The Pennsylvania State University
The Graduate School
Intercollege Graduate Program in Materials

ELECTRO-OPTICAL PROPERTIES IN RELAXOR FERROELECTRIC MATERIALS AND THE DEVICE APPLICATIONS

A Thesis in
Materials
by
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Doctor of Philosophy

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Abstract

The electro-optic (E-O) effects of the relaxor ferroelectric materials, Lead Magnesium Niobate-Lead Titanate $Pb(Mg_{1/3}Nb_{2/3})O_3 - PbTiO_3$ (PMN – PT) single crystals and poly(vinylidene fluoride-trifluoroethylene) [P(VDF – TrFE)] based polymers, are investigated here. The tetragonal 0.62PMN-0.38PT single crystals poled along the $<001>$ direction (the spontaneous polarization direction) have a stable single domain and show high transparency from the visible to Near-IR range. Using the Mach-Zender interferometry method, large linear E-O coefficients $r_{33} = 70 \text{ pm/V}$, $r_{31} = 25 \text{ pm/V}$, and $r_{15} = 558 \text{ pm/V}$ were characterized. P(VDF-TrFE) based terpolymers shows a large Kerr effect where a refractive index change of -2.6 % can be induced under an electric field of 80 $V/\mu m$. When combined with the electrostrictive strain, the terpolymer film exhibits a total -5.6 % optical pathlength change under a field of 80 $V/\mu m$. Calculations based on density functional theory suggest that such a large E-O effect was caused mainly by the reorientation of the C-F dipoles in the crystalline regions under external field.

With the large strain and E-O effect, the tunable grating and Fabry-Perot interferometers (FPIs) were fabricated. By changing the structure of comb-shape electrode for the bottom electrode and the polymer thickness, it was calculated that we could control the electric field distribution leading the different level of strain for grating. This new tunable grating has the advantage of simple fabrication and easy integration. In our first experimental demonstration, 24 % of the first order diffraction efficiency was observed with 100 $V/\mu m$. For the strain tunable FPI, which for the terpolymer films under mechanically clamped condition is 1.3 % under 100 $V/\mu m$ field, we show that a tunable range of 22.5 nm can be obtained at wavelengths near 1.5 $\mu m$. On the other hand, the FPI using a terpolymer film directly as the cavity of the etalon shows a smaller tunability (0.78 % under 100 $V/\mu m$) due to the opposite sign of the strain and refractive index change. In addition, since the conventional photolithograph technique damages the P(VDF-TrFE) based polymers, stencil mask method was tested to fabricate a strain tunable frequency selective surface.
In addition to the materials themselves, high performance tunable devices can be accomplished from the artificial periodic structures, so called Photonic Crystals (PCs). Near bandedge of PCs, optical properties can be very sensitive to the changes of the unit cell dimension and the refractive index of the constituents of the PCs. When calculating the optical properties in PCs, most calculations are based on the infinite size of PCs. However, real devices should have finite size and their properties are different from those of the infinite size of PCs. To predict the optical properties in real PCs device, we compared the light propagation properties between infinitely extended and finite size dielectric multilayer layer in terms of photonic crystals (PCs) along the wave propagation direction. It is shown that the multiple reflections at the two end interfaces of a finite size PC give an influence on both the transmittance and phase velocity (and also the group velocity as well as the effective refractive indexes \( n_{eff} \)). The results clearly demonstrate the importance of the two end interfaces of a finite size PC on the effective properties of photonic crystals, which could be quite different from those deduced from an infinitely extended photonic crystal. For device applications, finite size effect was applied to design the photonic crystals lenses.
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Chapter 1

Introduction

1.1 Electro-optic Effect

The speed of light propagation in a material is mainly determined by its refractive index \( n \), which is the most fundamental property of optics and is defined as the ratio of the velocity of light in vacuum \( c \) to that in the material \( v \)

\[
n = \frac{c}{v}
\]  

(1.1)

For non-magnetic materials, in which the relative magnetic permeability (\( \mu/\mu_0 \)) is taken as 1, Maxwell’s equations show that the propagation velocity of light is given by

\[
v = \frac{c}{\sqrt{K}}
\]  

(1.2)

and

\[
n = \sqrt{K}
\]  

(1.3)

where \( K \) is the dielectric constant or relative electric permittivity which associates the dielectric displacement \( D \) and electric field \( E \) at optical frequencies in the medium,

\[
D = \epsilon_0 KE
\]  

(1.4)

here, \( \epsilon_0 \) is the permittivity in vacuum \( (8.854 \times 10^{-12} \text{ F/m}) \), and \( K \) is the dielectric constant at optical frequencies, which is usually smaller than the dielectric constant measured at low frequencies.

Certain materials change their optical properties when subjected to an electric field. This is caused by forces that distort the position, orientation, or shape of the molecular constituting the material. The electro-optic (E-O) effect is the change in the
refractive index resulting from the application of a dc or low-frequency electric field. If materials have non-linear polarization properties, the linear Eq.1.4 should be added the non-linear terms as follows;

\[ D = \varepsilon_0 KE + \alpha E^2 + \beta E^3 + \ldots \]  

(1.5)

where \(\alpha\) and \(\beta\) are material’s non-linear coefficients. Therefore, the material’s permittivity, now defined by the slope of the curve, is

\[ \frac{dD}{dE} = \varepsilon_0 K + 2\alpha E + 3\beta E^2 + \ldots \]  

(1.6)

where the first term is a constant, and the other terms show the change of the permittivity due to the applied electric field. Since the material’s refractive index is directly related to its dielectric constant according to Eq.1.4, it will also change under the electric field due to the non-linear effect. This phenomenon is known as the E-O effect, which was first discovered by Kerr in 1875 [1].

For convenience, the change in the refractive index can be described as the modulation of the optical impermeability by the external electric field

\[ \Delta B_{ij} = \Delta \left( \frac{1}{n_{ij}^2} \right) = r_{ijk} E_k + R_{ijkl} E_k E_l \]  

(1.7)

where the first term is a linear E-O effect known as Pockels effect with the coefficient \(r_{ijk}\), and the second term is a quadratic E-O effect known as Kerr effect with the coefficient \(R_{ijkl}\) [2]. The coefficient \(r_{ijk}\) describing the linear E-O effect is a third-rank tensor and is absent in materials with a symmetry center. Typical values of \(r_{ijk}\) lie in the range \(10^{-12}\) to \(10^{-10} \text{ m/V}\) (1 to 100 pm/V). The most common crystals used as Pockels cells include \(\text{NH}_4\text{H}_2\text{PO}_4\), \(\text{KH}_2\text{PO}_4\), \(\text{LiNbO}_3\), \(\text{LiTaO}_3\), and \(\text{CdTe}\) [3]. However, for the quadratic E-O effect, since it is a fourth-rank tensor property, it can be found in all the materials although in most cases it is smaller than the linear effect. Typical values of \(R_{ijkl}\) are \(10^{-18}\) to \(10^{-14} \text{ m}^2/\text{V}^2\) in crystals and \(10^{-22}\) to \(10^{-19} \text{ m}^2/\text{V}^2\) in liquids [3].
In discussing the E-O effect, mechanical boundary condition is important for large strain materials. If the crystal is free, a static electric field will cause a strain by the converse piezoelectric effect, and this in turn will give a change in refractive index by the photoelastic effect [1, 2]. The E-O effect obtained under the constant strain is called the primary effect, and the effect due to piezoelectricity and photoelasticity is then called the secondary effect [2]. The observed effect in a free crystal is the sum of the primary and secondary effects. In practice, the primary effect at constant strain may be found by applying an AC of high frequency. The order of magnitude of the secondary effect may be found as follows. Electric field \(E\) produces a piezoelectric strain \(S\), 
\[
S = d \cdot E,
\]
where \(d\) is the piezoelectric constant. Then, this strain changes the refractive index through the photoelastic effect given by
\[
\Delta B = p \cdot S = (p \cdot d) E.
\]
(1.8)

Where \(p\) is the elasto-optical coefficients. As the \(p\) is of order magnitude \(10^{-1}\) for most materials [1, 2], it can be expected that the large piezoelectric materials will also have the large secondary effect.

From the fundamental materials viewpoint, the E-O effect is due to the change in optical susceptibility caused by molecular, ionic, and electronic polarization as a result of an applied electric field. The E-O effect due to electronic polarizability is typically small because the polarization changes that can be achieved are relatively small in comparison with the local fields already existing in the dielectric materials. The commonly used E-O materials are briefly summarized in Table 1.1.

Usually the change in the refractive index is very small. Nevertheless, its effect on an optical wave propagating a distance must greater than a wavelength of light in the medium can be significant. If the refractive index increases by \(10^{-5}\), for example, an optical wave propagating a distance of \(10^5\) wavelengths will experience an additional phase shift \(2\pi\). By applying an electric field to change the refractive index, the spatial and temporal distribution of the light waves traveling in an E-O medium can also be changed. Therefore, E-O effect can be used for optical communication and optical signal-processing applications, as indicated by the following examples:
<table>
<thead>
<tr>
<th>Materials</th>
<th>Symmetry</th>
<th>Coefficients</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiNbO₃</td>
<td>Rhombohedral</td>
<td>( n_o = 2.286 ), ( n_e = 2.200 )</td>
<td>Widely used for both thin film and bulk E-O modulation applications.</td>
</tr>
<tr>
<td><strong>Lithium Niobate</strong></td>
<td>3m</td>
<td>( r_{13} = 10.6 \text{pm}/\text{V} )</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>( r_{33} = 31.8 \text{pm}/\text{V} )</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>( r_{22} = 6.7 \text{pm}/\text{V} )</td>
<td></td>
</tr>
<tr>
<td>BaTiO₃</td>
<td>Tetragonal</td>
<td>( n_o = 2.412 ), ( n_e = 2.360 )</td>
<td>Widely used in E-O and photorefractive applications.</td>
</tr>
<tr>
<td><strong>Barium Titanate</strong></td>
<td>4mm</td>
<td>( r_{13} = 8 \text{pm}/\text{V} )</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>( r_{33} = 105 \text{pm}/\text{V} )</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>( r_{15} = 1300 \text{pm}/\text{V} )</td>
<td></td>
</tr>
<tr>
<td>Sr₀.₅Ba₀.₅Nb₂O₆</td>
<td>Tetragonal</td>
<td>( n_o = 2.312 ), ( n_e = 2.273 )</td>
<td>Solid solution system</td>
</tr>
<tr>
<td><strong>Strontium Barium Niobate</strong></td>
<td>4mm</td>
<td>( r_c = 205 \text{pm}/\text{V} )</td>
<td>Strong dependent on the composition &amp; temperature.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>[6]</td>
<td></td>
</tr>
<tr>
<td>KDP</td>
<td>Tetragonal</td>
<td>( n_o = 1.513 ), ( n_e = 1.471 )</td>
<td>Easy growing</td>
</tr>
<tr>
<td><strong>Potassium Dihydrogen Phosphate</strong></td>
<td>42m</td>
<td>( r_{41} = 26 \text{pm}/\text{V} )</td>
<td>Water soluble crystals.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( r_{63} = 32 \text{pm}/\text{V} )</td>
<td>Deliquescence problem.</td>
</tr>
<tr>
<td>PLZT(9/65/35)</td>
<td>Ceramics</td>
<td>( R = 9.1 \times 10^{-16} \text{m}^2/\text{V}^2 )</td>
<td>No single crystal available.</td>
</tr>
<tr>
<td><strong>Lead Lanthanum Zirconate Titanate</strong></td>
<td>ceramics</td>
<td>[7]</td>
<td>Kerr effect</td>
</tr>
</tbody>
</table>

Table 1.1. Properties of some widely used E-O materials.

- A tunable lens whose focal length can be changed by refractive index change.
- A prism whose beam bending ability is controllable can be used as an optical scanning device.
- Optical phase modulator in which light transmitted through a transparent plate of controllable refractive index undergoes a controllable phase shift.
- Wave retarder which can be used to change the polarization properties of light.
- Optical intensity modulator or optical switch.
1.2 Optics of Anistotropic Media

A dielectric medium is said to anisotropic if its macroscopic optical properties depend on direction. The macroscopic properties of matter are of course governed by the microscopic properties: the shape and orientation of the individual molecules and the organization of their centers in space [3]. In a linear anisotropic dielectric medium (a crystal, for example), each component of the electric flux density $D$ is a linear combination of the three components of the electric field

$$D_i = \sum_j \epsilon_0 K_{ij} E_j$$  \hspace{1cm} (1.9)

where $i,j = 1, 2, 3$ indicate the $x, y, z$ components, respectively. The dielectric properties of the medium are therefore characterized by a $3 \times 3$ array of nine coefficients $K_{ij}$ forming a tensor of second rank known as the dielectric constant tensor. Eq.1.9 is usually written in the symbolic form $D = \epsilon_0 K E$. The dielectric constant tensor is symmetrical, $K_{ij} = K_{ji}$, and is therefore characterized by only six independent numbers. For crystals of certain symmetries, some of these six coefficients vanish and some are related, so that even fewer coefficients are necessary.

Elements of the dielectric constant tensor depend on the choice of the coordinate system relative to the crystal structure. A coordinate system can always be found for which the off-diagonal of $K_{ij}$ vanish, so that

$$D_1 = \epsilon_0 K_1 E_1, D_2 = \epsilon_0 K_2 E_2, D_3 = \epsilon_0 K_3 E_3.$$  \hspace{1cm} (1.10)

where $K_1 = K_{11}$, $K_2 = K_{22}$, and $K_3 = K_{33}$. These are directions for which $E$ and $D$ are parallel. This coordinate system defines the principal axis and principal planes of the crystal. The dielectric constants $K_1$, $K_2$, and $K_3$ correspond to refractive indices

$$n_1 = \left(K_1\right)^{1/2}, n_2 = \left(K_2\right)^{1/2}, n_3 = \left(K_3\right)^{1/2},$$  \hspace{1cm} (1.11)
known as the principal refractive indices. In crystal with certain symmetries two of the refractive indices are equal \( n_1 = n_2 \) and the crystals are called uniaxial crystals. The indices are usually denoted \( n_1 = n_2 = n_o \) and \( n_3 = n_e \). \( n_o \) and \( n_e \) are called the ordinary and extraordinary indices, respectively. The \( z \) axis of a uniaxial crystal is called the optic axis. In other crystals the three indices are equal and the medium is optically isotropic. Media for which the three principal indices are different are called biaxial [2].

The rules that govern the propagation of light in crystals under general conditions are rather complicated. However, they becomes relatively simple if the light is a plane wave traveling along one of the principal axis of the crystal. A plane wave traveling \( z \) direction and linearly polarized in the \( x \) direction travels with phase velocity \( c/n_1 \) without changing its polarization. The reason is that the electric field then has only one component \( E_1 \) in the \( x \) direction, so that \( D \) is also in the \( x \) direction, \( D_1 = \varepsilon_0 K_1 E_1 \), and the wave equation derived from Maxwell’s equations will have a velocity \( \frac{1}{\sqrt{\mu_0 \varepsilon_0 K_1}} \) = \( c/n_1 \). A wave with linear polarization along the \( y \) direction similarly travels with phase velocity \( c/n_2 \) and experience a refractive index \( n_2 \). Thus the normal modes for propagation in the \( z \) direction are the linearly polarized waves in the \( x \) and \( y \) directions.

### 1.3 Characterization Method

#### 1.3.1 Interferometer Method for E-O Properties

To measure the individual refractive index change (\( \Delta n_o \) and \( \Delta n_e \)), the Mach-Zehnder type interferometer can be employed. The Mach-Zehnder interferometer is amplitude-splitting device. As shown in Fig.1.1, it consists of two beam-splitters and two totally reflecting mirrors. A linear polarized laser source generates a high coherent laser beam. After a beam splitter, this laser beam is separated into two beams. One can be used as the signal beam, which is transmitted through the crystal; the other is the reference beam. After two mirrors’ reflection, both beams intersect at another beam splitter and the final output is the interference of two beams. The interference intensity depends on the phase difference \( \delta \) from the optical path-length difference between the signal beam and the reference beam. Assuming the intensity of the signal and reference
beam, $I_s$ and $I_r$, respectively, the intensity after two beams' interference can be derived as [8, 9],

$$I = I_s + I_r + 2 \sqrt{I_s I_r} \cos \delta \quad (1.12)$$

At various points in space, the resulting intensity can be greater, less than, or equal to $I_s + I_r$, depending on $\delta$. So maximum and minimum in the intensity are obtained when $\cos \delta = \pm 1$, so that

$$I_{\text{max}} = I_s + I_r + 2 \sqrt{I_s I_r} I_{\text{min}} = I_s + I_r - 2 \sqrt{I_s I_r} \quad (1.13)$$

Using Eq.1.13, Eq.1.12 can be rewritten

$$I = \frac{I_{\text{max}} + I_{\text{min}}}{2} + \frac{I_{\text{max}} - I_{\text{min}}}{2} \cos \delta \quad (1.14)$$

Since the only difference between the two beams is an inserted crystal in the signal beam, by considering the phase retardation in the crystal, phase difference ($\delta$) can be expressed as

$$\delta = \frac{2\pi}{\lambda} (n - 1) l \quad (1.15)$$

where $\lambda$ is the wavelength of the light beam, $n$ is the refractive index of the crystal and $l$ the thickness of the crystal along the laser propagation direction.
If there is a small variation in the refractive index of the crystal with electric filed, it will cause a change in the phase retardation, \( \Delta \delta \), around the initial phase difference, \( \delta_0 \), resulting in an output intensity change. However, because the intensity modulated by phase difference follows a cosine function, intensity change is not linearly related to the crystal’s refractive index or phase change. Setting the \( \delta_0 = (2m - \frac{1}{2})\pi \), where \( m \) is an integer, \( \cos(\delta) = \cos(\delta_0 + \Delta \delta) = \sin(\Delta \delta) \approx \Delta \delta \), then the approximation can be obtained

\[
I = \frac{I_{\text{max}} + I_{\text{min}}}{2} + \frac{I_{\text{max}} - I_{\text{min}}}{2} \Delta \delta \propto \frac{I_{\text{max}} - I_{\text{min}}}{2} \Delta \delta 
\]  

(1.16)

Thus, at this particular initial phase position, the output intensity is linearly dependent on the small modulation of phase difference, which is also linearly related to the crystal’s refractive index change.

\[
\Delta \delta = \frac{2\pi}{\lambda} \Delta n l 
\]  

(1.17)

By measuring the output intensity change, which has the same frequency as the applied electric field, the refractive index change can be easily detected by a lock-in amplifier. This is the basic principle for this type of interferometer measurement [10]. In addition, from Eq. 1.17, the phase change is a ratio of the crystal’s optical path length change to the optical wavelength used (for the Helium-Neon laser operated in this work, the wavelength is only 0.633 \( \text{nm} \)), therefore, such a method performs effectively a magnification to create a relative large phase change from a small refractive index change. This is the reason for a high sensitivity achieved in the interferometer method.

However, to achieve the linear relationship between the output intensity change and crystal’s optical path length change, the interferometer system has to be operated at \( \delta_0 = (2m - \frac{1}{2})\pi \). Finding this point is relatively easy, because it is the center position of the cosine function in oscilloscope. By knowing the output interference intensity maximum and minimum, this point can be located. To reach this position experimentally, three variables, refractive index \( n \), thickness \( l \) and wavelength \( \lambda \) can be used to manipulate the phase difference between signal beam and reference beam.

An interferometer based on the above principle was realized by the combination of a piezoelectric driven mirror, which replaced the mirror in the reference beam.
to modulate the length of the reference beam [11]. The mirror’s driving voltage was controlled large enough to scan several wavelength distance and to measure the maximum and minimum of the output interference intensity in oscilloscope. Since the phase drift caused by noise is at low frequency range (below 1 Hz), the frequency response of piezoelectric driven mirror was carefully designed to separate the noise and the response from the driving voltage. Then, scanning the whole intensity cosine modulation function with piezoelectric driven mirror, if we apply the small electric field with high frequency, which can be separated from that of driving voltage for piezoelectric driven mirror, small intensity modulation from the refractive index change due to an E-O effect can be detected using a lock-in amplifier.

1.3.2 Senarmont Compensator Method

Although interferometer method can measure the individual refractive index change, it is required to know the ordinary and extraordinary refractive indices. However, since the induced refractive changes due to the E-O effects are usually quite small ($\Delta n < 10^{-3}$), it is not common to measure the absolute refractive index values first, and then calculate the difference to obtain the refractive index change. Instead of measuring the refractive index directly, other methods should be employed to measure the relative change in the refractive index.

Fig. 1.2. Optical set-up for the Senarmont compensator method.
In general, both ordinary and extraordinary refractive indices will change when the crystal is subjected to external fields. Senarmont compensator method, which is the birefringence-based method, can measure a small difference between the ordinary and extraordinary refractive indices rather than measuring the change of each individual refractive index. The birefringence in a crystal can be detected by placing the sample between a pair of crossed polarizers to convert the birefringence induced light polarization change to the output light intensity change. Therefore, any birefringence change caused by modulating the refractive index can be measured by recording the output intensity. As shown in Fig.1.2, the testing crystal is placed between a pair of crossed polarizers. In addition, a quarter wave plate is inserted between the sample and the analyzer. Here, $\alpha$ is the angle between the optical axis of the first polarizer and the principle refractive index axis of the crystal, $\beta$ is the angle between the optical axis of the quarter wave plate and the optical axis of the first polarizer, and $\gamma$ is the angle between the optical axes of the analyzer and the first polarizer, respectively. The incident light after passing through the first polarizer can be represented as $Ae^{j\omega t}$ along the y-axis. It can be decomposed into two orthogonal components along the crystal’s coordinate system ($x'$ and $y'$ are two principle refractive index axes). If we set the $\alpha$ as $45^\circ$, the phase delay ($\theta$) caused by birefringence after passing through the crystal thickness $l$ is

$$\theta = \frac{2\pi}{\lambda} \left(n_{y'} - n_{x'}\right) l$$  \hspace{1cm} (1.18)

If we set the optical axis of the quarter wave plate parallel to the optical axis of the first polarizer, then the angle $\beta$ is $0^\circ$. After passing through the quarter wave plate, there is a $\pi/2$ phase delay in the $x''$-axis. The final output intensity ($I$) after analyzer becomes [12]

$$I = \frac{1}{2} A^2 \left[1 - \cos (\theta - 2\gamma)\right].$$ \hspace{1cm} (1.19)

As the phase retardation $\theta$ includes both an initial phase $\theta_0$ due to the original birefringence in the crystal and a small variation $\Delta\theta$ caused by the crystal’s refractive index
modulation due to applied voltage, \( \theta = \theta_0 + \Delta \theta \), Eq.1.19 can be written as

\[
I = \frac{1}{2} A^2 \left\{ \left[1 - \cos\left(\theta_0 - 2\gamma\right)\right] + \sin\left(\theta_0 - 2\gamma\right) \cdot \Delta \theta + \cos\left(\theta_0 - 2\gamma\right) \cdot \frac{\Delta \theta^2}{2} \right\}
\]  

(1.20)

where \( \cos \Delta \theta \approx 1 - \Delta \theta^2 / 2 \) and \( \sin \Delta \theta \approx \Delta \theta \) are used when \( \Delta \theta \) is small. In Eq.1.20, the first term is not related to the sample’s refractive index change, so it is a constant light intensity (DC value). The second term is linearly proportional to sample’s phase change \( \Delta \theta \) and modulated by \( \sin(\theta_0 - 2\gamma) \), and hence it can be detected by Lock-in amplifier (1f value). The third term is modulated by \( \cos(\theta_0 - 2\gamma) \) by the \( \Delta \theta^2 \), and it is the second order AC signal (2f value). To increase the output magnitude, modulation factors, \( \sin(\theta_0 - 2\gamma) \) or \( \cos(\theta_0 - 2\gamma) \), should be tuned to maximum. Since \( \theta_0 \) is the initial phase retardation in the sample, which cannot be changed once the sample dimension is fixed, the \( \gamma \), which is the angle of the analyzer, can be rotated to compensate the initial phase \( \theta_0 \) and reach the maximal modulation, \( \sin(\theta_0 - 2\gamma) = 1 \) or \( \cos(\theta_0 - 2\gamma) = 1 \). In addition, rotation of the analyzer changes the DC level of the output light intensity from the maximum \( A^2 \) to minimum 0. Thus, the absolute phase change also can be calculated by measuring the maximum \( A^2 \).

### 1.3.3 Piezoelectric Effect in E-O Materials

It should be noted that in the interferometer configuration, as our materials show the thickness change as well as refractive index change, the actual measured quality is the crystal’s optical path length change, \( \Delta(nl) \), and can be expressed as [13, 14],

\[
\Delta(nl) = \Delta n \times l + (n - 1) \times \Delta l
\]

(1.21)

where the first term is the crystal’s refractive index change, and the second term is caused by crystal’s thickness change. Since the crystal is situated in air, which has the refractive index as 1, the optical path length change caused by a thickness change \( \Delta l \) should be multiplied by the refractive index difference between the crystal and air \( n \)
In order to measure the real refractive index change, pure E-O coefficients, the second term in Eq.1.21 has to be subtracted.

\[ \Delta \delta = \frac{2\pi}{\lambda} n \Delta l. \]  

(1.22)
Here, 2 was multiplied to consider the back and forth optical path length change due to the $\Delta l$. Then, the real E-O coefficients can be derived from the apparent value, which is obtained from the total optical path length change.

1.4 Relaxor Ferroelectrics

In crystal symmetry, eleven classes have centrosymmetry among the thirty-two crystal symmetry classes. With a symmetry center, the crystal does not possess any polarity and also has no any third-rank tensor properties, such as piezoelectric and linear E-O effect. The other twenty-one groups, which do not have any centrosymmetry, can possess one or more crystallographically unique directions (axes). All these noncentrosymmetric point groups, except the $432$ point group, exhibit third-rank tensor properties along a unique direction. Among them, ten point groups, $1$, $2$, $m$, $mm2$, $4$, $4mm$, $3$, $3m$, $6$, and $6mm$, have a unique rotation axis, but do not have any mirror plane perpendicular to this axis. Such crystals are called polar crystals since they display spontaneous polarization [6]. A crystal is said to be ferroelectric when it possesses a

![Dielectric polarization hysteresis loop of ferroelectrics.](image)
spontaneous polarization below a transition temperature \((T_c)\) that has two or more crystallographically equivalent orientation states. Ferroelectricity refers to the property that the spontaneous polarization can be switched between these states by application of an external electric field [15]. In most cases, the spontaneous polarization in a ferroelectric crystal is not uniformly distributed throughout the whole crystal, but rather forms small regions, called domains, with each domain having uniform polarization. The origin of the ferroelectric domain can be explained from the energy viewpoint, the polydomain system may be in the state of minimum energy balanced from both electric and mechanical contributions. The polarization direction of each domain is determined by the crystal symmetry of the ferroelectric crystal. The process of applying an electric field, which exceeds a certain field to orient the domains toward the field direction, is termed as poling. For a poled ferroelectric crystal, the switching of polarization direction to other orientation (or reverse) involves hysteresis due to the nucleation barrier resisting the polarization switching, as schematically shown in Fig.1.4. The reversing electric field needed to return to a zero polarization axis is known as the coercive field \((E_c)\). The spontaneous polarization \((P_s)\) can be found by extrapolating the linear saturating portion back to the polarization axis. The actual retained polarization after removing the poling field is called remanent polarization \((P_r)\), which is always smaller than the spontaneous polarization. For most ferroelectrics, there is a certain temperature, above which \(P_s\) becomes zero. The non-polar phase above this temperature is the paraelectric phase and this temperature marks the ferroelectric - paraelectric phase transition, which is signaled as a dielectric constant peak [16].

However, one kind of ferroelectric material which the dielectric constant maximum does not correspond to a transition from non-polar phase to a ferroelectric polar phase, such as Lead Magnesium Niobate (PMN), was grouped as relaxor ferroelectrics [17]. The other distinct features in the relaxor ferroelectrics are frequency dispersion of the dielectric maximum, slim-loop hysteresis behavior near \(T_{max}\), and the optical isotropy at the temperatures below the dielectric maximum when there is no external field [18]. These basic relaxor characteristics are illustrated in Fig.1.5. On the fundamental science side, because the interactions responsible for the relaxor ferroelectric phenomena are
Fig. 1.5. Basic relaxor characteristics. (a) Dielectric properties, (b) Polarization-Electric field curve behavior, and (c) X-ray diffraction and optical index [18].
on the mesoscopic scale, it is still a challenge to develop an understanding of the many interesting and peculiar features by this kind of materials [18]. On the application side, this class of materials offers a high dielectric constant and high electrostriction, which are attractive for a broad range of devices [19].

PMN-PT, the crystal used in this study, is typical ferroelectric relaxor. However, under external fields, if the crystals are poled into ferroelectric state at temperatures much below the dielectric constant maximum, these crystals show large piezoelectric effect and optical anisotropy. PMN-PT is the solid solution system, which has perovskite type structure such as $BaTiO_3$. This material has been of particular interest because of very high electromechanical responses presented at the Morphotropic Phase Boundary (MPB) between the tetragonal and rhombohedral phases [20, 21].

However, most of solid solution perovskite materials are in ceramic form because their single crystals are very difficult to grow. In the electromechanical applications, this ceramic form only causes a reduction of performance due to possible canceling effect among the misaligned ceramic grains, but in optical applications, light scattering due to grain boundaries renders the material impractical for device. Recently, PMN-PT and Lead Zinc Niobate-Lead Titanate (PZN-PT) can be grown into single crystal and this crystal demonstrates ultrahigh electromechanical performance near MPB [22, 23]. The reason for these types of materials showing a high performance is that there exists a morphotropic phase boundary between ferroelectric tetragonal phase and ferroelectric rhombohedral phase [22].

It is interesting to note that although the relaxor ferroelectric phenomenon has been observed in ceramic materials for nearly four decades, there is no direct observation of a relaxor ferroelectric phenomenon in polymer systems. Recently, relaxor ferroelectric phenomenon was observed from the modified $Poly(vinylidene~fluoride$-$trifluoethylene),P(VDF-TrFE)$, based polymers; high energy electron irradiation and copolymerizing the P(VDF-TrFE) with a small amount of chlorinated monomer to form a terpolymer [24, 25]. From Zhang et al.’s results, modification induces the defects in polymer and several effects occur when the defects are introduced into the ferroelectric crystalline region of the polymer. First of all, the defect structures weaken the inter-
Fig. 1.6. Polarization hysteresis loop of P(VDF-TrFE)50/50 mol% copolymer film measured at room temperature (a) before and (b) after irradiation with electrons of 2.5 MeV energy for 40 Mrad dose at 120 °C [24].

Fig. 1.7. The dielectric constant (solid lines) and dielectric loss (dashed lines) as a function of temperature of P(VDF-TrFE) 50/50 mol% copolymer films irradiated with 40 Mrad dose at 120 °C using 2.55 MeV electrons. The inset shows the fitting of the Vogel-Fulcher law. Here solid line is the fit and the circles are the data points [24].
and intra-chain dipolar coupling and hence, lower the Ferroelectric-Paraelectric phase transition to near room temperature. In addition, these defects also introduce inhomogeneity in the ferroelectric phase which broadens the transition region. Furthermore, they reduce and in some cases eliminate the energy barrier in the transformation between different molecular conformations which in turn reduce or eliminate the hysteresis associated with the transformation. As a result, the normal ferroelectric P(VDF-TrFE) copolymer is transformed into a relaxor ferroelectric polymer with a high electrostriction (up to 7% longitudinal electrostrictive strain) and improved the electromechanical coupling factor [24–26]. Fig.1.6 and 1.7 are the polarization loops and dielectric data of electron irradiated P(VDF-TrFE) copolymer, which show the relaxor behaviors.

1.5 Motivation of Optical Study

The physical properties of a crystal, such as the optical indicatrix, are related to its unit cell structure. For instance, the cubic unit cell imparts the crystal optically isotropic without birefringence; crystals with tetragonal unit cell are optically uniaxial, and the optic axis is parallel to the unit cell c-axis; crystals with rhombohedral unit cell are also optically uniaxial, but the optic axis is along the unit cell diagonal direction. In addition to the optic axis direction, the magnitude of the birefringence also relies on its lattice parameters. For PMN-PT and PZN-PT single crystals, there is the large lattice constant change near MPB, inducing the large change of birefringence, as shown in Fig.1.8 [21].

From the previous research work, it was found that an electric field induced phase transition can occur in the compositions near the MPB [22], which means without changing the crystal’s composition or temperature, the crystal can undergo a phase transition by only applying an external electric field. This phenomenon, as well as the fact that a large refractive index change associates with the phase transition, suggests that these crystals may also have a large refractive index change due to the proximity to the MPB. Therefore, it is expected that the external electric field can induce a large refractive index change, in other words, the crystal can have a large E-O effect. In addition to the primary E-O effect, as these materials have large piezoelectric effects, the large secondary E-O effect can be expected.
For relaxor ferroelectric P(VDF-TrFE) based polymers, large strain can be induced through either the phase transition between ferroelectric and paraelectric phases, which is associated with molecular structural change, or bond reorientations [24, 26]. Phase transition from paraelectric to ferroelectric phase generates the dipole moment and induces large polarizability change. For the same bond, for example, the polarizability between perpendicular and parallel to the C-F bond is quite different [28]. From these notions, large E-O effect can be expected through either phase transition or bond reorientation in the relaxor ferroelectric P(VDF-TrFE) based polymers. Thus, it is very interesting and promising to investigate E-O properties and associated applications of relaxor ferroelectric materials to tunable optical devices.

Fig. 1.8. (a) The change of lattice parameters in 0.9PZN-0.1PT single as a function of temperature [27]. (b) Temperature dependence of principal birefringence in 0.65PMN-0.35PT single crystal [21].
Optical materials with high E-O and acousto-optical (A-O) responses are highly desirable for uses in optical communications, optical signal processing and other commercial applications. As large E-O and/or A-O coefficients will allow for smaller size devices and lower operating voltages and power, a growing number of investigations has been focusing on new organic and inorganic materials or material systems to achieve high optical responses [1, 10, 14, 29–32]. Among many optical materials, $\text{LiNbO}_3$ and Liquid crystals are being popularly used for commercial devices. However, $\text{LiNbO}_3$ is suffering from the low E-O response ($r \approx 32 \text{ pm/V}$) and liquid crystals have some drawbacks in response time and polarization dependence [33]. Recently, although organic optical materials, which have large E-O responses and low driving voltage, have been reported, it is still far way for the device applications due to the difficulty in synthesis of stable materials [32].

Apart from the materials development itself, the artificial structures, called photonic crystals (PCs), were invented to manipulate the light. PCs are structures where the refractive index is a periodic function in space [34]. If the wavelength of the radiation is on the order of the lattice spacing, the propagation of electromagnetic radiation is strongly modified. Their periodicity gives rise to photonic band structures in a way that is analogous to electronic band structures. Since near bandedge the group velocity and phase velocity can be very sensitive to the changes of the unit cell dimension and the refractive index of the constituents of the PCs, the phenomena may be employed for stress sensors, for enhancing E-O effect, and for tunable focal length lens [35, 36]. As relaxor ferroelectric materials have the large strain and E-O effects, it is also interesting to study the high performance tunable PCs near photonic bandedge.

1.6 Scope of Thesis

In this thesis, researches were conducted on the materials, devices, and calculation. First, it will include the investigation and explanation of the E-O properties and related properties of ferroelectric relaxor PMN-PT single crystal and P(VDF-TrFE) based
polymers. Secondly, by using the high strain and/or large E-O properties, tunable optical devices will be demonstrated and analyzed. Finally, calculation will be conducted to understand the optical properties associated with the finite size of PCs.

1. Recently high electromechanical responses in the relaxor single crystals and P(VDF-TrFE) based polymers were discovered. The large electromechanical effect implies easy change in the structural configurations by external field, which may also have a high E-O effect. In chapter 2 and 3, optical properties of relaxor single crystals and P(VDF-TrFE) based polymers will be characterized. Furthermore, E-O effects will be explained by the phenomenological method for the single crystals and by the density functional theory for the P(VDF-TrFE) based polymer.

2. In the first section of chapter 4, a tunable grating will be demonstrated with the large strain of P(VDF-TrFE) based terpolymer, and some calculation will be conducted to design the best grating structure. In the second section, utilizing the electromechanical properties and/or E-O properties, tunable Fabry-Perot interferometers will be demonstrated and characterized. In making a metal pattern for mirror on the P(VDF-TrFE) based polymer, as most organic solvents damage the P(VDF-TrFE) based polymer, conventional lithography can not be used. In chapter 5, stencil method will be introduced to make a pattern on P(VDF-TrFE) based polymer and investigate the tunable 2-D PCs (Frequency Selective Surface) for optical filter applications in infrared range.

3. In using the abnormal optical properties near bandedge in PCs, precise calculation is required to predict the device performance. While calculating the optical properties in PCs, many calculations are based on the infinite size of PCs. However, since the real device has a finite size, real performance would be different from the calculation results. In chapter 6, calculations will be conducted to understand the finite size effect in PCs. Furthermore, this calculation will be extended to predict the performance of the tunable PC lens.

Finally, conclusion and future works will be presented in chapter 7.
References


Chapter 2

Electro-optical Properties of PMN-PT Single Crystals near MPB

2.1 Introduction

Ferroelectric single crystals with high E-O coefficients are widely used in many optic devices, such as E-O modulators, switches, frequency shifters and light valves [1, 2]. Recently, there has been an increased interest in ferroelectric PMN-PT and PZN-PT single crystals because the crystals show very large piezoelectric constants, high electromechanical coupling factors, and field-induced strain response over a broad composition range near the tetragonal-rhombohedral morphotropic phase boundary (MPB) [3, 4].

As E-O coefficients \( r_{ijk} \) are the third rank tensor and they are closely related to the field-induced changes in the crystal lattice structures, the large piezoelectric responses \( d_{ijk} \) suggest a large E-O coefficient in these crystals near the MPB. In addition, the fact that these single crystals can be grown to relatively large sizes with optical quality near the MPB opens the possibility for their use in optical applications [5–7]. Furthermore, single crystals with high E-O and piezoelectric response are attractive for multifunctional devices. The optical and E-O properties of PZN-PT single crystals have been investigated recently and large E-O effects have been reported [5, 6].

Here, we investigate the linear E-O coefficients of rhombohedral 0.67PMN-0.33PT and tetragonal 0.62PMN-0.38PT (the two compositions near the MPB).

2.2 E-O Coefficients of PMN-PT Single Crystals

PMN-PT single crystals, near room temperature, can be in either rhombohedral or tetragonal symmetries depending on their compositions [3, 4, 8–10]. In the tetragonal phase, the crystals belong to the 4mm point group, and according to the symmetry
operation, the linear E-O coefficient, which is a third rank tensor, can have the nonzero components as [11];

\[
[r_{ij}] = \begin{bmatrix}
0 & 0 & r_{13} \\
0 & 0 & r_{13} \\
0 & 0 & r_{33} \\
0 & r_{51} & 0 \\
r_{51} & 0 & 0 \\
0 & 0 & 0
\end{bmatrix}
\]  \tag{2.1}

where a matrix expression is used to simplify the tensor notation by index abbreviations, 11→1, 22→2, 33→3, 23→4, 31→5, 12→6 [12]. In the rhombohedral phase, the material belongs to the 3m point group, and the linear E-O coefficient is

\[
[r_{ij}] = \begin{bmatrix}
0 & -r_{22} & r_{13} \\
0 & r_{22} & r_{13} \\
0 & 0 & r_{33} \\
0 & r_{51} & 0 \\
r_{51} & 0 & 0 \\
-r_{22} & 0 & 0
\end{bmatrix}
\]  \tag{2.2}

According to Eq.1.7, 2.1 and 2.2, if an electric field \(E\) is applied on the sample along the 3-axis, which is the poling direction, the ordinary refractive index will show a change

\[
\Delta n_o = -\frac{1}{2} n_o^3 r_{13} E
\]  \tag{2.3}

and the extraordinary refractive index will experience a change.

\[
\Delta n_e = -\frac{1}{2} n_e^3 r_{33} E
\]  \tag{2.4}

Therefore, the E-O coefficient \(r_{13}\) and \(r_{33}\) can be characterized by measuring the electric field induced refractive index changes, \(\Delta n_o\) and \(\Delta n_e\) respectively.
While the poled crystals remain uniaxial with an electric field along the polar axis, they become biaxial under a field perpendicular to the polar axis. The application of an electric field perpendicular to the polar axis thus changes the principal axes. The angle between the new principal axes and the old ones is usually very small, given by \( \theta \approx \frac{r_{51}E_1}{(n_0^{-2} - n_e^{-2})} \) [13]. The E-O coefficients \( r_{51} (=r_{231}) \) were measured by the Senarmont compensator method, where the applied electric field \( E_1 \) is perpendicular to both the crystal poling direction and the light propagation direction [14]. It should be noted that in the measurement of \( r_{15} \), there is no need to make a correction for the piezoelectric effect.

### 2.3 Experiment

Crystals used in this investigation were grown by the Bridgman method [15]. The single crystals were oriented along the \(<001>\) and \(<111>\) directions using a Laue camera. Typical specimen dimensions were 2 x 2 x 1 mm\(^3\). Rhombohedral 0.67PMN-0.33PT single crystals were poled at room temperature and tetragonal 0.62PMN-0.38PT single crystals were poled at a temperature approximately 50 °C higher than the ferroelectric-paraelectric (FE-PE) phase transition and then slowly cooled to room temperature under a field. It was found that such a poling procedure yielded the best poled single crystals. The poled samples were carefully polished to an optical grade, without affecting the crystal polarization. Dielectric characterization (at 1 kHz) was carried out using a standard LCR meter (HP4284A) equipped with a temperature chamber. Spontaneous polarization was measured by the static Byer-Roundy method [16]. The transmittance was measured using an UV-visible spectrometer (HP 8453A). The domain patterns of the crystals at room temperature were characterized using a Zeiss Axioskop cross-polarized optic microscope.
2.4 Results and Discussion

Rhombohedral 0.67PMN-0.33PT has spontaneous polarization along the \(<111>\) direction so that the \(<001>\) poled single crystal has an engineered multidomain structure and scattering is quite large for the bulk crystals. The measured E-O coefficients correspond to the domain averaged values. In the 0.67PMN-0.33PT single crystals poled along the \(<111>\) direction (the spontaneous polarization direction) there exist some regions of unstable domain structures which affect the optical quality of the specimens. In contrast, the tetragonal 0.62PMN-0.38PT specimens poled along the \(<001>\) direction show a stable single-domain structure and high optical quality. Fig.2.1 presents the measured transmittance as a function of wavelength (200 \(nm\) - 1000 \(nm\)) for the 0.62PMN-0.38PT single crystals poled along the \(<001>\) direction. The transmittance begins to increase abruptly at around 410 \(nm\) and then increases gradually at wavelengths above 500 \(nm\). This transmittance continues into the IR region at least through 5 \(\mu m\) without any noticeable absorption bands being observed. Using the refractive index \(n = 2.7\) at 587.6 \(nm\) wavelength, the calculated reflection \(R = (n - 1)^2/(n + 1)^2\) is 21 \%.

![Transmittance graph](image)

Fig. 2.1. Transmittance of 0.62PMN-0.38PT \(<001>\) poled single crystal.
Table 2.1. The measured linear E-O coefficients ($r$) and calculated quadratic E-O coefficients ($g$) of PMN-PT single crystal at room temperature. Here, $r_{33}^*$ and $r_{13}^*$ are the apparent E-O coefficients, $d_{31}$ is the piezoelectric coefficient, $r_{33}$, $r_{13}$ and $r_{51}$ are the real E-O coefficients.

<table>
<thead>
<tr>
<th>Composition &amp; Poling direction</th>
<th>$r_{33}^*$</th>
<th>$r_{13}^*$</th>
<th>$-d_{31}$</th>
<th>$r_{33}$</th>
<th>$r_{13}$</th>
<th>$r_{51}$</th>
<th>$g$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.67PMN-0.33PT &lt;001&gt;</td>
<td>324</td>
<td>132</td>
<td>610</td>
<td>207</td>
<td>15</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.67PMN-0.33PT &lt;111&gt;</td>
<td>110</td>
<td>3</td>
<td>13</td>
<td>107</td>
<td>0</td>
<td>1050</td>
<td></td>
</tr>
<tr>
<td>($g_{11} - g_{12}$) = 0.015</td>
<td>($g_{11} - g_{12}$) = 0.023</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$g_{44}$ = 0.023</td>
<td>$g_{44}$ = 0.033</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.62PMN-0.38PT &lt;001&gt;</td>
<td>80</td>
<td>35</td>
<td>60</td>
<td>70</td>
<td>25</td>
<td>558</td>
<td></td>
</tr>
</tbody>
</table>

Table 2.1 summarizes the E-O coefficients measured at room temperature. Here, the apparent E-O coefficients ($r_{ij}^*$) is determined from the total optical pathlength change, and the real E-O coefficient ($r_{ij}$) can be determined after considering the piezoelectric coefficients ($d_{31}$) [5]. Rhombohedral 0.67PMN-0.33PT crystals exhibit larger $r_{33}$ and $r_{15}$ than the tetragonal 0.62PMN-0.38PT, whose composition is further away from the MPB. For 0.67PMN-0.33PT, the <001> poled sample shows a larger E-O coefficient than the <111> poled sample. This result is similar to that for the PZN-PT single crystal [6].

The measured linear E-O coefficients $r_{ij}$ can be linked to the polarization-related quadratic E-O $g_{ij}$ coefficients [17–19]. For crystals in the rhombohedral phase,

$$r_{33} = \frac{2}{3}K_{33}\varepsilon_0P_s(g_{11} + 2g_{12} + 2g_{44})$$

$$r_{13} = \frac{2}{3}K_{33}\varepsilon_0P_s(g_{11} + 2g_{12} - g_{44})$$

$$r_{15} = \frac{2}{3}K_{11}\varepsilon_0P_s(g_{11} - g_{12} - \frac{1}{2}g_{44}).$$
and for crystals in the tetragonal phase,

\[(r_{33} - r_{31}) = 2K_{33}\varepsilon_0P_s(g_{11} - g_{12})\]

\[r_{15} = K_{11}\varepsilon_0P_s g_{44},\]  \hspace{1cm} (2.6)

where \(g_{11} = g_{1111}, g_{12} = g_{1122}\) and \(g_{44} = 2g_{2323}; K_{33}\) and \(K_{11}\) are the dielectric constants along and perpendicular to the spontaneous polarization direction, respectively; \(P_s\) is the spontaneous polarization and \(\varepsilon_0\) is the vacuum permittivity (= 8.854 \times 10^{-12} \text{ F/m}).

For 0.67PMN-0.33PT single crystals poled along the \(<111>\) direction, \(K_{33}, K_{11}\) and \(P_s\) are 700, 17800 and 0.38 C/m², respectively. Using these values and Eq.2.18, \(g_{44} = 0.023 m^4/C^2\) and \((g_{11} - g_{12}) = 0.015 m^4/C^2\). For 0.62PMN-0.38PT single crystals poled along the \(<001>\) direction, \(K_{33}, K_{11}\) and \(P_s\) are 370, 6300 and 0.30 C/m², respectively. From Eq.2.6, \((g_{11} - g_{12}) = 0.023 m^4/C^2\) and \(g_{44} = 0.033 m^4/C^2\). It can be seen that the values of \(g\) in the tetragonal phase are larger than those in the rhombohedral phase. Similar to the PZN-PT single crystals, this large \(g\) values in tetragonal phase are supposed to be from the increases of PT contents [20].

Fig. 2.2. Temperature dependence of E-O coefficients for 0.62PMN-0.38PT \(<001>\) poled single crystal. Solid lines are drawn as a visual guide.
Fig. 2.2 presents the temperature dependence of the E-O coefficients for the tetragonal 0.62PMN-0.38PT poled along the <001> direction, which is an important property for the optical devices. Both the apparent and real E-O coefficients exhibit a weak increase with temperature. These results are different from those of the PZN-PT tetragonal single crystals which show temperature independence [6]. As \( r_{33} = 2K_{33}\epsilon_0 P_s g_{11} \) and \( r_{13} = 2K_{33}\epsilon_0 P_s g_{12} \), the E-O coefficient can be determined by the value of the dielectric constant multiplied by the spontaneous polarization \( (K_{33}P_s) \) and the \( g \) value. As quadratic E-O \( g \) coefficients should be temperature independent, the increase of linear E-O coefficients with temperature is due to the temperature dependence of \( K_{33}P_s \), as shown in Fig.2.3. Indeed, the ratio of \( r_{33} \) at 80 °C to that at 20 °C is 1.23 (deduced from
the average slope of the curve) which is very close to the ratio of $K_{33}P_s$ at 80 $^\circ$C to that at 20 $^\circ$C (1.24).

2.5 Conclusion

The E-O coefficients of PMN-PT single crystals in the rhombohedral and tetragonal phases were characterized. The tetragonal 0.62PMN-0.38PT single crystals poled along the $<001>$ direction (the spontaneous polarization direction) show $r_{33} = 70 \text{ pm/V}$, $r_{31} = 25 \text{ pm/V}$, and $r_{15} = 558 \text{ pm/V}$. In addition, $r_{33}$ and $r_{31}$ of crystals of this composition show a slight increase with temperature, which originates from the temperature dependence of polarization and dielectric constant. The quadratic E-O g coefficients were found using the linear E-O coefficients, the dielectric constant, and the remanent polarization. The rhombohedral 0.67PMN-0.33PT single crystals poled along the $<111>$ direction have $r_{33} = 107 \text{ pm/V}$, $r_{31} \sim 0$, and $r_{15} = 1050 \text{ pm/V}$.
References


3.1 Electromechanical Properties of Relaxor PVDF Based Polymer

Polymer based electroactive materials, which change shapes as an electric field is applied, have been attracted in many areas such as electromechanical actuators and sensors for robots, acoustic transducers for underwater navigation and medical imaging, artificial muscles and organs, fluid pumps and valves, and smart materials for vibration and noise control [1–3]. Polymers are renowned for their excellent mechanical properties including lightweight, flexible, and easy processing, and that polymers can be conformed to complicated shapes.

Fig. 3.1. The field induced longitudinal strain ($S_3$) as a function of the applied field for the unstretched terpolymer P(VDF-TrFE-CFE) 66/34/8.6 mol\% composition. Data points are shown and solid curve is drawn to guide eyes.
In designing the new materials, it is interesting to note that there are many unique phenomena in polymeric materials which can be made use of to generate high electromechanical responses. For example, in relaxor ferroelectric P(VDF-TrFE) [Poly(vinylidene fluoride-trifluoethylene)] based polymer, as can be seen in Fig.3.1 electric field can induce a high electrostriction (>7 % longitudinal electrostrictive strain), which accompanies the phase transformation between the ferroelectric and paraelectric (F-P) phases [4]. The origin of such a large strain in the F-P transition is attributed to the molecular conformation change or bond reorientations [5–9].

Similar to the inorganic single crystals, as phase transition accompanies the structural change, it is interesting to investigate the E-O properties of P(VDF-TrFE) based polymers.

3.2 Optical Properties of PVDF Based Polymer

Organic polymers for applications such as dielectric waveguides and optical fiber are increasingly attractive alternatives to inorganic components in telecommunication devices. Polymers offer flexibility, low cost fabrication and connection, high transparency in the visible and near-infrared spectra, and versatility in structure, properties, and grades for task specific integration such as local-area-network applications. However, glass-derived components remain formidable incumbents due to their lower density, high heat resistance, lower attenuation, wider bandwidth, and higher transmission speeds over the majority of common optical polymers. For example, PMMA exhibits a maximum transmission wavelength at 650 nm due to C-H vibrational overtone absorptions. Most telecommunication systems require low transmission losses (< 0.3 dB/cm) from 1535-1565 nm [10]. Due to their many complementary properties, fluoropolymers represent viable alternatives to current optical materials. Halogenated polymers in general show negligible transmission losses in the range desired and fluoropolymers represent the lowest loss examples of organic polymers to date [11]. Since P(VDF-TrFE) based polymers are also halogenated polymers, they might have good transmission properties in optical communication frequency. For materials properties,
relaxor ferroelectric PVDF based polymer have large strain from the molecular structural change so that large E-O properties can be expected [6]. In this part, we will investigate the optical and E-O properties of P(VDF-TrFE) based polymer.

3.2.1 Transmission and Refractive index

In order to be useful as an optical material light must be able to pass through an element made from the substance without being substantially absorbed. Therefore, an evaluation of how well electromagnetic radiation is transmitted and what portion is absorbed by the sample must be undertaken for a complete spectral range. Optical transmission measurements can reveal information about the electronic band structure, fundamental optical band gap, absorption from ionic lattice and molecules [11].

To obtain high transparency over an extended wavelength range, materials with low lattice resonance and high energy band gaps are required. Dielectric materials usually have large band-gap energy and only high energy light can excite the electronic structure. Dielectrics therefore tend to be transparent throughout the visible range. However, in the infrared range, the electromagnetic wave energy can excite the molecular vibrations and there can be intrinsic absorption. The measured optical transmission features of P(VDF-TrFE) film are presented in Fig.3.2. Partial reflection of the incident beam occurs at the boundary of two materials with differing refractive indices. The reflection can be calculated using Fresnel reflection values for normal incidence in a nonabsorbing region. With \( R = \frac{(n-1)^2}{(n+1)^2} \) and the refractive index \( n = \sim 1.45 \), R can be \( \sim 3.4 \% \). Although there are some losses originated from the sample preparation, P(VDF-TrFE) polymer still keeps > 80 % transparency in the visible and near-IR range. In Mid-IR range, P(VDF-TrFE) based polymer has a large absorption near 3000 \( cm^{-1} \) wavenumber (3.3 \( \mu m \)), which is attributed to the -CH\(_2\) vibration, and below 1500 \( cm^{-1} \) there are many absorption peaks. Thus, this P(VDF-TrFE) based polymer can be used at the optical window, 4000 \( cm^{-1} \) and 2900 \( cm^{-1} \) in Mid-IR range. In addition, above 25 \( \mu m \) wavelength range this polymer does not show any characteristic absorption peaks and shows high transparency up to 100 \( \mu m \).
Fig. 3.2. Optical transmission of P(VDF-TrFE) based polymer; (a) Visible, (b) Near-IR, (c) Mid-IR, and (d) Far-IR range.

In general, the index of refraction is not the same for all light wavelengths. This implies that, for a given incident angle, the refraction angle will depend on the wavelength of the incident light. Materials for which this dependence is relatively strong are called dispersive. The phenomenon whereby the index of refraction of a material measurably depends on the wavelength of the incident electro-magnetic radiation is called dispersion [12]. For PVDF polymer, knowing the positions and orientations of each bond in the crystal, one can calculate the polarizabilities. From these, using the Lorentz-Lorenz relationship, refractive index can be calculated. Fig.3.3(a) is the calculated refractive index of PVDF Form I (polar form) crystal when C-F bond is parallel to the polarization direction of light and Fig.3.3(b) is the calculated refractive
Fig. 3.3. The calculated refractive index of PVDF Form I: (a) when C-F bond is parallel to the polarization direction of light and (b) when C-F bond is perpendicular to the polarization direction of light.

Refractive index does not change much up to around $50000 \text{ cm}^{-1}$ ($>0.2 \mu m$), however, as wavelength becomes shorter, there appear abnormal refractive index. Interestingly, there is a big difference in refractive index for the different bond orientations. This implies that if we can change the bond orientations with an electric field, a large E-O effect can be expected in PVDF polymer.

3.2.2 E-O Response of the Ferroelectric Relaxor PVDF based Terpolymer

Optical materials with high E-O and acousto-optical (A-O) responses are highly desirable for uses in optical communications, optical signal processing and other commercial applications. As large E-O and/or A-O coefficients will allow for smaller size devices and lower operating voltages and power, a growing number of investigations
has been focusing on new organic and inorganic materials or material systems to achieve high optical responses [13–19].

Compared with inorganic materials, organic optical materials usually show smaller E-O coefficients. However, large E-O responses have recently been reported for organic material systems which incorporate the chromophores into a polymer matrix [18, 19]. These chromophores are π-conjugated organic compounds, having large molecular hyperpolarizabilities and dipole moments that give rise to the larger E-O effect. Although there has been a great deal of research to synthesize stable organic chromophores, this effort still remains a great challenge [19]. In this section, we will investigate the E-O properties of P(VDF-TrFE) based terpolymers.

3.2.2.1 Experiment

The terpolymer of P(VDF-TrFE-CFE), where CFE is 1-chloro-1-fluoroethylene, were prepared by the suspension polymerization process with an oxygen-activated initiator at 40 °C. In this study, the terpolymer with a composition of 68/32/9 mol% was investigated. As shown in Fig.3.1, the terpolymer with this composition exhibits an electrostrictive strain along the thickness direction of more than 7% under a field of 170 V/µm. For a polymeric material with such a large strain, even the secondary E-O effect, i.e., the elasto-optical effect, will produce a correspondingly large E-O response [20]. The polymer films were prepared using the solution cast method with dimethylformamide (DMF) as the solvent. The films were annealed at a temperature near 115 °C for 3 hours to improve the crystallinity. The typical film thickness used in this investigation is ~ 20 μm. For strain measurements, gold film of 40 nm thick was sputtered on both sides of polymer film to serve as electrodes. The strain along the thickness direction (longitudinal strain, S₃) was characterized by means of a modified optical method using piezoelectric bimorph based dilatometry [21]. The strain responses were measured under a 1 Hz AC electric field. No large differences in strain were detected in the 0.01 - 1 Hz frequency range.

In this study, the E-O effect of the P(VDF-TrFE-CFE) terpolymer in the infrared region was investigated using a Nicolet FT-IR spectrometer. To observe the changes in
the refractive index of the terpolymer films under external electric fields, the electrode should allow for the maximum transmittance of the IR signal, that is, it should have low loss in the optical frequency and be conductive for applied electric fields. As metallic films are known to absorb strongly in the infrared range [22, 23], which will be discussed later in this thesis, we employed the conductive polymer polypyrrole in this experiment.

Polypyrrole was deposited on both surfaces of the terpolymer films by an in situ deposition technique [24]. Anthraquinone-2-sulfonic acid, sodium salt monohydrate (2.45 g), 5-sulfo-salicylic acid dihydrate (13.35 g) and ferric chloridehexahydrate ($FeCl_3$-$6H_2O$) (8.75 g) were dissolved in 250 ml of distilled water. An aqueous solution of pyrrole (1.5 ml dissolved in 250 ml of distilled water) was poured into the above solution. While stirring the solution, terpolymer films fixed on metal frames were then immediately immersed in the solution for 60 min. To obtain the high quality polypyrrole electrodes, the terpolymer films were removed from the polymerizing solution after about 5 min and were rinsed with distilled water for about 10 sec. This procedure was repeated several times during the deposition process. The resultant polypyrrole electrodes were smooth, coherent and adhered well to the terpolymer films. The typical thickness of polypyrrole was about 300 Å. After connecting the wire to the conductive polymer, changes in the transmittance under different applied DC electric fields were recorded using a Nicolet 510 FT-IR spectrometer.

3.2.2.2 Results and Discussion

Presented in Fig.3.4 are the IR spectra of the terpolymer films coated with the polypyrrole electrodes. It is known that with the exception of the absorption peak near $\sim 3000 \, cm^{-1}$ due to the -CH$_2$ vibration, pure terpolymer shows high transparency from the visible to $1500 \, cm^{-1}$. However, terpolymer with conductive polypyrrole shows periodic Fabry-Perot interference fringes, as seen in Fig.3.4. These fringes are attributed to the multiple reflections from the polypyrrole electrodes, which act as mirrors in this case to form a Fabry-Perot interferometer.

As a mirror polypyrrole is supposed to have low reflectance in the measuring frequency range, which leads to the low finesse and fringe patterns with sinusoidal
behavior. As the-CH$_2$ vibration is the intrinsic characteristic of the polymer films, the peak near 3000 cm$^{-1}$ does not show much movement with the applied electric field. However, fringes from the Fabry-Perot interferometer exhibit marked shifts to large wavenumber, i.e. short wavelength with the applied electric field. It is noted that at normal incidence, the interference fringe pattern has its maxima when

$$2nd = m\lambda_1$$  \hspace{1cm} (3.1)

where $n$ is refractive index of polymer ($\sim 1.45$), $d$ is polymer thickness, $m$ is an integer, and $\lambda_1$ is wavelength of maximum peak. If the fringe pattern exhibits a shift with the electric field, Eq.3.1 can be modified to

$$2\{nd + \Delta (nd)\} = m\lambda_2$$  \hspace{1cm} (3.2)
where \( \lambda_2 \) is the wavelength for the new maximum peak. From Eq.3.1 and 3.2, the optical path length change \( \Delta(nd) \) can be expressed as,

\[
\frac{\Delta(nd)}{nd} = \frac{\Delta \lambda}{\lambda_1}
\]  

(3.3)

where \( \Delta \lambda = \lambda_2 - \lambda_1 \). It is assumed that this difference is much smaller than either \( \lambda_1 \) or \( \lambda_2 \) as indeed is the case here. Using Eq.3.3 and the measured fringe shift, a -5.4 % optical pathlength change was obtained for the films when the applied field was increased from 0 \( V/\mu m \) to 80 \( V/\mu m \). Compared with previous reported values in many E-O materials where the optical pathlength change is small (< 1%) [13–18], this change in the optical pathlength is quite large and attractive for tunable optical devices.

In this experiment, the observed optical pathlength change is due to two effects: the E-O effect as reflected by the change in the refractive index (\( \Delta n \)), and the thickness change due to the electrostrictive strain (\( \Delta d \)). To account for these two effects, Eq.3.3 can be rewritten as,

\[
\frac{\Delta(nd)}{nd} = \frac{\Delta d}{d} + \frac{\Delta n}{n}.
\]  

(3.4)

To obtain the pure refractive index change (\( \Delta n/n \)), the strain (\( \Delta d/d \)) was characterized for the terpolymer films under identical applied electric fields. Presented in Fig.3.5 are the electric field-induced strains as a function of the applied electric field amplitude. Using the -2.8 % longitudinal strain under 80 \( V/\mu m \) field of sample, a -2.6 % pure refractive index change can be obtained.

For the terpolymer film, the E-O effect can be explained in terms of the electric field (\( E_3 \)) or polarization (\( P_3 \)) as follows

\[
\Delta n_1 = -\frac{1}{2} n^2 R_{31} E_3^2, \text{or } \Delta n_1 = -\frac{1}{2} n^2 g_{31} P_3^2
\]  

(3.5)

where \( R_{31}, g_{31} \) are quadratic E-O coefficient known as Kerr coefficient [13–16]. Between these two equations, the equation with the polarization term is generally preferable when dealing with ferroelectric materials since the response in terms of the polarization...
relates more directly to the fundamental polarization changes that accompany ferroelectric transitions [25]. For the terpolymer investigated here, the two types of quadratic E-O coefficients are related through the dielectric permittivity as,

$$g_{31} = R_{31} / (K \cdot \epsilon_0)^2$$

(3.6)

where $K$ is the dielectric permittivity of terpolymer ($\sim 50$) and $\epsilon_0$ is the permittivity of free space ($8.854 \times 10^{-12} F/m$). With the -2.6% refractive index change at 80 $V/\mu m$, a value of $g_{31}$ equal to 21 $m^4/C^2$ can be obtained. Compared with oxygen-octahedra ferroelectrics [26], P(VDF-TrFE) based terpolymer has a 2-3 orders of magnitude larger $g$ value. On the other hand, the $R_{31}$ coefficient for the terpolymer here is $4.11 \times 10^{-18} m^2/V^2$, which is smaller than that observed for the PLZT (9.5/65/35) ceramics ($R \sim 2 \times 10^{-16} m^2/V^2$) [25]. For temperature dependence, which is crucial for real device applications, as terpolymer does not show big change in dielectric constant near room temperature, E-O may also be stable near room temperature. It should be mentioned
that our measurement was conducted near the DC condition. However, since $g_{31}$ can be assumed frequency independent, $R_{31}$ will decrease with frequency as the dielectric constant in relaxor ferroelectric materials decreases with frequency (see Eq.3.6) [7]. Although this dispersion is weak at low frequencies, it becomes strong when approaches 1 MHz [5, 27]. For example, if we assume that the frequency response of E-O effect is similar to that of the electromechanical response, which is also determined by the frequency dispersion of the dielectric constant, there would be $\sim 40\%$ decrease as the frequency increases from 100 Hz to 100 KHz [28].

<table>
<thead>
<tr>
<th>Direction</th>
<th>Form I polar</th>
<th>Form II non-polar</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt;100&gt;</td>
<td>1.52</td>
<td>1.20</td>
</tr>
<tr>
<td>&lt;010&gt;</td>
<td>1.46</td>
<td>1.21</td>
</tr>
<tr>
<td>&lt;001&gt;</td>
<td>1.36</td>
<td>1.16</td>
</tr>
</tbody>
</table>

Table 3.1. Refractive Indices of Forms I and II PVDF Crystals (calculated by Density Functional Theory). Here, <100> is perpendicular to chain; <010> is the polar and electric field direction; <001> is chain direction.

We discuss the underpinnings of the observed large E-O effect in the terpolymer. In the terpolymer studied here, the induced polarization under external electric field can result either from molecular conformational changes between the non-polar bonds (TGTG’ and T$_3$GT$_3$G’ conformations where T = trans and G = gauche) and polar bonds (all-trans conformation) or from nano-polar region reorientation. In the former case, a large volume strain should be observed since calculations of the volumes of the forms I (all-trans), II (TGTG’), and III (T$_3$GT$_3$G’) terpolymer superlattice crystals suggest that the change in volume when form II converts to III, which in turn converts to I is estimated to be about -6.4 % [29]. This estimated volume change is, however, greater than the
observed volume strain of -0.6 % (under a field of 170 V/µm. As has been pointed out, the thickness strain under this field is more than -7 %) [7]. The results imply that the interconversions between forms I, II, and III are not the main cause for the induced strain, polarization, and E-O effect. Furthermore, as can be seen in Table 3.1, calculations of the refractive index change by density functional theory (these calculations were performed using the Accelrys CASTEP code) show that the refractive index should increase on a conversion from form II or III to I, a prediction that is not consistent with the observed decrease of the refractive index with electric field [30].

The behavior observed in this section can be better interpreted in term of a rotation of the carbon-fluorine dipoles under electric field from the orientations less aligned with the field to the orientation more aligned with the field direction. The calculated values of the refractive index change support this notion. For a form I all-I crystallite, the calculated refractive index, assuming the polymer chain aligns along the film and does not rotate with the electric field, changes by -3.9 % in a dipolar reorientation from the perpendicular <100> to the parallel <010> direction with the electric field. Taking into account of the crystallinity in the terpolymer and a distribution of the dipole orientations and crystallite orientations, the observed -2.6 % value seems to be consistent with this interpretation.

3.2.2.3 Summary

In summary, E-O properties of P(VDF-TrFE) based terpolymers were characterized by the Fabry-Perot interference fringe measurements. The terpolymer film exhibits a -5.4 % of total optical pathlength change and -2.6 % pure refractive index change under a field of 80 V/µm. A calculation based on density functional theory suggests that this change in the optical refractive index is caused by the dipolar reorientation of the existing nano-polar regions in the terpolymer. This interpretation is also consistent with the small volume strain observed in the terpolymer. These results also support the notion that in the relaxor ferroelectric terpolymers, there exist nano-polar regions which are responsible for the observed polarization changes, the large electrostrictive strain and E-O properties.
References


Chapter 4

Tunable Optical Devices Using a PVDF Based Terpolymer

4.1 Tunable Optical Grating with High Strain of Terpolymer

4.1.1 Introduction

The light modulation becomes important in the large screen display and optical communications [1–3]. The light modulators with deformable mirror operate by deflecting a mirror, or an array of mirrors for a spatial light modulator [1–5]. Among the several modulation methods, with the ease of integration the deformable mirror modulator fabricated by silicon MEMS process has attracted the attentions for the future display and optical communication [1–3]. The Grating Light Valve (GLV), which was first developed at Stanford, is a type of optical MEMS; essentially a movable silicon nitride film with metal film for both the electrode and the reflecting mirror [1–4]. As GLV can be fabricated by the standard semiconductor process and equipment, many GLV devices are currently commercialized with the low cost [1, 2]. However, in detail process it is still hard to make a free standing flat thin silicon nitride film without bending and sealing is required for stable operation without air fluctuation. Similarly, an alternative technologies use thin viscoelastic materials between two electrodes instead of the micromechanical layer in GLV [2, 5, 6]. The viscoelastic modulator does not require any high temperature processing, so integration with drive circuits and active matrices is greatly simplified [6]. In addition, post process, such as sealing, is not needed. However, for example, since the maximum of the first order diffraction efficiency can be obtained with $1/4\lambda$ displacement in GLV device [1, 2, 7], its $\sim 50\ \text{nm}$ displacement was small for obtaining the high diffraction efficiency even in the visible range ($400 - 750\ \text{nm}$) [6]. As we have mentioned in Chapter 3, large electrostrictive strain ($\sim 7\%$) was observed from the free standing poly(vinylidene fluoride-trifluoroethylene) [P(VDF-TrFE)] based terpolymers [8]. This strain level is large enough for the display,
and optical communication applications with the moderate thickness. Interestingly, as
the large strain can be induced by external electric fields, these materials have been
exploited for many applications such as electromechanical actuators for robotic applica-
tions and artificial muscles, microfluidic devices, smart materials for vibration and noise
control, and acoustic transducers for underwater navigation and medical imaging [9].
In this section, first we will calculate the strain profile by changing the electrode struc-
ture and the thickness of the P(VDF-TrFE) based terpolymer. Then, we will demonstrate
a tunable polymer grating using a P(VDF-TrFE) based terpolymer.

4.1.2 Device Structure and Operation Principle

Polymer tunable grating uses a thin terpolymer sandwiched between a flexible
layer of metal and a rigid substrate with metal lines on the other. If a voltage is applied to
the lines, which are shaped with gratings, the terpolymer shrinks and top metal deform
together. Deformation shape of top metal is determined by electric field distribution
in the polymer. Essentially, this structure is similar to the micromachined GLV, with
difference implementation between the top and bottom metal layers, air vs. terpolymer.
The advantage of polymer based tunable light grating is that it does not require any high
temperature processing, so it is easy to integrate with driver circuit and active matrices.

![Schematic of a tunable polymer spatial light modulator](image)

*Fig. 4.1. The schematic of a tunable polymer spatial light modulator. (a) Without
electric field, the mirror acts as a flat mirror. (b) With electric field, polymer shrinks
according to the electric field distribution and forms the grating. $d$ is one period.*
The basic principle of operation for the polymer tunable grating is illustrated in Fig.4.1. Without electric field, top metallic electrode acts as a flat mirror reflecting the incoming light. When an electric field is applied between the comb-shape bottom electrode and the top electrode, there is an electric field distribution determined by the bottom electrode configuration, polymer thickness, and dielectric constant of polymer. Depending on the electric field distribution, polymer film generates the different level of strain and forms the grating. Then, optical path length will change according to the grating and diffraction pattern will be formed. If we change the applied electric field continuously, different level of strain can be obtained and consequently the diffraction intensity can be also modulated.

4.1.3 Calculation of Polymer Deformation Profile

To predict the polymer deformation profile with an electric field, we calculated the electric field distribution in polymer film using the ANSYS 7.0. Detail calculation can be referred in Appendices. Here, electric field distribution is determined by the configuration of comb-shape bottom electrode, polymer thickness, and dielectric constant of polymer. The dielectric constant of terpolymer is \( \sim 50 \). Shown in Fig.4.2(a) are the equipotential lines for the structure, which has the 1 \( \mu m \) width electrode, 15 \( \mu m \) gap between the electrodes and 15 \( \mu m \) polymer thickness. For this calculation, we set the electrode/gap/electrode as 0.5 \( \mu m/15 \mu m/0.5 \mu m \) for one period. It should be noticed that the minimum field is the center of the gap between the electrodes and shows \( \sim 42\% \) of the maximum field. This means that for example, 1 % strain between 42 \( V/\mu m \) and 100 \( V/\mu m \) in Fig.4.3 can be utilized in case of 100 \( V/\mu m \) applied electric field. Fig.4.2(b) presents the calculated polymer deformation profile for the 100 \( V/\mu m \) applied electric field.

Fig.4.4 shows the calculated polymer deformation profiles of 15 \( \mu m \) thickness terpolymer with the 1 \( \mu m \) electrode and 5, 10, 1\( \mu m \) gap between the electrodes. As the gap becomes smaller, the minimum electric field increases so that less strain can be utilized. For the 15 \( \mu m \) gap, the effect of electrode width was presented in Fig.4.5. As the electrode becomes wider, the minimum electric field increases. For the 0.5 \( \mu m/15 \)
Fig. 4.2. (a) Equi-potential plot in the polymer film and (b) Calculated polymer deformation profile and the electric field distribution for the applied 100 V/µm electric field. For this calculation, we set the electrode/gap/electrode = 0.5 µm/15 µm/0.5 µm, polymer thickness = 15 µm and the dielectric constant of polymer = 50.

µm/0.5 µm electrode structure, the thickness effect was shown in Fig.4.6. As thickness becomes thinner, electric field concentrated under the electrode and more strain can be used for the deformation. For example, compared with the 1.06 % strain between 42 V/µm and 100 V/µm for the 15 µm thickness polymer, 10 µm thickness polymer can use
Fig. 4.3. The field induced longitudinal strain under the clamped condition as a function of the electric field for the terpolymer P(VDF-TrFE-CFE) 68/32/9 mol%. Data points are shown and solid curve is drawn to guide eyes.

Fig. 4.4. Calculated deformation profile of the 15 µm thickness polymer with the different gap between the electrodes. Electrode/gap/electrode is (a) 0.5 µm/5 µm/0.5 µm, (b) 0.5 µm/10 µm/0.5 µm, and (c) 0.5 µm/15 µm/0.5 µm, respectively. The maximum applied electric field is 100 V/µm.
Fig. 4.5. Calculated deformation profile of the 15 μm thickness polymer with the different electrode width. Electrode/gap/electrode is (a) 0.5 μm/15 μm/0.5 μm, (b) 1 μm/15 μm/1 μm, and (c) 5 μm/15 μm/5 μm, respectively. The maximum applied electric field is 100 V/μm.

Fig. 4.6. Calculated deformation profile of the polymer with electrode/gap/electrode = 0.5 μm/15 μm/0.5 μm for the different thickness; (a) 10 μm and (b) 15 μm. The maximum applied electric field is 100 V/μm.
the 1.22 % strain between 27 V/µm and 100 V/µm. However, 10 µm thickness polymer shows the smaller the absolute displacement due to the smaller thickness.

4.1.4 Device Fabrication and Measurement

For polymer tunable grating, the terpolymer of P(VDF-TrFE-CFE) at the composition of 68/32/9 mol%, where CFE is chlorofluoroethylene, was used. As shown in Fig. 3.1, the free standing terpolymer at this composition exhibits an electrostrictive strain along the thickness direction of more than 7 % under a field of 170 V/µm [7]. Comb-shape gold electrode with 4 mm length, 10 µm width and 15 µm gap between the electrodes was made using the lift-off method on the optical grade glass substrate. The polymer films were then prepared using the solution cast method with dimethylformamide (DMF) as the solvent. The films were annealed at a temperature near 115 °C for 3 hours to improve the crystallinity. The typical film thickness used in this investigation is ~ 14 µm. 40 nm gold film was sputtered on the polymer film for both the mirror and top electrode. Typically sample size was 4 x 4 mm².

Fig. 4.7. Calculated deformation profile of the 14m thickness polymer with electrode/gap/electrode = 5 µm/15 µm/5 µm. The maximum applied electric field is 100 V/µm.
For the applied maximum $\sim 100\, V/\mu m$ electric field, the electric field distribution and deformation profile were shown in Fig.4.7. It should be noticed that 0.93 % strain between 100 $V/\mu m$ and 50 $V/\mu m$ was used in this structure, and 130 $nm$ height can be obtained with 14 $\mu m$ thickness.

![Diagram of measurement setup for detecting the first order diffraction.](image)

**Fig. 4.8.** Measurement setup for detecting the first order diffraction.

Applying the AC electric field, the first order diffraction was measured for the normal incident using the setup shown in Fig.4.8. The light source was a He-Ne laser of 632.8 $nm$ wavelength. Fig.4.9 presents the first order diffraction intensity and applied electric field. As strain changes continuously with the electric field in Fig.4.3, intensity can be also controlled continuously without the abrupt change. In addition, it should be noticed that this polymer shows electrostrictive strain ($S$), which is equal to $S = M E^2$, where $M$ is the electrostrictive coefficients, resulting that the first order diffraction intensity changes with the double frequency. With the 9.25 V for the zero order intensity, the maximum 24 % diffraction efficiency was obtained for 100 $V/\mu m$ electric field.
Fig. 4.9. The first order diffraction intensity (solid line) and applied electric field (dot line) for the time.

Fig. 4.10. The change of the deformation profile according to the electric field. This structure is consisted of the 14 µm thickness polymer and electrode/gap/electrode = 5 µm/15 µm/5 µm. Inset is the height between the minimum and the maximum displacement.
Here, since the strain does not change linearly with the electric field, it is interesting to trace the deformation profile for the applied electric field. Shown in Fig. 4.10 is the polymer deformation profile and inset is the deformation height for the applied electric field. In changing the electric field, it can be seen that both the height and shape change. These both changes implicate the possibility of modulation of diffraction angle and efficiency simultaneously.

4.1.5 Conclusion

We introduced the new method for a tunable grating using the high strain of P(VDF-TrFE-CFE) terpolymer. By changing the structure of comb-shape electrode for the bottom electrode and the polymer thickness, it was calculated that we could control the electric field distribution leading the different level of strain for grating. This new tunable grating has the advantage of simple fabrication and easy integration. In our first experimental demonstration, 24 % of the first order diffraction efficiency was observed with 100 V/µm.

4.2 Electrical Tunable Fabry-Perot Interferometer

4.2.1 Fabry-Perot Interferometer

The Fabry-Perot interferometer (FPI) consists of two optically flat plates, coated with semireflecting films and set parallel to each other [10]. Fringes are formed by interference of beams which are multiply reflected between the plates. (Fig. 4.11) To make the analysis as simple as possible, let unit amplitude of the incident light and let \( n_1 = n_2 \), thereby avoiding the need to introduce different reflection and transmission coefficients at each interface. The amplitude transmission coefficients are represented by \( t \), the fraction of the amplitude of a wave transmitted on entering into the film, and \( r' \), the fraction transmitted when a wave leaves the film. The intensity distribution of
Fig. 4.11. Multiple-beam interference from a parallel film.

The resultant transmitted $I_t(\delta)$ light is given by

$$I_t(\delta) = \frac{T^2}{(T + A)^2} \frac{1}{1 + \left[\frac{4R}{(1-R)^2}\right]^2 \sin^2 \left(\frac{\delta}{2}\right)}$$  \hspace{1cm} (4.1)

Here $R$, $r$, and $r'$, where minus sign indicates a phase shift, is the reflectance, $T$, the transmittance, and $A$ the absorbance of the films. The sum $R + T + A$ is equal to unity. $\delta$ is the phase change from an optical path length difference between adjacent rays ($\delta = k_0 \Lambda$). $k_0$ is a positive constant known as the propagation number in vacuum, and $\Lambda$ is the phase difference in optical path length between adjacent rays, which is given by $\Lambda = 2 n_f d \cos \theta_i$. If we introduce the coefficient of finesse $F$, such that

$$F \equiv \left[\frac{4R}{(1-R)^2}\right]$$

and the basic Airy formula, $A(\delta) = [1 + F \sin^2 (\delta/2)]^{-1}$,

$$I_t(\delta) = \frac{T^2}{(T + A)^2} \frac{1}{1 + F \sin^2 \left(\frac{\delta}{2}\right)} = \frac{T^2}{(T + A)^2} A(\delta)$$  \hspace{1cm} (4.2)
Airy formula expresses the transmitted intensity distribution and is plotted in Fig.4.12. If no energy is lost at the surfaces by absorption or scattering, the transmitted and the reflected intensity must be complementary.

![Fig. 4.12. Airy function [11].](image)

The intensity distribution may be examined by considering $I_t$ as a function of phase difference $\delta$. When $\delta = 2\pi m$, the Airy function is equal to unity for all values of $F$ and therefore $r$. When $R$ is small ($\leq 0.1$) and accordingly $F$ is small,

$$I_t(\delta) \approx 1 - F \sin^2 \left(\frac{\delta}{2}\right) = 1 - \frac{1}{2} F (1 - \cos \delta)$$

which are characteristic of only two interfering beams. Thus for low reflectivity the fringes are broad and only in the reflected system do the intensity minima approach zero. For increasing values of $R$ the value of $F$ rapidly becomes larger (e.g. $R = 0.90$, $F = 360$) and the fringes become sharper. In the transmitted system there is appreciable light only in the immediate vicinity of the maxima. Thus the transmitted fringe pattern consists of sharp bright fringes against a greatly reduced background. Correspondingly the reflected pattern is one of narrow dark fringes on a bright background.
For transmitted fringe, the peak intensity of the fringes is given by the factor 
\( \frac{T^2}{(T+A)^2} \). When there is no absorption the efficiency has its maximum value of unity. With increasing absorption the efficiency goes down rapidly. The sharpness of the fringes is determined by the quantity \( F \) which depends solely upon the reflectance \( R \).

The interference fringes are governed by the phase delay between successive beams given by \( \delta = \frac{4\pi}{\lambda_0} n f \cos \theta_i \). For a slightly different wavelength \( \lambda_0 + \Delta \lambda \) another system of interference fringes is similarly formed. At a fixed angle of incidence \( \theta_i \) the difference of phase delays for the two wavelengths is given by

\[
|\Delta \delta| = 4\pi n f \cos \theta_i \frac{\Delta \lambda}{\lambda_0^2}
\]  

(4.4)
supposing the any change of refractive index between the two wavelengths is negligible. The expression \( \Delta \lambda / \lambda_0^2 \) is of course the wavenumber difference between the two wavelengths.

As \( \Delta \delta \) becomes smaller the fringe systems of the two lines become closer and will eventually begin to overlap. For high order of interference, \( 2nf \cos \theta_i = m\lambda_0 \). Then,

\[
|\Delta \delta| \approx 2\pi m \frac{\Delta \lambda}{\lambda_0}.
\]  

(4.5)

In consequence the limiting resolving power is given by

\[
\mathcal{R}_0 = \frac{\lambda_0}{\Delta \lambda} = 2\pi m |\Delta \delta|_{min}^{-1}
\]  

(4.6)

It should be note that the resolving power calculated represents value for perfect plate with small detector aperture. However, in practice plate is degraded by many factors including plate imperfections and finite aperture.
4.2.2 E-O and Strain Tunable FPIs

4.2.2.1 Introduction

Wavelength division multiplexing (WDM) is a promising approach to satisfying the rapidly growing need for increased transmission capacity. Various tunable wavelength filters, a possible key component in WDM, have been energetically investigated including mechanically controlled grating, acoustooptic (AO) filters, silica based integrated Mach-Zehnder (MZ) interferometer filters, a FPI filters. The grating type and AO filters have a large tunable range of more than 100 nm, but their bandwidth is not narrow enough. Silica-based integrated MZ interferometer filters have a very narrow bandwidth, but they require a complicated drive to control several cascaded MZ's [12].

![Figure 4.13](image)

Fig. 4.13. Typical structure of the tunable liquid crystal Fabry-Perot interferometer. AR-antireflecting coating, G-glass substrate, ITO-transparent electrode, M-mirror, A-aligning layers, S-spacer, and LC-liquid crystal. In this arrangement the losses are minimized because the electrode are outside of the resonator formed by the two mirrors [13].

A FPI filter can be made to measure the fine spectral nature of materials with sub-Angstrom wavelength resolution by changing the reflecting mirror quality. FPI filter can
be tuned by changing the optical path length, which can be obtained from the change of the distance and/or reflective index between two reflecting mirrors. For example, Marinelli et al. used the Piezoelectric actuator and controlled the distance between two reflecting mirrors, which were deposited on ZnSe substrate [14]. Piezoelectrically controlled FPI filters have a large tunable range and a narrow bandwidth, but are difficult to fabricate due to very strict alignments. Another different way to change the optical length is to change the angle of incident beam [15]. Liquid crystal(LC) FPI filter is the typical tunable device by changing the reflective index between two reflecting mirrors. As it has several practical advantages, including low voltage drive, a wide tunable range as well as adequate optical filter performance, most researches have been focused on LC-FPI for 1.5 \( \mu m \) optical communication [12, 16–22]. Fig.4.13 is the typical structure of the LC-FPI. Here, it should be noted that as ITO has the plasma frequency in the near-IR region and shows high reflectance due to electronic scattering at 1.5 \( \mu m \) [23], reflecting mirrors are deposited on ITO electrode to minimize the losses [13]. However, it should be also noticed that the effective electric field across the liquid crystal will be reduced due to the voltage dropped in the dielectric reflecting mirrors [24]. Although LC-FPI shows large tunable range, a tuning speed is not faster than a few milliseconds. It also suffers polarization dependence due to the birefringence of the liquid crystals. Polarization independence, an important characteristic for tunable filter in optical-fiber communication systems, is not easily attainable in LC-FPI filters, except for those with additional components or through other means, because of the optical anisotropy caused by alignment of the liquid crystal molecules [21, 22].

Alternatively, recent development in the synthesis of organic polymeric E-O materials have seen the advent of new materials possessing E-O coefficients \( r \approx 100 \) \( pm/V \) larger than that of \( LiNbO_3 \) \( r \approx 32 \) \( pm/V \) and offering the potential of fast response times [25]. These materials are readily available as films by spin-coating on suitable substrates and are therefore ideal for developing thin-film E-O devices. The compatibility of these polymers with a variety of substrates implies that devices based on these thin films can be easily integrated with, for example, silicon and III-V semiconductor device. However, these materials is hard to synthesis and handle so that
it is still far way to make a cheap high performance devices. As discussed in chapter 3, P(VDF-TrFE) based terpolymer has a large strain and E-O effects. In addition, as terpolymer can be easily made into thin film using such as spin coating method, it is very interesting to fabricate a tunable Fabry-Perot interferometer using a large E-O and/or large strain.

4.2.2.2 Fabrication and Performance of E-O and Strain Tunable FPIs

The schematics of the FPIs used in this work are shown in Fig.4.14, where Fig.4.14(a) is for the terpolymer gaped FPI (hereafter referred to as the terpolymer FPI) and Fig.4.14(b) is for the air gap FPI tuned by the electrostrictive strain of the terpolymer which acts as the spacer (hereafter referred to as the strain tuned FPI). In Fig.4.14(a), silver films were employed as both electrodes and mirrors as the silver films were known to exhibit a relatively high reflectivity at 1.5 $\mu$m which is the wavelength used in this investigation [26, 27]. In this device, a 400 Å thick silver film was thermally evaporated onto the transparent (glass) substrate. Then, the terpolymer P(VDF-TrFE-CFE) 68/32/9 mol% was spin-coated on silver film. The films were annealed at a temperature near 115 $^\circ$C for 3 hours to improve the crystallinity. 400 Å silver film was then evaporated on the polymer film to form the mirror and electrode. The thickness of terpolymer film was about 2.5 $\mu$m as measured from Tencor Alpha-step 500 profilometer. The transmittance of the FPI under different applied fields was characterized using FT-IR at wavelengths near 1.5 $\mu$m.

The strain tuned FPI whose structure is shown in Fig.4.14(b) was fabricated as follows. Two transparent glass substrates were prepared. Gold electrode was sputtered on the first substrate with patterned mask which forms the electrode for the terpolymer films. Following that the terpolymer film was spin-coated to the first substrate and followed by the annealing. Typically film thickness was about 1.4 $\mu$m which determines the air gap space in the FP etalon. After removing the terpolymer film with acetone in the central area of the substrate which was not coated with gold electrode, silver mirror was evaporated on the substrate. Here, instead of dielectric multilayer, sliver mirror was employed for easy fabrication. Again gold electrode was sputtered on the top surface
of the terpolymer film to form another electrode. With low viscosity glue, top mirror of the cavity was attached to the terpolymer film. In this configuration, the tuning of the cavity optical pathlength is due to the strain in the terpolymer film. Transmittance spectra were measured using an UV-visible spectrometer (HP 8453A) under applied electric fields.

For characterizing the field induced strain of the terpolymer, thin film was fabricated using solution cast method and then glued to a solid substrate to mimic the mechanical clamping condition of the terpolymer films used in the FPIs. The strain along the thickness direction, which is the longitudinal strain and parallel to the applied electric field direction, was characterized by means of an optical method modified from the piezoelectric bimorph based dilatometer [28]. All the strain responses were measured under a 1 Hz AC electric field.

Shown in Fig.4.15 is the transmittance of the terpolymer FPI under 0 V/µm and 100 V/µm electric field, respectively. For normal incident, the transmittance of the FPI can be expressed as [10, 28];

\[
I_t = \frac{T^2}{(1 - R)^2} \frac{1}{1 + Fs\sin^2 \delta}
\]  

(4.7)
Fig. 4.15. Measured shift of resonant transmission peak of the terpolymer FPI. Solid curve is the transmission spectrum without applied voltage and the dotted curve is the transmission spectrum when the terpolymer film is under 100 V/\mu m.

\[ \delta = \frac{2\pi nl}{\lambda} + \phi, \]

where \( \phi \) is the phase shift introduced by the mirrors, \( l \) is the thickness of and \( n \) is refractive index of the spacer layer (~ 1.45), i.e., the terpolymer film. The coefficient of finesse \( F \) is defined as \( F \equiv \frac{4R}{(1 - R)^2} \), where \( R \) is the reflectivity of the mirror. It is noted that maximum peaks appear when \( \delta = m\pi \), i.e.,

\[ \frac{2\pi nl}{\lambda_1} + \phi = m\pi \] (4.8)

Where \( m \) is integer, and \( \lambda_1 \) is the wavelength of maximum peak. If an electric field is applied to the terpolymer film, maximum peak shifts to another wavelength \( \lambda_2 \) and Eq.4.8 can be modified into

\[ \frac{2\pi [nl + \Delta(nl)]}{\lambda_2} + \phi = m\pi \] (4.9)

where \( \Delta nl \) is the total optical pathlength change due to the application of the electric field. By combining Eq.4.8 and 4.9, total optical pathlength change \( \Delta nl \) can be obtained
from the wavelength difference $\Delta \lambda = \lambda_2 - \lambda_1$,

$$\frac{\Delta (nl)}{nl} = \frac{\Delta \lambda}{\lambda_1}$$

(4.10)

Fig. 4.16. The field induced longitudinal strain under the clamped condition (the lateral strains = 0) as a function of the electric field for the terpolymer P(VDF-TrFE-CFE) 68/32/9 mol%. Data points are shown and solid curve is drawn to guide eyes.

In these experiments, as electric field induces both the refractive index ($\Delta n$) due to the E-O effect and the dimension change ($\Delta l$), total optical pathlength change can be expressed as,

$$\frac{\Delta (nl)}{nl} = \frac{\Delta n}{n} + \frac{\Delta l}{l}$$

(4.11)

The data in Fig.4.15 yields the total optical pathlength change of -0.78 % when the applied field is increased from 0 to 100 V/\mu m. Here, negative sign represents the maximum peak position moving to shorter wavelength with electric field. As it is known that the terpolymer shrinks along the thickness direction with electric field, which has a negative strain of -1.3 % at 100 V/\mu m (see Fig.4.16), a 0.52 % of pure refractive index change ($\Delta n/n$)
can be deduced from Eq.4.11. It is noted that because of the opposite sign, the E-O effect cancels the strain effect, resulting in a smaller total optical pathlength change compared with the optical pathlength change due to pure strain effect.

To fully use the high strain of terpolymer, strain tunable FPI was fabricated. As shown in Fig.4.14(b), instead of using the terpolymer as the cavity of the etalon in Fig.4.14(a), air gap was introduced from removing the polymer between the mirrors. For air gap structure, tunability can be calculated as follows,

\[
\frac{\Delta (nl)}{nl} = \frac{\Delta l}{l} \quad (4.12)
\]

Based on the strain data in Fig.4.16, we calculated the transmittance of strain tunable FPI and compared with the measured transmittance at 100 V/\(\mu m\). As shown in Fig.4.17, these two spectra show good agreement. This result indicates that if we use the maximum strain change of 1.5 % of the terpolymer film under 130V/\(\mu m\) (see Fig.4.16), at near 1.5 \(\mu m\) wavelength the maximum tuning range of about 22.5 nm can be obtained, which is larger than that in the terpolymer FPI. In addition, if a lossless high reflective dielectric multilayer is employed for mirror, a high resolution can be also achieved for the strain tuned FPI (see Fig.4.17(c) which is the spectrum for \(R = 0.96\)).

Finally, we briefly discuss the E-O effect observed in the terpolymer films. The refractive index change measured here can be divided to

\[
\Delta \left( \frac{1}{n} \right)_T = \Delta \left( \frac{1}{n} \right)_S + pS \quad (4.13)
\]

where the first term is the change of refractive index under constant strain of the sample (the primary effect) which is due to the change of the polarizability of the material and the second term is due to the photoelastic effect (the secondary effect) where \(p\) is the elasto-optic coefficient and \(S\) is the corresponding strain [29]. For an isotropic dipolar system, it can be deduced from the Lorentz-Lorenz relation that [30, 31]:

\[
p = \frac{(n^2 + 2)(n^2 - 1)}{3n^4} \quad (4.14)
\]
Fig. 4.17. (a) Calculated transmittance spectra with the strain in Fig.4.16 at 100 $V/\mu m$. 81 % mirror reflectance was assumed for calculation. (b) Measured transmittance spectra at 100 $V/\mu m$. (c) Calculated transmittance spectra near 1.5 $\mu m$. For calculation, maximum 1.5 % strain in Fig.4.16, 1.5 $\mu m$ thickness and 96 % mirror reflectance were used.
For the PVDF terpolymer studied here, \( n \sim 1.45 \), which leads \( p \sim 0.34 \). Using the value of \( S = -1.3 \% \) yields a \( pS \sim -0.44 \% \). Comparing with the experimentally measured data of \( \Delta (1/n)_T^2 = -0.5 \% \) suggests that the photoelastic effect contributes quite significantly to the observed E-O effect.

In summary, we have demonstrated the E-O and strain tunable thin film FPI using the \( P(VDF-TrFE-CFE) 68/32/9 \) mol\% terpolymer films. In using terpolymer film directly as the FP etalon, a -0.78 \% total optical pathlength change was observed under a field of 100 \( V/\mu m \), which is smaller than the total strain of -1.3 \% of the terpolymer film due to the cancellation effect of the E-O effect (0.52 \% pure refractive index change under 100 \( V/\mu m \)). To obtain a large tunability, pure strain tuned FPI was also fabricated. This strain tunable FPI produces larger tuning range (22.5 \( nm \) under 130 \( V/\mu m \)) and provides the freedom to use the high quality dielectric mirrors or other high reflectivity mirrors for high resolution large tunability filters.
References


Chapter 5

Tunable Metallic Photonic Crystals in Infra-Red Frequency

To make a high performance tunable FPI using high strain and/or E-O properties, in which electric field induces the change of dimension or refractive index, electrode and reflecting mirrors should be together on both sides of polymer. Metal electrode has been usually employed for electromechanical applications. However, to use metal for electrode and reflecting mirror at the same time optical properties such as transmittance, reflection, and absorption should be also considered. In this chapter, we will review the optical properties of metal for electrode and reflecting mirror. As P(VDF-TrFE) based polymers can be easily damaged by organic solvents, which are used for conventional lithograph technique, it is not possible to direct apply the conventional photolithograph technique to fabricate patterns on P(VDF-TrFE) based polymers. Here, we will introduce a stencil mask method. Finally, by fabricating the 2-dimensional metallic patterns, the possibility of a strain tunable frequency selective surface will be investigated for a tunable filter application.

5.1 Optical Properties of Metallic Thin Film

The characteristic feature of conducting media is the presence of a number of free electric charges. When light [electric field, \( E(\omega) \)] shines the metal, free electrons move and generate the currents. Current density \( J = \sigma E \), \( \sigma \) is conductivity of metal. So in Maxwell’s equation, dielectric constant for nonconduction media \( \epsilon \) can be replaced with

\[
\tilde{K} = K + \frac{4\pi\sigma}{\omega}
\]  

(5.1)
Since the metal is actually resistive, light is finally converted to thermal energy - ergo absorption. This in turn leads to a complex index of refraction, which is given by

\[ \tilde{n} = n - ik \]  \hspace{1cm} (5.2)

where \( n \) is the real and \( k \) is imaginary indices. The quantities \( n \) and \( k \) may easily be expressed in terms of the materials constants \( K, \mu, \) and \( \sigma \).

\[ \tilde{n}^2 = \mu \tilde{K} = \mu(K + i\frac{4\pi\sigma}{\omega}) \]  \hspace{1cm} (5.3)

Writing the wave equation with the complex index yields

\[ \vec{E} = E_0 e^{i\omega(t-\tilde{n}cy)} = E_0 e^{-\omega k/c y} e^{i\omega(t-\tilde{n}cy)} \]  \hspace{1cm} (5.4)

where \( c \) is the light velocity in vacuum and \( y \) is the propagation vector. As the wave progresses into the conducting media, its amplitude, \( E_0 e^{-\omega k/c y} \), is exponentially attenuated. As the intensity is the square of the amplitude, we have

\[ I(y) = I_0 e^{-\alpha y} \]  \hspace{1cm} (5.5)

where \( I(0) = I_0 \); that is, \( I(0) \) is the intensity at \( y = 0 \) (interface), and \( \alpha \equiv 2\omega k/c \) is called the absorption coefficient or the attenuation coefficient. The intensity will drop by a factor of \( e^{-1} \) after the wave propagated a distance \( y = 1/\alpha \), known as the skin or penetration depth.

For a metal to be transparent the skin depth must be large in comparison to its thickness. The skin depth for metals, however, is exceedingly small. Table 5.1 presents the skin depth for selected metals at a certain wavelength. This small skin depth explains the generally observed opacity of metals, which nonetheless can become partly transparent when formed into extremely thin films. Now if we compute the reflectance using the complex index, \( \tilde{n} = n - ik \),

\[ R = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2} \]  \hspace{1cm} (5.6)
Note that if \( k \) is larger while \( n \) is comparative small, \( R \) in turn becomes large. Fig.5.1 shows the reflectance versus wavelength for different metals.

![Reflectance versus wavelength for different metals](image)

**Fig. 5.1.** Reflectance versus wavelength for silver, gold, copper, and aluminum [2].

If we look into the origin of loss in metal, \( k \) is related with conductivity \( \sigma \) from free electron. The conductivity \( \sigma \), just as the dielectric constant \( K \) which is largely determined by the bound electrons, is not a true constant of the medium, but that it depends on the frequency \( \omega \) of the field. Following the Drude’s model, conductivity due to the electric field can be derived into

\[
\sigma = \frac{Ne^2}{m(\beta - i\omega)}
\]  

(5.7)

Where \( N \) is free electrons per unit volume, \( m \) is mass of electron, \( e \) is the charge of the electron and \( \beta \) is decay constant for electron velocity. The time \( \tau = 1/\beta \) is called the decay time, or the relaxation time. It is typically of the order of \( 10^{14} \) sec. It is thus clear, from Eq.5.7, that when \( \omega \ll \beta \), \( \sigma \) may be approximated by its static value \( \sigma_0 = Ne^2/m\beta \), of course, is real. It is evident that for frequency \( \omega \ll \beta \) is one justified in separating the real and imaginary parts of the complex dielectric constant like Eq.5.2. On the other hand, when \( \omega \gg \beta \) (which is usually the case at optical frequencies), the imaginary part of \( \sigma \) will become large compared to its real part. Then, in Eq.5.1, \( \tilde{K} \) can have
<table>
<thead>
<tr>
<th>Al</th>
<th>Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wavelength</td>
<td>n</td>
</tr>
<tr>
<td>µm</td>
<td>µm</td>
</tr>
<tr>
<td>20.7</td>
<td>62.852</td>
</tr>
<tr>
<td>12.4</td>
<td>34.464</td>
</tr>
<tr>
<td>8.27</td>
<td>18.570</td>
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<td>11.733</td>
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<td>8.586</td>
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<td>3.55</td>
<td>5.438</td>
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<td>3.072</td>
</tr>
<tr>
<td>1.77</td>
<td>1.770</td>
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<td>1.55</td>
<td>1.444</td>
</tr>
<tr>
<td>1.03</td>
<td>1.260</td>
</tr>
<tr>
<td>0.83</td>
<td>2.745</td>
</tr>
<tr>
<td>0.73</td>
<td>2.143</td>
</tr>
<tr>
<td>0.62</td>
<td>1.304</td>
</tr>
<tr>
<td>0.52</td>
<td>0.826</td>
</tr>
<tr>
<td>0.41</td>
<td>0.523</td>
</tr>
<tr>
<td>0.31</td>
<td>0.294</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Au</th>
<th>Ag</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wavelength</td>
<td>n</td>
</tr>
<tr>
<td>µm</td>
<td>µm</td>
</tr>
<tr>
<td>12.4</td>
<td>8.17</td>
</tr>
<tr>
<td>6.20</td>
<td>2.13</td>
</tr>
<tr>
<td>4.14</td>
<td>0.99</td>
</tr>
<tr>
<td>3.10</td>
<td>0.59</td>
</tr>
<tr>
<td>2.48</td>
<td>0.39</td>
</tr>
<tr>
<td>2.07</td>
<td>0.28</td>
</tr>
<tr>
<td>1.77</td>
<td>0.22</td>
</tr>
<tr>
<td>1.55</td>
<td>0.15</td>
</tr>
<tr>
<td>1.24</td>
<td>0.13</td>
</tr>
<tr>
<td>1.03</td>
<td>0.10</td>
</tr>
<tr>
<td>0.87</td>
<td>0.08</td>
</tr>
<tr>
<td>0.69</td>
<td>0.09</td>
</tr>
<tr>
<td>0.62</td>
<td>0.13</td>
</tr>
<tr>
<td>0.52</td>
<td>0.50</td>
</tr>
<tr>
<td>0.41</td>
<td>1.54</td>
</tr>
<tr>
<td>0.31</td>
<td>1.55</td>
</tr>
</tbody>
</table>

Table 5.1. Calculated skin depth of Al, Cu, Au and Ag for selected wavelengths [1].
just real value, which means that metal must be expected to behave essentially as a dielectric without loss. For example, alkali metals are opaque and highly reflecting in the long wavelength, whereas at some critical wavelength in the visible or ultra-violet they become transparent, and have comparatively low absorption [3].

When metal film is used for mirror in FPI, as mentioned in Chapter 4 already, two main factors determine the quality of the fringes. The reflectance defines their sharpness and the efficiency \( \frac{T^2}{(T + A)^2} \) defines their brightness. In general, for a given metal, the reflectance increases steadily whereas the efficiency decreases with the thickness of the layer. A very thin layer has low reflectance and high efficiency whereas a thick layer has a high reflectance and low efficiency. For the purposes of interferometry a compromise has to be found by choosing layers of such thicknesses that they will have useful values of \( R \) and good or tolerable efficiencies. In practice this choice depends on the particular application.

For the FPI applications, aluminum film had been studied for wavelengths in the blue-violet below \( \sim 4800 \) Å and silver film above [4]. For a visible range, Kuhn and Wilson first reported the reliable and detailed investigation of silver films [5]. Typically at 6800 Å an absorption \( A \) of less than 2 % can be achieved for transmission \( T = 10\% \) for freshly prepared films. Nowadays, though most FPIs employ the low loss, high reflective dielectric mirrors, there are some recent papers on using metal mirrors in the visible region. To apply an electric field, Uchiki et al. made Al-polymer-Al structure and characterized the E-O properties measuring the transmittance change with electric field at the visible region [6]. Similarly, Eldering et al. measured the E-O properties of polymer from the transmittance change from the Au-polymer-Au structure using the visible He-Ne laser [7]. For an infrared interferometry, due to the large loss in metal, most metal have not been used for mirrors. However, silver films were investigated in detail in the 1 - 4 \( \mu m \) region by Oppenheim [8]. Different film thicknesses were made and \( R \) and \( T \) were measured at different wavelength. He also calculated theoretical value of efficiency, on the basis of bulk values of the refractive index \( n \) and absorption \( k \). Compared with experimental and calculated data, there was a big difference, which is
due to the well known fact that the optical constants of thin film (= 1000 Å) are radically different from those of the bulk metal.

5.2 Tunable 2-D Metallic Photonic Crystals - Frequency Selective Surface

5.2.1 Introduction

As metals act as a nearly perfect reflectors in IR range and longer wavelength, periodic metallic arrays on dielectric substrates, have been studied for filters and reflectors with a name of 2-D photonic crystal or Frequency Selective Surface (FSS) [9–17]. In principle, the incident electric field induces the currents in the conducting elements and induced currents determine the resonance behaviors associated with element shape, size, lattice geometry, dielectric substrate etc. As illustrated in Fig.5.3, an FSS is usually composed of a periodic array of aperture or patch elements. The aperture-element FSS reflects at low frequencies and transmits at high frequencies (similar to a high-pass filter), whereas the patch-element FSS transmits at low frequencies and reflects at high frequencies (similar to a low-pass filter) [16, 17].

In this section, simple metallic structure will be patterned on PVDF based polymer to form a 2-D photonic crystals using stencil method, and tuning behavior will be investigated.

5.2.2 Tunable 2-D Photonic Crystals

A surface on which two-dimensional (2D) metallic patches or aperture elements are regularly arrayed, the so-called FSS, provides a method for constructing optical filters from a single-layer of metallic structure [17, 18]. FSS was first used in the microwave region for signal processing. In order to make use of FSS in the infrared frequency region, the patch dimensions should be scaled down to the micrometer range to match the wavelength in that frequency region. With continuing advancements in microfabrication, FSS devices as beam splitters, polarizers, output couplers, and Fabry-Perot interferometers in the infrared region have been demonstrated [15, 19–23]. Since the position of the resonant frequency of a FSS depends on the configuration of the metallic
patches and the permittivity of the substrate, tunable FSS devices can be realized by several approaches [24–26]. For instance, FSSs on a ferrite substrate was proposed to exhibit tunable spectra via modifying the permittivity of the substrate [24, 25]. Tunable FSSs have potential applications in waveguide filters and reconfiguration reflector systems. In this section, we report that tunable FSSs can be realized by fabricating the FSS on the electrostrictive (PVDF-TrFE) copolymer films. The high energy electron irradiated PVDF-TrFE copolymer film exhibits giant electrostrictive strain and high E-O effect [27], and can be used as the substrate for tunable FSSs by external field induced strain (electrostriction) and/or refractive index change (E-O effect).

In general, 2D micro/submicro-scale metallic patterns for FSSs are obtained by photolithography techniques, such as UV lithography, electron-beam lithography, soft lithography, and microlens projection lithography [10, 15, 28–31]. However, it is not possible to apply photolithography techniques directly on the PVDF based copolymer films as they will be easily damaged by organic solvents used by the photoresist. In fact, many polymer and organic materials utilized in recent works on the micro-electromechanical systems and micro-opto-electro-mechanical systems are not compatible with the conventional photolithography techniques. A few alternative techniques in which no photoresist layer is applied to a sample substrate, such as nanotransfer printing technique [32], microcontact printing method [33], inkjet printing [34], and stencil mask method [35–37], have been proposed to make micro/nano-scale patterns. Among these techniques, the stencil mask method is the method that does not involve any solvents, substrate pre-treatment, or post-treatment during the fabrication procedure. In that method, the metallic patterns are formed by evaporating metal through a stencil mask. The stencil mask method, which has been used for fabricating metal point contacts and tunneling devices, utilizes ~ 100 nm-thick free-standing Si$_3$N$_4$ films. However, Si$_3$N$_4$ films have low fracture strength, and a free-standing thin Si$_3$N$_4$ film with an area of 5 × 5 mm$^2$ is very fragile. Here, we introduce an alternate stencil mask method to achieve the fabrication of FSSs on PVDF-TrFE substrates. In our experiment, instead of Si$_3$N$_4$, we fabricate the stencil mask with an area of ~ 5 × 5 mm$^2$ from micron-thick photoresist SU-8 films (MicroChem Corp.). The resulting stencil mask is chemically
and thermally stable, and of high mechanical quality. By using this type of mask, we succeed in fabricating strain tunable FSS.

![Diagram](image)

**Fig. 5.2.** The Scheme of the procedure for the fabrication of the SU-8 stencil mask and the deposition of metal through the stencil mask.

There are three major steps in the fabrication of FSSs on PVDF-TrFe films as illustrated in Fig. 5.2. Here we take the FSS's with the element configuration having a 45°-rotated crossed dipole as an example:

1. The SU-8 layer was patterned by photolithography, as shown in Fig. 5.2(a). $\text{Si}_3\text{N}_4$ layers were deposited by low-pressure chemical vapor deposition on both sides
of a $<100>$ silicon wafer. The Si wafer was about 400 $\mu$m thick, and the $Si_3N_4$ was about 100 $nm$ thick. A negative SU-8 photoresist layer was coated on the front side of the wafer. The SU-8 layer was about 2 $\mu$m thick. UV-light exposure patterned the FSS’s patch array on the SU-8 layer. Development in SU-8 developer (MicroChem Corp.) resulted in cross-shaped apertures in the SU-8 layer. After the development, the sample was cured at 180 $^\circ$C for 5 minutes to enhance the SU-8 layer’s mechanical strength.

2. The SU-8 stencil mask was formed by etching, as shown in Fig.5.2(b). A window of $5.5 \times 5.5$ $mm^2$ was patterned on the rear side of the wafer, and the $Si_3N_4$ film within the window was etched by using reactive ion etching (RIE). Then, the bulk silicon layer was etched down through the window using KOH wet etching, and the etching was stopped by the $Si_3N_4$ layer on the front side of the wafer. Finally, RIE was used again to remove the front $Si_3N_4$ layer, forming a suspended SU-8 membrane with an area of about $5 \times 5$ $mm^2$.

3. FSSs on P(VDF-TrFE) films were fabricated by evaporation of Au through the SU-8 mask, as illustrated in Fig.5.2(c). The SU-8 mask was clamped to the PVDF-TrFE substrate. Because there might be some protruded small particles or surface irregularities on the substrate, a few 2 $\mu$m thick polydimethylsiloxane (PDMS) bars were used as spacers between the stencil mask and the substrate before clamping the two together. A 50 $nm$ thick Au film was deposited through the stencil SU-8 mask by thermal evaporation, leaving 2D Au cross arrays on the P(VDF-TrFE) copolymer substrate.

The surface structure of the samples was characterized by a Philips XL20 W scanning electron microscope (SEM). Fig.5.3(a) is the SEM image of the top surface of the stencil SU-8 mask. The arm length ($L$) and the width ($b$) of the crosses are 24 and 4 $\mu$m, respectively. The 2D cross aperture arrays is in a regular square lattice with a spacing of 34 $\mu$m. The whole area of the sample is about $5 \times 5$ $mm^2$, and SEM images are taken at different regions. A statistical comparison between these images exhibits no differences in the size of crosses and the period distance between them, indicating
that the stencil mask is homogeneous over the whole area. For comparison, the SEM image of the SU-8 pattern of the first step is shown in the inset in Fig.5.3(a). The size of crosses and the period distance of the stencil mask are the same as those of the SU-8 pattern whose $Si_3N_4/Si/Si_3N_4$ layers have not been etched away, which indicates that the free-standing SU-8 film has good mechanical strength, and does not bend. In addition, SEM images were taken from the bottom surface of the stencil mask. The size of crosses, especially its arm width, from the bottom view is the same as that from the top view, indicating that the stencil mask made from SU-8 resist has vertical side wall profile. SU-8 resist has excellent imaging characteristics because of its high ultraviolet transparency, which makes it ideally suited for accurate high-aspect-ratio structures.
Fig. 5.3(b) shows the FSS structure on a P(VDF-TrFE) substrate, which is of high quality, as indicated by the smooth edge lines and the sharp angles of the crosses. The SEM measurement could not detect any divergence of the cross size between the patches in Fig. 5.3(b) and the aperture elements in the stencil mask in Fig. 5.3(a).

The resolution of the stencil mask method is limited by the divergence angle of the deposition beam and diffusion of atoms on the P(VDF-TrFE) surface [37], which is in nanometer scale in our case. In the experiment, the P(VDF-TrFE) substrate was placed right above the Au source, and the distance between the source and the substrate is around 40 cm. If the evaporation source is considered as a point source, the divergence angle of the deposition beam will make the deposited FSS patch on the substrate bigger than the corresponding aperture on the mask. The further the region is away from the center, the bigger the divergence angle is. At the edge of the 5 × 5 mm² area of the FSS sample, the broadening of the Au patch is about 25 nm. On the other hand, the P(VDF-TrFE) substrate is kept at room temperature during Au deposition, and the diffusion of atoms on the sample surface is also within nanometer scale. Therefore, the SU-8 stencil mask method is suitable for this μm scale fabrication.

The transmission spectra of the samples are measured at normal incidence by using a Bruker 55 Fourier transform spectrometer (FTIR). The P(VDF-TrFE) copolymer substrate has no characteristic absorption peaks within the measurement region (20-100 μm). All the transmission spectra of the FSS samples are normalized to that of the substrate. The inset of Fig. 5.3(b) shows the transmission responses of the obtained FSS sample, which shows a band-stop behavior. The stop-band is around 59 μm with attenuation in excess of 15 dB. The transmittance at the longer wavelength side is very high, with attenuation less than 1 dB. At the shorter wavelength side, there is a spurious peak around 40 μm. This is due to the finite thickness of the P(VDF-TrFE) film. When the reflections off the back surface of the film may be coherent with the diffractions from the FSS surface, standing-wave field forms within the substrate, which results in the dip in the transmission spectrum. The width of the stop band mainly depends on the lattice spacing, the aspect ratio of the cross, and the morphology of the FSS surface. Both rough edges and surface defects on the metallic patches will broaden the stop band.
The full width at half-maximum of the stop band is about 14 $\mu$m, similar to that from numerical simulation, indicating again a perfect FSS structure.

![Graph](image)

Fig. 5.4. Transmission spectra of an isolated dipole-type FSS before (solid curve) and after (dotted curve) stretching. Inset is the SEM image of the dipole FSS device.

It has been demonstrated that the uniaxially stretched electrostrictive PVDF-TrFE polymer substrate exhibits large transverse strain along the stretching direction ($\sim$ 3-4 % under a field of 100 $V/\mu m$) [27], so the arm length of the dipole along this direction can be tuned in $\sim$ 3-4 %, while the length of another vertical dipole does not vary significant, so the tuning of the resonance frequency along that direction is not obvious. To demonstrate the tuning of the resonance using the uniaxially stretched electrostrictive P(VDF-TrFE) polymer substrate, we fabricated dipole arrays on the P(VDF-TrFE) substrate as shown in the insert of Fig.5.4, which shows the SEM image of the FSS. The arm length and the width of the dipoles as shown in Fig.5.4 are 18 and 2 $\mu m$, respectively. The dipole arrays were deposited along the polymer film stretching direction. Due to the fact that the incident light is randomly polarized, the attenuation due to resonance by the
The dipole array is smaller than that by the crossed dipole array (Fig. 5.3) because the dipole array can only respond to one direction polarization (along the dipole direction). The resonance wavelength ($\lambda$) of crossed-dipole FSS can be given approximately by [31]:

$$\lambda = 2.1L \left( \frac{n_0^2 + n^2}{2} \right)^{1/2}$$  \hspace{1cm} (5.8)

where $L$ is the length of the dipole, and $n_0$ and $n$ are the refractive index of air and the P(VDF-TrFE) copolymer film. The resonance wavelength ($\lambda$) is approximately proportional to the length of the dipole. As shown in Fig. 5.4, when the P(VDF-TrFE) substrate was stretched by 3%, the resonance wavelength shows a red-shift from 47.1 $\mu$m to 48.5 $\mu$m, a shift close to 3% $\lambda$. The results also indicate that the deposited Au films are expanded the same strain level as that of the copolymer substrate (3%), and the stretch does not induce cracks on the Au dipole arrays’ surface. Previous experimental results have also shown that as long as the Au film thickness is thin and is much smaller than that of the substrate, Au films are expanded the same strain level as that of the substrate during the deformation of the substrate at strains of a few percent. [38] When the substrate is released, the resonance wavelength is recovered to its unstrained position.

In summary, we have fabricated FSS on high strain electrostrictive P(VDF-TrFE) copolymer substrate at far infrared frequencies using a stencil mask method and demonstrated the feasibility of strain tuning of FSSs on P(VDF-TrFE) based polymer substrates. The stencil mask method is useful for performing lithography on substrates for which the conventional photolithography technique can’t be used. The method of stencil mask using SU-8 films introduced here alleviates the problem associated with the high tensile stress in the $Si_3N_4$ masks, and hence relatively large stencil masks with high mechanical quality can be fabricated.
References


Chapter 6

Finite Size Effect in Photonic Crystals

6.1 Investigation of Finite Size Effect

6.1.1 Introduction

Photonic crystals (PCs) have been the research interests for more than a decade [1–3]. Most of the efforts were focused on the formation of the stop band as well as its related potential applications. More recently, experimental studies on the passing bands have revealed many interesting phenomena such as the super-prism effect, the near band edge group velocity anomaly and its use for the gain enhancement and low-threshold lasing [4–17]. In addition, at certain portion of dispersion curves the group velocity and phase velocity can be very sensitive to the changes of the unit cell dimension and the refractive index of the constituents of the PCs. The phenomena may be employed for stress sensors, for enhancing E-O effect, and for tunable focal length lens [18, 19]. In the analysis of these phenomena and related applications, the concept of effective refractive index has been introduced [19, 20]. Furthermore, in the literature, the effective refractive index has also been computed assuming PCs as an effective medium [21]. It is the purpose of this chapter to examine in detail of various quantities related to the effective properties for the wave propagations in photonic crystals. Especially, concerning the fact that a practical photonic device is always fabricated from photonic crystals with finite dimensions, we will examine the effect of the finite length (along the wave propagation direction) of photonic crystals on those effective properties [19, 22]. To simplify the discussion, one dimensional (1D) photonic crystals (PCs) are studied. It will be shown that the two end interfaces of a finite length 1D PC have profound effects on the effective properties associated with wave propagations. In the discussions to be presented, the effective refractive index $n_{eff}(g)$ is used to represent the ratio of $c/v_g$, where $c$ is the
vacuum light velocity and $v_g$ is the effective group velocity, and $n_{eff}$ is used for the effective index associated with the effective phase velocity.

6.1.2 Dispersion Relation and Band Structure in 1D Photonic Crystals

We first discuss the band structures of infinitely extended 1D PCs [22–24]. In fact, the derivation here is quite similar to that used to treat the electric transmission line problem [25]. Assuming that the layered structure is periodic in the $x$-direction and homogeneous in the $y$-$z$-plane, as schematically shown in Fig. 6.1, the refractive index profile $n(x)$ of the PC is a step-wise function,

$$n(x) = \begin{cases} 
  n_2, & 0 < x < h_2 \\
  n_3, & h_2 < x < h_3 \\
  n(x + m\Lambda) = n(x) 
\end{cases}$$

(6.1)

where $\Lambda = h_2 + h_3$ is the lattice period of the PC, and $m = \pm 1, \pm 2, \ldots$. The electric and magnetic fields at the two layers are related to each other through the boundary conditions at the interfaces. For the further discussion, it is adequate to assume that the wave propagates along the $x$-direction only and is a harmonic wave. At the interface $I$ of the $(m-1)^{th}$ cell in the layer $h_2$, the total electric and magnetic vectors are $\vec{E}_{m-1}^{(a)}$ and $\vec{H}_{m-1}^{(a)}$ and at the interface $II$ of the $(m-1)^{th}$ cell in the layer $h_3$, the total electric and magnetic vectors are $\vec{E}_{m-1}^{(b)}$ and $\vec{H}_{m-1}^{(b)}$, respectively.

$$\vec{E}_{m-1}^{(b)}(I) = \vec{E}_{m-1}^{(b)}(+)e^{-j\beta_3} + \vec{E}_{m-1}^{(b)}(-)e^{j\beta_3}$$

(6.2)
Fig. 6.1. (a) Schematics of infinite extended one dimensional photonic crystal (1D PC) with the unit cell consisting of two optic films of refractive indexes \( n_2 \) and \( n_3 \) and thickness \( h_2 \) and \( h_3 \), respectively; (b) a finitely extended (along the \( x \)-direction) 1D PC and the refractive index of the external medium interfacing with the PC is \( n_1 \).

Making use of Eq.6.2 and the continuity condition of the tangential components of the \( E \) and \( H \) fields across the interface \( I \) yields

\[
\begin{bmatrix}
E_{m-1}^{(a)} \\
H_{m-1}^{(a)}
\end{bmatrix}
= M' \begin{bmatrix}
E_{m-1}^{(b)} \\
H_{m-1}^{(b)}
\end{bmatrix}
= \begin{bmatrix}
m'_{11} & m'_{12} \\
m'_{21} & m'_{22}
\end{bmatrix}
\begin{bmatrix}
E_{m-1}^{(b)} \\
H_{m-1}^{(b)}
\end{bmatrix}
\tag{6.3}
\]

where \( m'_{11} = m'_{22} = \cos \beta_3, m'_{12} = \sin \beta_3 / Y_3, m'_{21} = -iY_3\sin \beta_3, Y_3 = \sqrt{\epsilon_0 / \mu_0 n_3}, i = \sqrt{-1} \).

Analogously, the relationship between the electric and magnetic fields \( E_{m-1}^{(b)} \) and \( H_{m-1}^{(b)} \) and those at the \( m^{th} \) cell of \( h_2 \) layer \( E_m^{(a)} \) and \( H_m^{(a)} \) can be found as

\[
\begin{bmatrix}
E_{m-1}^{(b)} \\
H_{m-1}^{(b)}
\end{bmatrix}
= M'' \begin{bmatrix}
E_m^{(a)} \\
H_m^{(a)}
\end{bmatrix}
= \begin{bmatrix}
m''_{11} & m''_{12} \\
m''_{21} & m''_{22}
\end{bmatrix}
\begin{bmatrix}
E_{m}^{(a)} \\
H_{m}^{(a)}
\end{bmatrix}
\tag{6.4}
\]

where \( m''_{11} = m''_{22} = \cos \beta_2, m''_{12} = -\sin \beta_2 / Y_2, m''_{21} = -iY_2\sin \beta_2, Y_2 = \sqrt{\epsilon_0 / \mu_0 n_2} \).
Combining Eq. 6.3 and 6.4, the electric vector $E$ and the magnetic vector $H$ in the layer $h_3$ between the $(m-1)^{\text{th}}$ and $m^{\text{th}}$ unit cells are related by the characteristic matrix $M$ of one primary period,

$$
\begin{bmatrix}
E_{m-1} \\
H_{m-1}
\end{bmatrix}
= M
\begin{bmatrix}
E_m \\
H_m
\end{bmatrix}
$$

where $M = M' M'' = 
\begin{bmatrix}
m_{11} & m_{12} \\
m_{21} & m_{22}
\end{bmatrix}$

$$
= 
\begin{bmatrix}
cos\beta_3 cos\beta_2 - \frac{n_2}{n_3} sin\beta_3 sin\beta_2 & -i \left( \frac{1}{2} cos\beta_3 sin\beta_2 + \frac{1}{3} sin\beta_3 cos\beta_2 \right) \\
-i \left( Y_3 sin\beta_3 cos\beta_2 + Y_2 cos\beta_3 sin\beta_2 \right) & cos\beta_3 cos\beta_2 - \frac{n_3}{n_2} sin\beta_3 sin\beta_2
\end{bmatrix}
$$

where $\beta_2 = \frac{2\pi n_2 h_2}{\lambda}$, $\beta_3 = \frac{2\pi n_3 h_3}{\lambda}$, $\lambda$ is the wavelength in the free space $\lambda = \frac{2\pi c}{\omega}$, and $\omega$ is the angular frequency of the wave, respectively. In Eq.6.5, we omitted the superscript $b$ for the sake of simplicity.

For an infinitely extended photonic crystal, according to the Bloch’s theorem, the electric and magnetic fields at the neighboring unit cells are related simply through

$$
\begin{bmatrix}
E_m \\
H_m
\end{bmatrix}
= e^{iK\Lambda}
\begin{bmatrix}
E_{m-1} \\
H_{m-1}
\end{bmatrix}
$$

where $K$ is the Bloch wave number, and $\Lambda$ is the lattice period. It follows from Eq.6.5 and 6.6 that the electric and the magnetic field vectors of the Bloch wave should satisfy the following eigenvalue problem,

$$
\begin{bmatrix}
m_{11} & m_{12} \\
m_{21} & m_{22}
\end{bmatrix}
\begin{bmatrix}
E_m \\
H_m
\end{bmatrix}
= e^{-iK\Lambda}
\begin{bmatrix}
E_m \\
H_m
\end{bmatrix}
$$

(6.7)
The phase factor $e^{-iK\Lambda}$ is thus the eigenvalue of the translation matrix
\[
\begin{bmatrix}
m_{11} & m_{12} \\
m_{21} & m_{22}
\end{bmatrix}
\]
and its solution is
\[
e^{-iK\Lambda} = \frac{1}{2}(m_{11} + m_{22}) \pm \left[\left\{\frac{1}{2}(m_{11} + m_{22})\right\}^2 - 1\right]^{1/2}
\]  
(6.8)

From Eq.6.8, the dispersion relation between $\omega$ and $K$ for the Bloch wave can be found,
\[
K(\omega) = \frac{1}{\Lambda} \cos^{-1}\left[\frac{1}{2}(m_{11} + m_{22})\right]
\]  
(6.9)

Fig. 6.2. Dispersion curves for the 1D PC with the parameters $n_2=1.5$ and $n_3=2.5$ and $n_2 h_2 = n_3 h_3$. $\Lambda = h_2 + h_3$ is the period of the 1D lattice.

Fig.6.2 presents the dispersion curves of $\omega$ vs $K$ (photonic band structure) for waves propagating along the $x$-direction in a 1D photonic crystal where the parameters $n_2 = 1.5$, $n_3 = 2.5$, and $\beta_2 = \beta_3$ are used. These parameters are used for the PCs discussed throughout this paper. Such a 1-D PC can be fabricated, for example, from alternating
polymer and ferroelectric crystal layers to form ferroelectric composites, which have been investigated extensively for more than two decades although at the ultrasonic wave length scale [26, 27]. For such a composite structure, an external applied electric field may change the refractive index through the E-O effect or the dimension of the unit cell through the piezoelectric or electrostrictive effect [28]. As a result, the band structure can be tuned and this phenomenon may be employed to enhance the E-O effect. Analogously, external stress field can also induce band structure changes which may be used as high sensitivity stress sensing devices.

Fig. 6.3. (a) The phase velocity $v_p$ and effective refractive index ($n_{eff}$) and (b) the group velocity $v_g$ and effective refractive index ($n_{eff(g)}$) derived from the dispersion curves in Fig.6.2(for the two lowest frequency bands).
It can be seen that in the 1D photonic crystal, a series of gaps occur, and the lowest bandgap is at frequencies around \( \omega = 0.27 \). From the dispersion curves, both the phase velocity \( (v_p = \omega/K) \) and group velocity \( (v_g = \partial \omega / \partial K) \) can be obtained and the results for the two lowest frequency bands are presented in Fig.6.3. At frequencies far away from the band edge, both the group velocity and phase velocity are nearly constant. Near the band edge, \( v_p \) exhibits a slight increase with frequency while \( v_g \) shows abnormal behavior and significantly slows down. In practice, the phase velocity \( v_p \) is often expressed in terms of the refractive index of the material \( v_p = c/n_{\text{eff}} \), here \( n_{\text{eff}} \) is used to indicate that this is an effective index for the PC and \( c \) is the vacuum light velocity. As shown in Fig.6.3(a), at frequencies far away from the band edge, \( n_{\text{eff}} \) is only weakly frequency dependent. When approaching the bandedge a large change of \( n_{\text{eff}} \) with frequency (frequency dispersion) occurs. Inside the bandgap, \( n_{\text{eff}} \) is actually complex and also exhibits abnormal dispersion.

Besides \( n_{\text{eff}} \) for the refractive index of the phase velocity in a PC, \( n_{\text{eff}}(g) \) was introduced by Sakoda to describe the ratio of \( c/v_g \) [29]. For the 1D PC, \( n_{\text{eff}}(g) \) thus obtained is also presented in Fig.6.3(b). It is apparent that only for the lowest branch of the dispersion curve and at low frequencies (long wavelength limit), \( n_{\text{eff}} \) and \( n_{\text{eff}}(g) \) are the same. Near the band edges \( n_{\text{eff}}(g) \) exhibits precipitous increase and is much larger than \( n_{\text{eff}} \), reflecting the marked slowing down of \( v_g \) [6, 10, 12].

### 6.1.3 The Influence of Finite Size PCs on the Wave Propagation Properties

PCs for practical device applications are often in finite size and for 1D systems dealt with here the most significant effect is from the finite length along the \( x \)-direction, as schematically shown in Fig.6.1(b). One of the interesting questions is how the effective properties discussed in the proceeding section are influenced by the finite dimension of a PC. Furthermore, in many experimental situations, it is the phase delay and the amplitude change of an optic wave when it passes through a PC that is measured. In other words, the effective refractive index of a PC is reflected in its effect on the transmission coefficient \( t \) and reflection coefficient \( r \) for a PC of finite length, respectively. For the discussion here, we will treat \( t \) only (\( r \) and \( t \) are related) and from \( t = |t| e^{i\beta} \),
one can determine the effective refractive index $n_{eff}(t)$ related to the phase velocity $(n_{eff}(t) = c/v_p)$ by assuming the phase factor $\beta = \frac{2\pi}{\lambda} n_{eff}(t) L$ where $L$ is the length along the $x$-direction ($L = N\lambda$). From the effective phase velocity $v_p$, one may estimate the effective group velocity $v_g$ from the well known relation [23]:

$$v_g = v_p + K \frac{\partial v_p}{\partial K}$$  \hspace{1cm} (6.10)

Following the results in the proceeding section, for $N$ periods of layers with alternately refractive indices $n_2$ and $n_3$ and thickness $h_2$ and $h_3$ (Fig.6.1(b)), the characteristic transmittance matrix $M^N$ can be obtained (T-matrix method),

$$\begin{bmatrix} E_1 \\
H_1 \end{bmatrix} = M \cdot M \cdots \cdots M \begin{bmatrix} E_{N+1} \\
H_{N+1} \end{bmatrix} = M^N \begin{bmatrix} E_{N+1} \\
H_{N+1} \end{bmatrix}$$  \hspace{1cm} (6.11)

where $E_1$ and $H_1$ are the total electric field and magnetic field at the interface of the external medium (with refractive index $n_1$) and PC at one end and $E_{N+1}$ and $H_{N+1}$ are those at the interface at the other end. The $N^{th}$ power of an unimodular matrix can be simplified by the Chebyshev Polynomials of the second kind and hence for $M^N$,

$$M^N = \begin{bmatrix} M_{11} & M_{12} \\
M_{21} & M_{22} \end{bmatrix} = \begin{bmatrix} (\cos \beta_2 \cos \beta_2 - \frac{2a}{n_3} \sin \beta_2 \sin \beta_2) U_{N,-1}(a) - U_{N,-2}(a) & -i (\frac{1}{2} \cos \beta_2 \sin \beta_2 + \frac{1}{3} \sin \beta_2 \cos \beta_2) U_{N,-1}(a) \\
-\frac{a}{n_3} (Y_3 \sin \beta_2 \cos \beta_2 + Y_3 \cos \beta_2 \sin \beta_2) U_{N,-1}(a) & (\cos \beta_2 \cos \beta_2 - \frac{a}{n_3} \sin \beta_2 \sin \beta_2) U_{N,-1}(a) - U_{N,-2}(a) \end{bmatrix}$$

where, $a = \cos \beta_2 \cos \beta_2 - \frac{1}{2} \left( \frac{n_3}{n_2} + \frac{n_2}{n_3} \right) \sin \beta_2 \sin \beta_2$, $U_N(a) = \frac{\sin((N+1)\cos^{-1}a)}{\sqrt{1-a^2}}$ [23]. To find the transmission (or reflection) coefficient, we assume that $E_1$ and $H_1$ consisting of incident ($E_1(+)$ and $H_1(+)$) and reflected waves ($E_1(-)$ and $H_1(-)$) so that $E_1 = E_1(+) + E_1(-)$, $H_1 = H_1(+) + H_1(-) = \sqrt{\frac{\varepsilon_0}{\mu_0}} n_1 \{E_1(+) - E_1(-)\}$ and $E_{N+1}$ and $H_{N+1} (H_{N+1} = \sqrt{\frac{\varepsilon_0}{\mu_0}} n_1 E_{N+1})$ consisting of transmitted wave only. It follows that the transmission coefficient $t$ of such a system is,

$$t = |t| e^{i\beta} = \frac{2n_1}{(M_{11} + M_{12} n_1) n_1 + (M_{21} + M_{22} n_1)}$$  \hspace{1cm} (6.12)
and from the phase shift $\beta = \frac{2\pi}{\Lambda} n_{\text{eff}}(t)L$, $n_{\text{eff}}(t)$ can be found where $L$ is the total thickness of the PC ($L = N\Lambda$) in the $x$-direction.

![Graph](image)

Fig. 6.4. (a) Transmittance and (b) Effective refractive index ($n_{\text{eff}}(t)$) for a finite size PC with $N=4$ and $n_1=1$ where $N$ is number of the unit cells in the PC. For the comparison, the effective refractive index $n_{\text{eff}}$ derived from the dispersion curves (Fig.6.3(a)) is also presented (dash curves in (b)).

We evaluated $t$ using the T-matrix method for several length of PC along the $x$-direction to obtain $n_{\text{eff}}(t)$. Fig.6.4,6.5, and 6.6 show the calculated $n_{\text{eff}}(t)$ for PCs with different number of layers ($N = 4$, $20$, and $100$, respectively). In the calculation, $n_1=1$
Fig. 6.5. (a) Transmittance and (b) Effective refractive index \(n_{\text{eff}}(t)\) of a finite size PC with \(N=20\) and \(n_1=1\). For the comparison, the effective refractive index \(n_{\text{eff}}\) derived from the dispersion curves (Fig.6.3(a)) is also presented (dash curves in (b)).

(a PC in air) was used. For comparison, \(n_{\text{eff}}\) obtained from the dispersion curve is also presented in the figures. In addition, the transmittance \(|t|^2\) for the corresponding PCs is also presented. As shown in the figures, \(n_{\text{eff}}(t)\) exhibits oscillations with the frequency, corresponding well with the oscillation in the transmittance. By using \(n_{\text{eff}}\) obtained from the dispersion curve, it can be shown that at low frequency region (long wavelength), the frequency interval between the neighboring maximums or minimums
Fig. 6.6. (a) Transmittance and (b) Effective refractive index ($n_{eff}(t)$) of a finite size PC with $N=100$ and $n_1=1$. For the comparison, the effective refractive index $n_{eff}$ derived from the dispersion curves (Fig.6.3(a)) is also presented (dash curves in (b)).

follows the relationship of

$$\Delta \omega = \frac{\pi c}{L n_{eff}}$$

(6.13)

in agreement with Sakoda and indicating that such oscillation originates mainly from the interference due to the multi-reflection from the two end interfaces of the PC [29]. Close to the band edges, the frequency interval $\Delta \omega$ between the neighboring maximums or minimums becomes smaller and does not match the relation described by Eq. 6.13, indicating the effect of individual internal layers becomes important as one would
Fig. 6.7. Effective refractive index ($n_{\text{eff}}(\omega)$, group velocity) calculated for finite size PCs: (a) $N=4$, $n_1=1$, (b) $N=20$, $n_1=1$, and (c) $N=100$, $n_1=1$. Dash curves are $n_{\text{eff}}(\omega)$ determined from the dispersion curves (Fig.6.3(b)).
Fig. 6.8. (a) Transmittance and (b) Effective refractive index ($n_{\text{eff}(t)}$) for a finite size 1D PC of $N=4$ and $n_1=1.94$. For the comparison, the effective refractive index $n_{\text{eff}}$ derived from the dispersion curves (Fig.6.3(a)) is also presented (dash curves in (b)).

expect. Analogously, one can also make use of Eq.6.10 and the data in Fig.6.4 to 6.6 to determine the effective group velocity as well as the related $n_{\text{eff}(g)}$ for a finite length PC. Those are presented in Fig.6.7. Due to the added reflections at the two end interfaces, the effective group velocity and $n_{\text{eff}(g)}$ for the finite size PC also exhibits oscillation. In addition, $n_{\text{eff}(g)}$ can become much larger than $n_{\text{eff}(t)}$ at near the bandedge, in analogy to the divergence of $n_{\text{eff}(g)}$ in an infinitely extended PC at the bandedge. As the length of the PC becomes long such as when $N = 100$ (Fig.6.6), the oscillation amplitude in
Fig. 6.9. (a) Transmittance and (b) Effective refractive index ($n_{\text{eff}(t)}$) for a finite size 1D PC of $N=20$ and $n_1=1.94$. For the comparison, the effective refractive index $n_{\text{eff}}$ derived from the dispersion curves (Fig. 6.3(a)) is also presented (dash curves in (b)).

$n_{\text{eff}(t)}$ decreases and $n_{\text{eff}(t)}$ approaches that obtained from the dispersion curve for an infinitely extended PC.

To further illustrate the effect of the two end interfaces, we also evaluated the transmission coefficient $t$ based on T-matrix method for the finite length PCs interfacing with an optical medium of $n_1 = \sqrt{n_2 \cdot n_3} = 1.94$. It is expected that the improved refractive index matching at the two end interfaces will significantly reduce the reflection at the two end interfaces. The transmittance and $n_{\text{eff}(t)}$ are presented in Fig. 6.8 and 6.9 for $N = 4$ and $N = 20$ two cases. Indeed, at frequencies away from the bandedge there is almost no sign of the interference induced oscillations in both the transmittance and
$n_{eff(t)}$ (related to the phase velocity), due to the much reduced reflections at the two end interfaces of the PCs. When the frequency approaches the bandedge, the interference induced oscillation occurs in both the transmittance and $n_{eff(t)}$, indicating the non-uniform structure of the PC now becomes increasingly important as the wavelength of the optic wave becomes comparable with the lattice constant of the PC. However, compared with the data in Fig.6.4 and 6.5, the oscillation amplitude is still much smaller.

The results clearly demonstrate the importance of the two end interfaces of a finite size PC on the effective properties of photonic crystals, which could be quite different from those deduced from an infinitely extended photonic crystal.

### 6.1.4 The Wave Propagation in a Single Layer with the Effective Properties of the PCs

In several publications, a PC is assumed as an effective medium with an effective refractive index $n_{eff}$ and effective thickness $N\Lambda$ (single layer assumption) [20, 21]. To examine this point, we calculated the transmission coefficient for a single layer which possesses the effective properties of the PC as derived in the section 6.1.2. We will compare the results here with those in the section 6.1.3. For an optic layer (refractive index $n_{eff}$ and length $L$ ($L = N\Lambda$)) interfacing with an external medium of refractive index $n_1$, the transmission coefficient is given by

$$t = \frac{2n_1n_{eff}}{2n_1n_{eff}\cos\beta + i\left(n_1^2 + n_{eff}^2\right)\sin\beta} \quad (6.14)$$

Fig.6.10 and 6.11 are the transmittance and $n_{eff(i)}$ (from $t = |t|e^{i\beta}$ and $\beta = \frac{2\pi}{\Lambda}n_{eff(i)}$ where $i$ indicates the parameter is from a single layer interference) for a film with $N = 4$ and $n_1 = 1$ and $N = 20$ and $n_1 = 1$, respectively. The results can be compared with the data presented in Fig.6.4 and 6.5. At the frequencies in the bandgap, the $n_{eff}$ is a complex number and no calculation is made here in Fig.6.10 and 6.11. Both the transmittance and $n_{eff(i)}$ exhibit oscillations, consistent with the conclusion that the oscillation observed in finite size PCs is mainly due to the multiple reflections at the two
Fig. 6.10. (a) Transmittance and (b) Effective refractive index ($n_{\text{eff}}$) calculated from a single layer with the effective refractive index $n_{\text{eff}}$ (Fig.6.3(a)) and thickness $L=4\Lambda$ (to be compared with the results in Fig.6.4).

end interfaces. At the reduced frequencies $\frac{\omega\Lambda}{2\pi c}$ below 0.1, the transmittance and $n_{\text{eff}}(i)$ in Fig.6.10 and 6.11 match quite well with those in Fig.6.4 and 6.5, which indicates that a PC can be treated as an effective medium at frequencies not too close to a bandgap. At the frequencies near the bandgap, the oscillation in the transmittance and $n_{\text{eff}}(t)$ in Fig.6.4 and 6.5 is much larger, which is caused by the multiple reflections at the internal interfaces in the PCs.
Fig. 6.11. (a) Transmittance and (b) Effective refractive index ($n_{\text{eff}}$) calculated from a single layer with the effective refractive index ($n_{\text{eff}}$) (Fig. 6.3(a)) and thickness $L=20\Lambda$ (to be compared with the results in Fig. 6.5).

### 6.1.5 Conclusion

The effective properties associated with the propagation of electromagnetic waves in photonic crystals are analyzed for 1D photonic crystals to illustrate the difference in those properties between infinitely extended and finite size photonic crystals (along the wave propagation direction). In infinitely extended PCs, at the long wavelength region, the phase velocity and group velocity are the nearly the same. As the bandgap is approached, the phase velocity decreases slightly while the group velocity exhibits a marked slowing down (the effective index $n_{\text{eff}}(g) = c/v_g$ approaches $\infty$). For finite
length (along the wave propagation direction) PCs, we evaluated the transmission coefficient $t$ and from that, the effective phase velocity and refractive index associated with it can be extracted (the results are the same as that from the reflection coefficient $r$). It is shown that the multiple reflections at the two end interfaces of a PC result in an oscillation in both the transmittance and $n_{\text{eff}}$. At the frequencies far away from the bandgap, the oscillation in both the transmittance and $n_{\text{eff}}$ can be modeled by assuming the PC as an effective medium with the effective properties derived from the dispersion curves of the corresponding infinitely extended PC. As the frequencies approach the bandgap, the oscillation in both the transmittance and $n_{\text{eff}}$ are enhanced markedly due to the reflections from the internal interfaces in the PC, which eventually result in the formation of the bandgap that normally does not exist in a single layer optical film. Therefore, in large frequencies regions away from the long wavelength region, a PC can not be simply approximated as an effective medium. Furthermore, the oscillation in $n_{\text{eff}}$ subsides as the length of the PCs increases. For instance when $N = 100$, $n_{\text{eff}}$ from the transmission coefficient becomes nearly the same as that derived from the dispersion curve of an infinitely extended PC.

6.2 Finite-Size Effect on Highly Dispersive PC Optical Components

Photonic crystals (PCs) exhibit many unique features that are very attractive for photonic integrated circuits [1, 3, 4], including the existence of photonic band-gaps (PBG), ultra-refraction, super-prism effect, and high dispersion in some frequency regions [4, 19, 22, 30–35]. Near the Brillouin zone edge, the effective refractive index $n_{\text{eff}}$ of PCs exhibits a strong frequency dependence, which can be utilized to construct highly dispersive optical devices and components. Such devices include high-resolution wavelength-division multiplexers/demultiplexers that have great potential for application in the telecommunication industry. Lin et al. proposed the concept of a PBG prism and realized it in the millimeter-wave spectral regime by arranging cylindrical alumina-ceramic rods parallel to one another in a triangular lattice structure [34]. Nelson et al. demonstrated experimentally that a 30-period one-dimensional (1D) GaAs/AlGaAs stack structure can spatially separate two beams with a 4 nm wavelength separation by
more than their beam width [35]. In this section, we propose the concept of a highly dispersive 1D PC thin lens, and study the effect of the finite-size along the propagation direction on the properties of the PC thin lens.

![Graph showing the focal length of an ideal 1D PC lens versus wavelength.](image)

**Fig. 6.12.** The focal length of an ideal 1D PC lens versus wavelength (solid curve). The 1D PC is a stack of alternating Si (78 nm thick, $n = 3.4$) and SiO$_2$ (182 nm thick, $n = 1.45$) layers, $a = 260$ nm is the period of the 1D lattice, and the spherical radius $R$ is 5 mm. These parameters are used for the PC lens discussed through the letter. The inset is the schematic of the 1D PC lens. The effective refractive index ($n_{eff}$) of the bulk PC is also shown (dash curve).

We begin by calculating the focal length of a thin lens fabricated from a 1D PC as shown in the inset of Fig. 6.12. Such a 1D PC thin lens can be made by depositing alternating layers of Si and SiO$_2$ on a SiO$_2$ substrate, and then the surface is polished to
form the spherical lens. The layers of Si and SiO₂ in the 1D PC alternate along the z-axis, which is also the optical axis of the lens (the x- and y-directions are in perpendicular to the z-direction and not shown in the Fig.6.12). When a unit-amplitude plane wave is normally incident on the surface of the PC lens, the field distribution at the plane \( z = z_0 \) is [36],

\[
E(x, y, z_0) = |t| \cdot \exp \left\{ -2j2\pi n_0 \cdot \left[ \Delta_0 - \Delta(x, y) \right] / \lambda \right\} \cdot \exp \left[ -j \cdot \beta(\Delta, \lambda) \right]
\] (6.15)

where \( |t|, n_0 \) and \( \lambda \) are PC’s transmission coefficient, the refractive index of air, and wavelength of light incident on the lens. \( \Delta_0 \) and \( \Delta(x, y) \) are the thickness of the lens at coordinates (0, 0) (center of the lens) and (x, y), respectively. \( \Delta(x, y) = Na \), where \( N \) is the number of periods at (x,y) and \( a \) is the lattice constant of the 1D PC. \( \beta(\Delta, \lambda) \) is the phase delay as the light propagates through a \( \Delta(x, y) \) thickness of PC. \( \beta(\Delta, \lambda) \) is a function of \( \Delta(x, y) \) and wavelength, and we define the effective refractive index \( (n_{eff}) \) as \( n_{eff} = \lambda \beta/(2\pi\Delta) \) [37–39]. If the PC can be approximated as infinite in extent along the z-direction \( (i.e., \Delta(x, y) = \infty) \), \( n_{eff} \) is thickness independent and can be obtained from the dispersion relation between the frequency \( \omega \) and the wave vector \( K \). From the dispersion relation, the phase velocity \( (v_p = \omega/K) \) can be obtained, and the phase velocity \( v_p \) can be expressed in terms of the effective refractive index of the material \( v_p = c/n_{eff} \), where \( c \) is the vacuum light velocity [37–39]. In this case, the property of the PC lens is similar to those of a traditional thin lens. The focal length of the lens is \( R/(n_{eff} - n_0) \), where \( R \) is the radius of curvature of the PC surface (Fig.6.12), and \( n_0 \) is the refractive index of air. The focal spot size is determined by the Fraunhofer diffraction pattern of a circular aperture, and the radius of the first bright ring can be written as \( 0.61f\lambda/A \) by Airy criterion [23], where \( A \) is the radius of the aperture of the PC lens.

The values of \( n_{eff} \) and focal length versus wavelength are shown in Fig.6.12 for an ideal PC lens with an infinite thickness. At frequencies removed from the band edges, \( n_{eff} \) is nearly constant. However, near the band edges, \( n_{eff} \) exhibits anomalous behavior and increases by as much as 20%. This high dispersion of \( n_{eff} \) with frequency...
Fig. 6.13. The calculated $n_{\text{eff}}$ for PCs with different number of layers (N=20, 50, and 80 respectively). For comparison, $n_{\text{eff}}$ for an infinitive PC is also presented in the figure (N=∞, dash curve).

introduces large differences in focal length for light with wavelengths near the band edges. At 1.53 $\mu$m, the difference of focal length ($\Delta f/f$) is about 0.07 % for two light beams with a wavelength difference of 1 nm. Using the Rayleigh criterion that two light beams of equal intensity are considered to be just resolved when the first intensity maximum of one coincides with the first intensity minimum of the other, this PC lens with a 1 mm aperture size ($A = 0.5$ mm) can resolve two light beams with wavelength difference of 2.7 nm. Moreover, the focal length is also very sensitive to the changes of the unit cell dimensions, and this can be used for tunable focal length PC lens. At 1.53 $\mu$m, if the thickness of one component (the low index layer in our example) is strained
Fig. 6.14. The $n_{\text{eff}}$ for PCs at a fixed wavelength $\lambda (1.53 \, \mu\text{m})$ as a function of number of layers $N$. The horizontal dash line is the $n_{\text{eff}}$ value of an infinitive PC.

by 5 %, which can be achieved readily with the electrostrictive polymers [40], the focal length ($\Delta f/f$) can be tuned by 2.9 %.

In practice, the number of periods $N$ of a PC for real devices is always finite and sometimes can be quite small. Contrary to the case of an infinitely extended PC, $n_{\text{eff}}$ is not a constant when $N$ varies. For a PC with finite thickness, we use the T-matrix method to determine $\beta$ and $n_{\text{eff}}$ as a function of wavelength. The results in Fig.6.13 show the values of $n_{\text{eff}}$ determined for PCs with different numbers of periods ($N = 20, 50, \text{and} 80$). For comparison, the values of $n_{\text{eff}}$ obtained from the dispersion curve (i.e., ideal PC with $N = \infty$) is also presented by the dashed line. As shown in Fig.6.13, the value of $n_{\text{eff}}$ for finite size PC oscillates above and below the value obtained for the ideal PC. The magnitude and period of the oscillations increase as the number of
Fig. 6.15. The intensity distribution around the focal point for a fixed wavelength $\lambda = 1.53 \ \mu m$.

periods in the PC decreases. Fig. 6.14 shows the value of $n_{\text{eff}}$ at a single wavelength $\lambda = 1.53 \ \mu m$ as a function of the number of periods $N = 1$ to 100 in the PC; the value of $n_{\text{eff}}$ for the ideal PC with $N = \infty$ is given by dashed line. At $\lambda = 1.53 \ \mu m$, the amplitude of the oscillation about the constant value of $n_{\text{eff}}$ determined from the ideal PC are 0.037, 0.014, and 0.0092 for PCs with $N = 20$, 50, and 80, respectively.

To determine the effect of the variation of $n_{\text{eff}}$ with $N$ on the focal spot size, the PC lens is divided into a series of rings with their common center at the optical axis as shown in the inset of Fig. 6.15. The thickness of the lens along each radial segment decreases from the center to the edge of the lens as the number of periods $N$ of the PC decreases. Because $n_{\text{eff}}$ at a given wavelength depends on the lens thickness (Fig. 6.14), light beams of a single wavelength will not be focused to the mean focal point
determined for the case of an ideal PC. Instead, the focal point will be smeared out around the mean focal point due to the oscillatory behavior of $n_{\text{eff}}$ with $N$ for small values of $N$. Fig. 6.15 illustrates the $z$-directed light intensity distribution around the mean focal point at $\lambda = 1.53 \mu m$ for lenses with maximum thickness along the principal optical axis equivalent to $N = 100$ and 200. The distributions are close to a Gaussian function, and the width of the focus spot of the thinner lens ($N = 100$) is larger than that of the thicker lens ($N = 200$), as expected. The full width at half maximum ($\delta f/f$) is about 0.9% and 0.5% for the thinner lens and the thicker lens, respectively. These results show that for a finite size PC lens, the size of the focus is no longer determined by Airy criterion. Instead, the finite-size effect determines the focal spot size, which is broadened significantly relative to that of an ideal PC. This reduces significantly the wavelength sensitivity of the PC lens. At $\lambda = 1.53 \mu m$, a PC thin lens with $N = 100$ at the center can only separate beams with wavelength difference of 13.5 nm. In contrast, a PC lens with $N = 1000$ approaches the sensitivity of an ideal PC lens, and can separate beams with a wavelength difference of only 2.7 nm.

The origin of the oscillation of $n_{\text{eff}}$ with $N$ in finite size PCs can be understood as follows. To simplify the analysis, the $N$-period 1D PC $<\text{HLHL.HL}>$ is approximated as $<\frac{L}{2}H\frac{L}{2}L\frac{L}{2}H\frac{L}{2}L\cdots H\frac{L}{2}>$, where $H$ and $L$ denote Si and SiO$_2$ layer thickness. $L/2$ denotes half-layer SiO$_2$. Using this notation, the symmetrical combination of thin-film layers $<\frac{L}{2}H\frac{L}{2}>$ can be seen as the new periodic unit that is mathematical equivalent to a single layer (ESL) with an equivalent index $E$ and thickness $a'$, and thus, the $N$-period multilayer can be equivalent to a single layer of thickness $Na'$ and index $E$. [41] $a'$ is chosen such that the equivalent phase thickness $2\pi Ea'/\lambda$ is nearest to the actual phase thickness of the combination $\frac{L}{2}H\frac{L}{2}$. The equivalent index $E$ is much larger than the refractive index of air ($n_0$) or SiO$_2$ ($n_s$) near the bandedge due to the reflections from the internal interfaces in the PC. The value of $E$ is 5.4 at $\lambda = 1.53 \mu m$. The reflections at the two interfaces air/ESL interface ($r_1 = (n_0 - E)/(n_0 + E)$) and the glass/ESL interface ($r_2 = (n_s - E)/(n_s + E)$) are so large that light with near band edge wavelength will be reflected multiple times as it passes through the thin film. In this case, phase delay $\beta$
and \( n_{\text{eff}} \) are given by, [42]

\[
\beta = 2\pi N \frac{Ea'}{\lambda} + \arctan \frac{r_1 r_2 \sin 2\gamma}{1 + n_1 n_2 \cos 2\gamma} \\
n_{\text{eff}} = Ea' + \frac{\lambda}{2\pi N a} \arctan \frac{r_1 r_2 \sin 2\gamma}{1 + n_1 n_2 \cos 2\gamma} 
\]

(6.16)

where \( \gamma \) is \( 2\pi \cdot 2NEa'/\lambda \). In Eq. (3), the first term of \( \beta \) is linear with thickness, and the second term results from the multiple-reflection at the air/ESL and glass/ESL interfaces. If \( N \) is large \((N = \infty)\), the second term of \( n_{\text{eff}} \) is negligible relative to first term, and \( n_{\text{eff}} \) becomes thickness independent. If \( N \) is finite, the second term cannot be neglected and \( n_{\text{eff}} \) is thickness dependent. This analysis indicates that the finite-size effect is due to the additional phase delay introduced by multiple-reflections from the internal interfaces in the PC and the two end interfaces of the PC. Hence the finite-size effect can be reduced if the PC lens is surrounded in an optical medium with an index close to the equivalent index \( E \), or the two composites of the 1D PC have a lower index contrast.

It should be pointed out that the effective index approach used in the present work only satisfies the particular conditions where the incident beam is a plane wave that propagates along the symmetry axis of the 1D PC. In this special case, the phase velocity \((v_p = \omega/k)\) and the group velocity velocity \((v_g = \partial \omega/\partial k)\) are parallel, and an effective refractive index can be defined. If the incident beam does not propagate along a symmetry axis, the correct approach for analyzing propagation in PCs should involve the concepts of dispersion surfaces and group velocity. The propagation direction of the incident wave in a PC should be obtained through the momentum conservation rule, and it is parallel to the group velocity \( v_g \) and not to the phase velocity \( v_p \) [43].

In summary, by making use of the large near bandedge of the effective refractive index of PCs, an ideal PC thin lens with an infinitely number of periods along the wave propagation direction can separate two beams with a 2.7 nm wavelength difference, which can be used as a effective wavelength-division demultiplexer. The finite-size effect induces oscillation in the effective refractive index of PCs, resulting in significant broadening of focal spot size along the optical axis of the lens and a corresponding reduction in the wavelength sensitivity of the lens. The oscillatory feature of \( n_{\text{eff}} \)
results from the additional phase delay due to the multi-reflection from the internal interfaces in the PC and the two end interfaces of the PC.
References


Relaxor ferroelectric materials, Lead Magnesium Niobate-Lead Titanate (PMN – PT) single crystals and poly(vinylidene fluoride-trifluoroethylene) [P(VDF – TrFE)] based polymers, have been well known to possess high performance electro-mechanical properties. As large strain accompanies with the structural changes with electric field, large electro-optic (E-O) effects can be also expected from these materials. In this thesis, E-O properties of these ferroelectric relaxor materials were characterized. By combining the E-O effect and/or the electro-mechanical properties, tunable optical devices, tunable grating, tunable Fabry-Perot interferometer, and metallic 2-dimensional photonic crystals, were investigated. For better understanding of the optical properties, calculations were conducted in terms of photonic crystals.

The tetragonal 0.62PMN-0.38PT single crystals poled along the $<001>$ direction (the spontaneous polarization direction) have a stable single domain and show high transparency from the visible to Near-IR range. Using the Mach-Zender interferometry method, large linear E-O coefficients $r_{33} = 70 \text{ pm/V}$, $r_{31} = 25 \text{ pm/V}$, and $r_{15} = 558 \text{ pm/V}$ were characterized. In addition, $r_{33}$ and $r_{31}$ of crystals of this composition show a slight increase with temperature, which originates from the temperature dependence of polarization and dielectric constant.

The E-O properties of the ferroelectric relaxor P(VDF-TrFE) based terpolymer were investigated in the wavelength region from 3 $\mu$m to 5 $\mu$m. A large Kerr effect was observed where a refractive index change of -2.6 % can be induced under an electric field of 80 V/$\mu$m. When combined with the electrostrictive strain, the terpolymer film exhibits a total -5.6 % optical pathlength change under a field of 80 V/$\mu$m. Calculations based on density functional theory suggest that such a large E-O effect was caused mainly by the reorientation of the C-F dipoles under external field in the crystalline region. Furthermore, the results support the notion that in the ferroelectric relaxor terpolymer,
there exist nano-polar regions which undergo reorientation under external field and generate the observed electrostrictive strain and E-O responses.

Large strain of P(VDF-TrFE-CFE) terpolymer was utilized to fabricate the tunable light graings. The electric field distribution was modulated by changing the structure of comb-shape electrode for the bottom electrode and the polymer thickness. Depending on the electric field distribution, polymer shows the different level of deformation and generates the grating. This new tunable grating has the advantage of simple fabrication and easy integration. In our first experimental demonstration, 24 % of the first order diffraction efficiency was observed with 100 V/μm.

In addition, by utilizing the large strain and E-O effect of a PVDF based terpolymer, electrical tunable Fabry-Perot interferometers (FPIs) were fabricated and characterized. Using pure strain tuning, which for the terpolymer films under mechanically clamped condition is 1.3 % under 100 V/μm field, we show that a tunable range of 22.5 nm can be obtained at wavelengths near 1.5 μm. Due to the opposite sign of the field induced strain and the refractive index change from the E-O, the FPI using a terpolymer film directly as the cavity of the etalon shows a smaller tunability (0.78 % under 100 V/μm).

As it is not possible to directly apply the conventional photolithograph technique to fabricate patterns on P(VDF-TrFE) based polymers, we investigated a stencil mask method. By fabricating the 2-dimensional metallic patterns, the possibility of a strain tunable frequency selective surface was also explored.

To understand and utilize the optical properties near bandedge in photonic crystals, calculations on the effective properties associated with the propagation of electromagnetic waves were conducted for the photonic crystals with finite size. It is shown that the multiple reflections at the two end interfaces of a PC result in an oscillation in both the transmittance and phase velocity (and also the group velocity as well as the effective refractive indexes $n_{\text{eff}}$), which are often determined experimentally from the transmitted or reflected wave. At the frequencies far away from the bandgap, the oscillation in both the transmittance and $n_{\text{eff}}$ can be modeled by assuming the PC as an effective medium with the effective properties derived from the dispersion curves.
of the corresponding infinitely extended PC. As the frequencies approach the bandgap, the oscillation in both the transmittance and $n_{eff}$ are enhanced markedly due to the reflections from the internal interfaces in the PC. The results clearly demonstrate the importance of the two end interfaces of a finite size PC on the effective properties of photonic crystals, which could be quite different from those deduced from an infinitely extended photonic crystal. For device applications, finite size effect was applied to design the photonic crystals lenses. Our calculations show that practical PCs of finite thickness exhibit an $n_{eff}$ with a thickness dependent oscillatory behavior. This results in broadening of the focal spot size along the optical axis when the number of periods in the PC lens is small, which limits the sensitivity of the lens.

An extension of the present study can be made into areas related to this work but not yet explored. Following are a few suggested topics for future research.

- Large strain and E-O effect of the P(VDF-TrFE) based terpolymer can be used for tunable photonic crystals. PCs with semiconductor and air hole are being fabricated in many places [1–5]. Attaching the large strain polymer actuator demonstrated in our group [6], pumping in or out the dielectric liquid into air hole can switch the light. For the large E-O effect, electric tunable PCs can be realized by infiltrating the polymer into air hole and applying the electric field on polymer. In reality, fabrication is so hard that precise simulation should be performed before making real devices.

- To increase the efficiency and to reduce the driving voltage of the tunable grating, new materials, which has large strain, should be developed. Since polymer usually has low dielectric constant, composite with large dielectric constant is one of the examples for increasing the dielectric constant and strain [7, 8]. Since rough polymer surface scatters light, smooth film surface is essential for a high efficiency tunable grating. It is known that depending on the process conditions, such as solvation temperature, concentration, and humidity, poly(vinylidene
fluoride) gives different surface morphologies [9]. Similar technique can be applied to find the smooth surface of P(VDF-TrFE) terpolymers.
References


Appendix A

Calculation of Electric Field Distribution in Polymer with the Comb-shape Bottom Electrode

This is the ANSYS code to calculate the electric potential distribution in polymer when 10 V is applied between the bottom and the top electrodes. Polymer has the dielectric constant (K) and thickness (t). The bottom electrode has the comb-shape configuration, which is electrode/gap/electrode (E/G/E). In this case, one period is 2E+G.

/prep7
antype,static
et,1,plane121

tair=t
tpol=t
w=E
s=G
per=8.85e-12
emunit,epzro,per
mp,perx,1,K
mp,perx,2,1

rectang,0,w/2+s+w/2,tpol,tpol+tair
rectang,0,w/2+s+w/2,0,tpol
rectang,0,w/2+s+w/2,0,-tair
aglue,all
asel,s,loc,y,0,tpol
aatt,1,,1
asel,s,loc,y,tpol,tpol+tair
aatt,2,,1
asel,s,loc,y,0,-tair
aatt,2,,1
esize,0.2e-6
asel,all
amesh,all
nsel,s,loc,y,0
d,all,volt,0
nsel,s,loc,y,tpol
nsel,r,loc,x,0,w/2
d,all,volt,10
nsel,s,loc,y,tpol
nsel,r,loc,x,w/2+s,s+w
d,all,volt,10
nsel,all
/solu
solve
finish
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