1995 North American Conference on
Smart Structures and Materials

26 February–3 March 1995
Catamaran Resort Hotel
San Diego, California USA

Smart Materials, Sensing, Processing, and Instrumentation

Industrial and Commercial Applications of Intelligent Systems

Smart Systems for Bridges, Structures, and Highways

Passive Damping
Smart Electronics

Including
Poster Sessions
Educational Short Courses
Tabletop Exhibition
Technical Program Updates (continued)

Conference 2447
Industrial and Commercial Applications of Smart Structures Technologies (Crowe, Anderson)

THURSDAY 2 MARCH
Session 2: Industrial Problems and Solutions II (Gackstatter, Sater)

Time Change: 5:00 pm: Active smart material system for butt load alleviations, K. B. Lazarus, E. Saarma, Active Control eXperts; G. S. Agnes, Air Force Wright Lab. ........ [2447-18]

Conference 2448
Smart Electronics (Varadan, Littlejohn, McWhorter)

THURSDAY 2 MARCH
Session 1: Millimeter Wave and Conformal Antennas (Varadan)

Canceled: 9:40 am: Overview of conformal antenna, R. E. Munson, Ball Aerospace Systems Group ....... [2448-02]
Added: 9:40 am: Intelligent circuit and conformal antenna elements using nonreciprocal materials, N.G. Alexopoulous, Univ. of California/Los Angeles ........ [2448-34]
Added: 9:40 am: Ferroelectric materials for microwave or millimeter wave applications, F. De Flavio, N. G. Alexopoulous, O. M. Stafsudd, P. Nelson, Univ. of California/Los Angeles ........ [2448-36]

Session 4: MEMS and Electronics Integration II (McWhorter)

Added: 5:20 pm: Low-cost 22 GHz active receiver, S. Mollenkopf, Qualcomm Inc.; L. P. B. Katehi, G. M. Rebeiz, Univ. of Michigan ........ [2448-35]
Added: 5:40 pm: Microsystem fabricated from free-standing structures, T. A. S. Srinivas, H. Ahmed, Univ. of Cambridge/Cavendish Lab. (UK) ........ [2448-33]

FRIDAY 3 MARCH
Session 5: Microelectronics and Applications (Rai-Choudhury)

Time Change: 9:40 am: Experiences with integral microelectronics on smart structures for space, T. Nye, S. Navarro, S. Casteel, TRW, Inc. ....... [2448-21]
Time Change: 10:00 am: Implementation of an active AlGaAs based 1 × 10 photonic polarization preserving fiber coupler in a fiber optic sensor demodulation system, J. M. Haake, B. C. Johnson, McDonnell Douglas Aerospace ........ [2448-22]
Time Change: Coffee Break ........ 10:20 to 11:10 am

Session 6: Characterization (Wolfson)
Canceled: 11:10 am: Mechanical properties of polysilicon-based composite films, F. A. Shoreansky, Jr., R. Ristic, D. Koury, R. Gutteridge, Motorola, Inc. ........ [2448-23]
Time Change: Lunch Break .......... 12:10 to 1:30 pm

Short Course Updates

SUNDAY 26 FEBRUARY
Robert E. Munson will not be a co-instructor on SC4, Microelectromechanical Systems: Processing and Integration with Smart Electronics for Smart Structures.
SC6, Smart Aircraft Structural Health Monitoring Systems (SHMS)—Requirements, Concepts, and Designs, has changed from a full-day to a half-day course.
Instructor: Jaihant N. Kudva.
SC6: $145/$155/$170 CEU J35 Sunday 8:30 am to 12:30 pm
Technology Overview, Smart Structures and Materials—An Overview, Actuators: 9:30 to 10:30 am
Speaker Change: Zaffir Chaudhry, Virginia Polytechnic Institute and State Univ.

MONDAY 27 FEBRUARY
Technology Overview, Smart Structures and Materials—Industrial Applications, has been canceled.

Proceedings

Editor Added:
Smart Structures and Materials 1995: Mathematics and Control in Smart Structures
Prepublication price $77

Editor Added:
Smart Structures and Materials 1995: Smart Structures and Integral Systems
Editors: Inderjit Chopra, Univ. of Maryland/College Park; Gareeb J. Knowles, Active Systems
SPIE Proc. Vol. 2443 • ISBN 0-8194-1792-0 • Approx. 91 papers
Prepublication price $95

Editor Added:
Smart Structures and Materials 1995: Industrial and Commercial Applications of Smart Structures Technologies
Editors: Robert Crowe, ARPA; Gary L. Anderson, U.S. Army Research Office; Janet M. Satter, Institute for Defense Analyses
SPIE Proc. Vol. 2447 • ISBN 0-8194-1796-3 • Approx. 64 papers
Prepublication price $77
Ferroelectric materials for microwave and millimeter wave applications
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ABSTRACT
Ferroelectric materials are nonlinear dielectrics, having a dielectric constant which is a function of the electric field. The nonlinear behavior of these materials makes them candidates for the realization of advanced high frequency devices which can operate up to the millimeter range. Ferroelectrics have been successfully employed in many optical devices, but their application at high frequency has been limited, mostly due to the large bias voltage required to significantly change the electrical properties of the bulk material. However, today there are several new techniques available to produce ferroelectric thin films and thin ceramics which only require low or medium bias voltage. These processes open the way for development of a new family of devices which are fully compatible with conventional analog and digital electronic circuits. Use of tunable dielectric material finds applications in many new devices including tunable phase shifters, tunable filters, and tunable beam scan antennas. High quality thin films and thin ceramics of PbTiO$_3$ (PTO), BaTiO$_3$ (BTO), Ba$_x$Sr$_{1-x}$TiO$_3$ (BST), and Pb$_x$Ca$_{1-x}$TiO$_3$ (PCT) have been produced and characterized. A 2.5 GHz tunable phase shifter, realized using BTO in microstrip configuration, is proposed and tested.

Keywords: ferroelectric, barium titanate, barium strontium titanate, lead titanium oxide, lead calcium titanium oxide, thin film, thin ceramic, microwave, phase shifter, millimeter wave.

1. INTRODUCTION
Chemical methods of preparation have generated considerable interest in the forming of ceramics\textsuperscript{1} for integrated circuit applications. These methods have the potential to control chemical composition, stoichiometry, purity, and homogeneity, which are critical features for fabrication of high-quality electronic components. A method well suited for the preparation of thin layer films and high purity thin ceramic is the sol-gel route.\textsuperscript{2} In this method, a chemical precursor of metal alkoxide, used with proper control of solution chemistry, allows the preparation of polymeric gel coating. Control of precursor alkoxide groups, solution concentration, hydrolysis content, pH\textsuperscript{1}, and deposition conditions for thin film (e.g. spinning speed, spinning time, etc.), determine the quality of the final product. Sol-gel processing has been used for the preparation of thin films of PTO and BTO, and thin ceramics of PTO, BTO, PCT, and BST. Thin films were deposited on nichrome-60 on alumina substrate, and on platinum on MgO substrate. Platinum growth on MgO substrate was done using an E-beam evaporator and preheating the substrate at 400° C. Multiple layers of film were spun. Finally, the film was dried at 680° C for one hour. Thin ceramics were produced by calcinating the precursor at 700° C, and by pressing the powder into a pellet of circular shape. The resulting sample was subsequently fired around 85% of its melting point for 2 hours. Finally, electrical devices were built by vacuum evaporation of copper.

2. PRECURSOR PREPARATION
2.1 PTO and PCT by sol-gel process
We have developed a new technique for the sol-gel synthesis of PTO and PCT. This new techniques is based on a process first developed by J.B. Blum and S.R. Gurkovich\textsuperscript{3}. The complex alkoxide precursor of PTO
is prepared by dissolving lead acetate trihydrate, Pb(C₂H₃O₂)₂·3H₂O, in 2-methoxyethanol (2-MOE) at a concentration of 0.5 molar. Acetic anhydride (AAA) is added at a molar ratio of 3:1 with respect to lead, to react with the 3H₂O, producing acetic acid. Finally, titanium isopropoxide, Ti(C₃H₇O₄), is added to the solution to yield a 1:1 molar ratio of lead to titanium. The PCT precursor is produced by introducing calcium acetate monohydrate, Ca(C₂H₃O₂)·H₂O, and lead acetate in the desired molar ratio prior to the addition of AAA. The amount of AAA is adjusted accordingly to transform all the H₂O to acetic acid. Due to the low solubility of calcium acetate, only methanol is used for PCT as solvent. Ultrasound is utilized to facilitate an even mixture of the components at each mixing stage. All procedures are carried out in room temperature in ambient air (not moisture-sensitive), and the precursor appears to have indefinite moisture shelf-life. This presents a major improvement over the previous process, which requires extensive refluxing of the solution above 100° C to remove water, and the addition of nitric acid to achieve the desired pH and prevent hydrolysis.

2.2 BTO and BST by sol-gel process

Barium titanate (BTO) powder and thin films are made by synthesizing a sol-gel derived precursor. This precursor is produced by starting with barium hydroxide octahydrate, Ba(OH)₂·8H₂O, which is first dissolved in methanol at a concentration of 0.1 M. Titanium isopropoxide Ti(C₃H₇O₄), is added to the solution to yield a 1:1 molar ratio of barium titanium. All procedures are followed at room temperature and in nitrogen atmosphere. BTO powder can be made by calcinating the precursor to 550° C. BTO films can be produced by first spin-coating the precursor onto a substrate, and subsequently firing the substrate at 750° C. A similar procedure is used for production of BST, where the Ba(OH)₂·8H₂O is replaced by strontium hydroxide octahydrate, Sr(OH)₂·8H₂O, diluted in methanol and subsequently mixed with titanium propoxide.

This new approach of producing BTO and BST ferroelectric material presents several advantages, such as high purity and absence of barium carbonate (which are usually difficult to remove simply with a firing process), low firing temperature, and very low cost (less than 3 dollars per ceramic sample).

Ability to control the grain size of the ceramic is important in order to understand and optimize electrical loss of the ceramic. Our technique synthesizes ceramic powder with grain size ranging from 1μm to 40μm. A picture taken by the electronic scan electroscope (SEM) shows two different grain-size powders of BTO, as shown in Fig. 1.

3. DEVICES PREPARATION

3.1 Thin film preparation

The substrate used was (100) MgO. It was cleaned by conventional procedures prior to deposition of platinum. Deposition of the sol-gel coatings was accomplished with a photoresist spinner. The solution was applied to the surface with a syringe containing a 0.2μm disposable filter. The sample was spun at 2000 rpm for 60 seconds. Multiple deposition was carried out to increase the thickness. Each layer was dried at 400° C in air atmosphere, and was approximately 0.5μm thick after drying. After the last layer of film was deposited, the film was heated in two steps. In the first step, the sample was heated at 400° C for 30 minutes, for removal of residual organic impurities, and for densification of the gel. In the second step, the sample was heated at 700° to obtain crystallization. All procedures were performed in air. X-ray diffraction data for PTO and BST thin films are shown in Figures 2 and 3. X-ray analysis confirms the high purity and random orientation of the film in both materials. Two parallel plate capacitors having thin film PTO as dielectrics were realized. In the first case, an alumina substrate is used to support the film, and nichrome-60 is used as ground contact (among low cost conductors, nichrome-60 seems to give
3.2 Thin ceramic preparation

Thin ceramics (with thicknesses below 0.2 mm) are very attractive ferroelectric materials for microwave applications. One advantage of thin ceramics over thin films is thickness, which is between 50 to 200µm, compared to 0.3-2µm for thin films. This allows low capacitance value (between 1-100 pF using a geometry between 1 to 0.1 mm), compatible with microwave designs. The sol-gel process guarantees high purity of the compound, is guaranteed by the sol-gel process, and absence of diffusion problems is assured by the fact that all metalization is carried out almost at room temperature, so no frequency dependence is observed. This also allows the use of electrical contacts with low cost metals such as copper or silver, instead of platinum.

A thin ceramic was produced by calcinating the precursor at around 700°C. Then the powder is preheated around 400°C to remove humidity, and pressed into a pellet using pressure between 4000-5000 Kg/cm². The sample was subsequently fired at 1170°C for PTO, and 1350°C for BTO. It was then sanded and polished, and the thickness reduced to 0.1 mm. Copper electrodes were evaporated on both sides, as shown in Fig. 5, to establish the electrical contact. The result of differential thermal analysis (DTA) carried out on a BTO sample is shown in Fig. 6; DTA for PTO and PCT with different concentrations of Ca (10% to 30%) are shown in Figures 7 through 10. The presence of calcium, as expected, reduced the Curie temperature of the PTO sample.

4. ELECTRICAL MEASUREMENTS

4.1 Thin film measurement

Electrical measurements of capacitance versus bias voltage and frequency for the PTO-based capacitor are shown in Fig. 11. The behavior is in perfect agreement with theory, and the frequency dependence of capacitance can easily be modeled by Debye relaxation, due to the interface layer between the film and the metal contact. Fig. 12 shows the electrical measurement versus bias voltage for the BTO-based capacitor. The film is grown on (111) platinum, on LaAlO₃ substrate. The curve in Fig. 12 clearly shows the presence of a hysteresis loop.

4.2 Thin ceramic measurements

Electrical measurements versus temperatures for BTOs and PCTs with different concentrations of calcium (20% to 30%) are shown in Figures 13 and 14. Clearly, the value of capacitance “blows up” at around the Curie temperature where the transition between tetragonal and cubic phase occurs. This confirms that our ceramic (at room temperature) is in the correct phase for exhibiting ferroelectric properties for exhibiting ferroelectric properties. Measurements of capacitance vs. temperature at 1 MHz were carried out by immersing the sample in a silicon oil bath, and by establishing the electrical contacts using a dedicated probe station. Electrical measurement of capacitance and losses vs. bias voltage for the BTO thin ceramic sample is shown in Figs. 15 and 16. High modulability is obtained, even when a field below 20 kV/cm (or 200V for the sample with 0.1mm thickness) is used. 40% modulability is achieved. The behavior of dielectric constants and losses vs. bias voltage is in perfect agreement with the theoretical behavior expected of material having a P-E hysteresis loop.

Fig. 17 shows the layout of a phase shifter built with a barium titanate lumped capacitor in a microstrip setup. Calibration was made at the connector section; therefore, losses due to the connector and the microstrip are not taken into account. Results for the S-parameters in a frequency range of 1.5 GHz and 2.5 GHz for two cases of unbiased (Vb = 0 V) and biased (Vb = 400 V) capacitor are reported in Figs. 18
and 19. An almost 10° phase shift is obtained at 2.0 GHz, with a change in magnitude of the $S_{21}$ below 0.3 dB, keeping the $S_{11}$ below –20 dB for both cases. The magnitude of $S_{21}$ decreases under bias conditions; at the same time, we know that the losses decrease. Thus, the change of $S_{21}$ is due to the mismatch of the capacitor, and not to the losses within it. By measuring the insertion loss due to both the microstrip and the connectors, we have found that they are of the same order as in the case of the capacitor with no bias. This clearly proves that the device can be used efficiently in this kind of configuration because of its small dimensions.

5. CONCLUSION

Use of thin ceramic phase shifters operating at 2.5 GHz shows how BTO thin ceramics can be used efficiently for microwave application. Use of PTO thin ceramics also seems to be very promising. Reduction of losses whenever extensive use of material is required (as in a 360° phase shifter based on a microstrip transmission line printed on ferroelectric material) can be achieved by doping it with strontium, in the case of BTO, or with calcium, in the case of PTO. When low bias voltage is required, use of thin films for microwave application is also possible.

6. ACKNOWLEDGMENTS

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7. REFERENCES


Fig. 1
PT04L.680, 4-layer on Nr60/Cu/Nr60/Alumina
3x(+5°C/m to 400°C/30m), +5°C/m to 680°C/2hr, -5°C/m

Fig. 2

Fig. 3
Fig. 6

Sample: BaTiO₃, ceramic disk, commercial
Size: 96.0000 mg
Method: DSC +50/–5°C/1Win 10°C/5°C/MIN
Comment: Air 30mL/min

Fig. 7

Sample: PT01098-2, 100% Pb, Methanol
Size: 135.0000 mg
Method: DSC +50/–5°C/1Win 50°C/5°C/MIN
Comment: Air 30mL/min, +/- 5/5 650°C/2 hr, press sinter ceramic disk
Fig. 8

Fig. 9
Fig. 10

Fig. 11
Fig. 12

PCT12020.C02, Pb0.8Ca0.2TiO3, ceramic, press 41 K Psi, 1150 C/8hr 2
powder 700 C/2hr, thick=0.175 mm, Area=8.8 mm²

Fig. 13
Fig. 14

Fig. 15
Fig. 16

Fig. 17