High-speed Deposition of Tetragonal-ZrO₂-dispersed SiO₂ Nanocomposite Films by Laser Chemical Vapor Deposition

Ling Fang Xu ^a, Akihiko Ito ^{b,*}, Takashi Goto ^b

^a Hubei Collaborative Innovation Center for Advanced Organic Chemical Materials, Faculty of Physics and Electronic Technology, Hubei University, Wuhan 430062, P.R. China

^b Institute for Materials Research, Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai 980-8577, Japan

* Tel: +81-22-215-2106; E-mail: itonium@imr.tohoku.ac.jp

Abstract: Tetragonal-ZrO₂ (t-ZrO₂)-dispersed amorphous SiO₂ composite films were prepared by laser chemical vapor deposition at high deposition rates of 40–300 μm h⁻¹. Without SiO₂ the films prepared at deposition temperatures of 869–1246 K contained monoclinic ZrO₂. ZrO₂ was stabilized in its tetragonal phase in an amorphous SiO₂ matrix at deposition temperatures of 867–1170 K. The t-ZrO₂ particle size decreased from 21 to 11 nm with increasing deposition temperature. In the amorphous SiO₂ matrix, t-ZrO₂ nanoparticles formed a network structure at lower deposition temperatures, whereas the t-ZrO₂ nanoparticles were homogeneously dispersed at higher deposition temperatures.

Keywords: Zirconia; Silica; Nanocomposite; Laser CVD; Film

1. Introduction

Tetragonal zirconia ($t\text{-ZrO}_2$) has been used as a structural material because of its excellent mechanical properties. In $t\text{-ZrO}_2$ -dispersed composites, $t\text{-ZrO}_2$ can prevent crack propagation because $t\text{-ZrO}_2$ undergoes a stress-induced phase transformation from $t\text{-ZrO}_2$ to monoclinic zirconia ($m\text{-ZrO}_2$) [1,2]. Because $m\text{-ZrO}_2$ is the stable phase at room temperature, $t\text{-ZrO}_2$ is commonly stabilized by substituting aliovalent cations such as Y^{3+} or Ca^{2+} for Zr^{4+} . $\text{ZrO}_2\text{-SiO}_2$ composites are definitely promising protective coatings with excellent corrosion and chemical resistances; however, Si^{4+} cannot substitute for Zr^{4+} in ZrO_2 because Si^{4+} possesses a smaller ionic radius when compared with Zr^{4+} , tends to exhibit lower coordination numbers and forms stronger covalent bonds with oxygen. Without substitution $t\text{-ZrO}_2$ can be stabilized in the forms of nanoparticles [3], films [4–7] and composites [8,9] because of thermodynamics [10,11], nucleation kinetics [8,12], and lattice strain and defects [7,9].

$\text{ZrO}_2\text{-SiO}_2$ glass composite powders have been prepared by wet-chemical processes [13–15], primarily by sol–gel methods. However, with these methods, high temperatures (1173–1623 K) are required to obtain crystalline $t\text{-ZrO}_2$, although high temperatures often result in a mixture of t - and $m\text{-ZrO}_2$ phases. On the other hand, the literature contains no reports of the vapor deposition of a $\text{ZrO}_2\text{-SiO}_2$ composite film in which $t\text{-ZrO}_2$ nanoparticles are stabilized and dispersed in the amorphous SiO_2 matrix.

Chemical vapor deposition (CVD) is advantageous for producing large-area conformal coatings and nanoparticle-dispersed films using multi-component source gases. We have reported that the use of laser irradiation in a CVD process, *i.e.*, laser chemical vapor deposition (LCVD) enhances chemical reactions, resulting in unique nanocrystal–matrix composite films such as SiC-SiO_2 [16], Rh-ZrO_2 [17], and

ZrO₂–Al₂O₃ [18] films. For example, t-ZrO₂ was stabilized in an Al₂O₃ matrix and the resulting films exhibited excellent mechanical and thermal properties [18]. In the present work, we prepared ZrO₂–SiO₂ nanocomposite films by LCVD and investigated the effect of the deposition temperature on the microstructural evolution of the films.

2. Experimental

Details of the LCVD apparatus have been reported elsewhere [19]. Zirconium acetylacetonate (Zr(acac)₄) and tetraethyl orthosilicate (TEOS) precursors were heated at 453 K and 343 K, respectively. The amounts of Zr(acac)₄ and TEOS transported were estimated from the mass change of the precursors after deposition. The ZrO₂ content in the source vapor (m_{ZrO_2}) was 14 ± 3 mol% ZrO₂. The precursor vapors were transported into the chamber using an Ar carrier gas; O₂ gas was separately introduced into the chamber through a double-tube nozzle. The total pressure in the chamber was maintained at 400 Pa. A continuous-wave InGaAs laser was employed. AlN plates ($8 \times 8 \times 1$ mm³) were used as substrates. The deposition temperature (T_{dep}) was measured using a thermocouple inserted into the backside of the substrate. The T_{dep} was increased from 867 to 1170 K by increasing the laser power from 100 to 200 W.

The phase composition of the resulting films was studied by X-ray diffraction (XRD) with a Cu-K α radiation source (Rigaku, Ultima-IV). The surfaces and cross-sectional microstructures were observed using a scanning electron microscope (SEM; Hitachi, S-3100H) and a transmission electron microscope (TEM; Topcon, EM-002B). The deposition rate was calculated from the film thickness and deposition time (0.6 ks). The compositions of the films were measured using an electron microprobe analyzer (EPMA; JEOL JXA-8621MX).

3. Results and Discussion

Figure 1 shows typical XRD patterns of a ZrO_2 film and the ZrO_2 – SiO_2 nanocomposite films. The ZrO_2 films prepared at $T_{\text{dep}} = 869$ – 1246 K without TEOS were indexed as m- ZrO_2 (ICSD #41572) (Fig. 1(a)); m- ZrO_2 is the stable phase formed at temperatures less than 1443 K in the absence of additives [2,20]. ZrO_2 – SiO_2 nanocomposite films prepared at $T_{\text{dep}} = 867$ – 1170 K were composed of a mixture of t- ZrO_2 and amorphous SiO_2 . The halo at approximately $2\theta = 22^\circ$ corresponds to amorphous SiO_2 , and the t- ZrO_2 phase (ICSD #68589) exhibited broad diffraction peaks (Fig. 1(b)).

Fig. 1 XRD patterns of (a) the ZrO_2 film prepared at $T_{\text{dep}} = 1055$ K, and (b) the ZrO_2 – SiO_2 composite film prepared at $T_{\text{dep}} = 1170$ K.

The t- ZrO_2 peaks became broader as the T_{dep} was increased from 867 to 1170 K; for example, the full width at half maximum (FWHM) of the t- ZrO_2 101 peak increased from 0.8 to 1.5° (open circles in

Fig. 2(a)). The t-ZrO₂ grain size (d) was estimated from the FWHM value by using the Scherrer equation, where a dimensionless shape factor k having a value 0.9 was used. The value of d decreased from 21 to 11 nm as T_{dep} was increased (closed circles in Fig. 2(a)). The ZrO₂ content in the films, as measured by EPMA, increased from 12% to 57 mol% ZrO₂ with decreasing T_{dep} (Fig. 2(b)). The high ZrO₂ contents at low deposition temperatures might be due to the higher pyrolysis temperature required to form SiO₂ from TEOS (~873 K [21]) than that required to form ZrO₂ from Zr(acac)₄ (~623 K [22]). At high T_{dep} , the ZrO₂ content in the films was similar to that in the vapor (m_{ZrO_2} = 14 mol%; dashed line in Fig. 2(b)).

Fig. 2 Effect of T_{dep} on (a) the FWHM of the t-ZrO₂ 101 peak (open circles) and the t-ZrO₂ grain size (closed circles) and on (b) the ZrO₂ content in the films. The dashed line indicates m_{ZrO_2} = 14 mol%.

Figure 3 shows typical cross-sectional SEM and TEM images of the ZrO₂-SiO₂ nanocomposite films prepared at T_{dep} = 867 and 1170 K. The ZrO₂-SiO₂ nanocomposite films had a dense cross-section and a dome-like surface microstructure (Fig. 3(a) and 3(c)). The films prepared at higher T_{dep} exhibited

smoother surfaces (insets of Fig. 3(a) and 3(c)). The deposition rate of the $\text{ZrO}_2\text{--SiO}_2$ nanocomposite films increased from 40 to $300\ \mu\text{m h}^{-1}$ as the T_{dep} was increased from 867 and 1170 K. In the $\text{ZrO}_2\text{--SiO}_2$ nanocomposite film prepared at $T_{\text{dep}} = 873\ \text{K}$, t- ZrO_2 nanoparticles formed a network structure in the amorphous SiO_2 matrix (Fig. 3(b)). Lower deposition temperatures reduced the deposition rate of the SiO_2 matrices and resulted in the formation of network structure of t- ZrO_2 particles, which might have increased the apparent grain sizes of t- ZrO_2 . The selected-area electron diffraction (SAED) pattern showed arc-like intensities, which were attributed to the t- ZrO_2 particles exhibiting a (101) orientation (inset of Fig. 3(b)).

Fig. 3 Cross-sectional SEM (a, c) and TEM images (b, d) of the $\text{ZrO}_2\text{--SiO}_2$ composite films prepared at (a, c) $T_{\text{dep}} = 867\ \text{K}$ and (c, d) $T_{\text{dep}} = 1170\ \text{K}$. Insets display corresponding SAED patterns.

ZrO_2 nanoparticles were uniformly dispersed in the amorphous SiO_2 matrix at $T_{\text{dep}} = 1170\ \text{K}$ (Fig.

3(d)). The SAED pattern showed a Debye ring, which was indexed as t-ZrO₂ (inset in Fig. 3(d)). The t-ZrO₂ particles were distributed with random orientation in the amorphous SiO₂ matrix. In high-magnification micrographs, lattice images were observed in the particles (Fig. 4(a)). Fast Fourier transform (FFT) patterns of the SiO₂ matrix showed a halo due to the amorphous structure (Fig. 4(b)), whereas those of ZrO₂ particles exhibited spot patterns, which were indexed as t-ZrO₂ (Figs. 4(c)). The lattice images and FFT patterns confirmed the presence of highly crystalline t-ZrO₂ particles.

Fig. 4 (a) High-resolution TEM image and (b, c) FFT patterns of the ZrO₂-SiO₂ composite film prepared at $T_{\text{dep}} = 1170$ K.

The m-ZrO₂ structure is thermodynamically stable at room temperature because of the small ionic radius of the Zr⁴⁺ cation (0.84 nm) [23]. The t-ZrO₂ structure is stabilized by replacing some of the Zr⁴⁺ cations with foreign cations with a larger ionic radius or a lower charge, such as Y³⁺ (1.02 nm) or Ca²⁺ (1.12 nm) cations. In contrast, Si⁴⁺ has a small ionic radius and low coordination numbers (*i.e.*, 0.26 and 0.4 nm for 4- and 6-coordinate environments, respectively); in addition, Si⁴⁺ forms strong covalent bonds

with O^{2-} anions. Thus, Si^{4+} cannot substitute 8-coordinated Zr^{4+} sites to stabilize the t- ZrO_2 structure.

CVD often produce t- ZrO_2 films without the use of additives [4–7], which might be a consequence of nucleation of t- ZrO_2 being favored from the vapor phase and of lattice strain and defects affecting the stabilization of t- ZrO_2 . In contrast, t- ZrO_2 -dispersed SiO_2 nanocomposite powders have been prepared by wet-chemical processes [13–15]. The presence of the SiO_2 matrix suppressed both t- ZrO_2 grain growth and the generation of nucleation sites necessary for t- ZrO_2 to transform into m- ZrO_2 [12,13,24].

To date, no study involving the vapor deposition of ZrO_2 – SiO_2 nanocomposite coatings has been reported. In the present study, we demonstrated that LCVD can be used to produce ZrO_2 – SiO_2 nanocomposite films in which t- ZrO_2 nanoparticles are dispersed in the amorphous SiO_2 matrix at relatively low temperatures (867–1170 K) and at high deposition rates (40–300 $\mu\text{m h}^{-1}$).

4. Conclusions

ZrO_2 – SiO_2 nanocomposite films were prepared by LCVD. m- ZrO_2 films were obtained without the use of TEOS. t- ZrO_2 – SiO_2 nanocomposite films were prepared at $T_{\text{dep}} = 867\text{--}1170$ K. The deposition rates were 40–300 $\mu\text{m h}^{-1}$. In the amorphous SiO_2 matrix, t- ZrO_2 nanoparticles were connected to each other, thereby forming a network structure at relatively low temperatures, whereas t- ZrO_2 nanoparticles were homogeneously dispersed at higher temperatures.

Acknowledgments

This research was supported in part by a Grant-in-Aid for Young Scientists (A) (No. 25709069) from the Japan Society for the Promotion of Science (JSPS). This work was also supported by the

Council for Science, Technology and Innovation (CSTI), Cross-ministerial Strategic Innovation Promotion Program (SIP) (Funding agency: JST).

References

- [1] Wang J, Stevens R. Zirconia-toughened alumina (ZTA) ceramics. *J. Mater. Sci.* 1989;**24**(10):3421–3440.
- [2] Chevalier J, Gremillard L, Virkar AV, Clarke DR. The Tetragonal-Monoclinic Transformation in Zirconia: Lessons Learned and Future Trends. *J. Am. Ceram. Soc.* 2009;**92**(9):1901–1920.
- [3] Djurado E, Meunier E. Synthesis of Doped and Undoped Nanopowders of Tetragonal Polycrystalline Zirconia (TPZ) by Spray-Pyrolysis. *J. Solid State Chem.* 1998;**141**(1):191–198.
- [4] Yamane H, Hirai T. Preparation of ZrO_2 -film by oxidation of ZrCl_4 . *J. Mater. Sci. Lett.* 1987;**6**(10):1229–1230.
- [5] Minet J, Langlais F, Naslain R. On the chemical vapour deposition of zirconia from $\text{ZrCl}_4\text{--H}_2\text{--CO}_2\text{--Ar}$ gas mixture: II. An experimental approach. *J. Common Met.* 1987;**132**(2):273–287.
- [6] Torres-Huerta AM, Domínguez-Crespo MA, Ramírez-Meneses E, Vargas-García JR. MOCVD of zirconium oxide thin films: Synthesis and characterization. *Appl. Surf. Sci.* 2009;**255**(9):4792–4795.
- [7] Chen Z, Ji G, Prud'homme N, Addad A, Ji V, Chevalier J, Bernard-Granger G. Stabilization of the tetragonal phase in large columnar zirconia crystals without incorporating dopants. *Scr. Mater.* 2013;**68**(8):559–562.

- [8] Heuer AH, Claussen N, Kriven W m., Ruhle M. Stability of Tetragonal ZrO₂ Particles in Ceramic Matrices. *J. Am. Ceram. Soc.* 1982;**65**(12):642–650.
- [9] Deb AK, Chatterjee P, Sen Gupta SP. Structural investigation of tetragonally stabilized ZrO₂ in α -Al₂O₃–ZrO₂ composites. *J. Appl. Crystallogr.* 2006;**39**(4):601–603.
- [10] Garvie RC. The Occurrence of Metastable Tetragonal Zirconia as a Crystallite Size Effect. *J. Phys. Chem.* 1965;**69**(4):1238–1243.
- [11] Wu N-L, Wu T-F, Rusakova IA. Thermodynamic stability of tetragonal zirconia nanocrystallites. *J. Mater. Res.* 2001;**16**(03):666–669.
- [12] Mitsuhashi T, Ichihara M, Tatsuke U. Characterization and Stabilization of Metastable Tetragonal ZrO₂. *J. Am. Ceram. Soc.* 1974;**57**(2):97–101.
- [13] Nagarajan VS, Rao KJ. Crystallization studies of ZrO₂–SiO₂ composite gels. *J. Mater. Sci.* 1989;**24**(6):2140–2146.
- [14] Wang S-W, Huang X-X, Guo J-K. Wet chemical synthesis of ZrO₂–SiO₂ composite powders. *J. Eur. Ceram. Soc.* 1996;**16**(10):1057–1061.
- [15] Meneghetti F, Wendel E, Mascotto S, Smarsly BM, Tondello E, Bertagnolli H, Gross S. Combined use of XAFS, XRD and TEM to unravel the microstructural evolution of nanostructured ZrO₂–SiO₂ binary oxides: from nanometres down to the molecular domain. *CrystEngComm* 2010;**12**(5):1639–1649.
- [16] Yu S, Tu R, Ito A, Goto T. SiC–SiO₂ nanocomposite films prepared by laser CVD using tetraethyl

orthosilicate and acetylene as precursors. *Mater. Lett.* 2010;**64**(20):2151–2154.

[17] Honda A, Kimura T, Ito A, Goto T. Rh-nanoparticle-dispersed ZrO_2 films prepared by laser chemical vapor deposition. *Surf. Coat. Technol.* 2012;**206**(11–12):3006–3010.

[18] Ito A, You Y, Ichikawa T, Tsuda K, Goto T. Preparation of Al_2O_3 – ZrO_2 nanocomposite films by laser chemical vapour deposition. *J. Eur. Ceram. Soc.* 2014;**34**(1):155–159.

[19] Ito A, Kadokura H, Kimura T, Goto T. Texture and orientation characteristics of α - Al_2O_3 films prepared by laser chemical vapor deposition using Nd:YAG laser. *J. Alloys Compd.* 2010;**489**(2):469–474.

[20] Torres-Huerta AM, Vargas-García JR, Domínguez-Crespo MA, Romero-Serrano JA. Thermodynamic study of CVD– ZrO_2 phase diagrams. *J. Alloys Compd.* 2009;**483**(1–2):394–398.

[21] Juárez H, Pacio M, Díaz T, Rosendo E, Garcia G, García A, Mora F, Escalante G. Low temperature deposition: Properties of SiO_2 films from TEOS and ozone by APCVD system. *J. Phys. Conf. Ser.* 2009;**167**(1):012020.

[22] Patil U, Winter M, Becker H-W, Devi A. Synthesis and structure of mixed isopropoxide- β -ketoester and β -ketoamide zirconium complexes: Potential precursors for MOCVD of ZrO_2 . *J. Mater. Chem.* 2003;**13**(9):2177–2184.

[23] Dhanaraj G, Byrappa K, Prasad V, Dudley M. Springer Handbook of Crystal Growth. 2010;

[24] Monte F del, Larsen W, Mackenzie JD. Stabilization of Tetragonal ZrO_2 in ZrO_2 – SiO_2 Binary

Oxides. *J. Am. Ceram. Soc.* 2000;**83**(3):628–634.

Graphical Abstract

High speed deposition of $\text{ZrO}_2\text{-SiO}_2$ nanocomposite films

t-ZrO₂ dendrite in SiO₂ matrix at a low temperature

t-ZrO₂ nanoparticle in SiO₂ matrix at a high temperature