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Final Report

Research on Lead Titanate Films For Radiation Detection

Barrett E. Cole, Robert D. Horning and Paul W. Kruse

4 November 1992

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13. ABSTRACT *(Maximum 200 words)*

The objectives of the contract were to prepare thin films of $PbTiO_3$, measure their properties and determine their performance for pyroelectric detection of infrared and millimeter-wave (94 GHz) radiation. Thin films of $PbTiO_3$ were deposited on silicon microstructures consisting of Si_3N_4 membranes over etch pits in silicon substrates. Upper and lower Pt electrodes formed electrical contacts to the $PbTiO_3$ pyroelectric films. Aluminum metallizations in the form of full-wave and half-wave dipoles contacting the $PbTiO_3$ pixels were developed for detection of 94 GHz radiation. Infrared detection was by direct absorption in the $PbTiO_3$ pixel. Two process runs incorporating single pixels and linear arrays were carried out and the results described.

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Honeywell Sensor and System Development Center
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Foreword

Honeywell received ARO contract DAAL03-89-C-0021 on 5 September 1989. The contract will end 30 September 1992. The objectives of the contract were to prepare thin films of $PbTiO_3$, measure their properties and fabricate and test pyroelectric detectors of infrared and millimeter-wave (94-GHz) radiation.

The application envisioned was the detection of infrared and millimeter-wave radiation by exploitation of the pyroelectric effect in thin films of $PbTiO_3$ on thermally isolated membranes and microbridges on silicon. The infrared radiation is detected by direct absorption within the $PbTiO_3$ film, whereas the millimeter-wave radiation is detected by 94-GHz microantennas coupled to the $PbTiO_3$ films.

Based upon Honeywell's long history of infrared detection by thermal mechanisms in thermally isolated membranes on silicon microstructures, our approach required that the $PbTiO_3$ be deposited upon a Si_3N_4 film on a silicon substrate. Because Si_3N_4 is amorphous, the $PbTiO_3$ film would not be single-crystal. However, a thin film of Pt, which served as the lower electrode, lay between the $PbTiO_3$ and the Si_3N_4. Honeywell therefore developed the technology for depositing partially c-axis-oriented polycrystalline $PbTiO_3$ thin films on Pt on Si_3N_4 on silicon. These films exhibited excellent electrical and pyroelectric properties. Ion beam sputtering using an alternating target assembly was the method developed for the $PbTiO_3$ deposition (see Section 2 for details).

Simple $PbTiO_3$ containing membranes were formed to demonstrate the basic process steps before fabrication of a mask set. These devices were not to be functional electrically but demonstrated the fabrication process. The full mask set contained half-wave and full-wave dipoles to couple 94-GHz radiation to the $PbTiO_3$ pixels. These microantennas were in the form of Pt metallizations on the silicon.

A linear array of IR and mm-wave pixels was also included in the mask design and a process run was carried out. Failure of the Si_3N_4 membrane allowed the KOH etchant to attack the $PbTiO_3$, thereby destroying the pixels. A passivation layer was incorporated in the pixel design to prevent this from happening. A second process run was started but not completed.

Some accomplishments under ARO Contract DAAL03-89-C-0021 are as follows:

- Infrared-sensitive pixels in a linear array were designed suitable for silicon micromachining, based upon the pyroelectric effect in thin films of $PbTiO_3$.
- A process to deposit thin films of $PbTiO_3$ on Pt films on Si_3N_4 membranes on silicon substrates by ion beam sputtering was developed. These films exhibit the required electrical and pyroelectric properties to make excellent pyroelectric detectors.
- Microantennas were designed to couple 94-GHz radiation to the pixels.
- A process run that revealed a need for a $PbTiO_3$ passivation layer was carried out . The layer was then incorporated in the redesign.

Seven oral presentations at scientific meetings were made. A paper was published describing $PbTiO_3$ thin film material development.

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1. Statement of the Problem

The objectives of contract DAAL03-89-C-0021 were to prepare thin films of $PbTiO_3$, measure their properties, and determine their performance for pyroelectric detection of infrared and millimeter wave (94 GHz) radiation.

Lead titanate ($PbTiO_3$) is a ferroelectric material which is of interest as an infrared detector because of its pyroelectric properties (generation of an electrical signal in response to a change in temperature). As such it has the potential of generating an electrical response to temporally modulated electromagnetic radiation which is absorbed by it. When prepared in thin film form on a thermally isolated substrate, it can find application as a detector of electromagnetic radiation. The wavelength to which it responds depends upon its absorption properties. If the radiation lies in the infrared region of the spectrum, say in the 8-12μm region, it can be absorbed directly by the $PbTiO_3$ thin film. If it lies in the millimeter wave region, where the wavelength is much greater than typical dimensions of the detection element (pixel), an antenna is required to couple the radiation to the film. Such antennas, in the form of a metallization on the $PbTiO_3$ film substrates, are termed microantennas. By combining on the same substrate both infrared and millimeter wave sensitive $PbTiO_3$ pixels, it is possible to prepare a dual mode array. Such arrays may find application in smart munitions and missile seekers.

To meet the objectives, Honeywell developed an ion beam sputtering process for $PbTiO_3$ film deposition, prepared thin films of $PbTiO_3$ by this technique and evaluated the physical optical, electrical and pyroelectric properties of these films. The influence of sputtering conditions upon these properties was studied in order to optimize the properties. Having then a clear understanding of the relationship between the film properties and the sputtering conditions, additional films were sputtered upon test structures suitable for evaluating the electrical performance of the films in response to temporally modulated infrared and millimeter wave radiation.

2. Technical Discussion

There are three primary criteria for a good quality $PbTiO_3$ film useful for pyroelectric infrared detection. First, the stoichiometry (i.e., the ratio of Pb to Ti) must be 1:1. Second, the stoichiometric films must be crystallized in the perovskite crystal structure. Finally, the loss tangent of the film must be low. The loss tangent is an indicator of defects in the material at both the microscopic (e.g., oxygen vacancies) and macroscopic (e.g., stress-induced film cracking) levels. Therefore, ARO contract DAAL03-89-C-0021 focused on developing films that met these three criteria and using those films in IR and mm-wave pixels.

Under contract DAAL03-89-C-0021, Honeywell developed a versatile ion beam-sputtering technique for depositing $PbTiO_3$ thin films for IR and mm-wave sensing[1]. Other sputtering techniques suffer from stoichiometry variations, particularly the depletion of lead in both the sputtering target and the film, at the elevated temperatures needed for deposition. In the Honeywell process (see Figure 1), individual PbO (or Pb) and Ti targets are used rather than a single target of $PbTiO_3$. PbO and TiO_2 films of about 10-Å thickness are ion beam sputtered from the individual targets. Many of these thin films are sequentially deposited to get a film of adequate thickness. Since the deposition occurs at 500– 600°C the thin films interdiffuse to form a homogeneous film of $PbTiO_3$. Therefore, stoichiometry is easily and accurately controlled simply by controlling the ratio of sputtering time from the individual targets. Thus, our technique overcomes the problems associated with some other techniques.

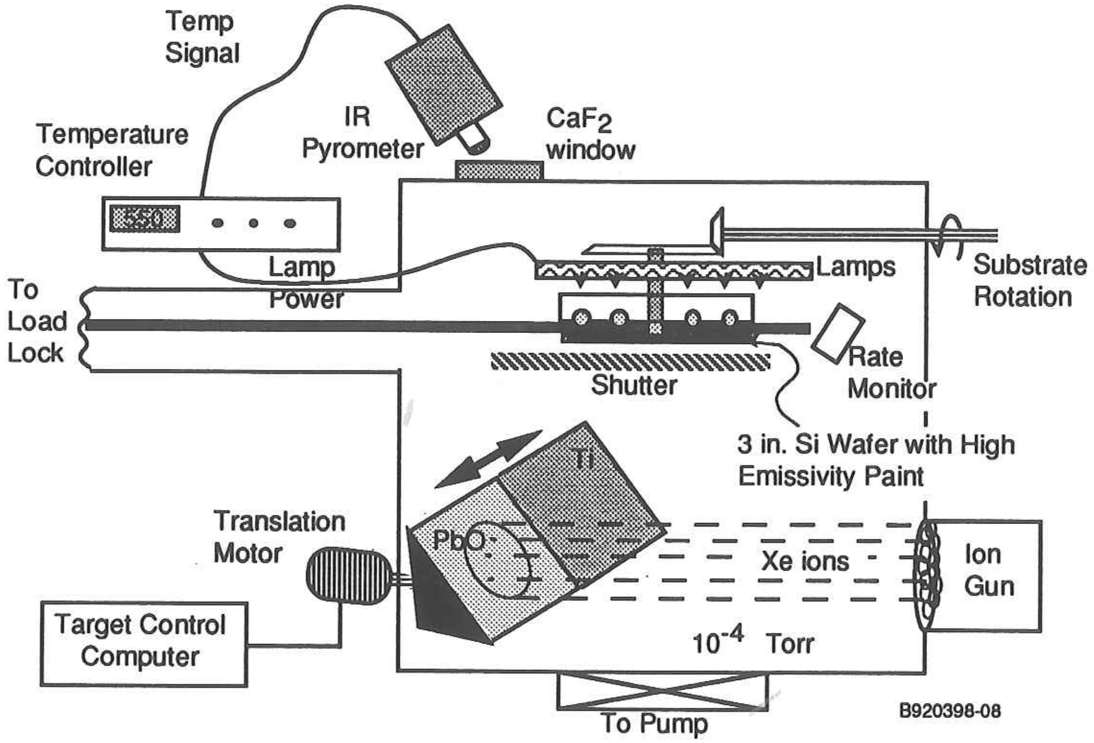


Figure 1. Honeywell Dual-Target Ion Beam Sputtering System for $PbTiO_3$ Film Deposition (The system features load lock wafer insertion, in situ substrate heating with real-time feedbackcontrol, and computer controlled translation of the sputtering targets.)

Figure 2 illustrates the stoichiometry control in the dual- target ion beam sputtering system at a fixed deposition temperature. The actual composition ratio, R_f=(atomic % Pb)/(atomic % Ti), as measured by Rutherford backscattering, is plotted against the ratio $R_t=t_{Pb}/t_{Ti}$ of sputtering times from the individual Pb and Ti targets. The composition varies linearly with the sputtering time ratio, and a ratio of about R_t=0.15 is needed for 1:1 stoichiometry at this temperature. Figure 3 shows the variation of this ratio (this time for PbO and Ti targets) as a function of the deposition temperature. The quantity R_t/R_f on the y-axis is roughly the value of R_t needed to get a stoichiometric film. As has been seen by others, less Pb is deposited per unit time at higher temperatures.

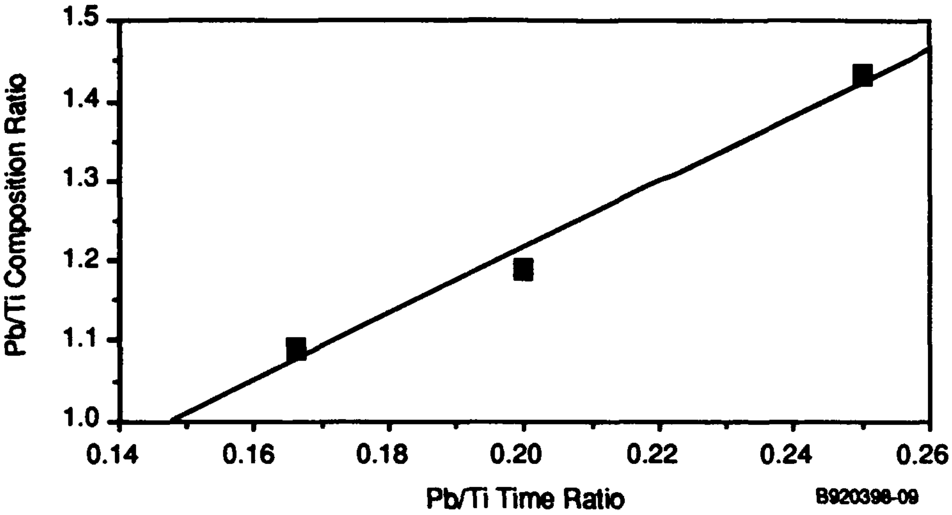


Figure 2. Measured Film Composition as a Function of the Ratio of Sputtering Times from the Pb and Ti Targets (The deposition temperature was 450°C.)

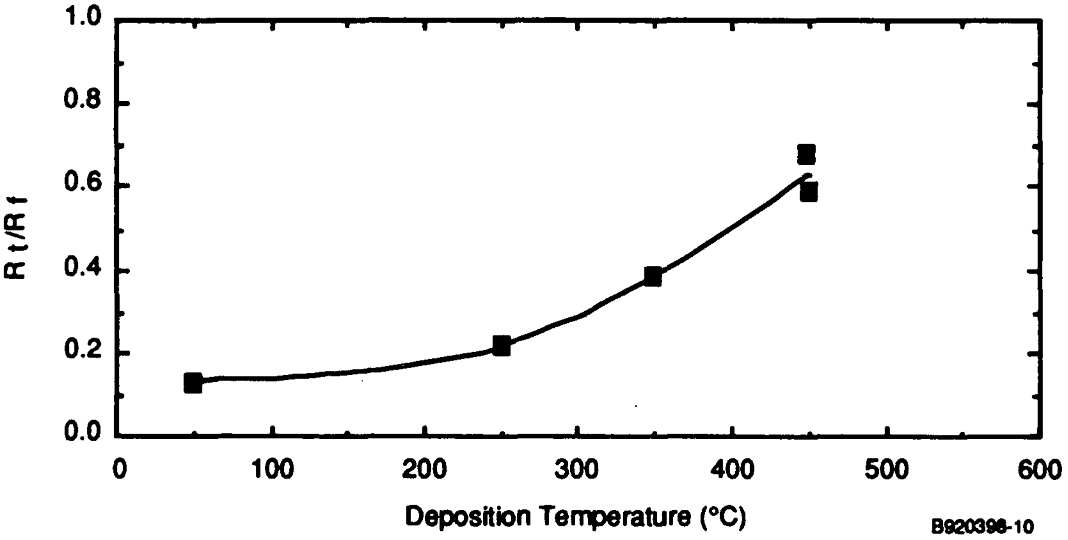


Figure 3. Variation of the Deposition Characteristics with Temperature (The vertical axis is approximately equal to the ratio t_{Ti}/t_{Pb} that is needed to achieve 1:1 stoichiometry.)

X-ray diffraction data show that these films crystallize in the tetragonal perovskite phase when deposited between about 500°C and 600°C. Figure 4 shows a typical spectrum. The (100)-(001) and (101)-(110) diffraction peaks are nicely split, showing that the films are well crystallized in the perovskite phase,and that the tetragonality (the difference between the (001) and (100) lattice parameters) is relatively high. The [001] axis is the polar axis, and it is important for good pyroelectric characteristics that the [001] direction be distinct from the nonpolar [100] direction. Figure 5 shows that the tetragonality is maximized at a deposition temperature of about 540°C.

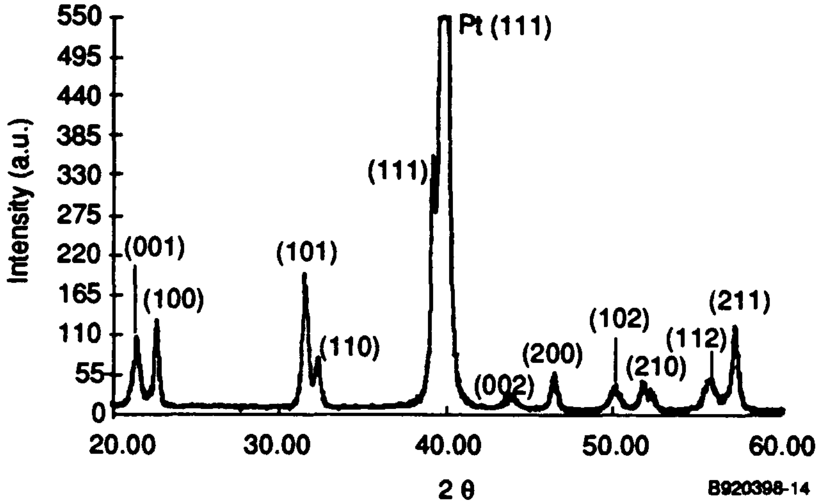


Figure 4. X-Ray Diffraction Spectrum of a $PbTiO_3$ Film Deposited by Honeywell's Dual-Target Ion Beam Sputtering Technique

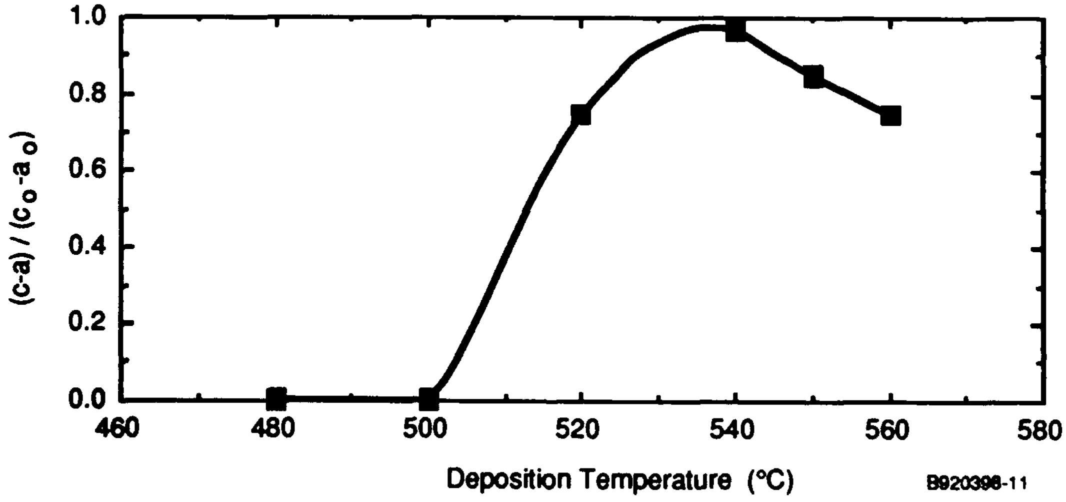


Figure 5. Tetragonality (the difference between the a and c axes, normalized to the value for bulk $PbTiO_3$) as a Function of the Deposition Temperature

All $PbTiO_3$ films are polycrystalline, and most have one or more crystallographic directions that are preferentially oriented perpendicular to the surface. It is desirable to have all grains with the polar (001) orientation, although (101) and (111) oriented grains have a component along the vertical.

Some degree of orientation control has been demonstrated with variations of the deposition parameters, but the films generally have not had a strongly preferential (001) orientation.

$PbTiO_3$ films deposited on Pt are fairly smooth, while $PbTiO_3$ deposited directly on Si_3N_4 tends to be rougher. This is due to both the lattice match with the Pt and the stress buffering effect of a metal between the $PbTiO_3$ and the Si_3N_4. The buffering effect of the metal can be seen in Figure 6. Identical $PbTiO_3$ films were deposited on Pt layers of varying thickness. $PbTiO_3$ deposited on thin Pt films (<500Å) are smooth but contain small cracks. The cracks are diminished for slightly thicker Pt, and disappear altogether when the Pt thickness exceeds about 1500 Å.

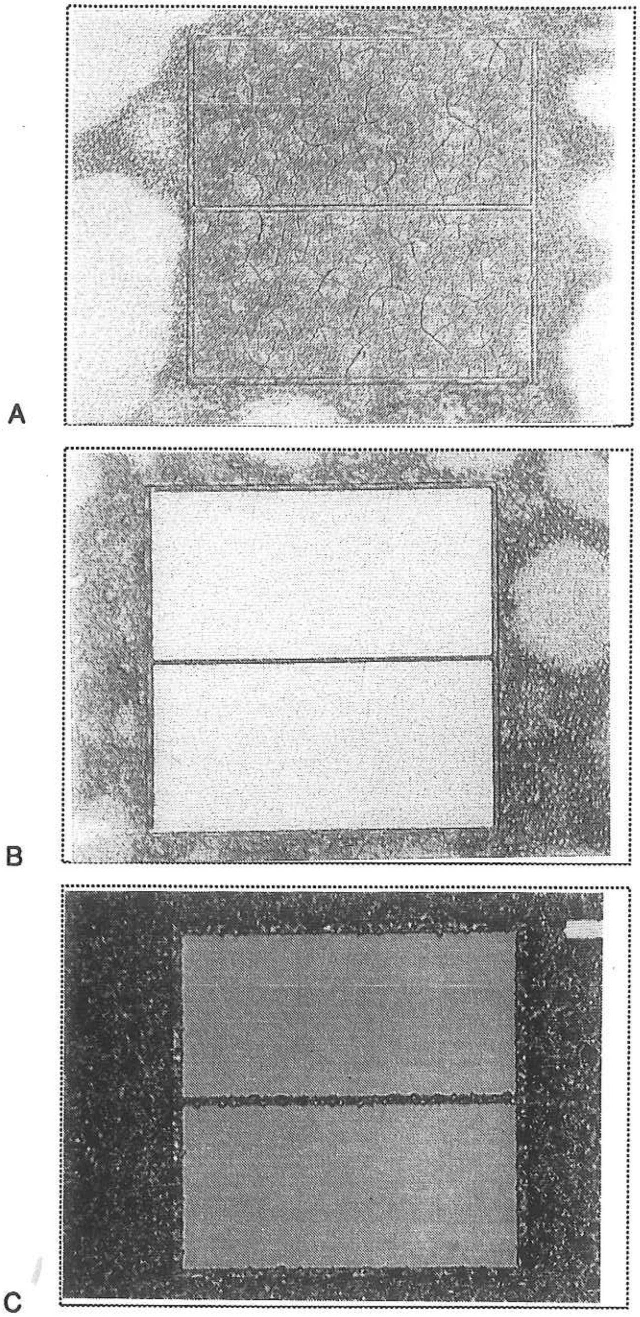


Figure 6. PbTiO₃ Films Deposited on Thin Pt Electrodes Showing Tendency To Be Rougher and Contain Small Cracks—A Thicker Pt Film Eliminates This Effect. (The Pt films are 750 Å thick in [A], 1000 Å thick in [B] and 1500 Å thick in [C].)

Electrical characterization of $PbTiO_3$ films is done by forming capacitor structures. The dielectric constant and loss tangent are measured at low fields (i.e., low enough that the $PbTiO_3$ behaves linearly) using an impedance analyzer. Ferroelectric hysteresis, such as is shown in Figure 7, is measured with a modified Sawyer-Tower circuit, with the wafer mounted on a temperature controlled chuck for poling. The pyroelectric coefficient is determined by measuring the current through a picoammeter while varying the temperature of the sample. The pyroelectric coefficient for our polycrystalline samples range between about 1×10^{-8} to 5×10^{-8} C/cm^2K, which compares favorably with the pyroelectric coefficient for single crystal $PbTiO_3$ at $8x10^{-8}$ C/cm^2K. Table 1 summarizes the dielectric properties of our films and compares them to values reported in the literature.

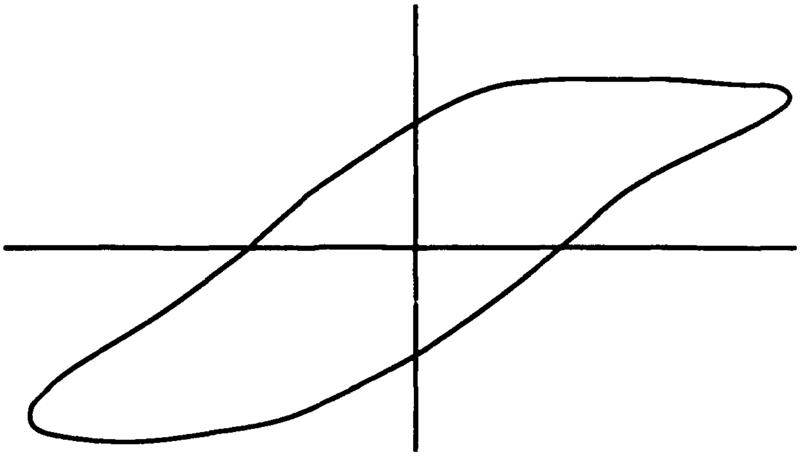


Figure 7. An Oscilloscope Trace from the Sawyer-Tower Circuit, Showing Ferroelectric Hysteresis

Table 1. A Comparison of the Dielectric Properties of Honeywell's Ion Beam Sputtered Films with Those Reported in the Literature

Property	Honeywell Films	Literature Value
Dielectric constant k	50–200	100–200[3]
tanδ	0.002–0.04	0.001–0.05[2]
Pyroelectric coefficient p (C/cm^2K)	1-5 $x10^{-8}$	8 $x10^{-8}$[3]

The single-level pyroelectric pixel design, which was developed under ARO contract DAAL03-89-C-0021, is shown schematically in Figure 8. The pixel consists of a silicon nitride membrane connected to the substrate with low thermal conductance legs. The legs are composed of the structural silicon nitride material and a metal used to make electrical contact to the pixel. The leg metal also forms a dual capacitor. The capacitor consists of a split-bottom electrode covered with $PbTiO_3$ and capped with a thin metal of NiCr with approximately 200-Ω/☐ impedance. The thin top metal has two purposes. It completes the electrical circuit and also absorbs IR radiation. Photomicrographs of the basic electrode structure are shown in Figures 9 and 10. We have used this detector fabrication process because it is the simplest technique to investigate fundamental fabrication and growth issues for $PbTiO_3$ films and can be carried over to more complex 2-D structures.

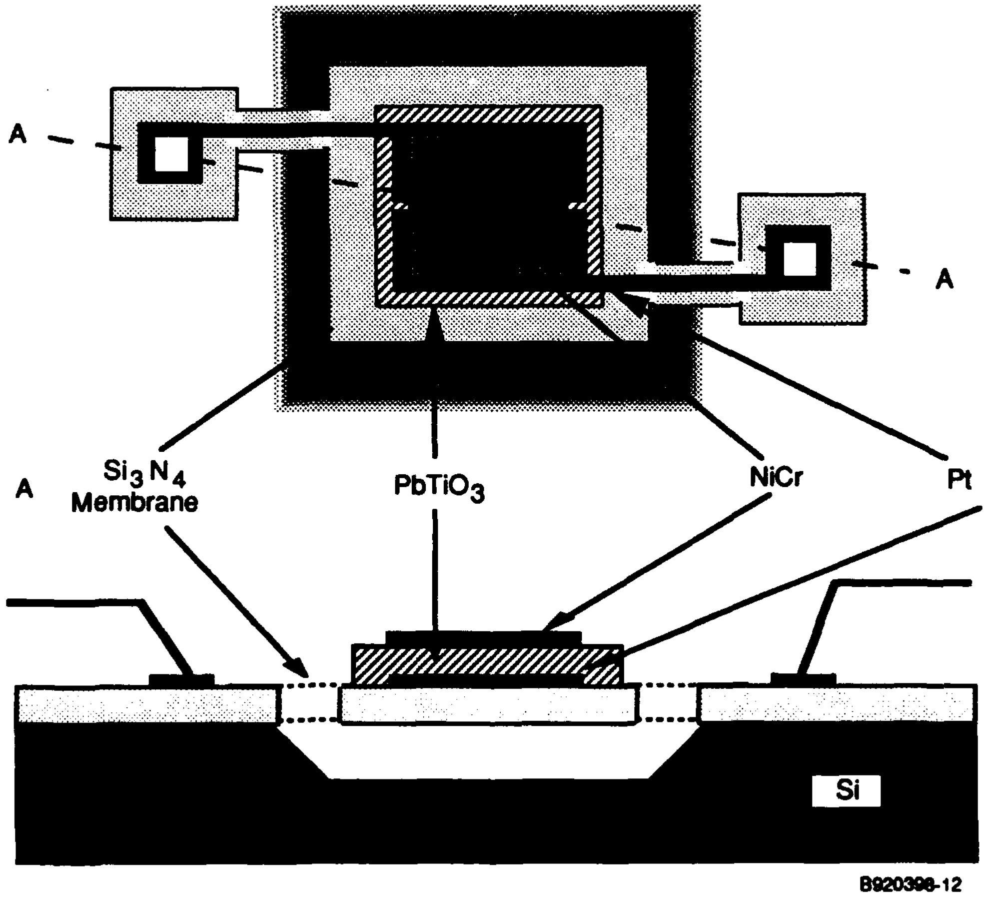
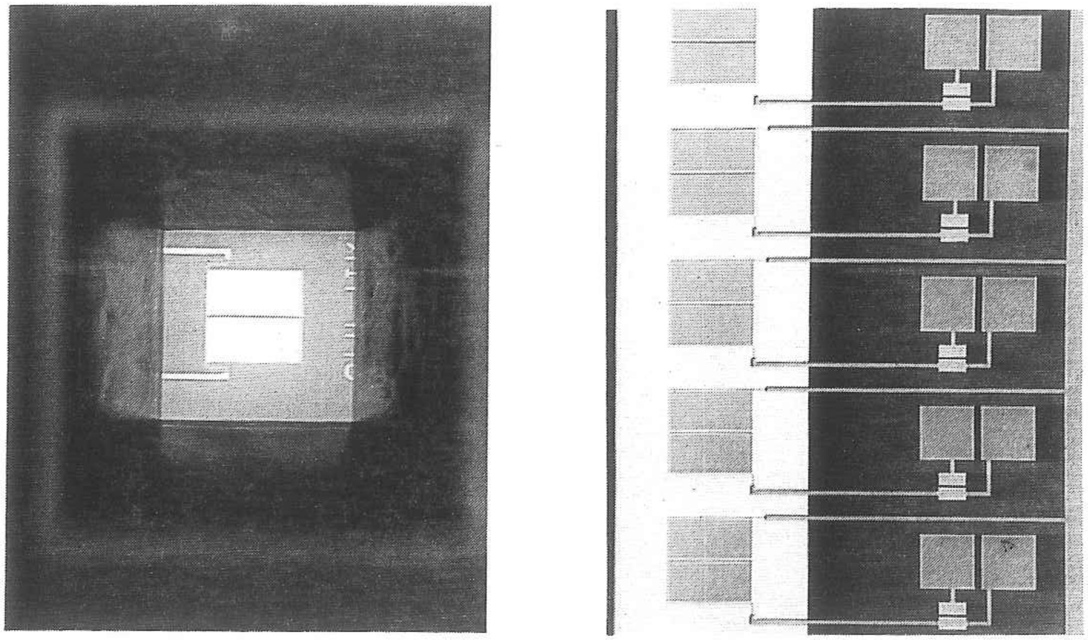


Figure 8. Single-Level Pyroelectric Pixel



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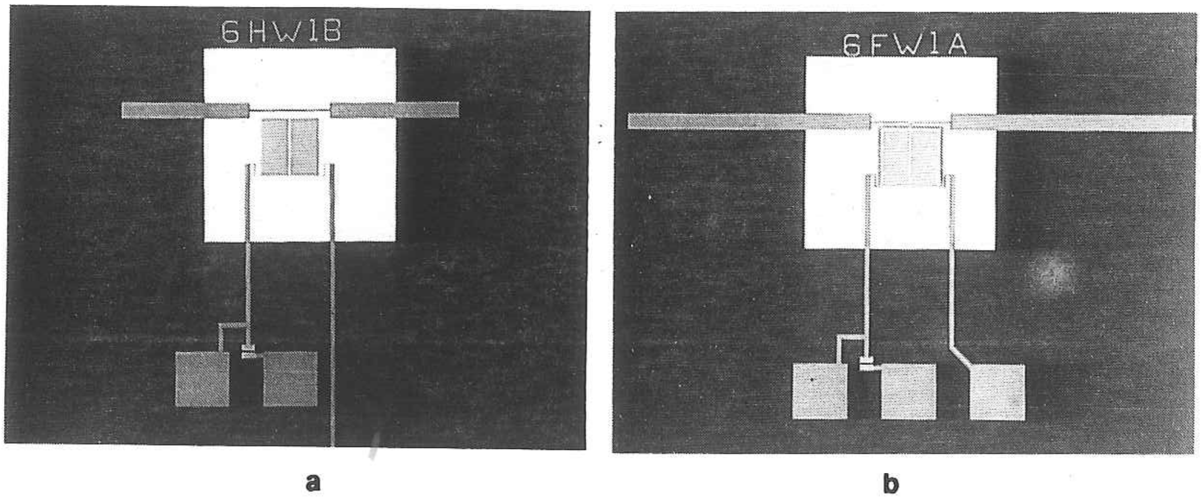
Figures 9. Photomicrographs of $PbTiO_3$ Pixel Electrodes for IR and Millimeter-Wave Structures a) A Single Element Pixel b) A Portion of a 64-Element Linear Array



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Figures 10. Photomicrographs of $PbTiO_3$ Pixel Electrodes for IR and Millimeter-Wave Structures a) A Half-Wave Microantenna for Millimeter-Wave Detection b) A Full-Wave Microantenna

A process development run was carried out to find and solve issues associated with processing the overall structure, aside from those related to the film deposition. Two areas of difficulty were found. First, the patterning and etching of the $PbTiO_3$ is done by ion milling. Endpoint detection becomes an issue because the mill is nonselective to materials, and because the Pt film underlying the $PbTiO_3$ is very thin. Second, pixels were fabricated, but were destroyed during the anisotropic backside etch. Failure of the nitride membrane was identified as the cause. The process was therefore modified to include additional passivation that would prevent $PbTiO_3$ dissolution even if some membranes failed during the etch.

More insight into the $PbTiO_3$ etching issue was gained during the first fabrication run. It was discovered that the growth rate and morphology of the $PbTiO_3$ is dependent on the material beneath it. In the fabrication runs the $PbTiO_3$ is deposited on Si_3N_4 coated silicon, with localized regions of Pt (the lower electrodes). The $PbTiO_3$ on the Pt was smooth, while the $PbTiO_3$ directly on the Si_3N_4 or on very thin metal lines was thicker and rougher. Because of the roughness, the integrity of the thin metal lines (e.g., the leadouts) was destroyed during ion milling. Because of this, a wet etch for $PbTiO_3$ was developed which is selective to both the nitride and the Pt.

The lessons learned during the process development run and the first fabrication run were to have been applied in a second fabrication run. Although the $PbTiO_3$ deposition was carried out, funding ran out and the fabrication run was stopped.

In summary, Honeywell developed a method of preparing high quality $PbTiO_3$ films on silicon microstructures. A pyroelectric detector structure was designed which would respond directly to infrared radiation and to 94 GHz radiation through microantennas. Some difficulties were encountered in the first process run which integrated the technology. The problems encountered in the first process run were typical of initial attempts to fabricate silicon microstructure devices. Although it was not possible to complete the second process run due to funding limitations, Honeywell remains convinced that thigh performance $PbTiO_3$ pyroelectric detectors and linear arrays on silicon microstructures which respond to infrared and millimeter waves are feasible.

3. Publications and Technical Reports

The following oral presentations were made describing research performed under contract DAAL03-89-C-0021.

B.E. Cole, R.D. Horning and P.W. Kruse, "$PbTiO_3$ Films Deposited by an Alternating Target Ion Beam Sputtering Technique," Materials Research Society Fall Meeting, Boston, MA, December 2-5, 1991.

R.D. Horning, "$PbTiO_3$ Films Deposited by an Alternating Target Ion Beam Sputtering Technique," Seminar at Department of Electrical Engineering, MIT, December 4, 1991.

P.W. Kruse, "Fundamental Limits of Infrared Detectors and Arrays," ARO Uncooled IR Imaging Workshop, Hilton Head, SC, November 14, 15, 1991.

B.E. Cole, "Pyroelectric-Based Infrared Microbolometer," ARO Uncooled IR Imaging Workshop, Hilton Head, SC, November 14, 15, 1991.

P.W. Kruse, "Fundamental Limits of Infrared Detectors and Arrays," Innovative Long Wavelength Infrared Detector Workshop, Jet Propulsion Laboratory, April 7-9, 1992.

P.W. Kruse, "Silicon Microstructure Imaging Arrays," Seminar at Army Research Office, March 30, 1992.

P.W. Kruse, "Focal Plane Arrays Based Upon Thermal Detection Mechanisms," JASON Imaging Infrared Detector Workshop, LaJolla, CA, June 29, 1992.

The following conference proceedings describing research performed under contract DAAL03-89-C-0021 is in press. A reprint is attached.

B.E. Cole, R.D. Horning and P.W. Kruse, "$PbTiO_3$ Films Deposited by an Alternating Target Ion Beam Sputtering Technique," in Ferroelectric Thin Films II, A.I. Kingon, E.R. Myers and B. Tuttle eds., Materials Research Society Symposium Proceedings, Vol. 243, p185 (1992).

MATERIALS RESEARCH SOCIETY SYMPOSIUM PROCEEDINGS VOLUME 243

Ferroelectric Thin Films II

Symposium held December 2-4, 1991, Boston, Massachusetts, U.S.A.

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$PbTiO_3$ FILMS DEPOSITED BY AN ALTERNATING DUAL-TARGET ION BEAM SPUTTERING TECHNIQUE

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ABSTRACT

Thin films, 0.2 μm to 2 μm thick, of ferroelectric $PbTiO_3$ have been deposit ed on Pt coated Si wafers using a novel dual target ion beam sputtering technique. The sputtering targets of PbO and Ti are shuttled back and forth into a Xe ion beam, depositing very thin (10 - 15 Å) alternating layers of PbO and TiO_2. The substrate is heated in situ, allowing interdiffusion of the thin layers into a homogeneous $PbTiO_3$ film. Film composition can be controlled accurately and repeatably by controlling the ratio of the sputtering times from each target. Structural characteristics were analyzed by x-ray diffraction, Rutherford backscattering as a function of the sputtering time ratio and the deposition temperature on Pt and Si_3N_4 coated Si substrates. The stoichiometric $PbTiO_3$ films have a tetragonal perovskite structure with a slight c-axis preference. Capacitor structures show ferroelectric hysterisis loops, dielectric constants of 100-250, loss tangents between 0.002 and 0.04 and a pyroelectric coefficient greater than
5×10^{-8} C/cm^2°C.

INTRODUCTION

Thin films of lead titanate, a perovskite phase pyroelectric material, have potential applications in IR and mm-wave sensing. The material's high pyroelectric coefficient, low dielectric constant, and relatively high Curie temperature make it one of the best suited for these applications.[1] Below the Curie temperature of about 480°C, spontaneous polarization arises along the [001] axis. Therefore it is best to have films with a preferred (001) orientation, although this is not necessary.[2]

Numerous techniques have been used to deposit thin films of $PbTiO_3$.[3] In this paper we report on an ion beam sputtering technique that solves some of the problems encountered with standard sputtering methods. Techniques for sputtering $PbTiO_3$ from a ceramic target generally suffer from a common problem: the Pb component in the surface of the target is preferentially sputtered more than the Ti component. Therefore, after a few depositions the stoichiometry of the active layer of the target has been altered, thereby changing the stoichiometry of the sputtered film.[4] This phenomenon is commonly seen during sputtering from other mixed targets as well, an example being the copper oxide based high temperature superconducting compounds. The most common methods of overcoming this are to dope the target with 5%-10% excess PbO or to add small pieces of Pb to the target. Others have used composite targets[5],[6],[7] made of Pb or PbO segments and Ti or TiO_2 segments. The film composition is then governed by the relative size and placement of the components.

DEPOSITION TECHNIQUE

An ion beam sputtering system was modified for $PbTiO_3$ deposition using multiple sputtering targets, as shown in Fig. 1. Two targets, one of Pb or PbO, and one of Ti are mounted on a moveable carriage. The carriage is driven by a computer-controlled stepper motor so that the PbO or Ti targets can be alternately positioned in the beam. A small oxygen

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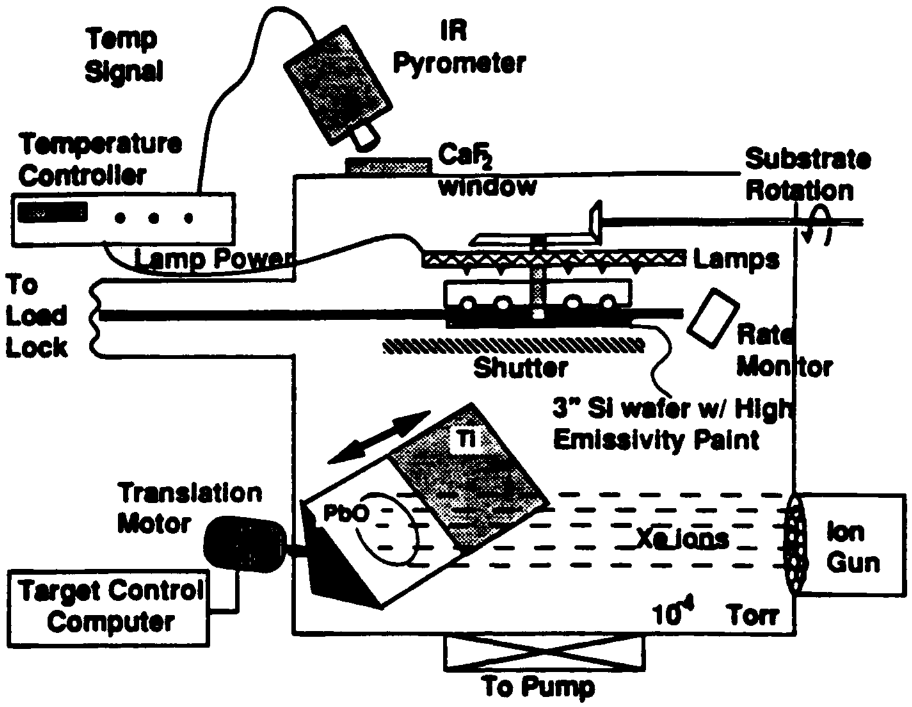

Figure 1. Multi-target ion beam sputtering system for deposition of $PbTiO_3$.

situ by a quartz lamp and is rotated during deposition for improved uniformity. A pyrometer monitors the wafer temperature and provides feedback control to the lamps, keeping the wafer temperature constant to within 5°C. The back surface of the wafers are coated with a 0.93 emissivity paint, eliminating wafer to wafer variations caused by the low emissivity and patterning of the platinum and by the transmission of the silicon substrate at the 5-6 µm monitor wavelength.

During deposition each target is sequentially placed in a Xe ion beam so that very thin layers of PbO and TiO_2, each about 10-15 Å thick, are deposited on the substrate. This sequence is repeated in excess of 200 times to deposit a film with a suitable total thickness. The thin layers diffuse together at the deposition temperature forming a homogeneous film of $PbTiO_3$. The exact film stoichiometry is controlled by the sputtering time from each target.

At the typical substrate temperatures of 550°C, the deposition rate is about 50 Å/min. Better repeatability is achieved when using a PbO target rather than a metallic Pb target since there is an appreciable flux of evaporated lead from the metal target.. It should be noted that additional target materials, such as La or Zr, can be easily added to make solid solution films of PZT, PLT or PLZT. Entirely different targets have been mounted for sputtering compounds including $YBa_2Cu_3O_7$.

EXPERIMENTAL RESULTS

Figure 2 is a plot of the Pb/Ti ratio in the deposited film as a function of the ratio of sputtering times from the PbO and Ti targets. These films were deposited at a constant temperature and the film composition was measured by Rutherford backscattering. The film composition varies linearly with the sputtering time ratio, as expected. The slope of the line is

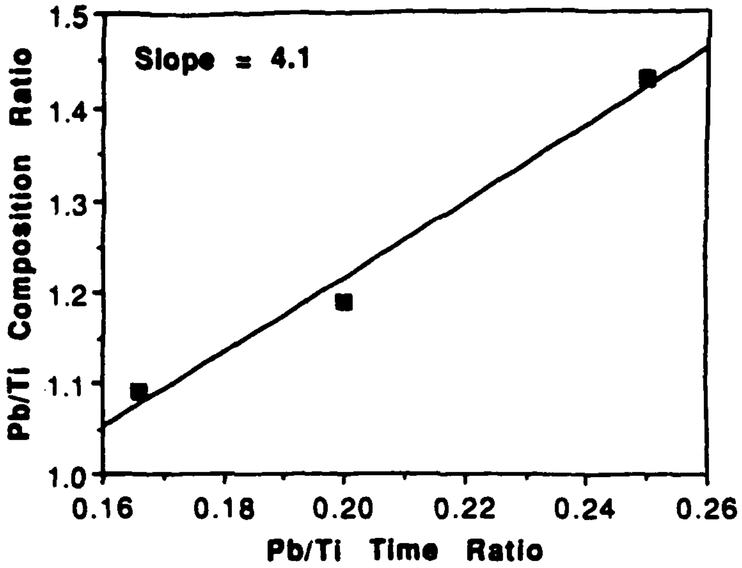

Figure 2. Rutherford backscattering data showing the linear dependence of the film composition on the ratio of the sputtering times from the PbO to Ti targets. The substrate temperature was 450°C during deposition.

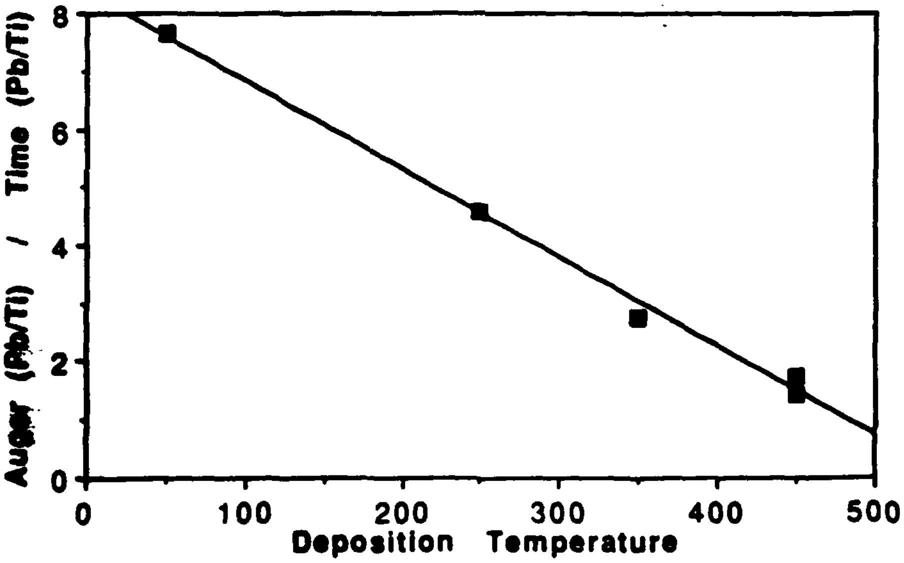

Figure 3. Variation in the film composition caused by the change in the sticking coefficient of lead with temperature. These films were sputtered from Ti and metallic Pb targets.

about 4.1 times faster than the TiO_2. To get a 1:1 stoichiometry in the film, the sputtering time from the Ti target must be 4.1 times longer than from the Pb target.

As the substrate temperature is increased the film composition changes, largely due to the decrease in the Pb sticking coefficient. This is shown in Fig. 3. The vertical axis is the film's Pb/Ti ratio, measured by Auger spectroscopy, divided by the sputtering time ratio. Therefore, the value is essentially the slope of the line obtained in a plot like Fig. 2 at each temperature. That is, the y-axis value represents the Ti/Pb sputtering time ratio needed to get a 1:1 stoichiometry film at each temperature. The deposition rate, of course, is due to both the rate of sputtering from the target and the sticking coefficient on the substrate. Lead sputters from the target much faster than Ti, and at a rate that is approximately constant with substrate temperature. However, the sticking coefficient decreases with increasing temperature, so less PbO is actually deposited on the substrate at the higher temperatures. This is the reason for the negative slope in Fig. 3. A comparison of Fig. s 2 and 3 shows that more lead, probably PbO, is actually deposited per unit time when using the PbO target than when using the metallic target. The probable explanation of this is that the metallic lead on the substrate, which will be more abundant when using the metallic target, desorbs from the surface at a much faster rate than PbO does. In contrast, most of the lead reaching the substrate is already oxidized if sputtered from the ceramic target. The net effect is that the deposition rate from a PbO target is higher than for a Pb target.

Structural characteristics of the films were measured by X-ray diffraction. Fig. 4 is diffraction data from a film deposited at about 550°C on a Pt coated Si wafer. Our films tend to have slightly more <110> and <111> character than a randomly oriented film, while the relative amounts of <100> to <110> vary with deposition conditions. There are usually more c-axis grains than in a random film. Typical grain sizes estimated from the diffraction peak widths are roughly 200-250 Å in the as-deposited samples. No lead poor phases or pyrochlore phases are observed in this sample, although these phases do appear under other deposition conditions.

The $PbTiO_3$ perovskite structure is tetragonal with lattice parameters a_0=3.89 Å and c_0=4.14 Å. Fig. 5 shows the measured lattice parameter difference, c-a, normalized to the maximum difference, c_0-a_0, as a function of the deposition temperature. All other conditions were held constant. Temperatures greater than 520°C are required to get acceptable tetragonality in the films.

The substrate plays an important role in the crystal structure and orientation of the film. Most $PbTiO_3$ films are deposited on a platinum layer. If, instead, the $PbTiO_3$ is deposited on a sputtered Si_3N_4 coating, under otherwise identical conditions, the grain size is roughly the same or a little smaller and pyrochlore peaks tend to be diminished. However, these films also tend to have much less of the desired <100> preferred orientation. Films deposited on Pt also tend to be smoother than those deposited on Si_3N_4.

Some films are given a post-deposition anneal at 650°C in air. The anneal has almost no effect on orientation. $PbTiO_3$ x-ray diffraction peaks get slightly more intense after the anneal and there is a noticeable decrease in the peak widths. The surface morphology after annealing also tends to be slightly more rough. These data point to $PbTiO_3$ grain growth during the anneal. Any pyrochlore peaks that may have been observed before annealing completely disappear.after the anneal.

Low field dielectric properties of 0.5 to 2.0 μm thick films were measured with an impedance analyzer from 10 Hz to 100kHz. At 1kHz the dielectric constants range between about 50 and 200 with loss tangents from about 0.002 to 0.04. Ferroelectric hysteresis loops, such as Fig. 6, were obtained with a Sawyer-Tower circuit at 60 Hz. The remanent polarization in as-deposited films is typically about 3-4 μC/cm^2. Poling the films at 100-150°C under an applied field of about 100 kV/cm results in increased polarization values.

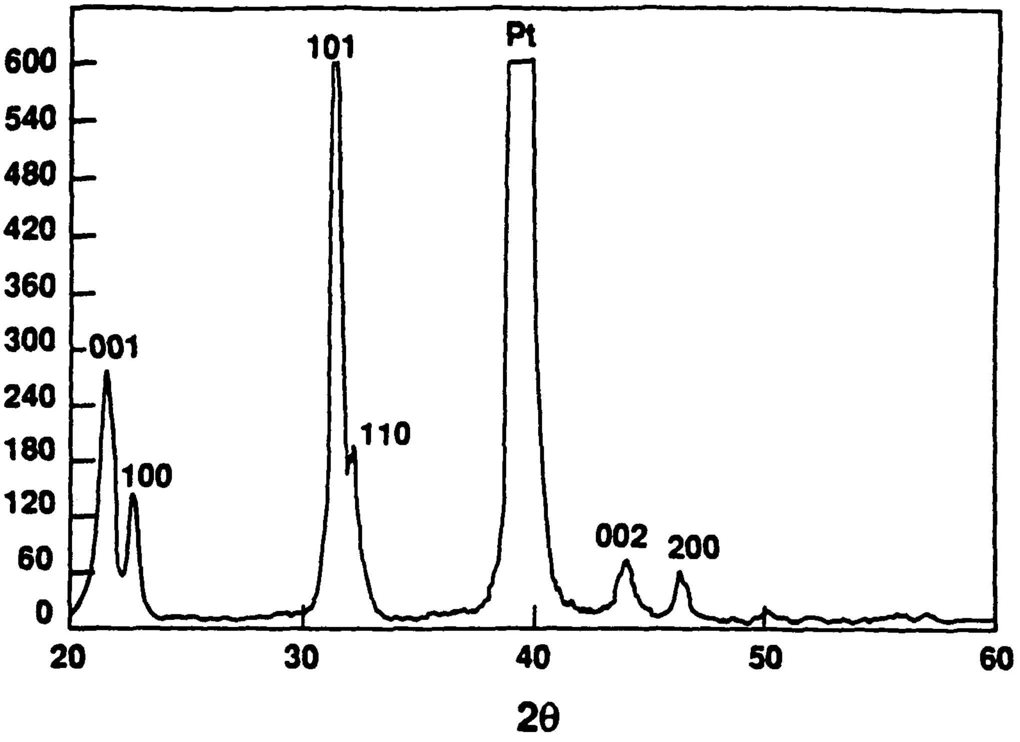

Figure 4. X-ray diffraction scan of a $PbTiO_3$ film deposited at about 550°C and a PbO/Ti sputtering time ratio of 1/4.

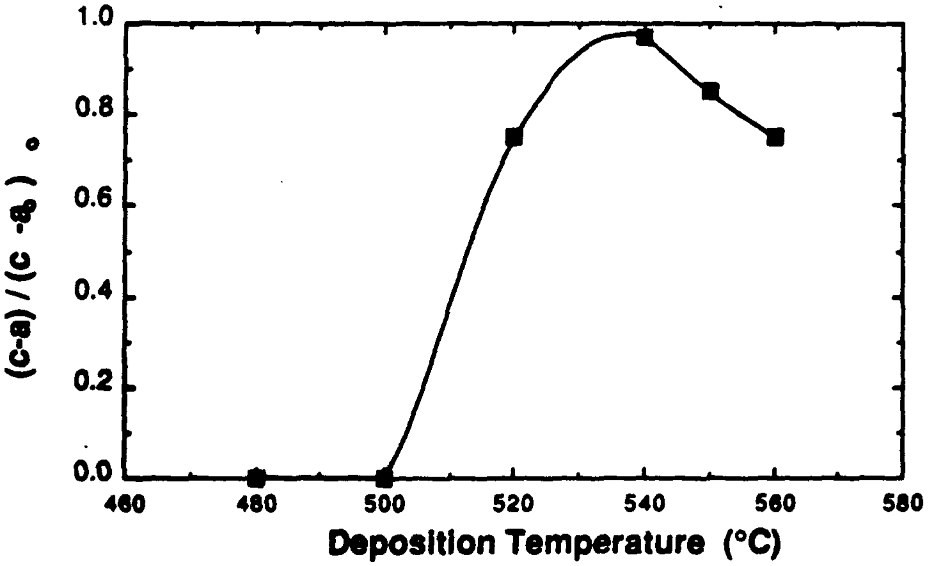

Figure 5. Lattice parameter splitting as a function of the deposition temperature.

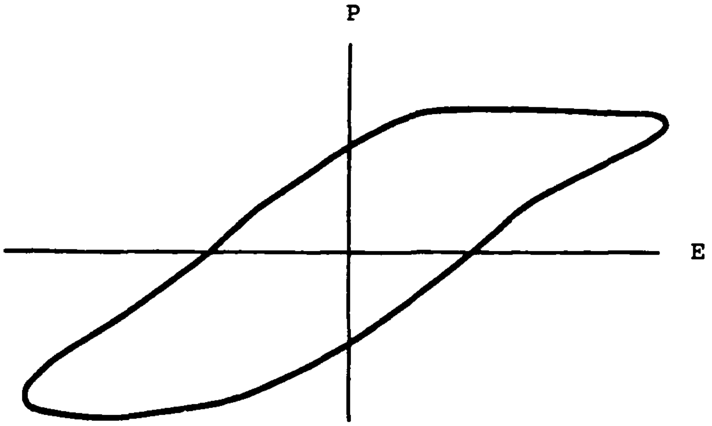

Figure 6. Ferroelectric hysteresis loop of a 0.5 µm thick $PbTiO_3$ film.

sufficiently large to allow high pyroelectric coefficients. The pyroelectric coefficient, measured with a picoammeter and a heat stage, ranges from about 1×10^{-8} to 5×10^{-8} C/cm^{2}K. These values compare well with pyroelectric coefficients reported in the literature. The figure of merit for pyroelectric detectors, FOM=$p/(\varepsilon\tan\delta)^{1/2}$, is typically $1\text{-}4\times10^{-7}$ C/cm^{2}K, which is comparable to the figures of merit for currently availabe IR sensors made from bulk, single crystal pyroelectric materials.

SUMMARY

A multiple target ion beam sputtering system has been used to deposit thin films of $PbTiO_3$. This technique eliminates problems associated with sputtering from a single ceramic target, allowing films to be deposited reproducibly. The films show good structural, dielectric and ferroelectric properties, making them good candidates for IR and mm-wave sensing technology.

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4. Participating Scientific Personnel

The following scientific personnel participated in contract DAAL03-89-C-0021

Dr. Barry Cole
Dr. Robert Horning
Dr. Paul Kruse
Mr. Rogers Anderson
Mr. Alan Beck
Mr. Harry Burke
Mr. James Detry
Mr. Robert Higashi
Mr. Leonard Hilton
Mr. Jim Holmen
Ms. Daryl LaMon
Mr. Duc Nguyen
Mr. Khanh Nguyen
Mrs. Peg Wilson
Mr. Chris Zins

5. Report of Inventions

There were no inventions under contract DAAL03-89-C-0021.

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Appendix

Theoretical Performance of $PbTiO_3$ Thin Film Pyroelectric Array

The theoretical performance of a pyroelectric infrared imaging array can be described by several performance parameters. These include the responsivity, noise, noise equivalent temperature difference, thermal response time, and electrical response time. The performance is a function not only of the pyroelectric material parameters but also the thermal isolation provided by the structure upon which the pyroelectric material is deposited. It is the combination of material and structure that comprises the pixel whose performance must be optimized.

Consider first the responsivity, R, which is the pixel output signal voltage per unit incident radiant power, expressed in V/W. The expression for it is

$$R = \frac{\eta \omega p A r}{G\left(1+\omega^2\tau_e^2\right)^{1/2}\left(1+\omega^2\tau_t^2\right)^{1/2}}$$

where

R = responsivity,
η = absorptance x fill factor,
ω = angular modulation frequency,
p = pyroelectric coefficient,
A = area of sensitive element,
G = thermal conductance from sensitive element to support structure.

Also, the electrical response time t_e is given by

$$\tau_e = rC_e$$

where r, the parallel resistance of the pixel and the readout electronics input, is

$$r = \frac{1}{\omega C_e \tan\delta}$$

Here

$\tan\delta$ = loss tangent and the pixel capacitance C_e is given by

$$C_e = \frac{(G.F.)K \epsilon_0 A}{d}$$

where

K = dielectric constant,
ϵ_0 = permittivity of free space.
d = capacitor thickness,
G.F. = geometrical factor.

The thermal response time t_t is given by

$$\tau_t = \frac{C}{G}$$

where

C = heat capacity (thermal mass) of the sensitive element.

The dependence of R upon modulation frequency is illustrated in Figure 11. In general, $\tau_e >> \tau_t$. The responsivity increases with frequency at low frequencies, reaches a plateau at $\omega\tau_e \approx 1$, then decreases at $\omega\tau_t \approx 1$. At high frequencies the responsivity is

$$R \approx \frac{\eta p A}{G C_e \omega \tau_t} \qquad \omega > \frac{1}{\tau_t} > \frac{1}{\tau_e}$$

These equations show that the responsivity is a function not only of the properties of the pyroelectric material through η, p, C,K and tanδ, but also the structure through A, d, G.F., C and G. Of special interest are the pyroelectric coefficient p and the thermal conductance G. Not only do we require materials with a large p value but also the structure should provide excellent thermal isolation (low value of G). In order that the thermal time constant τ_t be about 10 ms for typical thermal imaging applications (30-Hz frame rate), the ratio of pixel heat capacity C to thermal conductance G must be 10 ms. Given excellent thermal isolation, this means that the pixel heat capacity must be very small, obtained through very thin pixels.

The total noise voltage V_N is given by

$$V_N = \left(V_{N,J}^2 + V_{N,TF}^2 + V_{N,A}^2\right)^{1/2}$$

where

$V_{N,J}$ = Johnson noise associated with loss resistance = $\left(\frac{kT}{\omega C_e \tau_e}\right)^{1/2} = \left(\frac{kT \tan\delta}{C_e}\right)^{1/2}$

$V_{N,TF}$ = temperature fluctuation noise = $\left(\frac{kT^2}{C}\right)^{1/2} GR$,

$V_{N,A}$ = amplifier noise referred to input,
k = Boltzmann's constant,
T = absolute temperature.

The contribution to the total noise arising from the pyroelectric material is the Johnson noise, which depends upon tanδ. From the standpoint of optimal detector performance, noise is reduced by fabricating $PbTiO_3$ material with a small loss tangent. Values of 0.01 or less are desired and have been demonstrated under ARO contract DAAL03-89-C-0021.

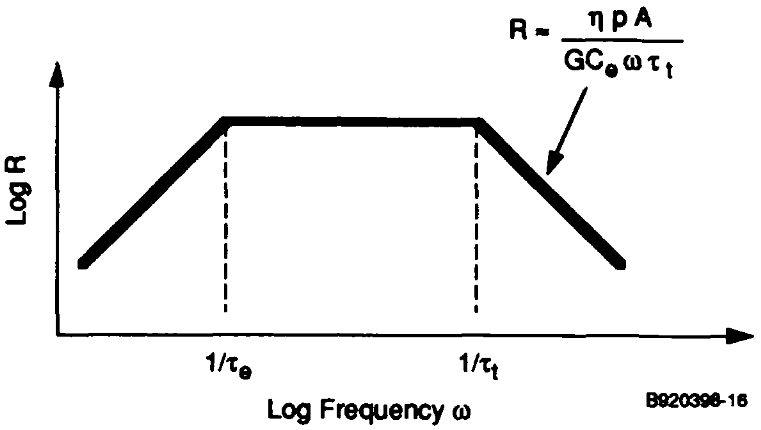

Figure 11. Responsivity vs. Frequency for Pyroelectric Detectors

The figure of merit describing the temperature sensitivity of an imaging system is the noise equivalent temperature difference (NETD), which is the change in temperature of a large black body imaged upon a focal plane array that causes a change of unity in the output signal-to-noise ratio.

For pyroelectric arrays operating in the 8–12 µm infrared window, it is given by

$$\mathrm{NETD} = \frac{\sqrt{2}\left(4F^2+1\right)V_N}{\tau_0 A\left(\frac{\Delta P}{\Delta T}\right)_{8\text{-}12} R}$$

where:

F = f/no. of optics,
τ_o = transmittance of optics,
$\left(\frac{\Delta P}{\Delta T}\right)_{8\text{-}12}$ = rate of change with temperature of black body emittance within 8–12 µm spectral interval

The factor $\sqrt{2}$ arises from the use of a chopper rotating at twice the frame rate.

Given the above expressions, the responsivity and NETD of a $PbTiO_3$ thin-film 2-D pyroelectric array can now be calculated. The parameters employed below are those of a HIDAD-like pyroelectric array (i.e., having 240 x 336 pixels on 50-µm centers operating in the 8 to 12-µm spectral interval with an f/1 lens at 30 frames per second. The pyroelectric properties are those of

$PbTiO_3$ thin films on Si_3N_4 membranes on silicon microstructures. Thus the values of the parameters used in the calculations are

A = 50 μm x 50 μm,
d = 0.5 μm,
K = 100,
G.F. = 0.25 (2 capacitors in series, each of area 25 μm x 50 μm),
$\tan\delta$ = 0.005,
η = 0.6 (absorptance) x 0.75 (fill factor),
τ_t = 10 ms,
G = 2×10^{-7} W/ K,
ω = 377 rad/sec,
p = 10×10^{-8} Coul/cm^2 K,
F = 1,
τ_o = 0.8,
T = 300 K.

The following values are derived from the above:

C_e = 1.11 pf,
r = $4.8 \times 10^{11}\ \Omega$,
τ_e = 0.53 sec,
$V_{N,TF}$ = 1.7 μV,
$V_{N,J}$ = 4.3 μV,
$V_{N,A}$ = 9.1 μV,
V_T = 10 μV.

The responsivity is therefore:

$$R = 1.35 \times 10^6 \text{V/W}$$

and the NETD is = 0.01°C.

An NETD of 0.01°C is excellent. For comparison, the DoD common modular FLIR used so successfully in Desert Storm, employing cryogenic (Hg,Cd)Te linear arrays, has an NETD of 0.1°C. The uncooled HIDAD microbolometer focal plane arrays also have an NETD of 0.1°C, although improvements are possible. A $PbTiO_3$ thin-film uncooled pyroelectric array of HIDAD-like complexity having an NETD of 0.01°C would be of great value for both military and commercial applications. Its performance would exceed that of cryogenic (Hg,Cd)Te linear arrays and be within an order of magnitude of the cryogenic (Hg,Cd)Te 2-D arrays now under development.

The assumed fill factor of 0.75 is attainable for 50μm x 50μm pixels only in two-level structures, not the single level structures investigated under Contract DAAL03-89-C-0021. A fill factor of 0.25 for a single level structure would result in a responsivity of 4.5×10^5V/W and an NETD of 0.03°C. Arrays with even this NETD would be useful for many military and commercial applications.