

Ultrathin barium titanate films by polyol thermal decomposition process

Hyeong Seok Lee · Sang Man Koo ·
Jung Whan Yoo

Received: 3 June 2010 / Accepted: 19 August 2010 / Published online: 2 September 2010
© The Author(s) 2010. This article is published with open access at Springerlink.com

Abstract We have successfully fabricated barium titanate (BaTiO_3) films on Si (100) and Pt(111)/Ti/SiO₂/Si substrates using the polyol thermal decomposition (PTD) process by spin-coating technique. In PTD process, we confirmed that the crystalline oxycarbonate $\text{Ba}_2\text{Ti}_2\text{O}_5\text{CO}_3$ films were directly formed as a consequence of evaporation of polyol precursor solution prepared simply by mixing metal chlorides and ethylene glycol, and then converting them into crystalline BaTiO_3 films through thermal decomposition at $>500^\circ\text{C}$. This feature makes it possible to grow densely packed and crack-free BaTiO_3 films as thin as 70 \AA per cycle. Although PTD is described here for a complex metal-oxide film of BaTiO_3 , other simple and complex metal-oxide thin films with high-dielectric constant materials are also likely to be suitable for deposition with accurate control of film thickness and composition using the polyol precursor solutions.

Metal-oxide thin films, such as AO and ABO_3 , are important components in a wide array of electronic and optical devices, and their study and manufacture involve major aspects of current science and technology [1]. The ability to deposit and tailor reliable metal-oxide films (with a particular recent emphasis on ultrathin systems) is indispensable for contemporary solid-state electronics. Many

different methods are used to make these thin films, such as various physical and chemical vapor depositions mainly dependent on vacuum deposition techniques, and many new techniques have been developed [1–3]. However, the use of these vacuum deposition techniques, the high cost of necessary equipment, and restriction of coatings on a relatively small area have limited their potential applications [4]. On the other hand, chemical solution depositions (CSD) such as sol–gel and metallo-organic decomposition (MOD) are more cost-effective, but many metal oxides cannot be deposited, and the control of stoichiometry is not always possible owing to differences in chemical reactivity among the metals [5]. In particular, precise control of film thickness, crystallinity, and morphology are significant problems to be overcome in CSD [6].

One of the challenges in solution-based processes of complex metal-oxide films has been to produce high-quality films with desired chemical composition. The sol–gel method among the CSD processes is one of the most important approaches, which are being extensively used for the fabrication of complex oxide thin films. The sol–gel method shows attractive advantages due to the fact that films with extremely uniform composition over large areas can be obtained from chemical solution deposition [7]. A key issue of any CSD thin films processing is the chemistry of precursor solution, which governs the properties of the final oxide layer. Even more challenging for sol–gel processing of complex metal-oxides is the identification of a solvent system in which the multiple organometallic precursors are reciprocally compatible. Recently, a few attempts have been reportedly made to add polymer during the sol preparation to increase the critical film thickness without cracks, and to modify the mechanical properties of the resulted films [5].

In this article, we introduce a novel method to grow the metal-oxide films using the “polyol thermal decomposition”

H. S. Lee (✉) · J. W. Yoo
Eco-Composite Materials Center, Korea Institute of Ceramic
Engineering and Technology, 233-5, Gasan-Dong,
Geumcheon-Gu, Seoul 153-801, Korea
e-mail: chemhslee@hotmail.com

H. S. Lee · S. M. Koo
Department of Chemical Engineering, Hanyang University,
Haengdang-dong, Seongdong-Gu, Seoul 133-791, Korea

(PTD) process, which is a simple methodology to enable accurate control of film thickness and composition by the spin-coating technique. To demonstrate the generality of the method, we describe the production of barium titanate (BaTiO_3) as a complex metal-oxide film, which is of interest for applications in electro-optic devices [8], multilayer ceramic capacitor (MLCC) [9, 10], tunable microwave devices [11, 12], and high-density dynamic random access memories (DRAMs) [13, 14]. In PTD process, we used a mixture of polyol precursor solution of metal chlorides (i.e., 0.2 M of barium chloride ($\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$, Showa, 99%) and 0.2 M of titanium tetrachloride (TiCl_4 , Aldrich, 99.9%) with sparingly soluble metal salts in water) with deionized water and ethylene glycol as a solvent under ambient conditions without the need for refluxing to grow the BaTiO_3 film. The preparation of polyol precursor solution is similar to the polyol process [15, 16], using diol or polyalcohol (for example, ethylene glycol or glycerol) as a solvent to reduce metal salts to metal particles, and the Pechini process [17, 18], except that citric acid or other chelating agents are not utilized. The polyol precursor solution also ensures a homogeneous metal distribution and prevents unwanted reaction that can lead to the formation of undesired phases. This solution can remain stable for months even when multiple metals are used.

In the deposition process reported here, the polyol precursor solution is applied onto a substrate and then spin-coated at 3,000 rpm for 30 s. When the coated substrate was heated at adequate temperature in ambient conditions, the solvent of the polyol precursor solution is immediately evaporated and then deposited into the crystalline intermediate phases (correspondingly small film volume) with desired metal species on the substrate surface, which enable the growth of the metal-oxide films through thermal decomposition. In contrast, the conventional sol-gel process deposits the amorphous gel films, which cause cracking or pore collapses due to the large weight loss and shrinkage under heat treatment and thicker films [5, 7]. The major distinction between the PTD and the existing sol-gel or CSD processes is that the deposited film is not amorphous gel but intermediate crystal with small volatile carbonate species. Therefore, we have successfully grown either continuous simple or complex metal-oxide films as thin as ~ 10 nm by spin coating using PTD process. These spin-coating cycles can be repeated to build up thicker films. The latter feature makes it possible to grow relatively thinner and crack-free metal-oxide films that are difficult to prepare by sol-gel or CSD.

We examine the evaporation for the polyol precursor solution of BaTiO_3 and characterization of crystalline thin films based on these solutions. As seen in Fig. 1, the weight loss in the temperature region up to 700 °C investigated by Thermodynamic gravimetric analysis (TGA) is about

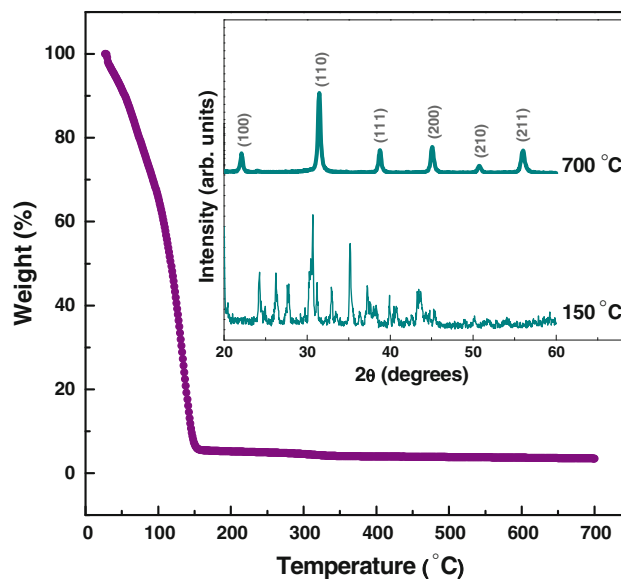


Fig. 1 Thermodynamic gravimetric analysis (TGA) for the polyol precursor solution. *Inset:* the powder X-ray diffraction pattern for the precursor after a TGA run terminated at two temperatures (between baking at 150 °C and annealing at 700 °C). The crystallinity was measured by X-ray diffractometer with Cu K α ($\lambda = 1.54056$ Å) radiation (Rikagu D/Max P/N: 3 kW/40, 45 mA)

97.4% of the initial sample weight, but mostly occurs below ~ 150 °C (about 92.7%), which was attributed to loss of solvents with ethylene glycol and water. There is no appreciable weight loss beyond 150 °C. Remarkably, we observe that the solvents of ethylene glycol with aqueous metal chloride solution have been evaporated below ~ 150 °C, ultimately leading to crystalline thin films. In the inset of Fig. 1, we also show the powder X-ray diffraction patterns for the polyol precursor solution after a TGA run terminated at two temperatures (between baking at 150 °C and annealing at 700 °C). The as-baked product at 150 °C is found to be in crystalline $\text{Ba}_2\text{Ti}_2\text{O}_5\text{CO}_3$ intermediate phase [19–23]. As the annealing temperature increased, the peaks of the crystalline intermediate phases formed at 150 °C decreased by thermal decomposition and then the peaks of the polycrystalline BaTiO_3 begins to form when annealed above 500 °C with weak diffraction peaks for the intermediate phase (not shown in figure). The XRD patterns annealed at 700 °C for 1 h are composed of cubic BaTiO_3 structure with lattice parameters (BaTiO_3 : $a = 3.996$ Å).

In the case of BaTiO_3 , the formation mechanism from solution-derived precursor is complicated and has been argued for a long time [24]. Considering the general formation mechanism, it has been reported that BaTiO_3 forms either by a nucleation process at the $\text{BaCO}_3/\text{TiO}_2$ interface or through a decomposition of crystalline $\text{Ba}_2\text{Ti}_2\text{O}_5\text{CO}_3$ intermediate phase [19–23]. The first of them proposed that the solution-derived metal organic precursors decompose

to form a finely divided mixture of BaCO_3 and TiO_2 , which subsequently reacts to form BaTiO_3 on heating at 600–700 °C [20]. Alternatively, it has been proposed that BaTiO_3 is formed directly through thermal decomposition of crystalline intermediate phases of the oxycarbonate $\text{Ba}_2\text{Ti}_2\text{O}_5\text{CO}_3$ [19, 20, 23] above 600 °C, in which it can be clearly identified as mainly those appearing at $2\theta = 21.3^\circ$, 24.6° , 26.8° , 28.2° , 29.3° , 30.36° , 32.3° , 34.1° , 41.1° , 44.9° , and 54.4° [22, 23]. From the XRD data (Fig. 1, inset), the as-baked film at 150 °C is consistent with neither diffraction peaks of the mixture of BaCO_3 and TiO_2 [21] nor amorphous phase but corresponding to diffraction peaks of the oxycarbonate $\text{Ba}_2\text{Ti}_2\text{O}_5\text{CO}_3$. We therefore mentioned that the intermediate phase formed at 150 °C is the oxycarbonate $\text{Ba}_2\text{Ti}_2\text{O}_5\text{CO}_3$ crystals. The oxycarbonate $\text{Ba}_2\text{Ti}_2\text{O}_5\text{CO}_3$ crystal is metastable, since it always decomposed to BaTiO_3 with increasing temperature or prolonged heating at a fixed temperature [20]. In PTD process, we found that the oxycarbonate $\text{Ba}_2\text{Ti}_2\text{O}_5\text{CO}_3$ crystals (correspondingly small film volume and volatile carbonate species) were directly formed as a consequence of evaporation of polyol precursor solution, before the formation of BaTiO_3 through thermal decomposition process.

Ultrathin BaTiO_3 films per cycle were spin coated onto silicon or Pt-coated substrates from the polyol precursor solution. The spin-coated film was then immediately backed in air for 2 min at about 150 °C on a preheated hot plate. Final annealing/decomposition treatments were in air at 700 °C. Transmission electron microscope (TEM) image of the cross-section of a device demonstrates the ultrathin, crystalline nature of the film, with average film thickness of ~ 70 Å. One representative high-resolution TEM image from BaTiO_3 film is also shown as an inset to Fig. 2a which displays clear lattice fringes; the distance between the fringes matches well with BaTiO_3 (4.0 Å). An AFM image of the BaTiO_3 film deposited per cycle (Fig. 2b) also shows a densely packed particle layer completely covering the surface. The films per cycle have very smooth surface as shown by AFM image (Fig. 2b: r.m.s. roughness = 0.45 nm for a BaTiO_3 film with about ~ 70 Å thick). From the AFM image, it can be seen that the deposited BaTiO_3 film per cycle has a smooth surface with a small grain size over conformal coverage.

The deposition rate and the surface morphology of the BaTiO_3 films grown by PTD process onto the silicon substrates at 700 °C for 1 h in each spin coating cycle was monitored by ellipsometry and scanning electron micrograph (SEM). As shown in Fig. 3a, the film thickness deposited in 40 cycles grew linearly with the number of cycles, demonstrating that the same deposition thickness occurs in each PTD cycle. The average increase in film thickness per cycle is about ~ 70 Å for BaTiO_3 films. In

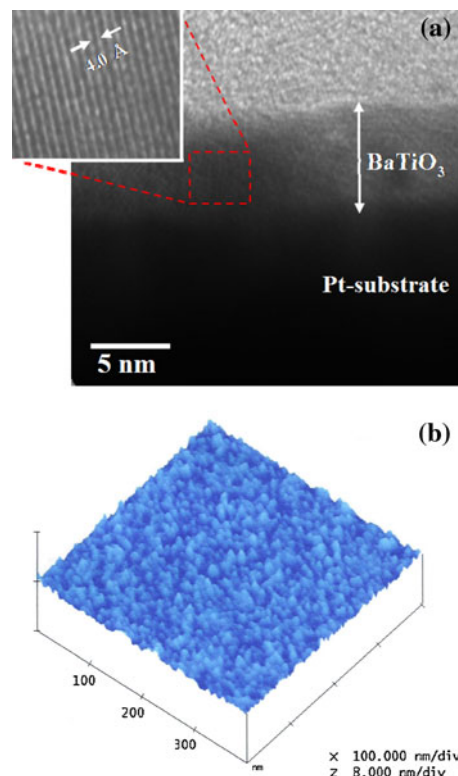


Fig. 2 **a** The cross-sectional TEM image of BaTiO_3 thin film deposited with one cycle by PTD on Pt(111)/Ti/SiO₂/Si substrate after annealing at 700 °C for 1 h in ambient atmosphere. *Inset*: HRTEM image of the BaTiO_3 thin film deposited with one cycle showing clear lattice fringes. **b** AFM image obtained after deposition of one cycle (the lateral dimensions are 400 × 400 nm)

particular, continuous crystalline perovskite films as thin as 70 Å can be formed by spin-coating technique using the PTD process. The thickness deposited in 40 cycles can also be visualized by a cross-sectional SEM (Fig. 3a, inset), which formed a BaTiO_3 film of nearly 290-nm thickness. Figure 3b shows an AFM image of a BaTiO_3 film deposited at 700 °C for 1 h in 40 cycles and characterized by a surface roughness with a uniform, densely packed and crack-free microstructure, which is in agreement with the SEM images (Fig. 3c). The average size and surface roughness of the densely packed spherical-shaped grains were close to 40–60 nm and 3.4 nm, respectively. It can be, therefore, described that the oxycarbonate $\text{Ba}_2\text{Ti}_2\text{O}_5\text{CO}_3$ crystals (corresponding to small film volume) deposited through evaporation of polyol precursor solution on the substrate probably contributes to the high quality of the resulting BaTiO_3 films and the ability to achieve ultrathin dimensions. The microcracks in amorphous gel films usually emerged from the conventional sol–gel-processed films. One of the explanations for microcrack formation in sol–gel-derived films is the condensation reaction and pore collapse in amorphous gel films under heat treatment [5]. However, in this PTD

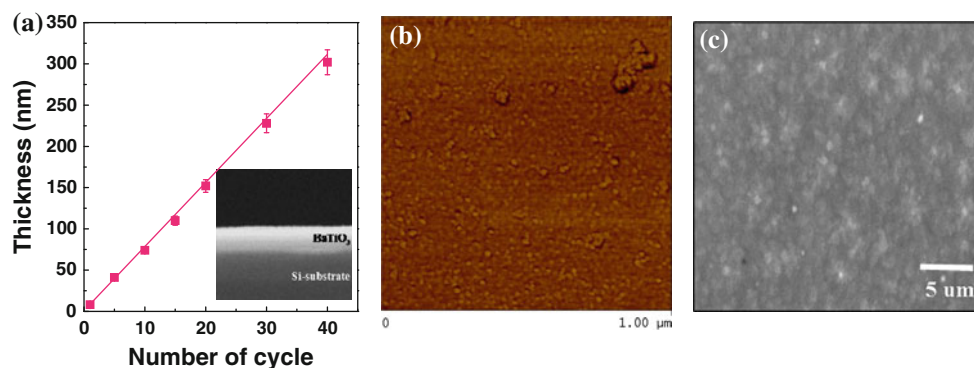


Fig. 3 The growth rate and surface morphology for BaTiO₃ film deposited from 1 to 40 cycles at 700 °C. **a** The linear relationship between BaTiO₃ film thickness on silicon substrate and the number of deposition cycles. *Inset*: cross-sectional scanning electron micrograph

process, because the oxycarbonate Ba₂Ti₂O₅CO₃ crystals were decomposed to the BaTiO₃ crystals by a small volatile carbonate species on the substrate without the condensation reaction in amorphous gel films, it is also possible to grow densely packed and crack-free BaTiO₃ films.

Using the PTD process, we developed BaTiO₃ film of about 200 nm at 700 °C for 1 h in 30 cycles on Pt/Ti/SiO₂/Si substrate. The X-ray diffraction patterns of the BaTiO₃ film are shown in Fig. 4a. Apart from the substrate peaks, the peaks of (100), (110), (200), and (211) were observed, indicating that the phase-pure BaTiO₃ film is obtained. In particular, it can be seen that BaTiO₃ thin film derived from the PTD process exhibited a perovskite phase of a (110) preferred orientation. In order to fabricate a BaTiO₃ capacitor structure, a platinum top electrode was deposited at room temperature using the sputtering with a shadow mask. The area of the top electrode was 1×10^{-4} cm². The dielectric constant and the dissipation factor of a BaTiO₃ capacitor was measured as a function of frequency. As shown in Fig. 4b, the dielectric constant and the dissipation factor at 1 GHz are about 160 and 0.015, respectively. Similar dielectric measurement results have been reported for BaTiO₃ thin films prepared by the sol-gel technique. The dielectric constant of the BaTiO₃ capacitor slightly decreases with increasing frequency. There are no sudden changes in the dielectric constant and the dissipation factor within the frequency range up to 1 GHz.

In conclusion, we have successfully fabricated barium titanate (BaTiO₃) films on Si (100) and Pt(111)/Ti/SiO₂/Si substrates using the polyol thermal decomposition (PTD) process by spin-coating technique. In PTD process, we confirmed that the crystalline oxycarbonate Ba₂Ti₂O₅CO₃ films were directly formed as a consequence of evaporation of polyol precursor solution, prepared simply by mixing metal chlorides and ethylene glycol, and then converting them into crystalline BaTiO₃ films through thermal

decomposition at >500 °C. This feature makes it possible to grow densely packed and crack-free BaTiO₃ films as thin as 70 Å per cycle. Although PTD is described here for a complex metal-oxide film of BaTiO₃, other simple and complex metal-oxide thin films with high-dielectric

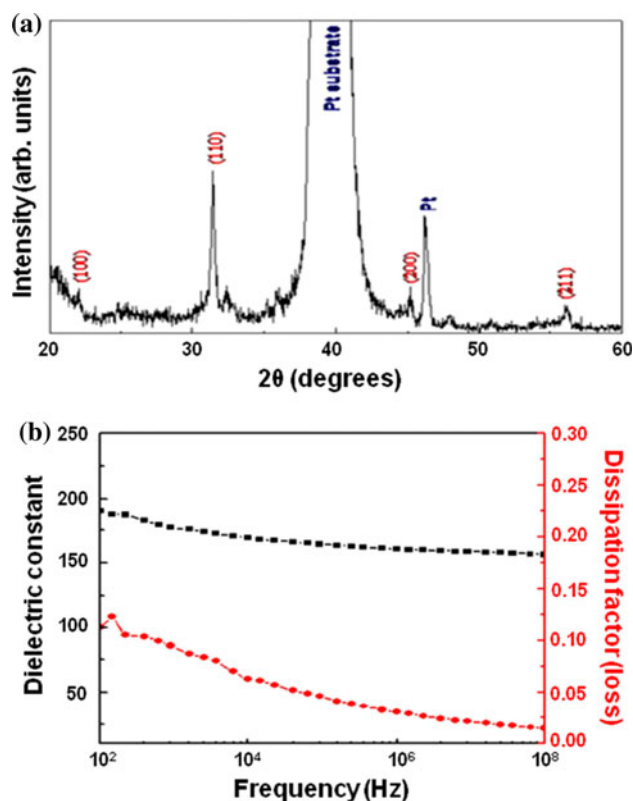


Fig. 4 **a** The X-ray diffraction pattern of BaTiO₃ thin film deposited with 30 cycles by PTD onto Pt(111)/Ti/SiO₂/Si substrate after annealing at 700 °C for 1 h in ambient atmosphere. **b** Dielectric constant and dissipation factor (loss) for Pt/BaTiO₃/Pt/Ti/SiO₂/Si films as a function of frequency at room temperature. The crystallinity of BaTiO₃ thin film was measured by X-ray diffractometer with Cu K α ($\lambda = 1.54056$ Å) radiation

decomposition at >500 °C. This feature makes it possible to grow densely packed and crack-free BaTiO₃ films as thin as 70 Å per cycle. Although PTD is described here for a complex metal-oxide film of BaTiO₃, other simple and complex metal-oxide thin films with high-dielectric

constant materials are also likely to be suitable for deposition with accurate control of film thickness and composition using the polyol precursor solutions.

Open Access This article is distributed under the terms of the Creative Commons Attribution Noncommercial License which permits any noncommercial use, distribution, and reproduction in any medium, provided the original author(s) and source are credited.

References

1. Park SM, Clark BL, Keszler DA, Bender JP, Wager JF, Reynolds TA, Herman GS (2002) *Science* 297:65
2. Mitzi DB, Kosbar LL, Murray CE, Copel M, Afzali A (2004) *Nature* 428:299
3. Hausmann D, Becker J, Wang S, Gordon RG (2002) *Science* 298:402
4. Gao Y, Masuda Y, Peng Z, Yonezawa T, Konmoto K (2003) *J Mater Chem* 13:608
5. Jia QX, McCleskey TM, Burrell AK, Lin Y, Collis GE, Wang H, Li ADQ, Foltyn SR (2004) *Nat Mater* 3:529
6. Kovtyukhova NI, Buzaneva EV, Waraksa CC, Martin BR, Mallouk TE (2000) *Chem Mater* 12:383
7. Tian HY, Luo YG, Pu XH, He XY, Qiu PS, Ding AL (2001) *Mater Chem Phys* 69:166
8. Zeng J, Wang H, Wang M, Shang S, Wang Z, Lin C (1998) *Thin Solid Films* 322:104
9. Tsuyumoto I, Kobayashi M, Are T, Yamazaki N (2010) *Chem Mater* 22:3015
10. Devaraju NG, Lee BI, Wang X, Viviani M, Nanni P (2006) *J Mater Sci* 41:3335. doi:10.1007/s10853-005-5390-1
11. Yang X, Yao X, Zhang L (2004) *Ceram Int* 30:1525
12. Kaiser DL, Vaudin MD, Rotter LD, Wang JL, Cline JP, Hwang CS, Marinenko RB, Gillen JG (1995) *Appl Phys Lett* 66:2801
13. Kingon AI, Maria JP, Streiffer SK (2000) *Nature* 406:1032
14. Lee EJH, Pontes FM, Leite ER, Longo E, Varela JA, Araujo EB, Eiras JA (2000) *J Mater Sci Lett* 19:1457
15. Sun S, Murray CB, Weller D, Folks L, Moser A (2000) *Science* 287:1989
16. Sun Y, Xia Y (2002) *Science* 298:2176
17. Simões AJ, Zaghete MA, Stojanovic BD, Gonzalez AH, Riccardi CS, Cantoni M, Varela JA (2004) *J Eur Ceram Soc* 24:1607
18. Pechini MP (1967) US Patent 3:330
19. Tian HY, Luo WG, Ding AL, Choi J, Lee C, No K (2002) *Thin Solid Films* 408:200
20. Kumar S, Messing GL, White WB (1993) *J Am Ceram Soc* 76:617
21. Kong LB, Ma J, Huang H, Zhang RF, Que WX (2002) *J Alloys Compd* 337:226
22. Durán P, Capel F, Tartaj J, Gutierrez D, Moure C (2001) *Solid State Ionics* 141:529
23. Durán P, Gutierrez D, Tartaj J, Bañares MA, Moure C (2002) *J Eur Ceram Soc* 22:797
24. Marssi ME, Marrec FL, Lukyanchuk IA, Karkut MG (2003) *J Appl Phys* 94:3307