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Summary of Research Findings:

1. Stoichiometry and Deposition Temperature Dependence of the Microstructural and Electrical Properties of Barium Strontium Titanate Thin Films

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Conclusions

The Group II/Ti ratio should be as close as possible, but should not exceed the stoichiometric value of 1.00, and the grain size should be as large as possible in order to optimize the electrical properties of BST thin films deposited using LS-MOCVD.

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The Effect of Deposition Temperature

Conclusions

The Group II/Ti ratio should be as close to 1.00 as possible. The effects of grain size and volume fraction on the amorphous phase are of secondary importance when the stoichiometry ratio is close to 1.00. The Group II/Ti ratio plays a far greater role in controlling the electrical properties of BST films than the deposition temperature, grain size, or amorphous phase volume fraction.

2. Microstructural and Electrical Characterization of Barium Strontium Titanate Thin Films[2]

Conclusions

A microstructure consisting of cubic BST plus a second amorphous phase is characteristic of BST thin films and not the deposition process used for their synthesis. When the Group II/Ti ratio is close to one, the grain size is not related to the electrical properties of the thin films.

The Genius Chip:

Three-Dimensional Ferroelectric Integrated Circuits - Prototype Fabrication and Interface Studies

Final Technical Report

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List of Manuscripts:

Microstructural and Electrical Characterization of Barium Strontium Titanate Thin Films
Y. Wu, E.G. Jacobs, R.F. Pinizzotto, R. Tsu, H.-Y. Liu, S.R. Summerfelt and B.E. Gnade
Materials Research Society Symposium Proceedings, **361** (1995) 269

Effect of a Ge Barrier on the Microstructure of BaTiO3 Deposited on Silicon by Pulsed Laser Ablation
E.G. Jacobs, Y.G. Rho, R.F. Pinizzotto, S.R. Summerfelt and B.E. Gnade
Materials Research Society Symposium Proceedings, **285** (1993) 379

Cross-Sectional TEM Studies of Barium Strontium Titanate Deposited on Silicon by Pulsed Laser Ablation
R.F. Pinizzotto, E.G. Jacobs, H. Yang, S.R. Summerfelt and B.E. Gnade
Materials Research Society Symposium Proceedings, **243** (1992) 463-468

M.S. Thesis:
Stoichiometry and Deposition Temperature Dependence of the Microstructural and Electrical Properties of Barium Strontium Titanate Thin Films
P. Peña
Master of Science in Chemistry, University of North Texas, May 1998

List of Presentations:

Deposition Temperature Dependence of Microstructural and Electrical Properties of BST Thin Films
P. Peña
Texas Society for Electron Microscopy Fall Meeting
Austin, Texas, October 1995

The Effect of Stoichiometry on the Microstructural and Electrical Properties of BST Thin Films
R.F. Pinizzotto
Materials Research Society Annual Meeting
Boston, Massachusetts, November 1994

The Genius Chip: Three-Dimensional Ferroelectric Integrated Circuits, Prototype Fabrication and Interface Studies
R.F. Pinizzotto
Army Research Office Workshop on Intelligent Materials
Boston, Massachusetts, August 1994

Ferroelectric Integrated Circuits: The Genius Chip
R.F. Pinizzotto
Center for Network Neuroscience 1994 Symposium - University of North Texas
Denton, Texas, March 1994

Microstructural and Electrical Characterization of Barium Strontium Titanate Thin Films
Y. Wu
Materials Research Society Annual Meeting
Boston, Massachusetts, November 1994

Three-Dimensional Ferroelectric Integrated Circuits: A New Category of Electronic Device
R.F. Pinizzotto
International Symposium on Integrated Ferroelectrics
Colorado Springs, Colorado, April 1993

The Genius Chip: Three-Dimensional Ferroelectric Integrated Circuits
R.F. Pinizzotto
University of North Texas Center for Materials Characterization Seminar
Denton, Texas, August 1993

A Dark Field TEM Study of the Microstructure of $BaTiO_3$ *on Si and Si/Ge*
Y. G. Rho
Texas Society for Electron Microscopy Fall Meeting
Galveston, Texas, October 1993

Effect of a Ge Barrier Layer on the Microstructure of $BaTiO_3$ *On Silicon*
E. G. Jacobs
International Symposium on Integrated Ferroelectrics
Colorado Springs, Colorado, April 1993

Effect of a Ge Barrier Layer on the Microstructure of $BaTiO_3$ *on Silicon*
Y. G. Rho
Texas Academy of Sciences Meeting
Denton, Texas, March 1993

Effect of a Ge Barrier on the Microstructure of $BaTiO_3$ *Deposited on Silicon by Pulsed Laser Ablation*
E. G. Jacobs
Materials Research Society Annual Meeting
Boston, Massachusetts, December 1992

Electron Microscopy of the $BaTiO_3$*/Ge Interface*
Y. G. Rho
Texas Society for Electron Microscopy Fall Meeting
Austin, Texas, October 1992

TEM Studies of Barium Strontium Titanate Deposited on Silicon by Pulsed Laser Ablation
E. G. Jacobs
ACS, ECS, MRS Eleventh Annual Joint Symposium on Electronic Materials, Processing and Characterization
Richardson, Texas, June 1992

Cross-Sectional TEM Studies of Barium Strontium Titanate Deposited on Silicon by Pulsed Laser Ablation
E. G. Jacobs
Texas Society for Electron Microscopy Spring Meeting
San Marcos, Texas, March, 1992

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4. Hong Yang

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Report of Inventions by Title:

A Three-Dimensional Ferroelectric Integrated Circuit:
R.F. Pinizzotto, C.L. Littler and B.E. Gnade (Texas Instruments).

List MS or PhD degrees conferred:

Stoichiometry and Deposition Temperature Dependence of the Microstructural and Electrical Properties of Barium Strontium Titanate Thin Films

P. Peña, Master of Science in Chemistry, May 1998

Summary of Research Findings:

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1. Stoichiometry and Deposition Temperature Dependence of the Microstructural and Electrical Properties of Barium Strontium Titanate Thin Films[1]

The Effect of Stoichiometry

Samples were prepared on substrates consisting of (100) single crystal silicon, 50 nm of thermally grown SiO_2, 50 nm of ZrO_2 and 100 nm of Pt. Thin films of barium strontium titanate (BST) were deposited using liquid-source metalorganic chemical vapor deposition (LS-MOCVD). All deposition conditions were held constant except for the concentration of the titanium precursor. This resulted in the Group II/Ti ratio varying from 0.658 to 1.022 (Table 1).

The microstructure of the samples was found to consist of three types of material: two different crystalline morphologies - equiaxed and triangular - embedded within an amorphous matrix (Figure 1). In this figure, several grains are indicated with arrows. The lighter contrast material between the grains is the amorphous phase.

The volume fraction of equiaxed grains increased with increasing Group II/Ti ratio up to a ratio of 1.00. The volume fraction of triangular grains was essentially random. Both the equiaxed and the triangular crystalline materials were found to be the cubic phase of BST using selected area electron diffraction. The average grain size varied from 20 to 40 nm, with an average of 30 nm, and was independent of stoichiometry. The amorphous phase was identified using micro-micro-diffraction, a form of focused beam electron diffraction in the scanning transmission electron microscopy mode. Micro-micro diffraction has a spatial resolution of approximately 10 nm.

The volume fraction of the amorphous phase decreased with increasing Group II/Ti ratio up to a ratio of 1.00 (Figure 2). When the Group II/Ti ratio exceeded 1, the volume fraction of amorphous phase increased.

The dielectric constant of the BST film increased with increasing grain size (Figure 3) and with increasing BST volume fraction (Figure 4). It should be noted that the outlier in both of these figures is sample 152, which is the only sample with a Group II/Ti ratio greater than 1. The capacitance per unit area (Figure 5) and dielectric constant increased with increasing Group II/Ti ratio for samples in which the ratio was less than 1.00.

Conclusions

The Group II/Ti ratio should be as close as possible, but should not exceed the stoichiometric value of 1.00, and the grain size should be as large as possible in order to optimize the electrical properties of BST thin films deposited using LS-MOCVD.

The Effect of Deposition Temperature

Samples were prepared on Si/SiO2/ZrO_2/Pt substrates as described above. The substrate temperature for LS-MOCVD was varied from 550 to 700C while all other deposition conditions were held constant. The reported deposition temperatures are approximate, since the actual deposition temperatures are proprietary information of ATM, Inc., the company that synthesized the samples. The Group II/Ti ratio was constant relatively constant, varying from 0.964 to 0.987 (Table 2).

The observed microstructures of the BST thin films were similar to those reported above for the stoichiometry series (Figure 6). In this figure, a typical equiaxed grain is labeled E and a triangular grain is labeled T. As expected, the grain size increased with increasing deposition temperature from 15 to 27 nm (Figure 7). The amorphous phase decreased from 40 to 10% of the projected area as measured in the transmission electron micrographs (Figure 8).

The strongest correlation observed was between Group II/Ti ratio and the dielectric constant (Figure 9). As can be seen, the dielectric constant increases dramatically when the Group II/Ti ratio is greater than 0.975, but there is significant scatter in the data. The dielectric constant and capacitance per unit area were independent of the deposition temperature. The dielectric constant was also independent of both average grain size and BST area.

Conclusions

The Group II/Ti ratio should be as close to 1.00 as possible. The effects of grain size and volume fraction on the amorphous phase are of secondary importance when the stoichiometry ratio is close to 1.00. The Group II/Ti ratio plays a far greater role in controlling the electrical properties of BST films than the deposition temperature, grain size, or amorphous phase volume fraction.

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2. Microstructural and Electrical Characterization of Barium Strontium Titanate Thin Films[2]

BST films were deposited on Pt electrodes on Si substrates using metalorganic decomposition. The BST films were rapid thermally annealed for 30 to 120 sec at temperatures ranging from 550 to 950C. The Group II/Ti ratio was held constant at 0.952.

The average grain size increased from 15 to 27 nm with increasing anneal temperature, but did not depend on the RTA anneal time (Figure 10). The amount of amorphous phase decreased from 40 to less than 10% of the total area as observed by TEM.

The dielectric constant did not depend on the grain size (Figure 11).

The microstructures of the films were similar to those described for the LS-MOCVD BST described above. They consisted of both a crystalline phase and an amorphous material between the grains (Figure 12).

Conclusions

A microstructure consisting of cubic BST plus a second amorphous phase is characteristic of BST thin films and not the deposition process used for their synthesis. When the Group II/Ti ratio is close to one, the grain size is not related to the electrical properties of the thin films.

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3. Effect of a Ge Barrier on the Microstructure of $BaTiO_3$ Deposited on Silicon by Pulsed Laser Ablation[3]

Barium titanate (BT) thin films were deposited using pulsed laser ablation. The substrates were either (100) silicon or (100) Si plus a 300 nm thick layer of Ge.

For BT deposited on Si, an amorphous interfacial layer was observed. The grains were columnar. There was weak electron diffraction evidence that $TiSi_2$ may be present near the interface.

For BT deposited on Ge, an amorphous interfacial layer was not observed. There is a strong preferred orientation of the grains indicating epitactic growth.

The grain sizes for BT on Si and Ge are lognormally distributed. The grain size is affected by the substrate type with the BT grain sizes on Ge substrates being slightly larger.

Table 1. Stoichiometry Series Samples

Sample No.	Group II/Ti Ratio
136	0.658
138	0.733
146	0.789
161	0.856
157	~0.9
152	1.022

Table 2. Deposition Temperature Series Samples

Sample No.	Approximate Deposition Temperature (C)	Group II/Ti Ratio
A1	**700**	**0.976**
A2	**700**	**0.973**
B	**650**	**0.970**
C1	**600**	**0.987**
C2	**600**	**0.964**
D	**550**	**0.970**

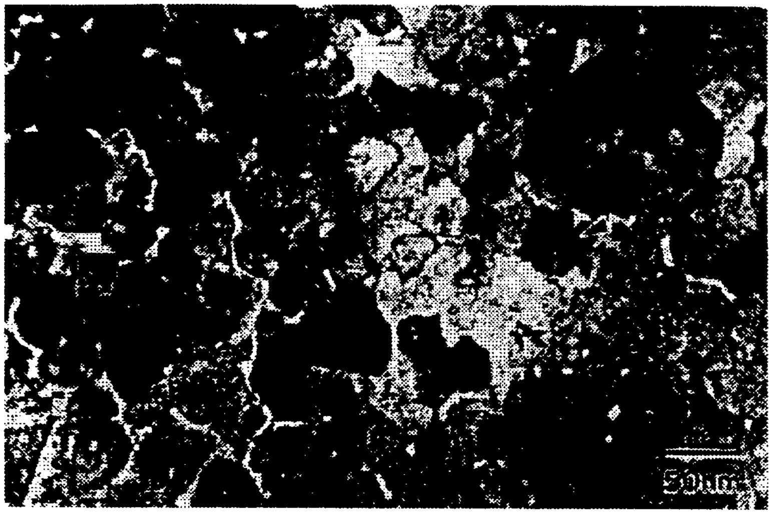

Figure 1. A typical microstructure for thin BST films synthesized using LS-MOCVD. This sample is part of the stoichiometry series. The arrows indicate typical equiaxed grains. The lighter contrast areas between the grains are the amorphous second phase.

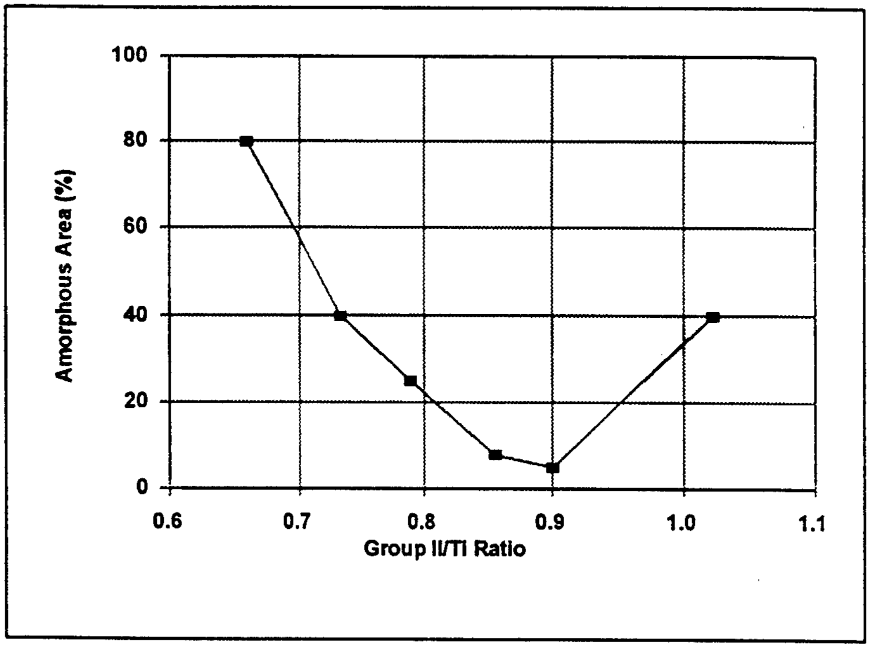

Figure 2. Amorphous area vs. Group II/Ti ratio for the stoichiometry series of BST thin films synthesized using LS-MOCVD.

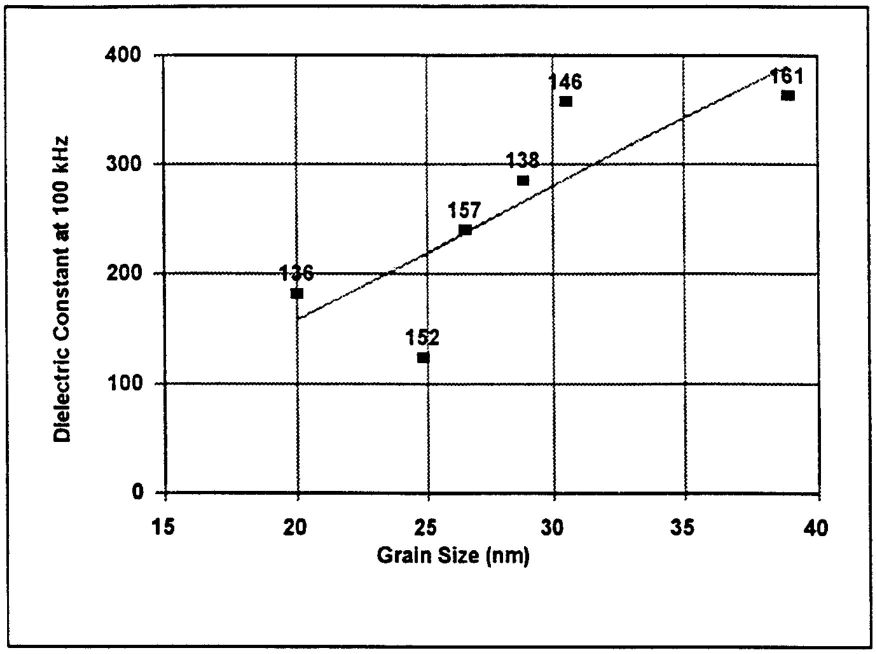

Figure 3. Dielectric constant at 100 kHz vs. grain size for the stoichiometry series of BST thin films synthesized using LS-MOCVD. The sample identifications are listed in Table 1.

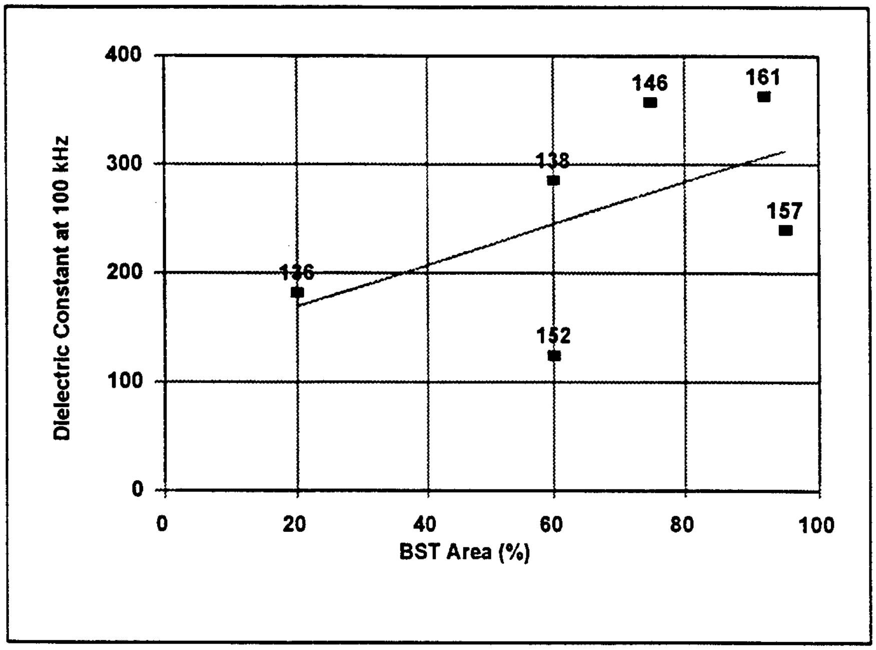

Figure 4. Dielectric constant at 100 kHz vs. BST area for the stoichiometry series of BST thin films synthesized using LS-MOCVD. The sample identifications are listed in Table 1.

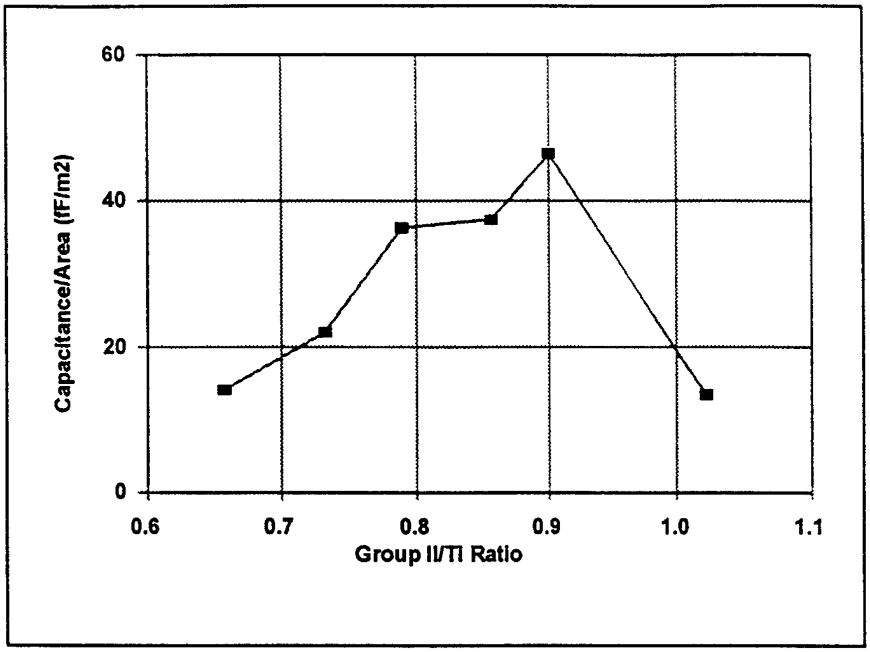

Figure 5. Capacitance per unit area vs. Group II/Ti ratio for the stoichiometry series of BST thin films synthesized using LS-MOCVD.

Figure 6. A typical bright field microstructure of thin BST films synthesized using LS-MOCVD. This sample is part of the deposition temperature series. E: equiaxed grain; T: triangular grain; A: amorphous material.

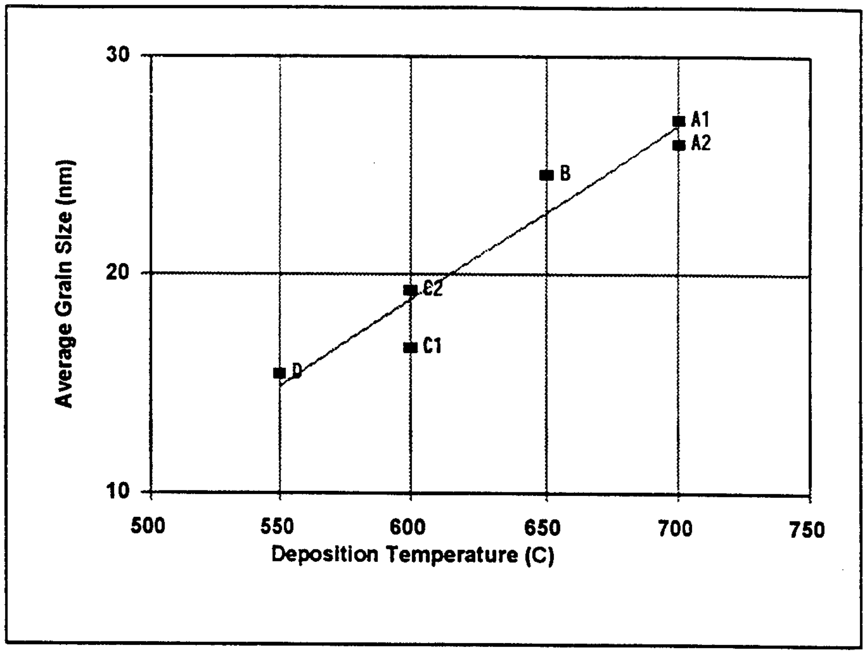

Figure 7. Average grain size vs. deposition temperature for the temperature series of BST thin films synthesized using LS-MOCVD. The sample identifications are listed in Table 2.

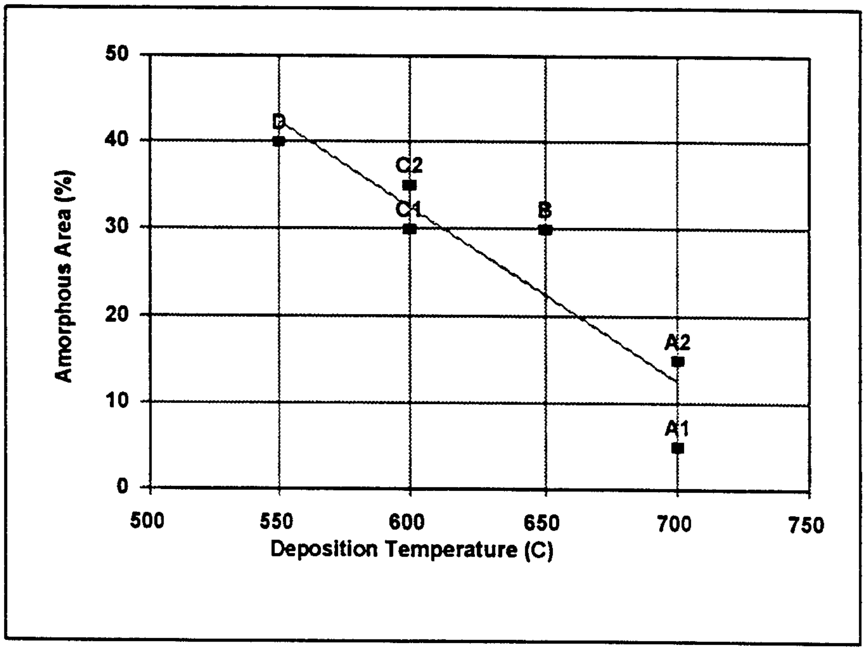

Figure 8. Amorphous area size vs. deposition temperature for the temperature series of BST thin films synthesized using LS-MOCVD. The sample identifications are listed in Table 2.

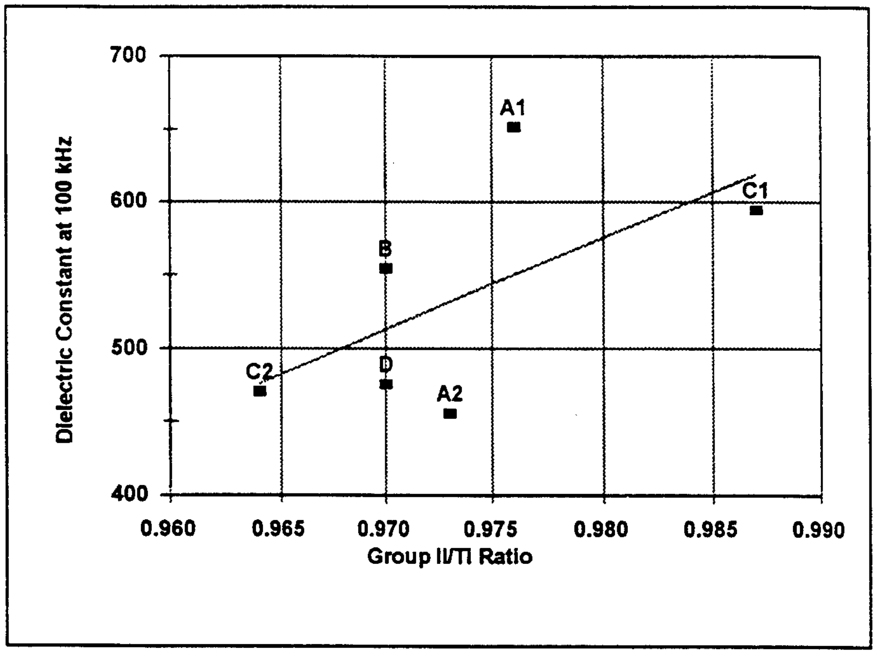

Figure 9. The effect of Group II/Ti ratio on the dielectric constant at 100 kHz for the temperature series of thin BST films synthesized using LS-MOCVD. The sample identifications are listed in Table 2.

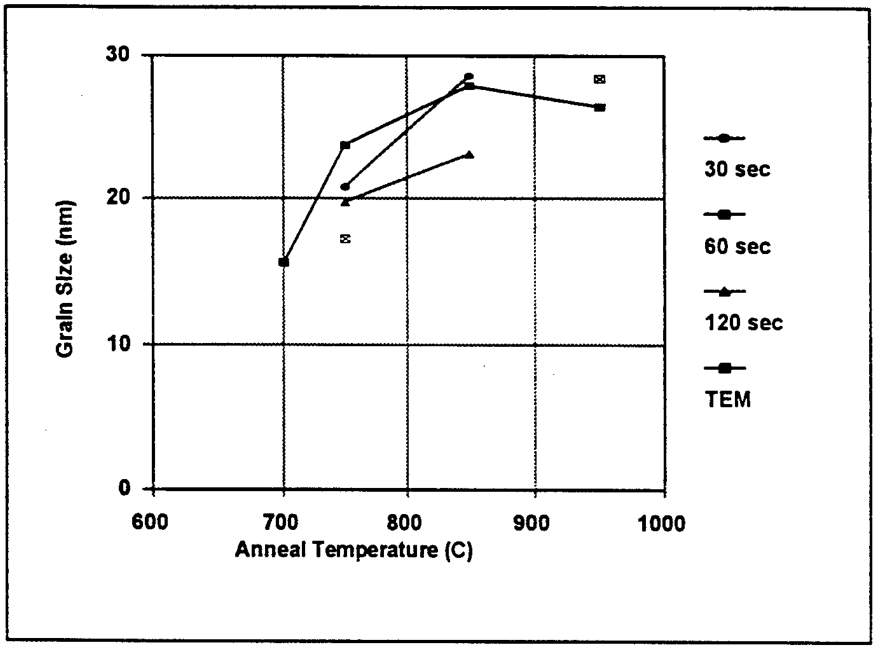

Figure 10. The effect of anneal temperature on grain size for the BT films synthesized using MOD. Except where indicated, the measurements were obtained using x-ray diffraction.

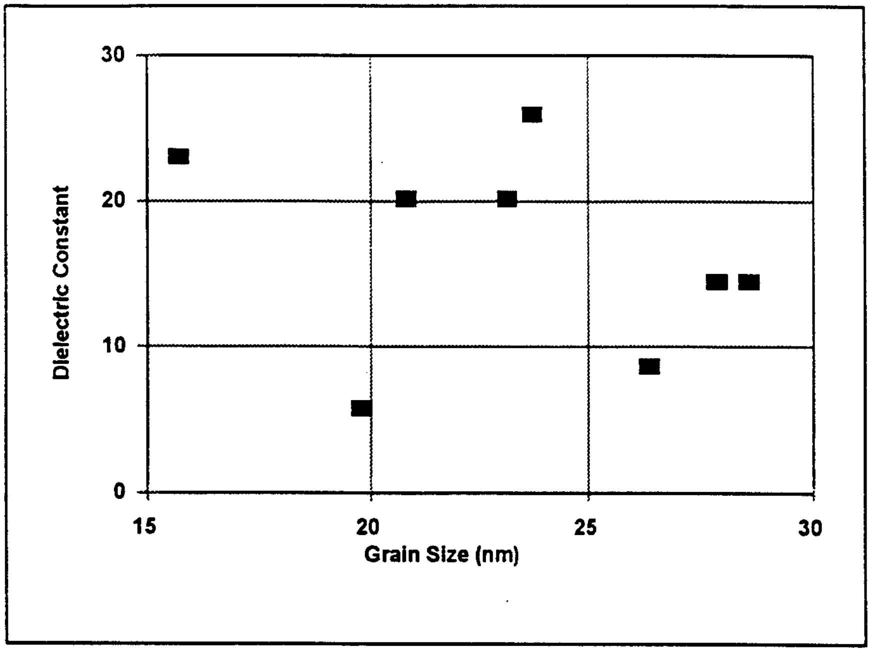

Figure 11. Effect of grain size on the dielectric constant of BT films synthesized using MOD and RTA.

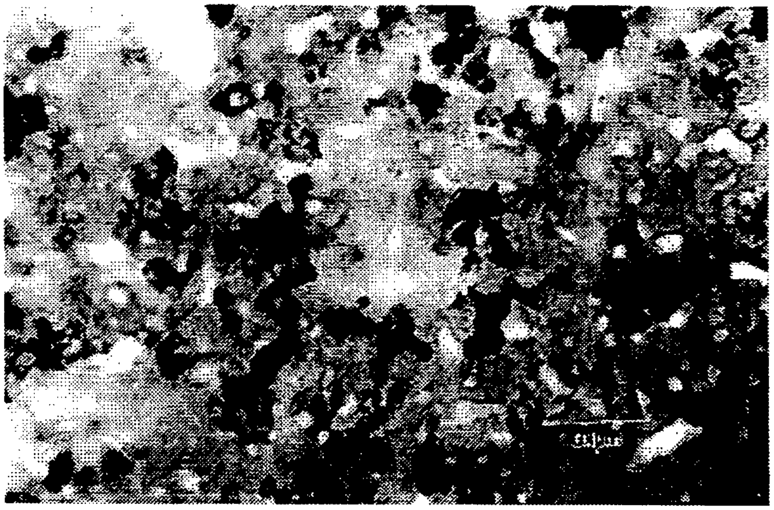

Figure 12. Typical microstructure of a BT thin film synthesized using MOD and RTA.

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1. P. Peña, *Stoichiometry and Deposition Temperature Dependence of the Microstructural and Electrical Properties of Barium Strontium Titanate Thin Films,* M.S. Thesis, University of North Texas, Denton, Texas, May 1998.

2. Y. Wu, E.G. Jacobs, R.F. Pinizzotto, R. Tsu, H.-Y. Liu, S.R. Summerfelt and B.E. Gnade, *Microstructural and Electrical Characterization of Barium Strontium Titanate Thin Films*, Materials Research Society Symposium Proceedings, **361** (1995) 269.

3. E.G. Jacobs, Y.G. Rho, R.F. Pinizzotto, S.R. Summerfelt and B.E. Gnade, *Effect of a Ge Barrier on the Microstructure of BaTiO3 Deposited on Silicon by Pulsed Laser Ablation*, Materials Research Society Symposium Proceedings, **285** (1993) 379.