Sensors and Materials, Vol. 34, No. 9 (2022) 3561–3567
MYU Tokyo

S & M 3060

Study of $Nd(Zn_{0.5}Ti_{0.5})O_3$ Dielectric Thin Films Fabricated Using Sol–Gel Method

Ching-Fang Tseng,[1] Bo-Yan Huang,[1] and Cheng-Hsing Hsu[2*]

[1]Department of Electronic Engineering, National United University,
No. 2 Lien-Da, Nan-Shih Li, Miaoli 36063, Taiwan
[2]Department of Electrical Engineering, National United University,
No. 2 Lien-Da, Nan-Shih Li, Miaoli 36063, Taiwan

(Received March 1, 2022; accepted September 15, 2022)

Keywords: sol–gel method, $Nd(Zn_{0.5}Ti_{0.5})O_3$ thin film, microstructure, electrical properties

We investigated the microstructures and electrical properties of $Nd(Zn_{0.5}Ti_{0.5})O_3$ thin films fabricated using the sol–gel method at various preheating temperatures and annealing temperatures. The composites and their morphological characteristics were analyzed using X-ray diffraction (XRD) and scanning electron microscopy (SEM) and were found to be sensitive to both the preheating temperature (100–300 °C) and annealing temperature (600–800 °C). The diffraction pattern indicated that the deposited films exhibit a polycrystalline microstructure. The dielectric constant and leakage current density of the $Nd(Zn_{0.5}Ti_{0.5})O_3$ thin films at a preheating temperature of 300 °C and an annealing temperature of 700 ºC were 16 and 2.13×10^{-8}, respectively. The experimental data for $Nd(Zn_{0.5}Ti_{0.5})O_3$ thin films can be applied to wireless communication microwave components, such as temperature-sensing antennas.

1. Introduction

The application of dielectric ceramics in wireless communication microwave components, including resonators, filters, dielectric resonator oscillators, and antennas, has garnered attention.(1–4) A dielectric ceramic often used in communication components is a perovskite ceramic system with a chemical formula of ABO_3. A common perovskite ceramic is $CaTiO_3$ [dielectric constant = 160, quality factor ($Q \times f$) = 12000 GHz, and temperature coefficient of resonant frequency (τ_f) = +850 ppm/°C], but it has low $Q \times f$ and large τ_f values; therefore, scholars have improved its composition.(5) Cubic complex perovskite ceramics such as $A(B'_{1/2}B''_{1/2})O_3$ and $A(B'_{1/3}B''_{2/3})O_3$, where the B-site position can be a single cation or several cations (Me^{2+}, Me^{3+}), have been developed. Common cubic complex perovskite ceramics are $Ba(Mg_{1/3}Ta_{2/3})O_3$, $Ba(Mg_{1/3}Nb_{2/3})O_3$, $Nd(Zn_{1/2}Ti_{1/2})O_3$, and $Nd(Co_{1/2}Ti_{1/2})O_3$, with dielectric constants of approximately 20–30 and $Q \times f > 50000$ GHz.(6–10)

Complex perovskite ceramics have been researched extensively because of their excellent microwave dielectric properties. $Nd(Zn_{0.5}Ti_{0.5})O_3$ ceramic has a dielectric constant (ε_r) of 31.6, a

*Corresponding author: e-mail: hsuch@nuu.edu.tw
https://doi.org/10.18494/SAM4041

ISSN 0914-4935 © MYU K.K.
https://myukk.org/

$Q \times f$ of 170000 (GHz), and a τ_f of −42 ppm/°C. $Nd(Zn_{0.5}Ti_{0.5})O_3$ is a complex perovskite ceramic that is a suitable substrate for passive components used in microwave applications.[10] In this study, we determined the electrical, dielectric, and physical properties of $Nd(Zn_{0.5}Ti_{0.5})O_3$ thin films fabricated using the sol–gel deposition method. The effects of the preheating temperature on the microstructural, electrical, and dielectric properties of $Nd(Zn_{0.5}Ti_{0.5})O_3$ were also investigated.

2. Experimental Procedure

High-purity ZnO powder, Nd_2O_3 powder, and titanium isopropoxide ($TiC_{12}H_{28}O_4$) were used in the sol–gel process with various preheating and annealing temperatures. First, ZnO powder was dissolved in acetic acid and water, which were then mixed to produce a solution. Simultaneously, Nd_2O_3 powder and titanium isopropoxide [$TiC_{12}H_{28}O_4$] were dissolved in the solution. The mixed solution was stirred at a temperature of 80 °C for 24 h to produce the final precursor sol. This sol was placed on n-type Si substrates and spun at 3000 rpm for 10 s and at 4000 rpm for 20 s to form the precursor thin films. The films were preheated at temperatures from 100 to 300 °C for 30 min. Finally, the films were annealed at annealing temperatures from 600 to 800 °C for 60 min in an air furnace to induce their crystallization. The final thickness of the $Nd(Zn_{0.5}Ti_{0.5})O_3$ thin films was approximately 105–229 nm, as shown in Table 1. The film structure was analyzed using X-ray diffraction (XRD) and Cu Kα radiation. The morphology of the film surface was determined using scanning electron microscopy (SEM). The dielectric and electrical properties of the $Nd(Zn_{0.5}Ti_{0.5})O_3$ thin films were evaluated using capacitance–voltage (*C*–*V*) and current–voltage (*I*–*V*) measurements. Test samples with metal–insulator–semiconductor (MIS) capacitor structures were prepared on Si substrates. The sample devices [$Ag/Nd(Zn_{0.5}Ti_{0.5})O_3/Si/Ag$] were fabricated using symmetrically deposited Ag electrodes (diameter = 1 mm) on both sides. All electrodes were prepared using ion sputtering. The *C*–*V* and *I*–*V* curves of the MIS capacitors were measured using an HP4284 LCR meter and an HP4155 semiconductor parameter analyzer, respectively.

3. Results and Discussion

Figure 1 shows the XRD patterns of $Nd(Zn_{0.5}Ti_{0.5})O_3$ thin films deposited on n-type Si substrates at various preheating and annealing temperatures. According to the XRD analysis, the $Nd(Zn_{0.5}Ti_{0.5})O_3$ thin films had an amorphous structure at an annealing temperature of

Table 1
Thickness data of $Nd(Zn_{0.5}Ti_{0.5})O_3$ thin films for various preheating and annealing temperatures.

Thickness		Annealing temperatures		
		500 °C	600 °C	700 °C
Preheating temperatures	100 °C	105 nm	106 nm	128 nm
	200 °C	208 nm	220 nm	211 nm
	300 °C	205 nm	220 nm	229 nm

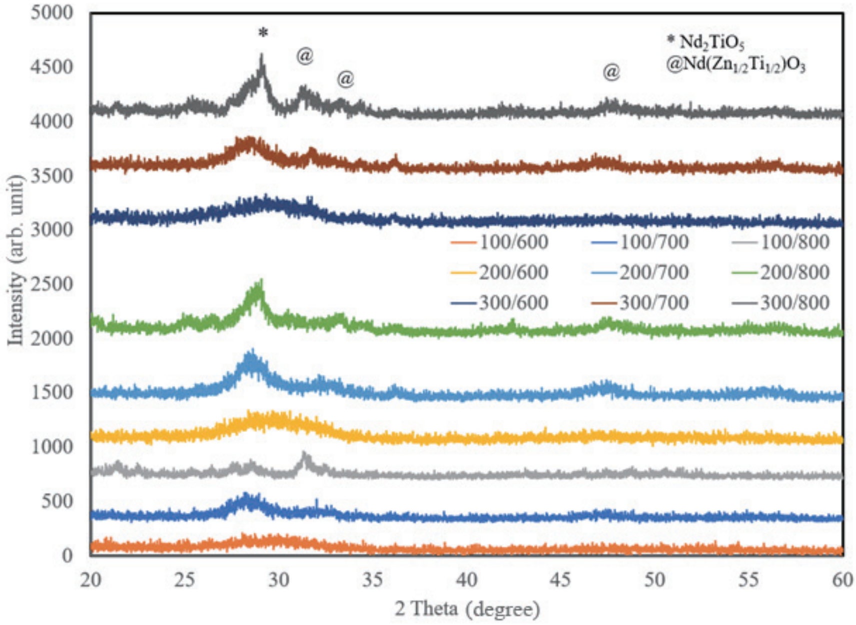


Fig. 1. (Color online) XRD patterns of $Nd(Zn_{0.5}Ti_{0.5})O_3$ thin films at various preheating and annealing temperatures.

600 °C. As the treatment temperature increased, the prepared thin films entered a crystalline phase, and the two crystal phases of the deposited specimens were identified as $Nd(Zn_{0.5}Ti_{0.5})O_3$ and Nd_2TiO_5. Additionally, the intensities of all peaks increased with the preheating and annealing temperatures.

SEM micrographs of the deposited $Nd(Zn_{0.5}Ti_{0.5})O_3$ thin films are illustrated in Fig. 2. When the annealing temperature was 600 °C, the grains were fine, which was consistent with the XRD results. Moreover, the films exhibited an amorphous structure at lower annealing temperatures. However, the grain size increased with the annealing temperature, and porous specimens were observed at an annealing temperature of 800 °C. A higher annealing temperature may increase the kinetic energy of the atoms deposited on the film surface.[11] Additionally, at higher preheating and annealing temperatures, flaky and irregularly shaped grains coexisted, which corroborated the XRD results of the two crystal phases of $Nd(Zn_{0.5}Ti_{0.5})O_3$ and Nd_2TiO_5. These changes may directly affect the dielectric and electrical properties of the $Nd(Zn_{0.5}Ti_{0.5})O_3$ thin films.

The *C–V* behavior of the $Nd(Zn_{0.5}Ti_{0.5})O_3$ thin films was evaluated to determine the $Ag/Nd(Zn_{0.5}Ti_{0.5})O_3/Si/Ag$ (MIS) structure. Through the use of capacitance characteristics, the dielectric constant at 1 kHz of the $Nd(Zn_{0.5}Ti_{0.5})O_3$ thin films can be calculated from the capacitance values (Fig. 3). The dielectric constant is affected by the porosity, secondary phase, grain size, and crystallinity.[12] According to the XRD patterns, the intensities of the peaks of the two phases of $Nd(Zn_{0.5}Ti_{0.5})O_3$ and Nd_2TiO_5 increased with the preheating temperature, which indicates that the microstructure and phase of Nd_2TiO_5 affect the dielectric constant of $Nd(Zn_{0.5}Ti_{0.5})O_3$ thin films.[13] However, the relationship between the dielectric constant and the

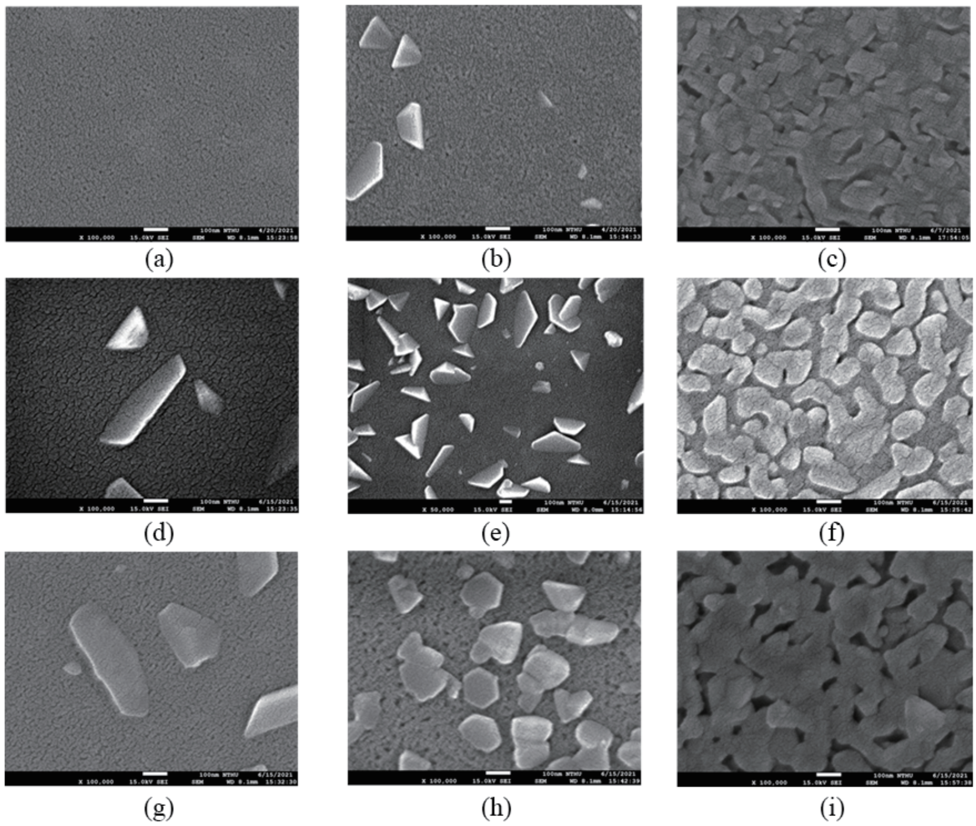


Fig. 2. SEM micrographs of $Nd(Zn_{0.5}Ti_{0.5})O_3$ thin films at various preheating and annealing temperatures. (a) 100–600 °C; (b) 100–700 °C; (c) 100–800 °C; (d) 200–600 °C; (e) 200–700 °C; (f) 200–800 °C; (g) 300–600 °C; (h) 300–700 °C; and (i) 300–800 °C.

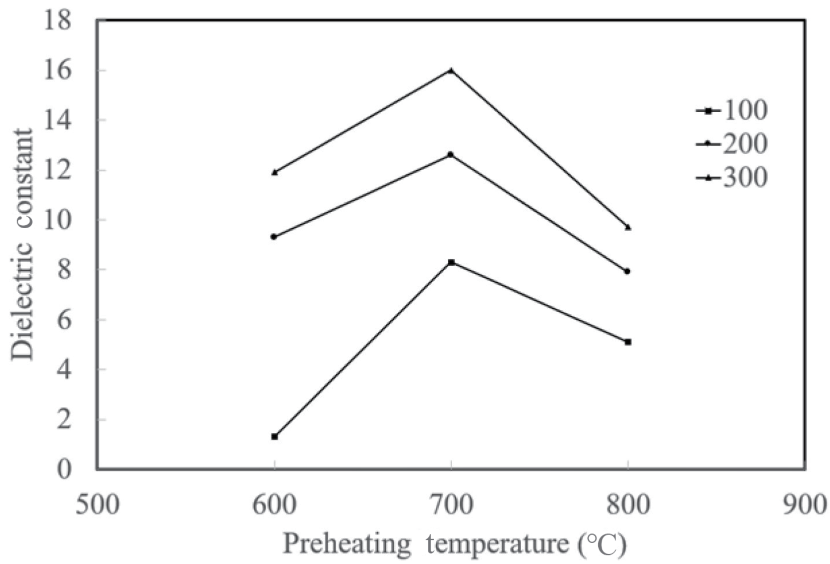


Fig. 3. Dielectric constants of $Nd(Zn_{0.5}Ti_{0.5})O_3$ thin films at various preheating and annealing temperatures.

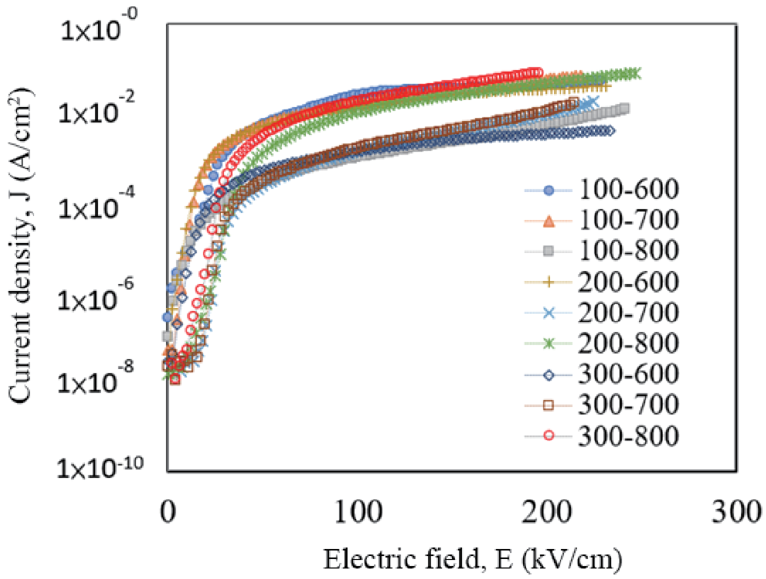


Fig. 4. (Color online) *I–V* curves of Ag/Nd($Zn_{0.5}Ti_{0.5}$)O_3/Si/Ag (MIS) structures at various preheating temperatures and annealing temperatures.

preheating temperature exhibited the same trend as that between the microstructure and the preheating temperature. Additionally, the dielectric constant at a preheating temperature of 300 °C for the Nd($Zn_{0.5}Ti_{0.5}$)O_3 thin films depended on the annealing temperature; the dielectric constant ranged from 9.3 at 600 °C to 12.6 at 700 °C.

Figure 4 shows the *I–V* curves of Nd($Zn_{0.5}Ti_{0.5}$)O_3 thin films deposited on n-type Si substrates at various preheating and annealing temperatures; the curves represent the relationship between the leakage current density and the electrical field. The leakage current is affected by the crystallinity and surface morphology. The leakage current density decreased with increasing annealing temperature and reached its minimum at 700 °C; thereafter, the value increased. Because the deposited atoms generate more kinetic energy at higher annealing temperatures, Nd($Zn_{0.5}Ti_{0.5}$)O_3 thin films with smaller surface roughness can be fabricated, resulting in a reduction in leakage current.[(1)] However, the higher surface kinetic energy produced at higher preheating temperatures may damage the microstructure, which is consistent with the results of XRD and the dielectric constant. Additionally, fewer crystal defects occur and the grain size increases with the preheating temperature.[(14,15)] A leakage current density of 2.13×10^{-8} A/cm^2 was observed near an electrical field of 10 kV/cm for a preheating temperature of 300 °C, which is similar to the leakage current density of SiO_2.

4. Conclusions

The effects of the preheating and annealing temperatures of Nd($Zn_{0.5}Ti_{0.5}$)O_3 thin films on their microstructural, dielectric, and electrical properties were investigated. The intensities of the Nd($Zn_{0.5}Ti_{0.5}$)O_3 and Nd_2TiO_5 peaks increase with the preheating and annealing temperatures. The Nd_2TiO_5 phase is observed in the $Nd(Zn_{0.5}Ti_{0.5})O_3$ thin films, whereas the dielectric constant is affected by the secondary phases. Moreover, grain growth increases with annealing temperature. However, the abnormal grain growth of the $Nd(Zn_{0.5}Ti_{0.5})O_3$ thin films occurs at an annealing temperature of 800 °C. For a preheating temperature of 300 °C and an annealing temperature of 700 °C, the films had a low leakage current density of 2.13×10^{-8} A/cm^2 and a dielectric constant of 16. The results of our study can contribute to applications employing wireless communication microwave components, such as temperature-sensing antennas.

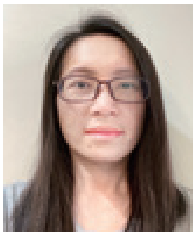
Acknowledgments

This work was sponsored by the Ministry of Science and Technology of the Republic of China under grant MOST 109-2221-E-239-006.

References

1 C. H. Hsu and S. F. Yan: J. Am. Ceram. Soc. **94** (2011) 822. https://doi.org/10.1111/j.1551-2916.2010.04174.x
2 C. H. Hsu and C. J. Huang: Int. J. Appl. Ceram. Technol. **10** (2013) 773. https://doi.org/10.1111/ijac.12119
3 Y. W. Tseng, J. Y. Chen, Y. C. Kuo, and C. L. Huang: J. Alloys Compd. **509** (2011) L308. https://doi.org/10.1016/j.jallcom.2011.06.010
4 W. S. Chen, M. L. Hung, and C. H. Hsu: J. Asian Ceram. Soc. **9** (2021) 433. https://doi.org/10.1080/21870764.2021.1889103
5 C. H. Hsu, P. S. Tsai, C. F. Tseng, S. H. Hung, and C. L. Huang: J. Alloys Compd. **582** (2014) 355. https://doi.org/10.1016/j.jallcom.2013.08.017
6 S. Nomura: Ferroelectrics **49** (1983) 61. https://doi.org/10.1080/00150198308244666
7 T. Shimada: J. Eur. Ceram. Soc. **23** (2003) 2647. https://doi.org/10.1016/S0955-2219(03)00191-2
8 J. B. Lim, J. O. Son, S. Nahm, W. S. Lee, M. J. Yoo, N. K. Kang, H. J. Lee, and Y. S. Kim: Jpn. J. Appl. Phys. **43** (2004) 5388. https://doi.org/10.1143/JJAP.43.5388
9 C. F. Tseng, C. L. Huang, and C. H. Hsu: J. Am. Ceram. Soc. **90** (2007) 1619. https://doi.org/10.1111/j.1551-2916.2007.01555.x
10 C. F. Tseng, C. L. Huang, W. R. Yang, and C. H. Hsu: J. Am. Ceram. Soc. **89** (2006) 1465. https://doi.org/10.1111/j.1551-2916.2005.00910.x
11 C. H. Hsu, P. H. Chou, Y. T. Chung, and C. W. Hsieh: J. Nanosci. Nanotechnol. **16** (2016) 12914. https://doi.org/10.1166/jnn.2016.13657
12 C. H. Hsu and C. Y. Chung: J. Am. Ceram. Soc. **94** (2011) 1837. http://doi.org/10.1111/j.1551-2916.2010.04320.x
13 T. M. Pan, J. C. Lin, M. H. Wu, and C. S. Lai: Biosens. Bioelectron. **24** (2009) 2864. https://doi.org/10.1016/j.bios.2009.02.018
14 M. Nayak and T. Y. Tseng: Thin Solid Films **408** (2002) 194. https://doi.org/10.1016/S0040-6090(02)00083-4
15 S. M. Chang and R. A. Doong: Thin Solid Films **489** (2005) 17. https://doi.org/10.1016/j.tsf.2005.04.076

About the Authors



Ching-Fang Tseng received her Ph.D. degree in electrical engineering from Cheng Kung University, Tainan, in 2007. Currently, she is a professor in the Electronic Engineering Department, National United University, Taiwan. She has been involved in the research and development of wearable and flexible antennas, implantable antennas, biomedical devices, microwave/mm-wave/sub-THz mobile antennas, wireless biosensors, and glass-free ULTCC, and LTCC microwave dielectric materials, as well as in biomedical signal analysis, nonintrusive biological signal measurement, and intelligent health monitoring systems. (cftseng@nuu.edu.tw)

Bo-Yan Huang received his B.E. degree from the Electronic Engineering Department, National United University (NUU), Miaoli, Taiwan, in 2020 and is currently working toward his M.S. degree in electronic engineering at NUU. His main research direction is the development of thin film technology. (potter870123@gmail.com)

Cheng-Hsing Hsu received his B.S. degree in electronic engineering from Fu Jen Catholic University, Taipei, Taiwan, in 1997 and his M.S. and Ph.D. degrees in electrical engineering from National Cheng Kung University, Tainan, Taiwan, in 1999 and 2003, respectively. From 2003 to 2005, he worked as a principal engineer with the Nano-Device Research Department, Macronix International Co., Ltd., where he was engaged in novel nonvolatile memory materials and devices. In February 2005, he joined the Faculty of the Department of Electrical Engineering, Da-Yeh University, Chang-Hua, Taiwan. In August 2005, he became an assistant professor of the Department of Electrical Engineering, National United University, Miaoli, Taiwan, where in 2008 he became an associate professor and in 2013 a professor. His research interests include dielectric ceramics, thin film technology, planar antenna design, microwave passive components, nonvolatile memory devices, thermoelectric materials, and optoelectronic materials. (hsuch@nuu.edu.tw)