J Sol-Gel Sci Technol (2013) 67:339–343
DOI 10.1007/s10971-013-3086-6

ORIGINAL PAPER

Fabrication of sol–gel derived ZrO_2 thin film for HR coatings via rapid thermal annealing process

Shengzhao Wang · Jun Shen

Received: 14 November 2012 / Accepted: 6 June 2013 / Published online: 15 June 2013

Abstract The properties of sol–gel derived ZrO_2 thin films heated via a novel method of rapid thermal annealing process were studied. We investigated the effects of heat-treatment schedules with different ramp rates on the refractive index and thickness of ZrO_2 thin films as well. By controlling the heating treatment parameter, the refractive index of the ZrO_2 coatings can be adjusted from 1.69 up to 1.9 continuously, which can meet different requirement for high reflectance well. The thickness of crack-free ZrO_2 coatings can be easily controlled by employing different experimental parameters. The result of X-ray diffraction shows that as-deposited film is amorphous, and it remains stable up to the heating temperature of 400 °C. However, it begins to crystallize as the temperature increases further attaining 500 °C. Meanwhile, the surface morphology was evaluated by atomic force microscopy and the result shows that the surface of the ZrO_2 coating is smooth and uniform with root means square of 0.63 nm for the measured area of 5×5 µm. As a typical example, ZrO_2 thin films with refractive index of 1.9 are chosen for highly reflective coatings. Nearly full reflective mirror at 1,064 nm was fabricated on fused silica substrate. The laser induced damage thresholds of 22 J/cm^2 (1,064 nm, 10 ns) and 14.6 J/cm^2 (1,064 nm, 10 ns) are obtained for ZrO_2 coating and ZrO_2/SiO_2 multilayer coatings respectively.

Keywords RTA process · Sol–gel method · ZrO_2 thin film · HR coatings

1 Introduction

High reflectance thin films fabricated on the surface of lots of optical components are necessary for high power laser systems of great potential application such as the ignition source of inertial confinement fusion (ICF) [1, 2]. Meanwhile, the fabrication of the HR mirrors is a real challenge and has recently attracted much attention in the world. Currently, HR coatings could be realized by means of physical vapor deposition (such as e-beam, magnetic sputtering) [3, 4], chemical vapor deposition [5, 6] and sol–gel method [7–9]. While the sol–gel process has become more effective and competitive candidate due to its low processing cost, simple processes, adjustable refractive index and high laser threshold [10, 11]. Among all the alternative materials, colloidal based ZrO_2 coatings are stress-free and the multilayered mirrors built up from ZrO_2 sols can withstand high peak flounces delivered by current and future high-power laser [12, 13]. In addition, the wide optical transparency range, high mechanical strength, high resistance to chemical reaction and thermal stabilities of ZrO_2 thin film make it to be a more potential candidate for the high refractive index film materials in the HR coatings [14, 15]. But progresses in the sol–gel deposition of ZrO_2 high-index layers are rather slow compared to the techniques for SiO_2 films used as low refractive index in HR coatings, which greatly restricts the development of sol–gel HR mirrors [16]. Especially, high refractive index ZrO_2

S. Wang (✉)
School of Electronic and Electrical Engineering, Nanyang Institute of Technology, Nanyang 473006, Henan, China
e-mail: 0610103017@tongji.edu.cn

J. Shen
Shanghai Key Laboratory of Special Artificial Microstructure Materials and Technology, Tongji University,
Shanghai 200092, China
e-mail: shenjun67@tongji.edu.cn

thin films are needed to reduce the stack layers of HR coating, however, many researches suggest that some challenges consists in obtaining high refractive index of ZrO_2 thin films in short fabrication time. Recently, rapid thermal annealing system, often employed in semiconductor process, is used to prepare high refractive index ZrO_2 thin films in our experiment. This system can provide very fast heating rates and thermal uniformity, which is one of the key facts to obtain ZrO_2 coatings with high refractive index and high densification in a few seconds [17–21]. It improves the efficiency of fabricating high quality HR coatings compared to conventional heating methods.

ZrO_2 coatings were prepared via hydrothermal synthesis method from $ZrOCl_2 \cdot 8H_2O$ as inorganic precursor. SiO_2 coatings were fabricated by ammonia catalyzed hydrolysis method. In order to obtain HR coatings, optical calculation was made before preparation. According to the calculation, HR coatings with alternating layers of quarter wave thick high and low refractive index components were prepared on fused silica substrates. The properties of the coatings proved that the HR coatings can reach very high reflectance and indicated that high refractive index ZrO_2 thin films prepared by RTA process have great potential in the manufacture of multilayer HR coatings.

2 Experimental

Zirconium dioxide colloidal suspension was synthesized via hydrothermal process. The solution of Zirconium Oxychloride Octahydrate ($ZrOCl_2 \cdot 8H_2O$, 99 %, Sinopharm Group Chemical Reagent Co. Ltd., Shanghai, China, AR) was first dissolved in water (0.4 mol/dm^3) and the pH value of the solution was <1.0. Weak base anion-exchange resin was added in the solution in order to adsorb and remove the acids. At the end of reaction the pH value of the solution was 4.0. The clear solution was held at the range from 120 to 200 °C for 1.5 to 2 h in a stainless steel autoclave coated with Teflon linear. Then it was quenched in an ice-bath to normal temperature. Finally the water was replaced by 2-methoxyethanol (99 %, Sinopharm Group Chemical Reagent Co. Ltd., Shanghai, China, AR) by distillation. The clear, stable, methoxyethanolic sol containing 3 wt% ZrO_2 with particle size of about 12 nm was obtained.

Low refractive index silica thin film was prepared by ammonia ($NH_3 \cdot H_2O$, Ammonia water, 25–28 %, Sinopharm Group Chemical Reagent Co. Ltd., Shanghai, China) catalyzed hydrolysis and the precursor of SiO_2 sol is teraethylorthosilicate (TEOS, $Si(OC_2H_5)_4$, 98 %, Sinopharm Group Chemical Reagent Co. Ltd., Shanghai, China, AR). TEOS is mixed with ethanol (EtOH, C_2H_5OH, 99.7 %, Sinopharm Group Chemical Reagent Co. Ltd., Shanghai, China, AR) which is as solvent. TEOS, $NH_3 \cdot H_2O$ and ethanol are mixed at room temperature with a molar ratio of 1:2.45:38. And the solutions aged in stable environment (with humidity lower than 30 % and temperature of 20–25 °C) for about 3–7 days. It will be under reflux at 80 °C for several hours after SiO_2 sol aging to showing light blue.

Single ZrO_2 and SiO_2 coating were fabricated on silicon wafers, K9 glass and fused silica substrates with spin coating machine (KW-4) of the speeds ranging from 1,000 to 5,000 rpm in clean room. And the coatings were heated by RTA process at different ramp-up rate for investigating its characteristics. The optical spectrum was measured by using UV/Vis/NIR spectrophotometer (Jasco V-570m, Japan) with reflectance angle of 5°. The thickness and refractive index of the coatings were measured by ellipsometer using a He–Ne laser as the light source. The crystallization behavior examined by XRD using Cu K_α radiation and the surface morphology of ZrO_2 coatings was observed by AFM (XE-100, PSIA Corporation, Korea).

Highly reflective coatings were prepared by stacking alternating quarter wave layers of high index ZrO_2 and low index SiO_2 thin films with spin coating machine.

SiO_2 thin film was the first layer on substrate and was heated for 1 h at 150 °C with conventional furnace. By this way solvent was evaporated and then the film was heated by rapid thermal annealing processing (AG Associates Heatpulse 610) with ramp-up rate of 30 °C/s and then stayed for 20 s. The second layer is ZrO_2 thin film and it was heated for 1 h at 150 °C too. And the ZrO_2 film was heated by rapid annealing thermal processing with the same ramp-up rate and stayed for 20 s. Then again and again, the highly reflective coating was formed.

3 Results and discussion

3.1 Characteristic of single layer ZrO_2 thin films

The refractive index of ZrO_2 and SiO_2 was measured by ellipsometer or UV/Vis/NIR spectrophotometer [22]. Meanwhile, from the refractive indices we can calculate relative density according to the Lorentz–Lorenz relationship [23]:

$$\frac{n^2 - 1}{n^2 + 2} = C * \rho \qquad (1)$$

where n is the refractive index of the film and C is constant. $C = 4\pi\alpha_m N_A/3$ M and N_A is the Avogadro constant, M is molecular weight, α_m is polarization ratio (unit is cm^3 in Centimeter-Gram-Second system of units), ρ is the density of the films. To the film of same nature, the relative density D of thin films can be obtained by formula 2:

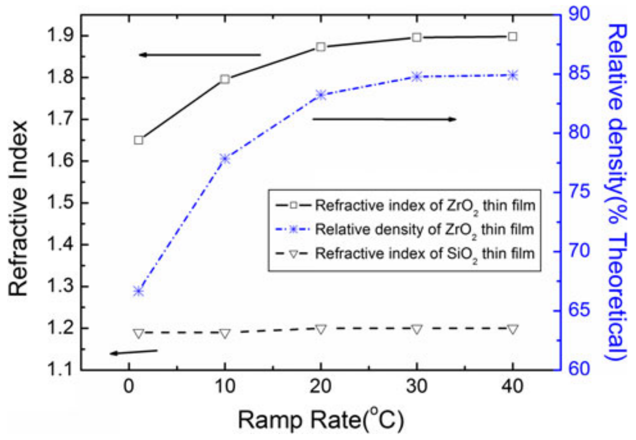

Fig. 1 Refractive index and density of ZrO_2 (SiO_2) thin films heated with different ramp rate

$$D = \frac{(n_f^2 - 1) * (n_c^2 + 2)}{(n_f^2 + 2) * (n_c^2 - 1)} \times 100\% \tag{2}$$

where n_f is refractive index of the films, n_c is refractive index of ideal crystals. To ZrO_2 and SiO_2, n_c was assumed of 2.15 and 1.46 respectively [24–26].

The effect of ramp-up rates on refractive index and film densification are investigated and the results are shown in Fig. 1. It shows that higher refractive indices and greater consolidation were obtained at higher heating rates. It was possible to prepare ZrO_2 film with a refractive index ranging from 1.69 of 1 °C/s to about 1.9 of 30 °C/s and 40 °C/s at 600 °C for 20 s by using different temperature and ramp rate. Meanwhile, we are able to control the film densification from 70 to 85 % of theoretical calculation under these conditions. It is particularly noteworthy that a refractive index of 1.9 for ZrO_2 was obtained within short time by using RTA process. Although such a high refractive is very useful in some optical applications including HR coatings, it is generally difficult to obtain with conventional heating treatment method in short time.

As shown from Figure, there are almost no changes in the refractive index of ZrO_2 when the ramp rate of 30 °C/s held at 600 °C for 20 s. Therefore the ramp rate of 30 °C/s is used to heat the ZrO_2 films.

Meanwhile, SiO_2 thin film was prepared by spinning coating method with the speed of 3,000 rpm and the film thickness of about 258.6 nm. The refractive index of SiO_2 film from 1.17 becomes 1.2 after heated by conventional furnace with 150 °C for 1 h. Its thickness becomes 223 nm in this process. And then the film was heated by RTA process. From the figure, the refractive index of SiO_2 films was essentially unchanged. Therefore, the relative density was almost uniform.

Zirconia thin films are held at 500, 600 and 700 °C for different heating treatment time and the thickness varies from about 220 to 120 nm around during the heating treatment process in Fig. 2. According to the result, the thickness decreases with the heating time, while they finally changes slightly as the heating treatment time is more than 20 s. In the process of HR preparation each film was heated before the next film fabrication.

3.2 Crystallization of ZrO_2 thin films

For examining the microstructure of the samples, XRD analysis was performed. As shown in Fig. 3, the as-deposited film yielded no other diffraction peak, which is the common feature for the amorphous ZrO_2 films. With the increasing of the heating temperature of the ramp rate at 30 °C/s, the XRD spectra is almost unchanged, which shows that the films remains stable in amorphous state up to 400 °C. But when the temperature increased to 500 °C, zirconia thin films began to crystallize and diffraction peaks appears at about 2θ–30.1°, corresponding to the (101) planes of tetragonal ZrO_2 [27]. Further heating treatment doesn't result in any change except for the intensity of peak in the XRD spectrum. According to the full width at half maximum (FWHM) of XRD pattern and Scherrer equation, the average crystallite size was estimated as about 1.2, 1.3, 1.3, and 1.4 nm as the temperature is 500, 600, 700, and 800 °C respectively. When the ZrO_2 films were heated by RTA system at these temperatures, only smaller crystallite size is measured. It reveals that the nucleation rate grows faster in our experiment, which is consistent with the result obtained by R. Pascual [28].

Based on the above results and analysis, ZrO_2 refractive index increases and films thickness declines during heating treatment (shown in Figs. 1, 2). Meanwhile, the sol–gel film is porous and amorphous after spin-deposition onto a substrate and crystallization occurs in the ZrO_2 films during the heating treatment as presented in Fig. 3. Some recent theories consider the competition between densification

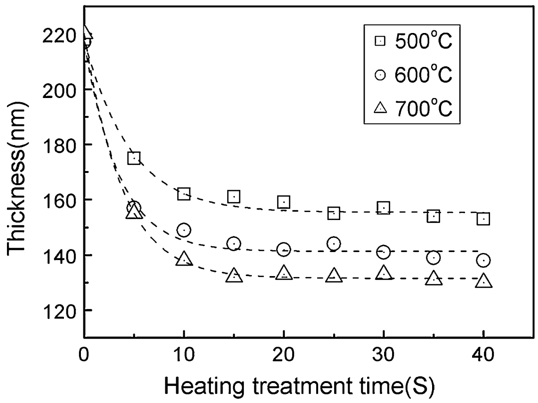

Fig. 2 Thickness of ZrO_2 thin films with different heating treatment time

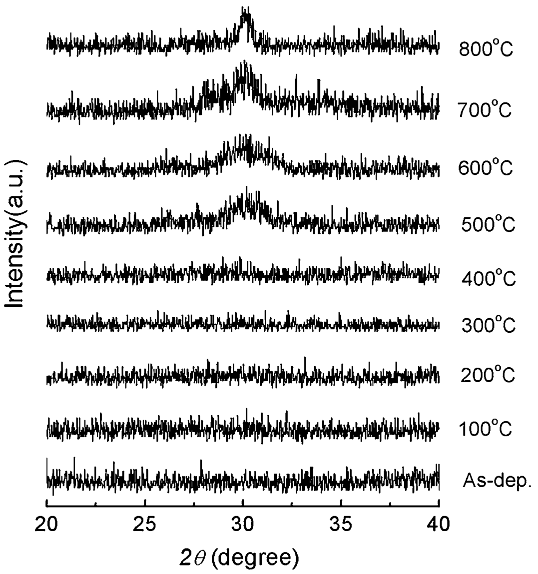

Fig. 3 XRD-patterns of rapidly heated ZrO_2 thin films with the ramp rate of 30 °C/s

and crystallization when sintering a porous, amorphous material [29, 30]. In the paper, we get high refractive index and high densification ZrO_2 thin films by using RTA system. We think that the film densification is supposed to precede crystallization and the maximum material density is obtained by using high ramp rate of RTA process.

In the experiment, a gel is expected to crystallize in a different manner than does a dense glass because of an extensive of nanometer size pores. As is well known, the rates of nucleation and crystal growth determine the crystal size and morphology that evolve in a gel material. In the theory, if the nucleation rate is moderately high when compared to the crystal growth rate. The crystals cannot grow equally in all directions, because of the porous gel structure. Instead, the growth of crystals is interrupted by the pore surfaces. Finally, the crystal radii are on the same size scale in the gel and the densities of the crystals approach maximum theoretical density [31–33]. In summary, the evidence was offered in support of the model concerning that the maximum material density is obtained prior to the onset of crystallization by using high ramp rate in this paper. Although, crystallization appears in ZrO_2 thin films at 500 °C, the relatively high densification and high refractive index films are obtained by RTA process.

3.3 Surface morphology

It is known that the crystallization of an oxide would cause significant increase in surface roughness. Therefore, to examine the surface morphology of the samples, AFM analysis was performed. In order to obtain a typical experiment result, 600 °C and ramp rate of 30 °C/s is chosen to heat the ZrO_2 films. The image (Fig. 4) clearly shows the surface characteristics of the ZrO_2 thin films heated by RTA system. The RMS representing surface roughness is about 0.63 nm for the measured area of $5 \times 5\ \mu m^2$. This roughness is typical and easy to reproduce for the whole specimen with an area $2 \times 2\ cm^2$. It should be noted that no cracks appeared to be present according to AFM observation. Furthermore, no cracks were observed when the film less than about 240 nm after annealing.

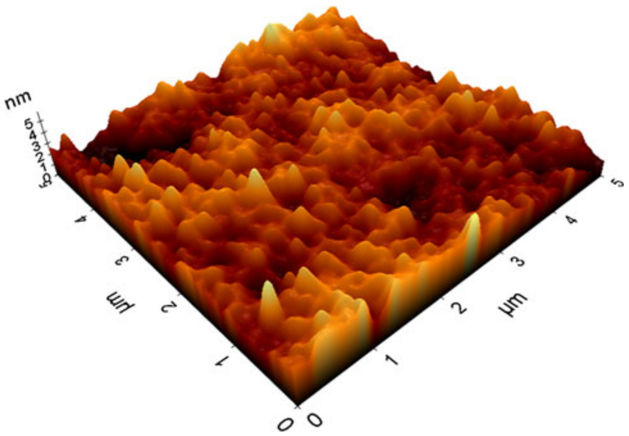

Fig. 4 Typical atomic force microscopy of heated ZrO_2 thin films over an area of $5 \times 5\ \mu m^2$

3.4 Optical properties of HR coatings

Twenty-four layers consisting of alternating quarterwave-thick layers of ZrO_2 and SiO_2 on fused silica substrates were obtained via RTA process. The typical experimental transmission spectrum and the minimum transmittance of about 1 % near 1,064 in the band of 1,030 to 1,080 nm was shown in Fig. 5. Such a result is consistent with that reported by Shen [7] and Liang [16]. Therefore, it is proved that ZrO_2 coatings heated by RTA process have high potential in fabrication of multilayer HR coatings.

One-on-one single shot laser damage tests at 1,064 nm wavelength with a pulse length of 10 ns were carried out on the single layer as well as multilayer systems. The thresholds averaged 22 and 14.6 J/cm^2 is obtained for thin ZrO_2-films and $[SiO_2–ZrO_2]^{12}$ multilayer HR coatings, respectively. The result of LIDT also shows that the coatings prepared by RTA process have great potential in the fabrication of HR mirrors.

4 Conclusions

Sol–gel derived high (low) refractive index with high LIDT ZrO_2 (SiO_2) thin films have been successfully prepared via RTA process. The refractive index and thickness of ZrO_2

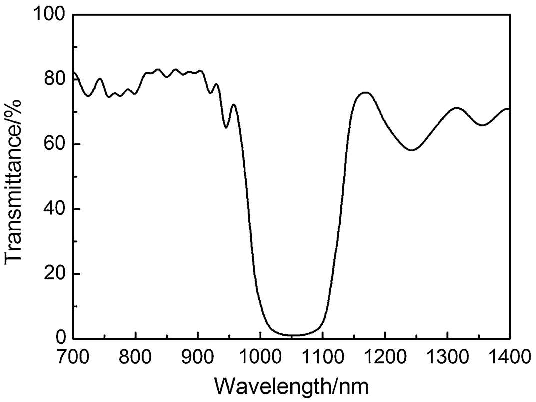

Fig. 5 Transmittance spectrum of HR coating fabricated with 12 pairs of alternated quarterwave-thick SiO_2 and ZrO_2 layers

thin films can be adjusted by choosing different preparation procedure such as 600 °C with 30 °C/s ramp rate. Its microstructure and surface morphology of ZrO_2 thin films can be controlled by using appropriate fabrication parameters such as pre-heated to 150 °C with 1 h in conventional furnace then 600 °C heat treatment temperature with 20 s in RTA process. As a typical example, multilayer $[SiO_2–ZrO_2]^{12}$ coatings were prepared on fused silica substrates. The minimum transmittance of the sample is about 1 % in 1,030–1,080 nm by using RTA process according to the experimental results.

Acknowledgments This subject is supported by Opening Project of Shanghai Key Laboratory of Special Artificial Microstructure Materials and Technology (No. ammt2012A-11).

References

1. Belleville PF, Bonnin C, Priotton JJ (2000) J Sol–Gel Sci Technol 19(1–3):223–226
2. Oliver JB, Kupinski P, Rigatti AL, Schmid AW, Lambropoulos JC, Papernov S, Kozlov A, Smith C, Hand RD (2012) Opt Express 20(15):16596–16610
3. Zhang D, Wang C, Fan P, Cai X, Zheng Z, Shao J, Fan Z (2009) Opt Express 17(10):8246–8252
4. Sprio S, Guicciardi S, Bellosi A, Pezzotti G (2006) Surf Coat Technol 4200(14–15):4579–4585
5. Jeon TS, White JM, Kwong DL (2001) Appl Phys Lett 78(3):368–370
6. Ferrer FJ, Frutos F, Garcia–Lopez J, Gonzalez–Elipe AR, Yubero F (2007) Thin Solid Films 516(2–4):481–485
7. Shen J, Zhang Q, Wang J, Yang T, Deng Z, Zhou B, Chen L (2000) J Sol Gel Sci Technol 19(1–3):271–274
8. Liang L, Yao X, Zhang L, Sheng Y, Dong W, Sun Y (2007) J Opt Soc Am B 24(5):1066–1074
9. Li H, Xiong H, Tang Y (2010) Chin Opt Lett 8(2):241–243
10. Shen J, Wang S-Z, Wang X-D, Liu Y, Li X-G (2009) Proc SPIE 7381:7381C1–7381C8
11. Wang X, Shen J (2012) J Sol Gel Sci Technol 61(1):206–212
12. Floch HG, Belleville PF, Pegon PM, Dijonneau CS, Guerain JR (1996) Proc SPIE 2633:432–445
13. Yang F, Shen J, Sun Q, Zhou B, Guangming W, Mugnier J (2006) Proc SPIE 6034:261–268
14. Thomas IM (1994) Proc SPIE 2288:50–55
15. Jun S, Shengzhao W, Xiaodong W, Zhihua Z, Bin Z, Guangming W (2010) Rare Metal Mater Eng 39(Suppl 2):52–56
16. Liang L, Yao X, Zhang L, Dong W, Sun Y (2008) J Sol Gel Sci Technol 47(2):173–181
17. Dieudonné X, Vallé K, Belleville P (2011) Opt Express 19(17):16356–16364
18. Pascual R, Sayer M, Vasant Kumar CVR, Zou L (1991) J Appl Phys 70(4):2348–2352
19. Bellessa J, Rabaste S, Plenet J-C, Mugnier J (2003) Proc SPIE 4944:15–22
20. Kobayashi Y, Katayama M, Kato M, Kuramochi S (2013) J Am Ceram Soc Article first published online: 26 APR 2013
21. Olevsky EA, Kandukuri S, Froyen L (2007) J Appl Phys 102(11):114913
22. Wang X, Shen J (2010) J Sol Gel Sci Technol 53(2):322–327
23. Born M, Wolf E (2003) Principles of optics: electromagnetic theory of propagation, interference and diffraction of light, 7th expanded Ed. United Kingdom at the University Press, Cambridge, p 92
24. Li X, Shen J (2011) J Sol Gel Sci Technol 59(3):539–545
25. Rujkorakarn R, Sites JR (1986) J Vac Sci Technol 4(3):568–571
26. Chin AK, Satyanarayan A, Zarrabi JH, Vetterling W (1988) J Appl Phys 64(3):994–999
27. Gao Y, Masuda Y, Ohta H, Koumoto K (2004) Chem Mater 16(13):2615–2622
28. Pascual R, Sayer M, Vasant Kumar CVR, Zou L (1991) J Appl Phys 70(4):2348–2352
29. Scherer GW (1997) J Sol Gel Sci Technol 8(1–3):353–363
30. Du XM, Almeida RM (1995) J Mater Res 11(2):353–357
31. Keddie JL, Giannelis EP (1991) J Am Ceram Soc 74(10):2669–2671
32. Keddie JL, Braun PV, Giannelis EP (1994) J Am Ceram Soc 77(6):1592–1596
33. Díaz–Parralejo A, Caruso R, Ortiza AL, Guiberteau F (2004) Thin Solid Films 458(1–2):92–97