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Atomic Layer Deposition of $Bi_{1-x-y}Ti_xSi_yO_z$ Thin Films Using H_2O Oxidant and Their Characteristics Depending on Si Content

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$Bi_{1-x-y}Ti_xSi_yO_z$ (BTSO) films were deposited on sputtered $Ru/SiO_2/Si$ substrates by the atomic layer deposition method using tris(1-methoxy-2-methyl-2-propoxy)bismuth, titanium tetraisopropoxide, and tetraethylorthosilicate as Bi, Ti, and Si precursors, respectively, and H_2O as an oxidant at temperatures ranging from 225 to 300°C. The film thickness ranged from 13 to 18 nm. The Si contents in the films ranged from 10 to 25 atom % and the dielectric constants ranged from 29 to 43 depending on the Si content. All of the BTSO films had very low carbon contents (<0.5 atom %), X-ray diffraction showed that the as-grown films were amorphous and, after annealing at 600°C for 30 min the films were crystallized to the pyrochlore structure.
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High dielectric constant (high-*k*) thin films are increasingly needed for use as capacitor dielectrics in dynamic random access memories (DRAMs) or gate dielectrics in transistors, as the design rule in ultralarge scale integrated devices aggressively scales down.[1] Recently, group 4 element based oxides, such as TiO_2, ZrO_2 and HfO_2, and multication oxides containing alkaline-earth metals, such as $SrTiO_3$, $(Ba,Sr)TiO_3$, have been intensively investigated as promising high-*k* dielectrics.[2] For capacitor dielectric applications, high dielectric constants and excellent insulating properties (low leakage current, low dielectric loss and high electric breakdown strength) are very important. For the films to be used as gate dielectrics, not only a high dielectric constant and good insulating properties, but also chemical and thermal stability, so as not to degrade the carrier mobility in transistors, are crucial factors.[3] In both applications, the uniformity of the film thickness and composition over three-dimensional (3D) structure is very important. This is an even more significant problem in DRAM capacitors, due to their extreme 3D structure. Conventional metallorganic chemical vapor deposition appears to fail to meet these requirements, especially in the case of multication oxide thin films.[4]

When considering the extreme 3D geometry of DRAM capacitors and the small thickness (<4 nm) of gate dielectric films with a design rule of <50 nm, it is believed that the atomic layer deposition (ALD) process should be the process of choice for the deposition of thin dielectric films, due to the better step coverage and thickness controllability that it provides. ALD is characterized by a self-limiting deposition mechanism, which makes it possible to obtain good step coverage over a severe trench structure with an aspect ratio as high as 1:40.[5] Therefore, ALD was chosen as the deposition process of the $Bi_{1-x-y}Ti_xSi_yO_z$ (BTSO) dielectric thin films in this study.

BTSO is a homogeneous mixture of $Bi_2Ti_2O_7$ (BTO) and SiO_2. BTO, which has a pyrochlore structure, has good insulating properties, due to its relatively large bandgap (3.4 eV),[6] and a high dielectric constant of ~150.[7] The deposition results of ALD-BTO films and their dielectric properties have recently been reported.[8,9] Using ALD, amorphous BTO films were deposited due to the low deposition temperature. Thanks to their amorphous nature, the films showed a very low leakage current ($\sim 10^{-8}$ A/cm^2 at 1 V). Their dielectric constants were as high as 40–65, although they have an amorphous structure. However, when the Bi concentration exceeded the stoichiometric value, metallic Bi was formed which in turn seriously degraded the insulating properties. In addition, Ti can have various valence states, Ti^{2+}, Ti^{3+}, and Ti^{4+}, depending on the deposition and postannealing conditions. This may create many defects that produce charge carriers and act as trap centers which can enhance the electrical conductivity. The incorporation of Si into the BTO film was an effective method for improving the leakage current by reducing the metallic Bi incorporation and Ti defects. Min et al. studied BTSO thin films which have a relatively high Si content (17–25%).[10-12] In these studies, ALD was performed with a liquid-delivery system using a single cocktail precursor solution and ozone[10,11] and H_2O[12] as an oxidant. In the case of H_2O oxidant, Bi-deficient BTSO film was deposited using the same precursors and the same precursor ratio of Bi and Ti in the precursor solution as that which was used for the growth of BTSO film using O_3 oxidant where a stoichiometric Bi:Ti ratio (1:1) was obtained.[11,12] This was believed to be due to the oxidizing power of H_2O being too low to sufficiently oxidize Bi and incorporate it into the film, as compared to that of O_3.[11,12] The dielectric constants varied between 24 and 64 depending on the Si contents and film thickness. A higher Si content generally results in a lower dielectric constant. Also, the deposition characteristics and other dielectric properties such as the breakdown voltage and leakage current density depend on the Si contents. The use of O_3 as an oxidant is considered to be beneficial in obtaining nonoxygen-deficient film. However, O_3 may raise an environmental concern once it is used in a mass-production process which requires extra cost for eliminating the residual O_3 extracted from the ALD reactor. In addition, the understanding of the ALD mechanism of oxide thin films using O_3 is still limited compared to the cases where H_2O is used as an oxidant. Therefore, in this case, the environmentally benign H_2O was used as an oxidant to grow BTSO film using the ALD process. In contrast to the method used in a previous study,[12] the Bi, Ti, and Si precursors were supplied separately by bubbling from the respective canisters, thereby allowing a stoichiometric Bi:Ti ratio to be achieved. The Si content was kept at lower values than those used in previous studies, in order to achieve higher dielectric constants.

Experimental

BTSO films were deposited at wafer temperatures ranging from 225 to 300°C using a 4 in. diam wafer scale, traveling wave-type ALD reactor (Quros Co., Plus-100). The ALD system can adopt four separate canisters for the precursor and reactant. The base pressure of the chamber was ~20 mTorr, and the deposition pressures were ~0.8 and ~1.5 Torr during the precursor/H_2O pulse and purging steps, respectively, which were maintained by a dry pump (BOC Edward, iQDP-80). Sputtered-Ru(50 nm)/Ta_2O_5(8 nm)/chemical

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vapor deposition-SiO_2(100 nm)/Si wafers were used as the substrates. Ta_2O_5 layer was used to enhance the adhesion between the Ru and SiO_2 films. In order to confirm the thickness and composition step coverage of the films, contact hole structure was fabricated in SiO_2 layer on Si wafer with the diameter of 0.15 μm and the aspect ratio of 8. In order to grow BTSO thin films with various Si contents, each precursor was injected separately using a normal bubbling system without any carrier gas. $Bi(OC(CH_3)_2CH_2OCH_3)_3$ [$Bi(mmp)_3$], $Ti(OCH(CH_3)_2)_4$ [TTIP], and $Si(OC_2H_5)_4$ [TEOS] were used as the Bi, Ti, and Si precursors, respectively. The $Bi(mmp)_3$, TTIP, and TEOS were evaporated at 130, 65, and 25°C, respectively, and no carrier gas was used to deliver the metallorganic precursors. Water was used as the oxygen source and was evaporated at 14°C. No carrier gas was used for the water delivery either.

The quaternary oxide film was deposited by the successive deposition of the binary oxide layers. This was achieved by exposing the substrate surface to water vapor after each metal precursor pulse, thus forming submonolayer metal oxide layers. One cycle of binary oxide deposition consisted of the metal precursor pulse, the first Ar pulse for purging excessive metal precursor, the water pulse, and the second Ar pulse for purging excessive water. The length of the $Bi(mmp)_3$, TTIP, and TEOS pulses were 2, 1, and 0.5 s, respectively, and that of the H_2O pulse was 0.5 s. The length of the Ar purge pulses was 30, 5, 5, and 15 s after the Bi, Ti, and Si precursor pulses and H_2O pulses, respectively.

The film thickness (physical thickness) was measured by a single-wavelength ellipsometer (Gaertner Scientific Corporation, L116S300) which was calibrated by spectroscopic ellipsometry and cross-sectional high-resolution transmission electron microscopy (TEM, JEOL, JEM-3000F). The cation ratio in the deposited quaternary oxide film was defined using X-ray photoelectron spectroscopy (XPS, ThermoVG, SIGMA PROBE) and X-ray fluorescence spectroscopy (XRF, QuanX, 8000/TCD, Spectrace Co.), which was calibrated by inductively coupled plasma mass spectroscopy. In the case of XRF, the Si concentration cannot be obtained due to the interference caused by the Si signal originating from the Si substrate. Therefore, it was used to measure the Bi to Ti concentration ratio. The Si concentration was mainly calculated from the XPS results, wherein the substrate Si was not detected. The crystalline structure of the film was investigated by X-ray diffraction (XRD, MAC Science, M18XHF-SRA). The thickness and composition step coverage on a contact hole (0.15 μm diameter) whose aspect ratio was 8 were confirmed by cross-section TEM and energy dispersion spectroscopy (EDS, Oxford EDS 6989).

For the electrical measurements, metal-insulator-metal (MIM) capacitors were fabricated using electron-beam-evaporated Pt through a shadow mask (circular electrode diameter of 250 μm) as the top electrode. The fabricated MIM capacitors were annealed at 400°C in air. The dielectric properties were measured using a Hewlett-Packard 4194 impedance analyzer at 10 kHz and a 4149B picoammeter.

Results and Discussion

TEOS is known not to react with H_2O to form SiO_2 film by ALD in this temperature region.[13] This was also confirmed in this experiment; ALD SiO_2 film was not obtained from any conditions using TEOS and H_2O on Si, TiO_2/Si, and Ru substrates. However, Ferguson et al. reported that the ALD of SiO_2 using TEOS with H_2O was possible when NH_3 was used as a catalyst.[13] TiO_2 is also known as a good catalyst material which activates chemical reactions on the surface.[9,14] The authors recently reported that the deposition of a lead-oxide layer in the ALD of $PbTiO_3$ is greatly enhanced on the TiO_2 layer compared to that on the lead-oxide layer.[15,16] Therefore, the ALD of SiO_2 using TEOS and H_2O was expected to occur when the TiO_2 layer was deposited prior to the SiO_2 ALD cycles. The thickness of the single component TiO_2 film deposited at 250°C was ~4 nm after 100 (TTIP + H_2O) cycles. However, when one (TEOS + H_2O) pulse was added after each (TTIP + H_2O) pulse, the film thickness increased to ~5.8 nm, suggesting that SiO_2 was grown on top of each of the partial TiO_2 layers. Therefore, it was found that the catalytic activity of the TiO_2 layer working on SiO_2 deposition[17] rendered the incorporation of Si into the BTSO film possible.

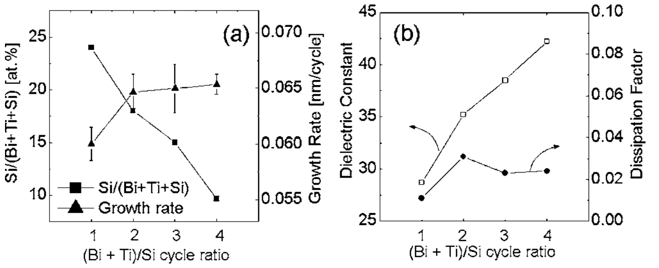

Figure 1. (a) The variation in the Si content in the film [Si/(Bi + Ti + Si)] and growth rate, and (b) the variation in the dielectric constants and dissipation factors of the BTSO films deposited at 225°C as a function of R_{cy}.

In order to control the Si contents in the films, different binary oxide deposition cycle ratios (R_{cy}), defined as [the number of (Bi cycles + Ti cycles)/number of Si cycles], were used. Here, the Bi, Ti and Si cycles are defined as the Bi-precursor pulse-purge-H_2O pulse-purge, and so on. Based on a previous study of ALD-BTO where a Bi/Ti ratio in the film of ~1 was obtained from a 1:1 cycle ratio of Bi and Ti cycles,[8] the Bi and Ti-cycle ratio was fixed at 1. The R_{cy} value was varied from 1 to 4. Figure 1a shows the variation in the Si content in the film [Si/(Bi + Ti + Si)] and growth rate (GR) as a function of R_{cy} at a growth temperature (T_g) of 225°C. Here, the number of cycles that was used to calculate the growth rate was the sum of each number of binary oxide cycles, i.e., for instance, when R_{cy} was 2, the number of cycles was 5 (2 Bi cycles + 2 Ti cycles + 1 Si cycle). Here, the Si content was obtained from XPS. It was observed that the Si content varied almost linearly with R_{cy} suggesting that the Si content can be easily controlled by adjusting the value of R_{cy}. It was noted that the Si content in this study varies from 10% to 25% which is a lower Si content than that observed in previous studies.[10-12] When the Si content was high ($R_{cy} = 1$) the GR was lower (~0.06 nm/cycle) compared to the cases where R_{cy} was >2 (0.065–0.066 nm/cycle), suggesting that the SiO_2 growth rate is still lower than that of the BTO film in the BTSO. It should be noted that the GR of BTO under otherwise identical conditions was ~0.075 nm/cycle (Fig. 3 of Ref. 8). The observation of a low Si content for a high R_{cy} value explains the recovery of the GR of BTSO to that of the BTO films as the R_{cy} increases. The GR value of 0.060–0.066 nm/cycle is almost three times higher than that obtained with the same precursor and O_3 (Ref. 11) which is one of the crucial merits of this process.

Figure 1b shows the variations in the dielectric constants and dissipation factors of the BTSO films, which were deposited at a T_g of 225°C, as a function of the R_{cy} value. The dielectric constant increases almost linearly from 29 to 43 with R_{cy} and, thus, is inversely proportional to the Si content in the film. The dissipation factor was ~2%. These dielectric constant values are lower than those obtained in the study by Min where a dielectric constant of 55 was obtained when the Si content was 20%.[11] Therefore, the use of O_3 appears to allow a higher dielectric constant to be obtained than that using H_2O, although the reason for this is not clearly understood at this moment.

Figures 2a and b show the variations in the cation concentration ratio [Bi/(Bi + Ti + Si), Ti/(Bi + Ti + Si), and Si/(Bi + Ti + Si)], and GR as a function of T_g in the temperature range from 225 to 300°C. The relative error limits in the XRF measurements were <~1.5%, which were too small to be depicted for the given symbol size, so there is no error bar in this plot. Also shown in Fig.

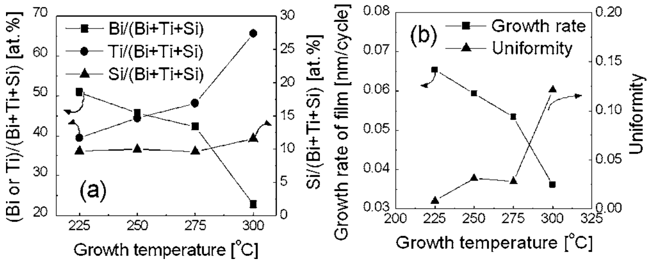

Figure 2. (a) The variation in the cation concentration ratio [Bi/(Bi + Ti + Si), Ti/(Bi + Ti + Si) and Si/(Bi + Ti + Si)] in the BTSO films, and (b) growth rate and uniformity as a function of the growth temperature in the range from 225 to 300°C.

2b is the variation in the thickness uniformity, which is defined as (max. thickness-min. thickness)/2(average thickness), over the 4 in. diam wafer. This actually represents the relative error limits of GR. Here, the value of R_{cy} was 4. The Si content in the films is almost constant (~9% for $T_g < 275°C$ and ~11% for $T_g = 300°C$) irrespective of T_g. However, the Bi and Ti content moderately decreases and increases, respectively, with increasing T_g up to 275°C and then abruptly decreases and increases at a T_g of 300°C. GR also decreases moderately with increasing T_g up to 275°C and then decreases abruptly at 300°C. The decrease in the Bi content and increase in the Ti content with increasing T_g was also observed in the case of BTO film prepared by ALD.[8] It is considered that the increase in the volatility of Bi and increase in the GR of TiO_2 from TTIP with increasing T_g in the T_g range from 200 to 275°C[18,19] constitute the reason for the gradual change in the same T_g region. The abrupt increase in the Ti content at 300°C might originate from the thermal decomposition of TTIP at this temperature. This conclusion is supported by the large degradation in the thickness uniformity at this temperature. Note that the ALD reactor used in this study was of the traveling wave type, so that once the deposition reaction starts by thermal decomposition, the uniformity is seriously degraded. The film thickness on the portion of the wafer close the precursor inlet port of the reactor becomes thicker. As T_g increases the Bi content decreases due to its volatilization, and this makes the film closer to the Ti–Si–O. Because the GR of the Ti–Si–O film is lower than that of BTSO, the GR of the BTSO film decreases with increasing T_g.

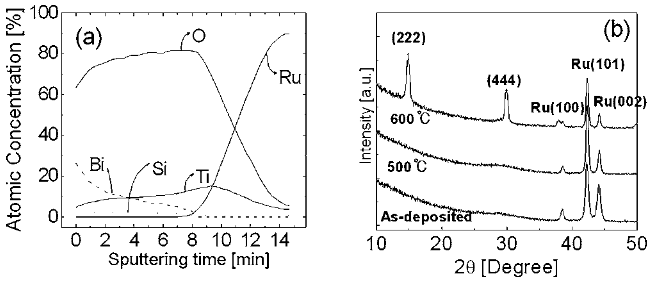

Figure 3. (a) The AES depth profile results of a 13.7 nm thick BTSO film, and (b) XRD patterns of the films before and after the postdeposition annealing for 30 min in an N_2 atmosphere at 500 and 600°C.

Figures 3a and b show the Auger electron spectroscopy depth profile results for a 13.7 nm thick BTSO film grown at a T_g of 225°C and the XRD patterns of the films before and after the postdeposition annealing, respectively. Although it is not included in Fig. 3a, the residual carbon content was <0.5% throughout the film. Figure 3a shows obviously that Bi was piled up near the film surface, and Ti was piled up near the interface with Ru substrate in contrast to Bi, while the Si content shows a relatively constant value throughout the film thickness. Similar Bi and Ti distributions along the film thickness were also observed in ALD-BTO film.[8] Lee et al. also reported that the Bi content increases near the surface of $Bi_4Ti_3O_{12}$ films which were deposited by metallorganic chemical vapor deposition.[20] Using the two-step process, as has been performed in the ALD of BTO film,[8] a more uniform cation distribution along the film depth was achieved (data not shown). This phenomenon might be attributed to the less active oxidation and much higher volatility of the Bi atoms compared to Ti atoms. Postdeposition annealing was performed under a N_2 atmosphere for 30 min at temperatures of 500 and 600°C. The XRD patterns (Fig. 3b) of the BTSO films show that the as-deposited film ($T_g = 225°C$) was amorphous and that the amorphous structure was maintained up to 500°C, and then crystallized to the pyrochlore structure at 600°C. The crystalline peak positions are close to those of the BTO crystalline phase (Joint Committee on Powder Diffraction Standards no. 32-0118) but not exactly identical. The incorporation of Si produced a slight difference in the lattice parameters.

Figures 4a and b show the variation of the current density (J) with the apparent electric field (E_a), which was calculated by dividing the applied voltage by the film thickness, of the films deposited at different temperatures with a common R_{cy} value of 4, and deposited with different R_{cy} values at a common T_g of 225°C, respectively. When the film was grown at 300°C the J value was slightly higher at $E_a > \sim 1$ MV/cm. The other films show stably low J values up to an E_a of 1.2 MV/cm. Figure 4c shows the J value (at 1.2 MV/cm) vs equivalent oxide thickness (t_{ox}) performance of the BTSO films deposited in this study. The t_{ox} is defined by the following equation and calculated from the measured capacitance (C_m), area (A) and physical thickness (t_{phy})

$$t_{ox} = (k_{SiO_2}/k) \cdot t_{phy} = \varepsilon_0 k_{SiO_2}(A/C_m) \quad [1]$$

where ε_0, k_{SiO_2}, and k are the permittivity in a vacuum, dielectric constant of SiO_2 (3.9), and measured dielectric constant of the film, respectively. In Fig. 4c, data from previously reported ALD BTSO

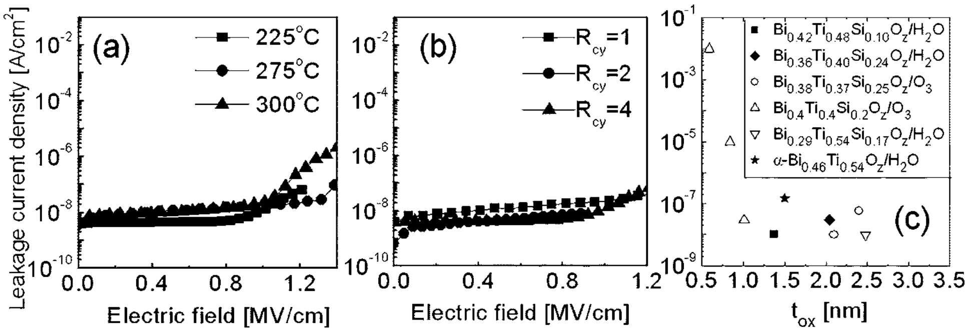

Figure 4. (a) The variation of the current density as a function of the apparent electric field of the films deposited at different temperatures with a common R_{cy} value of 4, and (b) deposited with different R_{cy} values at a common T_g of 225°C. (c) The various results of J_g vs t_{ox} of the amorphous BTO film used as a reference, which was deposited using ALD with H_2O [★: Hwang et al. (Ref. 8)], and BTSO films where the BTSO films were grown using ozone and a single cocktail precursor solution [○: Min et al. (Ref. 10), △: Min et al. (Ref. 11)], grown using H_2O and a single cocktail precursor solution [▽: Min et al. (Ref. 12)], and grown using H_2O in this study (■, ◆).

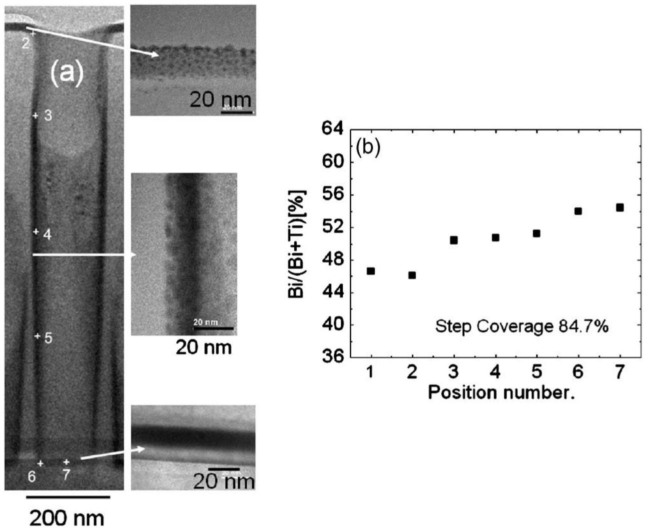

Figure 5. (a) The cross-sectional TEM image of the BTSO films grown at 225°C on a contact-hole-type structure formed in SiO_2 and (b) Bi/(Bi + Ti) ratio at the various positions shown in (a).

films using O_3 oxidant[10,11] and H_2O oxidant,[12] and ALD BTO using H_2O oxidant[8] were also included for the purpose of comparison. The J vs t_{ox} performance of the BTSO film grown in this study cannot be compared with those of the $Bi_{0.4}Ti_{0.4}Si_{0.2}O_z/O_3$ film in the t_{ox} region <1.0 nm, since such thin films were not prepared in this study. However, it can be observed that the J vs t_{ox} performance of the slightly thicker films ($t_{ox} > 1.3$ nm) in this study is comparable or slightly better than that of the BTSO films grown using the O_3 oxidant. This is an important merit of this H_2O-based ALD process, considering the environmentally benign process conditions that were used and almost three times higher GR that was obtained. Compared to the BTO film, the BTSO film appears to have an approximately ten times lower J value at a similar t_{ox} value. This shows the merit of incorporating Si into the BTO film in terms of reducing the J value.

Finally, the film step coverage in terms of its thickness and composition was investigated using a patterned wafer having circular-shaped holes with a depth of 1200 nm and an opening of 150 nm that were etched in the SiO_2 layer, as shown by the cross section TEM images in Fig. 5a. Here, the film was grown at a T_g of 225°C with an R_{cy} of 4. Because it is difficult to measure the Si content of BTSO films on SiO_2, only the Bi and Ti compositions were measured by TEM-EDS along the wall of the hole, as shown in Fig. 5b. The thickness step coverage was as high as $\sim 90\%$, as can be seen in the magnified images in Fig. 5a. Although there was a slight difference in the composition according to the positions in the hole, the step coverage of the composition was $\sim 85\%$, which is a reasonably good value considering the accuracy of local composition measurement by TEM-EDS. It can be observed that the Bi concentration slightly decreases near the opening area of the hole, possibly due to the higher volatility of Bi in that area.

Conclusion

The growth behavior and various properties of the BTSO film prepared by ALD using H_2O as an oxidant for use as an alternative high-dielectric material for DRAM capacitors or gate dielectric applications were studied. Based on the previously reported BTO ALD results with the same chemistry, ALD reactor and process conditions,[8] the Si content in the BTSO films was controlled by adjusting the (Bi + Ti) cycle to Si-cycle ratio. It was found that the Si content varied almost linearly with the cycle ratio. The dielectric constant varied inversely with the Si concentration. The Bi content was significantly decreased at a high deposition temperature due to the volatility of Bi and insufficient oxidizing power of H_2O. The growth rate of the BTSO film varied from 0.060 to 0.067 nm/cycle depending on the conditions, which is almost three times higher than that obtained for the growth of BTSO film using O_3 oxidant. A higher Si concentration generally decreases the growth rate. The as-deposited BTSO films have an amorphous structure and postannealing at 600°C induced their crystallization into the pyrochlore structure. Although the growth rate was much higher, the amount of carbon residue was very low (<0.5 atom %) and the electrical performance was almost identical to that of the O_3-based BTSO film in the t_{ox} region $> \sim 1.3$ nm. The ALD-BTSO film grown at 225°C showed a good thickness ($\sim 90\%$) and composition ($\sim 85\%$) step coverage over the contact hole structure with an aspect ratio of 8.

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References

1. *International Technology Roadmap for Semiconductors 2005*, Semiconductor Industry Association (http://public.itrs.net)
2. G. D. Wilk, R. M. Wallace, and J. M. Anthony, *J. Appl. Phys.*, **89**, 5243 (2001).
3. L. Manchanda, M. D. Morris, M. K. Green, R. B. van Dover, F. Klemens, T. W. Sorsch, P. J. Silveran, G. Wilk, B. Busch, and S. Aravanmudhan, *Microelectron. Eng.*, **59**, 351 (2001).
4. C. S. Hwang, S. Y. No, J. Park, H. J. Kim, H. J. Cho, Y. K. Han, and K. Y. Oh, *J. Electrochem. Soc.*, **149**, G585 (2002).
5. R. G. Gordon, D. Hansmann, E. Kim, and J. Shepard, *Chem. Vap. Deposition*, **9**, 73 (2003).
6. Y. Hou, T. Lin, Z. Huang, G. Wang, Z. Hu, J. Chu, X. Xu, and M. Wang, *Appl. Phys. Lett.*, **85**, 1214 (2004).
7. S. W. Wang, H. Wang, X. Wu, S. Shang, M. Wang, Z. Li, and W. Lu, *J. Cryst. Growth*, **224**, 323 (2001).
8. G. W. Hwang, W. D. Kim, Y.-S. Min, Y. J. Cho, and C. S. Hwang, *J. Electrochem. Soc.*, **153**, F20 (2006).
9. M. Schuisky, K. Kukli, M. Ritala, A. Hårsta, and M. Leskelä, *Chem. Vap. Deposition*, **6**, 139 (2000).
10. Y.-S. Min, Y. J. Cho, I. P. Asanov, J. H. Han, W. D. Kim, and C. S. Hwang, *Chem. Vap. Deposition*, **11**, 38 (2005).
11. Y.-S. Min, Y. J. Cho, and C. S. Hwang, *Electrochem. Solid-State Lett.*, **7**, F85 (2004).
12. Y.-S. Min, Y. J. Cho, J.-H. Ko, E. J. Bae, W. Park, and C. S. Hwang, *J. Electrochem. Soc.*, **152**, F124 (2005).
13. J. D. Ferguson, E. R. Smith, A. W. Weimer, and S. M. George, *J. Electrochem. Soc.*, **151**, G528 (2004).
14. A. L. Linsebigler, G. Lu, and J. T. Yates, Jr., *Chem. Rev. (Washington, D.C.)*, **95**, 735 (1995).
15. G. W. Hwang, H. J. Lee, K. Lee, and C. S. Hwang, *J. Electrochem. Soc.*, **154**, G69 (2007).
16. T. Watanabe, S. Hoffmann-Eifert, S. Mi, C. Jia, R. Waser, and C. S. Hwang, *J. Appl. Phys.*, **101**, 014114 (2007).
17. G. Li, X. Wang, X. Guo, S. Liu, Q. Zhao, X. Bao, and L. Lin, *Mater. Chem. Phys.*, **71**, 195 (2001).
18. W. D. Kim, G. W. Hwang, O. S. Kwon, S. K. Kim, M. Cho, D. S. Jeong, S. W. Lee, M. H. Seo, C. S. Hwang, Y. -S. Min, and Y. J. Cho, *J. Electrochem. Soc.*, **152**, C552 (2005).
19. M. Ritala and M. Leskela, *Chem. Mater.*, **5**, 1174 (1993)
20. S. K. Lee, J. H. Kim, D. H. Choi, M. W. Hwang, M. Y. Um, Y. H. Kim, J. Y. Kim, and H. J. Kim, *J. Korean Vac. Soc.*, **9**, 373 (2000).