ABSTRACT

CHANG, WEI-YI. Novel Nanocomposites for Piezoelectric and Photoacoustic Transduction Structures. (Under the direction of Dr. Xiaoning Jiang and Dr. Chin-Hao Chang).

Efficient transduction structures and materials have been widely used and developed for several decades. Transduction structures are usually employed at the boundaries of measurement systems, where the electrical energy is converted to and from other physical quantities, such as force or motion. In this thesis, two types of electromechanical transduction materials/structures were studied, including the nano-patterned electrode and alternating current electrical field poling for enhancing the properties of PMN-PT single crystal and candle soot nanoparticle composite transduction for photoacoustic evaluation. With a brief review of ferroelectric relaxor-PT single crystals, the fabrication and development of nano-patterned electrode was presented. The piezoelectric properties measurements and domain observation results suggest that nanocomposite electrodes are promising for domain engineering of PMN-PT single crystals. The other domain engineering method we studied is ACP. Compared with the traditional DCP method, PMN-PT single crystal with ACP method exhibits 20% higher dielectric coefficient, piezoelectric coefficient and smaller domains. For the photoacoustic transduction material, we propose an efficient broadband light absorption material, candle soot nanoparticles. Combining with PDMS, the energy conversion efficient composite was fabricated.
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Novel Nanocomposites for Piezoelectric and Photoacoustic Transduction Structures

by
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The following publications were authored or coauthored by Wei-Yi Chang in peer-reviewed journals and conference proceedings during his doctoral study at North Carolina State University.

Journal Articles


9. Chang, W.-Y., W. Huang, A. Bagal, C.-H. Chang, J. Tian, P. Han, X. Jiang, “Study on dielectric and piezoelectric properties of 0.7 Pb(Mg\textsubscript{1/3}Nb\textsubscript{2/3})O\textsubscript{3} -0.3 PbTiO\textsubscript{3} single crystal with nano-patterned composite electrode”, Journal of Applied Physics, 114, 11, 114103 (2013)

Conference Proceedings


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CHAPTER 1

INTRODUCTION

1.1. Motivation

Efficient transduction structures and materials have been widely used and developed for several decades. Transduction structures are usually employed at the boundaries of measurement systems, where the electrical energy is converted to and from other physical quantities, such as force or motion. The most common applications include the non-destructive test (NDT), underwater acoustic ultrasound, high intensity focused ultrasound, and medical imaging[1–5]. The advantages of ultrasound transduction application include non-irradiation, real-time ability, high resolution and cost-effectiveness. The output performance of the transduction structure dramatically relies on the properties of chosen active materials. To further enhance output performance for applications, transduction structure studies aim to improve the converting efficiency of electromechanical devices. In the past decades, the material of transduction structure is mainly focused on piezoelectric materials, for example, quartz, lead zirconate titanate (PZT) and, lead magnesium niobate-lead titanate (PMN-PT)[5–7]. Thus, the first part of the thesis addresses the development of outstanding properties of piezoelectric single crystal by domain engineering and alternating current poling method.

Other than the conventional piezoelectric materials, the unconventional transduction structure was also paid research attention. Recently, photoacoustic transduction is widely used in many medical and industrial areas because of their high pressure output and broadband signal[8–10], and hence, many applications rely on the photoacoustic transduction, for instance, drug delivery, imaging, and et al. Thus, the second part of the thesis is focused on the investigation of candle soot based photoacoustic transduction with high energy conversion efficiency.
1.1.1. Piezoelectric transduction

The piezoelectric transduction material study can be traced back to 1880 by the brothers Pierre Curie and Jacques Curie[6]. They demonstrated the piezoelectric effect using crystals of quartz and Rochelle salt. For the following decades, the definition of crystal structures with piezoelectricity was established. Sonar was the first practical application and developed during World War I for detecting submarines[11,12]. A piece of piezoelectric material (quartz crystal) was glued between two steel plates as the electrodes, resulting in a transducer capable of generating and receiving the acoustic pulses. Due to the availability of improved materials, continual development in piezoelectric transduction devices has been made since the end of World War II[12,13]. A well-known material, PZT, was first reported as ferroelectric solid-solution system in 1952[14]. PZT exhibit excellent piezoelectric properties in comparison with other counterparts of piezoelectric materials[14]. Recently, the next generation of piezoelectric transduction material, PMN-PT single crystal, has been developed and applied to sonar systems and medical imaging devices[15,16]. Compared with PZT, PMN-PT single crystal shows some advantages, such as, high energy density, high piezoelectric coefficients and electromechanical coupling coefficients[17]. More piezoelectric single crystal properties and testing methods will be introduced in chapter 2.

1.1.2. Photoacoustic transduction

Photoacoustic transduction is the second topic discussed in the thesis. The research in this part was focused on carbon-based transduction composite material. Photoacoustic transduction is based on photoacoustic effect which can be used to generate high frequency, broadband ultrasound with high pressure output. In general, high frequencies show short wavelength, good axial resolution with decreased spatial pulse length, and longer near field. In order to enhance the
resolution of medical images, the high frequency, broadband signal are required[18]. The cavitation effect needs high pressure output ultrasound to generate cavitations in the liquid[19]. In conventional photoacoustic imaging and techniques, the laser light is directly shined on the objects; thermo-elastic wave generation occurs and propagates in the medium. In general, photoacoustic transduction requires high laser absorbing and thermal elastic materials to excite ultrasound[20]. Pulse laser excitation of these photoacoustic transduction materials results in the ultrasound wave with high frequency and amplitude[21,22]. Although, photoacoustic transduction shows a lot of advantages, traditional piezoelectric-based transducer still dominate the medical image market[23,24]. Most of traditional piezoelectric-based medical transducer array fabrications are relying on lapping technique and dice-and fill method[25,26]. Especially in high frequency (> 15 MHz) transducer fabrication, the thickness of piezoelectric material is important[16]. However, the ultrasound with high amplitude and high frequency are difficult to obtain in the traditional piezoelectric-based transduction method[27].

1.2. Objectives

For the piezoelectric transduction structure study, there are several ways to enhance the piezoelectric properties, such as doping method, and electrode patterning method[28,29]. Many works have been done on the domain engineering[30,31]. Owing to the inhibited domain wall motion by the acceptor doping or the enhance domain wall motion by the donor doping, the piezoelectric crystal properties can be changed[32]. For the domain patterning method, most of researchers focus on the micro-scale pattern because of the fabrication limitation[33]. However, the nano-scale lithography fabrication process is widely used in industry. Currently, there are no such articles and research mentioning the combination of domain engineering and nano-scale lithography fabrication process.
In the first part of this thesis, it is proposed to develop a novel nanocomposite electrodes to enhance the piezoelectric transduction performance. The specific goals of this study are:

1. To design and develop the nanocomposite electrode on PMN-PT single crystal;
2. To understand the mechanism of the nanocomposite electrode by simulation and experimental methods;
3. To enhance the piezoelectric transduction properties by alternating current poling method.

For the study of the photoacoustic transduction, a carbon-based nanocomposite usually has better light absorption. Here, we bring up one simple but effective material which is candle soot nanoparticles with polydimethylsiloxane (PDMS) composite. Candle soot can play a role of light absorbing material and PDMS is a thermal expanding material. Based on the optical properties of candle soot nanoparticle, the excited laser energy can be absorbed by the particles without scattering. Thus, the nanocomposite layer was designed and fabricated to enhance the photoacoustic conversion efficiency. The objectives of this research include:

1. To design and develop a cost-effective nanocomposite and fabrication process for photoacoustic transduction structure;
2. To evaluate the photoacoustic transduction efficiency of candle soot nanocomposite transmitters

1.3. Outline

This dissertation includes topics of the background of piezoelectric and photoacoustic transduction materials (Chapter 2 and 3), patterned nanocomposite electrode for domain engineering (Chapter 4), alternating current poling method (Chapter 5), and candle soot nanocomposite based photoacoustic transduction research (Chapter 6). The rest of this dissertation is organized as follows:
In Chapter 2, the background of the ferroelectric relaxor-PbTiO$_3$ single crystal is described. An overview of the primary parameters for the piezoelectric and ferroelectric material is given. The description of the morphotropic phase boundary (MPB) and domain engineering are also mentioned.

In Chapter 3, the background of laser generated ultrasound transmitter is described. The mechanism of photoacoustic between different active layers is given. The photoacoustic transduction materials are introduced briefly. Last but not least, the applications of photoacoustic transducer are described.

Chapter 4 and 5 cover the topics of nanocomposite electrode fabrication, domain engineering, and poling method. In chapter 4, a brief review of domain engineering by patterning method is given, followed by the experimental design. The analytical method and the finite element method are introduced as well. The fabrication process of nanocomposite electrode is presented. With the fabricated nanocomposite electrode, the domain engineered PMN-PT single crystal is developed to evaluate the performance. The main theme of Chapter 5 is the research of alternating current poling method applied on PMN-PT single crystal. The domain observation and piezoelectric performance evaluation are given.

Chapter 6 mainly focuses on photoacoustic transduction structure. A brief background of laser generated ultrasound is presented. The optical and acoustic simulation of candle soot nanocomposite is also given. The optimized nanocomposite transduction layer is demonstrated and the photoacoustic conversion efficiency is evaluated as well.

Finally, Chapter 7 summarizes the research findings, followed by suggestions for the future research.
CHAPTER 2

BACKGROUND OF FERROELECTRIC RELAXOR-PbTiO3 SINGLE CRYSTAL

2.1. Overview of piezoelectricity and ferroelectricity

Nowadays, most of devices and applications are based on the piezoelectric or ferroelectric materials. The definitions of piezoelectric and ferroelectric is different. Figure 2.1(a) simply shows the classification of non-centrosymmetric crystal. The generation of charge in response to the applying stress to a material is called piezoelectricity, such as, quartz. A change in the spontaneous polarization of a material follows a temperature change is called pyroelectricity, such as, aluminum nitride. A spontaneous electric polarization that can be reversed by the external electric field is called ferroelectricity, such as, barren titanate (BT), lead titanate (PZT). Figure 2.1(b) shows the milestone and history of piezoelectric material since 1880[6]. More details about piezoelectricity and ferroelectricity will be introduced in the following sections.

Figure 2.1. (a) Schematic of ferroelectricity and piezoelectricity. (b) History map for piezoelectric transducer material development. KDP/ADP: KH$_2$PO$_4$/($\text{NH}_4$)H$_2$PO$_4$; BT: BaTiO$_3$; LN: LiNbO$_3$; PZT: Pb(Zr,Ti)O$_3$; PN: PbNb$_2$O$_6$; PMN: Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$; PMN–PT: Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$–PbTiO$_3$.[5]
2.2. Piezoelectricity and related parameters

Piezoelectricity is the ability of certain crystalline materials which can create an electric charge by the applied stress. Such piezoelectric effect is also called direct piezoelectric effect since it is a reversible process. Thus, there is a converse piezoelectric effect, which is developing a mechanical strain proportional to an applied electric field. In 1880, the direct piezoelectric effect was discovered by Pierre Curie and Jacques Curie in quartz[6]. One year later, Gabriel Lippmann mathematically deduced the converse effect from the fundamental thermodynamic principles; and the confirmed experimentally by Curie brothers in the same year[34].

Recently, piezoelectric materials have been used in several applications, such as sensor, actuators and ultrasonic transducers; they are important in both academic and industrial field. The generally used piezoelectric materials include bulk ceramic, single crystals, thin film, and composites[4,35,36]. Relaxor based ferroelectric single crystals, such as Pb(Mg_{1/3}Nb_{2/3})-PbTiO_3 (PMN-PT) and Pb(Zn_{1/3}Nb_{2/3})-PbTiO_3 (PZN-PT), have attracted attentions due to their high piezoelectric properties. The longitudinal piezoelectric strain coefficient d_{33} and electromechanical coupling factor k_{33} are larger than 1500 pC/N and 90%, respectively. Compare to the state-of-art polycrystalline ceramics Pb(Zr, Ti)O_3 (PZT), the relaxor based ferroelectric single crystals show higher d_{33} and k_{33} which are great promise for electromechanical applications[5,37].

2.2.1. Dielectric permittivity

The electric displacement (D_i) in a dielectric material is related to the applied E-field (E) through the:

\[ D_i = \varepsilon_{ij} \cdot E_j \]  

(2-1)

, where \( \varepsilon_{ij} \) is the dielectric permittivity of the material, and the relative dielectric permittivity
(\varepsilon_r) can be calculated according to

\[ \varepsilon_r = \frac{\varepsilon_{ij}}{\varepsilon_0} \tag{2-2} \]

where is the permittivity of free space, \( \varepsilon_0 = 8.854 \times 10^{-12} \) farads per meter (F/m). The dielectric permittivity is a complex number including real and imaginary components \( \varepsilon'_r \) and \( \varepsilon''_r \), respectively. The real part of relative dielectric permittivity is also called dielectric constant. Following the equation

\[ \varepsilon''_r = \varepsilon'_r \cdot \tan \delta \tag{2-3} \]

where \( \tan \delta \) is the dielectric loss. The dielectric constant of crystal plates was calculate from geometry and capacitance measurement, according to

\[ \varepsilon_r = \frac{1}{\varepsilon_0} \frac{d}{A} C \tag{2-4} \]

where \( d \) and \( A \) are the area and thickness of the element, \( C \) is the measured capacitance. For practical applications, the free dielectric permittivity \( \varepsilon^T \) and clamped dielectric permittivity \( \varepsilon^S \) are needed in theoretical and device analysis. \( \varepsilon^T \) may be measured at constant stress (1 kHz), and \( \varepsilon^S \) may be measured at constant strain (5 MHz). The free and clamped dielectric permittivity may differ greatly for piezoelectric materials. The difference is related to the electromechanical coupling factor (\( k \)) and the relationship between two dielectric permittivity is the following expression:

\[ \varepsilon^S = \varepsilon^T (1 - k^2) \tag{2-5} \]

### 2.2.2. Piezoelectric coefficients

Piezoelectricity has two types of effects: direct effect and converse effect. Direct effect is the additional electric charge generated by the applied mechanical stress; and converse effect is the mechanical strain created by the applied E-field[5,29]. Before discussing more piezoelectric parameters, notice that the equations above and my whole work use Voigt notation for higher
rank of tensors. For example, the symmetric tensors like strain and stress are usually relabeled in the following fashion: 11 → 1; 22 → 2; 33 → 3; 23 → 4; 13 → 5; 12 → 6. Thus, \( d_{ij} \) (\( i=1,2,3 \) and \( j=1,2,3,4,5,6 \)) can have up to 18 independent tensor coefficients depending upon the crystal symmetry of the material systems. According to different independent electrical and mechanical variables, there are four forms of piezoelectric coefficients [29]. First, the piezoelectric strain coefficient \( d \) is only related to a constant E-field (E) and mechanical stress (T), as the following equation,

\[
d_{ij} = \left( \frac{\partial S_j}{\partial E_i} \right)_T = \left( \frac{\partial D_i}{\partial T_j} \right)_E \tag{2-6}
\]

\( d \) is usually used in low frequency or non-resonant device application. This equation also marks the unity of the direct piezoelectric effect (S-E relation) and converse direct piezoelectric effect (D-T relation). Thus, the piezoelectric strain coefficient \( d \) has also two identical units, m/V and C/N. In practical cases, the smaller pm/V and pC/N are more widely used.

Second, the piezoelectric voltage coefficient is \( g \) which gives the field produced by applied stress, where the electrical displacement (D) and mechanical stress (T) are selected independent variables, given by:

\[
g_{ij} = \left( -\frac{\partial E_j}{\partial T_i} \right)_D = \left( \frac{\partial S_i}{\partial D_j} \right)_T \tag{2-7}
\]

Third, the piezoelectric stress coefficients is \( e \), where E-field (E) and strain (S) are selected as independent variables, following

\[
e_{ij} = \left( -\frac{\partial T_j}{\partial E_i} \right)_S = \left( \frac{\partial D_i}{\partial S_j} \right)_E \tag{2-8}
\]

\( e \) is generally employed at high frequency or under mechanical clamped conditions. Fourth, the piezoelectric clamped voltage coefficient \( h \) is defined by the independent variables strain (S) and electrical displacement (D), according to the equation

9
\[ h_{ij} = \left( -\frac{\partial T_{ij}}{\partial D_i} \right)_S = \left( -\frac{\partial E_i}{\partial S_j} \right)_D \] (2-9)

Jaffe and Berlincourt define these piezoelectric constants as partial derivatives evaluated at constant T, E, D, and S [38].

### 2.2.3. Electromechanical coupling

The electromechanical coupling factor \((k)\) is a property that measures the ability of a poled piezoelectric material to convert the energy between electrical and mechanical form. In the design of resonant devices, \(k\) is related to the bandwidth of devices. The relationship between electromechanical coupling and the piezoelectric coefficients is showing below [39]:

\[
 k^2_{i\mu} = \frac{d_{i\mu}^2}{\varepsilon_{ii}^T e_{i\mu}^T s_{\mu}} = \frac{e_{i\mu}}{\varepsilon_{ii}^T e_{i\mu}^T s_{\mu}} = \frac{g_{i\mu}^2}{\rho_{ii}^T \rho_{\mu}^T} = \frac{a_{i\mu}^2}{\rho_{ii}^T \rho_{\mu}^T} \] (2-10)

, where \(s\) and \(c\) are the elastic compliance and stiffness constant, respectively. \(\beta\) is the dielectric impermeability. The superscripts T, E, S, and D indicate different boundary conditions, with subscripts \(i, j=1, 2, 3;\) and \(\mu= 1,2, 3, 4, 5,\) and 6. Owing to the conversion of mechanical to electric energy is always incomplete, \(k\) is always <1. The electromechanical coupling factor is highly related to the vibration modes, which depends on the sample geometry. The coupling can calculated from the resonance \((f_r)\) and antiresonance \((f_a)\) frequencies measured on the piezoelectric samples, as following equation [28]:

\[
k^2 = \frac{\pi f_r}{2 f_a} \cot \left( \frac{\pi f_r}{2 f_a} \right) \] (2-11)

The coupling factor of longitudinal excitation and transverse excitation is \(k_{33}\) and \(k_{31}\) respectively.

### 2.2.4. Mechanical quality factor

Mechanical quality factor \((Q_m)\) is the ratio of reactance to the resistance in the series equivalent circuit representing the piezoelectric resonator. \(Q_m\) is also related to the sharpness of
the resonance frequency. Owing to the energy loss to mechanical damping, it heats the crystal. Therefore, the ultrasonic resonators require a piezoelectric crystal with a high $Q_m$, which can suppress the heat generation. $Q_m$ is calculated by the resonator’s bandwidth relative to its center frequency, according to:

$$Q_m = \frac{f_r}{\Delta f}$$  \hspace{1cm} (2-12)

, where $\Delta f$ is the frequency difference at -3 dB of the maximum admittance. In ferroelectric single crystals, the existence of movable domain walls (including motion/ polarization rotation) dominates $Q_m$. Some other factors also affect the $Q_m$, such as polarization rotation angle, domain state, and domain size. Other than the crystal’s factor, the external conditions will also affect the measured $Q_m$, for instance, the contact resistance and measurement frequency.

2.3. Ferroelectricity and related parameters

Ferroelectricity is a characteristic of certain materials show a spontaneous electric polarization and that can be reoriented by the external E-field[40,41]. A ferroelectric crystal consists of multiple grains, and each grain is including some regions which are called domains. In the same domain has the same polarization direction. The boundary or interface between each domain is domain wall. The domain wall density is strongly related to the crystal performance in applications. In general, the higher domain density in the ferroelectric crystal the better piezoelectric properties are. Thus, the domain engineering is a new method to manipulate the domain wall density in ferroelectric crystals[42]. Changing the composition of crystal is another method to enhance the piezoelectric properties. Near the morphotropic phase boundary (MPB) region, the piezoelectric response is enhanced because of the diversity and instability of ferroelectric phases. Therefore, the ferroelectric domain structure, MPB, and domain engineering will be discussed in the following dissertation.
2.3.1. **Morphotropic phase boundary (MPB)**

The morphotropic phase boundary (MPB) marks the temperature independent phase transitions that occur because of the composition changed. The MPB studies started from the PZT solid solution systems by Shirane et al. and Jaffe et al. who discovered that PZT with near the MPB compositions was importance for piezoelectric transducer applications[43–45]. Learning from the successful PZT system, the following relaxor-PT development is focused on those solid solutions with the similar phase diagram, showing MPB between the relaxor component and classic ferroelectrics, such as PZN-PT single crystal and PMN-PT single crystal[46,47].

Near the MPB composition, the structure is relatively less stable. The two phases (two different crystallographic symmetries) can be existed at the same time which can enhance the dielectric and piezoelectric properties. The reason is the spontaneous polarization can be rotated easily between different symmetries[48–50]. For example, figure 2.2 shows some common material of phase diagram around MPB regions, such as, PZT ceramic[51], PZN-PT single crystal[46] and PMN-PT single crystal[47]. The MPB composition is given in a range between 30% and 35% of PbTiO$_3$ for PMN-PT single crystals (PZN-PT single crystals are similar with 8% to 15%), which means that the MPB is not a single line but a composition range. PZN-0.08PT single crystal shows a rhombohedral symmetry before poling, but an orthorhombic phase can be irreversibly induced by an external electric field[21]. A monoclinic phase with different angles of polarization rotation was observed phase coexisted (rhombohedral and tetragonal) in the PMN-33PT single crystal at room temperature by polarized optical microscope[53]. It also worth to mention there are some important properties, such as high piezoelectric coefficients, extremely large strains, and high electromechanical coupling factors.
Take PMN-33PT as example, the existence of the monoclinic phase is regarded as the main cause of the high piezoelectric properties of PMN-PT single crystals because the polarization vector can be rotated in response to the poling field[49].

Figure 2.2. The comment materials of phase diagram around MPB region. (a) PZT ceramic, (b) PZN-PT single crystal, and (c) PMN-PT single crystal.

2.3.2. Ferroelectric domain structures

As shown in figure 2.3, ferroelectric crystal is cooled from paraelectric cubic (above Curie temperature, $T_c$) to ferroelectric phase (below $T_c$) with lower symmetry. Each region shows uniform polarization which is called ferroelectric domain, ranging in scale from few nanometers to micrometers. The interface between two domains is domain wall. In general, domain wall is relatively thin in order to reduce the elastic energy generated by the strain. In the ferroelectric crystals, the domain patterns and the type of domain walls is based on the number of conceivable polarization occurs form the prototype phase[28,54]. For the rhombohedral (R) case, the polarization direction alone one of eight $\langle 111 \rangle$ directions; and it existed $180^\circ$ (red solid arrow to red dash arrow), $71^\circ$ (red solid arrow to blue solid arrow) and $109^\circ$ (red solid arrow to green solid arrow) domain wall orientations, as figure 2.3(a). For the tetragonal (T) case, the polarization direction alone one of six $\langle 001 \rangle$ directions; and it existed $180^\circ$ (red solid arrow to
red dash arrow) and 90° (red solid arrow to purple solid arrow) domain wall orientations lie in (001) and (10-1) plane, as figure 2.3(b). The switching of 180° domain walls may reduce the effects of depolarizing E-field, but it does not involve elastic deformation. However, the formation of non-180° domain walls not only reduce the depolarizing E-field but also can minimize the elastic energy[29]. Ferroelectric materials can be poled by certain E-field, in other words, E-field is applied to switch the polarization vector of each domain toward to the poling direction. Polarized light microscopy (PLM), scanning electron microscopy (SEM), and piezoresponse force microscopy (PFM), can be used to observe the domains.

Figure 2.3. Schematic drawing of orientation states. (a) Rhombohedral shows three different domain wall orientations which are 180°, 71°, and 109°; (b) Tetragonal shows two domain wall orientations which are 180°, and 90°.

Park and Shrout had reported that E-field induced strain response in [001] oriented rhombohedral (R) relaxor-PT is related to the “domain engineered configuration” [55]. Before discussing the details of domain engineering, the domain configuration should first be discussed according to different crystal symmetries and crystallographic orientation the comparisons is in Table 2.1 [29]. Take R-phase for example, the symbol “4R” represent the existed 4 equivalents.
(111) spontaneous polarization for [001] oriented sample after poling alone [001] direction. Owing to the easy tilt of spontaneous polarization by applied external E-field, the relaxor-PT single crystal show high piezoelectric coefficients.

Table 2.1. Domain engineered configuration in relaxor-PT systems [29]

<table>
<thead>
<tr>
<th>Crystal phase</th>
<th>Polar directions</th>
<th>Poling direction</th>
<th>Engineered domain configuration</th>
<th>Exist domain walls</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rhombohedral (R)</td>
<td>(111)</td>
<td>[001] [011] [111]</td>
<td>4R 2R 1R</td>
<td>109°, 71° 71° Single domain</td>
</tr>
<tr>
<td>Orthorhombic (O)</td>
<td>(011)</td>
<td>[001] [011] [111]</td>
<td>4O 1O 3O</td>
<td>90° Single domain 60°</td>
</tr>
<tr>
<td>Tetragonal (T)</td>
<td>(001)</td>
<td>[001] [011] [111]</td>
<td>1T 2T 3T</td>
<td>Single domain 90° 90°</td>
</tr>
</tbody>
</table>

2.3.3. Domain engineering

The method used to control or manipulate the desirable domain configuration is called domain engineering. The basic understanding of domain engineering of ferroelectric crystal is to change the field induced displacement of specific mode to another mode through the manipulating techniques, such as, inhibited/enhanced domain wall motion, and domain wall engineering [28].

With the development of relaxor-PT single crystal, three generation crystals were proposed[29], as showing in Table 2.2. First generation crystals exhibit some advantages, such as, high electromechanical coupling and piezoelectric coefficients. Second generation crystals shown higher electric field and mechanical stress, and extend the electromechanical coupling to a broader range of temperature. Third-generation crystals include small amount of dopant in order
to manipulate the electromechanical parameters. Other than changing the composition of crystals, domain wall can be further engineered by altering the poling conditions. Wada et al. utilized mathematical calculation and experiment results to demonstrate the micron-scale patterning electrode could increase the piezoelectric properties with decreasing domain size in BaTiO₃ single crystal[56]. In comparison with the 5 µm domain size achieved with whole plane electrode, crystals with patterning electrodes exhibited a gradient domain sizes from 3 µm to 9 µm and showed a high d₃₁, and d₃₃ value of 243.2pm/V, 486.4 pm/V, respectively[57]. Urenski et al. reported that the periodic domain structures can be success fully induced in KTiOPO₄ single crystal by patterning electrodes[58]. Few years later, Yamashita et al. put the nano-scale Mn oxide patterning electrode on PMN-PT single crystal to enhance over 20 % of piezoelectric and dielectric properties[59]. Two oxide nano-islands surface were fabricated through heat treating a spin-coated sol-gel manganese oxide layer. Further information will be discussed in chapter 4 and chapter 5.

Table 2.2. Properties of relaxor-PT single crystals with different generations in 4R engineered domain configuration[29]

<table>
<thead>
<tr>
<th>Crystal</th>
<th>T_c(°C)</th>
<th>T_RT(°C)</th>
<th>E_c(kV/cm)</th>
<th>K^T_{33}</th>
<th>d_{33}(pC/N)</th>
<th>k_{33}</th>
<th>Q_m</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMN-0.29PT (Gen I)</td>
<td>135</td>
<td>96</td>
<td>2.3</td>
<td>5400</td>
<td>1700</td>
<td>0.91</td>
<td>150</td>
</tr>
<tr>
<td>PMN-PT (MPB) (Gen I)</td>
<td>155</td>
<td>65</td>
<td>2.8</td>
<td>8200</td>
<td>2800</td>
<td>0.95</td>
<td>100</td>
</tr>
<tr>
<td>PIN-PMN-PT (Gen II)</td>
<td>191</td>
<td>125</td>
<td>5.0</td>
<td>4400</td>
<td>1500</td>
<td>0.92</td>
<td>180</td>
</tr>
<tr>
<td>PIN-PMN-PT (MPB) (Gen II)</td>
<td>197</td>
<td>96</td>
<td>5.5</td>
<td>7200</td>
<td>2700</td>
<td>0.95</td>
<td>120</td>
</tr>
<tr>
<td>Mn: PIN-PMN-PT (Gen III)</td>
<td>193</td>
<td>119</td>
<td>6.0</td>
<td>3700</td>
<td>1100</td>
<td>0.90</td>
<td>800</td>
</tr>
<tr>
<td>Mn: PMN-PT (Gen II)</td>
<td>203</td>
<td>141</td>
<td>6.3</td>
<td>3400</td>
<td>1100</td>
<td>0.92</td>
<td>1050</td>
</tr>
</tbody>
</table>
CHAPTER 3

BACKGROUND OF LASER-ULTRASOUND TRANSDUCERS

A laser ultrasound transducer is based on the photoacoustic mechanism. In this chapter, the introduction of photoacoustic effect and mechanism will be described first, including the absorption layer and thermal-elastic layer. Thus, the choosing materials for transduction material are also the key element of photoacoustic mechanism. The requirement of thermal-elastic layer was also discussed. In this chapter, the absorption layer can be separated into metal-based and carbon-based materials. Metal-based materials include three types (thin metal film, sub-wavelength nanostructure, and metal nanoparticles); and carbon-based materials include brief introduction of carbon nanotube, carbon nanofiber and candle soot nanoparticles. In the end of chapter 3, the application of photoacoustic transducers will be introduced, such as, imaging and drug release, etc.

3.1. Introduction of photoacoustic effect

Photoacoustic effect refers to sound wave generation by the material vibration excited by the light. In order to enhance the acoustic pressure, the high power light source (laser) was used for the photoacoustic applications. Thus, photoacoustics is also called laser generated ultrasound. The photoacoustic waves can be detected by piezoelectric sensors (including microphones and hydrophones) and lase interferometry.

Photoacoustic effect was discovered by Alexander Graham Bell in 1881 [60]. He observed the acoustic signal can be generated by moving the reflected sunlight through mirror to the light receiver. The effect was caused by the light energy absorption resulting in thermal expansion of the receiver. With the improvement of acoustic sensor and light sources, the photoacoustic effect has received more attention since 1971[21,61]. The high frequency and broadband ultrasound
can be generated by the short pulse laser excitation, and it has been applied in the imaging field requiring high spatial resolution in biological tissues and material defect detection [1,62].

### 3.2. Mechanism of photoacoustic effect

Photoacoustic ultrasound can be generated by the incident light source in two ways. The first is material ablation, and second is thermoelastic effect. The material ablation-induced ultrasound usually needs ultrahigh light energy, but this ultrasound generation method may cause damages to the target. Thus, the ablation-induced ultrasound will not be discussed in this dissertation. In contrast, the thermoelastic effect generates photoacoustic ultrasound via relatively low-intensity light source, which is a nondestructive method. Photoacoustic effect includes three coupled physical fields, which are light, thermal, and acoustics (mechanical vibration). Figure 3.1 shows the schematic of photoacoustic transduction.

![Photoacoustic transducer diagram](image)

Figure 3.1. Schematic of photoacoustic transducer. The transducer includes absorption layer and expansion layer, which can convert the laser energy into acoustic energy.

The light pulses are shined on the transducer, and the light turns into heat on the transducer surface. The local and short light pulses can heat up small area and generate thermal expansion of part of the transducer. Owing to the periodic thermal expansion, the mechanical sound wave can be obtained. One important requirement of photoacoustic effect is that the heating rate should be faster than the thermal expansion, which is also called stress confinement.
condition[63]. Under the stress confinement condition, high thermo-elastic pressure in the sample can build up rapidly[64]. Based on the conservation of energy, the incident optical energy equals to the thermal energy. The optical-thermal convert equation can be derived as following equations[8,9],

$$
\Delta V = A \cdot S \cdot F \cdot \frac{\beta_T}{\rho C_P}
$$

Where, $A$ is the light absorption, $S$ is surface area, $F$ is the laser fluence, $\beta_T$ is the thermal coefficient of volume expansion, $\rho$ is mass density, and $C_P$ is the heat capacity at constant pressure. The photoacoustic amplitude can be rewritten as,

$$
P_0 = \Gamma \cdot A \cdot \frac{F}{l}
$$

Where, $\Gamma = \frac{\beta_T c^2}{C_P}$ is Grüneisen parameter, and $l$ is the length. Usually, strong light absorption and thermal coefficient of volume expansion is required for high photoacoustic amplitudes.

The thermo-mechanical coupled wave equation in the given media can be expressed as,[65]

$$
\nabla^2 P_i - \frac{1}{C_{L_i}^2} \frac{\partial^2 P_i}{\partial t^2} = -\frac{\beta_T}{C_P} \frac{\partial \overline{h_i}}{\partial t}
$$

, where $\overline{h_i} = \kappa \nabla^2 T_i + S_i$ is the heat supply per unit time and unit volume in each medium, $\kappa$ is the thermal conductivity (W/m·k), $i = 1, 2, 3$, $P$ is pressure, $C_L$ is the isentropic wave speed. From this governing equation, we can conclude that the following two layers, absorption layer and expansion layer, play an important role in photoacoustic transducers.

3.2.1. Absorption layer

In the photoacoustic mechanism, the quality of absorption layer determines how much of the light energy can be converted to thermal energy. Thus, a good absorption layer includes some specific features, such as, low light reflection, and high thermal conductivity. In other words, low light reflection can let more light energy be absorbed on the absorption layer, and high thermal
conductivity refers to the fact that the thermal energy will not accumulate in local region.

Based on the low reflection (anti-reflection) requirement, there are several methods to reach the goal. The sub-wavelength structures and nanoparticles can highly reduce the optical reflection[66,67]. For the sub-wavelength structure, if the light wavelength is greater than the arbitrary structure size, the structure behaves like a gradient-reflection index film which can reduce the reflection. The effective medium approximation can be applied to calculate the reflection [68]. Using nanoparticles to reduce reflection is strongly dependent on the size and shape. The nanoparticles have shown the surface plasmon resonance which can be explained by solving Maxwell’s equations for the absorption and scattering of electromagnetic radiation [69].

These two methods were used to enhance photoacoustic efficiency, and the following are two examples. First, Hou et al. used two dimensional gold nanostructure to convert the short and high intensity laser energy to high frequency and broadband ultrasound [70]. Second, Zou et al. coated gold nanoparticles with around 20 nm in diameter on the tip of optical fiber, and it showed high optical energy absorption capability and photoacoustic efficiency [66].

One of important factors of absorption material is thermal conductivity. In general, materials of high thermal conductivity are used in heat sink application, and materials of low thermal conductivity are used in thermal insulation. In photoacoustic effect, higher thermal conductivity materials can receive more thermal energy. Table 3.1 shows some thermal conductivity of comment materials. Metallic materials have higher thermal conductivity than polymer material, such as, PDMS[71,72]. The thermal conductivity of carbon-based absorbing materials is between metals and polymers[73,74]. A detailed review of the absorption materials is given in Section 3.3.
Table 3.1. The thermal conductivity of comment materials

<table>
<thead>
<tr>
<th></th>
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<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermal conductivity (W/m·K)</td>
<td>317</td>
<td>400</td>
<td>1.38</td>
<td>2.15</td>
<td>0.596</td>
<td>0.15</td>
<td>2.34</td>
</tr>
</tbody>
</table>

3.2.2. Thermo-elastic layer

To enhance the photoacoustic signal, a thermal elastic expansion layer is required. The expansion layer is used to convert the thermal energy to the kinetic energy. Recently, researchers have started to study the polymer, polydimethylsiloxane (PDMS), for photoacoustic effect. Among many polymers, PDMS shows high optical transparency and high thermal conversion[75–77]. High thermal conversion means that under the same exciting thermal energy, PDMS can expand more than other polymers or metals, to generate more kinetic energy. For the photoacoustic transducer, heat transfer between absorbers and the surrounding medium is the most important part for efficient energy conversion. The volume expansion ($\Delta V$) of PDMS can be calculated by the thermoelastic equation.

$$\Delta V = \frac{E_{th} \beta}{\rho C_p}$$  \hspace{1cm} (3-4)

Where $E_{th}$ is thermal energy, $\beta$ is thermal expansion coefficient, $\rho$ is the density. The $\beta$ value of metals is relatively small, for instance, aluminum (24×10^{-6}/K), and copper (19×10^{-6}/K), while the thermal expansion coefficient of PDMS is about 310 × 10^{-6}/K, which is higher than water tissue, ceramics, and metals [78]. The heat capacity is based on the molecular motion and vibration. Usually, metals have lower $C_p$, such as aluminum (24.3 J/K·mol) and copper (24.5 J/K·mol). However, compared to other polymers, PDMS shows lower $C_p$ which is about 120.3 J/(K·mol) at room temperature[79]. These materials properties of PDMS allow larger thermal
expansion, compared with common polymers and metals, making it a suitable material for expansion layer.

3.3. Photoacoustic transduction materials

Based on the photoacoustic mechanism, the photoacoustic transducer can be designed and fabricated. A short pulse laser light source is the requirement of generating high frequency ultrasound. The light is captured by the absorption layer and transferred to heat energy. Thus, in the following sections, different absorption materials will be discussed. Because the high $\beta$ and optical transparent characteristics, polymer is chosen as the expansion material. The surrounding high $\beta$ material is expanded because of obtaining the heat energy from the absorption materials. Combining the light absorbing material and expanding polymer, the application of new type photoacoustic transduction composite will be discussed.

3.3.1. Metal-based materials

The first photoacoustic experiment was demonstrated based on metal-based film in 1976 by Dr. Melcher [80]. During the experiment, the thin metallic film, such as Mo or W, was deposited on the transparent polished quartz or sapphire. The metallic side was bounded to the solid sample with bounding agents. Then, the pulsed laser beam was focused and shined on the quartz side. The advantage of this method is that the acoustic wave can be propagated into solid sample since the specimen surface does not need to be absorbing to the incident radiation. Two years later, Gutfeld et al. first generated mega Hz elastic wave from metallic-liquid interfaces [81]. However, the thermal expansion of metals is relatively low. To enlarge the photoacoustic signal, the polymer layers were coated on a metal layer [82]. With the rapid evolution of manufacturing methods, the efficient light absorbing methods was discovered, such as two-dimensional gold nanostructure, or gold nanoparticles, as depicted in figure 3.2 [66,70]. The
two-dimension gold sub-wavelength array combined with PDMS thermal-elastic layer exhibited peak absorption at resonance due to localized surface plasmon around the nanoparticles. For the gold nanoparticles mixture with PDMS, the optimized gold composite was observed to have magnitude of acoustic output ten times higher than a single metal film [83].

![Diagram](image)

**Figure 3.2.** The efficient light absorbing method illustration. (a) Traditional metal layer, (b) 2D Au nanostructure array, and (c) Au nanoparticles.

### 3.3.2. Carbon-based materials

Compared to metal-based absorbing materials, carbon-based absorbing materials is an alternative method. In 1880, Alexander Graham Bell used lampblack for photoacoustic effect; carbon black has been used for photoacoustic generation since then. Carbon black is continually applied on solids for the photoacoustic experiment in 1973[84]. The photoacoustic wave can be propagated into solids. The carbon particles absorb the light energy, and transfer this energy to the surrounding mediums. However, the excitation laser source, absorbing particle size, and expanding materials are not fully developed. The photoacoustic performance was not impressive during that time. Since the improvement of nano-scale carbon particles preparation, highly absorbing carbon-based materials can be created, such as, carbon nanotubes (CNT), carbon nanofibers (CNF), candle soot nanoparticles (CSNPs), and so on.[76–78]. Dr. Guo’s group developed a composite combining CNT and PDMS. They claimed that the thick CNT layer can
absorb almost 100% of light. But the thinner absorbing layer, the better thermal transmission and lower wave attenuation it is. Thus, thin CNT film layer (absorption up to 80%) with a gold layer (20-30 nm) sputtering on the top shows better photoacoustic output pressure [85]. The light absorption enhancement is due to the high absorption of CNTs, and localized surface plasmon resonance of Au particles, which caused significant heating of the Au particles and the surrounding medium. Figure 3.3 shows the scanning electronic microscope of main carbon-based absorption materials, CNT, CNF and candle soot nanoparticles. A vertically aligned multi-walled CNT forest shows perfect broadband light absorption, because of the sub-wavelength random roughness surface[75,78]. CNF with PDMS layer as a photoacoustic transmitter exhibits some advantages, such as the simple and cost-effective fabrication[76]. The candle soot nanoparticles can be deposited on any geometry surface through an easy fabrication[77].

![Figure 3.3. Carbon-based absorbing materials. (a) CNT [85] (reproduced from Ref. 85 with permission from the Royal Society of Chemistry), (b) CNF [76], (c) candle soot [77].](image)

### 3.4. Applications of photoacoustic transducers

The application of photoacoustic transducer is depending on the transducer configuration, as depicted in figure 3.4. The planar glass and concave lens has different advantages. Planar glass transducer is easy to fabricate using spin-coating method. The high power amplitude photoacoustic waves can be generated by coating absorption material on a transparent concave
substrate. High power ultrasound waves are very useful to induce cavitation effect, which has many applications in medical therapies[86,87]. The cavitation effect is the formation of vapour cavities in a liquid which can be generated by high power amplitude ultrasound. The instant high power amplitude could rapidly change the pressure that causes relatively low pressure in the cavities. When the cavitation imploded, the shock wave can be generated. Most of cavitation application is based on the shock wave, such as, ultrasound cleaning, cavitation therapy. Baac et al. had demonstrated that the laser generated focused ultrasound (LGFU) enabled high amplitudes pressure (>50 MPa) at 15 MHz. The LGFU-induced cavitation was deterministic and controllable, in other words, the cavitation can precisely fragment kidney stone [78]. The cavitation will also induce micro-scale disturbance which can be applied on molecular delivery [88]. Drug release or drug delivery is another application of photoacoustic effect. Di et al. showed the drug delivery ability using LGFU [10]. The drug released by LGFU was proportional to the output pressure and treating time. This effect resulted from the cavitation generated by LGFU.

Figure 3.4. Different geometry illustration of photoacoustic application. (a) Planar transmitter, (b) focused transmitter, (c) optical fiber with planar transmitter, and (d) optical fiber with focused transmitter.
Other than the cavitation effect, the high resolution imaging is another important application for photoacoustic transducers. Compared to the traditional piezoelectric ultrasound probes, the all-optical photoacoustic transducer has some advantages such as, the high frequency and the simple fabrication. The all-optical ultrasound probe combine laser-generated ultrasound and fiber ultrasound detector, which can be applied in ultrasound imaging. Hou et al. used gold nanostructure and carbon black PDMS as absorbing material to generate three dimension ultrasound imaging [67,89]. Moreover, ultrasound can be generated in a light-absorbing material on an optical fiber tip. Colchester et al. integrated photoacoustic transducer and receiver into the optical fiber based ultrasound probe [90]. With 200 μm diameter of optical fiber, the ultrasound probe can be moved precisely to enhance the pulse-echo ultrasound imaging resolution.
CHAPTER 4

PATTERNED NANO-DOMAINS USING NANOCOMPOSITE ELECTRODES

The content in this chapter was published with the title “Patterned nano-domains in PMN-PT single crystals”, in Acta Materialia 143 (2018): 166-173, as reference[91]. Further piezoelectric materials and domain engineering related work were also published[92–96].

The domain structure, dielectric, and piezoelectric properties of 0.7 Pb(Mg\(_{1/3}\)Nb\(_{2/3}\))O\(_3\)-0.3PbTiO\(_3\) (PMN-PT) single crystals with nanocomposite electrode, which includes MnO\(_x\) semiconductor nanogratings and a Ti/Au conductive layer, were studied in this paper. These artificial MnO\(_x\) nanogratings can alter the electric field distribution and then enhance the domain density. PMN-PT crystals with Ti/Au-MnO\(_x\) nanocomposite electrodes showed high piezoelectric constant of 2250 pm/V and dielectric constant of 5400 at 1 kHz, respectively. Compared to ones with conventional planar electrodes, the piezoelectric and dielectric constants of the samples with nanocomposite electrodes were increased 36.7\% and 38.3\%, respectively. Piezoresponse force microscopy (PFM) images revealed the domain pattern near the electrode/single crystal interface. A linear domain structure induced by the MnO\(_x\) nanocomposite electrode was found in the samples with thickness less than 200 µm.

Time-of-flight secondary ion mass spectrometry (TOF-SIMS) results showed the diffusion of Mn about 300 nm in depth in PMNPT crystal after heat treatment during MnO\(_x\) nanocomposite electrode. It is believed that the localized high electric fields induced by fringe effects caused by the nanocomposite electrode can enhance nucleation of new domains, and that diffusion from the patterned Mn layer may also lead to an enhancement in domain wall mobility. Our findings open up a new domain engineering technique for tailoring the dielectric and piezoelectric properties of PMN-PT single crystals.
4.1. Introduction

Relaxor ferroelectric single crystals have been widely used in electro-active devices due to their excellent piezoelectric and dielectric properties near the morphotropic phase boundary (MPB)[37,97]. It is widely accepted that the enhanced piezoelectric response and poling efficiency near the MPB are due to an increased number of allowable domain states[29,98–100]. Moreover, the piezoelectric and dielectric properties of a ferroelectric material are highly related to its domain wall features[101]. Thus, the piezoelectric properties of ferroelectric materials can be tailored by domain engineering techniques[102,103]. The most commonly used domain engineering technique is the manipulation of the domain wall mobility by adding acceptor or donor type dopants[104].

In recent years, it was also reported that domain engineering can be achieved by using micro-patterned metal electrodes. Uneven electric fields could form in a single crystal with patterned electrodes during electrical poling, which can be used for tailoring the domain structure and piezoelectric properties of ferroelectrics[28,105,106][30,107]. Wada et al. reported that the domain size in BaTiO$_3$ single crystal could be effectively reduced by using a patterned electrode during the electrical poling process. The domain size of BaTiO$_3$ with a planar electrode was larger than 5 µm, and the domain size of BaTiO$_3$ with a patterned electrode was smaller than 3 µm[57]. The piezoelectric coefficient ($d_{31}$) of BaTiO$_3$ with smaller domain sizes (i.e., patterned electrodes) was found to be -243.2 pC/N, which is significantly higher in absolute amplitude than -62.0 pC/N of the ones with larger domain sizes (i.e., planar electrodes)[57]. The enhanced piezoelectric coefficient in the BaTiO$_3$ with a patterned electrode has evidenced that the patterned electrode method is a powerful technique for manipulating the properties of ferroelectrics.
The dielectric and piezoelectric properties of PMN-PT have been studied using metal-based electrodes for several years[97,108]. Recently, a composite electrode method including conductive and semi-conductive layer on the ferroelectric relaxors has been developed for better piezoelectric properties[59]. Mn oxides (MnO$_x$) are considered to be the suitable semiconductor materials for the semi-conductive layer since the electrical resistivity is ranging from 1 to 10$^5$ $\Omega$cm[109]. Yamashita et al. used a sol-gel method to coat a high density, but randomly distributed MnO$_x$ patterns, on PMN-PT single crystals as a part of the composite electrode. PMN-PT with a composite electrode exhibited nearly a 40% improvement in their longitudinal piezoelectric ($d_{33}$) values[59]. The authors attributed the enhanced $d_{33}$ values to the effects of the composite electrodes on the domain structure. Similar behavior was also observed in a PMN-PT single crystal with a periodical nanocomposite electrode, which exhibits an enhanced piezoelectric properties$^{24}$. The composite electrode may prevent rapid domain reversal when electric fields are applied to the PMN-PT crystal, as the electrical flux in the sample is nonuniform[59]. Furthermore, more new domains may nucleate at the interfaces between patterned composite electrodes and single crystal due to surface doping effect[110]. Based upon Landauer’s nucleation theory, the nucleation of new domains is the initial stage of domain evolution during polarization reversal[111]. Formation of smaller domains is the key approach for enhancing piezoelectric properties[112], which is usually defect-assisted[113]. Surface doping effect has been observed in the lithium tantalite substrate with a periodic nickel grating[114]. The diffused ions could enhance the domain nucleation probability and enhance domain wall motion[115]. A powerful tool to quantify oxide ion diffusion and evaluate diffusion depth profile is time-of-flight secondary ion mass spectrometry (ToF-SIMS)[116,117]. The existing known fact is an enhancement in the piezoelectric properties with a
micro/nano-patterned composite electrode can be achieved in ferroelectric single crystals[59,92]. However, the influence of the MnO$_x$ nanocomposite electrode on the mechanisms of domain formation in PMN-PT single crystals is still not clear.

In this paper, the relationship between the domain structure and piezoelectric properties in a PMN-PT crystal with a MnO$_x$ nanocomposite electrode was investigated. Two methods, electron beam lithography and focused ion-beam milling, are commonly used for fabricating nanoscaled patterned electrodes with specific structures[118–120]. Although a complicated patterned metal electrode with size in the nanoscale can be fabricated using these techniques, the throughput is relatively low and the process can be costly. In this work, MnO$_x$ nanocomposite electrodes were fabricated using Lloyd’s mirror interference lithography (LIL), a proved scalable nanofabrication technique[121,122]. After the heat treatment, Mn from the MnO$_x$ nanocomposite was found to be diffused into PMN-PT crystals. ToF-SIMS was used to analyze the depth profile of diffused Mn. The influence of the nanocomposite on electric fields in PMN-PT single crystals was simulated using COMSOL. The dielectric and piezoelectric properties of the PMN-PT single crystals were measured using LCR meter and laser vibrometer system, respectively. To provide a better understanding of how the domain structure is modified by the patterned electrodes, samples with different thicknesses were studied using piezoresponse force microscopy (PFM). The mechanisms contributing to the enhanced property in the PMN-PT single crystals with nanocomposite electrodes will be elucidated using the combined ToF-SIMS, COMSOL simulation, and PFM results.
4.2. Experimental Section

4.2.1. Fabrication of nanocomposite electrodes

For the nanocomposite electrode fabrication, LIL is an effective technique for fabricating nanograting structures, which allows for control of electrode structure sizes and features on large exposure areas[92]. The distance between the nanogratings could be controlled by using the interference equation: \( \Lambda = \frac{\lambda}{2n \sin \theta} \), where \( \Lambda \) is the grating period, \( n \) is the refractive index \( (n_{\text{air}} = 1) \), \( \lambda \) is the wavelength of the ultraviolet laser (325 nm), and \( \theta \) is the incident angle of light/laser. In this experiment, a precise pitch of 800 nm was obtained with a light incident angle of 11.7°. First, a 200 nm layer of photoresist (Sumitomo PFI-88A1/2) was coated on the [001]-grown PMN-PT single crystal (CTS Corporations, IL, USA). Then, the light intensity pattern was recorded by the photoresist to form a 1D grating nanostructure. The nanograting was fabricated parallel to [010] \(_C\) direction, as shown in figure 4.1(a). After the photoresist exposure and development, a 100 nm thick Mn metal layer was deposited on the PMN-PT crystal with a nanostructured photoresist by electron-beam evaporation. The lift-off of Mn was implemented by using acetone. After the lift-off process, a Mn nanograting layer was left on the top surface of the PMN-PT crystal. After that, the sample was annealed at 800 °C for 3 h in air. During the high temperature (800 °C) treatment, the conducting Mn metal layer was oxidized forming a semiconducting MnO\(_x\) layer [59,123]. The surface morphology of the MnO\(_x\) nanograting is shown in figure 4.1(b). Lastly, a blanket layer of 5 nm thick Ti and 100 nm thick gold was deposited on the entire top surface of the sample as the conducting layer, as shown in figure 4.1(c). This nanocomposite electrode was then finally prepared including MnO\(_x\) semiconductor nanogratings with the pitch of 800 nm (MnO\(_x\) line width of 500 nm and spacing between two
neighboring MnO$_x$ lines of 300 nm) and a Ti/Au conductive layer (5/100nm thick). The direction of nanocomposite electrode was along [010]$_c$.

![Diagram of nanograting and SEM image](image)

Figure 4.1. The schematic and SEM image of fabrication results. (a) The MnO$_x$ nanograting was fabricated parallel to [010]$_c$ direction (b) the MnO$_x$ nanograting pattern on PMN-PT single crystal surface, (c) it shows the clear MnO$_x$ nanocomposite electrodes after 100 nm gold electrode deposition.

### 4.2.2. PMN-PT sample preparation

After the nanocomposite electrode fabrication process, a [001]-grown PMN-PT single crystal wafer with dimension of 25 mm $\times$ 25 mm $\times$ 0.6 mm was diced into rectangular plates (4 $\times$ 4 $\times$ 0.6 mm$^3$) for experiments. Different thicknesses of samples were prepared by lapping and polishing from the bottom of samples. The root mean squared roughness ($R_q$) was well controlled below 5 nm, as measured by scanning probe microscopy (Dimension Icon, Bruker, Santa Barbara, CA). Ti/Au electrodes were deposited on the bottom surface of the PMN-PT samples to create the parallel-plate capacitors. Lastly, all samples were poled at an electric field amplitude of 10 kV/cm for 30 min at room temperature in air.

### 4.2.3. PFM measurements

The domain morphology of PMN-PT single crystals was characterized by a piezoresponse force microscopy, PFM (Dimension Icon, Bruker, Santa Barbara, CA). PFM is a versatile method for studying ferroelectric domain structure by applying an electrical voltage to the sample surface with a conductive tip of a scanning force microscope$^{18}$. PFM requires detection
of small tip displacements induced by inverse piezoelectric oscillations from the sample. A sample with rough surfaces could significantly affect the PFM image. Thus, careful lapping and polishing are needed to ensure the sample surface is smooth. The samples were waxed on the glass substrate and lapped down to certain thicknesses (200 µm, 50 µm, and 30 µm). To avoid contacting and destroying the nanocomposite electrode, the lapping and polishing were done on the non-composite side (bottom side). Polishing was conducted right after the lapping process. The samples were polished with a 300 nm Al₂O₃ slurry (a mixture of deionized water and Al₂O₃ in volume ratio of 6:1) and finally with a 50 nm Al₂O₃ slurry. After the polishing, the Rq of the samples were measured below 5 nm.

4.2.4. Time-of-flight secondary ion mass spectrometry (ToF-SIMS)

In ToF-SIMS measurements, a finely focused, pulsed primary ion beam is rastered across the sample surface and the secondary ions emitted to each pixel are extracted into a time of flight mass spectrometer, mass filtered, and then counted[124]. With dual beam operation, a depth profile of ions can be obtained, and a quantification of elements can be achieved that is standardized. ToF-SIMS analyses were conducted using a TOF-SIMS V (ION TOF, Inc. Chestnut Ridge, NY) instrument equipped with a Biₙᵐ⁺ (n = 1 - 5, m = 1, 2) liquid metal ion gun, Cs⁺ sputtering gun. Both the Bi and Cs ion columns were oriented at 45° with respect to the sample surface normal. A pulsed Bi³⁺ primary ion beam at a 25 keV impact energy with less than a 1 ns pulse width was used. For depth profiles acquired in this study, 1 keV Cs ion with a 7.5 nA current was used to create a 120 µm by 120 µm area, and the middle 50 µm by 50 µm area was analyzed using a 0.3 pA Bi³⁺ primary ion beam. The sputtering time for with and without diffusion samples was 560 sec and 335 sec over the area, respectively.
4.2.5. Piezoelectric properties measurement

The dielectric properties were measured using a LCR meter (KEYSIGHT technologies, E4980A, Santa Clara, CA). To measure the piezoelectric coefficient of the PMN-PT single crystals, a $d_{33}$ measurement setup that combined with a high-resolution (< 10 pm) laser vibrometer (Polytec, OFV-5000, Irvine, CA) and a function generator (Tektronix, AFG3101, Lake Mary, FL) was used. The displacement of the sample was recorded by the laser vibrometer and an oscilloscope (Agilent Technologies Inc., DSO7104b, Santa Clara, CA).

4.3. Results and discussion

4.3.1. Simulation of the electric flux distribution

In domain engineering, nucleation of new domains is a critical step in the evolution of polarization reversal[107,125]. However, the mechanism of domain nucleation during application of electric fields is still not clear, because it is difficult to observe the appearance of an individual nanoscaled domain[110,126]. The key factors that may affect domain nucleation are the activation electric field for the domain nucleation, the averaged electric field over the volume of individual nuclei, the shape of the nuclei, and temperature[107]. Previous experimental studies of a LiNbO$_3$ single crystal with a micron-scaled stripe-patterned electrode revealed that most of the domain nucleation sites occur near the edge of the electrodes, and that this enhancement of domain nucleation result from the spatial electric field distribution[110,127]. The stripe-patterned electrodes had a 2.6 µm periodicity on the surface of the LiNbO$_3$ ceramic and resulted in the nucleation of needle-like domains[105].

Yamashita et al. reported a PMN-PT crystal with random-patterned MnO$_x$ composite electrodes could exhibit a ~40% enhancement in the dielectric and piezoelectric constants [59]. The random-patterned MnO$_x$ composite electrodes did change the piezoelectric properties.
However, the mechanisms of the pattern effects were not mentioned in the report. In our previous study, uneven electric fields were found beneath the nanocomposite electrodes[92]. In the present work, the nanocomposite electrodes consist of a periodical MnO$_x$ semiconductor nanograting and a coating with a Ti/Au conductive layer. The nanocomposite electrodes could screen part of the electric field based on different materials. To have a better understanding of the influence of nanocomposite electrodes on the local electric fields in the sample, COMSOL was used to simulate the electrical flux distribution in PMN-PT crystals with a patterned electrode. The width and thickness of the MnO$_x$ nanograting used for simulation were 500 nm and 100 nm, respectively. The spacing between MnO$_x$ nanogratings was 300 nm. Thus, the pitch size of the MnO$_x$ nanograting on the surface of PMN-PT crystal was 800 nm. A ground boundary condition was assigned to the bottom electrode, and 100 V was applied across a 600 µm thick PMN-PT crystal. Figure 4.2 shows the simulated electric flux distribution in the PMN-PT crystal. On the edge of each MnO$_x$ nanograting, a strongly non-uniform electric field was generated by a fringe effect. Beneath the edge of the MnO$_x$ nanograting, the electric field was found to be three to six times higher than the area between the two nanogratings or at the center area of the nanograting. Consequently, a larger quantity of the new domains was formed at the edge of the MnO$_x$ nanograting, since the region had a higher electric field that could easily exceed the activation field of domain nucleation. The needle-like domains propagated, forming nuclei that were parallel to the direction of applied field[107]. The non-uniform electric fields created by the nanocomposite electrodes on the PMN-PT crystal may lead to a higher domain density at the edge of the MnO$_x$ nanograting, as well as prevent rapid domain reversal during application of electric field[59]. The difference in domain reversal timing may produce larger charged domain boundary regions and dense domains of the PMN–PT single crystal. Thus, the
simulation result illustrates the electric field spatial distribution and the favored regions for
domain nucleation. The fringe effect observed in the simulation result is similar with the work
reported by Shur et al[110].

![Mn Oxide Nanocomposite Electrode](image)

Figure 4.2. The fringe effect simulation of MnO$_x$ nanocomposite electrode. The MnO$_x$
nanograting has an 800 nm period with pattern size 500 nm and 100 nm in width and thickness,
respectively. The color bar denotes the electric field intensity.

### 4.3.2. Mn doping/diffusion analysis

Heat treatment of the PMN-PT crystals during the nanocomposite electrode fabrication
process may result in the doping/diffusion of Mn ions into PMN-PT. In order to maintain charge
neutrality, it is known that the formation of oxygen vacancies is needed when acceptor dopants
(Mn$^{2+}$) substitute onto the B-site (e.g., Ti$^{4+}$, Mg$^{3+}$, and Nb$^{5+}$) in PMN-PT[128]. The oxygen
vacancies tend to diffuse along the direction opposite to that of the orientation of polarization,
forming a defect dipole[129]. These oxygen vacancies may promote the domain nucleation rate
in PMN-PT crystals with MnO$_x$ nanocomposite electrodes. ToF-SIMS was employed to quantify
the diffusion of Mn ions. Two PMN-PT crystals with Mn oxide nanogratings, with and without
heat treatment, were prepared for the ToF-SIMS analysis and the results are shown in figure 4.3.
There are three regions in each figure; they are a MnO$_x$ region, an interface region and a PMN-PT single crystal region (from left to right). The material was sputtered using a Cs ion beam from the top surface of the nanocomposite which is the MnO$_x$ layer. Atomic force microscopy with a tapping mode was used to measure the crater depth in the bombarded area, and the measured crater depth was used to calculate the sputtering rate. As the material was progressively removed, the intensity of Mn ion decreased, and the intensities of Ti and Pb ions increased, commensurate with the location of the interface region. The intensity of Mn ion reached a plateau in the PMN-PT single crystal region as the top nanocomposite electrode and interfaces were being completely removed by the ion beam. The sample without heat treatment shows the Mn ion intensity starts to drop significantly at a depth of ~80 nm (in the interface region) and reaches a minimum at a depth of ~130 nm, as shown in figure 4.3(a). Below this depth (the red region of the figure), the intensity of Ti and Pb ions were stable, which means that the sputtered materials mostly come from PMN-PT. On the other hand, a significant doping/diffusion of Mn into PMN-PT was found in the sample that was heat treated, as shown in figure 4.3(b). The intensity of the Mn ion curve evidenced that the depth of Mn doping/diffusion was ~300 nm.

Figure 4.3. ToF-SIMS results of MnO$_x$ nanocomposite electrodes with and without heat treatment (a) PMN-PT without heat treatment; (b) PMN-PT after heat treatment.
4.3.3. Domain structure analysis

In order to understand the influence of nanocomposite electrodes on the domain structure, domain morphologies of the PMN-PT crystals with different thicknesses were acquired using PFM. The high spatial resolution of PFM makes it ideal for the study of domain morphology changes on the nanometer scale[130]. In a control group, the domain structure of 30 µm and 200 µm thick crystals with planar electrodes were measured by PFM. The out-of-plane polarization phase images are shown in figure 4.4(a) and 4.4(b), and their topography images are shown in the insets. The surface roughnesses (root mean square) were less than 5 nm. The PFM images revealed that both samples (of different thickness) with planar electrodes had a randomly distributed ribbon-shaped domain structure as previously reported by Shvartsman et al.[131].

The PFM images of PMN-PT crystals (thicknesses of 30, 200 and 600 µm) with nanocomposite electrodes are shown in figure 4.5. The PFM image of the 600 µm thick crystal had a similar ribbon-shaped domain structure to the crystal with a planar electrode (see figure 4.4(a) and 4.4(b)). When the sample thickness was decreased to 200 µm, linear domain structures which were parallel to the direction of the MnO$_x$ nanogratings, [010]$_C$ direction, were observed. Similar linear domain structures were also observed in the 30 µm thick crystal. The linear domain structure may be induced by the fringe effect at the edges of nanocomposite electrode. The fringe effect provides a high electric field gradient locally, which may favor nuclei formation. Thus, more domains may be nucleated along the edge of the MnO$_x$ nanograting, resulting in the linear domain structures. The nucleation probability (P) is proportional to \( \exp\left(\frac{-E_{active}}{E_{local}}\right) \), where \( E_{active} \) is the activation field and \( E_{local} \) is the electric field averaged over the volume of the nucleus[110]. When the thickness of the crystal is above a critical value, the polar nuclei forming near the nanocomposite electrodes do not grow throughout the crystal volume. Part of the
new-forming domains merge together in the crystal, resulting in a randomly oriented ribbon-shaped domain morphology (see figure 4.5(a)). However, as the sample thickness is reduced, the fringe effect can only influence the process up to a depth of 200 µm, resulting in a linear domain morphology (See figure 4.5(b) and 4.5(c)). A schematic of the domain growth process in crystals with different thickness is given in figure 4.5(d), summarizing our plausible explanation for why the nanocomposite electrode can generate two different types of domain distributions in crystals of different thicknesses. Similar linear domain patterns were also found in a 50 µm thick PMN-PT crystal, as shown in figures 4.6(a) and 4.6(b). The zoomed-in PFM image (figure 4.6(c)) shows the linear domain pattern had a width of 150 nm. This figure also demonstrates near-periodic linear domain structures with a periodicity of ~300 nm. Figure 4.6(d) shows the phase intensity, which is illustrated as a dash-line in figure 4.6(c). Changes in the phase signal intensity matched well with the MnO$_x$ nanocomposite electrode pattern. Furthermore, the MnO$_x$ nanocomposite electrode on the 50 µm thick PMN-PT crystal clearly generated a periodic linear domain pattern over the entire sample surface.

Based on these experimental observations, a MnO$_x$ nanocomposite electrode can be used to generate different nanodomain patterns in PMN-PT single crystals. A patterned domain structure with a high domain density could be generated by a combination of the fringe effect and the diffusion of Mn. When the domain density increased, the piezoelectric properties have shown significant enhancement[132].
Figure 4.4. The PFM domain image of PMN-PT with conventional planar electrodes in different thicknesses. (a) The thickness of the sample is 30 µm, and (b) 200 µm; the insert images are the topography and surface roughness.

Figure 4.5. The PFM domain image result of PMN-PT with MnO$_x$ nanocomposite electrodes in different thicknesses. (a) 600 µm (b) 200 µm (c) 30 µm (d) schematic images of nucleation of new domain observation by PFM for samples in different thickness.
4.3.4. Ferroelectric hysteresis measurements

Figure 4.7 shows the polarization-electric field loops ($P$-$E$ loop) of PMN-PT crystals with and without nanocomposite electrodes. The samples were treated with the same poling condition. The 600 µm thick PMN-PT crystals with and without nanocomposite electrodes exhibited similar and well-saturated $P$-$E$ loops under application of a triangular bipolar waveform ($f = 1$ Hz) with an amplitude of 10 kV/cm. Before each measurement of hysteresis loop, a preset pulse E-field (10 kV/cm) is applied on the sample. The hysteresis loop was recorded after 20 loop cycles. PE curves of each sample were collected under two different electric field conditions, which we designate here as normal and inverted electric fields. The normal electric field is along the direction from the nano-electrodes to the opposite surface, and the inverted field is reversed. Figure 4.7(a) shows the $P$-$E$ loops for a sample without a nanocomposite electrode under both normal and inverted electric fields. Similar $P$-$E$ loops with a remnant polarization ($P_r$) of 20.48 µC/cm$^2$ and a coercive electric field ($E_c$) of 2.45 kV/cm were observed in both cases. On the
the other hand, the $P$-$E$ loops of PMN-PT with nanocomposite electrodes are shown in figure 4.7(b). The values of $P_r$ and $E_c$ were 24.42 $\mu$C/cm$^2$ and 2.24 kV/cm, respectively. Under the normal electric field, the Mn nanograting induced oxygen vacancy was accumulated on the surface and formed a lower internal bias field, $E_i=0.05$ kV/cm. Under the inverted electric field, the oxygen vacancy migrated to the whole crystal and formed a higher internal bias field, $E_i=0.18$ kV/cm. Compared to the sample without nanocomposite electrodes, the $P$-$E$ loops of samples with the nanocomposite electrodes were slim (decrease 5.7%) and non-symmetric (internal bias field $E_i=0.18$ kV/cm). Also, the $E_c$ of normal and inverted electric fields were clearly not equal. The slimmer loop demonstrates reduced hysteretic losses under high amplitude drive. The non-symmetric nature results in a horizontal shift in the $P$-$E$ loops, indicating the presence of internal dipolar fields that bias the crystal[133]. The inverted electric field hysteresis data for PMN-PT with nanocomposite electrodes showed a partially poled phenomenon. The PMN-PT samples with nanocomposite electrodes were partially poled during the $P$-$E$ measurement with lower field amplitudes. This dipolar field from the Mn doping might be leading to the asymmetry offset in the $P$-$E$ loops.

![Figure 4.7](image)

Figure 4.7. Normal and inverted electric field (E-field) induced ferroelectric (P-E) hysteresis loop. (a) PMN-PT with conventional planar electrodes. (b) PMN-PT with nanocomposite electrodes on one surface and a plane electrode on the other surface.
4.3.5. Piezoelectric constant measurements

The illustration of the setup is shown in figure 4.8(a). A sine wave with an electric field amplitude of 1.6 kV/cm was applied to the crystal at a frequency of 1 Hz. The piezoelectric coefficient ($d_{33}$) was then calculated by dividing the measured displacement by the applied voltage. PMN-PT crystals with three different thicknesses (30 µm, 200 µm, and 600 µm) and different electrodes (nanocomposite electrodes and conventional planar electrodes) were studied. To minimize the compositional differences between the samples, the samples used in this work were prepared from the same section of the PMN-PT crystal. The thickness variation will cause the measuring error of the piezoelectric constant. The thickness of samples was measured by using length gauge (CT 6000, Heidenhain, Traunreut, Germany) three times for each sample and the error of thickness measuring was less than 1%. Before measuring $d_{33}$, the samples were put away for 24 hours after poling to reach a stable state. For each condition, three samples were prepared. And the $d_{33}$ were measured at three different locations of each sample. The data shown in the figure 4.8(b) is the statistical average $d_{33}$ and the measuring error was less than 3%. The $d_{33}$ value of PMN-PT crystal with the plane electrode is consistency with Tian’s works[134] and Zhang’s works [135] around 1600 pC/N. PMN-PT samples with nanocomposite electrodes showed a higher $d_{33}$ value of 2050 ± 150 pm/V than the ones with planar electrodes. Three samples with same conditions were prepared, and the data were averaged from three samples with three different locations. The standard deviation of the piezoelectric constant for plane electrode sample 20 µm, 200 µm and 600 µm were 37 pC/N, 82 pC/N, and 100 pC/N respectively. The standard deviation of the piezoelectric constant for structured electrode sample 20µm, 200 µm and 600 µm were 234 pC/N, 37 pC/N, and 150 pC/N respectively. The dielectric constant was measured by a LCR meter. PMN-PT samples with nanocomposite electrodes
showed a dielectric constant value of 5400, and the ones with planar electrodes were 3905. The values of the dielectric and piezoelectric constants of the PMN-PT crystal with the nanocomposite electrodes were 38.3% and 36.7% higher than the crystal with a conventional planar electrode, respectively. The $d_{33}$ value of the crystal with conventional electrodes did have a modest increase of about 8% as the thickness was increased from 30 µm to 600 µm because of the clamping/pinning of domain wall motion was reduced in the thicker samples[136]. These improvements could be explained directly due to the patterned electrodes.

![Diagram](image)

Figure 4.8. Piezoelectric coefficient measurement system and results. (a) The piezoelectric coefficient measurement system which including a laser vibrometer system, a function generator, an amplifier and an oscilloscope. (b) The piezoelectric constant of PMN-PT with MnO$_x$ nanocomposite electrodes and conventional planar electrodes in three different thicknesses, 30 µm, 200 µm and 600 µm. The standard deviation (error bar) of piezoelectric constant for plane electrode sample 20µm, 200 µm and 600 µm were 37 pC/N, 82 pC/N, and 100 pC/N respectively. The standard deviation of piezoelectric constant for structured electrode sample 20 µm, 200 µm and 600 µm were 234 pC/N, 37 pC/N, and 150 pC/N respectively.

### 4.4. Conclusion

Single crystals of PMN-PT with MnO$_x$ nanocomposite electrodes showed a high $d_{33}$ value and dielectric constant, which were 36.7% and 38.3% higher than the ones with a conventional planar gold electrode, respectively. The enhanced $d_{33}$ may be due to the higher domain densities which originate from two domain nucleation mechanisms: Mn doping/diffusion and the fringe effect. ToF-SIMS investigations demonstrated that the doping/diffusion of the Mn into PMN-PT
may result in defect dipoles, which resulted in a slightly asymmetric characteristic in the P-E loops. PFM images revealed an increase in the domain density for crystals with nanocomposite electrodes when the crystal thickness was less than 200 µm. The simulation results show a fringe effect beneath the edge of the patterned MnO$_x$ nanograting. The non-uniform electric fields resulting from the MnO$_x$ nanocomposite electrode in the PMN-PT may increase the domain nucleation rate and prevent rapid domain reversal. Thus, nucleation of small domains with reversed polarization will occur first in local regions that have higher electric fields. This work provides a better understanding of PMN-PT single crystals with tailored MnO$_x$ nanocomposite electrodes for improving piezoelectric properties.
CHAPTER 5

PROPERTY ENHANCEMENT OF PMN-PT USING ALTERNATING CURRENT POLING

The content in this chapter was published with the title “Dielectric and piezoelectric properties of 0.7 Pb(Mg\textsubscript{1/3}Nb\textsubscript{2/3})O\textsubscript{3}-0.3 PbTiO\textsubscript{3} single crystal poled using alternating current”, in Materials Research Letters 6.10 (2018): 537-544, as reference[137].

In this chapter, 0.7Pb(Mg\textsubscript{1/3}Nb\textsubscript{2/3})O\textsubscript{3}-0.3PbTiO\textsubscript{3} (PMN-30%PT) single crystal samples were electrically poled using an alternating current (electric field) poling (ACP) method. Compared to the traditional poling method, the piezoelectric coefficient, free and clamped dielectric constants were improved more than 20%. X-ray diffraction result suggests the existence of monoclinic phase ($M_A$) in ACP samples and piezoresponse force microscopy (PFM) result further depicts the phase coexistence finer domain structures. The ACP sample also showed the different phase transition sequences during the depoling process. Our work could provide a novel domain engineered method to enhance piezoelectric properties of PMN-PT single crystal.

5.1. Introduction

Solid solution of $(1-x)$Pb(Mg\textsubscript{1/3}Nb\textsubscript{2/3})O\textsubscript{3}-xPbTiO\textsubscript{3} (PMN-xPT) and other relaxor ferroelectric single crystals have attracted intense research interest over the past decades because of their outstanding piezoelectric electromechanical properties, and the associated applications in sensors, actuators, and transducers.[5,29,138,139] In particular, their high piezoelectric coefficient and dielectric permittivity are critically important in advanced transducers.[29,140,141] There are several ways to manipulate dielectric and piezoelectric properties of PMN-xPT single crystal, such as modifying the compositions,[104] applying nanocomposite electrodes,[92,142] and utilizing different poling methods.[92,143] Among these
methods, using different poling methods has the greatest potential from its advantages of low cost and high efficiency. In general, direct current (electric field) poling (DCP) method is widely used in academia and industry.[28] DCP-based domain engineering study by Wada et al. revealed that piezoelectricity of domain engineered crystals can be enhanced from higher domain wall densities.[33,144] Recently, Yamamoto and Yamashita et al. reported an alternating current (electric field) poling (ACP) method that could further enhance the dielectric and piezoelectric properties of PMN-PT crystals.[143,145] While ACP may be a promising method for piezoelectric material properties enhancement, it has not been reported whether or not the domain engineering mechanism realized in DCP is similarly derived through the ACP, and this question needs to be answered for crystal applications.

One important stability concern in the piezoelectric materials is aging, which can be observed in most of the ferroelectrics such as barium titanate (BaTiO$_3$) and lead zirconate titanate (PZT).[146–151] Devonshire and Plessner described that aging is a gradual transformation from the free state to the clamped state, which means the domain boundary migrates from high energy polarizability to a lower energy polarizability.[146,152] Aging strongly affects the application of ferroelectrics, and many investigations have been devoted to elucidate the aging phenomena in relaxor ferroelectrics.[153,154] However, there are only a few reports that mention the aging characteristics of PMN-PT single crystals,[155] not mentioning the influence brought from the new ACP method.

This chapter reports the different poling conditions of DCP and ACP for PMN-30%PT single crystals, and their aging characteristics. The piezoelectric and dielectric properties of DCP and ACP crystal samples were measured. X-ray diffraction (XRD) was used to mark the field-induced phase transition from rhombohedral to monoclinic phase ($M_A$) in ACP samples,
while piezoresponse force microscopy (PFM) was utilized to find the domain structures in ACP samples. The temperature dependent dielectric constant curves of both ACP and DCP samples were measured and their phase transition sequences during the depoling process were compared.

5.2. Experimental section

5.2.1. PMN-PT sample preparation

The [001]-grown PMN-30%PT single crystal (CTS Corporations, IL, USA) was cut, diced and polished to obtain samples with dimension of 9.2×9.2×0.6 mm³. Titanium/gold electrodes (5/100 nm) were sputtered on the top and bottom surfaces of the samples. For the DCP samples, an external electric field (E-field) of 10 kV/cm was applied to pole the sample at room temperature for 30 minutes.[28] Its piezoelectric coefficients and dielectric constants were then measured using a Berlincourt-type $d_{33}$ meter (YE2730A $d_{33}$ meter, APC International Ltd., Mackeyville, PA, USA) and an LCR meter (KEYSIGHT technologies, E4980A, Santa Clara, CA, USA). The free dielectric permittivity ($\varepsilon^{T}_{33}$) and clamped dielectric permittivity ($\varepsilon^{S}_{33}$) were calculated from the measured capacitance by using an impedance analyzer (Agilent 4294A, Palo Alto, CA, USA) at 1 kHz and the frequency at two times of anti-resonant frequency (2$f_a$), respectively. The clamped dielectric permittivity was measured because of the fact that electrical impedance of a transducer is determined by $\varepsilon^{S}_{33}$ and dimensions of the piezoelectric material.[5] For ACP samples, a bipolar triangular voltage with a designated frequency (e.g., $f = 1$ Hz) was applied to the samples to generate an alternating E-field (e.g. with the peak-to-peak 10 kV/cm). The ACP samples were poled for up to 20 cycles or 20 seconds.

5.2.2. Measurement of properties

After each poling process, the piezoelectric coefficient, free ($\varepsilon^{T}_{33}$) and clamped ($\varepsilon^{S}_{33}$) dielectric permittivity were measured by the $d_{33}$ meter and impedance analyzer mentioned earlier,
respectively. Structure properties of PMN-30%PT single crystal with different poling conditions were studied using an X-ray diffractometer (SmartLab, Rigaku, Tokyo, Japan) with monochromatic CuKα radiation. The domain morphology was observed and characterized by a piezoresponse force microscopy, PFM (Dimension Icon, Bruker, Santa Barbara, CA, USA). The temperature dependent dielectric properties of PMN-PT single crystal were acquired by an LCR meter at every 1°C in a temperature range of 25°C to 200°C. During the measurement, the sample was heated in a silicone oil bath with a heating rate of 1°C/minute to ensure a homogeneous heating process. For repeating the experiments, the five samples were fully depoled in silicone oil at 250°C for 30 minutes, with top and bottom electrodes shorted during the depoling process. Each sample was tested three times to collect data.

5.3. Results and discussion

5.3.1. Piezoelectric, dielectric constant, and electromechanical coupling coefficient

The piezoelectric coefficients of PMN-30%PT single crystals with different poling conditions (ACP and DCP) are shown in figure 5.1(a). The inset is an illustration showing the poling conditions for ACP and DCP methods. The DCP sample used 30 minutes, whereas ACP sample used less than 1 minute during total poling process. Five samples were prepared and tested three times. The applied E-field (10 kV/cm) in this ACP method is about four times of the coercive field (E_c) of PMN-PT crystals (~2.3 kV/cm).[156] The piezoelectric coefficient of the sample poled with the ACP method (ACP sample) was 1992±7 pC/N which is 21% higher than the sample poled with the conventional DCP method (DCP sample), 1650±18 pC/N. It should be noted that high piezoelectric coefficients were observed in ACP samples which were poled for less than 1 minute. The poling process of DCP samples took 30 minutes with E-field of 10 kV/cm. With 2 alternative cycles or 2 seconds, the ACP sample has exhibited a piezoelectric
coefficient of 1845±10 pC/N, which is already higher than that of the DCP samples. Free and clamped dielectric constants of the PMN-30%PT single crystal with different poling conditions are shown in figure 5.1(b). The inset chart shows the dielectric constant consistency in five ACP samples. Free and clamped dielectric constants of ACP sample were 8500±100 and 970±70, respectively. These values are larger than the DCP samples, which is 6900±105, and 715±70, respectively. Compared to the PMN-PT with DCP method, $d_{33}$, $\varepsilon_{33}^T$, and $\varepsilon_{33}^S$ were improved 21%, 23% and 35%, respectively. Piezoelectric coefficient and dielectric constant of the PMN-30%PT single crystal samples increase with the ACP cycles up to 7 cycles (or 7 seconds), and the values saturated after 7 cycles. The saturated piezoelectric coefficients and dielectric constants were at around 1980±5 pC/N and 8140±150, respectively. Thus, the ACP single crystals showed clearly enhanced piezoelectric and dielectric properties over the DCP samples.

In addition, electromechanical coupling coefficient ($k_t$) of ACP and DCP samples are calculated according to the IEEE standards, using the following equations.[157]

$$ k_t^2 = \frac{\pi}{2} \times \frac{f_r}{f_a} \times \tan \left( \frac{\pi \Delta f}{2 f_a} \right) \quad (5-1) $$

$$ \Delta f = (f_a - f_r) \quad (5-2) $$

where $f_r$ and $f_a$ are the resonance and antiresonance frequency, respectively. The DCP and ACP samples both showed the similar coupling coefficient $k_t = 0.57$. 


Figure 5.1. The piezoelectric and dielectric properties of ACP and DCP. (a) the piezoelectric coefficient of DCP and ACP with different number of cycles; the inset shows the poling electrical field and duration time, (b) the free and clamped dielectric constant of DCP and ACP with different number of cycles; the inset shows the stability of ACP method in five samples.

5.3.2. XRD measurement

Figure 5.2 shows 400 peaks of PMN-30%PT single crystal with different poling conditions. XRD reference patterns are also listed in the bottom of the figure 5.2. According to the phase diagram and electric field-temperature diagram,[158,159] the field-induced phase transition for PMN-30%PT single crystal under the electric field along [001] direction will be rhombohedral ($R$) $\rightarrow$ monoclinic ($M_A$) $\rightarrow$ monoclinic ($M_C$)$\rightarrow$ tetragonal ($T$). (The notation $M_A/ M_C$ follows definitions of Vanderbilt and Cohen.[160]) Thus, the unpoled sample peak marks the $R$ phase. Since the peak center of the DCP sample is almost at the same $2\theta$ position as the unpoled sample peak, it shows that DCP sample is still in the same $R$ phase. In contrast, the peak center of ACP is obviously shifted, showing the likely existence of an $M_A$ phase based on the reference pattern.
Figure 5.2. The XRD 400 reflection of PMN-PT single crystal resulting from different poling methods, including ACP, DCP and unpoled sample in the room temperature. The peak intensities have been normalized and the reference patterns are shown in the bottom of the figure.

5.3.3. Domain observation

In addition to the average crystal structure characterization using XRD, the local domain structure was observed by PFM as shown in figure 5.3(a) shows clear lamellar domain structures (921 ± 75 nm in width), which are engineered by conventional DCP method.[161] In figure 5.3(b), the ACP sample depicted heterogeneous domain structure constructed by wide (694 ± 8 nm), nearly [100]-oriented domains and finer (162± 3 nm), 90-degree, [101]-oriented domains, which are significantly different from the ones observed in DCP samples. Additionally, domains generated from ACP samples were distributed more uniformly than those from DCP sample, which is believed corresponding to the lower full width half maximum (FWHM) in the XRD result shown in figure 5.2. This unique domain structure likely originates from the domain wall motion due to the electrical field polar switching.

As it is discussed in XRD results above, DCP samples remain $R$ phase and ACP samples experience $R\rightarrow M_A$ field-induced phase transition. Here, the heterogeneous domain structure
demonstrates that such phase transition was not complete since there was still remained 90-degree $R$ phase. Thus, the wide, nearly [100]-oriented domains represent $M_A$ phase, and the phase transition caused by ACP is actually $R \rightarrow M_A + R$. The finer $R$ phase domains generated by ACP method indicate the enhancement of domain wall density, which is the origin of outstanding dielectric and piezoelectric properties in ferroelectric materials after the domain engineering[132,162,163].

![Figure 5.3](image.jpg)

Figure 5.3. The PFM images of domain morphology for (a) DCP method and (b) ACP method. Electrodes are attached to vertical direction of the photos.

### 5.3.4. Temperature-dependent dielectric constant measurement

The temperature-dependent dielectric constant measurement result is shown in figure 5.4. The ACP samples poled with 7 AC cycles and 20 cycles had a maximum dielectric constant value ($\varepsilon_{33,max} \sim 40,000$), which was higher than the DCP sample ($\varepsilon_{33,max} \sim 20,000$). It has been reported that the poled rhombohedral PMN-x%PT has a phase transition sequence of $R \rightarrow T \rightarrow C$ during the zero field heating.[164] In this work, the similar dielectric constant curve in figure 5.4(a) shows the phase transition temperatures of DCP PMN-30%PT single crystal are 90°C (363 K) for $R \rightarrow T$ and 130°C (403 K) for $T \rightarrow C$. In addition to the same phase transition temperature near 90°C and 130°C, extra anomalies at 93°C ~ 97°C (366 K ~ 370 K) are shown.
in dielectric constant curves of ACP samples, as shown in figure 5.4(b). It demonstrates that the different poling conditions lead to different phase transition sequences. Here, dielectric constant for ACP samples dropping at 90°C and 93°C ~ 97°C is likely caused by the appearance of the $T$ phase and totally transformed $T$ phase, respectively.

As it is discussed in XRD and PFM results above, in ACP samples $M_A+R$ phase exists at room temperature. Based on phase transition study,[158,159] the phase transition sequence of ACP samples is $M_A+R \rightarrow M_A+R+T \rightarrow T \rightarrow C$. Other explanation might be $M_A+R \rightarrow R(M_A)+T \rightarrow T \rightarrow C$ and further XRD and PFM at high temperatures would be needed to further confirm this sequence. Figure 5.4(b) also shows that the $M_A+R \rightarrow M_A+R+T$ phase transition temperature is ACP-cycle-number-independent. In other words, the field-induced-$M_A$-phase domain wall energy is also ACP-cycle-number independent. Interestingly, comparing to the ACP-cycle-number independent $M_A+R \rightarrow M_A+R+T$ phase transition temperature, $M_A+R+T \rightarrow T$ phase transition temperature of ACP samples is ACP-cycle-number dependent and ranges from 93°C to 97°C. Such dependence can be explained by domain wall energy difference between ACP and DCP samples. First, the extra anomalies at 93°C to 97°C are from the domain wall energy increment of ACP samples. The higher ACP-cycle-number sample has higher domain wall energy and it needs higher temperature to make the whole sample transformed into $T$ phase. This result corresponds to the higher 90-degree domain wall density in the $R$ phase of ACP samples from PFM results.
5.3.5. Properties stability measurement

Considering the new domain structure shown in PFM result, the property stability of such phase coexistence heterogeneous structure was tested by the following aging experiment. In the experiment, the aging characteristics of the piezoelectric coefficient and dielectric constant were collected right after the poling process and after a certain period of time at room temperature. The properties of aging data were measured using a $d_{33}$ meter and an impedance analyzer at room temperature. Figure 5.5(a) shows the aging characteristics of the piezoelectric coefficient with different poling methods. The aging behaviors of poled PMN-30%PT single crystals follow the logarithmic law similar to BaTiO$_3$ and PZT,[165,166] and the aging equation can be written as follows.

$$P_t = P_i - A_p \log(t)$$

(5-3)
where \( P_t \) is the piezoelectric or dielectric constant after aging time \( t \), \( P_i \) is the initial value of property. \( A_p \) is the absolute aging rate which is the absolute decrease for one decade. The relative aging rate is expressed as

\[
R_p = \frac{A_p}{P_i} \times 100 \text{ (%/decade)}
\]

(5-4)

It was observed that the piezoelectric aging of the ACP and DCP samples follow linear, logarithmic time dependence with aging rate \((R_p)\) of 0.5 %/decade and 0.6 %/decade, respectively. The aging of free and clamped dielectric constant is shown in figure 5.5(b). The aging rate of free dielectric constant around 1.3–2.0 %/decade by DCP and ACP method, which is similar to the Mn-doped \( \text{Pb(In}_{1/2}\text{Nb}_{1/2})\text{O}_3-\text{Pb(Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3-\text{PbTiO}_3 \) (~1.5%/decade) with the dielectric constant of 4000.[129] The ACP and DCP samples also have similar aging rate of clamped dielectric constant. Therefore, ACP method can be used to enhance the dielectric and piezoelectric properties with reduced time of poling process without any aging concerns.

Figure 5.5. The aging rate of DCP and ACP. (a) The aging rate of piezoelectric coefficient, (b) The aging rate of free and clamped dielectric constant.
5.4. Conclusion

In summary, the ACP single crystal samples (alternating current E-field with 7 cycles or 7 seconds) exhibit a higher piezoelectric coefficient of $1992\pm7$ pC/N and dielectric constant of $8500\pm100$ that those of their DCP counterparts (continuities E-field for 30 minutes). The enhanced piezoelectric coefficient and dielectric constant in ACP samples may originate from a higher degree of field-induced $M_A$-phase. Both XRD and PFM results depict that ACP method induced coexisted phases $M_A+R$ at room temperature. The finer $R$ phase domain structures generated by ACP method indicate the enhancement of domain wall density and hence, the better piezoelectric performance. The aging rate of the piezoelectric coefficient and dielectric constants of the ACP samples are 0.5 %/decade and 2.0%/decade, respectively. Thus, the reported ACP method exhibits a great potential to enhance the piezoelectric and dielectric propertied of relaxor-PT single crystals without aging concerns.
CHAPTER 6

CANDLE SOOT NANOPARTICLES-PDMS COMPOSITES FOR LASER ULTRASOUND TRANSDUCERS


Generation of high power laser ultrasound strongly demands the advanced materials with efficient laser energy absorption, fast thermal diffusion and large thermoelastic expansion capabilities. In this chapter, candle soot nanoparticles-polydimethylsiloxane (CSNPs-PDMS) composite was investigated as the functional layer for an optoacoustic transducer with high-energy conversion efficiency. The mean diameter of collected candle soot carbon nanoparticles is about 40 nm, and the light absorption ratio at 532 nm wavelength is up to 96.24%. The prototyped CSNPs-PDMS composite laser ultrasound transducer was characterized and compared with transducers using carbon black (CB)-PDMS and carbon nano-fiber (CNF)-PDMS composites, respectively. The unprecedented laser ultrasound transduction performance using CSNPs-PDMS composites is promising for a broad range of ultrasound therapy applications.

The effect of candle soot structure and thickness on the photoacoustic transduction efficiency was also studied. Optical properties of the CSNP/PDMS composites were characterized through both experimental measurements and finite difference time domain (FDTD) analysis in the visible wavelength range, indicating that the carbon volume fraction and thickness
of CSNPs-PDMS composite are highly relevant with light absorption. With a low laser energy input (<1 mJ/pulse), the CSNPs-PDMS composite with 2.15 μm thickness exerts an output pressure of 3.78 MPa and a conversion efficiency of 9.69×10⁻³.

6.1. Introduction

Ultrasound transducers with high intensity or high peak pressure can be used in a broad range of biomedical ultrasound therapy and drug delivery applications[173,174]. Optoacoustic transducers are attractive because of their high power density, high frequency and broad bandwidth. Furthermore, laser generated ultrasound offers an easy and efficient way to transform laser energy into short acoustic pulses without direct interaction between laser and the subjects. Instead, a laser ultrasound transduction structure, usually consisting of a laser light absorption layer and an thermal expansion layer[75,89]. In order to obtain high performance laser ultrasound transducers, active research has been focused on the absorbing materials such as carbon black, carbon nanotubes (CNT)[75], graphite, metallic films[175], gold nano-structures[89,176] and gold nano-particles[177]. These single phase materials are known with high light absorption ratio and thus high temperature can be generated locally under laser exposure. Owing to their nanometer spatial configuration, thermal energy can be transferred into the expanding layer or matrix with high efficiency. Moreover, thermal expanding material with high thermal expansion coefficient is greatly demanded to achieve a high pressure acoustic pulse. Polydimethylsiloxane (PDMS) has been widely used as a thermal expanding layer because of its high thermal coefficient of volume expansion ($\alpha = 0.92 \times 10^{-3}$ K⁻¹), which is much higher than water, tissue, ceramics and metals[78,178]. As an example, Buma et al. proved that the conversion efficiency of thermoelastic effect was improved over 20 dB by using PDMS film instead of metallic film[179].
In addition to single phase light absorption layer and thermal expansion layer configurations, composite materials capable of both light absorption and expanding have also been studied. Flat composite films with graphene and carbon nanotube showed the capability of generating high acoustic pressure over 7.5 MPa near the transducer surface under a laser input of 43.28 mJ/cm$^2$[78]. By employing PDMS/gold nanoparticle nanocomposite, the laser ultrasound transduction efficiency was increased by 3 orders of magnitude compared with the aluminum thin film[180]. Baac et al. claimed that CNT-PDMS composite-based laser ultrasound transducer generated strong optoacoustic pressure: 18 times stronger than a Cr film reference and 5 times stronger than gold nanoparticle-PDMS composite[75]. Hsieh et al. used CNF-PDMS composite as a light absorption material and the optoacoustic energy conversion efficiency was measured to be $15.6 \times 10^{-3}$ Pa/(W/m$^2$), which is much higher than that of carbon black composite[76]. Bao et al. used finite difference time domain (FDTD) simulations to analyze the relation between absorption, volume fraction, and thickness. [181]. The non-uniform, carbon black/PDMS mixture is even more efficient than the metal film/PDMS composite, which shows great potential in sonothrombolysis using a laser generated focused ultrasound transducer [89,182]. Recently, candle soot nanoparticles (CSNP) have attracted increasing attention due to its simple synthesis process. Owing to the excellent electrical properties and branch-like nanostructures, candle soot (CS) has been used to build superhydrophobic surfaces, fabricate infrared sensors, and improve volumetric receivers [183–185].

However, current fabrication process for the absorbing layer preparation not only lacks precise dimension control but also is complicated, expensive and less scalable. the transduction mechanism and the relationship between the CS structural property and the photoacoustic transduction efficiency have not been fully addressed yet. In this chapter, we demonstrate the
effects of CS absorption layer structure and thickness on the photoacoustic transduction. We studied the contribution of light absorption property to the photoacoustic transduction of CSNPs-PDMS composites. The constitutive materials were modeled with FDTD simulations and characterized using a spectrophotometer. The photoacoustic transduction efficiency was analyzed based on the characterized results.

6.2. Experiment section

6.2.1. Fabrication of CSNPs-PDMS composite

A flame synthesis using a paraffin wax candle flame was executed to generate carbon nanoparticles [183]. The overall fabrication procedure was modified from our previous work [77]. This modification was made for gaining more precise control of the CS layer deposition. The CS was deposited on a glass slide placed about 2 cm above the wick, resulting in a coated area of approximately 25 mm by 25 mm, as shown in figure 6.1(a). By changing the deposition time, different thicknesses of CS can be deposited. The cross section of a sample with a 30 sec CS deposition time is shown in figure 6.1(b). The diameter of each particle shown is 40 ± 5 nm. When gas molecules collide against evaporated CS nanoparticles, CS nanoparticles lose their kinetic energy and form clusters [183]. The CS particles stick at the point of impact on the glass surface and then develop branch-like porous structures with mechanical stability [17, 21]. The mechanism is molecular diffusion, which depends on the ratio of the characteristic pore dimension ($r_p$) and mean free path ($\lambda$). The branch-like structures can be predicted and simulated by Knudsen diffusivity calculations [186].

Meanwhile, a PDMS thermal expansion layer was fabricated. The PDMS was prepared with a base and curing agent (Sylgard 184) with a ratio of 10:1, and then degassed for 30 min in a vacuum chamber. For lowering viscosity of the uncured PDMS, toluene was added to the PDMS
by a weight ratio of 1:100 (toluene: PDMS). Next, PDMS was spin-coated directly on the CS-coated glass slide to clear away extra PDMS, as well as control the thickness of the pure PDMS layer shown in figure 6.1(c). The CSNPs-PDMS composite samples were later placed on a hot plate at 65°C for 1h (VWR, standard series 7×7 hotplate, PA) to fully cure the PDMS and eliminate the added toluene. A cross section view of the laminar (PDMS, CSNPs-PDMS, and glass layer) stack is shown in figure 6.1(d). Each CS nanoparticle was fully covered with PDMS, with an average inter-particle spacing of about 70 nm.

6.2.2. Optical and acoustic measurements

The thicknesses of each constitutive layers were measured using a field emission scanning electron microscope (FE-SEM, FEI Verios 460L, OR). The measured thickness of PDMS and CSNPs-PDMS composite layer on five different points were averaged. Light absorption properties of the CSNPs-PDMS composites were measured. The absorption properties for the visible wavelength range were measured using a spectrophotometer and an integrating sphere.
(Agilent, Cary 5000, CA) at normal incidence at the samples with different CSNPs-PDMS composite thicknesses. Total transmission, $T$, and reflection, $R$, of each sample were measured, and absorption was obtained as $1-T-R$.

The acoustic pressure output and bandwidth of prototyped transmitters were measured using the setup reported in our previous work [77]. We used the laser source of 532 nm wavelength Q-switched Nd:YAG pulse laser with a pulse duration of 6 ns and a repetition rate of 10 Hz (SL-III-10, Continuum, San Jose, CA). The calibrated hydrophone (HGL-0085, ONDA Crop., Sunnyvale, CA) was positioned 7.5 mm away from the transmitter radiation surface. The measurement location was in the near field region to acquire Gaussian pulse shape with less attenuated pressure amplitudes [72]. The detected shock wave signals were monitored and acquired using a digital oscilloscope (DSO7104B, Agilent, Santa Clara, CA), as shown in figure 6.2. In this work, low laser energy was used for the following reason. In the low laser energy region, the output acoustic pressure is proportional to the input laser energy, as reported by Bacc et. al [78] and Chang et. al [77]. Hence, the low laser energy values from 0.3 mJ/pulse to 1 mJ/pulse with various absorption layer thicknesses were investigated.

![Figure 6.2. Experimental setup for laser ultrasound generation and characterization.](image)
6.2.3. Optical simulation

Light absorption properties of the CSNPs-PDMS composites were simulated using Lumerical’s FDTD Solutions 8.9. This simulation enabled an analysis of light absorption properties with different volume fractions of CSNPs. In the simulation, the diameter of carbon nanoparticles was set uniformly to be 40 nm, as observed in the scanning electron micrographs. Since the inter-particle distance and particle diameter are roughly ten times smaller than the visible wavelengths, the distribution of the carbon particles was simplified to three-dimensional periodic square lattices in the simulation. The inter-particle distances were fixed at about 65 nm and 72 nm for carbon volume fractions of 12% and 9%, respectively. The simulation was conducted in three dimensions with periodic boundary conditions along x and y directions, and absorption boundary conditions in z direction. The structures were directly illuminated by a pulsed light source for spectral analysis in the visible wavelength range. The PDMS volume was assumed to be non-dispersive with a constant refractive index of 1.41, and the refractive index of amorphous carbon was from the reference work [31]. For both experimental and numerical measurements, transmission spectra under unpolarized illuminations were calculated by averaging transverse-electric (TE) and transverse-magnetic (TM) results.

6.3. Results and discussion

6.3.1. Characterization of CSNPs-PDMS composites

The fabricated CSNPs-PDMS composite films were then characterized for a photoacoustic transduction study. The scanning electron micrographs of the CSNPs-PDMS composite samples with 10 sec, 30 sec, and 120 sec CS deposition times are shown in figure 6.3(a-c). Based on the observation of sample cross section, a linear relationship between the thickness of the CSNPs-PDMS layer (t) and CS deposition time (τ) is shown in figure 6.3(d). The standard
deviation of the CSNPs-PDMS layer thickness for each sample is less than 0.3 µm, which suggests that the thickness of the light absorption layer (CSNPs-PDMS) can be effectively controlled under the deposition time control. The dashed line in figure 6.3(d) shows the thickness of the pure PDMS layer \( (h) \) on different samples that were prepared with a spin speed of 3000 rpm, which is about 16 µm (standard deviation is less than 0.65 µm). Previous work confirmed that the acoustic attenuation of the pure PDMS layer \( (< 0.1 \text{ dB/µm at 100 MHz}) \) was negligible, and a PDMS layer greater than 2 µm thickness was necessary to isolate light-induced-thermal waves from the water-composite interface [75]. Thus, we maintained the pure PDMS thickness (16 µm) as a constant variable, and evaluated the effect of different thicknesses of CSNPs-PDMS layers on the photoacoustic transduction performance.

The optical absorption measurement results were compared with the simulation results. The measured absorption spectra are shown in figure 6.4(a), where candle soot deposition time varies from 5 sec to 30 sec. It can be observed that higher absorption occurs with longer carbon deposition time due to longer absorption path length. For carbon deposition times longer than 120 sec, the composite becomes very absorptive and the absorption saturates at around 96% due to the Fresnel reflection from the flat glass/air interface. The absorption measurements for 20 sec, 60 sec and 120 sec CSNPs-PDMS samples were performed using the spectrophotometer as described above. The data plot is shown in figure 6.4(b), where 60 sec and 120 sec samples show similar absorption near 96% while 20 sec sample exhibits lower absorption. The reflection could be mitigated by using anti-reflection coatings [20]–[22].
Figure 6.3. (a)-(c) Scanning electron micrographs of the CSNPs-PDMS composites with CS deposition time of 10 sec, 30 sec and 120 sec, respectively. (d) Linear relationship between CSNPs-PDMS composite thickness, $t$, and the CS deposition time, $\tau$. The pure PDMS layer thickness remains constant.

Figure 6.4 (a) Optical absorption measurement (solid lines) and FDTD simulation results (dashed lines) for CSNPs-PDMS composites with CS deposition time of 5 sec, 10 sec and 30 sec, respectively. (b) Measured absorption for 20 sec, 60 sec and 120 sec CSNPs-PDMS composites.

6.3.2. Optical simulation results

Commonly-used hexagonal and square lattices were used in FDTD simulations with same solid fraction of carbon. The absorption spectra for both lattice types are shown in figure 6.5. The
absorption difference is also plotted. In terms of the periodic order type, it was found that the simulated absorptions from simple squares and hexagonal lattices with the same carbon volume fraction were not significantly different, both lattices follow the same trend and the maximum absorption difference is about 0.006. Therefore, both lattices can be used to model the carbon composites without significant difference. For simplicity, square lattice was chosen in our FDTD modeling. From this observation, we anticipated that the solid volume fraction of the carbon particles would determine the absorption of the composite, while the carbon nanoparticle arrangement would play a less important role. The refractive index of the amorphous carbon was taken from previous work [189]. For the sample with a 10 sec carbon deposition time, the simulated light intensity distribution within the composite is depicted in figure 6.6, where a decaying intensity pattern along the thickness direction is observed. Similar decaying intensity patterns are also found in other simulations with different carbon deposition time, but the decay lengths can vary. Here, we only show one simulated intensity map with 10 sec carbon deposition in figure 6.6 as an example.

![Absorption Comparison](image)

Figure 6.5. Simulated absorption results between square and hexagonal lattices with the same carbon solid volume fraction. The absorption difference is about 0.006.
Figure 6.6. Light intensity distribution within the CSNPs-PDMS composite with 10 sec CS deposition using FDTD simulation. Three-dimensional periodic square lattice is used for carbon particle configurations.

To estimate the carbon volume fraction, the lattice constant of the square carbon lattice in the FDTD simulation was varied to fit the measurement results. Using this method, the estimated carbon volume fractions for the composites with 5 sec and 10 sec candle soot depositions were about 12% and 9%, respectively. For samples with carbon deposition times longer than 10 sec, the above fitting method can no longer yield accurate results because the differences in light absorption for different high carbon volume fractions are so small that a small error in absorption measurement can lead to large error in volume fraction calculations. Therefore, the carbon volume fractions for samples with carbon deposition times longer than 10 sec were all assumed to be 9%, based on the assumption that the three-dimensional carbon nanoparticle arrangement would be more stable for longer deposition times, thus the carbon volume fraction would remain
unchanged. However, at a 5 sec deposition time, the carbon structures could easily collapse during spin-coating, resulting in a larger volume fraction of about 12%. Although 5 sec deposition results in the higher volume fraction (12%) than >10 sec deposition cases (9%), a thin, porous layer of carbon particles (< 1 µm) absorb lower amount of light (< 88%), whereas the thicker carbon layers (> 2 µm) enable enhanced light absorption (> 94%) despite the slightly lower volume fraction (9%). The FDTD simulations agree well with the experimental measurement for thicker samples, as shown for the sample with a 30 sec CS deposition time in figure 6.4(a). The wavelength-dependent absorption coefficients of the nanocomposites were calculated as well, using the Maxwell-Garnett effective medium approximation [190]. Due to the coherent light source in the simulation, a pattern as a result of interference can be observed along the thickness direction. Incoherence was considered when comparing absorption spectra between simulation and experiments using a Lorentzian spectral averaging method described in literature [191]. Maxwell-Garnett theory takes the following form, Eq. (1):

\[
\frac{\varepsilon_{\text{eff}} - \varepsilon_{\text{PDMS}}}{\varepsilon_{\text{eff}} + 2\varepsilon_{\text{PDMS}}} = f \frac{\varepsilon_{C} - \varepsilon_{\text{PDMS}}}{\varepsilon_{C} + 2\varepsilon_{\text{PDMS}}}
\]

(6-1)

where \(\varepsilon_{\text{eff}}\) is the effective dielectric constant for the CSNPs-PDMS composite, \(\varepsilon_{\text{PDMS}}\) is PDMS dielectric constant, \(\varepsilon_{C}\) is the dielectric constant for amorphous carbon, and \(f\) is the carbon volume fraction. By solving the effective dielectric constant of the composite, the extinction coefficient, \(k\), can be obtained by taking the imaginary part of the effective refractive index. The absorption coefficient, \(\alpha\), is calculated by the following Eq. (2),

\[
\alpha = \frac{4\pi}{\lambda} k
\]

(6-2)

where \(\lambda\) is the wavelength. Figure 6.7 illustrates that the absorption coefficient for CSNPs-PDMS composite is between 0.9 µm\(^{-1}\) and 2.3 µm\(^{-1}\) for 9% carbon volume fractions within the visible wavelength range.
Figure 6.7. Absorption coefficients calculated by Maxwell-Garnett theory as a function of carbon solid volume fraction and wavelength. Contours are plotted for absorption coefficients.

6.3.3. Acoustic pressure output measurement results and energy conversion efficiency calculation

The photoacoustic transduction efficiency was determined by measuring the peak-to-peak pressure amplitudes. Figure 6.8 shows acoustic output as a function of laser energy for CSNPs-PDMS composites with CS deposition times longer than 5 sec. The results of CSNPs-PDMS composites with 5 sec CS deposition times were separately analyzed, due to the unstable structure and different carbon volume fractions (12%) of the nanocomposites. The 5 sec CSNPs-PDMS ($t = 0.8 \, \mu m$) nanocomposite showed the lowest acoustic output due to its lack of absorption material. The 10 sec and 20 sec CSNPs-PDMS ($t = 2.2 \, \mu m$ and $4.3 \, \mu m$) exhibit higher acoustic output pressure than the 5 sec CSNPs-PDMS. On the other hand, as the thickness of CSNPs-PDMS increases, extra CSNPs-PDMS consumes most of the laser energy and high-frequency acoustic waves that have been attenuated in the extra CSNPs-PDMS. Thus, the acoustic pressure decreases as the CSNPs-PDMS layer increases in thickness, as shown in the
results from the 60 sec and 120 sec CSNPs-PDMS nanocomposite. Both positive and negative pressures showed highly linear relationships with laser energy for each sample in figure 6.8(a) and 6.8(b), which supports recent findings [192].

Figure 6.8. The photoacoustic transduction measurements. (a) Peak positive pressure and (b) peak negative pressure output as a function of laser energy for three different CSNPs-PDMS composite samples: 5 sec CSNPs-PDMS, 10 sec CSNPs-PDMS, 20 sec CSNPs-PDMS, 30 sec CSNPs-PDMS, 60 sec CSNPs-PDMS and 120 sec CSNPs-PDMS.

The -6dB fractional bandwidth and peak pressure decrease when the thickness of the CSNPs-PDMS layer increased. The waveforms and frequency spectra of photoacoustic transducers are shown in figure 6.9. The -6 dB frequency bandwidths of 10 sec, 30 sec and 120 sec CSNPs-PDMS samples are 22.8 MHz, 22.6 MHz and 19 MHz, respectively. At a laser energy of 1 mJ/pulse, the peak pressure of a 10 sec CSNPs-PDMS sample is as high as 3.78 MPa, and it is close to the output value of a focused optoacoustic transducer [78]. This can be explained by the fact that the thermal elastic properties of thin layers outperform those of thicker layers when the light absorption of both layers is equal. The acoustic attenuation is negligible in pure PDMS film due to a lack of absorption material [10, 29]. In other words, when the thickness of the absorption layer (CSNPs-PDMS layer) is greater than the optical absorption thickness, the output acoustic pressure increases as the thickness of the absorption layer decreases. As the composite thickness exceeds the optical absorption thickness, the majority of the light energy can
be absorbed by the CS, becoming thermal energy. The thermal energy is finally transferred into PDMS to generate thermo-elastic expansion.

![Figure 6.9. The acoustic pressure and frequency spectra for different samples using a low laser input (1 mJ/pulse). (a) 10 sec CSNP-PDMS, (b) 30 sec CSNPs-PDMS, and (c) 120 sec CSNPs-PDMS.](image)

However, due to the large conductivity of CS and the branch-like structure, thermal energy can travel along the CS thickness simultaneously, resulting in a deeper heating domain in thicker CSNPs-PDMS layers. Therefore, thermal energy is distributed more evenly in thicker layers than
that in thinner layers, and therefore, lower acoustic pressure, given the identical total energy absorption. In addition, the observed acoustic wave has two parts. One is the forward traveling wave when PDMS is heated, and the other is the wave reflected by the glass substrate. The time delay between these two waves depends on the thickness of absorption layer, and is much shorter than the acoustic pulse duration over acoustic traveling depth[194]. These two waves interfere constructively, and shorter time delay between them results in higher acoustic output. In addition to acoustic pressure and bandwidth, photoacoustic efficiency, which is defined as Eq. (3)[77]

\[ \eta = \frac{E_a}{E_{optical}} \]  

is also important in a photoacoustic transduction evaluation. In the above equation, \( E_{optical} \) is the laser energy normalized with the actual absorbed laser energy in the layer, and \( E_a \) is the output of acoustic energy. \( E_a \) can be estimated by the following Eq. (4), assuming that the pressure was measured in water:

\[ E_a = \frac{1}{\rho c} A \int_0^\infty p^2(t) dt \]  

Where \( \rho \) is water density, \( c \) is sound velocity in water (~1500 m/s), \( p \) is the acoustic pressure measured by hydrophone, and \( A \) is the acoustic aperture area which can be considered as the same size of the laser beam in the near field. The normalized laser energy, \( E_{optical} \), was measured by a pyroelectric energy sensor (J-50MB-YAG, Coherent, Portland, OR) and multiplied with the absorption of CSNPs-PDMS composite. For the Gaussian pulse laser with a pulse energy of 1 mJ/pulse, the calculated photoacoustic transduction efficiency for CSNPs-PDMS composites with different CS depositions can be found in figure 6.10. In region I, the photoacoustic efficiency of a CSNPs-PDMS sample with a 5 sec CS deposition time is about \( 2.1 \times 10^{-4} \). This low efficiency is likely caused by the insufficient thickness of the absorption layer (~ 0.8 \( \mu \)m, too thin to absorb most laser energy). The measured absorption and reflection are about 80.8% and 3.5%,
respectively, indicating that about 15.7% of the laser energy passes through the CSNPs-PDMS layer at a wavelength of 532 nm. In region II, the photoacoustic efficiency reaches its peak at a CSNPs-PDMS composite thickness of 2.15 µm, suggesting an optimal photoacoustic transduction thickness may exist in a photoacoustic transduction structure. The photoacoustic efficiency exhibits a clear exponential decay profile when \( t \) increases. The photoacoustic efficiency is \( 9.60 \times 10^{-4} \) and \( 3.89 \times 10^{-4} \) for CSNPs-PDMS thicknesses of 12.7 µm and 25.9 µm, respectively. We speculate that the occurrence of the highest photoacoustic efficiency at the thickness of 2.15 µm is due to the full absorption of the laser energy while the lowest acoustic attenuation compared to that in thicker samples. The measured photoacoustic transduction efficiency of \( 9.02 \times 10^{-3} \) is 51% more than that of our previous work \([77]\), about six times higher than 2.6 µm thickness of carbon nanotube composite \([75,78]\), and about 50 times higher than gold nanoparticles composite which is about 105 µm in thickness \([195]\). The comparisons are shown in Table 6.1.

Figure 6.10. The relationship between the photoacoustic transduction efficiency and the thickness of CSNPs-PDMS composites; the inset shows the schematic of photoacoustic effect.
Table 6.1. Photoacoustic efficiency in different material

<table>
<thead>
<tr>
<th>Material</th>
<th>Thickness of composite total thickness (absorption material thickness/PDMS thickness)</th>
<th>Laser power (mJ/cm²)</th>
<th>Photoacoustic efficiency</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>CNT/PDMS</td>
<td>2.6 µm (1.2 µm/1.4 µm)</td>
<td>42.4</td>
<td>1.4 ×10⁻³</td>
<td>[75,78]</td>
</tr>
<tr>
<td>Gold-nanoparticle/PDMS</td>
<td>105 µm</td>
<td>8.75</td>
<td>1.8×10⁻⁴</td>
<td>[195]</td>
</tr>
<tr>
<td>Cr/PDMS</td>
<td>25 (100 nm/25 µm)</td>
<td>3.57</td>
<td>8×10⁻⁵</td>
<td>[77]</td>
</tr>
<tr>
<td>Carbon black/PDMS</td>
<td>30 µm</td>
<td>3.57</td>
<td>3.4×10⁻⁴</td>
<td>[77]</td>
</tr>
<tr>
<td>Carbon nanofiber/PDMS</td>
<td>57.8 µm (24.4 µm/33.4 µm)</td>
<td>3.57</td>
<td>1.66×10⁻³</td>
<td>[76,77]</td>
</tr>
<tr>
<td>Candle soot/PDMS</td>
<td>25 µm (6 µm/19 µm)</td>
<td>3.57</td>
<td>4.41×10⁻³</td>
<td>[77]</td>
</tr>
<tr>
<td>Candle soot nano-composite/PDMS</td>
<td>18 µm (2 µm/16 µm)</td>
<td>1</td>
<td>9.02×10⁻³</td>
<td></td>
</tr>
</tbody>
</table>

The superior performance of the CSNPs-PDMS composite photoacoustic transducer is the result of the nano-scale spatial configurations, and the reason can be explained in two ways. The first explanation is that heat diffuses from CS particles into adjacent PDMS by the temporal temperature gradient. The CSNPs-PDMS layer has a low interfacial thermal resistance thus a high rate at which heat releases into PDMS [77,196]. The other explanation is based on the collectively-diffusive thermal effect, which explains the thermal properties of nanoparticles. Depending on the spacing between neighboring nanoparticles, the thermal transport may be significantly different. When the spacing of a neighboring heat source is small compared to the dominant mean free paths, the phonons originating from neighboring heat sources can interact
with each other, resulting in a more efficient thermal diffusion [197]. In other words, nano scale heat sources cool faster when placed closer together, which is an effect that can explain the efficiency of the CSNPs-PDMS absorption layer. The three-dimensional structures of ball-shaped CS particles are much more conductive for thermal energy releasing than two-dimensional and one-dimensional structures, such as carbon nanofibers or carbon nanotubes [76,85]. Furthermore, PDMS, as a highly thermal elastic material, makes direct contact with the carbon nanoparticles to receive most of the heat energy generated from the three-dimensional nanostructures, resulting in low thermal transfer loss [198]. Herein an efficient photoacoustic conversion can be obtained. We also speculate that the small volume fraction of carbon nano-particles (9%) leaves a larger volume for PDMS (91%), which would allow for more thermal expansion. As a result of the efficient CSNPs-PDMS thermal transfer and thermal expansion, high amplitude acoustic waves could then be generated.

6.4. Conclusion

This study develops new photoacoustic transduction material and explores the relationship between the structural property and device performance of photoacoustic transducers by utilizing CSNPs-PDMS composites. The optical absorption of CSNPs-PDMS composites are up to 96% in the experiment. The optical interactions with the carbon nanoparticles in the composite are examined with FDTD simulations, which indicates that the solid volume fraction of carbon particles is a critical factor. At the same time, photoacoustic experiments show a promising relationship between linear output acoustic pressure and laser input, as long as the laser pulse energy is lower than 1 mJ/pulse. For samples with a CS deposition time longer than 10 sec, photoacoustic efficiency decays exponentially as the thickness of CS increases. At the laser pulse energy of 1 mJ/pulse, the measured maximum acoustic output pressure and efficiency are 3.78
MPa and $9.69 \times 10^{-3}$, respectively. These findings suggest that the design optimization of CSNPs-PDMS composite photoacoustic transmitters can realize highly efficient laser-ultrasound patches for industrial and biomedical applications.
CHAPTER 7

CONCLUSIONS AND FUTURE WORK

In this thesis, two types of electromechanical transduction materials/structures were studied, including the nano-patterned electrode and alternating current electrical field poling for enhancing the properties of PMN-PT single crystal and candle soot nanoparticle composite transduction for photoacoustic evaluation. With a brief review of ferroelectric relaxor-PT single crystals, the fabrication and development of nano-patterned electrode was presented. The piezoelectric properties measurements and domain observation results suggest that nanocomposite electrodes are promising for domain engineering of PMN-PT single crystals. The other domain engineering method we studied is ACP. Compared with the traditional DCP method, PMN-PT single crystal with ACP method exhibits 20% higher dielectric coefficient, piezoelectric coefficient and smaller domains. For the photoacoustic transduction material, we propose an efficient broadband light absorption material, candle soot nanoparticles. Combining with PDMS, the energy conversion efficient composite was fabricated. In the following sections, the major accomplishments in domain engineering and photoacoustic transductions are summarized, followed by the future work suggestions.

7.1. Patterned nano-domains using nanocomposite electrodes

The background on patterned nano-domain and nanocomposite electrode development are presented. By creating artificial MnOx nanogratings, the domain density can be enhanced because of changing the electric field distribution. In the characterization, PMN-PT single crystals with Ti/Au-MnOx nanocomposite electrodes showed high piezoelectric constant of 2250 pm/V and dielectric constant of 5400 at 1 kHz, respectively. Compared with the conventional planar electrodes, the sample with nanocomposite electrodes showed 36.7% and 38.3% of
piezoelectric and dielectric constant enhancement, respectively. These properties enhancement showed a good accordance with the domain observation using piezoresponse force microscopy (PFM). Time-of-flight secondary ion mass spectrometry (ToF-SIMS) results showed that Mn was diffused about 300 nm in depth in PMN-PT single crystal after the heat treatment forming the MnOx layer. It is believed that the localized high electric fields induced by fringe effects caused by nanocomposite electrode can enhance nucleation of new domains, and that diffusion from the patterned Mn layer may also leads to an enhancement in domain wall mobility. From this research, the new domain engineering technique was presented for tailoring the dielectric and piezoelectric properties of PMN-PT single crystals.

7.2. Property enhancement of PMN-PT using alternating current poling

In this study, the alternating current poling (ACP) method was studied for PMN-0.3PT single crystal along [001]c. Compared with the conventional direct current poling (DCP) (state-of-the-art), the dielectric constant and piezoelectric coefficient of single crystal samples were both enhanced more than 20%. The unique phase coexistence of monoclinic type A ($M_A$) and rhombohedral ($R$) phases was observed in ACP single crystal samples from X-ray diffraction (XRD) results. Under the same poling electric field, DCP sample exhibited in $R$ phase while $M_A + R$ phase appeared in ACP samples. The corresponding heterogenous domain structure observed by the piezoresponse force microscopy (PFM) depicted how the domain wall was uniquely engineered by ACP method. This ultra-fine domain in PMN-PT single crystals was, for the first time, observed and reported, and the findings may lead to advanced domain engineering of relaxor-PT single crystals for novel piezoelectric devices.

7.3. Candle soot nanoparticles-PDMS composites for photoacoustic transducer

In this work, candle soot nanoparticles-PDMS (CSNPs-PDMS) composite was fabricated as
the functional layer for a photoacoustic transducer with high-energy conversion efficiency. The effect of candle soot light absorption composite thickness on the photoacoustic transduction was investigated. We report a novel approach for fabricating CSNPs-PDMS composite with different thicknesses, which presents the highest photoacoustic energy conversion efficiency compared with the reported existing photoacoustic transduction materials. The experimental study and finite difference time domain (FDTD) analysis were performed to obtain the optical properties of the prepared nano-composites material, and the results agree well with each other for interpreting the light absorption mechanism. Owing to the arborized nanostructure, CSNPs-PDMS composite material exhibits excellent light absorption and heat conduction capabilities, resulting in unprecedented optoacoustic energy conversion efficiency. With a low laser energy input, this CSNPs-PDMS nanocomposite can generate output pressure about 3.78 MPa, and the energy conversion efficiency is two orders higher than other reports.

7.4. Future work

7.4.1. Prospective study of new domain engineering methods

Going forward, the 2D nanostructure composite electrodes or smaller nanostructure composite electrodes may be the potential method for tailoring the dielectric and piezoelectric properties of PMN-PT single crystals. Based on the interference lithography technique, the 2D nanostructure can be fabricated by multi-exposure; and the smaller nanostructure can be obtained by changing the ambient index[199]. (The light wavelength is scaled by the refractive index of the immersion fluid, reducing the minimum interference pattern period and increasing the spatial resolution.)

The ACP is still a new domain engineering method to enhance the crystal’s properties. Thus, how to obtain higher piezoelectric and dielectric constant by changing poling conditions
will be another interesting research topic. There are several parameters for the poling conditions optimization, such as, alternating current poling frequencies (single frequency verses multi frequency), poling electrical field, poling cycles, poling temperature, poling directions, et al. Other than changing the ACP parameters, the application of ACP sample are also an important topic. Take medical imaging for instance, the electromechanical coupling of ACP sample needs to be proven in high frequency transducer designs.

7.4.2. Prospective study of photoacoustic transducer

Candle soot coating is a cost effective method to deposit light absorption material on the subjects. This coating technique is suitable to deposit candle soot on any size and geometry surface, such as, micro-scale concave lens, optical fiber. Candle soot based optical fiber photoacoustic transducer can generate up to 10 MPa output pressure with central frequency at 10 MHz under a low laser energy (< 1mJ/cm²); and the -6 dB fractional bandwidth is up to 180% in our initial experiment. We believe that the higher resolution imaging can be obtained by combining the optical fiber photoacoustic transducer and traditional piezoelectric receiver.
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