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Multilayer Ceramic Capacitors with Thin (Ba,Sr)TiO_3 Layers by MOCVD

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Abstract. Barium strontium titanate ((Ba,Sr)TiO_3; BST) thin films were prepared on platinum-coated MgO substrates at 650°C by metalorganic chemical vapor deposition (MOCVD). Perovskite single phased BST thin films were obtained. Dielectric constant at 1 kHz–100 mV was 1000. Multilayer ceramic capacitor with twelve BST dielectric layers of 0.26 μm thick was formed on the MgO substrate. Capacitance and dissipation factor (tanδ) at 1 kHz–100 mV were 32 nF and 1.5% respectively. Capacitance per unit volume of 33 μF/mm^3 provided 10 to 20 times larger volumetric efficiency than the conventional multilayer ceramic capacitors. Temperature coefficient of capacitance was -4000 ppm/°C. The leakage current at 1 V was 2.3×10^{-9} A that yielded an acceptable CR product of 12.8 MΩ-μF. MOCVD was proposed as one of the promising manufacturing technologies for multilayer ceramic capacitors of high performance with sub-micron thick dielectric layers.

Keywords: chemical vapor deposition, barium strontium titanate, multilayer ceramic capacitors, ferroelectric thin film

1. Introduction

With the advent of advanced electronic circuits, the increasing need for miniaturized passive components is continuing. Under these circumstances, significant advances have been achieved in the technology of high volumetric multilayer ceramic capacitors (MLCs) composed with hundreds of dielectric layers less than 3 μm in thickness. We believe that a conventional sheet and/or printing method has a technical limit of the dielectric thickness of around 1 μm. Therefore, new techniques are required to prepare the multilayer ceramic structure with high dielectric constant materials of sub-micron thickness. Several attempts to design the MLCs with thin film technology of metalorganic chemical vapor deposition (MOCVD) have been reported by the present authors [1,2].

Barium strontium titanate ((Ba,Sr)TiO_3; BST) thin films of high dielectric constant have been applied for high-density dynamic random access memory (DRAM) and the monolithic microwave integrated circuit (MMIC). For these applications, thin film technologies with MOCVD [3–6], sputtering [7–10], laser ablation [11–13] and sol-gel process [14] have been developed. Among these techniques, MOCVD has several advantages such as excellent coverage, high deposition rate and precise control of the composition. The gap coverage is particularly important factor for MLCs, because the thickness gaps between active electrodes and side margin area increase with layer count.

In this work, we investigated the microstructure and dielectric properties of BST thin films prepared by MOCVD, and designed the MLCs to demonstrate the new technologies for next generation of capacitor manufacturing.

2. Experimental

A schematic diagram of our MOCVD system is shown in Fig. 1. Bis-dipvaloylmethanate barium phenanthroline adduct ($Ba(DPM)_2(phen)_2$), bis-dipvaloylmethanate strontium phenanthroline adduct ($Sr(DPM)_2(phen)_2$) and titanium isopropoxide ($Ti(i-OC_3H_7)_4$) were used as MOCVD sources. A cold-wall type reactor was used to prevent the reaction

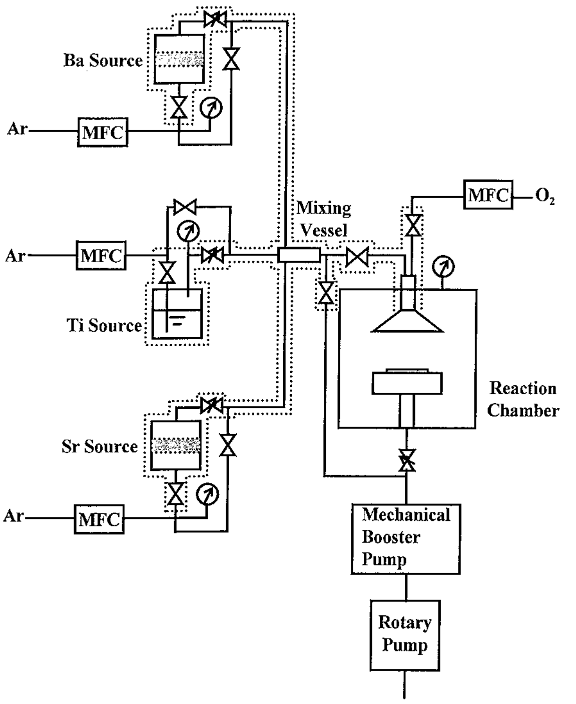

Fig. 1. Schematic diagram of the MOCVD apparatus for the preparation of BST films.

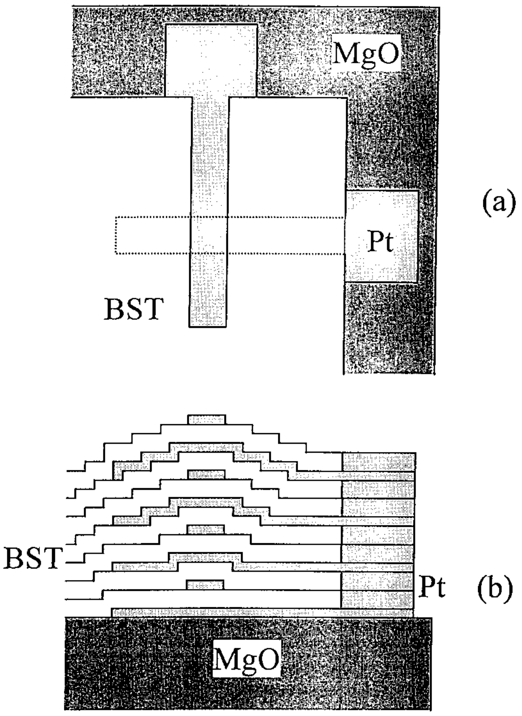

Fig. 2. Schematic (a) upper view and (b) cross section of the multilayer capacitor with BST thin layers.

of the metalorganic sources from occurring in the vapor phase. Oxygen as an oxidant, and argon as a carrier gas were used. Vapor pressure of Ti source was controlled by needle valve located between the source and mixing vessel. Temperature of a tube between Ti source vessel and mixing vessel was controlled at 80°C, and the other tubes and mixing vessel was hold at 250°C. Metalorganic vapors containing argon were transported separately to the mixing vessel and then mixed. The mixed metalorganic vapor was introduced to the reaction chamber with argon and oxygen gases. The substrate temperature was measured by an optical pyrometer and controlled at 650°C. The deposition conditions of the BST thin films are summarized in Table 1.

Substrates of Pt(111)/MgO(100) and Pt(100)/MgO(100) were used for dielectric deposition. Pt(111) films were deposited as electrode at temperature lower than 100°C using the RF magnetron sputtering. Pt(100) films were epitaxially grown at 600°C.

A schematic structure of MLC with BST dielectrics and Pt electrode is shown in Fig. 2. Pt electrode was formed by RF magnetron sputtering. Pt electrode of 0.4 mm wide overlapped to the counter Pt electrode at a right angle. The MLC samples on the MgO(100) substrate were prepared by alternative depositions of the BST ultra-thin dielectrics layer and Pt electrode. After the deposition process, the capacitor was annealed at 650°C for 100 h in air.

Table 1. Deposition conditions of BST films

Source temperature	
$Ba(DPM)_2(phen)_2$	210–220°C
$Sr(DPM)_2(phen)_2$	195–205°C
$Ti(i-OC_3H_7)_4$	35°C
Pressure of Ti source vessel	15–21 kPa
Ar carrier gas flow rate	
$Ba(DPM)_2(phen)_2$	50 CCM
$Sr(DPM)_2(phen)_2$	50 CCM
$Ti(i-OC_3H_7)_4$	35 CCM
O_2 gas flow rate	480 CCM
Substrate temperature	650°C
Total pressure	130–670 Pa
Deposition time	60–120 min

The crystalline phases and crystal orientation of the single layer BST thin films were identified by the X-ray diffraction (XRD). Microstructure and composition of the films were analyzed by a scanning electron microscope (SEM) and energy dispersive X-ray spectroscopy (EDX). Electrical properties of the BST thin film were measured with Pt top electrodes of 0.5 mm in diameter. Capacitance and dissipation factor were measured by LCR meter (HP 4284A). Leakage current was measured by electrometer (KEITHLEY Model 6517). Roughness of the BST thin films was measured by an atomic force microscope (AFM) (Nanoscope 3A).

3. Results and Discussion

3.1. *BST Thin Film*

Dielectric properties of the BST film were studied under several process conditions to obtain the optimal composition and deposition conditions for the MLCs. The maximum dielectric constant of 1000 was obtained in the composition of $(Ba_{0.6}, Sr_{0.4})TiO_3$. Dielectric constant change with oxygen pressure in the reaction chamber is shown in Fig. 3. Dielectric constant increased with increasing oxygen pressure. Growth rate of the thin films decreased at higher oxygen pressure than 500 Pa. It was supposed that the vapor pressure of both Ba and Sr decreased with increasing pressure of their source vessel.

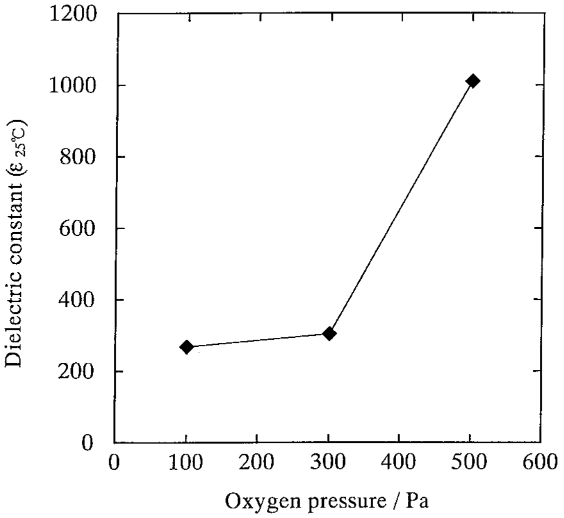

Fig. 3. Dielectric constant of BST thin films as a function of oxygen pressure in the reaction chamber.

The XRD patterns of the BST thin films deposited on Pt(100)/MgO substrates under several oxygen pressures are shown in Fig. 4. As shown in this figure, the BST films had perovskite phase symmetry and oriented to the [100] direction. The peak intensity of (100) diffraction increased with increasing oxygen pressure. It was confirmed that the change of dielectric constant with oxygen pressure was attributed to the crystallinity of the BST thin films. On the other hand, any peak without the peaks of MgO substrate and Pt film were hardly observed in the XRD patterns of the BST thin films on Pt(111)/MgO. The BST films deposited on Pt(111)/MgO substrates were oriented to the [111] direction, and the peak of BST(111) overlapped with Pt(111) peak. SEM images of the BST on the Pt(100)/MgO and Pt(111)/MgO substrate are shown in Fig. 5. The BST thin film on the Pt(100)/MgO substrate had a rectangular shaped grains. On the other hand, the film on the Pt(111)/MgO substrate was composed of triangle shaped grains. It was confirmed that the orientation of the Pt electrode characterized the orientation and morphology of the BST dielectric layer.

The dielectric properties of the BST thin films deposited on Pt(111)/MgO substrates are summarized in Table 2. Dielectric constant at room temperature, (at 1 kHz and 100 mV) was 1000 and the highest value in this work. The capacitance slightly degreased with frequency, which was similar result with the BST bulk ceramics [15]. The $(Ba_{0.6}, Sr_{0.4})TiO_3$ bulk ceramics gives maximum value of dielectric constant at Curie temperature around −10°C. However, capacitance of the dielectric film changed with temperature at a rate of −4000 ppm/°C in the range from −55°C to +125°C. Curie point of the film was supposed to be shifted to the temperature lower than −55°C due to the external stress from the substrate and/or grain size effects. The leakage current density was of the order of 10^{-8}A/cm^2 at voltage stress below 200 kV/cm. Withstanding voltage field was above 500 kV/cm. The dielectric properties of the BST thin films deposited on Pt(100)/MgO were comparable to those of the films on Pt(111)/MgO. The single layer BST thin film obtained in this work was applied for MLCs with sub-micron thick dielectrics.

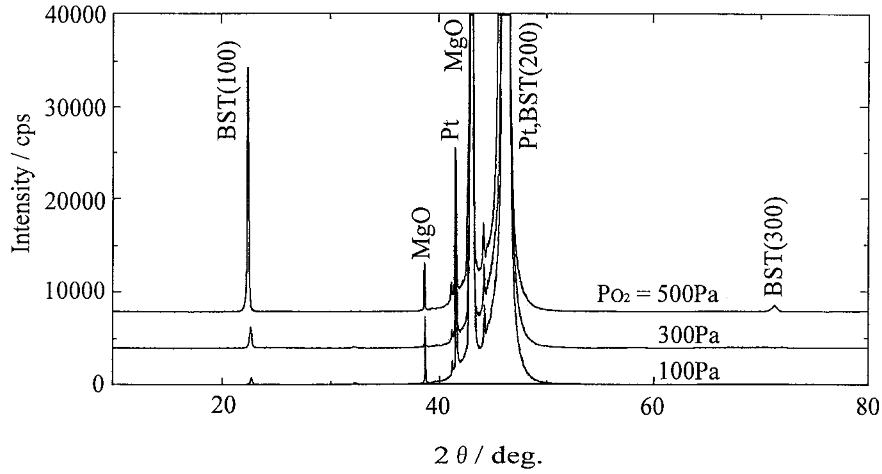

Fig. 4. XRD patterns of BST thin films deposited at various oxygen pressures.

3.2. Multilayer Ceramic Capacitor with BST Thin Layers

MLCs with sub-micron dielectric layer on MgO substrate were prepared to demonstrate the technical potentials of MOCVD method for manufacturing the advanced MLCs providing the highest volumetric efficiency. Figure 6 shows the SEM image of the cross sectional view of the capacitor. The capacitor was constructed with twelve BST dielectric layers and thirteen Pt electrode layers. The average thickness of dielectric and electrode was 0.26 μm and 0.20 μm respectively, which result in total thickness of 5.7 μm. Thickness uniformity of the dielectric layer was poor at layer by layer. This could be caused by unstable vapor pressure of source materials in our MOCVD system. The deposited layers were wavy in shape. This layer deformation was magnified with increasing the layer count. The morphology of the substrate surface was transferred to the newly deposited layer on it. The dielectric properties of the capacitor are summarized in Table 3. The MLC of 0.4 mm by 0.4 mm in size provided capacitance of 32 nF, and dissipation factor (tanδ) of 1.5% at 1 kHz–100 mV. Capacitance per unit volume of 33 μF/mm^3 was derived from the capacitance value and dimension of 0.4 mm × 0.4 mm × 5.7 μm. This volumetric efficiency was 10 to 20 times larger than that of the conventional chip MLCs and tantrum electrolytic capacitors. As can be seen from Table 2 comparing

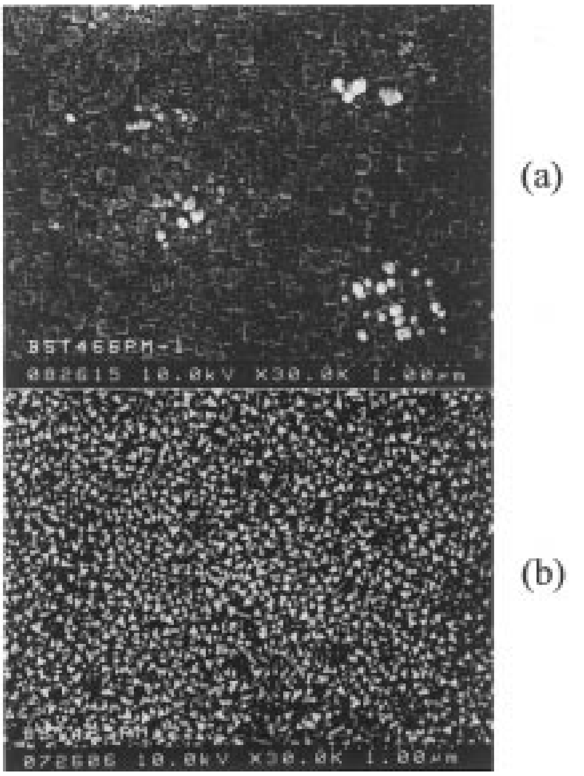

Fig. 5. SEM images of BST film on (a) Pt(100)/MgO(100) substrate and (b) Pt(111)/MgO(100) substrate.

Table 2. Dielectric properties of the BST thin film

Dielectric constant at 1 kHz	1000
Dissipation factor (tanδ)	2.2%
Capacitance change (ΔC/C)	
− 55°C– + 125°C	− 4000 ppm/°C
100 Hz–1 MHz	− 11%

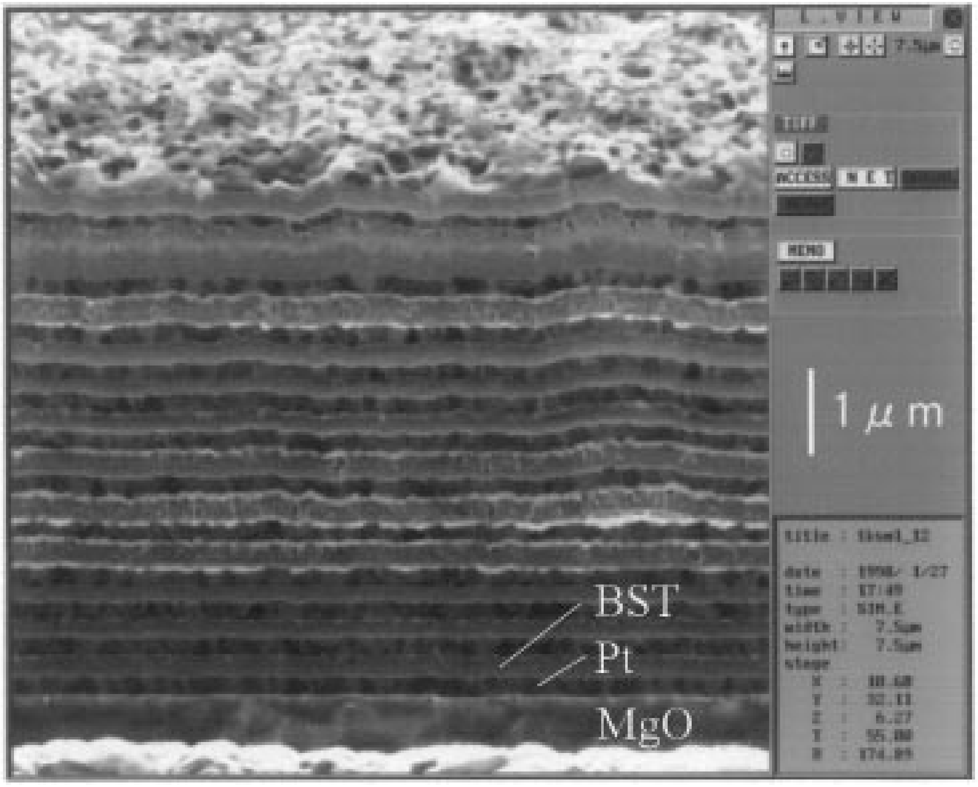

Fig. 6. Cross sectional SEM image of the multilayer capacitor with twelve BST dielectric layers. (Average thickness of dielectric layer is 0.26 μm.).

with Table 3, frequency and temperature dependence of the single layer and multilayer capacitance agreed fairly well with each other. It was confirmed that the dielectric properties of the BST single layer capacitor were reproduced on MLC.

Table 3. Characteristics of the multilayer ceramic capacitors by MOCVD

Dimension	0.4 mm × 0.4 mm × 5.7 μm
Materials	$(Ba_{0.6}, Sr_{0.4})TiO_3$ (dielectric) Pt (electrode)
Substrate	MgO
Average thickness of the layer	0.26 μm (dielectric) 0.20 μm (electrode)
Capacitance at 1 kHz	32 nF
Capacitance per unit volume	33 $\mu F/mm^3$
Dissipation factor (tanδ)	1.5%
Capacitance change (ΔC/C)	
− 55°C to + 125°C	− 4100 ppm/°C
100 Hz to 1 MHz	− 7.7%
Leakage current at 1 volt	2.3×10^{-9} A
CR product	12.8 MΩ-μF

As mentioned before, the MLC was annealed at 650°C in air for 100 h. With this heat treatment, tanδ and leakage current was so much improved. This improvement was attributed to reoxidation of the dielectrics. Before this annealing, the capacitor showed tanδ of more than 10%, which was caused by leaky characteristic of the dielectrics. The BST dielectrics deposited at early deposition cycles were exposed in a low oxygen atmosphere for long time, which resulted in dissociation of oxygen from the dielectrics. The high dielectric loss and leakage current were attributed to the oxygen deficiency. The dielectrics had a large capacitance change with dc bias field as shown in Fig. 7.

Figure 8 shows the I-V curve of the MLC with the twelve BST thin layers. The leakage current at 1 V was 2.3×10^{-9} A that yielded an acceptable CR product of 12.8 MΩ-μF. Insulation resistance of the mulitilayer capacitor was strongly affected by quality and homogeneity of the dielectric layer. Table 4 shows the roughness of the BST films. The BST single

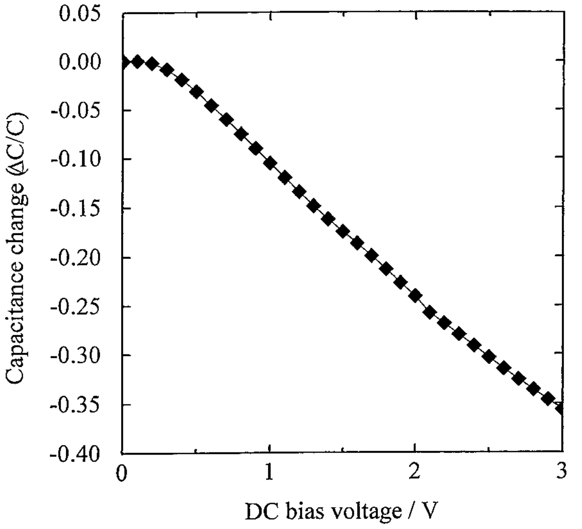

Fig. 7. DC bias voltage dependence of capacitance.

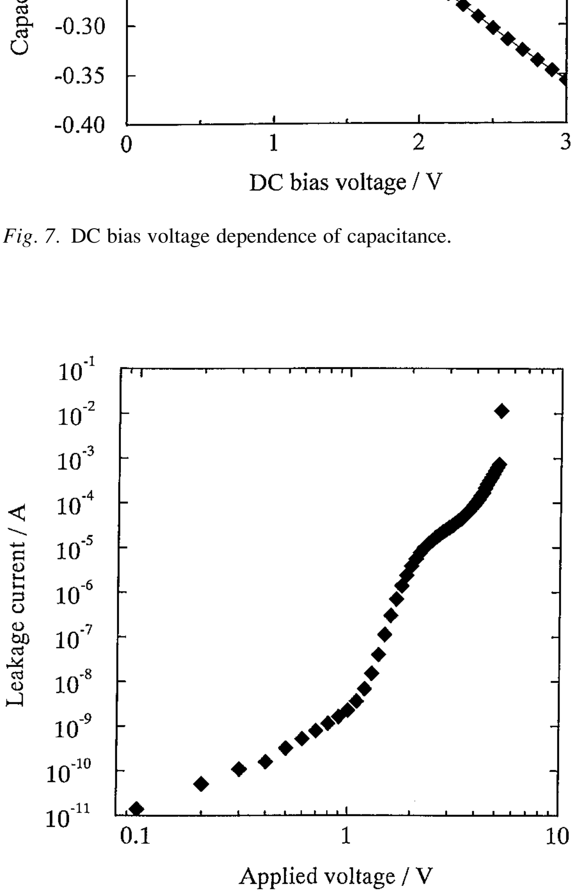

Fig. 8. I-V curve of the multilayer capacitor with twelve BST dielectric layers.

layer showed rather smooth surface of roughness 12 nm. But the homogeneity of the dielectric layers was getting poor with stacking cycle. Extended studies on MOCVD are required to control the multilayer structure and quality of dielectric layers for highly reliable MLCs.

Table 4. Roughness of the BST films

Number of BST layers	Average roughness (Ra)
1	12 nm
8	42 nm
12	37 nm

4. Summary

$(Ba_{0.6}, Sr_{0.4})TiO_3$ thin films were prepared by MOCVD in oxygen atmosphere using $Ba(DPM)_2(phen)_2$, $Sr(DPM)_2(phen)_2$ and $Ti(i - OC_3H_7)_4$ as starting materials. The perovskite single phased BST were obtained on the Pt/MgO substrate. The dielectric constant at room temperature was 1000 at 1 kHz-100 mV. The MLCs (0.4 mm x 0.4 mm x 5.7 μm) with twelve $(Ba_{0.6}, Sr_{0.4})TiO_3$ layers of 0.26 μm were formed on MgO substrates. Capacitance and dissipation factor (tanδ) at 1 kHz-100 mV were 32 nF and 1.5%, respectively. Capacitance per unit volume of 33 μF/mm^3 provided 10 to 20 times larger volumetric efficiency than the conventional MLCs. The temperature coefficient of capacitance was -4100 ppm/°C. The leakage current at 1 V was 2.3×10^{-9} A that yielded an acceptable CR product of 12.8 MΩ-μF. The insulation resistance of the MLC was strongly affected by the quality and homogeneity of the dielectric layer. The BST dielectric and the process conditions were applicable for preparing the multi-layers capacitor. The MOCVD method gave us one of the promising manufacturing technologies for high performance ceramic capacitors with sub-micron thick dielectric layers of high layer count.

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