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Microwave dielectric properties of nanocrystalline TiO_2 prepared using spark plasma sintering

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Abstract

TiO_2 bulk ceramics were fabricated by using both spark plasma sintering (SPS) and the conventional sintering method (CSM). Starting materials were ultra fine rutile powders (<50 nm) prepared via the sol–gel process. CSM achieved the relative sintering density of 99.2% at 1300 °C. The grain size of 1300 °C sintered specimen was 6.5 μm. However, the sintering temperature of SPS for the density of 99.1% was as low as 760 °C, where the grain size was only 300 nm. In order to re-oxidize the Ti^{3+} ions due to the reducing atmosphere of the SPS process and the high temperature of the CSM process, the prepared TiO_2 specimens were annealed in an oxygen atmosphere. The dielectric constant (ε_r) and quality factor ($Q \times f$) of SPS-TiO_2 re-oxidized specimens in a microwave regime were 112.6 and 26,000, respectively. These properties were comparable to those of 1300 °C sintered CSM specimens ($\varepsilon_r \sim 101.3$, $Q \times f \sim 41{,}600$). These microwave dielectric properties of nanocrystalline TiO_2 specimens prepared using SPS were discussed in terms of grain size variation and Ti^{4+} reduction.

Keywords: TiO_2; Dielectric properties; Nanocomposites; Spark plasma sintering; Defect

1. Introduction

TiO_2 has been widely used for gas and temperature sensing devices,[1] photocatalytic devices[2] and photoelectric devices.[3] Recently, the dielectric properties of TiO_2 have been of great interest for applications in the telecommunications industry due to its unusually high dielectric constants and low dielectric loss.

Nanocrystalline materials have unique electrical, magnetic, mechanical, and optical properties in various fields due to their extremely small grain size, which are not available in conventional materials. Recently, major research efforts have been placed on the fabrication characterization of nano-sized dielectric material, because the current technology requires very small size particles to miniaturize microwave devices and components. In spite of the technological importance, nanostructured TiO_2 samples have not been fully realized due to the high sintering temperature. Several researchers have shown that high-density nanostructured TiO_2 can be achieved by using uniform nano-size TiO_2 particles,[4] an excess energy released from the anatase–rutile phase transformation of TiO_2,[5] and hot press.[6]

Recently, the spark plasma sintering (SPS) process has recently received a great deal of attention in densifying nanocrystalline TiO_2 samples.[7–9] The SPS process can enhance densification by applying a pulsed voltage and a uniaxial pressure to a specimen during sintering. However, the exact spark plasma sintering mechanism has not been well-elucidated.[10–13] Although SPS is utilized to fabricate a fully densified bulk having nanocrystalline grains, it leads to a reduction in the bulk sample due to the applied high voltage and vacuum condition. This reduction of Ti^{4+} is the main reason why many studies involving the SPS of TiO_2 have only focused on sintering behavior and have not reported the dielectric characteristics of TiO_2 obtained through SPS.

The purpose of present work is to explore the microwave dielectric properties of fully dense nanocrystalline TiO_2 samples. The fully dense nanocrystalline TiO_2 specimen was fabricated by using SPS. The microwave dielectric properties of the re-oxidized nanocrystalline TiO_2 (300–400 nm) were compared with those of the microcrystalline TiO_2 specimen prepared by the conventional sintering method (CSM).

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2. Experimental procedure

Nano-sized rutile powders were prepared via the sol–gel method.[14] The prepared particles were granulated with deionised water and then 2.4 g of powders were placed into graphite mold. Then, SPS sintering was performed at the scheduled temperatures (680–760 °C) for 10 min. The temperature on the surface of the graphite mold was measured by a pyrometer. During the SPS process, an electric current of 1 kA passed through the specimen and a uniaxial pressure of 40 MPa was applied to the specimen in a vacuum chamber of 65 mTorr. For the CSM samples, granulated powder compacts that were prepared at a uniaxial pressure of 100 MPa, were sintered at temperatures ranging from 1000 to 1300 °C for 2 h in a normal furnace. To remove the effect of the reduction during the sintering process, both the SPS and CSM specimens were annealed in an oxygen atmosphere (i) at 780 °C for various time periods (1–6 h) or (ii) at 1200 °C for 1 h.

The density of the sintered specimens was measured using the Archimedes method. Microstructure of samples was observed using field emission scanning electron microscopy (FESEM: Model JSM6330F, Japan Electronic Optics Laboratory, Japan). The reduction and oxidation of Ti^{4+} ions was measured using X-ray photoemission spectroscopy (XPS: Model SIGMA PROBE, ThermoVG, UK). The XPS binding energy (BE) was calibrated using a C 1s peak of 284.5 eV. The dielectric properties in the frequency range from 100 Hz to 10 MHz were measured using an impedance analyzer (Model HP4194A, Hewlett-Packard, Palo Alto, CA). The microwave dielectric properties at c-band frequencies (5–7 GHz) were measured using a network analyzer (Model HP8720C, Hewlett-Packard, Palo Alto, CA).

3. Results and discussion

To obtain the dense nanocrystalline TiO_2 specimen, we used nano-sized powders as starting materials. Also, to remove the ambiguities of the dielectric properties, the crystal structure of nano-sized powders was controlled to be a rutile phase. A phase transformation of TiO_2 from anatase to rutile during sintering is accompanied with the reduction of Ti^{4+}, which irreversibly deteriorates the quality factor ($Q \times f$).[15]

The relative density and the average grain size of the SPS-TiO_2 specimens and CSM-TiO_2 specimens as a function of sintering temperature are summarized in Table 1. The density of a sample prepared using SPS at 760 °C for 10 min was larger than 99.0%, while a sample with the same density was obtained using CSM at 1300 °C for 2 h. Only fully densified specimens were used for the measurement of microwave dielectric properties to exclude the porosity effect on the dielectric properties. The fully dense specimens obtained through SPS at 760 °C for 10 min and CSM at 1300 °C for 2 h were designated as SPS and CSM specimens, respectively. Fig. 1 shows the microstructure of the SPS and CSM specimens. The average grain size of the SPS specimen and the CSM specimen are 300 nm and 6.5 μm, respectively. In the CSM, a long sintering time and a high sintering temperature, which are needed to obtain a fully densified specimen, result in large grains. However, low temperature and short time SPS process does not allow for grain growth and yields a fully densified TiO_2 bulk having nano-sized grains. A detailed mechanism for the densification of TiO_2 samples via SPS is under investigation.

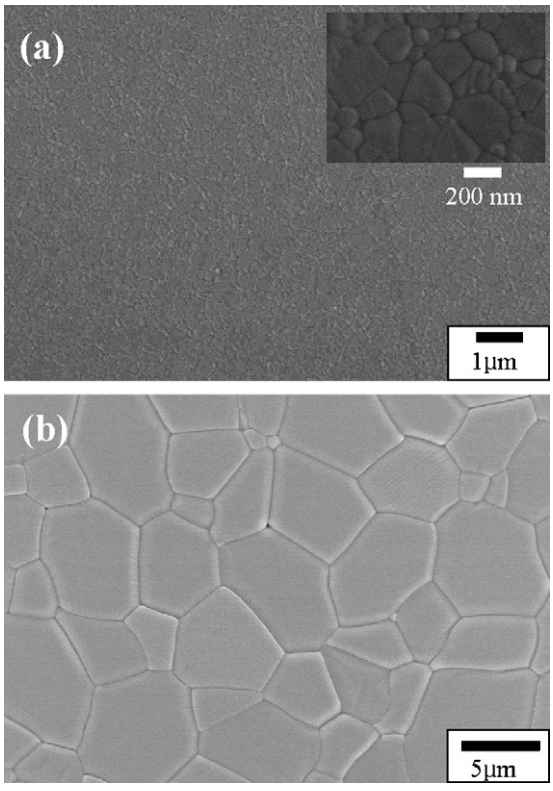

Fig. 1. SEM images of (a) the SPS specimen at 760 °C for 10 min and (b) the CSM specimen at 1300 °C for 2 h.

Although SPS has the merit of low temperature sintering for nanocrystalline grains, it leads to a reduction of samples due to its vacuum environment. Therefore, the color of SPS specimens was black due to the reduction of Ti^{4+} ions. Fig. 2 shows the XPS spectra of the SPS specimen and the CSM specimen before and

Table 1
Relative density and average grain size of the SPS specimens and the CSM specimens as a function of sintering temperature

	Temperature					
	SPS			CSM		
	680 °C	720 °C	760 °C	1000 °C	1150 °C	1300 °C
Relative density (%)	88.2	97.3	99.1	91.0	97.5	99.2
Average grain size (nm)	100	200	300	1000	3500	6500

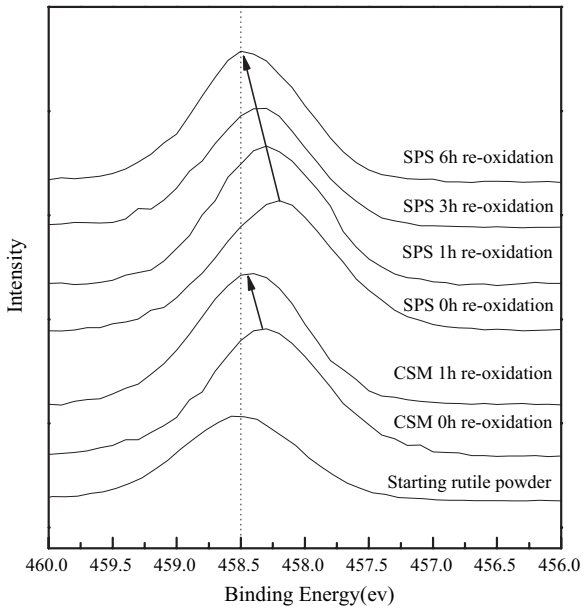

Fig. 2. XPS spectra of initial rutile power and the CSM specimens before and after the oxidation for 1 h, and the SPS specimens as a function of re-oxidizing time.

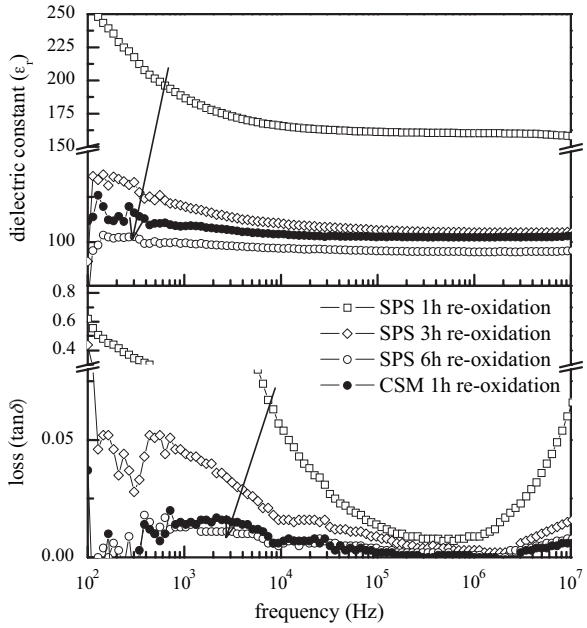

Fig. 3. The dielectric constant (ε_r) and loss (tan δ) as a function of the frequency for the re-oxidized SPS specimens and the re-oxidized CSM specimen.

after the re-oxidation. Ti $2p_{3/2}$ peaks of Ti^{4+} and Ti^{3+} ions are observed in the range of 458.5–458.9 eV and 456.9–458.2 eV, respectively.[16] Endle et al.[17] and Jiang et al.[18] reported that the binding energy of Ti^{4+} shifts to lower energy when the reduction from Ti^{4+} to Ti^{3+} ions occurs. The position of Ti $2p_{3/2}$ peak for the starting rutile powders is 458.5 eV, indicating that the amount of Ti^{3+} ions is negligible. In SPS, however, the Ti $2p_{3/2}$ peak of the as-made SPS specimen shifted significantly toward lower energy. With increasing re-oxidation time, the Ti $2p_{3/2}$ peak SPS specimens were recovered to the original peak of the starting rutile powders. This result clearly shows that the SPS process induces the reduction of Ti^{4+} ions and that the subsequent oxygen annealing annihilates Ti^{3+} ions. Although the binding energy of the as-made CSM specimen also shifted toward lower energy, its variation was less than that of the as-made SPS specimen. The slightly oxidized CSM specimen recovered the Ti $2p_{3/2}$ peak of the starting materials via the re-oxidation process, as shown in Fig. 2.

Microwave dielectric properties such as the relative dielectric constant (ε_r) and the quality factor ($Q \times f$), as well as the average grain size of the SPS specimen and the CSM specimen before and after the re-oxidizing process, are summarized in Table 2 . The dielectric properties of the SPS specimens, which were re-oxidized for 0 and 1 h, could not be measured in the microwave range, since these specimens were exceedingly lossy due to the presence of Ti^{3+} ions.[19] Fig. 3 shows the dielectric constant (ε_r) and loss (tan δ) of the re-oxidized SPS and CSM specimens in the frequency range from 100 Hz and 10 MHz. The 1 h-oxidized SPS specimen shows a relaxation behavior and abnormally large dielectric constant and large loss, confirming the negative effect of Ti^{3+} ions on the dielectric properties.

Templeton et al.[20] attributed a large microwave dielectric loss of pure TiO_2 to the oxygen vacancy, which was accompanied by the reduction of Ti^{4+}. They also argued that a small fraction of reduced Ti^{3+} could drastically increase the dielectric loss. Non-reduced TiO_2 has a dielectric constant (ε_r) of 100–105 and a quality factor ($Q \times f$) of 40,000 GHz.[21] The microwave dielectric properties of the CSM specimen, which was re-oxidized for 1 h were similar to those of non-reduced TiO_2. In Fig. 3, the 1 h-oxidized CMS specimen shows no relaxation behavior and possesses a low dielectric in frequency range of 100 Hz to 10 MHz. This result indicates that the reduced Ti^{3+} ion of the CSM specimen was almost re-oxidized by 1 h oxygen annealing. Fig. 3 also shows that the dielectric loss (tan δ) of the SPS specimen became almost similar to that of the 1 h-oxidized CSM specimen when the subsequent annealing time was larger than

Table 2
Microwave dielectric properties and average grain size of the SPS specimens and the CSM specimens as a function of re-oxidizing time

	Oxidation time					
	SPS specimen				CSM specimen	
	0 h	1 h	3 h	6 h	0 h	1 h
ε_r	–	–	112.6	112.6	101.0	100.3
$Q \times f$	–	–	19,100	26,000	19,100	41,600
Grain size (nm)	300	300	330	400	6,500	6,500

6 h. Also, it is noted in Table 2 that the dielectric loss is more sensitive to the subsequent oxidation than the dielectric constant.

The combination of the XPS results (Fig. 2) and the dielectric properties (Fig. 3) shows that both the 6 h-oxidized SPS specimen and the 1 h-oxidized CSM specimen had a negligible amount of Ti^{3+} ion. However, the grain size of each specimen was significantly different, as shown in Fig. 1. The dielectric constants of the 6 h-oxidized SPS specimen and the 1 h-oxidized CSM specimen were 112.6 and 100.3, respectively. Given that their dielectric constant was larger than 100, this difference was not significant. However, the quality factor ($Q \times f$) showed considerable difference between these specimens. The 6 h-oxidized SPS specimen having nano-sized grains, 400 nm, which slightly grew during the re-oxidation from 300 nm, had $Q \times f$ of 26,000 GHz, while the 1 h-oxidized CSM specimen having micro-sized grain, 6.5 μm, had $Q \times f$ of 41,600 GHz. There have been intensive studies on grain size–dielectric loss relationships. For example, Penn et al.[22] reported that dielectric loss very strongly depends on the grain size and that the dielectric constant is less sensitive to grain size in alumina. However, these studies did not exclude the effect of other parameters such as porosity and liquid phase in addition to a grain size. Since the effect of porosity and liquid phase, and the existence of Ti^{3+} were excluded in this study, it was expected that the nanocrystalline SPS specimen would show a lower $Q \times f$ value than that of the microcrystalline CSM specimen. The increase in the number of grain boundaries per unit volume in a nanocrystalline material would result in higher loss, because the grain boundary is a defective region and suppresses the harmonic oscillation of dipoles under an external field.

4. Conclusion

Fully dense nanocrystalline TiO_2 (300–400 nm) was fabricated through SPS from nano-sized rutile powder prepared via the sol–gel process, and then the resulting microwave dielectric properties were studied. Because the as-made SPS specimen was significantly reduced, the exact microwave dielectric properties could be characterized after re-oxidizing process for 6 h. The reduction of TiO_2 did not affect the dielectric constant (ε_r) and resulted in deterioration of the quality factor ($Q \times f$) in the microwave range. The dielectric constant (ε_r) of the nanocrystalline TiO_2 was similar to that of the microcrystalline TiO_2. However the quality factor ($Q \times f$) was found to strongly depend on the grain size. The nanocrystalline TiO_2 with the number of grain boundaries per unit volume had a lower quality factor ($Q \times f$) of 26,000 GHz than that (41,600 GHz) of the microcrystalline TiO_2.

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References

1. Kulwicki, B. M., Ceramic sensors and transducers. *J. Phys. Chem. Solids*, 1984, **45**, 1015–1031.
2. Levy, B., Photochemistry of nanostructured materials for energy applications. *J. Electoceram.*, 1997, **1**, 239–272.
3. Barbe, C. J., Arendse, F., Comte, P., Jirousek, M., Lenzmann, F., Shklover, V. *et al.*, Nanocrystalline titanium oxide electrodes for photovoltaic applications. *J. Am. Ceram. Soc.*, 1997, **80**, 3157–3171.
4. Yan, M. F. and Rhodes, W. W., Low temperature sintering of TiO_2. *Mater. Sci. Eng.*, 1983, **61**, 59–66.
5. Kumar, K. N. P., Keizer, K., Burggraaf, A. J., Okubo, T., Nagamoto, H. and Mrooka, S., Densification of nanostructured titania assisted by a phase transformation. *Nature*, 1992, **358**, 48–51.
6. Liao, S. C., Pae, K. D. and Mayo, W. E., High pressure and low temperature sintering of bulk nanocrystalline TiO_2. *Mater. Sci. Eng. A*, 1995, **204**, 152–159.
7. Zhan, G. D., Kuntz, J., Wan, J., Garay, J. and Mukherjee, A. K., A novel processing route to develop a dense nanocrystalline alumina matrix (<100 nm) nanocomposite material. *J. Am. Ceram. Soc.*, 2003, **86**, 200–202.
8. Luan, W., Gao, L., Kawaoka, H., Sekino, T. and Niihara, K., Fabrication and characteristics of fine-grained $BaTiO_3$ ceramics by spark plasma sintering. *Ceram. Int.*, 2004, **30**, 405–410.
9. Gao, L., Li, Q. and Luan, W., Preparation and electric properties of dense nanocrystalline zinc oxide ceramics. *J. Am. Ceram. Soc.*, 2002, **85**, 1016–1018.
10. Wang, S. W., Chen, L. D., Kang, Y. S., Niino, M. and Hirai, T., Effect of plasma activated sintering (PAS) parameters on densification of copper powder. *Mater. Res. Bull.*, 2000, **35**, 619–628.
11. Shen, Z., Johnsson, M., Zhao, Z. and Nygren, M., Spark plasma sintering of alumina. *J. Am. Ceram. Soc.*, 2002, **85**, 1921–1927.
12. Omori, M., Sintering, consolidation, reaction and crystal growth by the spark plasma system (SPS). *Mater. Sci. Eng. A*, 2000, **287**, 183–188.
13. Yamazaki, K., Risbud, S. H., Aoyama, H. and Shoda, K., PAS (plasma activated sintering): transient sintering process control for rapid consolidation of powders. *J. Mater. Process. Technol.*, 1996, **56**, 955–965.
14. Jung, H. S., Shin, H., Kim, J. R., Kim, J. Y. and Hong, K. S., In situ observation of the stability of anatase nanoparticles and their transformation to rutile in an acidic solution. *Langmuir*, 2004, **20**, 11732–11737.
15. Kim, D. W., Ko, K. H., Kwon, D. K. and Hong, K. S., Origin of microwave dielectric loss in $ZnNb_2O_6$–TiO_2. *J. Am. Ceram. Soc.*, 2002, **85**, 1169–1172.
16. Moulder, J. F., *Handbook of X-ray Photoelectron Spectroscopy*. Physical Electronics, Minnesota, 1995, pp. 72–73.
17. Endle, J. P., Sun, Y. M., White, J. M. and Ekerdt, J. G., X-ray photoelectron spectroscopy study of TiN films produced with tetrakis-(dimethylamido)titanium and selected N-containing precursors on SiO_2. *J. Vac. Sci. Technol. A*, 1998, **16**, 1262–1267.
18. Jiang, N., Zhang, H. J., Bao, S. N., Shen, Y. G. and Zhou, Z. F., XPS study for reactively sputtered titanium nitride thin films deposited under different substrate bias. *Phys. B: Condens. Mater.*, 2004, **352**, 118–127.
19. Kim, D. W., Park, B., Chung, J. and Hong, K. S., Mixture behavior and microwave dielectric properties in the low-fired TiO_2–CuO system. *Jpn. J. Appl. Phys.*, 2000, **39**, 2696–2700.
20. Templeton, A., Wang, X., Penn, S. J., Webb, S. J., Cohen, L. F. and Alford, N. M., Microwave dielectric loss of titanium oxide. *J. Am. Ceram. Soc.*, 2000, **83**, 95–100.
21. Kim, D. W., Kim, J. H., Kim, J. R. and Hong, K. S., Phase constitutions and microwave dielectric properties of $Zn_3Nb_2O_8$–TiO_2. *Jpn. J. Appl. Phys.*, 2001, **40**, 5994–5998.
22. Penn, S. J., Alford, N. M., Templeton, A., Wang, X., Xu, M., Reece, M. *et al.*, Effect of porosity and grain size on the microwave dielectric properties of sintered alumina. *J. Am. Ceram. Soc.*, 1997, **80**, 1885–1888.