Dielectric response of TiO₂ Ceramics: The crucial role of Ta₂O₅

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Abstract

Colossal permittivity in tantalum-doped TiO₂ (Ta_xTi_{1-x}O₂) ($x = 1\%$, 2% , 3% , 4% , 5% and 6%) fabricated by the conventional solid-state reaction method in N₂ atmosphere were achieved. Especially, by optimizing components and sintering temperatures, the dielectric loss could significantly decreased. The effects of Ta doping on their microstructure, dielectric properties, and temperature stability were revealed in detail. When the composition with $x=5\%$ and sintered at $1400\text{ }^{\circ}\text{C}$, the dielectric constant reached to ~ 30000 and the dielectric loss decreased to 3% . Interestingly, all the samples also exhibit good temperature stability of dielectric properties in a wide temperature range from 100 to 350 K . Based on XPS analysis, the formation of defect-dipole clusters, e.g. $2(\text{Ta}^{5+})_{\text{Ti}}^{\bullet} \rightarrow 4(\text{Ti}^{3+})_{\text{Ti}}^{\bullet} \leftarrow \text{V}_{\text{O}}^{\bullet\bullet}$ should be mainly responsible for the improved dielectric properties in tantalum-doped TiO₂.

Keywords: Ta-doped TiO₂; Giant permittivity; Low dielectric loss; Temperature stability; XPS analysis.

1. Introduction

High-performance dielectric materials have been attracting increasing attentions because of their applications in myriad types of miniaturized devices and in high-energy-density storage applications.[1-2] High-dielectric-constant oxides have become essential for modern microelectronic devices, such as dynamic random access memory (DRAM) devices and on-chip capacitors.[3]

During the past several decades, several types of Colossal permittivity (CP) material have been available, [4-19] such as BaTiO_3 , [4-7] $\text{ACu}_3\text{Ti}_4\text{O}_{12}$ (ACTO), [8-15] NiO , [16,17] SrTiO_3 , [18] and $(\text{Pb}, \text{La})\text{TiO}_3$, [19] as well as their substitutions by acceptor and donor dopants. For these CP materials, a higher ϵ_r is always accompanied by a higher $\tan\delta$, while there is a poor dependence of dielectric properties on temperature and frequency, [4-19] limiting their practical applications. For example, a strong temperature dependence of dielectric properties appeared from room temperature to 120 °C in the BaTiO_3 ceramics, which is induced by the tetragonal-cubic phase transition, seriously hindering the applications of their devices. Furthermore, although a higher ϵ_r were obtained in $\text{ACu}_3\text{Ti}_4\text{O}_{12}$ and $\text{La}_{1.7}\text{Sr}_{0.3}\text{NiO}_4$, their $\tan\delta$ were always greater than 20%. [8-15,19] As a result, it is very necessary to reduce $\tan\delta$ under a large ϵ_r in the CP materials for application.

TiO_2 materials have been extensively investigated because of their good electrical properties.[20-23] Recently, (Nb, In)-co-doped TiO_2 ceramics with both high permittivity and low dielectric loss have been produced.[23] This research work also opens up a new way to comprehend the origin of colossal permittivity, which is

completely different from other mechanisms, such as, the surface barrier layer capacitors (SBLC) and the internal barrier layer capacitors (IBLC).[12.15] It was thought that the triangular $\text{In}_2^{3+}-V_o^{\bullet\bullet}-\text{Ti}_4^{3+}$ ($V_o^{\bullet\bullet}$ stands for the oxygen vacancies with positive charge) complex and diamond-shaped $\text{Nb}^{5+} 2\text{Ti}_4^{3+} \text{A}_{\text{Ti}}$ complex hold together, resulting in large defect-dipole clusters.[23] It was also speculated that other trivalent elements may yield CP in Nb modified TiO_2 ceramics.

In this work, to further describe the colossal permittivity mechanism in TiO_2 based ceramics, Ta_2O_5 was selected as a donor additive substitution into the host materials to aim to obtain the giant permittivity as well as low dielectric loss. The Ta-doped TiO_2 ceramics were sintered in N_2 atmosphere to hold back the delocalized electrons by providing an oxygen-deficient environment, which can give rise to the formation of defect dipoles. In order to prove the existence of defect dipoles and clarify the correlation between defect dipoles and colossal permittivity, the short-range structure and element valence information were characterized and acquired mainly by the X-ray photoelectron spectroscopy (XPS) measurement. The results showed that the Ta-doped TiO_2 could exhibit a giant $\epsilon_r (>10^4)$ and an unexpected low $\tan \delta$ (0.03). Additionally, the $2(\text{Ta}^{5+})_{\text{Ti}}^{\bullet} \rightarrow 4(\text{Ti}^{3+})_{\text{Ti}}^{\bullet} \leftarrow V_o^{\bullet\bullet}$ defect complex, in which electrons and oxygen vacancies were located in the limited lattices to induce the electron-pinned defect-dipoles, was evidenced in this study. Moreover, the connection of the defects states and the dielectric properties of Ta-doped TiO_2 was explored in detail.

2. Experimental procedure

$\text{Ta}_x\text{Ti}_{1-x}\text{O}_2$ ($x=1\%, 2\%, 3\%, 4\%, 5\%, 6\%$) (short as TTO1, TTO2, TTO3, TTO4, TTO5 and TTO6 respectively), ceramics were prepared by conventional solid reaction. Raw materials used in this work were rutile TiO_2 (99.99%), Ta_2O_5 (99.99%). These powders were weighed accurately as their chemical formula, and then ball mixed for 16 h with ethanol as medium. All of the mixed powders were calcined at 1060°C for 10 h in air. The calcined mixture was ball-milled again for another 12 h and then pressed into disk pellets with a diameter of 15 mm under 100 MPa pressure. TTO pellets were sintered in N_2 at $1300^\circ\text{C} \sim 1500^\circ\text{C}$ for 10 h. For electrical measurements, silver paste was coated on each side of the pellets. The thickness and diameter of our pellets are 0.8 mm and 10 mm. The information on phase structure of sintered ceramics was characterized by X-ray diffraction (XRD, D/max-2550/PC, Rigaku, Japan $\text{Cu K}\alpha$) technique and Raman spectrometer (Renishaw, inVia) with a back scattering geometry. The laser source was 532 nm line obtained from an Ar ion laser. The surface morphologies and compositions of the ceramics were obtained using a field emission scanning electron microscope (FE-SEM, Hitachi SU8000). The X-ray photoelectron spectroscopy (XPS) measurements were carried out on an ESCA--PHI5400 (PerkinElmer, Santa Clara, CA) photoelectron spectrometer. Dielectric dispersion was measured by Agilent 4294A impedance analyzer within the frequency range from 40 Hz to 10 MHz at room temperature. The temperature dependence of the dielectric properties of the samples was conducted upon heating from -150 to 150°C at $3^\circ\text{C}/\text{min}$ at 5 kHz.

3. Results and discussion

Fig. 1(a) shows the X-ray powder diffraction of $\text{Ta}_x\text{Ti}_{1-x}\text{O}_2$ samples. It can be seen from Fig. 1(a) that all major diffraction peaks are indexed as pure rutile phase according to JCPDS # 65-1119. Furthermore, it is clearly seen from Fig. 1(a), the peaks at $2\theta = 26.85^\circ$ shows a slight shift to small angle with the increasing of the Ta^{5+} content. As the ionic radius of Ta^{5+} ($r_{\text{Ta}^{5+}}=70\text{pm}$) is bigger than that of Ti^{4+} ($r_{\text{Ti}^{4+}}=60.5\text{pm}$), substitution of Ta for Ti will lead to the expansion of the unit cell. Such as the crystal plane of the (110), when the content of Ta^{5+} increasing from 1% to 6%, the 2θ decreasing from 26.85° to 26.12° , It indicates the volume of the unit cell is enlargement. Fig. 1(b) shows the Raman spectra of the ceramics with various compositions. There are three Raman active fundamental modes in rutile TiO_2 : B_{1g} (143 cm^{-1}), E_g (447 cm^{-1}), A_{1g} (612 cm^{-1}). The 143cm^{-1} (B_{1g}) Raman peak is an O-Ti-O bond bending mode, the 612cm^{-1} (A_{1g}) relates to Ti-O stretch mode, [24-27] while the 447 cm^{-1} (E_g) mode is due to oxygen atom liberation along the c-axis out of phase.[27] In addition, there is also a second-order scattering feature located at 234cm^{-1} . These results confirm that all the Ta-doped ceramics possess a rutile phase [26,28] which is compatible with the analysis of XRD patterns. It is clearly seen from Fig. 1(b), the A_{1g} mode shows slightly redshift in the Raman frequency, which is also indicates the expansion of the unit cell. In other word,

the increased O-Ti-O bond length after Ta doping induces the redshift of A_{1g} mode which arises from O-Ti-O bond-stretching vibrations.[26]

In order to visualize the evolution of the microstructures, we acquired FE-SEM images. The surface morphologies and the element analysis of the $Ta_xTi_{1-x}O_2$ ceramics ($x= 1\%$, $x=3\%$, $x =5\%$ and $x =6\%$) are presented in Fig. 2. All of the characterized ceramics were clearly observed to possess a dense microstructure. The grain were developed with terraced and with prominent angularities. Furthermore, the grain sizes decreases with increasing x , The mean grain sizes of $Ta_xTi_{1-x}O_2$ ceramics with $x = 0.01$, 0.03 , 0.05 and 0.06 are 35.14 , 27.23 , 19.05 and $13.47 \mu m$, respectively (shown in Fig.2b). Alternatively, significant suppression of the grain growth in Ta-doped TiO_2 ceramics is likely associated with the solute drag mechanism which is an important phenomena to investigate the depressed grain boundary mobility in polycrystalline ceramics [29,30]. It is known that the difference in ionic radii between dopant and host ions will introduce lattice strain energy (ΔG_{strain}) in the crystal lattice, following to the relation

$$\Delta G_{strain} = 4\pi EN_A [(r_0/2)(r_M - r_0)^2 + (1/3)(r_M - r_0)^3]$$

where r_0 and r_M represent the optimal radius of the lattice site and the ionic radius of dopant, respectively. N_A is Avogadro's Number, E is Young's modulus [28,29]. ΔG_{strain} induced by size mismatch between the dopant Ta^{5+} ions and host Ti^{4+} ions together with the electrostatic potential energy at grain boundary could give rise to interaction between the boundary and the dopant [28,30]. As a result, the grain growth of Ta-doped samples was inhibited significantly.

Fig.3(a) shows the temperature dependence of dielectric properties of Ta-doped TiO_2 ceramics at 5 kHz and in the temperature range of 100 to 350 K . As shown in

Fig.3(a), it can be clearly observed that the dielectric permittivity maintains similar value over a wide temperature range from 100 to 350 K, which verify that there is a good temperature stability of ϵ_r at 100 to 350 K in all Ta doped TiO_2 samples. Furthermore, the optimum dielectric properties are obtained at $x = 5\%$ and the samples show the lowest dielectric loss in the temperature range from 150 to 330 K. Fig.3(b) shows the temperature dependence of dielectric properties of $\text{Ta}_{0.05}\text{Ti}_{0.95}\text{O}_2$ ceramics at different frequency and in the temperature range of 100 to 350 K. It can be seen that the ceramics exhibit good temperature stability of dielectric response at all measured frequency.

Fig.4 shows the frequency dependence of the dielectric properties of $\text{Ta}_x\text{Ti}_{1-x}\text{O}_2$ ceramics in the frequency range of 40 to 10^7 Hz at room temperature. As shown in Fig. 4(a), The permittivity of the ceramics declined slowly with the frequency increasing in the frequency range of 40 to 10^6 Hz. and their dielectric loss reveal strong dependency to the frequency, while, the $\tan \delta$ of TTO5 remained nearly steady with varied frequencies from 10^3 to 10^6 Hz (Fig. 4(b)). And the minimum value of dielectric loss reached about 0.03. Furthermore, it can be seen in Fig. 4(a) that ϵ_r obviously becomes larger for $0.01 \leq x \leq 0.05$ and then drops slowly as $x > 0.05$. It is noted that TTO5 samples did not exhibit the highest permittivity and dielectric loss being on the order of 30000 and 3%. But the low level of dielectric loss and high stability made it most suitable for practical applications. The dielectric permittivity of ceramics is found to decrease at high frequency region ($f > 10^6$ Hz), while the dielectric loss increase greatly.

Herein, the composition, frequency, and temperature dependence of the dielectric properties have been investigated in detail. In the following part, special attention will be paid to the underlying physical mechanisms for the enhanced dielectric properties. Previously, the formation of electron-pinned defect dipoles is as the main reason for the origin of colossal permittivity in doped TiO_2 ceramics [31]. Therefore, it is necessary to identify the valences of the involved elements (such as, Ta, Ti, and O). Figs. 5(a)-(i) show the XPS of the etched surfaces of Ta-doped TiO_2 ceramics. Fig. 5(a) shows the XPS of Ta elements in Ta-doped TiO_2 ceramics. The binding energies of Ta $4d$ electrons were 229.6 eV and 241.1 eV, respectively, for $4d5$ and $4d3$, and no other $4d5$ low-binding-energy peaks are involved. These results show that only Ta $4d$ exists in Ta-doped TiO_2 samples, and the oxidation state of Ta is +5 [32]. Figs. 5(b)-(e) illustrate XPS of the Ti 2p core level for the $\text{Ta}_x\text{Ti}_{1-x}\text{O}_2$ ceramics. The dominant Ti $2p_{3/2}$ peak is at 458.5 eV binding energy, and Ti $2p_{1/2}$ is at 464.3 eV [35,36]. The spin-orbit splitting of Ti $2p_{3/2}$ and Ti $2p_{1/2}$ peaks is 5.8 eV, corresponding to that of rutile TiO_2 (5.7 eV). However, there are two small peaks surrounding the 458.5 eV peak, corresponding to the three valence states of Ti. After subtracting a Shirley background for the narrow region of Ti $2p_{3/2}$ and Ti $2p_{1/2}$, the Ti^{3+} $2p_{3/2}$ component is fitted as an additional symmetric peak at about 457.15 eV [35] and the Ti^{3+} $2p_{1/2}$ peak is at about 458 eV. A slight difference could be observed in the XPS spectrum of Ti 2p in TTO1, TTO3, TTO5 and TTO6 ceramics. From Fig. 5(e), it is found that the Ti^{3+} content of TTO6 ceramics is 0.36%, which is much less than the initially introduced dopant Ta^{5+} amount.

While for the TTO1 ceramics, Ti^{3+} content of **11.39% (Fig.5(b))** is much more than the initially introduced dopant Ta amount 1%. Then it could be concluded that there are two main factors responsible for the existence of Ti^{3+} . In this work, the introduction of Ta^{5+} is considered to be responsible for the reduction of Ti^{4+} . Meanwhile, the presence of oxygen vacancies in the ceramics sintered in N_2 atmosphere can also induce the extra Ti^{3+} ions, and the related reaction equations about the partial reduction of Ti^{4+} to Ti^{3+} are as follows:

In equation upon, “ $\cdot$ ” and “ $'$ ” separately represent an extra positive charge and negative charge. It suggests that the substitution of $(\text{Ta}^{5+})_{\text{Ti}}^\bullet$ for Ti^{4+} with an added positive charge as well as the formation of $V_\text{o}^{\bullet\bullet}$ induce the surrounding Ti^{4+} to reduce into Ti^{3+} ions, at low Ta doped level, through obtaining a negative electron for the demand of charge balance. Then the content of Ti^{3+} increases with increasing Ta doped level as shown in Fig. 6. However, the higher Ta doped level (more than 5%) will provide excessive electrons, which can be captured by oxygen vacancies $V_\text{o}^{\bullet\bullet}$ in equation (2) to further transform into O_o . The reverse reaction equation (2) will decrease the concentration of electrons, which restrains the occurrence of equation (3) and results in the decrease of Ti^{3+} content at higher Ta doped level as shown in Fig. 6.

As described above, the substitution of Ta^{5+} for Ti^{4+} as well as the formation of $V_\text{o}^{\bullet\bullet}$, at low Ta doped level, being considered to be responsible for

the existence of Ti^{3+} . While higher Ta doped level will provide excessive electrons and make oxygen vacancies $V_0^{\bullet\bullet}$ to further transform into O_o , leading to the decrease of $V_0^{\bullet\bullet}$. To check the change of oxygen vacancies with the increase of the content of Ta ions in TTO samples, XPS analysis of O 1s is carried out on these samples and shown in Figs. 5(f)-(i). As shown in Figs. 5(f)-(i), the O 1s XPS spectrum of the doped TiO_2 consists of a broad asymmetric peak, which can be fitted by two peaks. The strongest peak at 529.11 eV correspond to bulk Ti-O. A higher-energy peak at 530.5 eV, which corresponds to the presence of oxygen vacancies and surface hydroxyl (OH). The highest-energy peak at 532.09 eV is attributed to the adsorb surface H_2O , [36,37] From Figs. 5(f)-(i), with the increase of Ta content, the peak of 530.5 eV which relate to the oxygen vacancies is continue to decrease, is accord with the change of the content of Ti^{3+} .

As mentioned above, $(\text{Ta}^{5+})_{\text{Ti}}^{\bullet}$, $(\text{Ti}^{3+})_{\text{Ti}}^{\cdot}$ (produced by the Ta^{5+} and $V_0^{\bullet\bullet}$), $V_0^{\bullet\bullet}$ (caused by the sintering process in N_2 atmosphere) all coexist in the Ta-doped TiO_2 ceramics. oxygen vacancies and electrons are located in the limited lattices owing to the demand for charge balance to form complex clusters, such as $(\text{Ta}^{5+})_{\text{Ti}}^{\bullet} \rightarrow (\text{Ti}^{3+})_{\text{Ti}}^{\cdot}$, $(\text{Ti}^{3+})_{\text{Ti}}^{\cdot} \rightarrow V_0^{\bullet\bullet} \leftarrow (\text{Ti}^{3+})_{\text{Ti}}^{\cdot}$, $2(\text{Ta}^{5+})_{\text{Ti}}^{\bullet} \rightarrow 4(\text{Ti}^{3+})_{\text{Ti}}^{\cdot} \leftarrow V_0^{\bullet\bullet}$ etc.

Leading to a high permittivity and low dielectric loss performance in the high frequency range.

It was reported that the sintering temperatures would strongly affect the dielectric properties of TiO_2 -based ceramics [38]. In this study, we studied the effects of sintering temperature on ϵ_r and $\tan \delta$ of $\text{Ta}_{0.05}\text{Ti}_{0.95}\text{O}_2$ ceramics. The dielectric properties of the ceramics sintered at different temperature were measured at different

frequency and temperatures are shown in Fig. 7. It could be observed that ϵ_r obviously increased with increasing of the sintering temperatures ($T \leq 1400^\circ\text{C}$) and then decreased ($T > 1400^\circ\text{C}$), reaching a peak ϵ_r value at $T = 1400^\circ\text{C}$. Moreover, $\tan\delta$ also increased with increasing of sintering temperature except $T = 1400^\circ\text{C}$, which the $\tan\delta$ sharply decreases to 3%. Subsequently, we investigated the temperature and frequency dependence of dielectric properties of the ceramics with various sintering temperatures, as shown in Fig. 7. From these figures, it could be observed that the ceramics sintered at $T \geq 1300^\circ\text{C}$ shown high dielectric constant ($\epsilon_r \geq 25000$). In addition, the improved temperature and frequency stability of dielectric properties on the samples with $T \geq 1300^\circ\text{C}$ are obtained in TTO5 samples. In a word, good dielectric properties ($\epsilon_r = 50000$ and $\tan\delta = 3.07\%$) of TTO5 samples could be achieved at $T = 1400^\circ\text{C}$.

4. Conclusions

In this study, a large dielectric constant ($\epsilon_r = 30000$ and $\tan\delta = 3\%$) and dielectric can be obtained in $\text{Ta}_{0.05}\text{Ti}_{0.95}\text{O}_2$ and sintering at 1400°C . In addition, the dielectric properties of the ceramics exhibited relatively stable temperatures ($-170 \sim 100^\circ\text{C}$) and frequency ($40 \sim 10^6 \text{ Hz}$) behaviors. The Raman and XPS analysis indicated the concentration of oxygen vacancies decreased and the ratio of Ti^{3+} went upward to a maximum, and then fallen down with increasing the Ta doped level. It was suggested that Ta^{5+} as a donor doped into TiO_2 , killed the oxygen vacancies, formed $2(\text{Ta}^{5+})_{\text{Tl}}^{\bullet} \rightarrow 4(\text{Ti}^{3+})_{\text{Tl}}^{\bullet} \leftarrow \text{V}_{\text{O}}^{\bullet\bullet}$ defect complex, in which electrons and oxygen vacancies were located in the limited lattices leading to electron-pinned defect-dipoles leading to a high permittivity and low dielectric loss performance in the high frequency range.

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Figure captions

Fig.1 (a) XRD patterns of $\text{Ta}_x\text{Ti}_{1-x}\text{O}_2$ ceramics. (b) Raman spectra of $\text{Ta}_x\text{Ti}_{1-x}\text{O}_2$ ceramics. The wavelength of Ar^+ laser was 532 nm.

Fig.2 (a) Surface morphologies of the $\text{Ta}_x\text{Ti}_{1-x}\text{O}_2$ ceramics with different doped contents: (a) $x=1\%$, (b) $x=3\%$, (c) $x=5\%$, (d) $x=6\%$.

(b) The statistic of grain sizes of surface FE-SEM images in $\text{Ta}_x\text{Ti}_{1-x}\text{O}_2$ ceramics.

Fig.3 Temperature dependence of permittivity and $\tan\delta$ of (a) Ta-modified TiO_2 ceramics, measured at 5 kHz and 80-360K. (b) $\text{Ta}_{0.05}\text{Ti}_{0.95}\text{O}_2$ ceramics, measured at 1, 5, 50, 100 kHz and 80-360K.

Fig.4 (a) Dielectric constant and (b) dielectric loss of Ta-doped rutile TiO_2 ceramics in the frequency range of 40 to 10^6Hz , measured at room temperature. The inset of (b) shows dielectric loss in the frequency range of 10^3 to 10^6Hz .

Fig.5 Valence state of $\text{Ta}_x\text{Ti}_{1-x}\text{O}_2$ ceramics: (a) Ta 4d of $\text{Ta}_{0.05}\text{Ti}_{0.95}\text{O}_2$ ceramics (b)-(e) Ti 2p of $\text{Ta}_x\text{Ti}_{1-x}\text{O}_2$ ceramics with $x=1\%$, 3%, 5% and 6%, (f)-(i) O 1s of $\text{Ta}_x\text{Ti}_{1-x}\text{O}_2$ ceramics with $x=1\%$, 3%, 5% and 6%.

Fig.6 The % At concentration of Ti^{3+} and [O-H] with different x .

Fig.7 (a) Frequency and (b) temperature dependence of permittivity and $\tan\delta$ of $\text{Ta}_x\text{Ti}_{1-x}\text{O}_2$ ceramics with $x=0.05$, in which the ceramics were sintered at various temperatures.

a **b**

a **(b)**