Pyroelectric response of spray-deposited $BaTiO_3$ thin film

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ABSTRACT

Pyroelectric photoresponse of aqueous spray deposited thin films containing $BaTiO_3$ nano-crystals is reported. X-ray diffraction data indicate the presence of hexagonal $BaTiO_3$ nano-crystals with ~20 nm crystalline domains in a matrix of some as yet unidentified nano-crystalline material. When the film is annealed at 600 C, the X-ray pattern changes significantly and indicates a conversion to one of the non-hexagonal phases of $BaTiO_3$ as well as a complete change in the matrix. With suitable amplifier, the measured photoresponse was 40V/W. Ferroelectric hysteresis on a film with significant presence of hexagonal $BaTiO_3$ shows saturated polarization which is about 5-times smaller than for the bulk tetragonal phase. A potential application is a patternable infrared detector for photonic and plasmonic devices, such as chip-scale spectral sensors.

Keywords: pyroelectric, thin film, barium titanate, infrared, spray deposit

1. INTRODUCTION

Motivation for the subject research is to develop an in-house IR detector material that can be deposited, patterned, and integrated with on-chip infrared photonic and plasmonic devices, such as spectral sensors [1,2]. Barium titanate (BaTiO3) was selected because this well-known ferroelectric material is amenable to our spray deposition technique, known as Streaming Process for Electrodeless Electrochemical Deposition SPEED. SPEED is superficially similar to spray pyrolysis, except that it does not involve thermal splitting of molecules, and hence operates at lower temperature. SPEED results in perfectly conformal nano-crystalline thin films with strong adhesion[3-5]. Pyroelectric photoresponse of SPEED grown $BaTiO_3$ thin films was first reported in ref.[6]. A purpose of the present paper is to further investigate this response and the dependence of materials properties on processing conditions.

SPEED deposits inorganic thin films over large areas, without a vacuum, a scalable and manufacturing friendly process. Water-soluble compounds with complexing agents grow films by heterogeneous reaction on the substrate, with little wasteful homogeneous reaction. Hydrophilic substrates bind hydroxyl ions, which serve as attachment and nucleation sites with density exceeding 1012 cm^{-2}. The nebulized aqueous precursor impinges on a substrate heated to ~300 ℃, giving growth rate exceeding 200 nm/min. Substrate heating provides reaction activation energy, and it decomposes and volatilizes reaction byproducts.

The five known phases of bulk crystalline $BaTiO_3$ are hexagonal, cubic, tetragonal, orthorhombic, and rhombohedral. Tetragonal is the stable phase at room temperature. The cubic phase exists above the 120 ^{o}C Curie temperature. The high temperature hexagonal phase can be meta-stable at room temperature. The orthorhombic and rhombohedral phases occur at lower temperatures. All but the cubic phase are capable of a pyroelectric photoresponse[7], which is the appearance of a small voltage difference across opposite faces of the material due to a temperature-induced change in the film's intrinsic polarization. The actual stable phase of $BaTiO_3$ film at room temperature can differ from that of bulk

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crystal due to interaction with the substrate, and it can depend on processing history. We previously reported both cubic and hexagonal phase for room temperature SPEED-grown $BaTiO_3$ thin films.[6]

2. EXPERIMENTAL DETAILS

Self-assembled nano-crystalline $BaTiO_3$ films on stainless steel foil substrates were grown by SPEED (Figure 1). The precursor solution included $Ba(NO_2)_2$ and $TiCl_3$ as the source of Ba and Ti ions. The likely reaction is

$$\text{(BaTi)-Ligand}^{(p+6)} + \text{substrate-OH}^{-} \rightarrow \text{substrate-BaTi(OH)}^{5+} + \text{Ligand}^{(p)}\text{(gas)} \qquad (1)$$

$$\text{(substrate)-BaTi(OH)}^{5+} + 5\text{OH}^{-} \rightarrow \text{(substrate)-BaTiO}_3 + 3\text{H}_2\text{O (gas)} \qquad (2)$$

The superscript "p" is the ligand charge, which may be positive, negative, or zero. Thirty spray cycles were applied at 300 ^{o}C, and then the films were annealed at 450 or 500 ^{o}C for 2 hours. Subsequent annealing at 600 ^{o}C was also performed on some samples. A purpose of the post growth anneal was to decompose and volatize residual byproducts and recrystallize the formed nanoparticles based film.

Scanning electron microscopy (SEM, Hitachi SU70) with energy dispersive X-ray spectroscopy (EDX) was used for surface and cross sectional imaging and elemental analysis. Asymmetric out-of-plane X-ray diffraction (XRD, PANalytical Empyrean) was performed to determine crystalline phases. The Cu Kα X-ray beam at 0.1540598 nm was incident at a fixed angle of $\omega = 10$ deg. The scattered intensity was recorded as a function of scattering angle 2θ.

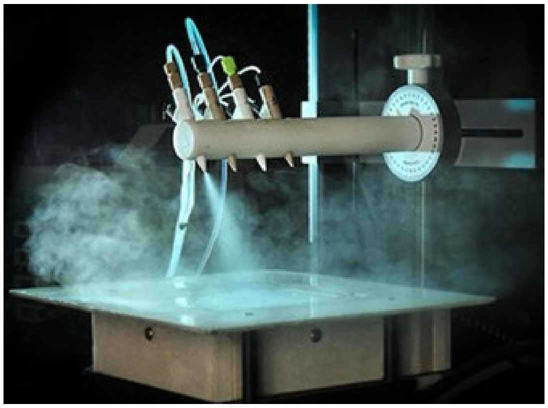

Figure 1. Photograph of SPEED deposition system.

For photo-response measurements, a ~1-μm-thick film on stainless steel substrate was coated with a ~30 μm thick conducting carbon-black IR absorbing layer. Sample area was 1 to 4 cm^2. Photo-response measurements were made using two different IR sources and amplifiers.

System A comprised a CO_2 laser (Access Lasy 3S) with ~100 mW CW power, which was mechanically chopped at 70 Hz. Laser spot size on the sample was ~1-2 mm. A spring contact was made to the carbon black layer and connected to the inverting input of a type 741 operational amplifier with 1 MΩ negative feedback resistor. The substrate and non-inverting input of the op-amp were grounded. There was no electronic filtering. A digital oscilloscope averaged 64 traces of the photoresponse.

System B measured pyroelectric current based on the dynamic capacitance method[8]. A broadband black-body source chopped at 1 Hz illuminated the sample with ~13 mW/cm^2. A low-noise high-gain pre-amplifier converted the pyroelectric current into a voltage with gain of 1V/100 pA. The signal was filtered by a 7.2 Hz low-pass. A digital oscilloscope averaged 16 traces.

Ferroelectric hysteresis was measured by the Sawyer Tower method[9]. A sawtooth voltage V_x was applied across the series combination of a capacitor made from our ~1 μm thick film with area $A = 1$ cm^2 and a sense capacitor $C_s = 1$ μF. Since most of V_x is dropped across the much smaller sample capacitor, the electric field in the film is V_x divided by film thickness. The polarization is determined by the extraneous charge on the sample capacitor, which is the same as that on the sense capacitor, so that $P = (C_s/A)\ V_y$, where V_y is the voltage dropped on C_s.

3. RESULTS

Figure 2 presents a top-view SEM image of the grown thin film. We refer to our films as "$BaTiO_3$ thin films" even though subsequent analysis shows that they are only partially composed of this compound, in contrast to our previously reported films[6], in which $BaTiO_3$ was the dominant crystalline phase. The SEM image reveals grains with a size distribution of about 50 to 200 nm. Additional SEM images reveal a fine grained matrix that contains cracks.

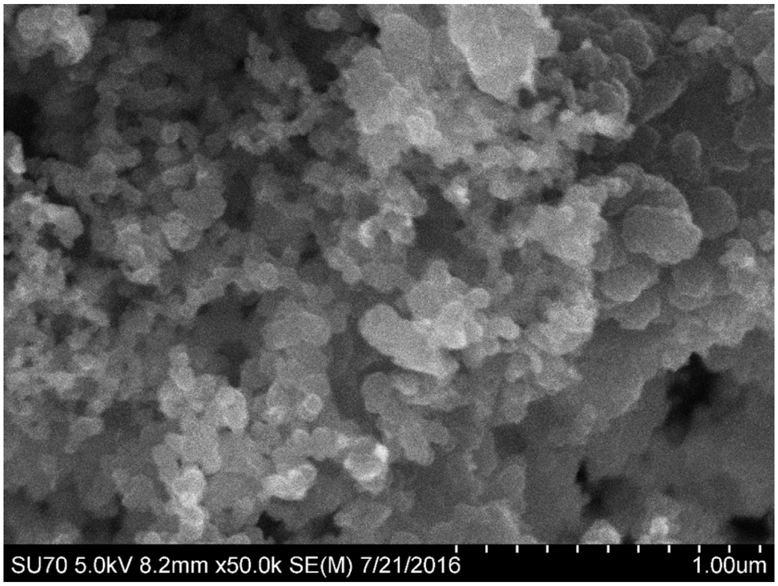

Figure 2. High resolution SEM image of SPEED-grown $BaTiO_3$ thin film.

Figure 3 presents an SEM image of the surface at the edge of the carbon-black coating at low magnification. The $BaTiO_3$ film has a white crust, which EDX shows to be up to 35% Cl. This indicates that the Cl byproduct was incompletely volatized, and it suggests the need for longer and hotter anneals. EDX on the carbon-black film shows almost exclusively carbon. Cross sectional SEM imaging shows the $BaTiO_3$ and C-black films to be ~1 and ~30 μm thick, respectively.

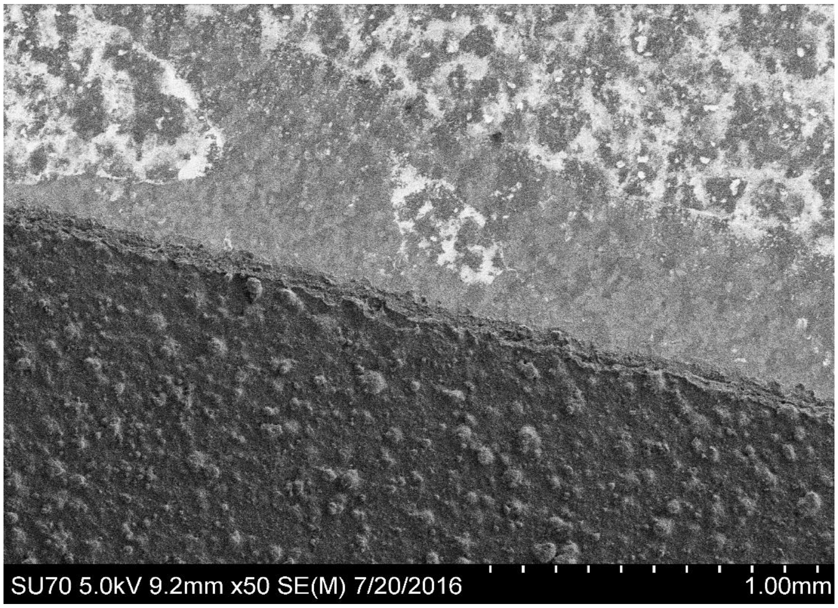

Figure 3. SEM image of surface of SPEED-grown $BaTiO_3$ film with carbon-black coating (lower region).

Figure 4 presents powder XRD reference data for the various phases of $BaTiO_3$. The signal-to-noise ratio is sufficiently low in the XRD data for our thin films that the non-hexagonal phases would be difficult to distinguish from each other. The XRD pattern for the hexagonal phase is much different than the others. The relative intensities of XRD peaks for nano-crystalline thin films can differ significantly from those of the powder due to interactions with the substrate.

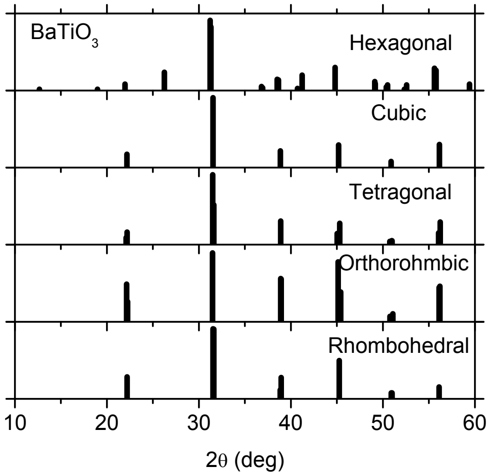

Figure 4. Reference Powder XRD spectra for the five phases of $BaTiO_3$.

Figure 5 compares our measured XRD data for films annealed after growth at the three different temperatures 450, 500, and 600 ^{o}C. The annealing times were 1, 2, and 4 hours respectively. At a given annealing temperature, the XRD spectrum was independent of annealing time in the range 1-4 hours. The substrate spectrum was taken on the backside of the substrate and reveals substrate lines at ~44 and 51 degrees. These substrate lines appear as artifacts in the XRD of the two lower-temperature annealed samples. The expected peak positions for hexagonal and cubic $BaTiO_3$ are indicated. In all three spectra, the dominant peaks do not belong to any of the 5 $BaTiO_3$ phases. In the two lower temperature annealed samples there are several weak peaks that could correspond to the hexagonal phase, but they could with equal probability be assigned to phases of residue $TiCl_2$, $TiCl_3$, or $TiCl_4$, and the strongest peaks in these spectra belong with high confidence to a hexagonal phase of $TiCl_3$, which itself could be pyroelectric.

In the 600 ^{o}C annealed sample there are a few small XRD peaks that can be identified with one of the non-hexagonal phases. Thus it appears that the films are a mixture of $BaTiO_3$ nano-crystals in a matrix of some other polycrystalline material. The transition from hexagonal to one of the other phases with increasing annealing temperature agrees with our previous observation on a different set of films [6], which were more nearly pure $BaTiO_3$. Scherrer's formula[10] indicates that the lower bound on the mean size of the ordered crystalline domains of $BaTiO_3$ is ~20 nm.

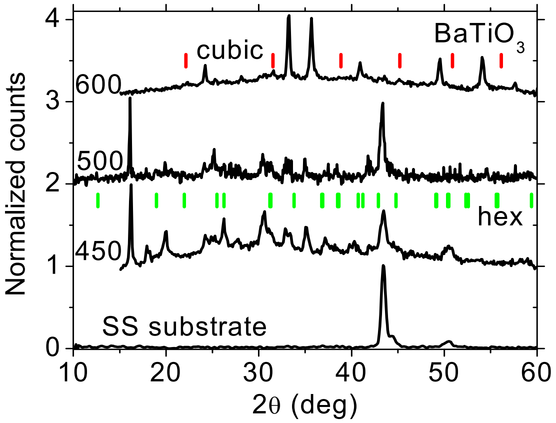

Figure 5. XRD spectra of SPEED-grown $BaTiO_3$ thin films. Annealing temperatures in degrees C and the reference positions of XRD peaks for cubic and hexagonal phases are indicated.

Figure 6 (left) presents photoresponse data for a carbon-black coated sample annealed at 500 ^{o}C for 2 hours using measurement system A. The signal comprises a peak when the chopped laser first illuminates the sample, and a smaller and slower signal when the laser is chopped off. The response time is about 1 ms. The responsivity is about 100 mV/W, which is considerably more than the ~1 μV/W we previously reported for a more-nearly pure hexagonal $BaTiO_3$ film using a 100 ns pulsed CO_2 TEA laser with a similar amplifier.[6] That earlier peak response was reduced by the ratio of laser pulse duration to system response time, 100 ns/5 ms = 20 x 10^{-6}. Scaling the earlier result by that ratio gives ~50 mV/W as the probable response that would be measured for that earlier film using measurement system A. Thus, the present measurement is in agreement with the earlier one.

Figure 6 (right) presents photo-response using measurement system B. The signal is now symmetric with respect to the on-off chopping of the source. The peak output voltage was 0.5 V. The response has a 400 ms time constant, which is slower than expected for the 7.2 Hz filter cut-off frequency. With system B, we achieve responsivity of 40 V/W.

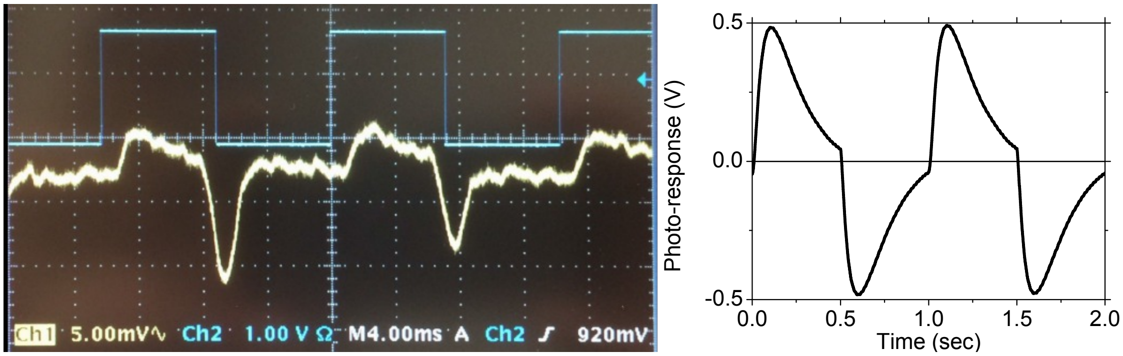

Figure 6. (left) Oscilloscope screen shot showing pyroelectric response to 100 mW CO_2 laser chopped at 70 Hz, amplifier A. (right) Response to 13 mW/cm^2 broad-band IR source chopped at 1 Hz, amplifier B.

Previously we reported the appearance of a short-lived (1 min) photoresponse that appeared after poling the film with a few volts bias at room temperature. The sign of the photoresponse depended on the sign of the applied bias. We now interpret this effect as poling-induced charging of traps, whose spatial distribution depends on the sign of the applied bias. When the sample is hit by infrared, these traps are thermally discharged, giving a current that is comparable to pyroelectric current. As soon as the traps are all emptied, the effect disappears. This effect is known to be especially significant in thin films.[11]

Figure 7 presents ferroelectric hysteresis measured on the film studied in ref.[6]. The saturated polarization is of order 0.05 C/m^2, which is 5x smaller than the value for bulk $BaTiO_3$.[12] That film was primarily hexagonal phase, with significant admixture of some other material, which can explain the relative smallness of its P_s compared to bulk tetragonal $BaTiO_3$.

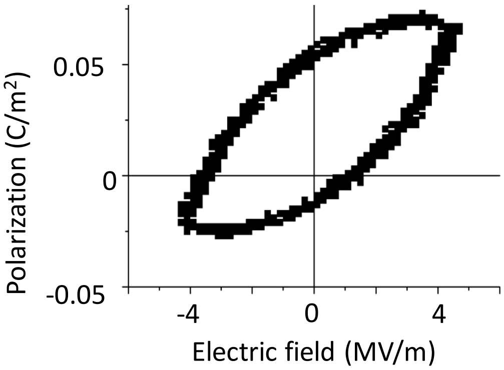

Figure 7. Ferroelectric hysteresis curve of $BaTiO_3$ thin film.

4. DISCUSSION

Refs.[1,2] described a design for spectrometer on a chip. The design comprised a broad-band IR source, rectangular photonic waveguide, interaction region, dispersion region, and detectors. In that paper, only the waveguide section formed by deep reactive ion etching of silicon had actually been fabricated. The proposed sources were IR LEDs, but integrating these onto the chip had not been considered. An adiabatic taper transduced the photons in the waveguide to surface plasmons polaritons that existed in a gap between the outer side walls of the narrowed waveguide and vertical side walls of border material coated with suitable conductor. We have since demonstrated perfectly conformal conducting SnO_2: F that can be deposited by SPEED on such sidewalls to support surface plasmons in this interaction region.[5] With Ref.[6] and this paper we have presented first results on a pyroelectric $BaTiO_3$ detector material, which can be deposited by SPEED, and which in principle can be positioned at the end of a waveguide by standard photolithographic patterning. Clearly, considerable work remains to optimize the film, to develop processes, and to design suitable amplifiers.

5. CONCLUSIONS

$BaTiO_3$ thin films were grown by an aqueous spray deposition process. Two phases were observed, depending on annealing temperature, in a matrix of some other material. The sample with hexagonal phase demonstrated a pyroelectric infrared photoresponse.

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