# Supporting Information:
# Design of Experiment for Photonic Sintering of PZT Thick Films

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In order to optimize the sintering parameters to obtain a photonically sintered PZT film without damaging the ITO glass slide, a full factorial design of experiment (DOE) with three variables (voltage, pulse duration, and number of cycles), two levels, and two replicates was carried out. Based on previous research, frequency is the least significant factor for the sintering quality. Therefore, the frequency was not considered as a variable, and the value was fixed at 2 Hz. 20 pulses gave the best sintering quality based on the empirical analysis. Therefore, for all DOE experiments, the number of pulses was fixed to 20. The factor and level matrix are shown in the Table S1. The response was estimated from the qualitative observation of the sintered PZT films with the assistance of SEM images. A quality number ranging from 0 to 1 was defined to represent the sintering quality and to serve as the response for the DOE. The quality number of 0 represents an unsintered film, where the individual unsintered particles can still clearly be seen; while 1 represents the film has been highly overheated to form large balls, which affects the uniformity of the film and causes the porosity and delamination due to the poor intra-layer bonding [1]. Therefore, the closer to 0.5, the better the sintering quality of the PZT film. SEM images of PZT film with quality number = 0.10, 0.40, and 1.0 are shown in the Fig. S1 (a), (b), and (c), respectively. The main effects plots of the DOE are shown in Fig. S2. It indicates that the higher voltage/duration/number of cycles, the higher quality number. Also, the effect of the voltage and duration to the quality number is more important than number of cycles. The ANOVA table is shown in Table S2. It shows that within the specified range of the factors, voltage and duration had the greatest impact to the sintering quality, as well as the interaction between these two factors, due to the low p-value ($< 0.05$). Moreover, the high R-square (99.4%) shown in Table S2 indicates that this ANOVA model is reliable. In addition, the residual plots are shown in the Fig. S3. The normal probability plot shows discrete data because of the discontinuous experimental results. The random scatter around the horizontal “zero error line” and the constant spread in the residual versus fit plot, plus marginally skewed normal distribution of residual frequency plot further verifies that there are no violations in using the aforementioned ANOVA model. The best response was obtained when using the combination of voltage = 600 V, duration =130μsec, frequency = 2 Hz, number of pulses = 20, and number of cycles = 2. However, the response for this combination was 0.40, indicating a slight underexposure. Further optimization was performed based on this by fine tuning the least important parameters (frequency and number of pulses). The final optimized parameters were: voltage = 600 V, duration = 130μsec, frequency = 2 Hz, number of pulses = 23, and number of cycles = 2.  This yielded a quality factor of 0.45. It is important to note that the parameter combination for achieving 0.5 quality number started to damage the ITO glass, giving rise to conductivity reduction and negatively affecting the poling process. Therefore, in order to ensure the good quality of both sintering and poling, a 0.45 quality number was chosen practically.

Table S1. Factor table and experimental response results for photonic sintering parameter optimization.

| RunOrder | Voltage (V) | Duration (μsec) | No of Cycles | Response |
|---|---|---|---|---|
| 1 | 400 | 130 | 1 | 0.10 |
| 2 | 600 | 500 | 1 | 1.00 |
| 3 | 600 | 130 | 2 | 0.40 |
| 4 | 400 | 130 | 1 | 0.15 |
| 5 | 400 | 130 | 2 | 0.15 |
| 6 | 600 | 130 | 1 | 0.30 |
| 7 | 400 | 500 | 1 | 0.25 |
| 8 | 600 | 130 | 2 | 0.40 |
| 9 | 400 | 500 | 2 | 0.40 |
| 10 | 400 | 500 | 1 | 0.35 |
| 11 | 600 | 500 | 1 | 1.00 |
| 12 | 600 | 130 | 1 | 0.35 |
| 13 | 600 | 500 | 2 | 1.00 |
| 14 | 600 | 500 | 2 | 1.00 |
| 15 | 400 | 130 | 2 | 0.20 |
| 16 | 400 | 500 | 2 | 0.35 |

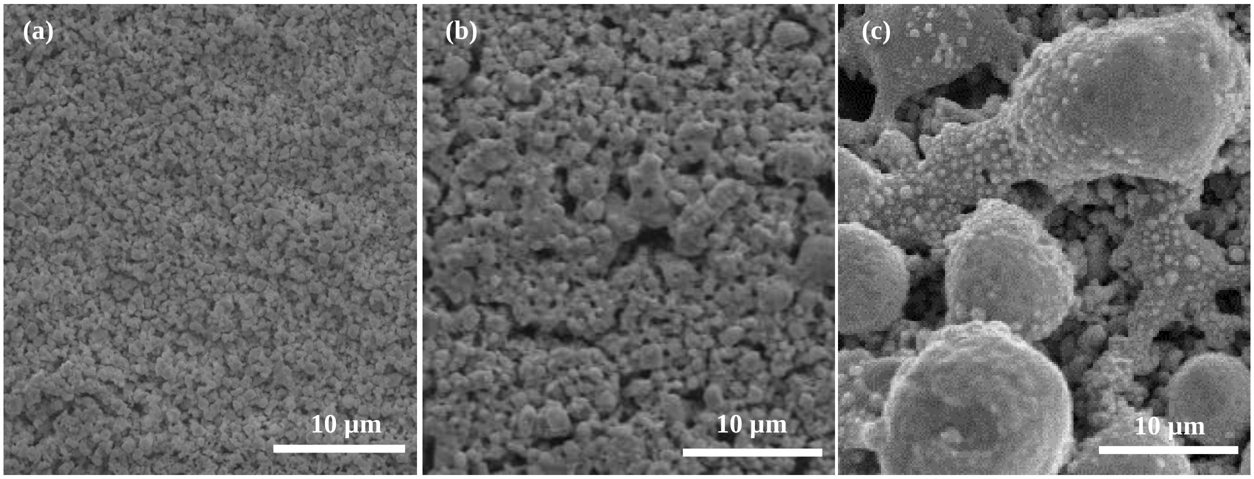


Figure S1. The SEM images were used to qualitatively estimate the quality number, which is the response of the DOE. Examples of the topography of photonically exposed PZT film with quality number of (a) 0.10, (b) 0.40, and (c) 1.0.

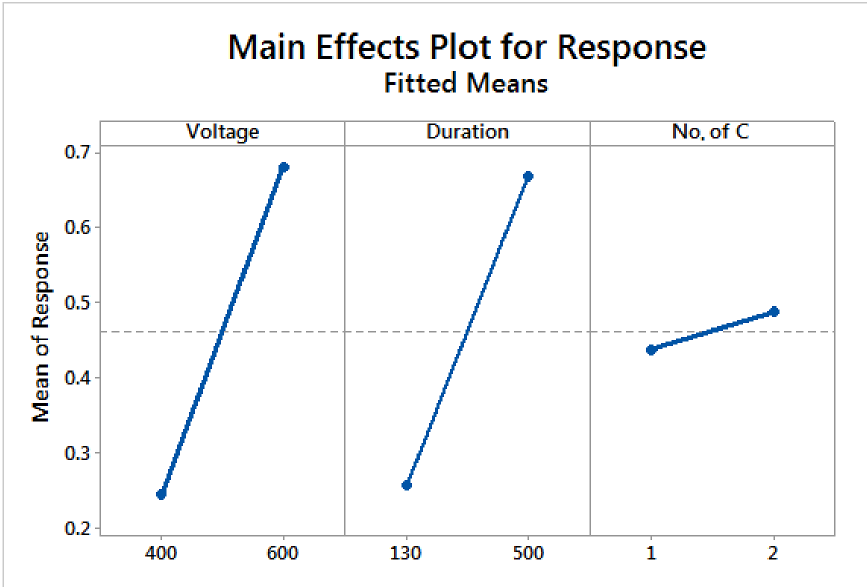


Figure S2. The main effects plot of the response. The voltage and duration show significant impact to the sintering quality, while the number of cycles has less impact.

Table S2. ANOVA table for all three factors and two-factor interactions.

| Source | DF | Adj SS | Adj MS | F-Value | P-Value |
|---|---|---|---|---|---|
| Model | 7 | 1.66250 | 0.237500 | 190.00 | 0.000 |
| Linear | 3 | 1.45625 | 0.485417 | 388.33 | 0.000 |
| Voltage | 1 | 0.76563 | 0.765625 | 612.50 | 0.000 |
| Duration | 1 | 0.68062 | 0.680625 | 544.50 | 0.000 |
| No of Cycles | 1 | 0.01000 | 0.010000 | 8.00 | 0.022 |
| 2-Way | 3 | 0.20375 | 0.067917 | 54.33 | 0.000 |
| Voltage*Duration | 1 | 0.20250 | 0.202500 | 162.00 | 0.000 |
| Voltage*No of C | 1 | 0.00062 | 0.000625 | 0.50 | 0.500 |
| Duration*Noof C | 1 | 0.00062 | 0.000625 | 0.50 | 0.500 |
| 3-Way | 1 | 0.00250 | 0.002500 | 2.00 | 0.195 |
| Voltage*Duration*No. of C | 1 | 0.00250 | 0.002500 | 2.00 | 0.195 |
| Error | 8 | 0.01000 | 0.001250 | | |
| Total | 15 | 1.67250 | | | |
| S: 0.0353553 | R-Sq: 99.40% | R-sq (adj): 98.88% | R-sq(pred): 97.61% | | |

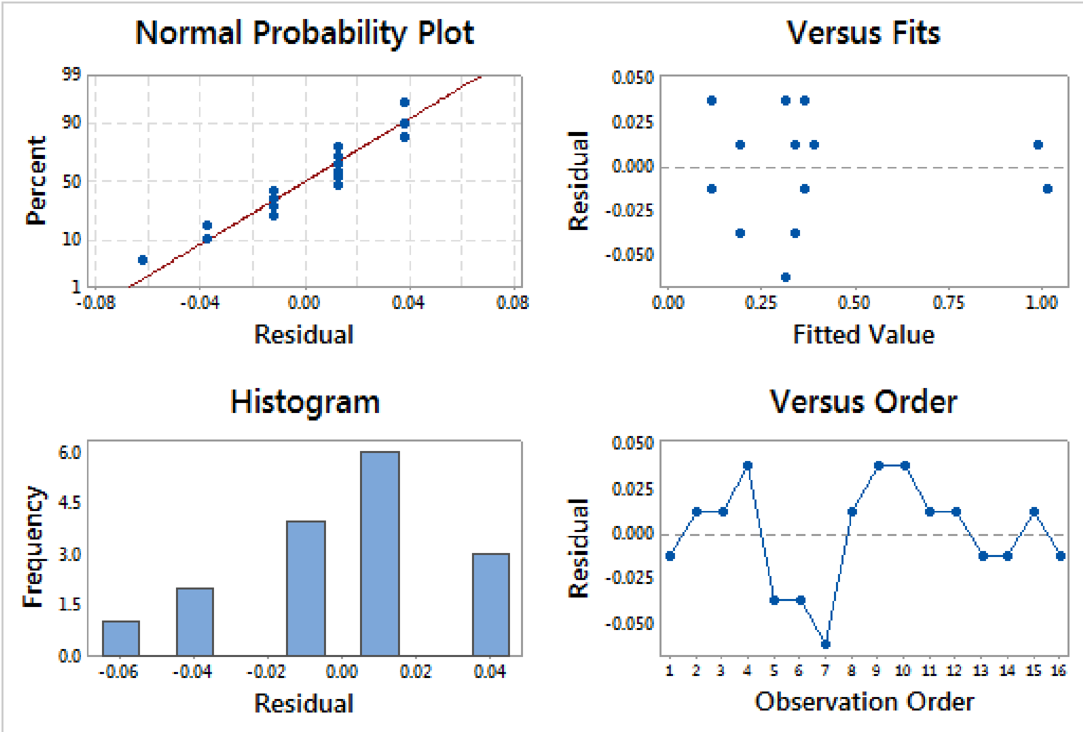


Figure S3. The normal probability plot shows discrete data because of the discontinuous experimental results. The random scatter around the horizontal "zero error line" and the constant spread in the residual versus fit plot, plus marginally skewed normal distribution of residual frequency plot further verifies that there are no violations in using the ANOVA model.

**References:**

(1) Gu, D.; Shen, Y.BallingPhenomena in Direct Laser Sintering of Stainless Steel Powder: Metallurgical Mechanisms And Control Methods, *Mater.Des.***2009**, 30, 2903-2910.