Journal of ELECTRONIC MATERIALS
https://doi.org/10.1007/s11664-017-5995-6

Study on Structural and Dielectric Properties of Ultra-Low-Fire Integratable Dielectric Film for High-Frequency and Microwave Application

SHENG QU,[1,2] JIHUA ZHANG,[1,2,3] KAITUO WU,[1,2] LEI WANG,[1,2]
and HONGWEI CHEN[1,2]

1.—State Key Laboratory of Electronic Thin Films and Integrated Devices, University of Electronic Science & Technology of China, Chengdu 610054, Sichuan, People's Republic of China. 2.—Collaboration Innovation Center of Electric Materials and Devices, University of Electronic Science & Technology of China, Chengdu 610054, Sichuan, People's Republic of China. 3.—e-mail: jhzhang@uestc.edu.cn

In this study, ultra-low-fire ceramic composites of $Zn_2Te_3O_8$-30 wt.%$TiTe_3O_8$ (ZTT) were prepared by a solid-state reaction method. Densified at 600°C, the best microwave dielectric properties at 8.5 GHz were measured with the ε_r, tanδ, $Q \times f$, and τ_f as 25.6, 1.5×10^{-4}, 56191 GHz and 1.66 ppm/°C, respectively. Thin films of ultra-low-fire ZTT were prepared by a radio-frequency magnetron sputtering method. ZTT films which deposited on Au/NiCr/SiO_2/Si (100) substrates at 200°C showed good adhesion. From ultra-low-fire ceramic to ultra-low-fire ZTT thin films, the latter maintained all the good high-frequency dielectric properties of the former: high dielectric constant ($\varepsilon_r \sim 25$) and low dissipation factor (tan$\delta < 5\times10^{-3}$), low leakage current density ($\sim 10^{-9}$ A/cm^2) and ultra low processing temperature. These excellent properties of the ultra-low-fire ZTT thin film make it possible to be integrated in MMIC and be applied in the research of GaN and GaAs MOSFET devices.

Key words: Ultra-low-fire, high-frequency, microwave application dielectric properties, thin film, low processing temperature

INTRODUCTION

Microwave dielectric materials are widely used in microwave devices. With the development of microwave integrated circuits and the integration of microwave devices, size of ceramics is becoming smaller and smaller, which is desirable to make bulks into thin films. Good permittivity, high Q value and low temperature coefficient integrated microwave dielectric thin film makes it possible to achieve functions on small chips and to realize complanation and integration of microwave device. Metal–insulator–metal (MIM) thin film capacitors play an important role in monolithic microwave integrated circuit (MMIC). Thin film research of microwave dielectric ceramic has become a trend in the development of microwave dielectric integration. Device of high-performance dielectric properties generally required a high processing temperature (> 800°C) to prepare. However, high processing temperature may be not compatible with the technology of monolithic microwave integrated circuit (MMIC). So it is important to find ultra-low-fire materials.

Under the requirements of International Technology Roadmap for Semiconductors (ITRS), the capacitors of microwave circuit should achieve 10 fF/μm^2 of capacity density and meanwhile possess low leakage current density (< 10 nA cm^{-2}@5 V), low electric nonlinearity (< 100 ppm/V^2), and high quality factor ($Q > 50$@1 GHz). Considering the dielectric loss, some materials were reported to be used in MIM capacitors as thin films. SiNO ($\varepsilon_r \sim 4$–7)[1,2] and

(Received July 30, 2017; accepted November 22, 2017)

Al_2O_3 ($\varepsilon_r \sim 10$)[3] thin films had low leakage current density, and the disadvantages was low capacity density and the VCC value was high ($Al_2O_3 \sim 2000$ ppm/V^2). HfO_2 ($\varepsilon_r \sim 22$)[4–7] thin films, showed good performance in high capacity density and low leakage current density, but still have inability to keep a low VCC value. Ta_2O_5 ($\varepsilon_r \sim 25$)[8] doped Al_2O_3 thin film did not meet the requirement in Q value. The Crystalline TiO_2 had a high dielectric constant ($\varepsilon_r \sim 80$), but the crystallization would cause unacceptably high leakage current. In recent years, application of ferroelectric thin films was also tried in MIM capacitors because of high permittivity. Materials such as (Ba, Sr)TiO_3 (BST), (Pb, Zr)TiO_3 (PZT),[9] $Bi_{1.5}Zn_{1.0}Nb_{1.5}O_7$ (BZN),[10] $Pb(Mg_{0.33}Nb_{0.67})_{0.65}Ti_{0.35}O_3$ (PMNT)[11] were reported as being candidates of this field. However, ferroelectric thin films were not ideal microwave dielectric materials because of their large dielectric loss and instability of dielectric constant to temperature and voltage, which hinders their practical application in ordinary microwave circuits.

Additionally, radio frequency or analog/mixed MIM capacitors in semiconductor devices such as GaAs, or on printed circuit boards (PCBs) require not only low processing temperatures,[12,13] but also high-performance dielectric properties. Therefore, it is important to find ultra-low-fire materials with good microwave dielectric properties to apply for GaN/GaAs MOSFET devices and MMIC.[14–19] It was reported that TeO_x, TaTiO, $Bi_2Mo_2O_9$, and $Bi_6Ti_5TeO_{22}$ thin/thick films were developed for their low processing temperatures, but the dielectric properties were still imperfect for their low Q values exactly resulting from such low processing temperatures that could match semiconductor process.[20–25]

Recent progress in high-K ULTCC microwave dielectric materials was reported that the $0.45BiVO_4$-$0.55TiO_2$ ceramics could sinter at 900°C for 2 h possessed excellent microwave dielectric properties with a $\varepsilon_r \sim 86$, a $Qf \sim 9500$ GHz and a near-zero TCF ~ -8 ppm per °C[26] and $0.06BiVO_4 - 99.94LaNbO_4$ could obtain $\varepsilon_r > 75$ with a fluctuation of $\sim 1.24\%$ (TCF $\leq \pm 85$ ppm per °C) accompanied by a $Qf \sim 10{,}000$ GHz in the range of 25–140°C were obtained in ceramic sintered at 800°C for 2 h.[27]

It has been recently reported that $Zn_2Te_3O_8$ and $TiTe_3O_8$ were good low firing microwave dielectric materials: $Zn_2Te_3O_8$ had a sintering temperature of 585°C, ε_r value of 16.2, $Q \times f$ value of about 66,000 GHz, τ_f value of -60 ppm/°C; $TiTe_3O_8$ had a sintering temperature of 720°C, ε_r value of 50, $Q \times f$ value of about 30600 GHz, τ_f value of 133 ppm/°C. The composites of the two can obtain the microwave ceramic whose τ_f is nearly zero (0–10 ppm/°C).[28]

Ultra-low-fire $Zn_2Te_3O_8$-30 wt.%$TiTe_3O_8$ (ZTT) ceramic composites with excellent dielectric properties: densified at 600°C, high $Q \times f$ value of 50042 GHz (at a measurement frequency of 11.8 GHz), ε_r value of 19.8, and τ_f value of + 3.0 ppm/°C, could be used as a potential material of preparing ultra-low-fire thin films and promised to be applied in MMIC.[29] Therefore, in this study, ZTT ceramic was prepared as a sputtering target to grow thin films on Au/NiCr/SiO_2/Si (100) substrates under various processing conditions. Delectric properties were investigated in order to evaluate the qualification of being ultra-low-fire thin film capacitors. In this study, we have prepared and studied ultra-low-fire thin films that would be compatible with MMIC technology and have good high-frequency dielectric properties. It is believed that there will be some dedication to integration process.

EXPERIMENTAL

$Zn_2Te_3O_8$ and $TiTeO_8$ were prepared by using high purity ($\geq 99\%$ purity) of ZnO, TiO_2 and TeO_2 powders at a ratio of Zn:Te of 2:3 and Ti:Te to 1:3. After sufficiently mixing in ethanol, the pre-calcined $Zn_2Te_3O_8$ and $TiTeO_8$ powders were obtained at 500°C and 640°C, respectively. The mixed powders were mixed in ethanol at a weight ratio of $Zn_2Te_3O_8$:$TiTeO_8$ = 1:0.3 for 24 h. After drying, 4% by weight of PVA powder was pressed into a disk at a pressure of 20 MPa and then sintered at 560°C, 580°C, 600°C, and 620°C for 2 h. The bulk density of the sample was determined by the Archimedes method. The $Q \times f$ values were measured in the TE011 mode using the Hakki and Coleman method by a vector network analyzer (VNA; Agilent E5071C). Measurements of the τ_f (temperature coefficient) of the resonant frequency in the temperature range from 25°C to 85°C were performed in a automatic temperature control box.

In order to ensure the best performance of the ZTT target synthesized by the conventional solid phase method, the optimum process conditions should be found. ZTT films were grown on Au/NiCr/SiO_2/Si (100) substrates by RF magnetron sputtering using ZTT targets, which is a common method to deposit thin films.[30–33] When the temperature was 200°C and the total pressure was 0.27 Pa, the ratio of oxygen to argon was 5:3; 1:1; 1:2; 1:3; 1:4; Sputtering was performed at a power of 200 W for 8 h, then the film exhibited good adhesion to the substrate. The film was grown at a different sputtering power and atmospheric pressure at a temperature of 200°C. After the deposition process, the films were annealed at different temperatures (350°C, 400°C, 450°C, and 500°C). The structural properties of the films were analyzed by x-ray diffraction (XRD; Bede QC200), scanning electron microscopy (SEM; FEI Inspect-F, Holland) and atomic force microscopy (AFM). Composition analysis was performed using energy dispersive spectroscopy (EDS, FEI Inspect-F, Holland). To measure the dielectric properties, Au/NiCr was deposited on the ZTT film by evaporation to form the top electrode of the MIM capacitor. The top electrode was patterned using a shadow mask to form a disc with a diameter of 0.8 mm. Capacitance and dielectric losses were measured in the range of 1 kHz to 10 MHz using a precision LCR instrument (Agilent 4294A, USA). The leakage current density was measured by using a precision material analyzer (RADIANT Precision LC, USA).

RESULTS AND DISCUSSION

Properties of the ZTT Bulk

As shown in Table I, density of the ZTT ceramics slightly increases with the increase of sintering temperature, and the maximum density at 600°C reaches 5.41 g/cm^3. While the sintering temperature rose to 620°C, the density of the ceramics decreased rapidly because TeO_2 would sublimate at 450°C as the gas state. Meanwhile, Table I shows dielectric properties of the ZTT ceramics sintered at 560°C, 580°C, and 600°C, respectively. Samples sintered at 620°C had not been tested since they could not maintain cylindrical after melting. When the sample sintered at 600°C, the $Q \times f$ value and dielectric constant both were the highest in this study, and the dielectric loss was the lowest because the ZTT ceramic composites were densified at this temperature. Processed with the vector network analyzer, we obtained the $Q \times f$ value up to 56,191 GHz (at a measurement frequency at 8.5 GHz), which is higher than most of other ultra-low-fire materials.The dielectric loss could be as low as 1.5×10^{-4} and the dielectric constant was 25.6. For the τ_f at 600°C, by f_{25} = 9.43125 GHz, f_{85} = 9.43219 GHz, we can obtain the value of τ_f is 1.66 ppm/°C which is nearly zero. These advantages make the sample annealed at 600°C as a target to grow films have excellent dielectric properties and the films can be well used for MMIC application..

Figure 1 shows that there was no heterogeneous phase in the ceramic sintered under the sintering system except for the phase of zinc telluride and titanium telluride, and no chemical reaction between the two compounds proved that the ZTT ceramic could be in the range of as low as 600°C sintering into porcelain. The relative intensities between the peaks of the ZTT ceramics prepared at different temperatures are not the same, and the two peaks near 27°are obvious, because the loss as sublimation of TeO_2 during sintering was different, resulting in the difference of compositional mass ratio of the synthesized compound, so tthere was relative change in the spike ratio.

Structural Properties of the ZZT Film

Figure 2 shows the XRD patterns of ZTT thin films grown on SiO_2/Si substrates annealed at various temperatures at (200). As shown in Fig. 3, the annealed film of 500°C or less has no obvious peaks except for the (200) peak of the Si substrate. The broad peak represented by the asterisk orresponds to (202) of $Zn_2Te_3O_8$ and (220) of $TiTe_3O_8$ crystalline phases. It indicates that all the ZTT thin films annealed from 350°C to 500°C have a tendency to crystallize. A small amount of nanocrystalline phases of $Zn_2Te_3O_8$ and $TiTe_3O_8$ could be found after annealing from 350°C to 450°C. Since the eutectic reaction between $Zn_2Te_3O_8$ and $TiTe_3O_8$ compounds and no other phase was observed in the ZTT ceramic. So it can be concluded that the ZTT thin films would not crystallized after annealed below 450°C. This good stability after thermal treatment is important to reduce the leakage current of being the MIM capacitors, because the current would be scattered when running through the amorphous and disordered structures.[22–25] Figure 3a and b shows the SEM and AFM images of the ZTT thin films annealed at 450°C, No significant crystalline grain was observed, confirming that the ZTT film after thermaltreatment at 450°C was in an amorphous state.

In Fig. 2, it can also be noticed that a only new peak appeared after the thin films were annealed at 500°C, which belonged to neither $Zn_2Te_3O_8$ nor $TiTe_3O_8$. It is asummed to correspond to a new phase. As shown in Fig. 4, the thin film dehisced and shrank into several parts, and the structures of ZTT thin films were broken after 500°C thermal treatment which is high than sublimation point of the Te element. So Te elements sublimated in the state of gas after 500°C thermal treatment. Obvious crystalline grains surrounded by amorphous substance were observed after magnified 40,000 times. The amorphous substance might be ZTT, and the crystalline grains were newly formed because of the composition loss possibly due to the Te elementary compounds (such as TeO_2) sublimation during thin

Table I. Sintered densities and dielectric properties measured at 8.5 GHz of the ZTT ceramics with various of sintering temperatures

Sintering temperature (°C)	Density (g/cm^3)	Permittivity	$Q \times f$ (GHz)	tanδ
560	5.378	21.0	27715	2.65×10^{-4}
580	5.392	21.3	30317	2.38×10^{-4}
600	5.410	25.5	56191	1.51×10^{-4}
620	5.321	–	–	–

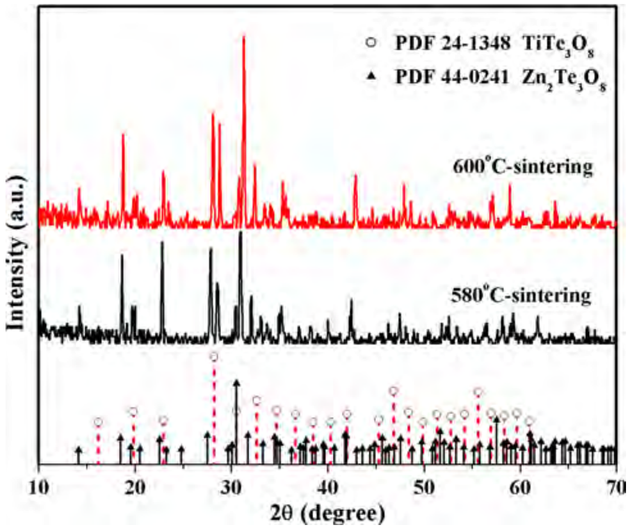

Fig. 1. XRD patterns of the ZTT ceramics with different sintering temperature.

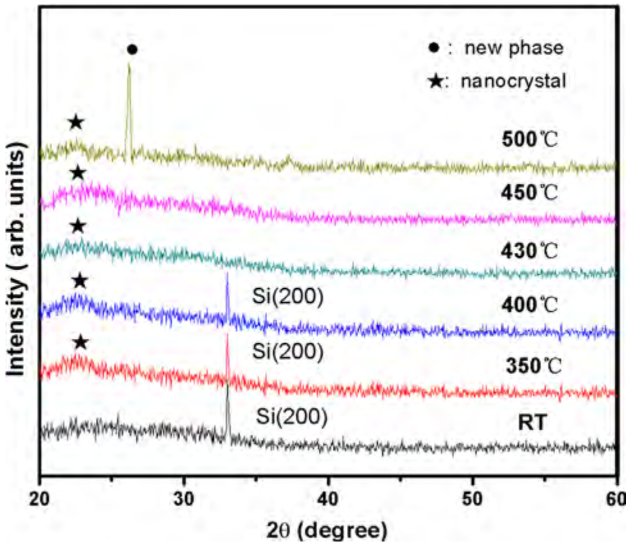

Fig. 2. XRD patterns of the ZTT films grown under a pressure of 0.48 Pa with O_2:Ar = 1:2 which annealed at various amounts of temperatures on SiO_2/Si substrates.

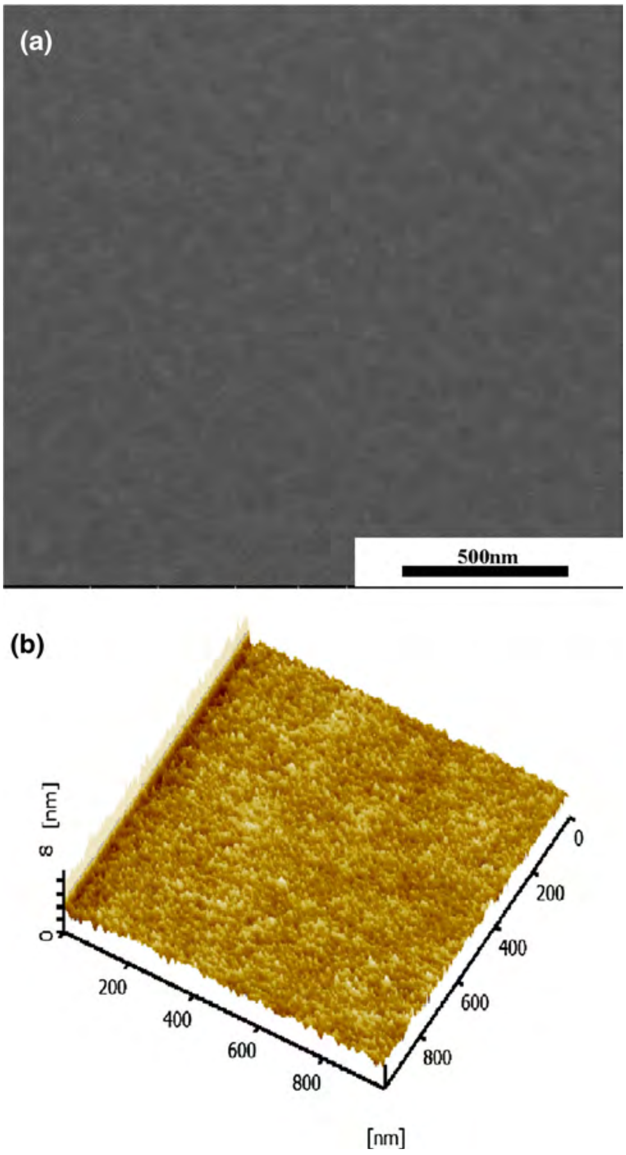

Fig. 3. (a) Scanning electron microscope image, (b) atomic force microscope image of the ZTT thin film annealed at 450°C on SiO_2/Si substrate.

films annealed at a high temperature. The cyclic and hollow structure in some part of the film indicated that some components volatilized from the film. In order to verify the sublimation of the Te element, Energy Dispersive Spectroscope (EDS) were taken from the ZTT thin films annealed at 400°C and 500°C respectively, and the compositional analysis were exhibited in Table II. The concentration of Te in the thin film annealed at 400°C was approximately 64.30%, which was close to the 63.29%, theoretical concentration of Te. However, under the circumstance of thermal treated at 500°C, an obvious decrease of the concentration of Te was observed, with the value reduced approximately 8%, in comparison with the theoretical value, indicating that the Te elementary was sublimated as compounds (such as TeO_2) because TeO2 begins to sublimate at 450°C.

Dielectric Properties of the ZTT Film

Figure 5 shows the dielectric constant and dissipation factors, measured at 1 MHz, of the ZTT films grown at various conditions, which could give the optimal sputtering conditions. While the deposition temperature was 200°C, O_2/Ar was 1/2, and the total pressure was 0.48 Pa, different sputtering powers were performed. As shown in Fig. 5a, the dielectric constant of the ZTT film was approximately 16, and the dissipation factor was relatively high as 2.8% for the film when sputtering power was

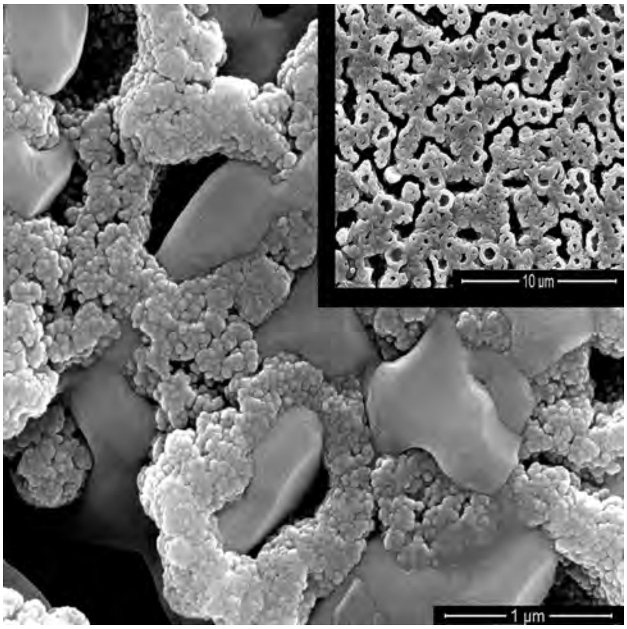

Fig. 4. The scanning electron microscope images of ZTT thin film annealed at 500°C.

Table II. Chemical composition of the ZTT thin films annealed at 400°C and 500°C

	Theoretical composition	400°C	500°C
Ti (at.%)	5.48	4.03	5.00
Zn (at.%)	31.23	31.67	39.59
Te (at.%)	63.29	64.30	55.41

150 W. As the sputtering power increased, performance of the ZTT film would change. For example, when 300 W sputtering power was used, the dielectric constant increased to 21 and the dissipation factor reduced to 5‰. However, when the sputtering power increased to 350 W, the dielectric constant of the film did not rise, but decreased to 18, and the dissipation factor increased significantly, reaching to 1.8%. Likewise, with the similar change, Fig. 5b exhibits the influence of different atmospheric pressures on dielectric constant. It could be interpreted as that when sputtering power and pressure increased, the density of the Ar^+ ions subsequently increased, and the energy of the sputtering atoms increased when arriving to the substrate, which led to strengthening migration and diffusion of atoms.It resulted in better adhesion and densification and defect-free of the ZTT film. While the conditions went beyond a certain limit, the particles were frequently hit by high-concentration gas molecules, with low energy left to reach to the substrate, which led to low diffusivity. Meanwhile, the critical core of film nucleation was small. Thus, on the surface of the film, the particles would form new cores continually, so that the film would be loose and low intensity.[34,35] Figure 5c shows the dielectric properties of the ZTT films grown in various proportion of oxygen and argon (O_2:Ar = 5:3; 1:1; 1:2; 1:3; 1:4; 1:5) atmospheres under a total pressure of 0.27 Pa in the same sputtering temperature of 200°C, and

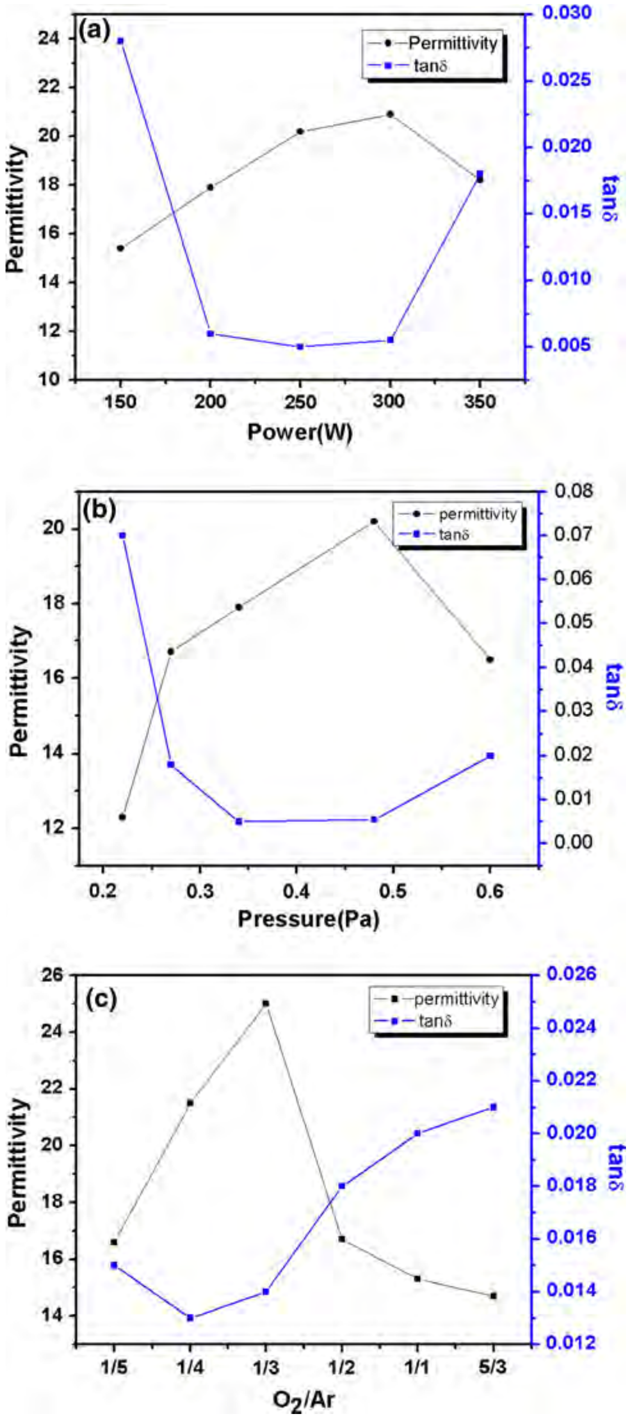

Fig. 5. Dielectric properties of the ZTT films grown at (a) different various of sputtering powers, (b) different various of atmospheric pressures, and (c) different various of O_2/Ar values measured at 1 MHz.

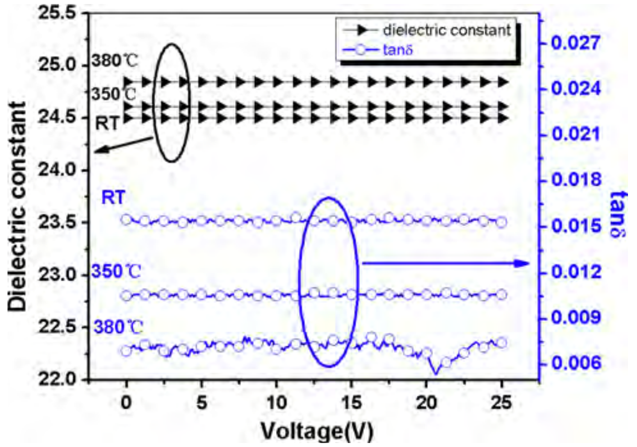

Fig. 6. Dielectric properties of the ZTT films grown at same conditions and annealed at 350°C and 380°C, and not thermal treated, measured at 1 MHz.

the same sputtering power of 250 W. When the O_2/Ar was 1/5, the dielectric constant was relatively low being approximately 16.5 and the dissipation factor was 1.5%. The dielectric constant increased to 25 when the O_2/Ar value increased to 1/3. For ZTT films deposited under the low oxygen pressure, lots of oxygen vacancies were considered to exist. Based on the equation as follows

$$\mathrm{O_O} = V_{\mathrm{O}}^{\bullet\bullet} + 2e' + \frac{1}{2}\mathrm{O_2} \tag{1}$$

where $\mathrm{O_O}$ is the oxygen ion at its normal site, $V_{\mathrm{O}}^{\bullet\bullet}$ is the oxygen vacancy and e' is the free electron. In low oxygen pressure, the chemical equilibrium is offset to the right. Therefore, a large number of oxygen vacancies and free electrons would be produced, leading to the poor dielectric properties of the ZTT film. The oxygen vacancies and free electrons were reduced gradually with the increasing oxygen pressure during deposition, which made the dielectric properties became better when the O_2/Ar value increased. Over this value, the oxygen pressure continued to rise, but the dielectric constant decreased, the dielectric loss increased rapidly, it could be considered that the interstitial oxygen ions and the holes started to be formed in the ZTT films. The reaction is showed as the following equation

$$\frac{1}{2}O_2 = O_i'' + 2h^{\bullet} \tag{2}$$

where O_i'' is an interstitial oxygen ion and $h^{\bullet}$ is the hole.[36] Overlarge oxygen pressure may produced interstitial oxygen ions and plenty of holes, making the ZTT films tend to semi-conducted. Meanwhile, excessive oxygen pressure might transform a part of Te^{4+} into Te^{6+}, which could not only changed the dielectric properties but also decreased the breakdown field of the films.[37]

Figure 6 shows the dielectric constant and dissipation factors, measured at 1 MHz, of the ZTT films grown at the same conditions and annealed at different temperatures. The dielectric constant of films annealed at 350°C and 380°C and room temperature were almost equal. It indicated that annealed at 380°C had extremely little improvement in increasing dielectric constant of the ZTT films. Compared with the stability of dielectric constant, dissipation factor was more sensitive when the annealed temperature changed. After annealing at 380°C, the dielectric loss was down from 1.5% to 7‰. However, the change of dielectric loss was still less than those of most other crystalline films, since the ZTT film could always keep an amorphous state after thermal treatment. It could be observed that the dielectric properties of the ZTT film was maintaining at a good level, particularly for the loss factor. Even if not annealing, loss factor of 1.5% still remains acceptable.

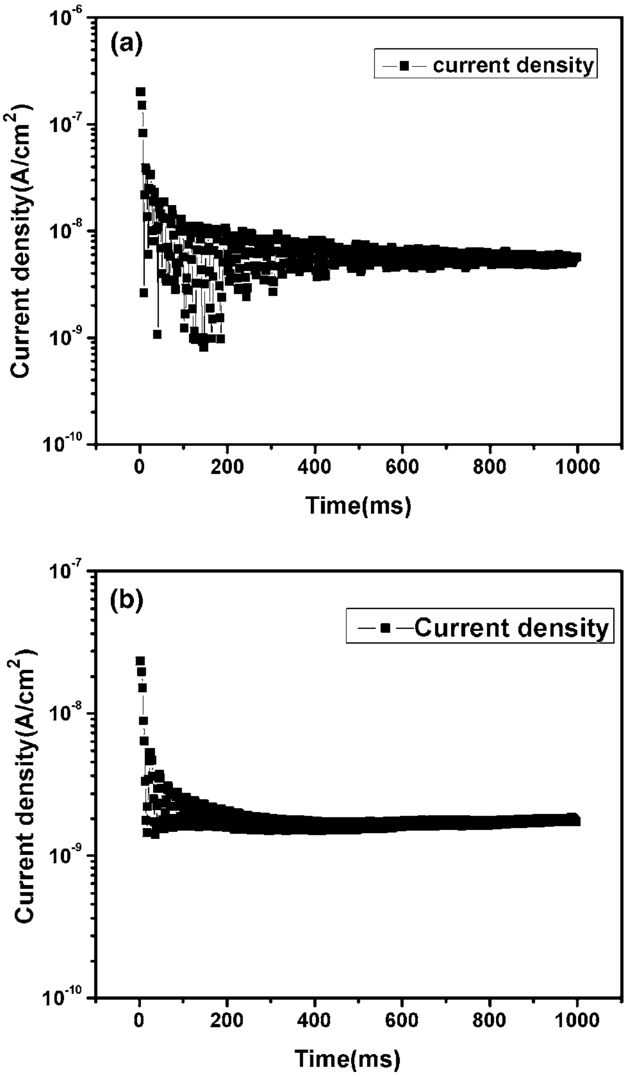

Fig. 7. Leakage current density of the 800 nm ZTT films grown at 200°C, 250 W, under O_2/Ar = 1/3 with a total pressure of 0.48 Pa, (a) not thermal treated, and (b) annealed at 380°C, measured at a voltage of 100 V.

The leakage current density of the ZTT film grown under appropriate conditions was measured, as shown in Fig. 7a. For the 800 nm unannealed ZTT films, the leakage current density could be as low as approximately 5×10^{-9} A/cm^2. Because under ideal conditions, defects and the concentration of electrons or holes would remain at a minimum level. Figure 7b shows that after 380°C thermal treated, the current density curves became smooth. That is because of densifying and defect reducing of the ZTT film after annealed, the current density became uniform and the average value of current density was as low as approximately 2×10^{-9} A/cm^2. Since the difference in the leakage current density after the thermal treatment was small, both unannealed and annealed at 380°C ZTT films can meet the MIM capacitor dielectric performance requirements.

CONCLUSIONS

The ZTT ceramic composites were densified at 600°C and the highest dielectric constant of 25.6 was obtained, and the $Q \times f$ value was 56191 GHz (at a measurement frequency at 8.5 GHz), the τ_f value was 1.66 ppm/°C. The 200°C-Grown ZTT films can not be crystallized at any annealing temperature, but there is a nanosized ZTT crystal phase at a certain temperature. A new crystalline phase formed when the annealing temperature rose up to 500°C, at which the structure of the ZTT film was broken, since the Te element sublimates in the form of compounds during annealing. High-performance dielectric properties could be obtained when the suputtering conditions were: O_2/Ar = 1/3, total pressure was 0.48 Pa, and the sputtering power was 250 W. After annealing at 380°C, the ZTT film exhibited dielectric constant as high as 25 and extremely low dissipation factor ($< 5‰$ at 1 MHz and could be as low as $1.5‰$ when measured at 1 kHz). Excellent dielectric properties ($\varepsilon_r \sim 25$, $\tan\delta < 1.5 \times 10^{-2}$) could be kept without thermal treatment. At 100 V, the 800 nm ZTT thin film annealed at 380°C had a leakage current density as low as 2×10^{-9} A/cm^2 and a leakage current density of 5×10^{-9} A/cm^2 of the unannealed ZTT film could be maintained in the same order of magnitude.

At 100 V, the leakage current density of 800 nm thick ZTT film annealed at 380°C was as low as 2×10^{-9} A/cm^2, while in the same order of magnitude, the leakage current density of unannealed ZTT film was 5×10^{-9} A/cm^2. Excellent dielectric constant and extremely low dissipation factor, low leakage current density, almost no crystallization, and most importantly, low process temperature and good stability to thermal treatment, make the ZTT film highly suitable for MIM capacitors. With the excellent microwave dielectric properties of ceramics composites and high-frequency dielectric properties of the film, it is believed that the ZTT film for MMIC application can be expected in the future.

ACKNOWLEDGEMENTS

This work was supported by the Innovation Foundation of Collaboration Innovation Center of Electronic Materials and Devices (No. ICEM2015-4002).

REFERENCES

1. C.H. Ng, K.W. Chew, and S.F. Chu, *IEEE Electron Device Lett.* 24, 506 (2003).
2. L.Y. Tu, H.L. Lin, L.L. Chao, D. Wu, C.S. Tsai, C. Wang, C.F. Huang, C.H. Lin, and J. Sun, *Symposium on VLSI Technology* (2003), p. 79–80.
3. S.B. Chen, J.H. Lai, K.T. Chan, A. Chin, J.C. Hsieh, and J. Liu, *IEEE Electron Device Lett.* 23, 203 (2002).
4. C. Zhu, H. Hu, X.Yu, A. Chin, M.F. Li, and D.L. Kwong, *IEDM Technical Digest* (2003), p. 379–382.
5. S.J. Kim, B.J. Cho, M.-F. Li, C. Zhu, A. Chin, and D.L. Kwong, *Symposium on VLSI Technology* (2003), p. 77–78.
6. S.J. Kim, B.J. Cho, S.J. Ding, M.-F. Li, M.B. Yu, C. Zhu, A. Chin, and D.-L. Kwong, *Symposium on VLSI Technology* (2004), p. 218–219.
7. C. Zhu, H. Hu, X. Yu, and S.J. Kim, *IEDM Technical Digest* (2003), p. 879–882.
8. T. Ishikawa, D. Kodama, Y. Matsui, M. Hiratani, T. Furusawa, and D. Hisamoto, *IEDM Technical Digest* (2002), p. 940–942.
9. R.A. Bakar, S. Sulaiman, and N.F.M. Lazim, *International Conference on Nanoscience and Nanotechnology,* (*NANO-Sci-Tech 2008*), p. 385.
10. K. Sudheendran, K.C.J. Raju, and M.K. Singh, *J. Appl. Phys.* 104, 104104 (2008).
11. W. Chen, K.G. McCarthy, and A. Mathewson, *IEEE Electron Device Lett.* 31, 996 (2010).
12. T. Kim, A.I. Kingon, J.P. Maria, and R.T. Croswell, *J. Mater. Res.* 19, 2841 (2004).
13. A.I. Kingon and S. Srinivasan, *Nat. Mater.* 4, 233 (2005).
14. D. Zhou, C.A. Randall, H. Wang, L.X. Pang, and X. Yao, *J. Am. Ceram. Soc.* 93, 1096 (2010).
15. D. Zhou, C.A. Randall, L.X. Pang, H. Wang, X.G. Wu, J. Guo, G.Q. Zhang, L. Shui, and X. Yao, *J. Am. Ceram. Soc.* 94, 802 (2011).
16. W.H. Liu, H. Wang, D. Zhou, and K.C. Li, *J. Am. Ceram. Soc.* 93, 2202 (2010).
17. K.T. Kang, M.H. Lim, H.G. Kim, Y. Choi, H.L. Tuller, I.D. Kim, and J.M. Hong, *Appl. Phys. Lett.* 87, 242908 (2005).
18. K.C. Chiang, C.H. Lai, A. Chin, T.J. Wang, H.F. Chiu, J.R. Chen, S.P. McAlister, and C.C. Chi, *IEEE Electron Device Lett.* 26, 728 (2005).
19. C.H. Choi, J.Y. Choi, K.H. Cho, M.J. Yoo, J.H. Choi, S. Nahm, C.Y. Kang, S.J. Yoon, and H.J. Lee, *J. Electrochem. Soc.* 155, G87 (2008).
20. N. Dewan, V. Gupta, K. Sreenivas, and R.S. Katiyar, *J. Appl. Phys.* 101, 084910 (2007).
21. Y.H. Jeong, J.B. Lim, S. Nahm, H.J. Sun, and H.J. Lee, *IEEE Electron Device Lett.* 28, 17 (2007).
22. S.F. Wang, Y.F. Hsu, Y.R. Wang, and C.C. Sung, *J. Am. Ceram. Soc.* 94, 812 (2011).
23. S.F. Wang, Y.R. Wang, Y.F. Hsu, and J.S. Tsai, *J. Eur. Ceram. Soc.* 30, 1737 (2010).
24. S.J. Fiedziuszko, I.C. Hunter, T. Itoh, Y. Kobayashi, T. Nishikawa, S.N. Stitzer, and K. Wakino, *IEEE Trans. Microwave Theory Tech.* 50, 706 (2002).
25. D.K. Kwon, M.T. Lanagan, and T.R. Shrout, *Mater. Lett.* 61, 2007 (1827).
26. D. Zhou, D. Guo, W.B. Li, L.X. Pang, X. Yao, D.W. Wang, and I.M. Reaney, *J. Mater. Chem. C* 4, 5357 (2016).
27. L.X. Pang, D. Zhou, Z.M. Qi, W.G. Liu, Z.X. Yue, and I.M. Reaney, *J. Mater. Chem. C* 5, 2695 (2017).
28. S.-F. Wang, Y.-F. Hsu, Y.-R. Wang, and C.-C. Sung, *J. Am. Ceram. Soc.* 94, 812 (2011).
29. M. Udovic, M. Valant, and D. Suvorov, *J. Am. Ceram. Soc.* 87, 591 (2004).
30. G. He, J. Liu, H. Chen, Y. Liu, Z. Sun, X. Chen, M. Liu, and L. Zhang, *J. Mater. Chem. C* 2, 5299 (2014).

31. G. He, J. Gao, H. Chen, J. Cui, Z. Sun, X. Chen, and A.C.S. Appl, *Mater. Interfaces* 6, 22013 (2014).
32. J. Zhang, G. He, L. Zhou, H. Chen, X. Chen, B. Deng, J. Lv, and Z. Sun, *Alloys Compd.* 611, 253 (2014).
33. G. He, B. Deng, H. Chen, X. Chen, J. Lv, Y. Ma, and Z. Sun, *APL Mater.* 1, 012104 (2013).
34. J.C. Yang, X.Q. Meng, C.T. Yang, and Y. Zhang, *Appl. Surf. Sci.* 287, 355 (2013).
35. H.B. Zhou, H.Y. Zhang, L.W. Han, and J.C. Han, *Superlattice Microst.* 64, 563 (2013).
36. C.H. Choi, J.Y. Choi, K.H. Cho, M.J. Yoo, S. Nahm, C.Y. Kang, S.J. Yoon, and J.H. Kim, *Electrochem. Solid St.* 11, G51 (2008).
37. C.H. Choi, J.Y. Choi, K.H. Cho, M.J. Yoo, S. Nahm, C.Y. Kang, S.J. Yoon, and J.H. Kim, *J. Electrochem. Soc.* 155, G199 (2008).