leads to flaking. To decrease the stress one must either increase the argon flow or decrease the electric power, keeping the argon flow stable at the same time. For new parameters of the argon flow and plasma source flow other hysteresis curves were observed. A lower argon pressure gives a lower slope of the curve between the metallic and oxide modes. As one can see from comparison of Figs. 1 and 2, the slope decreases as the efficient argon flow decreases. In Fig. 1, the efficient flow is about twice as small because a power of 3500 W and flow of 40 sccm correspond to a flow of 23 sccm at a power of 2000 W. The deposition rate decreased due to the lower electric power.

The working point must be chosen at the point equal to 15 sccm of the oxygen flow, as shown in Fig. 2. The transmission curves of films prepared at the cathode power of 2000 W, 15 sccm of oxygen and 40 sccm of argon are shown in Fig. 3. To achieve a stable MS process and operate closer to the oxide mode (i.e. to “sit” on the slope of the curve between the metallic and oxide modes), lambda control was applied. The lambda sensor was stabilized at a value of 345 mV. Stable lambda-sensor indication guarantees a constant oxygen flow in the vicinity of the sputtering target by changing the electric power applied.

The system was pumped by turbomolecular pumps to $1 \cdot 10^{-4}$ Pa before the deposition. Argon and oxygen gases

were used for both magnetrons. The cathode power of the Si target was 4500 W. The gas pressure was about $1 \cdot 10^{-1}$ Pa during the sputtering process. Oxygen was fed near the targets to

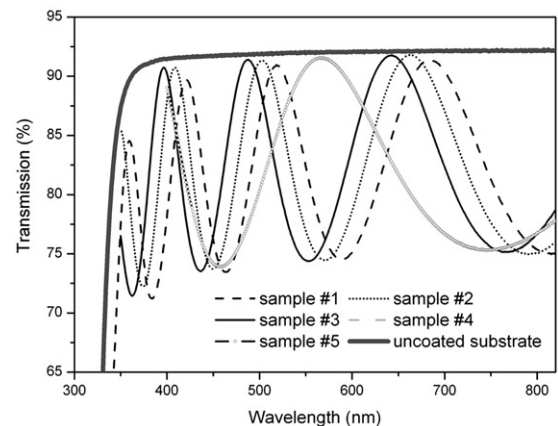


Fig. 3. Transmission curves of the samples. All curves are for the plasma source parameters: constant power of 1200 W and oxygen flow of 15 sccm. The cathode power of 3500 W and argon pressure of 40 sccm were constant for sample #1 — 19 sccm oxygen flow, sample #2 — 20 sccm oxygen flow, sample #3 — 21 sccm oxygen flow. The cathode power of 2000 W and argon pressure of 40 sccm were constant for sample #4 and sample #5, both for 15 sccm oxygen flow. The gray curve is for an uncoated substrate. Curves for samples #4 and #5 are undistinguishable in the figure.

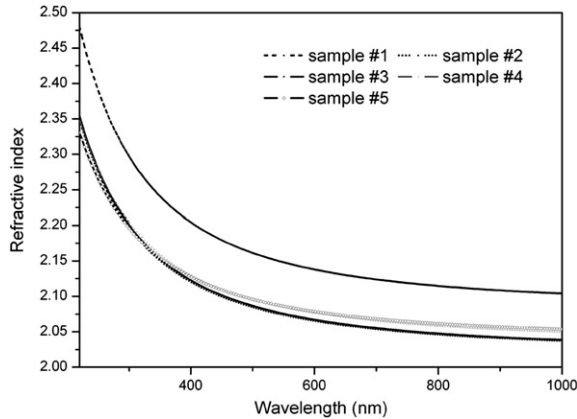


Fig. 4. The dispersion of the refractive index of the samples.

oxidize the sputtering films. The distance from the targets to the substrates was 100 mm. The purity of the Si target was 99.999% and that of the Hf target was 99.9%. By changing the electric power applied to the cathode it was possible to vary the deposition rate. The film quality was found to degrade at a high rate. A good film quality was realized at a rate of around 0.3 nm/s for both targets. In the experiments we used BK7 and FS substrates. The transmission and reflection spectra were measured with PerkinElmer spectrophotometer (Lambda 950). Helios uses an optical monitoring system OMS-4000 (Leybold Optics GmbH). It allowed measuring the transmission with a precision of 0.02%.

3. Optical properties of films

We determined the optical constants of the films by the known method, viz. the measured transmission spectrum shown in Fig. 3 is fitted to find both the dispersion of the refractive index and extinction coefficient and the thickness of the layer. The relevant details for determining the refractive index and extinction coefficient can be found in [1]. One of the useful formula for the refractive index is Cauchy's formula

$$n = a_0 + \frac{a_1}{\lambda^2} + \frac{a_2}{\lambda^4}, \quad (1)$$

where n is the refractive index, a_0 , a_1 and a_2 are constants and λ is the wavelength. In the first step we found only the dispersion of the refractive index on the assumption that the films are non-absorbing.

The dispersions of the refractive indices of samples #1–5 are shown in Fig. 4. All the samples were made with time control and a deposition time of 900 s. The relevant data are shown in Table 1. For samples #1–3 it can be seen that oxygen decreases the deposition rate and leads to lower absorption. The hafnium oxide films realized revealed unexpected behavior during the deposition process. The transmission signal of the optical monitor system (at a wavelength of 500 nm) changed from the value corresponding to the transmission of an uncoated substrate to the minimum where the optical thickness of the film was equal to a quarter of the wavelength, i.e. 125 nm. The same signal corresponding to the transmission of an uncoated substrate was expected at an optical thickness of 250 nm, but it reached the value that is 0.3% lower. Usually this is an indication that the film has absorption. But then, at an optical thickness of the film of 500 nm, the transmission once more reached the same value which is 0.3% lower than that for an uncoated substrate. In the case of absorption, the transmission must be of a lower value than that measured at this film thickness. We thus concluded that the reason for such behavior of the transmission curve is the interface between the film and substrate. It is rather interesting that similar behavior for different substrate materials and polishing qualities of the substrates was observed. For a film thickness of 300 nm, this feature leads to losses of 0.4–0.5% of the film–substrate sandwich. Losses were estimated by subtracting the transmissions of the uncoated and coated substrates in the maxima of their transmission around 500 nm (Fig. 3). Therefore, in the first stage we assumed that the films produced have no losses, because conventional estimation of losses of such films was impossible. In the second stage below we made an estimate of the absorption in hafnium oxide films on the basis of the properties of a whole multilayer stack. The loss effect observed in the interface between the substrate and the film needs further investigation with a special technique.

Sample #5 was prepared by using the same parameters as for sample #4. Its spectrum is presented in Fig. 5(a). By using Optichar, the transmission spectrum of sample #5 was fitted by the procedure already described. The fitting (crosses) is shown in Fig. 5(a). The dispersion of the refractive index and extinction coefficient are shown in Fig. 5(b). The hafnium oxide films prepared by MS can be used for coatings for the spectral range starting from at least 250 nm. Unfortunately, the approach to determining the optical constants from the transmission spectrum does not work satisfactorily in a region near the fundamental absorption edge, where sharp behavior of

Table 1
Results of the measurements of samples #1–5

Number of the sample	Power of plasma source, W	Power of cathode, W	Argon flow in sccm	Oxygen flow in sccm	Physical thickness, nm	Deposition rate, nm/s	Difference in transmission, %
1	1200	3500	40	19	480.7	0.534	0.96
2	1200	3500	40	20	479.9	0.532	0.55
3	1200	3500	40	21	464.7	0.516	0.4
4	1200	2000	40	15	272.3	0.302	0.49
5	1200	2000	40	15	273.5	0.304	0.45

the constants is observed. We believe that the data obtained up to a wavelength of 250 nm are reliable.

As one can see from Fig. 5(b), the MS process provides films of high refractive index close to that of the bulk material [4]. For comparison, all other deposition techniques give smaller values of the refractive index [8–13].

In fact, the property of the very first film deposited onto the substrate described above is not of importance for high reflection coatings because the incident radiation does not penetrate down to the very substrate. This was confirmed by the subsequent experiments. Two stacks were prepared: a 12-quarter-wavelength stack of alternating $\text{HfO}_2/\text{SiO}_2$ and a very broadband chirped mirror consisting of 83 alternating $\text{HfO}_2/\text{SiO}_2$ layers [6]. The reflection and transmission measurement curves of these stacks are shown in Fig. 6. The solid curve in both cases was calculated by subtracting the measured transmission spectra values from 100%. The reflectivity of a stack is described by the relation $R=1-T-A$, where R is the reflectivity, T the transmission and A the losses. In Fig. 6, two measurements of the reflectivity are shown by different types of circles. The vertical difference between the blank and the solid circles in the figure indicates the precision of the measurements. From comparison of the curves one can conclude that $A=0$ within the experimental accuracy of 0.1%. The wavelength shift

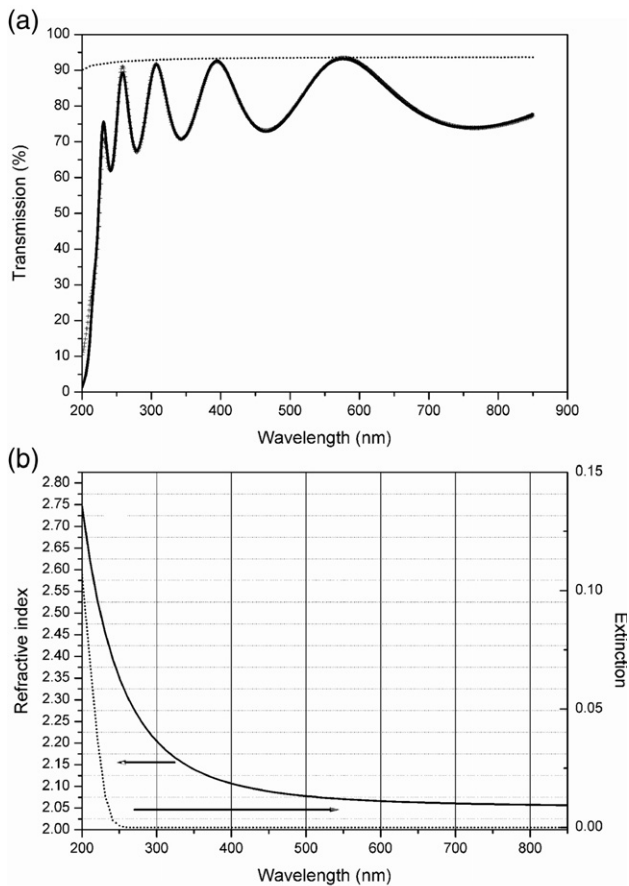


Fig. 5. (a) Transmission of sample #5 (the black curve) and the uncoated substrate (the gray dashed curve) measured in the wavelength range 220–1000 nm; the crosses show the fitting result. (b) The dispersions of the refractive index and extinction coefficient.

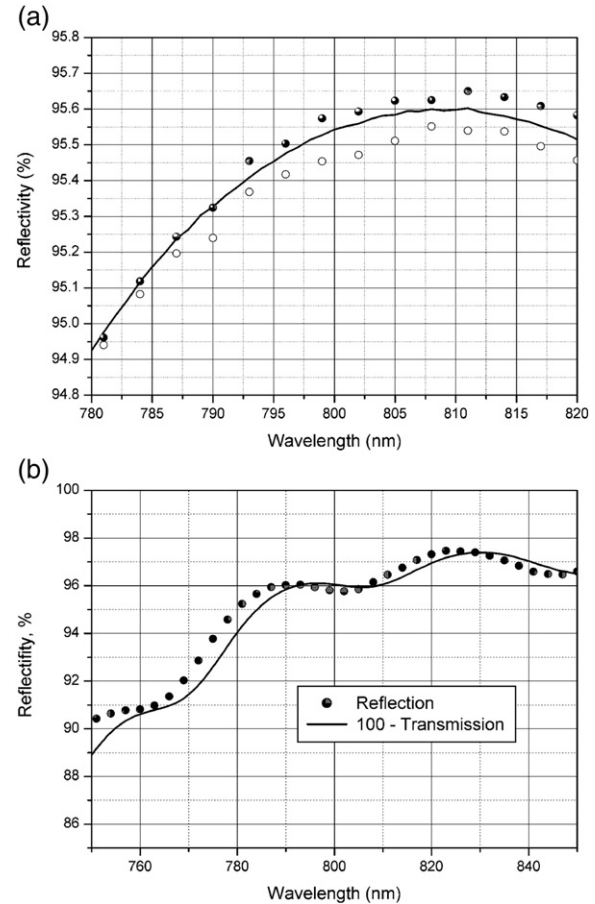


Fig. 6. The reflectivity of a quarter-wavelength $\text{HfO}_2/\text{SiO}_2$ stack (a) and a chirped mirror consisting of a sandwich of 83 alternating $\text{HfO}_2/\text{SiO}_2$ layers (solid curves), calculated from the transmission spectrum as $1-T$. The circles are the results of the reflection measurement.

visible in Fig. 6(b), can be explained by a small tilting of the mirror.

4. Conclusions

Hafnium oxide thin films were prepared with a reactive middle-frequency dual MS system. The films can be used for optical coatings due to the low absorption achieved. The parameters of the MS process were investigated and optimized, and films with different parameters were prepared and analyzed. The dispersion curves were obtained and the operational parameters were found. The deposition rate in the working range was found to be as high as 0.3 nm/s. The MS process rate is comparable to the rates of other technologies such as electron beam evaporation. The refractive index of films prepared by MS is higher than that of films prepared by electron evaporation [4]. Losses in stacks of alternating $\text{HfO}_2/\text{SiO}_2$ are not observed and are estimated at $<0.1\%$. The wavelength range where the MS system can be used has now been extended from 350 nm [1] to 250 nm. The next step toward advanced UV $\text{HfO}_2/\text{SiO}_2$ mirrors calls for additional investigation of losses in the wavelength range 220–250 nm. To decrease the film absorption further, a hafnium target of higher purity is required.

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References

- [1] V. Pervak, S. Naumov, A.V. Tikhonravov, M.K. Trubetskov, F. Krausz, A. Apolonski, *Appl. Phys.*, B 87 (2007) 5.
- [2] V. Pervak, S. Naumov, G. Tempea, V. Yakovlev, F. Krausz, A. Apolonski, in: Claude Amra, Norbert Kaiser, H. Angus Macleod (Eds.), *Advances in Optical Thin Films II*, Proc. SPIE, vol. 5963, 2005, p. 490.
- [3] V. Pervak, A.V. Tikhonravov, M.K. Trubetskov, J. Pistner, F. Krausz, A. Apolonski, *Appl. Opt.* 46 (2007) 1190.
- [4] S.M. Edlou, A. Smajkiewicz, G.A. Al-Jumaily, *Appl. Opt.* 32 (1993) 5601.
- [5] R. Chow, S. Falabella, G.E. Loomis, F. Rainer, C.J. Stolz, M.R. Kozlowski, *Appl. Opt.* 32 (1993) 5567.
- [6] V. Pervak, F. Krausz, A. Apolonski, *Opt. Lett.* 32 (2007) 1183.
- [7] J.M. Zukic, D.G. Torr, J.F. Spann, M.R. Torr, *Appl. Opt.* 29 (1990) 4284.
- [8] J.D. Traylor Kruschwitz, W.T. Pawlewicz, *Appl. Opt.* 36 (1997) 2157.
- [9] D. Smith, P. Baumeister, *Appl. Opt.* 18 (1979) 111.
- [10] J.P. Lehan, Y. Mao, B.G. Bovard, H.A. Macleod, *Thin Solid Films* 203 (1991) 227.
- [11] M. Gilo, N. Croitoru, *Thin Solid Films* 350 (1999) 203.
- [12] P.J. Martin, R.P. Netterfield, *Thin Solid Films* 199 (1991) 351.
- [13] S. Capone, G. Leo, R. Rella, P. Siciliano, L. Vasanelli, M. Alvisi, L. Mirengi, A. Rizzo, *J. Vac. Sci. Technol.*, A 16 (1998) 3564.