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# The effect of processing conditions and porosity on the electrical properties of $Y_2O_3$ -doped SrTiO<sub>3</sub> internal boundary layer capacitors

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Internal boundary layer capacitors of 0.8 mole%  $Y_2O_3$ -doped SrTiO<sub>3</sub> were prepared by a co-milling process and then sintered in an oxidizing atmosphere between 1450-1550 °C for hold periods of 1-15 h. Large enhancements in the dielectric constant as a function of sintering conditions were observed, as compared to pure SrTiO<sub>3</sub>. The electrical properties of effective dielectric constant and effective conductivity were strongly correlated with each other depending on the frequency, and both properties decreased strongly with increasing porosity. To account for this strong dependence, three microstructural models were developed based on random porosity, porosity intersecting the grain boundary region, and porosity localized in the grain boundary region. For cases when the porosity preferentially reduces the grain boundary area, the models qualitatively predict a very strong dependence for the both the dielectric constant and conductivity on the pore volume fraction.

Key words: strontium titanate, porosity, dielectric constant, conductivity.

## Introduction

Although pure strontium titanate has a moderate dielectric constant of approximately 350 [1-4], effective dielectric constants of up to 200,000 can be realized [5] when this material is doped with small amounts of acceptor or donor compounds. This enhancement in the effective dielectric constant is attributed to the formation of thin insulating layers around grains of semiconducting SrTiO<sub>3</sub>, and capacitors fabricated by this route are termed internal boundary layer capacitors (IBLCs).

To fabricate IBLCs, several different processing routes have been developed [1, 5-16]. In one approach [8, 10, 12], SrTiO<sub>3</sub> substrates are first sintered in a reducing atmosphere during which the SrTiO<sub>3</sub> becomes n-type semiconducting as oxygen vacancies are formed. The sintered substrates are next coated with a dopant, which is then diffused into the substrate under oxidizing conditions, where it creates an insulating layer around each SrTiO<sub>3</sub> grain [10].

As an alternative method [1, 5-7, 13-18], the dopant powder can be mixed or milled directly with  $SrTiO_3$ powder. The green bodies are directly formed from this powder mixture and then sintered to obtain the internal boundary layer microstructure. This approach is advantageous in that the dopant powder is well dispersed throughout the  $SrTiO_3$  substrate; a disadvantage is that the dopant may impede the sintering of the substrates [14] to full density.

In earlier work, we have used the co-milling method to prepare 0.8 mole%  $Y_2O_3$ -doped SrTiO<sub>3</sub> compositions [18]. These compositions were formed into substrates and then sintered in an oxidizing atmosphere over a range of temperatures for different times. The effective dielectric constant ( $\varepsilon_{eff}$ ) and conductivity ( $\sigma_{eff}$ ) at 1000 Hz were found to be highly correlated, which in turn was attributed to the effect of porosity. In this study, we examine the electrical properties over a range of frequencies for a 0.8 mole% Y<sub>2</sub>O<sub>3</sub>-doped SrTiO<sub>3</sub> composition sintered at different conditions. Three models are then developed for describing how porosity, which decreases the area of the grain boundary region, influences the effective dielectric constant and conductivity.

#### Experimental

To prepare the 0.8 mole%  $Y_2O_3$ -doped SrTiO<sub>3</sub> composition, SrTiO<sub>3</sub> and  $Y_2O_3$  powders (Sigma-Aldrich Chemicals, Milwaukee, WI) were co-milled for 6 h in ethanol with 1 weight% poly(vinyl butyral) as a binder. After drying at 50 °C, the powder mixture was dry pressed into disks of 19 mm diameter and then sintered in a box furnace in air at soak temperatures of 1450-1550 °C for 1-15 h. The sintering cycle consisted of a 4 K minute<sup>-1</sup> ramp from room temperature to 900 °C, then an 8 K minute<sup>-1</sup> ramp to the soak temperature for a hold period, followed by cooling at 10 K minute<sup>-1</sup> to room temperature. The sintered density was determined by the sample weight and dimensions and by the Archimedes technique.

To characterize the electrical properties, gold electrodes

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were sputtered onto the substrates, and the capacitance and resistance were measured with a Hewlett-Packard 4274A *LCR* meter. The microstructures of the samples were characterized by scanning electron microscopy (SEM), by transmission electron microscopy (TEM), and by composition profiling of the grain boundary region by energy dispersive X-ray spectroscopy (EDS). The grain size and pore size were determined by image analysis of the SEM and TEM micrographs.

### **Results and Discussion**

Figure 1 shows representative micrographs of the microstructures of 0.8 mole% Y2O3-doped SrTiO3 samples sintered at different conditions. The grains are generally facetted in shape, and the curvature of most of the grain boundaries is near zero. Pores, when present, are generally found at the grain boundaries and at triple points, and are generally elongated in shape. Although some pores may have been caused by polishing, this was not taken into account in the pore size analysis. A summary of the microstructural features of the IBLC substrates sintered at different conditions is contained in Table 1 and Fig. 2. Although differences in average grain size and average pore size were observed versus sintering conditions, Fig. 2 indicates that, in light of the large standard deviations, neither average quantity varies over a wide range for the sintering conditions examined here. We thus take as representative of the data average values of the grain size,  $d_g=1.2 \mu m$ , and of the pore size,  $d_p=2.3 \mu m$ .

A representative TEM micrograph of the grain boundary region is shown in Fig. 3a and indicates a grain boundary thickness of 2-3 nm. Composition profiling of the Y and Ti compositions across the grain boundary region (see Fig. 3b) demonstrates that the extent of yttrium penetration is a factor of ten larger than based on the appearance of the grain boundary region in Fig. 3a. Table 1 also summarizes the grain boundary thickness versus sintering conditions for selected samples, and again no strong trends were evident with the processing conditions. An average grain boundary thickness,  $d_1$ =0.021 µm, is thus taken as being repre-



3µm



Fig. 1. SEM micrographs of 0.8 mole%  $Y_2O_3$ -doped SrTiO<sub>3</sub> samples. Sample #4 (top) was sintered at 1500 °C for 15 h, and Sample #8 (bottom) was sintered at 1550 °C for 15 h. The large pore in Sample #8 is likely an artifact of polishing.

sentative of the samples.

The electrical properties as a function of frequency were also analyzed (see Table 2), and Fig. 4 shows that the effective dielectric constant and effective conductivity

Table 1. Effect of sintering conditions on the porosity, grain size, and grain boundary width for 0.8 mole%  $Y_2O_3$ -doped SrTiO<sub>3</sub>. The ranges denote  $\pm 1$  standard deviation

Sample ID	Sintering temperature (°C)	Sintering time (h)	Porosity (-)	Pore diameter (µm)	Pore aspect ratio (-)	Grain diameter (µm)	Grain boundary width (nm)
1	1450	15	0.076	1.0±0.7	2.4	0.9±0.16	25.4±1.8
2	1450	15	-	-	-	-	-
3	1500	15	0.059	2.7±2.0	2.2	1.3±0.33	-
4	1500	15	-	2.2±3.9	1.9	1.2±0.26	-
5	1550	1	0.061	1.4±0.9	2.2	0.8±0.16	-
6	1550	5	0.025	3.0±2.2	1.6	1.2±0.25	-
7	1550	10	0.020	2.0±1.3	1.8	1.3±0.22	21.2±4.6
8	1550	15	0.035	3.9±1.3	1.3	1.4±0.33	17.6±7.0



Fig. 2. Average grain size and pore size for 0.8 mole%  $Y_2O_3$ -doped SrTiO<sub>3</sub> samples sintered at different conditions. The error bars indicate  $\pm 1$  standard deviation.

are highly correlated with each other at each frequency over a range from  $10^2$ - $10^5$  Hz. Both the effective dielectric constant and effective conductivity are also highly correlated with the porosity, and Figs. 5 and 6 show that each of these quantities decreases with increasing porosity for each frequency. In order to further analyze the data, the effective dielectric constant and effective conductivity at zero porosity for each frequency were obtained by linear extrapolation.

The extrapolated values were then used to normalize the effective dielectric constant and effective conductivity data. Figure 7 shows that the data for normalized dielectric constant versus fractional porosity now lie on a single curve with a nearly constant slope ranging from 9.0-9.4. For the normalized conductivity in Fig. 8, however, this collapsing of the data onto a single curve is less effective, and the slope now ranges from 6.9-9.5, with the slope of the lower frequency conductivity data





**Fig. 3.** (a) TEM micrograph of the grain boundary region for a 0.8 mole%  $Y_2O_3$ -doped SrTiO<sub>3</sub> sample sintered at 1450 °C for 15 hours. (b) Ratio of the Y: Ti signals determined by EDS across the grain boundary region. The experimental data (solid circles), the fitted baseline (dashed line), the fitted Y: Ti ratio (solid curve), and the thickness of the grain boundary region (bracket) are shown in the figure.

Table 2. Effective dielectric constant and effective conductivity versus frequency for  $0.8 \text{ mole} \% \text{ Y}_2\text{O}_3$ -doped SrTiO<sub>3</sub> sintered at different conditions

ID	Sintering Temp.	Sintering Time	Porosity		$\mathcal{E}_{eff}\left(- ight)$ @			$\sigma_{e\!f\!f} \left(  ext{microohm-cm}  ight)^{\!-\!1} @$			
	(°C)	(h)	(-)	100 Hz	1,000 Hz	10,000 Hz	100,000 Hz	100 Hz	1,000 Hz	10,000 Hz	100,000 Hz
1	1450	15	0.076	47000	28900	18400	11200	7	50	310	1940
2	1450	15	-	38100	23400	15100	9400	6	40	260	1730
3	1500	15	0.059	142000	93800	57500	27900	28	150	690	2690
4	1500	15	-	124300	81800	50500	25500	24	140	640	2660
5	1550	1	0.061	75900	49900	32100	17600	14	90	470	2220
6	1550	5	0.025	117100	78800	50400	27900	23	140	720	3170
7	1550	10	0.020	195700	132000	79600	38800	40	210	930	3590
8	1550	15	0.035	146900	102900	69100	38100	31	210	1000	3680



**Fig. 4.** Effective conductivity versus effective dielectric constant at different frequencies for 0.8 mole%  $Y_2O_3$ -doped SrTiO<sub>3</sub> samples sintered at different conditions (see Table 2).



Fig. 5. Effective dielectric constant at different frequencies versus porosity for 0.8 mole%  $Y_2O_3$ -doped SrTiO<sub>3</sub> samples sintered at different conditions.

agreeing better with the dependence on porosity seen in Fig. 7 for the dielectric constant.

To account for the effect of porosity on the effective dielectric constant and effective conductivity, we follow the approach of Wernicke [7] and now include probabilistic models for describing how porosity is distributed in the microstructure. Figure 9 shows three ways in which porosity can be envisioned to reside within the microstructure of cubic grains: Model A treats pores that are randomly distributed, Model B treats pores intersecting the grain boundary region, and Model C treats pores localized entirely within the grain boundary region.

For one single cubic grain, as depicted in Fig. 9, the capacitance,  $C_1$ , is given in terms of the effective grain boundary area,  $A_{eff}$ , as:



Fig. 6. Effective conductivity at different frequencies versus porosity for 0.8 mole%  $Y_2O_3$ -doped SrTiO<sub>3</sub> samples sintered at different conditions.



Fig. 7. Normalized dielectric constant at different frequencies versus porosity for 0.8 mole%  $Y_2O_3$ -doped SrTiO<sub>3</sub> samples sintered at different conditions.

$$C_1 = \varepsilon_0 \varepsilon_1 \frac{A_{eff}}{d_1} \tag{1}$$

where  $\varepsilon_0$  is the permittivity of free space and  $\varepsilon_1$  is the permittivity of the grain boundary region. As a consequence of porosity in the grain boundary area, the effective grain boundary area is related to the maximum grain boundary area,  $A_1$ , by:

$$A_{eff} = A_1(1 - P') \tag{2}$$

where P' is the fraction of the grain boundary area missing due to pores. The quantity P' will be different for the three models proposed above. We note further that the total fractional porosity in a sample, P, differs



Fig. 8. Normalized conductivity at different frequencies versus porosity for 0.8 mole%  $Y_2O_3$ -doped SrTiO<sub>3</sub> samples sintered at different conditions.



**Fig. 9.** Schematic 2-D representation of a cubic array of grains showing the grain boundary region in light gray. Cubic pores in white are shown randomly distributed (Model A), intersecting the grain boundary region (Model B), and localized entirely in the grain boundary region (Model C). The characteristic dimensions that appear in the model are also indicated.

from the porosity localized at the grain boundaries, P'; the two quantities, however, are related. The total porosity, P, can be represented in terms of the number of grains and pores,  $n_g$  and  $n_p$ , and their corresponding volumes,  $V_g$  and  $V_p$ , as:

$$P = \frac{n_P V_P}{n_g V_g} = \frac{n_P d_P^3}{n_g d_g^3} \tag{3}$$

The number of grains can also be expressed in terms of other microstructural features as:

$$n_{g} = \frac{d_{c}}{d_{g}} \tag{4}$$

where  $d_c$  is the spacing between the electrodes. For a large number of grains spanning the total thickness of the device,  $n_g$  is approximately equal to the number of insulating layers,  $n_1$ .

The fraction of missing grain boundary area P' arising from porosity for Model A (random pores), Model B (intersecting pores), and Model C (localized pores) can be expressed in terms of microstructural features by:

$$P'=P$$
 Model A (5a)

$$P' = \frac{n_p d_1 d_p^2}{n_1 d_1 d_2^2} \qquad \text{Model B} \qquad (5b)$$

$$P' = \frac{n_P d_P^3}{n_1 d_1 d_e^2} \qquad \text{Model C} \qquad (5c)$$

The quantity  $n_p$  in Eqs. (5a)-(5c) can be expressed in terms of the observable total porosity *P* from Eq. (3) as:

$$n_p = \frac{n_g d_g^3}{d_p^3} P \tag{6}$$

The value of P' in Eqs. (5a)-(5c) can then be represented with this value of  $n_p$  for the three models as:

$$P'=P$$
 Model A (7a)

$$P' = \frac{d_g}{d_p} P$$
 Model B (7b)

$$P' = \frac{d_g}{d_1} P$$
 Model C (7c)

where we have used that  $n_g/n_1 \approx 1$ . With these expressions for *P'*, the effective area at the grain boundary region for the three models is given by:

 $A_{eff} = A_1(1 - P) \qquad \text{Model A} \qquad (8a)$ 

$$A_{eff} = A_1 \left( 1 - \frac{d_g}{d_P} P \right) \qquad \text{Model B}$$
(8b)

$$A_{eff} = A_1 \left( 1 - \frac{d_g}{d_1} P \right) \qquad \text{Model C}$$
(8c)

Thus, the reduction in effective area of dielectric from Models B and C is now in terms of the microstructural features of the substrate, namely, the pore size, grain size, and grain boundary region thickness. In light of Eqs. (8a)-(8c), the effective dielectric constant for the three models can be expressed as:

$$\varepsilon_{eff} = \varepsilon_1 \frac{d_g}{d_1} (1 - P)$$
 Model A (9a)

$$\varepsilon_{eff} = \varepsilon_1 \frac{d_g}{d_1} \left( 1 - \frac{d_g}{d_P} P \right)$$
 Model B (9b)

$$\varepsilon_{eff} = \varepsilon_1 \frac{d_g}{d_1} \left( 1 - \frac{d_g}{d_1} P \right)$$
 Model C (9c)

The effective dielectric constant thus depends on the permittivity of the insulating layer,  $\varepsilon_1$ , and on other microstructural features. Equations (9a)-(9c) all reduce to the equation derived by Wernicke [7] for no porosity,  $\varepsilon_{eff} = \varepsilon_1 d_g/d_1$  and thus the term in parentheses in each equation represents a correction factor to account for the presence of porosity in the grain boundary region. This correction factor has a straightforward physical interpretation in that large grain size, small pore size, small grain boundary thickness, or a combination thereof strongly magnify the effect of porosity because the area of dielectric is small.

The effect of porosity in the grain boundary region can also be applied to the effective conductivity. For the case where the grain boundary resistance controls the conductivity, the effective conductivity for the three models is given by:

$$\sigma_{eff} = \sigma_1 \frac{d_g}{d_1} (1 - P) \qquad \text{Model A} \qquad (10a)$$

$$\sigma_{eff} = \sigma_1 \frac{d_g}{d_1} \left( 1 - \frac{d_g}{d_p} P \right) \qquad \text{Model B} \tag{10b}$$

$$\sigma_{eff} = \sigma_1 \frac{d_g}{d_1} \left( 1 - \frac{d_g}{d_1} P \right) \qquad \text{Model C} \qquad (10c)$$

Each of these equations has the same dependence on the microstructural quantities and on the porosity as for the effective dielectric constant in Eqs. (9a)-(9c), respectively. One way to test this dependence is to plot the normalized



Fig. 10. Normalized conductivity versus normalized dielectric constant at different frequencies for 0.8 mole%  $Y_2O_3$ -doped SrTiO<sub>3</sub> samples sintered at different conditions.



**Fig. 11.** Normalized dielectric constant at different frequencies versus porosity as compared to the predictions from Models A, B, and C. The best fit line with slope of 9.2 is also shown.

conductivity ( $\sigma_{eff}/\sigma_{eff@P=0}$ ) versus the normalized dielectric constant ( $\varepsilon_{eff}/\varepsilon_{eff@P=0}$ ). When this normalization is applied to Eqs. (9a)-(9c) and Eqs. (10a)-(10c), the right-hand sides for Models A-C, respectively, are identical, and thus a plot of ( $\sigma_{eff}/\sigma_{eff@P=0}$ ) versus ( $\varepsilon_{eff}/\varepsilon_{eff@P=0}$ ) should have unit slope. As Fig. 10 shows, most of the data obtained in this work exhibits this type of behavior. As the frequency becomes higher, however, the conductivity data no longer lie exactly on the line. Thus, it appears that using dielectric constant data obtained at any frequency or the low frequency conductivity data leads to a set of data consistent with the behavior predicted by Eqs. (9) and (10).

Figure 11 is a graph of the normalized dielectric constant versus porosity as compared to the model predictions from Eqs. (9a)-(9c) using the average values of  $d_g$ =1.2 µm,  $d_p$ =2.3 µm, and  $d_1$ =0.021 µm. For randomly distributed porosity, Eq. (9a) under predicts the decrease in normalized dielectric constant with increasing porosity. This arises because, as seen in Fig. 1, the porosity is in fact not random but instead is localized near the grain boundary region.

Equation (9b), which is based on pores intersecting the grain boundary region, also under predicts the effect of porosity on the dielectric constant, and, in fact, is worse than Model A for random porosity. This arises because of the large pore size measured here, as compared to the grain size. Although Model B does not adequately take into account the effect of porosity, it has the potential to do so if the pore size is small. It may also be that because of their size, small pores as seen in Fig. 1 were not adequately accounted for in determining an average pore size, whereas large pores arising from polishing were over counted.

Equation (9c), which is based on pores residing

entirely in the grain boundary region, predicts too strong a decrease of the normalized dielectric constant with increasing porosity. Thus, we see that although none of the models exactly fits the experimental data, this is not surprising in light of the simplifications in the scaling law models developed here. In any real IBLC device, distributions of grain size, pore size, and grain boundary thickness are present. The pore shape has also not been included here, and we see that in Fig. 1, the porosity often has a high aspect ratio [18]. Finally, because we have used average quantities in this analysis, some of the specific dependences on differences in grain size, pore size, and grain boundary thickness arising from the sintering conditions may be obscured.

In summary, the data shown here indicate that the measured effective dielectric constant and effective conductivity are highly correlated with each other, and also with the porosity. Models have also been derived to account for how the presence of porosity can lead to such a strong dependence. The results presented here also suggest that effective dielectric constant data over the frequency range of  $10^2$ - $10^5$  Hz or effective conductivity data at low frequency are useful for analyzing the correlations of both properties with each other and with the porosity. The lack of consistency of the high frequency conductivity data may be related to the fact that the relaxation times of the effective dielectric constant and effective conductivity become more dissimilar at high frequency.

#### Conclusions

Capacitors of IBLC-type device architecture were fabricated from a 0.8 mole% Y<sub>2</sub>O<sub>3</sub>-doped SrTiO<sub>3</sub> composition and then sintered over a range of temperatures and times. The effective dielectric constant and effective conductivity were found to be highly correlated with each other, at each frequency of analysis. The two electrical properties were in turn found to strongly decrease with increasing porosity. Three scaling law models were developed to account for how porosity in the grain boundary region can lead to decreases in electrical properties with increasing porosity. Although none of the scaling law models directly predicted the observed dependence of the electrical properties on porosity, the models were able to show how such a dependence can arise, and furthermore point out the importance of accurately accounting for porosity in the grain boundary region.

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