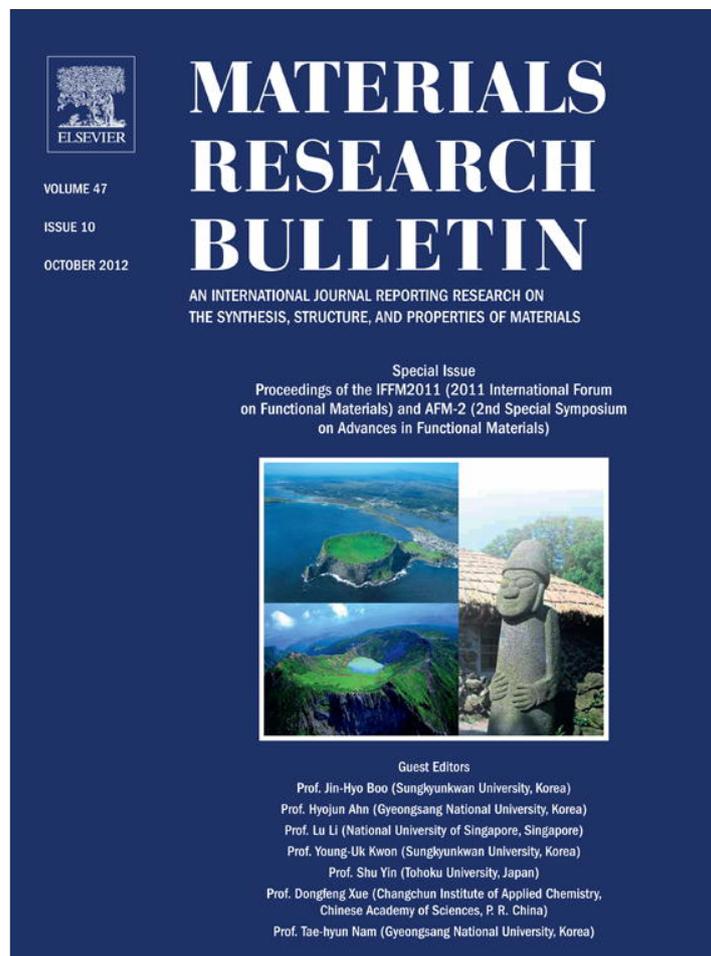


Provided for non-commercial research and education use.  
Not for reproduction, distribution or commercial use.



This article appeared in a journal published by Elsevier. The attached copy is furnished to the author for internal non-commercial research and education use, including for instruction at the authors institution and sharing with colleagues.

Other uses, including reproduction and distribution, or selling or licensing copies, or posting to personal, institutional or third party websites are prohibited.

In most cases authors are permitted to post their version of the article (e.g. in Word or Tex form) to their personal website or institutional repository. Authors requiring further information regarding Elsevier's archiving and manuscript policies are encouraged to visit:

<http://www.elsevier.com/copyright>



Contents lists available at SciVerse ScienceDirect

## Materials Research Bulletin

journal homepage: [www.elsevier.com/locate/matresbu](http://www.elsevier.com/locate/matresbu)

# Studies on optical, chemical, and electrical properties of rapid SiO<sub>2</sub> atomic layer deposition using tris(tert-butoxy)silanol and trimethyl-aluminum

Dongwon Choi<sup>a</sup>, Boo-Kyung Kim<sup>b</sup>, Kwun-Bum Chung<sup>b</sup>, Jin-Seong Park<sup>a,\*</sup>

<sup>a</sup> Department of Materials Science and Engineering, Dankook University, Cheonan 330-714, Republic of Korea

<sup>b</sup> Department of Physics, Dankook University, Cheonan 330-714, Republic of Korea

## ARTICLE INFO

## Article history:

Available online 25 April 2012

## Keywords:

SiO<sub>2</sub> thin film  
Atomic Layer Deposition  
tris(tert-butoxy)silanol

## ABSTRACT

Rapid SiO<sub>2</sub> atomic layer deposition (ALD) was used to deposit amorphous, transparent, and conformal SiO<sub>2</sub> films using tris(tert-butoxy)silanol (TBS) and trimethyl-aluminum (TMA) as silicon oxide source and catalytic agent, respectively. The growth rate of the SiO<sub>2</sub> films drastically increased to a maximum value (2.3 nm/cycle) at 200 °C and slightly decreased to 1.6 nm/cycle at 275 °C. The SiO<sub>2</sub> thin films have C–H species and hydrogen content (~8 at%) at 150 °C because the cross-linking rates of SiO<sub>2</sub> polymerization may reduce below 200 °C. There were no significant changes in the ratio of O/Si (~2.1) according to the growth temperatures. On the other hand, the film density slightly increased from 2.0 to 2.2 although the growth rate slightly decreased after 200 °C. The breakdown strength of SiO<sub>2</sub> also increases from 6.20 ± 0.82 to 7.42 ± 0.81 MV/cm. These values suggest that high cross-linking rate and film density may enhance the electrical property of rapid SiO<sub>2</sub> ALD films at higher growth temperature.

© 2012 Elsevier Ltd. All rights reserved.

## 1. Introduction

Recently, SiO<sub>2</sub> thin films have been intensively investigated as functional materials to apply in various applications such as nano-electronics, energy production, optoelectronics, and flexible electronics [1–6]. The required properties of a SiO<sub>2</sub> thin film are low cost, lower deposition temperature, damage/particle free process, high throughput, and excellent step coverage. However, conventional deposition techniques for SiO<sub>2</sub> (e.g., chemical vapor deposition, sputtering, electron beam evaporation, etc.) have critical problems: a high growth temperature, particle generation, poor surface coverage, and low deposition rate.

Atomic layer deposition (ALD) methods can be used to obtain conformality and atomic layer control of thin film growth. ALD is a growth method based on sequential, self-limiting surface reactions. A variety of materials including oxides, nitrides, and various metals have been deposited using ALD [7,8]. SiO<sub>2</sub> ALD using SiCl<sub>4</sub> and H<sub>2</sub>O requires high temperatures of >325 °C and large reactant exposure of >10<sup>9</sup> L (1 L = 10<sup>-6</sup> Torr s) [9]. Silicon precursors beside SiCl<sub>4</sub> have been utilized for SiO<sub>2</sub> ALD, including Si(NCO)<sub>4</sub> and H<sub>2</sub>O, (H<sub>3</sub>CO)Si(NCO)<sub>3</sub> and H<sub>2</sub>O<sub>2</sub>, and Si(NCO)<sub>4</sub> and N(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub> [11,12]. Ozone has also been employed for SiO<sub>2</sub> ALD with SiH<sub>2</sub>Cl<sub>2</sub> at 300 °C and required reactant exposures >10<sup>9</sup> L [13]. Despite many reports on SiO<sub>2</sub> ALD, practical SiO<sub>2</sub> ALD has been difficult to obtain because of high growth temperature and slow growth rate [14–16].

Recently, a SiO<sub>2</sub> deposition method using silanols with Al catalysts has been developed: this method is known as rapid SiO<sub>2</sub> ALD [17,18]. While maintaining self-limiting behavior, the growth rate of SiO<sub>2</sub> thin film is >10 times higher than conventional SiO<sub>2</sub> ALD approaches. Rapid SiO<sub>2</sub> ALD has been accomplished using tri(tert-butoxy)silanol (TBS) or tri(tert-pentoxo)silanol (TPS) in a temperature range below 250 °C. Despite the high growth rate of SiO<sub>2</sub> thin film, there have been only a few papers reporting on the film properties of rapid SiO<sub>2</sub> ALD using tri(tert-pentoxo)silanol (TPS) and Al catalysis. In this study, we performed the rapid SiO<sub>2</sub> ALD process using TBS and trimethyl-aluminum (TMA) and investigated the SiO<sub>2</sub> thin film in terms of optical, chemical, and electrical properties.

## 2. Experimental details

Rapid SiO<sub>2</sub> ALD was performed from 150 °C to 275 °C by using TBS and TMA. N<sub>2</sub> gas flow produced a pressure of 0.3 Torr in the reactor. The TBS was held in a stainless steel canister and maintained between 65 and 95 °C to control the range of vapor pressures. The TMA was contained in a stainless steel cylinder and was maintained at 10 °C.

The thickness and the refractive index of the SiO<sub>2</sub> thin films were measured by spectroscopy ellipsometry. The film densities and thickness were also confirmed by X-ray reflectivity (XRR). Auger electron spectroscopy (AES) depth profile and Rutherford back-scattering spectroscopy (RBS) were performed to obtain the composition ratio and impurity. The chemical bonds of the deposited films were investigated by Fourier transform infrared

\* Corresponding author. Tel.: +82 41 550 3514.

E-mail address: [jinseongpark@dankook.ac.kr](mailto:jinseongpark@dankook.ac.kr) (J.-S. Park).

spectroscopy (FTIR). Current–voltage ( $I$ – $V$ ) measurements were performed to investigate the breakdown voltage, leakage current level, and dielectric constant. A home-made tube furnace was used to anneal the  $\text{SiO}_2$  thin films under air ambient for 1 h. The annealing temperatures were 400 and 500 °C.

### 3. Results and discussion

The self-limiting character of these two surface reactions is demonstrated at the growth temperature of 200 °C by the saturation of the growth rate as the doses of TMA shown in Fig. 1. As the TMA injection time increases to 0.5 s, the growth rate of  $\text{SiO}_2$  films saturated at 2.3 nm/cycle after 0.3 s. After a certain amount of TBS doses, the  $\text{SiO}_2$  film also saturated to a constant value at 200 °C. The rapid  $\text{SiO}_2$  ALD is believed to result from the growth of siloxane polymer chains at the Al-catalytic sites and the cross-linking of these polymer chains to form a dense  $\text{SiO}_2$  film [17,18]. Unlike conventional  $\text{SiO}_2$  ALD processes using silicon precursors and oxygen reactants, the TBS and TMA precursors in rapid  $\text{SiO}_2$  ALD may play roles as a  $\text{SiO}_2$  source and a catalytic agent, respectively. Despite the different roles of the reactants, the growth of  $\text{SiO}_2$  film is quite followed by conventional ALD mechanism, which is a self-limited surface reaction. However, the saturated growth rate of rapid  $\text{SiO}_2$  ALD is different from that in the previous report [17], showing that the saturated growth rate at 225–250 °C is 12 nm/cycle. It is possible to consider a few reasons: (1) the use of partially decomposed TBS precursors, (2) precursor condensation from a different design of ALD reactor and (3) small dose of TBS precursors. In fact, the first reason should be excluded because all precursors (TBS and TMA) were purified before the  $\text{SiO}_2$  deposition. In the case of the second reason, previous rapid  $\text{SiO}_2$  results also reported that a large dependence on the exposure pressure was observed during the experiment [18] due to TBS precursor condensation (solid precursor at room temperature). Thus, a large amount of TBS dose might be necessary to reach the reported growth rate (12 nm/cycle). In this work, the real dose of TBS was also 10 times smaller than that of previous report. Unfortunately, the lower growth rate in this study might be the result of the second and third reasons given above. However, in terms of ALD throughput (growth rate per total growth time), the result for this system (about 0.2 nm/s) is better than that of the previous system (about 0.1 nm/s).

Fig. 2 shows the dependence of the growth rate and refractive index on the growth temperature. As the growth temperature increase from 150 °C to 200 °C, the growth rate drastically

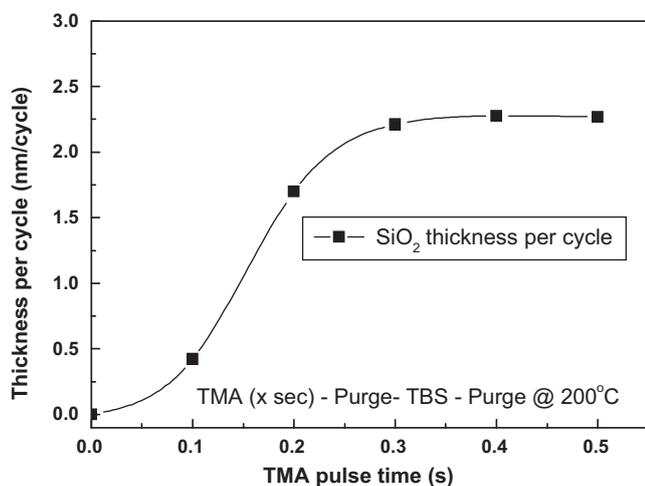


Fig. 1. The growth rate (thickness per cycle) of  $\text{SiO}_2$  thin film as a function of TMA pulse time. The growth temperature was 200 °C.

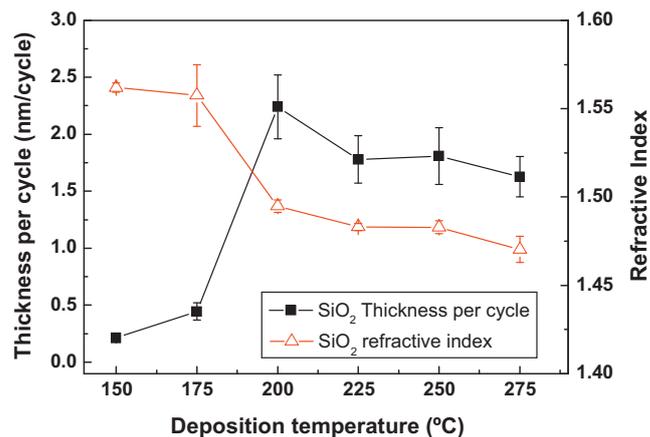


Fig. 2. The growth rate (thickness per cycle) and refractive index of  $\text{SiO}_2$  thin films depending on growth temperatures.

increases from 0.21 to 2.3 nm/cycle. After the growth temperature of 200 °C, the growth rate significantly decreased from 2.3 nm to 1.6 nm. However, the refractive index of the  $\text{SiO}_2$  films steps down from 1.56 to 1.48 after the growth temperature of 200 °C. UV–VIS was also performed from 300 nm (UV) to 800 nm (Visible) to determine the transmittance of the  $\text{SiO}_2$  thin films (not shown here). 100 nm thick  $\text{SiO}_2$  thin films made by rapid ALD have an excellent transmittance of over 95% for the whole spectral range. There is no significant difference in either transmission or reflectance at the various growth temperatures.

In terms of growth rate behavior, D. Hausmann suggested the following mechanism: [17] the decrease in the growth rate at temperature  $>200$  °C can be attributed to the higher cross-linking rates that limit the diffusion of silanol reactants though the growing film to the Al catalytic center. Also, the decrease in the growth rate at temperature  $<200$  °C might be explained by the thermal dependency of cross-linking and silanol diffusion rates. Thus, the cross-linking rate and silanol diffusion rate are faster at high and low growth temperatures, respectively.

On the other hand, a higher refractive index of  $\text{SiO}_2$  film was shown below the growth temperature of 200 °C, which can be compared to the refractive index of thermally oxidized  $\text{SiO}_2$  film (1.46). This suggests that the catalytic reaction between TBS and TMA is incomplete at low growth temperature. Based on quantum chemical calculation [19], the activation energy of tri(tert-butoxy)silanol catalyzed by Al–O bonding is predicted at a modest activation energy of 74 kJ/mol, which is a much lower activation energy than that (197 kJ/mol) of the uncatalyzed elimination of tert-butanol. However, the predicted activation energy for the aluminum-catalyzed reaction is still not enough to polymerize the  $\text{SiO}_2$  thin film at low growth temperature. The high refractive index of the  $\text{SiO}_2$  film at low growth temperature might be correlated with the film compositions. To investigate the  $\text{SiO}_2$  film stoichiometry and impurity, 100 nm thick  $\text{SiO}_2$  thin films were measured by AES and RBS (not shown here). Carbon impurity (~4 at%) in the  $\text{SiO}_2$  films was detected at 150 °C and the other  $\text{SiO}_2$  films above 200 °C do not have any carbon impurity (under the AES detect-limit, below 0.5 at%). RBS also exhibits that the ratios of Si/O at 150, 200, 225, and 250 °C are 0.44, 0.47, 0.47, and 0.48, respectively. As the growth temperature increases from 150 °C, the oxygen content in the  $\text{SiO}_2$  slightly decreases. After 200 °C, there are no significant changes of Si/O ratios. As mentioned before, this is the evidence that the cross-linking reaction is not complete below 200 °C. This means that the polymerization of  $\text{SiO}_2$  by rapid ALD will react completely above the growth temperature of at least 200 °C.

**Table 1**

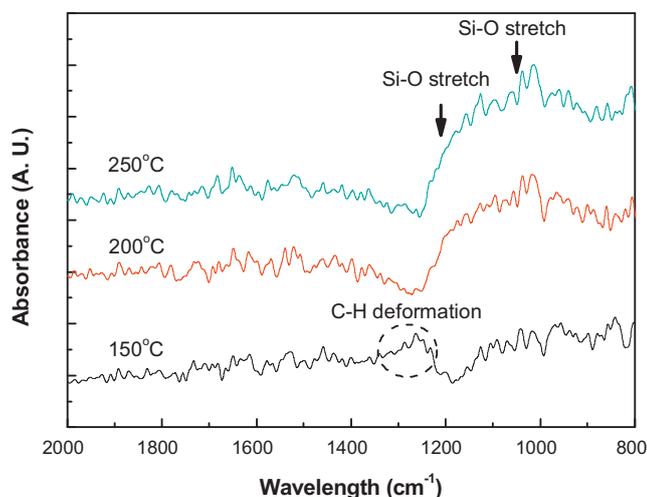
RBS, ERD, AES, and XRR results for SiO<sub>2</sub> films with 100 nm thickness, deposited at 150–250 °C.

	Si	O	C	H	Si:O	Density (g/cm <sup>3</sup> )
150 °C	0.27	0.61	0.04	0.08	0.44	2.02
200 °C	0.31	0.66	ND	0.03	0.47	2.18
225 °C	0.31	0.66	ND	0.03	0.47	2.20
250 °C	0.32	0.66	ND	0.02	0.48	2.28

ND: no detection.

The XRR investigations also yielded the density of the deposited SiO<sub>2</sub> films. The film density at the low growth temperature of 150 °C was 2.02 g/cm<sup>3</sup>. When the growth temperature increased to 200 °C, the density increased to 2.18 g/cm<sup>3</sup>. The density then increased further to ~2.28 g/cm<sup>3</sup> at 250 °C. The change of film density could be related with the ratio of Si/O and the carbon impurity between 150 °C and 250 °C. After the growth temperature of 200 °C, this increase in film density may be expected based on the increase in the cross-linking rate, which yields denser SiO<sub>2</sub> films. Another implication of the increased cross-linking rate and the larger film density would be the smaller growth rate (from 2.3 nm/cycle to 1.6 nm/cycle) observed after the growth temperature of 200 °C. The film composition and film density of the SiO<sub>2</sub> films are summarized in Table 1 Table 1 for various growth temperatures.

To understand between the reaction mechanism and the film property, the hydrogen contents and the chemical bonds were investigated by ERDA and FTIR, respectively. ERDA enabled the quantification of the hydrogen content. The amount of hydrogen in the films increased as a function of growth temperatures (not shown here). After the growth temperature of 200 °C, the hydrogen content drastically decreased as summarized in Table 1. Fig. 3 shows the FTIR spectrums at various growth temperatures (150 °C, 200 °C, and 250 °C). There are two prominent peaks between 2000 cm<sup>-1</sup> and 800 cm<sup>-1</sup>. One broad peak is located between 1000 cm<sup>-1</sup> and 1230 cm<sup>-1</sup>, indexing the Si–O–Si stretching mode (1216 and 1052 cm<sup>-1</sup>) and the other peak is near 1300 cm<sup>-1</sup>, indexing the CH<sub>x</sub> symmetric deformation (1304 cm<sup>-1</sup>) [20]. It might be that the increase of the absorbance of the C–H deformation mode results from the incomplete cross-linking at low temperature. Also, the increase of hydrogen at lower temperature (150 °C) is expected based on incomplete cross-linking reaction, which leads to a higher concentration of the C–H species. The higher C–H species may also correlate with the lower density and higher refractive index of the SiO<sub>2</sub> films at low growth temperature.



**Fig. 3.** Fourier transform infrared spectroscopy (FTIR) of SiO<sub>2</sub> thin films deposited on 150, 200, and 250 °C, respectively. The 100 nm thick SiO<sub>2</sub> film deposited on Si substrate.

**Table 2**

Results for breakdown field strength of SiO<sub>2</sub> thin film according to growth temperature (150–250 °C) and annealing temperature (400 and 500 °C). The average breakdown field and error bar range are extracted from 10 samples.

Substrate temperature (TC)	Average breakdown (MV/cm)	Error bar range (MV/cm)	Anneal temperature (°C)	Average breakdown (MV/cm)	Error bar range (MV/cm)
150	6.20	±0.82	As-dep	6.97	±0.60
200	6.97	±0.60	(200 °C)		
225	7.72	±0.78	400	7.85	±1.56
250	7.42	±0.81	500	8.34	±1.38

Table 2 summarizes the breakdown voltages as functions of growth temperatures and annealing temperatures. As shown before, the compositions of all SiO<sub>2</sub> films showed very similar ratios of Si/O and hydrogen contents except for the low temperature SiO<sub>2</sub> films (150 °C). Only the film densities of SiO<sub>2</sub> films slightly increased linearly according to the growth temperatures. As in the previous report, this indicates that a higher growth temperature may lead to the formation of dense SiO<sub>2</sub> films and that this temperature increase correlates with an increase of breakdown strength [21]. Therefore, rapid SiO<sub>2</sub> thin films had excellent breakdown strength (7 MV ± 0.78) even at the low growth temperature (200 °C), compared with that of plasma enhanced ALD SiO<sub>2</sub> films [3,22] (8–10 MV/cm over 300 °C).

Furthermore, the as-deposited state and the furnace-annealed sample (air ambient) were investigated in order to improve the electrical property of SiO<sub>2</sub> thin film. The breakdown strengths exhibited 6.97 ± 0.60, 7.85 ± 1.56, and 8.34 ± 1.38 MV/cm when the sample states were as-deposition, 400 and 500 °C annealing, respectively. Interestingly, without change of refractive index (~1.48), the thickness of the SiO<sub>2</sub> thin films slightly decreased after annealing in air ambient for 1 h. The decrement of the thickness was about 3.5% after 500 °C annealing. This implies that the composition of the SiO<sub>2</sub> film may not be changed and the decrement of the thickness may induce the formation of dense SiO<sub>2</sub> films under the annealing processes.

#### 4. Conclusion

In summary, SiO<sub>2</sub> films have been grown using tri(tert-butoxy)silanol as a silicon oxide source and trimethyl-aluminum as a catalytic agent. Based on detail investigations, the lower temperatures reduced the cross-linking rates between the siloxane polymers that self-limit the SiO<sub>2</sub> deposition. The C–H species and the hydrogen content suggest that the cross-linking process is progressed incompletely and/or slowly during rapid SiO<sub>2</sub> ALD. On the other hand, high growth temperature may enhance the cross-linking rate and suppress the silanol diffusion rate. Although the growth rate of SiO<sub>2</sub> films slightly decreases due to those kinetic competitions, the film properties are almost same except for the film density. Also, the film density of SiO<sub>2</sub> films is strongly correlated with electrical properties such as breakdown strength. A higher growth temperature and annealing process may form a denser SiO<sub>2</sub> film, resulting in better breakdown strength (~8 MV/cm). Since the rapid SiO<sub>2</sub> ALD process has several advantages such as accurate thickness control, high throughput, conformal coating, and reasonable optical/electrical properties, it might be a promising material and process technique in functional material applications.

#### Acknowledgement

This work was supported by the RFID R&D program of MKE/KEIT. [10035225, Development of core technology for high performance AMOLED on plastic].

## References

- [1] L. Zhong, W.L. Daniel, Z. Zhang, S.A. Campbell, W.L. Galdfelter, *Chem. Vap. Dep.* 12 (2006) 143.
- [2] A.A. Dameron, S.D. Davidson, B.B. Burton, P.F. Carcia, R.S. McLean, S.M. George, *J. Phys. Chem. C* 112 (2008) 4573.
- [3] S.J. Won, S. Shu, M.S. Hur, H.J. Kim, *IEEE Electron Dev. Lett.* 31 (2010) 857.
- [4] J.S. Park, H. Chae, H.K. Chung, S.I. Lee, *Semicond. Sci. Technol.* 26 (2011) 034001.
- [5] J. Liu, D. Xue, *Nanoscale Res. Lett.* 5 (2010) 1619–1626.
- [6] J. Wu, D. Xue, *Mater. Res. Bull.* 45 (2010) 295–299.
- [7] M. Ritala, M. Leskela, *Handbook of Thin Film Materials*, Academic Press, San Diego, CA, 2001.
- [8] S.M. George, *Chem. Rev.* 110 (2010) 111.
- [9] J.D. Ferguson, A.W. Weimer, S.M. George, *Chem. Mater.* 12 (2000) 3472.
- [10] S. Morishita, Y. Uchida, M. Matsumura, *Jpn. J. Appl. Phys.* 1 34 (1995) 5738.
- [11] K. Yamaguchi, S. Imai, N. Ishitobi, M. Takemoto, H. Miki, M. Matsumura, *Appl. Surf. Sci.* 132 (1998) 202.
- [12] J.W. Lim, S.J. Yun, J.H. Lee, *ETRI J.* 27 (2005) 118.
- [13] J.D. Ferguson, E.R. Smith, A.W. Weimer, S.M. George, *J. Electrochem. Soc.* 151 (8) (2004) G528–G535.
- [14] G. Dingemans, M.C.M. van de Sanden, W.M.M. Kessels, *Phys. Status Solidi RRL* 5 (1) (2011) 22–24.
- [15] K.-S. Kim, *Ceram. Process.* 43 (11A) (1997).
- [16] D. Hausmann, J. Becker, S.L. Wang, R.G. Gordon, *Science* 298 (2002) 402.
- [17] B.B. Burton, M.P. Bolelaski, A.T. Desombre, S.M. George, *Chem. Mater.* 20 (2008) 7031.
- [18] M.J. Frisch, et al., *Gaussian 98 (Revision A.9)*, Gaussian Inc., Pittsburgh, PA, 1998.
- [19] B.B. Burton, S.W. Kang, S.W. Rhee, S.M. George, *J. Phys. Chem. C* 113 (2009) 8249.
- [20] H.U. Kim, S.W. Rhee, *J. Electrochem. Soc.* 147 (2000) 1473.
- [21] S.W. Lee, K. Park, B. Han, S.H. Son, S.K. Rha, C.O. Park, W.J. Lee, *Electrochem. Solid-State Lett.* 11 (2008) G23.