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Core-shell TiN@SrTiO$_3$ structure for grain boundary barrier layer capacitor

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ABSTRACT

A novel TiN@SrTiO$_3$-based (TiN@STO-based) grain boundary barrier layer capacitor (GBBLC) was proposed to decrease dielectric loss (tgδ) of SrTiO$_3$-based GBBLC at high frequency region through reducing the electrical resistivity of GBBLC by introducing conductive core. The TiN@STO composite was synthesized by utilizing the surface electrostatic interaction between TiN and STO. The TiN@STO-based GBBLC was prepared by spark plasma sintering at 1150 °C under N_2 atmosphere and annealed at 600 °C in air to remove the carbon contamination and insulate grain boundary. XRD and SEM results prove TiN phase was intact reserved in the annealed TiN@STO-based GBBLC. Compared with SrTiO$_3$ GBBLC, the tgδ of 1TiN@5STO GBBLC remarkably decreased by 83.7% and 66.7% with the high dielectric constant reserved at 5 kHz and 10 MHz, respectively. The electric-conductor@semi-conductor core-shell structured composite GBBLC proposed in the paper can be expected to develop other high frequency ceramic capacitor with low dielectric loss.

1. Introduction

The increasing demand of electronic component has led to a worldwide interest in ceramic capacitors in view of their high service temperature, specific capacity, humidity resistance and low dielectric loss [1,2]. Grain boundary barrier layer capacitor (GBBLC) with high dielectric property is one of the research hotpots in the ceramic capacitor family, which can contribute to the miniaturization and high volume capacity of ceramic capacitors [3,4]. The high dielectric constant of GBBLC was attributed to its unique structure composed by large size semi-conductive grains and thin insulator grain boundary (Fig. 1a). The semi-conductive grains act as the electrodes of numerous microcapacitors. However, the series resistance caused by internal electrical resistivity of semi-conductive grains can affect the dielectric loss and stability for high frequency region application. It is noted that the relationship between the dielectric loss (tgδ) of GBBLC and the electric resistivity (ρ_g) of grains is as follows: $tg\delta = 2\pi f \varepsilon_0 K_{eff} \rho_g$, where f, ε_0 and K_{eff} represent the frequency, vacuum and effective dielectric constant of semi-conductive grains, respectively [5,6]. In addition, the dielectric constant is another important factor to describe the performance of GBBLC, whose change is always observed with the same trend of dielectric loss in SrTiO$_3$-based GBBLC [4,5]. Thus, it is important to design a novel GBBLC with lower ρ_g which could decrease the dielectric loss of GBBLC while retaining its high dielectric constant.

As a traditional GBBLC material, SrTiO$_3$ (STO) always exhibits low dielectric loss, excellent frequency property, and high dielectric constant since it was found in the 1970s [7,8]. Metal nitride (e.g. TiN) is usually reported as a common conductive material and owns a good chemical compatibility with STO [9]. In view of the above relationship between tgδ and ρ_g, we aimed at developing a new type GBBLC composed by an electric-conductor@semi-conductor core-shell structured composite to decrease the electrical resistivity of SrTiO$_3$-based GBBLC (Fig. 1b). Here TiN was introduced as a conductive core into SrTiO$_3$ semi-conductive shell to fabricate the electric-conductor@semi-conductor composite. This GBBLC is named as TiN@STO-based GBBLC. The whole structure of our TiN@STO-based GBBLC is very similar to that of traditional SrTiO$_3$-based GBBLC. However, the grain in TiN@STO-based GBBLC is composed of TiN@STO composite, which was sintered by spark plasma sintering (SPS). This TiN@STO-based GBBLC is expected to improve SrTiO$_3$-based GBBLC's dielectric properties due to its decreased electrical resistivity. Herein we reported the preparation, characterization and dielectric performance of this new ceramic capacitor material.

2. Experimental

2.1. Preparation process

The pH value of 1 wt.% polyethyleneimine (PEI, *M*w 10,000, Alfa Aesar) aqueous solution was adjusted from 11 to 5 by HNO$_3$ for complete ionization. TiN powder (10–20 μm, Alfa Aesar) was dispersed in the PEI solution and refluxed with stirring for 4 h. TiN@PEI composite was obtained after filtration and washing carefully to remove residual PEI. The samples in 1:25, 1:5, 1:1 and 0:1 molar ratios for TiN@PEI to SrTiO$_3$ (STO, 0.5–1 μm, Alfa Aesar) were refluxed in distilled water for 4 h at 100 °C. After filtration, the powders were collected and dried at 110 °C. Sintering was conducted in N_2 atmosphere at 1150 °C for

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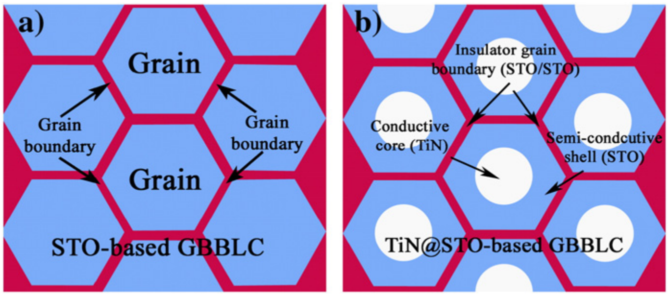

Fig. 1. Structure comparison of GBBLC: (a) the $SrTiO_3$-based GBBLC; (b) the TiN@$SrTiO_3$-based GBBLC.

2 min by SPS. The resultant plates were annealed at 600°C for 8 h in air. In order to exclude the interference of other impurities, we added no sintering aid in our experiment.

2.2. Characterization

Scanning electron microscopy (SEM, Instrument JSM 6700F) was employed for powder morphology observation. X-ray diffraction (XRD, Model D/MAX-RB) was used for crystalline phase identification. The zeta potential of STO and TiN particles was measured at several pH values using a zeta meter (Model 3000, Penkem). And Dr Sinter 1020 SPS apparatus (Sumitomo Coal Mining Co., Ltd., Japan) was used for sintering. Silver paint electrodes were formed on both sides of the sintered ceramic disks for electrical measurements by Precision impedance analyzer (Model 4294A, Agilent).

3. Results and discussion

The preparation process of TiN@STO-based GBBLC is illustrated in Fig. 2. The surfaces of TiN and STO particles are both proved negative by their zeta potential values (−36 and −45, respectively) in distilled water at pH = 7. First, the TiN particle was modified by the fully ionized cationic dispersant PEI to form TiN@PEI composite with positive charge surface (Fig. 2b), and the zeta potential value of TiN particle changed from −36 to 68, correspondingly. Second, STO particles in different molar ratios were added to be absorbed onto the positive surface of TiN@PEI composite, forming micro TiN@-STO composite with core-shell structure utilizing the charge interaction (Fig. 2c). Finally, the TiN@STO composites were sintered by SPS to prepare the compact TiN@STO-based GBBLC (Fig. 2d).

Considering the importance of large grain size for the performance of GBBLC and the big diameter difference between core and shell for the coating procedure, TiN with particle size ranging from 10 to 20 μm and STO with the relatively small particle size (0.5–1 μm) was used to fabricate micro TiN@STO composite (Fig. 3a) [10]. Fig. 3b–d shows the SEM images of TiN@STO composite with different TiN/STO ratios. As shown in Fig. 3c, most of the STO particles are coated on the surface of TiN. Furthermore, the partly naked TiN in 1TiN@1STO composite (Fig. 3b) and the large amount of the residual STO particles in 1TiN@25STO composite (Fig. 3d) indicate that the optimal STO/TiN molar ratio is about 5/1.

The XRD patterns of the sintered samples are shown in Fig. 3f. There are only peaks of cubic STO for $SrTiO_3$ GBBLC observed in Fig. 3f (1). For the TiN@STO-based GBBLC, XRD peaks of TiN are observed and the peak intensity increases in good agreement with the increasing TiN content in samples (Fig. 3f (3) and (4)). On the other hand, it was reported that TiN can be oxidized to TiO_2 when heated

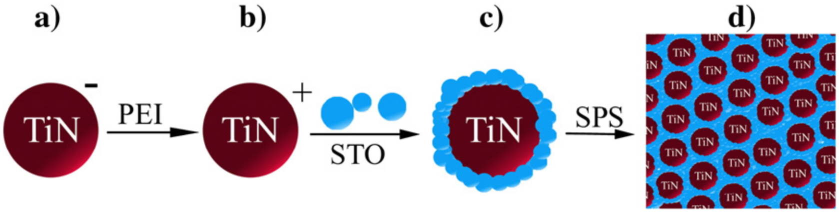

Fig. 2. Schematic illustration of the procedures for preparing TiN@STO-based GBBLC: (a) TiN particle with negative surface; (b) TiN@PEI composite; (c) TiN@STO composite; (d) TiN@STO-based GBBLC.

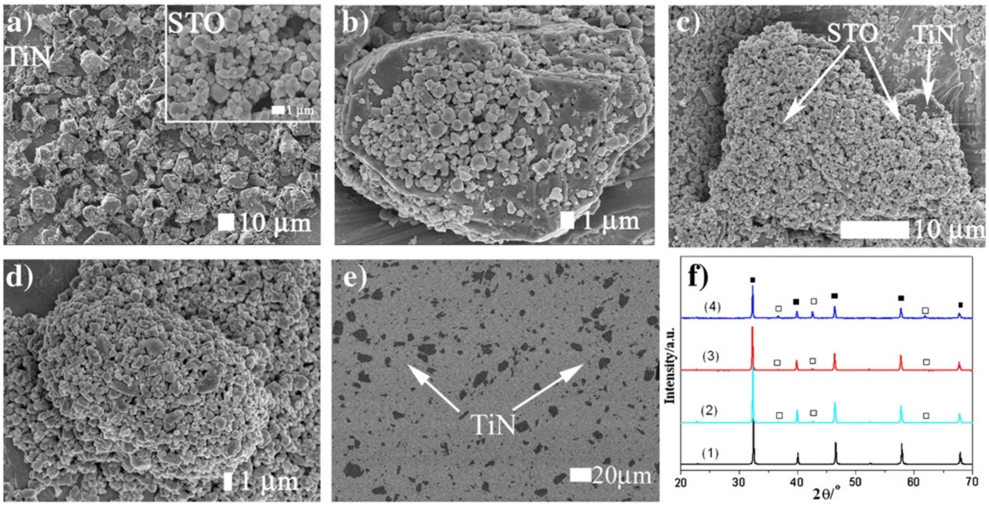

Fig. 3. SEM images of (a) pristine TiN powder and STO powder; (b) 1TiN@1STO composite; (c) 1TiN@5STO composite; (d) 1TiN@25STO composite; (e) 1TiN@5STO GBBLC surface. (f) XRD patterns of (1) $SrTiO_3$ GBBLC; (2) 1TiN@5STO GBBLC after annealing at 600°C; (3) 1TiN@5STO GBBLC; (4) 1TiN@1STO GBBLC; where ■ and □ represent STO and TiN, respectively.

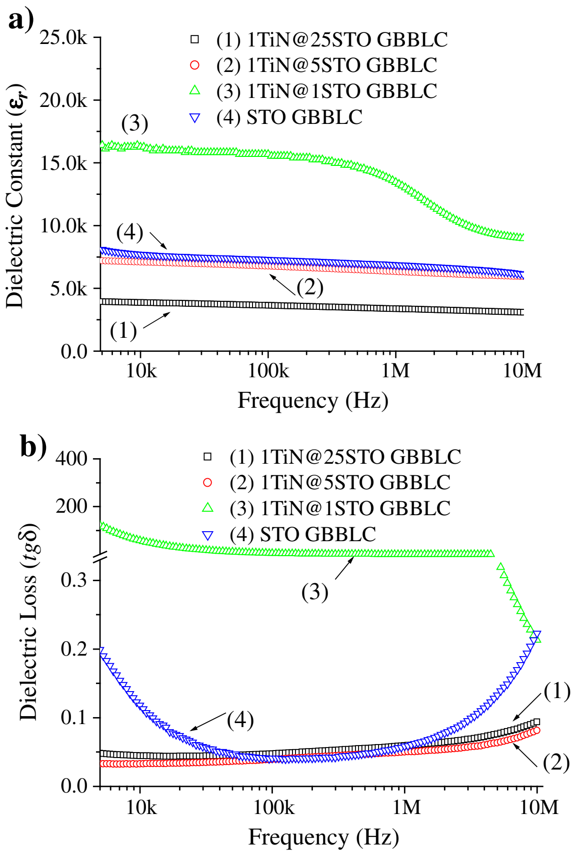

Fig. 4. The frequency dependence of (a) the dielectric constant (ε_r) and (b) dielectric loss (tgδ) of $SrTiO_3$ GBBLC and TiN@STO-based GBBLC; where □, ○, △, and ▽ represent 1TiN@25STO-based GBBLC, 1TiN@5STO, 1TiN@1STO, and $SrTiO_3$ GBBLC, respectively.

in air at temperatures above 450 °C [11]. In view of the absence of TiO_2 phase in all our TiN@STO-based GBBLC samples and the TiN phase reserved after annealing in air (Fig. 3f (2)), it is suggested that the oxidation of TiN should be depressed due to the protection of the STO matrix on TiN surface and the large diameter of TiN particles.

The frequency dependence of the values of dielectric constant (ε_r) and dielectric loss (tgδ) of TiN@STO-based GBBLC from 5 k to 10 MHz at room temperature are shown in Fig. 4, in which TiN significantly affects the dielectric loss and dielectric constant of $SrTiO_3$-based GBBLC. The tgδ and ε_r of TiN@STO-based GBBLC almost increase with the increasing TiN molar ratio. 1TiN@1STO GBBLC shows the highest tgδ in the four samples in Fig. 4b(3), because the contact of the partly naked TiN destroyed the insulator grain boundary of TiN@STO GBBLC. In contrast with 1TiN@1STO GBBLC, an excess of STO of 1TiN@25STO GBBLC and 1TiN@5STO GBBLC can insure the presence of insulator grain boundary of TiN@STO GBBLC. It is known that the dielectric loss and the dielectric constant of $SrTiO_3$-based GBBLC usually change with the same trend. Compared with $SrTiO_3$ GBBLC, TiN decreases the dielectric loss in 1TiN@25STO GBBLC, but the insufficiency of TiN also results in the drop of its dielectric constant. In the case of 1TiN@5STO GBBLC (Fig. 4b), nearly same ε_r (~7500) to that of $SrTiO_3$ GBBLC (~7700) and the lowest tgδ in four samples were observed. Compared with $SrTiO_3$ GBBLC, the tgδ of 1TiN@5STO GBBLC exhibits a significant decrease ranging from 5 to 13 kHz and from 1.1 MHz to 10 MHz. The tgδ of 1TiN@5STO GBBLC remarkably decreases by 83.3% at 5 kHz and 66.7% at 10 MHz, respectively. All results are consistent with our design that the separated TiN conductive core with proper proportion (Fig. 3e) introduced to GBBLC can improve its dielectric property by decreasing the dielectric resistivity.

4. Conclusions

In summary, a novel TiN@STO-based GBBLC composed by electric-conductor@semi-conductor core-shell structured composite has been developed. The tgδ of TiN@STO-based GBBLC has been decreased by import proper molar ratio TiN conductive core into $SrTiO_3$ semi-conductive grains without decreasing the dielectric constant, especially in the high frequency range. Furthermore, the metal nitride conductive core design presented in this study for GBBLC was expected to be suitable for fabricating other types of high dielectric property GBBLC (e.g. NbN and ZrN).

Acknowledgments

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