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Piezoelectric Property Enhancement of PZT Thick Film via Pulsed Flash Poling during Sintering

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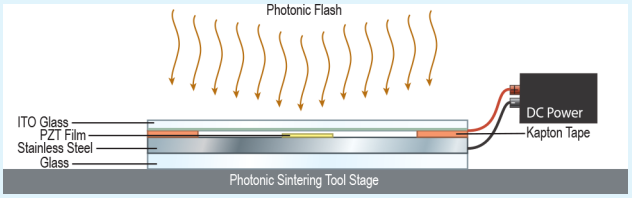
Supporting Information

ABSTRACT: Lead zirconate titanate (PZT) is a widely used piezoelectric material due to its high piezoelectric response. High-temperature thermal sintering and poling are two important steps to obtain a high piezoelectric property PZT film by densifying the film and reorienting the dipoles along the desired direction, respectively. However, these two steps are processed separately, which increases the duration and complexity of the process. Moreover, a high-temperature process limits the selection of electrode and substrate material to those materials with very high melting points. This paper experimentally demonstrates the feasibility of sintering and poling simultaneously, providing a novel approach to prepare PZT film. Moreover, this paper investigates the effect of cyclic temperature excursions above and below the Curie temperature on the piezoelectric properties of PZT thick film. Photonic sintering with high-intensity, short-duration pulsed flashes was used to fuse and merge PZT particles. Simultaneously, an electrical poling field (20 kV/cm) was applied through the PZT film to reorient the PZT dipoles. The entire processing duration was less than 5 min. The resultant piezoelectric property of the PZT film was analyzed, yielding high g_{33} (22.6×10^{-3} Vm/N), d_{33} (626×10^{-12} m/V), and permittivity (3130) values, indicating good sensing and actuating capabilities. This enhanced piezoelectric performance is superior to the groups of PZT films prepared using traditional processes. This approach has potential applications for obtaining high-performance piezoelectric devices, such as piezoelectric energy harvesters, memory storage devices, or bulk acoustic wave resonators.



KEYWORDS: *piezoelectric, PZT, photonic sintering, poling, pulsed flash, additive manufacturing*

INTRODUCTION

Lead zirconate titanate (PZT) ceramic piezoelectric devices have a current worldwide market of over a billion dollars.[1] This material has been widely used in various transducers, such as actuators,[2] sensors,[3] and energy harvesters,[4] due to its conversion efficiency between electrical and mechanical forces. Sintering and poling are vital steps to enhance the electric properties of the PZT film via densifying the film and reorienting the dipoles along the desired direction, respectively. These two steps are processed separately, which increases the duration and complexity of the process. Moreover, processing PZT at a high temperature (>800 °C) for sintering can impact the piezoelectric properties, due in part to the volatility of the Pb.[5] High sintering temperatures also limit the selection of electrode and substrate materials to those with very high melting points. For example, platinum is a common high-temperature electrode exhibiting high chemical resistance, making patterning the electrode features difficult.[6] Substrates exhibiting high melting points lack flexibility desired in many applications. To address challenges in electrode and substrate material, film transfer methods are often employed, with the sintered PZT film transferred to low melting point substrates which enables the utilization of a range of electrode materials.[7] However, the process complexity limits the utility of this approach; there is a need for low-temperature processing of PZT films to expand the range of substrate/electrode materials and to simplify the process.

Many methods have been developed to lower the PZT sintering temperature. Adding a sintering aid is the most popular approach.[8−10] However, in principle, the sintering aids have to be considered as an impurity in the PZT film. Therefore, optimized control of the type and quantity of the sintering aid is essential to minimize potential deterioration of the piezoelectric properties of the resulting film.[1] There is a need for processes that move beyond the limitations of sintering aids, enabling low-temperature sintering of PZT films while maintaining robust piezoelectric performance.

Poling is an essential process that reorients the dipole direction in the material, to enhance the piezoelectric property of the ferroelectric film. Ideally poling uses a relatively low electric field with short duration to achieve dipole reorientation along the field. However, due to the low mobility of the dipoles, it is difficult to meet both requirements (low field and short duration) and achieve high poling quality. Poling at elevated temperature is accordingly widely used to increase dipole mobility. High poling refers to the process that starts

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from a temperature above the Curie temperature (T_c) which is then gradually reduced below T_c, which has been demonstrated to improve piezoelectric properties.[11] However, cyclically raising and lowering the temperature to above and below the T_c has not previously been investigated.

Recently, a high-energy pulsed flash technique known as photonic sintering was demonstrated to sinter PZT thick films in extremely short duration (<1 min) with a low substrate temperature increase (<200 °C).[10] Due to the low secondary pyrochlore phase exhibited in the photonically sintered PZT film, high piezoelectric properties were achieved. This process utilizes repetitive sub-millisecond pulses to drive rapid temperature excursions in the PZT film to above and below the Curie temperature. While this process has previously demonstrated robust sintering quality,[12] the effect of cyclic temperature fluctuations around T_c on dipole reorientation has not been explored.

In this paper, we have investigated the effect of cyclic temperature excursions above and below the Curie temperature on the piezoelectric properties of printed PZT thick films. Moreover, we experimentally demonstrated the feasibility of performing poling and sintering simultaneously. The resultant piezoelectric property of the PZT film was analyzed, demonstrating enhanced piezoelectric performance over traditional processing.

EXPERIMENTAL SECTION

1. Ink and Film Preparation. The ink was prepared from commercially available PZT nanoparticles (LQ-S2-P, Choko Co., Ltd., Japan) with an approximately 480 nm average size and 1.6 μm largest particle size with a T_c of 220 °C. A liquid-phase sintering aid (combination of Cu_2O and PbO in a molar percentage ratio of 1:4) was added to lower the required sintering temperature of the PZT film.[8] Polyvinylpyrrolidone (PVP) was added to serve as a particle dispersant and to promote adhesion between the substrate and the PZT film following drying. The ink composition is listed in Table 1.

Table 1. PZT Ink Composition

material	weight percent
PZT	30
DI Water	65.4
PVP	3
Cu_2O	0.22
PbO	1.38

Because the particles are on the nanosize scale, they tend to agglomerate together. Therefore, the mixture was first mixed with an ultrasonic horn (F60 Sonic Dismembrator, Fisher Scientific International, Inc., Hampton, NH) for 5 min to separate the particles. Then, it was stirred using a homogenizer (PRO 250; PRO Scientific Inc., Oxford, CT) for 5 min to mix all components to achieve a homogeneous solution.

The PZT ink was then transferred to the aerosol jet printer jar and printed using an aerosol jet printing technique (AJ300, Optomec Inc., Albuquerue, NM) as described in our prior work.[12] Before sintering, the printed film was baked on a hot plate at 150 °C for 1 h in atmospheric conditions for dehydration. The hot plate was then turned off, and the dried PZT film was kept on the hot plate to cool to room temperature.

2. Photonic Sintering with ITO Glass. The PZT film was sintered in a photonic sintering system (PulseForge 3300, Novacentrix Corporation, Austin, TX). This system contains a broadband (ultraviolet to infrared) Xenon flash lamp which can generate high-intensity flash pulses with a <1 ms duration. The energy profile generated by the system is defined by five parameters: applied voltage, pulse duration, pulse frequency, number of pulses, and number of cycles. The photonic energy is absorbed by the target film, raising the temperature to above that required for sintering within an extremely short time (msec). Control of the energy profile through the system parameters enables sintering of the printed PZT film while limiting the temperature rise of the underlying substrate. Printed PZT has been processed directly on low melting point substrates using this technique.[12] Here, we modified this capability to enable sintering through a transparent, conductive film that will allow simultaneous application of an electric field for electrical poling of ferroelectric films.

In order to apply an electric field across the PZT film, the film was sandwiched between a bottom electrode formed by the substrate and a top electrode formed by indium tin oxide (ITO)-coated glass. ITO is commonly used in the semiconductor industry as a transparent ohmic contact, especially for optoelectronic applications[13,14] due to its relatively high transparency and low resistivity.[15] In this work, an ITO glass slide (ITO-111-25, Nanocs Inc., Boston, MA) with an approximately 0.6 μm ITO layer with a 10 Ω/sq sheet resistance served as the top electrode. The light absorption spectrum of the ITO glass slide (Figure 1) shows some absorbance in ultraviolet, reducing

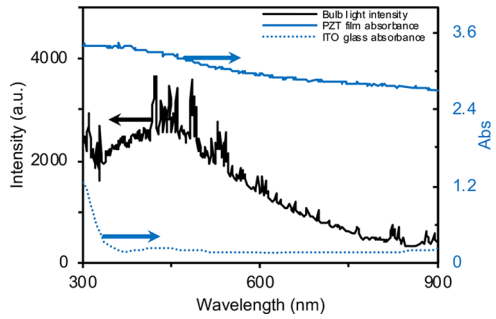

Figure 1. Light intensity spectrum of the Novacentrix bulb generated at a 600 V level pulse setting (black), with a peak emission in the violet regime. The dried PZT film light absorbance spectral curve (blue) has significant overlap with the bulb emission, with the greatest absorbance in the ultraviolet (<400 nm) range. The ITO glass slide also has the greatest absorbance in the ultraviolet region, impacting effective energy transfer to the PZT film.

the effective flash energy transferred to the PZT film and impacting the film sintering quality. There was also risk of conductivity loss of the ITO due to absorbance, necessitating a reduction of the energy in each pulse as compared to our prior work.[12] To optimize the process for effective sintering without damage to the ITO, a two-level, three-variable, full-factorial design of experiments was performed with two replicates on 7 mm × 7 mm× 0.006 mm PZT films on stainless steel substrates (described in the Supporting Information). A qualitative investigation by scanning electron microscopy (SEM) imaging (MIRA3, TESCAN, Czech Republic) was used for the response of the DOE (described in the Supporting Information). The DOE statistical analysis indicates that the effect of the voltage and duration, which directly contribute to the energy generated from the lamp and the energy transferred to the PZT film for sintering, is more important to the sintering quality than the other parameters. The optimized parameter combination yielded an applied voltage of 600 V, pulse duration of 130 μs, pulse frequency of 2 Hz, number of pulses of 23, and number of cycles of 2. This parameter combination resulted in an energy density of 2.75 J/cm^2 delivered from the lamp for each flash pulse. However, due to the light absorption of the ITO layer, the effective energy density transferred to the targeted PZT film from each pulse was only 1.90 J/cm^2 (total = 87.4 J/cm^2) as measured by a pulsed light energy meter (BX-100, Novacentrix, Austin, TX). The light intensity spectrum of the photonic sintering bulb generated at a 600 V pulse setting is shown in the Figure 1. It has peak emission in the violet regime, which has significant overlap with the dried PZT film light absorbance.

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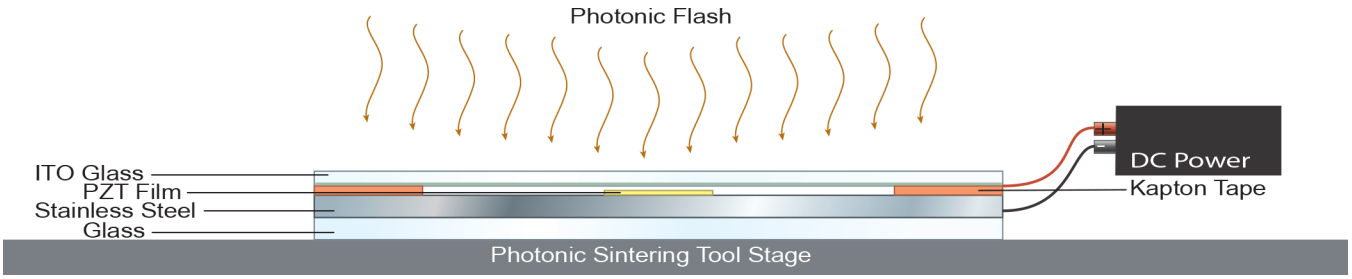

Figure 2. Setup for photonic sintering of the PZT film with simultaneous poling. The PZT film was sandwiched between a top (ITO-coated glass with the ITO layer facing down) and bottom (stainless steel) electrodes. Photonic flashes were transferred through the transparent top ITO glass electrode to create a rapid temperature transient in the film. An electric field is continuously applied to the sample during sintering to reorient the electric dipoles in the PZT film.

3. Poling while Photonic Sintering. To simultaneously pole the PZT films during photonic sintering, an electric field was provided across the film, as shown in Figure 2. The stainless steel substrate served as the bottom electrode, while the ITO glass slide served as the top electrode, with the ITO layer facing down to minimize the electrode separation and maximize the electric field. To avoid contact between the electrodes, Kapton tape (thickness = 60 μm, width = 12 mm) was used as an insulator layer separating the top and bottom electrodes. A plain glass slide (thickness = 1 mm) (Thermo Fisher Scientific, Inc., USA) was placed between the bottom stainless steel electrode and photonic sintering tool stage to avoid electrical shorting. During photonic sintering, a DC voltage of 120 V was applied across the electrodes, providing an electric field of 20 kV/cm across the PZT film to reorient the electric dipoles.

4. Testing Groups. To investigate the effect of sintering and poling techniques on the resulting piezoelectric properties of printed PZT films and to demonstrate the advantages of poling while photonic sintering, six techniques were explored using combinations of the conditions outlined in Table 2.

Table 2. Processing Conditions for Experimental Design

abbreviation	technique	conditions
TS	thermal sintering	1000 °C for 1 h in an N_2 environment
PS	photonic sintering	202 J/cm^2 energy[a], no ITO
RP	regular poling	170 °C, 20 kV/cm, 1 h
SP	short poling	170 °C, 20 kV/cm, 5 min
PDS	poling during sintering	87 J/cm^2 energy[b], ITO, 20 kV/cm for 5 min

[a]Voltage = 400 V; pulse duration = 650 μs; pulse frequency = 2 Hz; number of pulses = 20; and number of cycles = 2 (this parameter combination was processed without ITO glass, yielding a fully sintered PZT film along both the $X-Y$ plain and the Z direction). Single pulse energy density at film = 5.06 J/cm^2. [b]Voltage = 600 V; pulse duration = 130 μs; pulse frequency = 2 Hz; number of pulses = 23; and number of cycles = 2. Single effective pulse energy density at film = 1.90 J/cm^2.

(1) **TS-RP**: traditional sintering and regular poling.
(2) **PS-RP**: photonic sintering with regular poling.
(3) **PDS**: poling during sintering.
(4) **TS-SP**: traditional sintering with a short-duration poling equivalent to the PDS process.
(5) **PS-SP**: photonic sintering with short duration poling.
(6) **PDS-RP**: poling during sintering followed by a regular poling process.

5. Characterization Methods. To study the sintering quality along both the $X-Y$ plane and in the Z direction of the film, a qualitative evaluation was performed using SEM to observe the morphology (i.e., $X-Y$ plane) and cross-sectional structure (i.e., Z direction) of unsintered, thermally sintered, and photonically sintered films. Sintering is the process to densify the film by fusing and merging particles, resulting in a larger particle size after sintering. A monolithic layer is preferred, indicating a fully consolidated film.

Transmission electron microscopy (TEM) (JEOL 2010, Japan; operated at 200 kV using a LaB_6 filament) was used to investigate the PDS-processed PZT films. The TEM sample was prepared by scraping the PDS-processed film off from the substrate using a scalpel. The film scraps were transferred to a small ceramic vial. A few drops of isopropyl alcohol (IPA) were added for dispersion. The vial then underwent ultrasonication for 5 min to disperse the particles in the fluid. Then, 10 μL of dispersed PZT sample was taken using a pipet and put on a TEM carbon mesh. After 10 min of rest to completely evaporate the solvent (i.e., IPA), the sample was ready for TEM analysis.

The piezoelectric voltage coefficient (g_{33}) and relative permittivity (ε_r) of all six groups of PZT films were measured using a self-built cylinder system and an RC bridge circuit, respectively, as described in our previous work.[12] Prior to measurement, the samples were allowed to rest at room temperature overnight to eliminate aging effects,[16] and the top surface was coated with a layer of silver epoxy (EJ2189, Epoxy Technology, Inc., Billerica, MA) that was served as the top electrode (5 × 5 mm^2) for electrical characterization measurements. The d_{33} piezoelectric charge coefficient was calculated using eq 1 for quantitative comparison.

$$d_{33} = g_{33}\varepsilon_r\varepsilon_0 \quad (1)$$

where $\varepsilon_0 = 8.854 \times 10^{-12}$ F/m, and g_{33} and ε_r are average measured values.

RESULTS AND DISCUSSION

SEM imaging was used to study the sintering quality of ITO glass-covered PZT film, as shown in the Figure 3. Before sintering, an approximately 6 μm thick film was achieved with a consistent thickness and uniformly distributed particles (Figure 3 (a) and (e)). After the performance of traditional thermal and photonic (PS parameter combination) sintering, the particles were fused and merged into a monolithic layer, indicating a high sintering quality (Figure 3 (b) and (f) for traditional sintering; Figure 3 (c) and (g) for photonic sintering). However, to protect the ITO layer from burning and accordingly losing its electric conductivity, a low flash energy was used for the PDS process. Moreover, the effective sintering energy was further lowered due to the energy absorption of the ITO layer. Therefore, pores and gaps between the particles are visible in the PDS-prepared film (Figure 3 (d) and (h)).

The TEM result is shown in the Figure 4. Bright spot arrays are clearly observed on the selected area electron diffraction (SAED) pattern, indicating good crystallization in the PDS-processed PZT film (Figure 4 (a)). The TEM micrograph showing the sample used for TEM analysis is presented in

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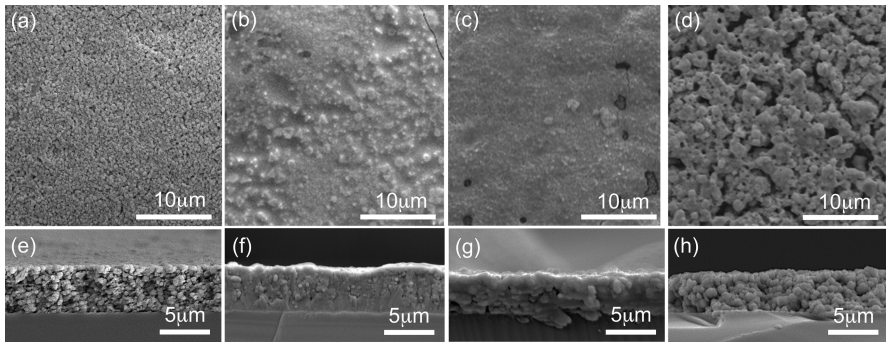

Figure 3. Prior to sintering (a), the particles were uniformly distributed in the film. After traditional thermal (b) and photonic (c) sintering (PS parameter combination), the particles were fully fused and merged to form a monolithic film. After the PDS process (d), the particles in the prepared film were expanded and also merged. However, because a lower sintering energy was used and the ITO layer further absorbed the light energy, gaps and pores between particles were visible. Images (e–h) are cross-sectional views of the unsintered, traditionally sintered, photonically sintered (PS parameter combination), and PDS-processed films, respectively.

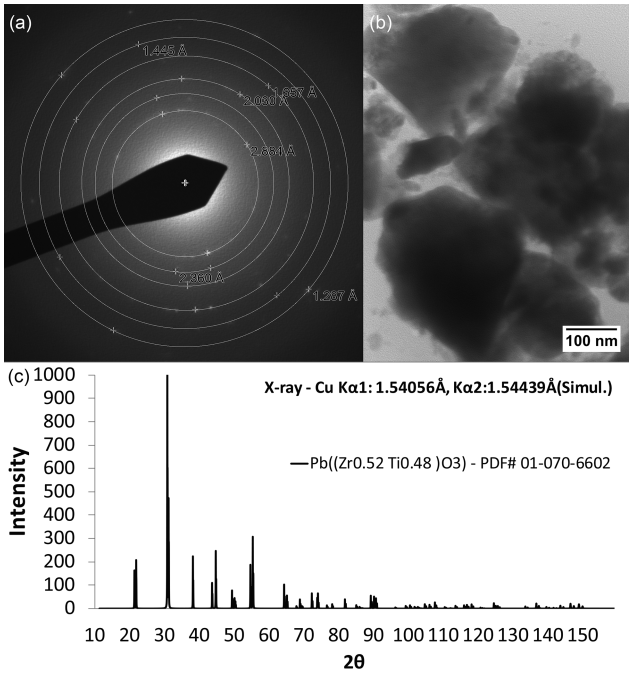

Figure 4. TEM analysis of PDS-processed PZT film. The selected area electron diffraction (SAED) pattern (a), which was captured from the sample shown in (b), shows clear white dot arrays, indicating good crystallization in the processed PZT film. The pattern-peak positions agree well with the standard ICDD database for PZT crystallization, indicating a pure perovskite phase existing in the processed PZT film (c).

Figure 4 (b). The diffraction-peak positions extracted from the SAED pattern agree very well with the ICDD (International Center for Diffraction Data) powder diffraction files (PDF-4+, 2018, PDF#: 00-033-0784, 01-070-6602, 01-080-6049, 01-083-4007, 01-083-4008, 01-083-4010, 01-083-4011, 01-082-2857), with the best match to file 01-070-6602, as shown Figure 4 (c). This demonstrates that there is only perovskite phase existing in the processed PZT film.

The electrical characterization results of all six groups are summarized in Table 3, presented as the average and standard deviation of five samples for each group. The d_{33} values were calculated from the averaged g_{33} and ε_r values using eq 1. The PDS-prepared PZT yielded superior piezoelectric properties, demonstrating enhancement via poling during photonic

Table 3. Measured Piezoelectric Properties of the Processed PZT Films

methods	g_{33} (10^{-3} Vm/N)	d_{33} (10^{-12} m/V)	ε_r
TS-RP	21.3 ± 1.4	341.2	1810 ± 246
PS-RP	22.1 ± 2.0	516.3	2640 ± 305
PDS	**22.6 ± 1.9**	**626.0**	**3130 ± 242**
TS-SP	6.6 ± 0.8	21.6	370 ± 57
PS-SP	8.0 ± 1.0	26.4	373 ± 40
PDS-RP	22.5 ± 2.0	597.2	2999 ± 261

sintering. Therefore, the high g_{33} (22.6×10^{-3} Vm/N) and d_{33} (626.0×10^{-12} m/V) values should provide the best sensing and actuation performance among all six groups. There are two elements of the PDS processing that may contribute to this enhancement.

During traditional processing, prior to poling, the dipoles are randomly oriented to yield an electrically balanced state. Application of the electric field during poling must provide sufficient energy to overcome interdomain stress to reorient the dipoles along the poling direction.[17] One hypothesis for the enhanced piezoelectric properties with the PDS processing is dipole formation under an applied electric field as the film temperature is rapidly cycled from above to below the Curie temperature (T_c = 220 °C). This avoids the need to overcome traditional interdomain stress, enabling higher piezoelectric properties to be achieved with a relatively low poling field. The second hypothesized contribution to PDS enhancement is the UV photoactivation provided by the broadband lamp of the photonic sintering tool. As proposed by Kholkin and Setter, UV light can generate photoexcited charge carriers that drift under the applied electric field and are trapped by defects near the film/electrode interface. This results in compensation of the depolarization field and enhanced piezoelectric coefficients.[18] Researchers continue to work to fully understand the underlying mechanisms leading to the enhanced performance.

The entire poling and sintering duration for PDS group is only 5 min. This short poling duration is not sufficient to reorient the dipoles using an applied electric field following either traditional or photonic sintering (TS-SP: g_{33} = 6.6 × 10^{-3} Vm/N, d_{33} = 21.6 × 10^{-12} m/V; PS-SP: g_{33} = 8.0 × 10^{-3} Vm/N, d_{33} = 26.4 × 10^{-12} m/V). During PDS processing, the dipoles are directly formed along the poling field direction during the phase transition while the temperature decreases below the T_c value. Since this phase transition occurs on the

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order of nanoseconds,[19] the short duration PDS processing can still achieve high piezoelectric properties.

By comparing the PDS-RP group (g_{33} = 22.5 × 10^{-3} Vm/N, d_{33} = 597.2 × 10^{-12} m/V) with the PDS group, we identified that both the g_{33} and d_{33} values obtained from PDS group cannot be further improved by post-regular poling. In fact, the performance of regular poling following PDS processing results in a slight reduction in piezoelectric properties. This may be attributed to the usage of the lower poling temperature giving rise to the relatively lower poling energy. Therefore, this leads to a slight depolarization to the PZT film.

Photonic sintering (PS-RP) provides improvements over traditional thermal sintering (TS-RP) when processed with the same poling conditions. This is likely due to the photonic processing limiting the time spent at high temperature and associated Pb loss from the film. This loss of Pb leads to a secondary phase pyrochlore phase which negatively impacts the piezoelectric properties.[12]

These results were limited by the requirement for lower photonic energy to prevent damage of the transparent ITO layer. The sintering quality is inferior as evidenced by Figure 3 (c) and (d). Because a lower sintering energy was used to protect the ITO layer, the particles in Figure 3 (d) are not merged and fused as great as the one shown in Figure 3 (c). An exploration of alternative transparent and conductive top electrodes to allow greater energy transfer to the PZT film is required.

The pulsed poling during sintering technique can be used to realize many piezoelectric applications. For instance, flexible energy harvesters have been studied extensively in the past decade[20] to achieve high deflection and accordingly obtain high electrical energy. However, due to the mismatch of PZT sintering temperature and the substrate melting temperature, the film transfer method[7] is the main method to realize flexible energy harvesters. Direct sintering of the PZT film on the low melting point substrate has been demonstrated via the photonic sintering technique.[12] By further employing the pulsed poling during sintering technique, we expect that the performance of flexible energy harvesters can improve further.

CONCLUSIONS

The feasibility of performing electric poling of PZT thick films during photonic sintering was demonstrated, with the entire process completed in ∼5 min. The PZT particles were fused and merged together after photonic sintering. Five additional PZT film groups processed using different sintering and poling technique combinations were prepared for comparison, and their piezoelectric and dielectric characteristics were measured. The group prepared using the approach of poling while photonic sintering (PDS) yielded superior piezoelectric properties, which cannot be further enhanced using a conventional poling approach. The high piezoelectric properties cannot be obtained in this short, 5-min time scale using a traditional poling approach, suggesting a unique capability enabled through the rapid cycling to above the Curie temperature in combination with strong pulsed UV illumination. This approach has potential applications for obtaining high-performance piezoelectric devices, especially on low melting temperature flexible substrates.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsaem.8b01337.

Additional details on the design of the experiment to optimize the pulsed-flash PZT film sintering process (PDF)

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Author Contributions

The manuscript was written with contributions from all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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