Influence of purity of HfO_2 on reflectance of ultraviolet multilayer

Jingmei Yuan (袁景梅), Hongji Qi (齐红基), Yuan'an Zhao (赵元安), Zhengxiu Fan (范正修), and Jianda Shao (邵建达)

R and D Center for Optical Thin Film Coatings, Shanghai Institute of Optics and Fine Mechanics, Chinese Academy of Sciences, Shanghai 201800

Received June 27, 2007

The impurities in two kinds of HfO_2 materials and in their corresponding single layer thin films were determined through glow discharge mass spectrum technology and secondary ion mass spectrometry (SIMS) equipment respectively. It was found that ZrO_2 was the main impurity in the two kinds of HfO_2 either in the original HfO_2 materials or in the electron beam deposited films. In addition, the difference of Zr content in the two kinds of HfO_2 single layer films was much larger than that of the other impurities such as Ti and Fe, which showed that it was just ZrO_2 that made the difference between the optical performance of the film products including the two kinds of HfO_2. With these two kinds of HfO_2 and the same kind of SiO_2, we deposited HfO_2/SiO_2 multilayer reflective coatings at the wavelength of 266 nm. Experimental results showed that the reflectances of these two mirrors were about 99.85% and 99.15% respectively, which agreed well with the designed results what were based on the optical constants obtained from the corresponding single layer thin films.

OCIS codes: 310.6860, 160.0160.

As ultra-low loss optical mirrors are needed in high-power laser systems, dielectric materials are generally adopted as coatings to fulfill this requirement due to their lower absorptance and higher stability compared with metals[1]. Most of the high refractive index optical materials absorb ultraviolet light at 266 nm, so only enumerable materials are applicable in this spectrum. And hafnium oxide (HfO_2) is one kind of competitive material in the ultraviolet spectrum below 250 nm because of its high refractive index and relatively low absorptance loss. In addition, it has good thermal and mechanical stability and high damage threshold[2−5].

In the HfO_2 material product, ZrO_2 is usually not looked as impurity because of their similar properties in some aspects. But as HfO_2 is transparent from 220 nm while ZrO_2 is transparent from 300 nm, ZrO_2 has a higher extinction coefficient than HfO_2[6,7], when it comes to 266 nm. So ZrO_2 will inevitably influence the optical performance of the ultraviolet components made with HfO_2. In this paper, it was tested that a different Zr content of about 3% in HfO_2 made the HfO_2/SiO_2 $(HL)^{11}H$ mirrors at 266 nm had a difference of 0.7% in the reflectance. The measured spectra fitted well with the calculated results.

Two kinds of HfO_2 marked as A and B were adopted in this experiment. A was ultraviolet HfO_2 whose rated pureness is 99.99% (from Merck Company of Germany), shortened as HfO_2(A). B was HfO_2 who had a rated pureness of 99.99% (from General Research Institute for Nonferrous Metals of Beijing, China), shortened as HfO_2(B). Impurity mass percents of these two kinds of HfO_2 were determined by glow discharge mass spectrograph (England Thermal Electricity Company) which has a measurement accuracy of ppm order. The tested results were shown in Table 1.

From Table 1, we could see that in the initial HfO_2, the amount of Zr in both materials were higher in two to three orders than those of Ti and Fe. All the impurities in HfO_2(B) were higher than those in HfO_2(A), in which Zr in HfO_2(B) were about six times to those in HfO_2(A).

As is well known, when a starting material, containing the main component and impurities, is evaporated onto a substrate to form a thin film, the relative proportion of their components will change based on the different deposition conditions. In order to know what would happen in our deposition environments, we deposited single layer thin films of about 500 nm with these two kinds of HfO_2 respectively on both ultraviolet fused silica and Si substrates.

All the substrates were cleaned ultrasonically in alcoholic solution. The films were deposited by electron beam evaporation method at the deposition temperature of 230 °C. The base pressure was controlled at 3×10^{-3} Pa and working pressure at 1.5×10^{-2} Pa. The electron beam current was controlled at 160 mA. During depositing HfO_2 thin film, a proper proportion of O_2 was introduced into the chamber.

With IMS 6F secondary ion mass spectrometry (SIMS) equipment (CAMECA Company in France), we obtained the fluctuation of Zr, Hf, Ti, O, Fe, Si contents in the two kinds of HfO_2 single-layer thin films with the depth of the films respectively, which was shown in Fig. 1.

From Fig. 1, it could be seen clearly that Ti, Fe and Si contents were neglectable. To know the contrasts of Zr, Ti and Fe contents between these two samples, we normalized O and obtained the Zr, Ti, Fe contents in both

Table 1. Impurities Mass Percent in the Two Kinds of HfO_2

Impurity	Zr	Ti	Fe
HfO_2(A)	0.6445	0.0014	0.00014
HfO_2(B)	3.5936	0.01679	0.00399

1671-7694/2008/030222-03 © 2008 Chinese Optics Letters

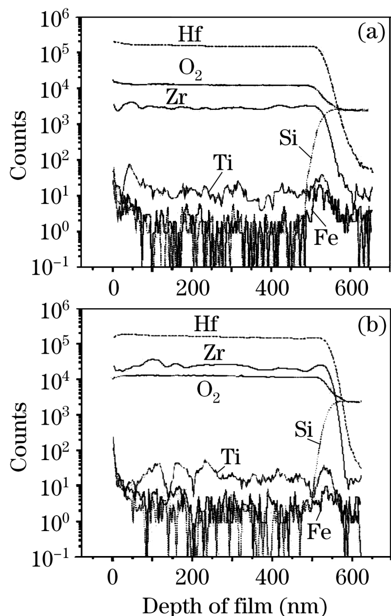

Fig. 1. Fluctuation of Zr, Hf, Ti, O, Fe, and Si contents versus the depth of the films. (a) HfO_2(A) and (b) HfO_2(B) single layer films deposited with electron beam bombardment.

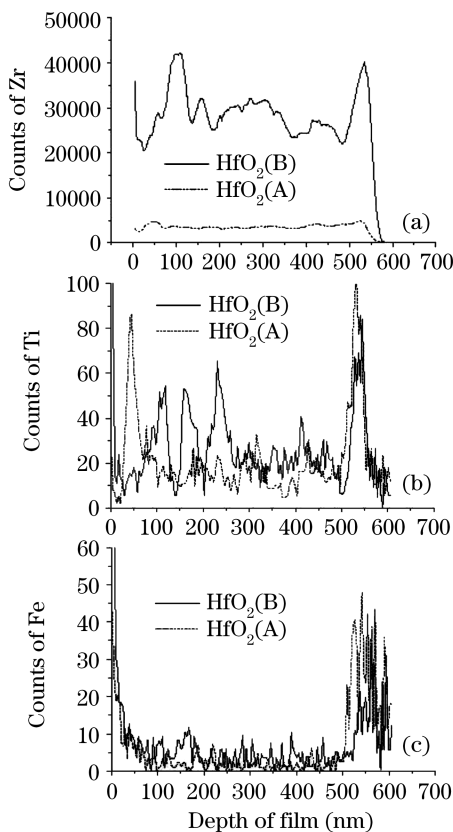

Fig. 2. Contrast of Zr, Ti, and Fe content in the two kinds of HfO_2 films versus the depth of the films. (a), (b), and (c) represent Zr, Ti, and Fe in the two kind of HfO_2, respectively.

of the two samples which were shown in Figs. 2(a), (b), and (c) respectively.

We could see from Fig. 2 that under our specialized deposition conditions, the difference of Zr content between the two kinds of HfO_2 single layer thin films was larger than that in the original materials. On the contrary, there is a smaller variance of Ti and Fe contents between the films. It was proved further that the different Zr content was the main reason to cause the difference of the optical performance of thin films including this two kinds of HfO_2.

Transmittance spectra of the two kinds of HfO_2 single layer thin films on the substrate of fused silica were measured by Lambda 900 spectrometer (from Perkin Elmer company of USA, transmittance accuracy is $\pm 0.08\%$), and the measured spectra results are shown in Fig. 3.

Figure 3 shows that the two kinds of HfO_2 single layer thin films have little transmittance difference in the near ultraviolet spectra. But with the wavelength becoming shorter, the difference became larger and larger. It is clear that the difference was caused by the different impurity contents especially by the content of ZrO_2, which absorbed the ultraviolet light and then influenced the extinction coefficient of the thin film materials directly. Simulating with Tfcalc software, we calculated the optical constants of these two kinds of HfO_2 at 266 nm, as shown in Table 2.

We calculated the reflectance of 266 nm mirrors with the multilayer stack of $(HL)^{11}H$, where H and L represent high and low refractive index layers respectively. Each layer had an optical thickness of a quarter of the design wavelength, which was 266 nm. 11 was the number of the repeating periods of (HL). The calculated reflectance curves of the two kinds of HfO_2 combined with the same kinds of SiO_2 respectively are shown in Fig. 4.

From Fig. 4, it could be seen that the two kinds of HfO_2 may build up a reflectance difference of 0.7% at the wavelength of 266 nm with the film stack of $(HL)^{11}H$.

To testify the calculated results, HfO_2(A)/SiO_2 and HfO_2(B)/SiO_2 multilayer films $(HL)^{11}H$ were deposited on BK7 substrates by electron beam evaporation method. The deposition conditions of HfO_2 were the same as those of their corresponding single layer thin films. SiO_2 was deposited at a pressure of 4×10^{-3} Pa and the beam current was 80 mA. We prepared four samples A1, A2, B1

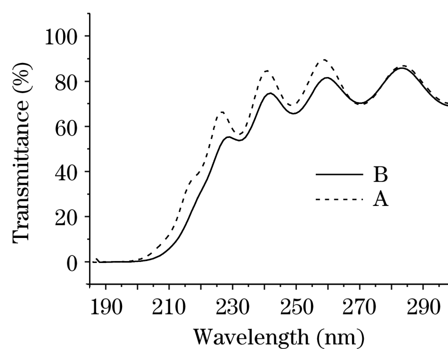

Fig. 3. Transmittance of single layer HfO_2 coatings, A is HfO_2(A) film and B is HfO_2(B) film, thickness for both films are about 500 nm.

Table 2. Optical Constants of the Two Kinds of HfO_2 at the Wavelength of 266 nm

Material	Refractive Index	Extinction Coefficient
HfO_2(A)	2.1	0.0003
HfO_2(B)	2.1	0.003

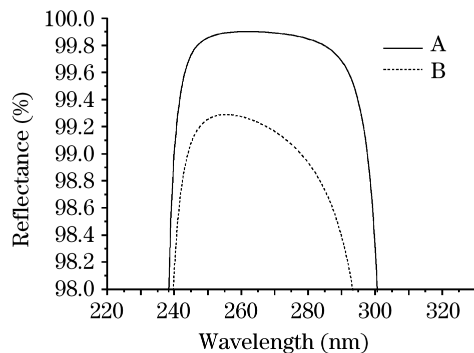

Fig. 4. Calculated reflectance spectrum for film stack of $(HL)^{11}H$, where A stands for the stack of HfO_2(A)/SiO_2, and B stands for HfO_2(B)/SiO_2.

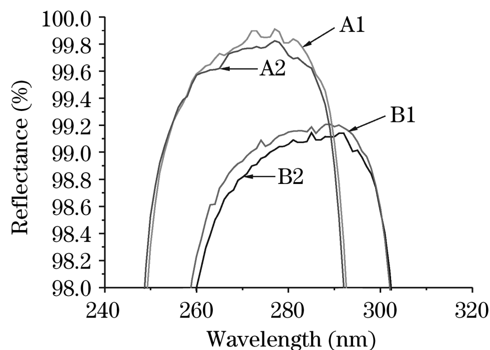

Fig. 5. Measured reflectance spectra of 266 nm mirrors with the stack of $(HL)^{11}H$. Curves A1, A2 are the reflectance curves of HfO_2(A)/SiO_2, curves B1, B2 are the reflectance curves of HfO_2(B)/SiO_2.

Table 3. RMS Roughness of the Sample Surfaces and Peak Reflectance of These Samples

Sample	A1	A2	B1	B2
RMS (nm)	0.931	1.296	1.001	1.286
Peak Reflectance (%)	99.9	99.8	99.22	99.11

and B2, whose reflectance spectra were also determined by Lambda 900 spectrometer, as shown in Fig. 5.

From Fig. 5, we can obtain the peak reflectance of these four samples, as shown in Table 3. We could see that the peak reflectance difference of A1 and A2 or B1 and B2 was about 0.1%. This was caused by the scattering loss of samples which were correlated with the root mean square (RMS) roughness of the sample surfaces[8]. We measured the surface RMS roughness of the samples with Maxim 3D 5700 profiler (Zygo Company, USA), and got the result as shown in Table 3. The experimental result of 0.1% difference agreed well with the theoretical calculated value[8]. This result indicated that when the RMS roughness of the sample surface is of 1-nm order, it will show less influence on the reflectance of the mirrors than the absorptance loss caused by the ZrO_2 content in HfO_2.

HfO_2/SiO_2 multilayer coatings at 266 nm with the kinds of HfO_2 were deposited on BK7 glass substrates with electron beam evaporation technology. They had a difference of 0.7% in the reflectance because HfO_2(A) and HfO_2(B) had different contents of impurities, especially the content of ZrO_2. RMS roughness of the sample surface had some influence on the reflectance of $(HL)^{11}H$ mirrors, because the dispersion would get stronger when the surface got more rough. Whereas comparing to the influence of ZrO_2 content in HfO_2, it was neglectable. These were all congruent with the theoretical results. It showed that the selecting of HfO_2 with low ZrO_2 content was very important to prepare high quality optical mirrors at 266 nm.

The authors are grateful to Mr. Yongming Cao and Peiyuan Fang from National Microanalysis Center in Fudan University for the SIMS measurement. J. Yuan's e-mail address is jmyuan@siom.ac.cn.

References

1. J. I. Larruquert and R. A. M. Keski-Kuha, Opt. Commun. **215,** 93 (2003).
2. J. P. Lehan, Y. Mao, B. G. Bovard, and H. A. Macleod, Thin Solids Films **203,** 227 (1991).
3. C. Fournet, B. Pinot, B. Geenen, F. Ollivier, W. Alexandre, H. Floch, G. Herve, A. Roussel, C. Cordillot, and D. Billon, Proc. SPIE **1624,** 282 (1991).
4. M. Zukic, D. G. Torr, J. F. Spann, and M. R. Torr, Appl. Opt. **29,** 4284 (1990).
5. P. Torchio, A. Gatto, M. Alvisi, G. Albrand, N. Kaiser, and C. Amra, Appl. Opt. **41,** 3256 (2002).
6. J. Yuan, Z. Tang, H. Qi, J. Shao, and Z. Fan, Acta Opt. Sin. (in Chinese) **23,** 984 (2003).
7. F. Rainer, W. H. Lowdermilk, D. Milam, C. K. Carniglia, T. T. Hart, and T. L. Lichtenstein, Appl. Opt. **24,** 496 (1985).
8. J. F. Tang and Q. Zheng, *Applied Optical Thin Films* (in Chinese) (Shanghai Science and Technology Press, Shanghai, 1984) p.197.