CHARACTERIZATION OF PEROVSKITE FILMS GROWN BY A NOVEL LOW-TEMPERATURE PROCESS FOR UNCOOLED IR DETECTOR APPLICATIONS

W.L. Sarney* and J.W. Little
U.S. Army Research Laboratory, Sensors & Electron Devices Directorate
Electro-Optics/Infrared Materials & Devices Branch
Adelphi, MD 20783

A.R. Tao and D.E. Morse
Institute for Collaborative Biotechnologies
University of California, Santa Barbara, CA 93106

F.E Livingston
Micro/Nano Technology Department, Space Materials Laboratory
The Aerospace Corporation, El Segundo, CA 90245

ABSTRACT

Many Army applications, such as driver vision enhancement (DVE), rifle sights, seekers, physical security, target acquisition, and fire control, would benefit from affordable, passive uncooled infrared (IR) sensor options. The main considerations for uncooled IR sensors are cost, weight, and power. We have begun a three-year effort to develop a novel approach to the fabrication of uncooled IR focal-plane array (FPA) detectors using bio-inspired, low-temperature, multimetallic perovskite nanoparticle deposition, direct-write digitally-scripted laser phase conversion, and MEMS fabrication and optimization techniques. Success is contingent on fully characterizing the perovskite films and resolving basic materials issues during the first year of this project.

1. INTRODUCTION

The objectives of this program are to use a unique direct-write, digitally-scripted laser pulse modulation technique (Livingston and Helvajian, 2007; Livingston et al, 2007; Livingston et al, 2006; Livingston and Helvajian, 2005; Livingston and Helvajian, 2004) in conjunction with a novel low-cost, low-temperature, kinetically controlled catalytic process for the growth of nanostructured multimetallic perovskites and semiconductor thin-films (Schwenzer et al., 2006; Kisailus et al, 2006; Brutchey and Morse, 2006). The resulting pyroelectric, perovskite-based material will be fabricated using a room-temperature infrared FPA process compatible with ultimate monolithic integration of the detector elements directly onto a readout integrated circuit (ROIC). The long-term potential is a lower-cost option for integration into Army systems and applications requiring uncooled IR detectors.

To successfully transition this technology into IR imaging systems that would be of use to the Army, we are fully characterizing the electrical and IR optical properties of a variety of films deposited and fabricated into test devices. Characterization is performed both before and after post-deposition laser-induced transformation of the nanoparticles into the appropriate pyroelectrically-active crystalline phase. For these films to be compatible with monolithic integration with commercially-fabricated ROICs, the process steps cannot subject the substrates to excessive temperatures or caustic chemicals, and the entire process must be scalable to wafer-level fabrication techniques.

2. BIO-INSPIRED FILM GROWTH

ARL has extensive materials research programs based on film growth by molecular beam epitaxy (MBE) and metal organic chemical vapor deposition (MOCVD). IR photon detectors based on III-V semiconductor quantum structures such as type-II superlattices (Little et al, 2007) and quantum well IR photodetectors (Choi et al, 2007) require the atomically flat interfaces allowed by MBE. Other MBE IR programs at ARL include HgCdTe on Si (Chen et al, 2003) and IV-VI films on Si and SiO_2. ARL also has a thermal detector research program based on MOCVD-grown ferroic oxides operating as pyroelectrics. Alternate routes to supplement these cost-intensive, high vacuum, high temperature growth techniques are being explored in response to demands for more flexible and lower energy

Report Documentation Page

Form Approved
OMB No. 0704-0188

1. REPORT DATE	2. REPORT TYPE	3. DATES COVERED
DEC 2008	**N/A**	**-**

4. TITLE AND SUBTITLE
Characterization Of Perovskite Films Grown By A Novel Lowtemperature Process For Uncooled Ir Detector Applications

5a. CONTRACT NUMBER
5b. GRANT NUMBER
5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)

5d. PROJECT NUMBER
5e. TASK NUMBER
5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
U.S. Army Research Laboratory, Sensors & Electron Devices Directorate Electro-Optics/Infrared Materials & Devices Branch Adelphi, MD 20783

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

10. SPONSOR/MONITOR'S ACRONYM(S)
11. SPONSOR/MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release, distribution unlimited

13. SUPPLEMENTARY NOTES
See also ADM002187. Proceedings of the Army Science Conference (26th) Held in Orlando, Florida on 1-4 December 2008, The original document contains color images.

14. ABSTRACT

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			
unclassified	**unclassified**	**unclassified**	**UU**	**7**	

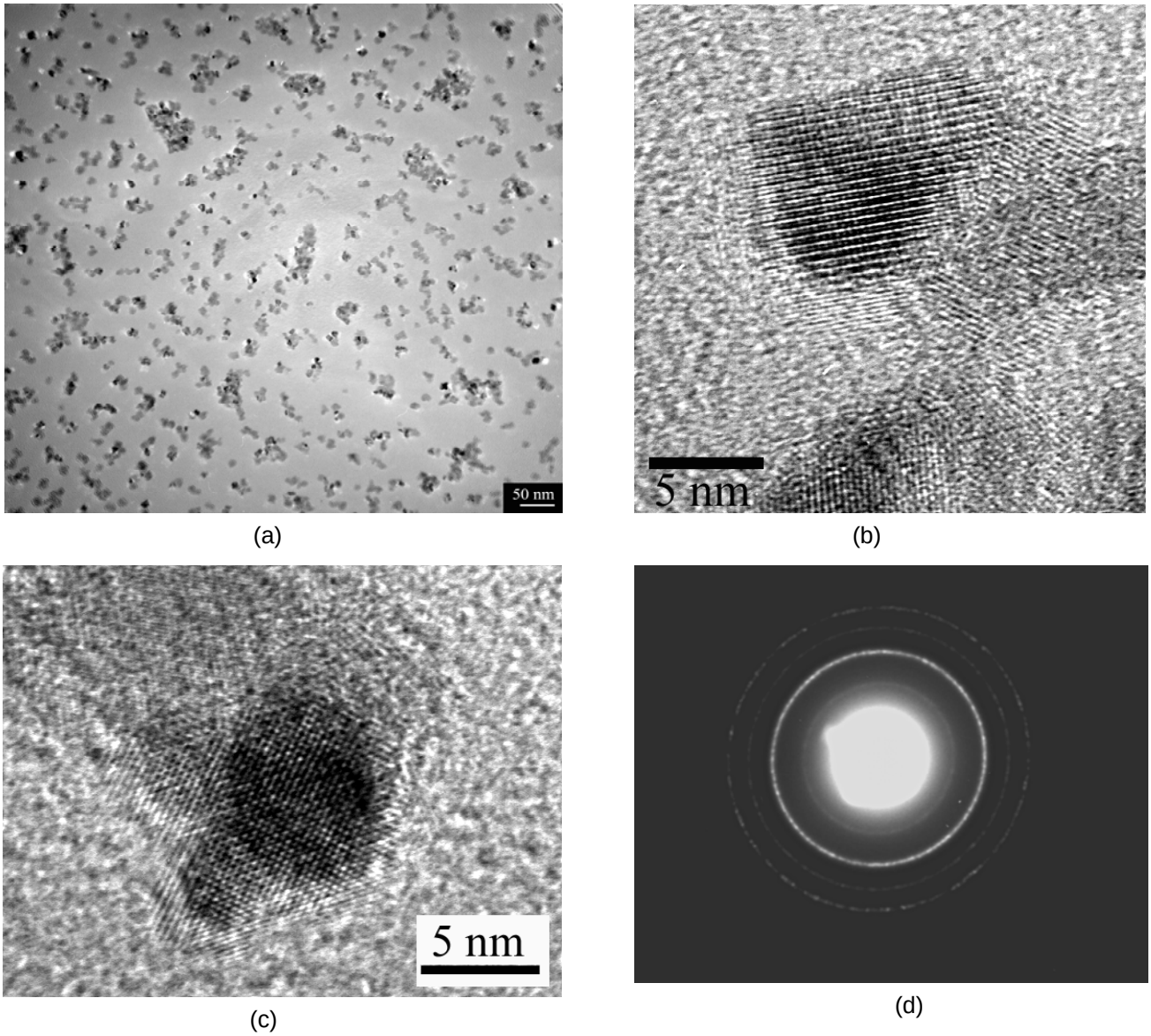
synthesis strategies for certain IR detector applications. One technique studied at ARL is metalorganic solution deposition (MOSD) for the growth of paraelectric thin films such as BST (Cole and Geyer, 2004). Techniques that mimic biomineralization have received attention because of the inherently benign physiological conditions of synthesis. One such biomineralization process has been studied intensively at UCSB (Morse, 1999). Molecular cloning, sequence analyses and mechanistic studies of the SiO_2 structures in a marine sponge led to the discovery that the process is mediated by catalytically active, structure-directing enzymes called silicateins. Purified silicatein fibers are able to catalyze and structurally direct the hydrolysis and polycondensation of molecular precursors in vitro to form SiO_2, anatase-TiO_2, and γ-Ga_2O_3 under very mild conditions, whereas traditional synthetic routes to these materials typically require high temperatures and/or extreme pH (Sumerel et al, 2003). The success of silicatein in forming high temperature crystalline polymorphs of TiO_2 and Ga_2O_3 lies in kinetically controlled, slow catalytic hydrolysis and growth.

In an effort to overcome the disadvantage of using biomolecules for the synthesis of high purity materials, while still preserving the fundamental concepts and success of biomineralization, a biologically-inspired and kinetically controlled vapor diffusion nanofabrication method was developed that yields nanocrystalline material at room temperature and ambient pressure (Schwenzer et al, 2006). The fundamental biochemical mechanisms underlying enzyme-mediated catalysis and templating have been translated to an approach wholly controlled by chemical physics, using vapor diffusion to establish temporal and vectorial gradients of catalyst for the kinetically controlled, slow growth of metal oxide nanocrystals. The resulting biologically-inspired, vapor diffusion-mediated catalytic approach affords a revolutionary low temperature and environmentally benign method for the nanofabrication of crystalline metal oxides based on the integrated tuning of molecular precursors, catalysts, solvents and concentrations that captures the advantages of the biomolecular synthesis mechanisms without using organic molecules.

One successful development for capacitive detectors is the use of perovskites as a thermally sensitive dielectric layer in uncooled detectors (Whatmore, 2004). In such a device, IR energy is absorbed by the perovskite, which results in a temperature change that gives rise to current (the pyroelectric effect) that is registered by an external circuit. Pyroelectric-based IR photodetectors have demonstrated broad wavelength response, high stability, and high sensitivity. The figure of merit (F_D) is a useful metric for assessing the potential of a pyroelectric perovskite for thermal imaging, with higher values of F_D having greater potential for detector performance. F_D is defined as: $F_D = p \Big/ c_v \sqrt{\varepsilon \varepsilon_o \tan\delta}$ where p is the pyroelectric coefficient, c_v is the volume specific heat, $\varepsilon\varepsilon_o$ is the permittivity, and $tan\delta$ is the dielectric loss tangent.

Two key challenges must be overcome for utilization of pyroelectric perovskites in next-generation IR photodetectors (Whatmore, 2004). The first is fabrication of well-defined nanostructures via low-cost, low energy processes. Traditional solid-state routes to pyroelectric $BaTiO_3$ (BT) require temperatures in excess of 1100 ˚C and yield a wide range of grain sizes (0.5-3 μm) with very little control over the shape of the particles. The second challenge is the deposition of high quality, stoichiometric, and homogeneous thin-films to minimize $tan\delta$ (and thereby yield higher F_D values). This requires new synthetic capabilities in order to push the size limit and uniformity of crystalline pyroelectric nanoparticles past what is currently feasible.

Our growth process utilizes a novel vapor diffusion sol-gel route that offers a very low temperature (16°C) pathway to BT nanoparticles (Fig. 1). Traditional solid-state reaction pathways to BT require high temperatures that offer little structural control, while newer solution based methods require elevated temperatures (>100 °C) and/or highly alkaline solutions to achieve small, well-defined nanoparticles (Wang et al, 2005). Our synthesis method is based on vapor phase delivery of water and a catalyst in a temporally controlled gradient to promote the slow, kinetically controlled growth of highly crystalline 6 nm nanoparticles, which are among the smallest reported for BT. Low temperature synthesis of perovskite nanocrystals is inherently difficult since accurate control over elemental stoichiometry, closely matched reaction rates of the constituent precursors, and specific conditions for crystallization (such as temperature, pressure and pH) are all critically important. Using a single-source bimetallic alkoxide with the vapor diffusion approach provides the necessary conditions for facile crystallization and growth of small, well-defined BT nanoparticles at very low temperatures.



(a) (b)

(c) (d)

Figure 1. TEM images of (a-c) $BaTiO_3$ nanoparticles and (d) corresponding diffraction pattern.

X-ray diffraction analysis revealed that the nanocrystals are comprised of cubic BT (space group *Pm*3*m*, simple cubic with a 5-atom basis). A lattice constant of *a* = 4.052 Å was calculated for the cubic nanoparticles, which is in excellent agreement with the literature value of 4.058 Å (JCPDS no. 75-0215). Bulk BT is a room temperature pyroelectric material in which the thermodynamically stable crystal polymorph is the non-centrosymmetric tetragonal phase (space group *P*4*mm*; *a* = 3.992 Å, *c* = 4.036 Å). The stability of the cubic phase in very small domains (<30 nm) for BT and other perovskites has been the subject of much interest and research. For small particles, a high temperature annealing step (900-1100°C) is typically necessary to convert the as-prepared cubic BT to the pyroelectric tetragonal phase (Lines and Glass, 1977). Once in the tetragonal phase, the perovskite remains pyroelectric until the Curie temperature (T_c ≈ 130˚C for BT) at which point a reversible phase transformation to the cubic phase occurs.

The pyroelectric material will be deposited as a thin-film for IR array detector applications. In order to minimize $tan\delta$, and maximize F_D, a high quality and stoichiometric film comprised of uniform particles is ideal. Traditional high temperature routes to BT yield nonuniform and coarse material, in addition to being incompatible with temperature restraints of device fabrication (<550˚C). The Institute for Collaborative Biotechnology's (ICB) unique synthesis of BT nanoparticles is perfectly suited for thin-film

applications because it is a low temperature route that yields small, uniform particles. The nanoparticles can be dispersed in common organic solvents (such as methanol) and then deposited as thin-films using dip coating or spin coating techniques at low temperature. Figure 2 is a scanning electron micrograph of an initial attempt at depositing BT onto a Si substrate with a thermal oxide. The image is a cross-section of two samples that were epoxied together and polished (this sample was being prepared for transmission electron microscopy). The film is reasonably uniform in thickness, but some cracks were observed. Current experiments include depositing Cr onto the substrate surface prior to depositing the BT film in an attempt to improve the film's adhesion to the substrate. Another experiment involves controlling the evaporation process within small (100s of microns) channels to relieve stress within the films and control cracking.

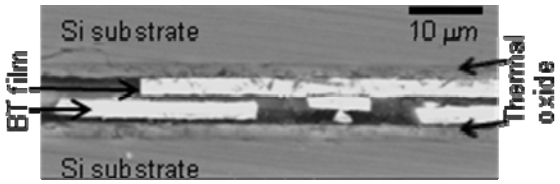


Figure 2. Cross-section SEM image of BT on Si.

3. LASER-INDUCED PHASE TRANSFORMATION

Following nanoparticle preparation and film deposition, The Aerospace Corporation's novel direct-write laser pulse modulation process will be utilized to induce site-selective and local phase transformation of nanoscale aggregates of these nanoparticles from the inactive (non-pyroelectric) crystalline cubic polymorph to the active (pyroelectric) crystalline tetragonal polymorph.

The special pyroelectric properties of BT fine particles and thin-films are principally associated with the structural phase of the material, and are also influenced by the crystallite size and density, film thickness, impurity and intrinsic defect concentration, and dispersion processing effects (Hoshina et al, 2006; Ahmad et al, 2005; Fong, 2004; Zhao et al, 2004]. Crystalline cubic BT is non-pyroelectric, but crystalline tetragonal BT is an active ferroelectric material. The cubic-to-tetragonal phase transformation occurs at temperatures of approximately 900-1100°C, and is typically accomplished with conventional resistive heating. Traditional thermal processing techniques unfortunately lead to global phase transformations, where the entire deposited BT film undergoes structural conversion. This eliminates spatial control and pattern capability, and prevents the highly selective and localized activation/deactivation of pyroelectric/non-pyroelectric domains in the thin-film BT substrates.

Fortunately, lasers provide a unique and attractive processing tool that is physically non-intrusive and capable of delivering spatially-focused action at a distance. We will use a digitally-scripted laser genotype pulse modulation technique to induce patterned local phase transformation of pyroelectrically inactive microscale and nanoscale clusters of ICB's BT nanoparticles to the pyroelectrically active polymorph (Fig. 3). Since the cubic-tetragonal phase transformation is a thermally-mediated process, development of initial laser pulse scripts will be based on the critical temperature-dependent parameters, including the heat capacity, thermal diffusivity and conductivity, and optical absorption properties of the BT nanostructured thin-films.

Another powerful feature of the direct-write laser genotype pulse modulation technique is the ability to incorporate genetic algorithms or intelligent feedback loops for real time process monitoring and control. For the laser-scripted processing of the BT nanostructured thin-films, we propose to utilize optical second harmonic generation (SHG) techniques for direct in situ monitoring of the phase transformation to the pyroelectric structure. SHG represents an attractive tool for examining structural phase transitions since it is inherently a non-contact

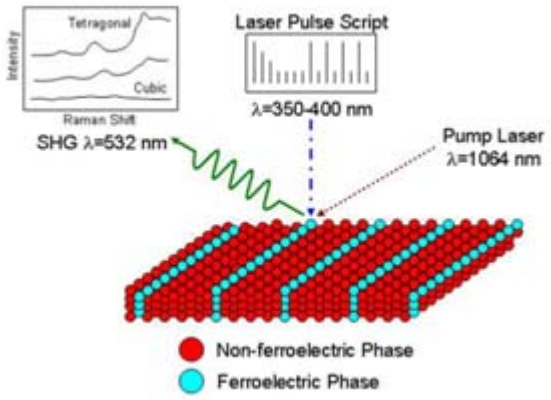


Figure 3. Schematic representation of the laser-scripted patterned phase transformation of the BT nanoparticle thin films with direct in-situ SHG signal monitoring for end-point control.

method with high non-linear sensitivity. SHG has proven to be a useful and reliable method for the detection of crystalline non-centrosymmetry in a variety of materials, including BT thin-films and monodisperse BT nanoparticles (Bihari et al, 1994; Lu et al, 1993; Dougherty and Kurtz, 1976). The non-linear SHG process is allowed only for the non-centrosymmetric (tetragonal) pyroelectric phase of BT, while the centrosymmetric (cubic) non-pyroelectric phase of BT does not exhibit SHG behavior.

4. IR PROPERTIES CHARACTERIZATION

A Nicolet Fourier transform IR (FTIR) spectrometer was used to measure the room temperature IR optical transmission of the BT films on crystalline SiO_2 substrates in the 1.5 to 5 μm wavelength region. The transmission of a bare substrate was measured to distinguish between features associated with the BT film and those due to the substrate. A typical result is shown in figure 4. A number of features are common to both the substrate and the film and are due to phonon replicas (multi-phonon absorptions) in the SiO_2. In addition to a broadband absorption (or scattering) associated with the film, there is a strong absorption feature at about 2.9 μm (3446 cm^{-1}). This absorption has been identified (Frey and Payne, 1996) as the stretching mode of OH ions incorporated in the film and is commonly found in perovskite films grown at low temperature by more conventional sol-gel techniques. These ions are referred to as hydroxyl defects because of the high mobility of hydrogen in perovskite materials (with associated degradation of the electrical properties of devices), and are usually annealed out at temperatures near the phase transformation temperature (750–800°C). Determining the effects of laser processing of the BT films on the hydroxyl defects will be an important part of the ongoing program.

5. DEVICE FABRICATION

ARL has historically provided single-pixel and focal-plane array characterization for internal Army programs and for devices provided to the Army by outside contractors. FTIR spectrometers, calibrated point source and extended source blackbody radiators, capacitance meters, spectrum analyzers,

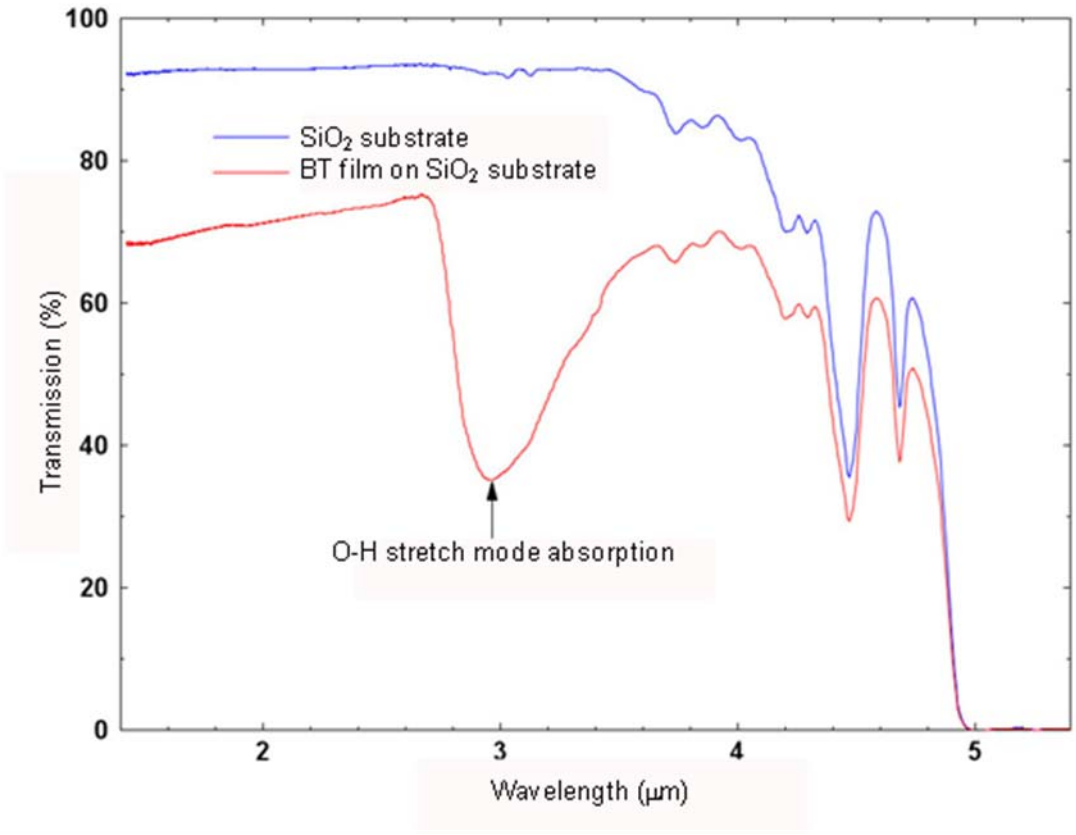


Figure 4. Infrared transmission measurements of a BT film grown on a crystalline quartz substrate (red). The transmission of a bare substrate is shown in blue. Note the strong transmission dip associated with the stretching mode of O-H ions incorporated in the film.

and semiconductor parameter analyzers are available for room-temperature and temperature-dependent detector characterization.

The second year of work at ARL will involve the development of a thermally-isolated prototype detector pixel based on micro-electromechanical systems (MEMS) processing technology. In order to maximize the pyroelectric response to absorbed IR radiation, it is important that each pixel of a detector array be thermally isolated from its surroundings and that it has a minimum thermal mass. This ensures a maximum rate of change of the temperature of the pyroelectric material (in response to a typically chopper-modulated IR scene) and a corresponding maximum in polarization current.

Thermal isolation and thermal mass management has been successfully accomplished in room-temperature IR detector applications through the use of MEMS techniques for fabricating free-standing detector membranes supported by long, thin arms that also serve as electrical contacts. ARL has an active MEMS processing group available for this stage of the device development.

Figure 5 outlines a potential set of processing steps (a-f) for fabricating a single pixel (in cross section) and shows a top-down view (g) of the pixel membrane. The starting substrate could be a custom-designed CMOS readout integrated circuit or, as will be the case for this program, a silicon fanout chip comprising a silicon chip with a thermal oxide grown on top and gold lines deposited to connect the two contacts of each pixel to wire bonding pads. The steps shown here are compatible with processing a functional readout circuit, but the use of in-house fabricated fanout circuits gives the flexibility of varying the dimensions or other properties of the substrate chip without the formidable cost of full CMOS chip runs for each design. Processes of this type are routinely done by the MEMS team at ARL, and will be developed in collaboration with the ICB team (for nanoparticle deposition) and the Aerospace team (for localized phase transformation).

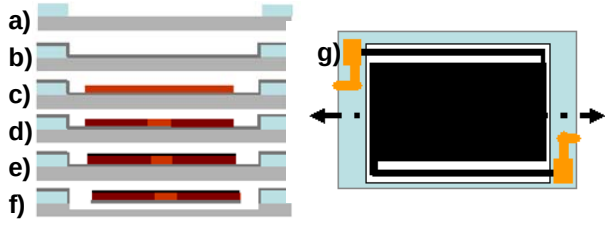


Figure 5. (a) Starting substrate (CMOS or fanout chip), (b) structural layer deposition, (c) perovskite deposition, (d) perovskite laser-induced phase transformation, (e) infrared absorbing layer deposition, (f) membrane release, (g) top view of released membrane. The arrow shows location of cross section shown in (a-f).

6. SUMMARY

The objective of this project is to combine novel techniques of low-temperature nanostructured multimetallic perovskite thin-film growth and direct-write digitally-scripted laser phase transformation to fabricate precision patterned 2-D focal-plane arrays. Since the necessary cubic-tetragonal phase transformation is a thermally-mediated process, the critical temperature-dependent parameters of the BT nanostructured thin-films must be assessed in the first year. The potential outcome of this project is to demonstrate a novel architecture for fabricating high sensitivity and low-cost uncooled IR FPAs suitable for many Army platforms such as Drivers' Vision Enhancement devices, IR cueing sensors, helmet mounted IR sensors, UAVs, UGVs and UGSs.

ACKNOWLEDGEMENTS

The authors acknowledge support by the Institute for Collaborative Biotechnologies through grant DAAD19-03-D-0004 from the U.S. Army Research Office and The Aerospace Corporation Independent Research and Development (IR&D) Program and the Product and Development (PDP) Program.

REFERENCES

Ahmad, T., Kavitha, G., Narayana, C., and Ganguli, A.K., 2005*:* Nanostructured barium titanate prepared through a modified reverse micellar route: Structural distortion and dielectric properties *J. Mater. Res.*, **20,** 1415-1421.

Bihari, B., Kumar, J., Stauf, G. T., Van Buskirk, P. C., and Hwang, C.S., 1994: Investigation of barium titanate thin films on MgO substrates by second-harmonic generation, *J. Appl. Phys.*, **76**, 1169-1174.

Brutchey, R. and Morse D.E., 2006: Template-Free, Low-Temperature Synthesis of Crystalline Barium Titanate Nanoparticles under Bio-Inspired Conditions, *Angew. Chem. Int. Ed.,***128**, 10288.

Chen, Y.P., Brill, G., and Dhar N.K., 2003: MBE growth of CdSeTe/Si composite substrate for long-wavelength IR HgCdTe applications, *J Crystal Growth,* **252,** 270–274.

Choi, K.K., Monroy, C., Swaminathan, V., Tamir, T., Leung, M., Devitt, J., Forrai, D., and Endres, D., 2007: Optimization of corrugated-QWIPs for large format, high quantum efficiency, and multi-color FPAs, *Infrared Physics & Technology*, **50,** 124–135.

Cole, M.W. and Geyer, R.G., 2004: Novel tunable acceptor doped BST thin films for high quality tunable microwave devices, *Revista Mexicana de Fisica*, **50**, 232-238.

Dougherty, J.P., and Kurtz, S.K., 1976: A second harmonic analyzer for the detection of non-centrosymmetry, *J. Appl. Cryst.*, **9**, 145-158.

Fong, D.D., Stephenson, G.B., Streiffer, S.K., Eastman, J.A., Auciello, O., Foss, P.H., and Thompson, C., 2004: Ferroelectricity in Ultrathin Perovskite Films, *Science*, **304**, 1650-1653.

Frey, M.H. and Payne, D.A., 1996: Grain-size effect on structure and phase transformations for barium titanate, *Phys. Rev. B*, **54**, 3158.

Hoshina, T., Kakemoto, H., Tsurumi, T., Wada, S., and Yashima, M., 2006: Size and temperature induced phase transition behaviors of barium titanate nanoparticles, *J. Appl. Phys.*, **99,** 0543111-0543118.

Kisailus, D., Schwenzer, B., Gomm, J., Weaver, J.C., and Morse, D.E., 2006: Kinetically controlled catalytic formation of zinc oxide thin films at low temperature, *J. Am. Chem. Soc.,* **128**, 10276-10280.

Lines, M.E. and Glass, A.M., 1977: Principles and Applications of Ferroelectrics and Related Materials, Claredon Press, Oxford.

Little, J.W., Svensson, S.P., Beck, W.A., Goldberg, A.C., Kennerly, S.W., Hongsmatip, T., Winn, M., and Uppal, P., 2007: Thin active region, type II superlattice photodiode arrays: Single-pixel and focal plane array characterization*, J. Appl. Phys.*, **101**, 044514.

Livingston, F.E. and Helvajian, H., 2004: Genotype Pulse Modulation Laser Writing System," U.S. Patent filed under Docket No. D526.

Livingston, F.E. and Helvajian, H., 2005: Development of a new laser material processing technique using digitally-scripted genotype sequencing and electro-optic pulse modulation, *SPIE Proc. Laser Precision Microfabrication*, **1**, 329-335.

Livingston, F.E. and Helvajian, H., 2006: Photophysical processes that activate selective changes in photostructurable glass ceramic material properties, *Proc. NATO Advance Sciences Institutes – Photon-based Nanoscience and Nanobiotechnology*, **239**, 225-265.

Livingston, F.E. and Helvajian, H., 2006: Selective activation of material property changes in photostructurable glass ceramic materials by laser photophysical excitation, *J. Photochem. and Photobiol. A: Chemistry*, **182**, 310-318.

Livingston, F.E. and Helvajian, H., 2007: The Symbiosis of Light and Matter: Laser-Engineered Materials for Photo-Functionality, *Special Issue MRS Bulletin: Direct Write Technologies*, **32**, 40-46.

Livingston, F.E., Steffeney, L.F., and Helvajian, H., 2007: Tailoring light pulse amplitudes for optimal laser processing and material modification, *Appl. Surf. Sci.*, **253**, 8015-8021.

Lu, H. A., Willis, L.A., Wessels, B.W., Lin, W.P., Zhang, T.G., Wong, G.K., Neumayer, and D.A., Marks, T.J., 1993: Second-harmonic generation of poled $BaTiO_3$ thin films, *Appl. Phys. Lett.*, **62**, 1314-1316.

Morse, D.E., 1999: Silicon biotechnology: Harnessing biological silica production to make new materials, *Trends in Biotechnology,* **17**: 230-232.

Schwenzer, B., Roth, K.M., Gomm, J.R., Murr, M., and Morse, D.E, 2006**:** Kinetically controlled vapor-diffusion synthesis of novel nanostructured metal hydroxide and phosphate films using no organic reagents, *J. Mater. Chem.*, **16**, 401-407.

Sumerel, J.L., Yang, W., Kisailus, D., Weaver, J., Choi, J.H., and Morse, D.E., 2003: Biocatalytic structure-directing synthesis of titanium dioxide, *Chem. Mater*., **15**, 4804-4809.

Wang, X., Zhuang, J., Peng, Q., and Li, Y., 2005: A general strategy for nanocrystal synthesis: The chimpanzee genome, *Nature*, **437**, 121-124.

Whatmore, R.W., 2004: Pyroelectric Arrays: Ceramics and Thin Films, *J. Electroceram,* **13**, 139-147.