CHAPTER 1

Introduction

II-VI semiconductor nano-crystal quantum dots and electro-optic active polymers, which exhibit electro-optic and nonlinear optical properties different from those of corresponding bulk materials, are a new class of materials which hold considerable promise for numerous applications in electronics and photonics.[1-6] Incorporating such quantum dots into polymer films is of increasing interest because of their application in guided wave nonlinear optics[7,8] and optical communication devices.[9,10] Traditionally, for such devices, films are normally formed by spin-coating, followed by a poling process. A poling electric field (typically, several tens of volts per micron of thickness are required) must be applied to films to align the chromophores and obtain nonzero even-order electrooptic or nonlinear optical susceptibilities since they have a center of inversion at the macroscopic level.[11-13] Several novel methods for creating noncentrosymmetric polymer films incorporating organic molecules with large molecular susceptibilities have been developed during the past decade. These materials include Langmuir-Blodgett films,[14-16] covalent self-assembled monolayer structures,[17] and materials formed by electrostatic self-assembly (ESA).[18-20]

In this dissertation, we report detailed studies of the ESA method for the creation of noncentrosymmetric CdSe quantum dot-doped thin films and electro-optic polymeric

films with substantial electro-optic response. The advantages of this technique include simple, rapid, inexpensive production, long term and thermal stability, and most importantly, the avoidance of a high electric poling fields to produce even-order nonlinear optical properties, and the applications of such materials in electro-optic devices.

In this chapter, some general theories of electro-optic materials are briefly introduced, with emphasis on two kinds of electro-optic materials: one being nano-sized II-VI semiconductors (CdS, CdSe), and the other one being electro-optic active polymers (chromophores). Their potential use in electro-optic devices, such as optical modulator, an important device and is widely used in telecommunications area, is discussed. The remainder of this chapter describes this background and frames the objectives of the dissertation.

1.1 **Electro-optic and nonlinear optical properties of materials**

The electro-optic effect is that the refractive index of materials changes with external field by

$$\frac{1}{n_{ij(E)}^2} - \frac{1}{n_{ij(0)}^2} = \gamma_{ijk} E_k + s_{ijkl} E_k E_l \quad , \qquad (1.1)$$

where γ_{ijk} are the linear electro-optic (Pockels) tensor components of the medium, and s_{ijkl} are the quadratic electro-optic (Kerr) tensor components of the medium. Higher order terms are omitted in the above equation, because they are weak compared with the linear and quadratic terms, and can be neglected in most cases. For centrosymmetric systems,

the linear electro-optic effect vanishes. For noncentrosymmetric systems, both linear and quadratic terms determine material behavior. The electro-optic effect depends on the ratio of the applied electric field (E) to the intra-atomic electric field (E_i). The minimum E_i can be estimated as

$$E_i = \frac{(1/4\pi\varepsilon_0)q}{a^2} \quad , \tag{1.2}$$

where a is the lattice constant, q is the elementary electric charge and ε_0 is the vacuum permittivity. If $E_i >> E$, the Kerr effect is small enough compared with the Pockles effect so the quadratic term in (1.1) may be ignored.

Nonlinear optical (NLO) phenomena refer to how the polarization (P) varies with an applied electric field nonlinearly, as

$$P = \chi^{(1)}E+\chi^{(2)}EE + \chi^{(3)}\,EEE + \ldots\ldots , \tag{1.3}$$

where $\chi^{(n)}$ is the n^{th}-order susceptibility of the medium.

In general, NLO phenomena are characterized as second-order or third-order harmonic generation (SHG or THG), depending on whether they are described primarily through the $\chi^{(2)}$ or $\chi^{(3)}$ terms. SHG is an example of a second-order phenomenon in which two photons, each of angular frequency ω, combine to produce a third photon with angular frequency 2ω. Commercially, some of the inorganic materials such as potassium dihydrogen phosphate (KDP), lithium niobate ($LiNbO_3$), and barium titanate ($BaTiO_3$)

having large $\chi^{(2)}$ values have found many applications in optical engineering field, in applications such as frequency doubling, parametric oscillation of laser beams.

The second-order NLO phenomenon is also the base of the electro-optic Pockels effect. The Pockels effect mediated by a $\chi^{(2)}$ terms arises from the change in the index of refraction in the presence of an external electric field. The index of refraction of such materials changes linearly with the strength of the applied electrical field. This electro-optic effect can find applications in electro-optic devices used in data processing and optical communication systems. Examples of these devices include active optical interconnects and switches, and electro-optic intensity and phase modulators, which can operate at much higher speed and bandwidths than non-optical devices.

Traditionally, electro-optic materials are inorganic crystals, they are acentric in crystal symmetric classes, such as monolinic, triclinic, hexagonal. For materials in centrosymmetric crystal classes, such as cubic (432), there is no Pockels electro-optic effect. Only a small number of crystals have large Pockels electro-optic coefficients. Recently, more and more attention has been given to organic electro-optic materials (polymer dyes, chromophores). that also need acentric molecular structure. Many organic electro-optic materials with high Pockels electro-optic coefficient have been synthesized. The third kind of electro-optic material is nano-clusters, and the origin of electro-optic behavior for them is quite different from that for the first two materials. As mentioned above, the structural base of SHG for inorganic crystals is the lack of central symmetry of the unit cells. Since most such materials exhibit symmetry, only a few inorganic crystals exhibit SHG. For organic chromophores, the asymmetry of the molecular structure is the primary source of SHG, and the molecules should be aligned in the same direction to

optimize noncentral symmetry. But for nano-crystals, things are quite different. The nano-crystals represent the intermediate regime between these two cases in the sense that they can be viewed as a class of large molecules, composed of a limited number of bulk-like unit cells. An additional feature of the nanocrystal size regime, with possible significance for their SHG response, is the enhancement of the ratio of surface atoms to volume atoms. SHG is forbidden in centrosymmetric media, but at an interface, the centrosymmetry intrinsically breaks, and as the nanocrystal size decreases, the surface contribution to SHG is more and more important.

The third-order nonlinearity (THG) phenomenon is more general, because no asymmetric structure is required. There are many aspects of third-order nonlinearity such as third harmonic generation (THG), three-wave and four-wave mixing, Raman and Brillouin scattering and other effects. Third order nonlinearity is related to the intensity-dependent change in the order of refraction coefficient $^{(21)}\mathrm{N}_2$ given by

$$n(\omega) = n_0(\omega)+N_2 I , \tag{1.4}$$

$$N_2[\frac{cm^2}{kW}] = \frac{1}{3}(\frac{4\pi}{n_0(\omega)})^2 \chi^{(3)}[e.s.u.] \quad , \tag{1.5}$$

where the intensity I is

$$I = \frac{\varepsilon_0 n_0 c}{2}\left|E\right|^2 . \tag{1.6}$$

At sufficiently high laser intensities, the deviation of P from a linear dependence on E also must be considered. For isotropic media, such as nano-crystals dispersed in a dielectric matrix (such as glasses or polymers), only odd powers of E come into play. Here we can write P as $P = P^{l} + P^{NL}$, where P^{l} is the linear part and P^{NL} is the nonlinear part, noting that usually $P^{l} >> P^{NL}$.

1.2 Electro-optic devices

Electro-optic modulators are a kind of device important in optical networks and communication systems. The demand for electro-optic modulators has, to a large extent, been driven by the desire for greater bandwidth, for high capacity local area networks (LANs), for video and audio transmitters, for optical detection of radar and phased-array radar signals, for ultra-fast information processing such as analog to digital conversion, and for many other applications. There are several kinds of modulators, depending on their structure, such as electro-optic, acousto-optic, magneto-optic and electro-absorption modulators. Each employs a different physical mechanism and has different applications. The electro-optic modulator is the most important type in optical communication systems. Different configurations have been adopted, such as the Mach-Zehnder interferometer (MZI) modulator, and the directional coupler modulator. The MZI modulator is now the most widely used type.

Figure 1-1 illustrates the structure of an MZI modulator. The input signal is first split equally into two separate channels, separated enough to prevent any cross talk and coupling. The two channels are recombined later into one channel father along the propagation path. An electric field is applied across one of the channels, resulting in a

phase shift of the beam propagating through that channel. When a sufficiently large electric field is applied to the channel, the phase difference between the fields propagating in the two channels reaches π. The applied voltage that produce this critical electric field is then the half-wave modulation voltage V_π, and the output becomes zero due to destructive interference. By periodically switching the applied voltage on and off, on-off modulation of the optical signal can be performed. The modulation voltage V_π can be expressed as

$$V_\pi = \frac{\lambda h}{n^3 \gamma_{33} L \Gamma} \quad , \tag{1.7}$$

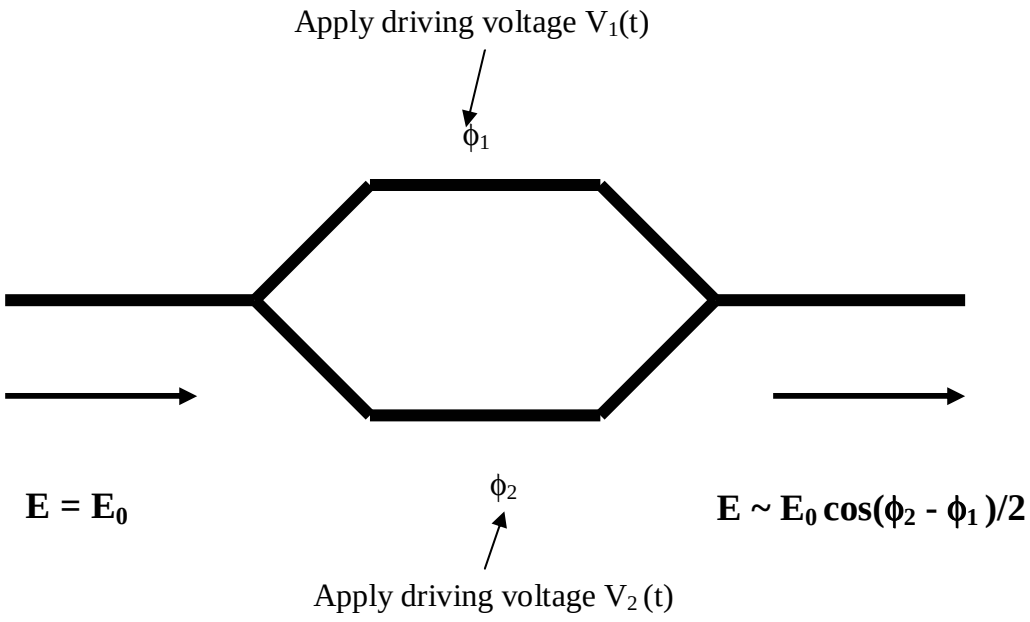

Fig. 1-1. Structure of MZI modulators: Basic cosine response of a MZI modulator.

where λ is the optical wavelength, h is the gap between the electrodes, n is the index of refraction, r_{33} is the EO coefficient of the EO wave-guide layer, L is the interaction length, and Γ is a modal overlap integral, a measure of the interaction intensity of the optical field and the rf modulation electrical field. This is given by

$$\Gamma = \frac{h}{V}\iint E_e |E_0|^2 dxdy \quad , \tag{1.8}$$

where E_e is external electrical field, E_o is normalized optical field of the waveguide mode, and V is the applied voltage.

V_π is an important parameter of the EO modulator. Low V_π is desirous and can be achieved by adjusting one or several parameters in the above equation. But the most effective way lower V_π is to increase the EO coefficient r_{33}.

Another important parameter is the optical response (OR(f)), or the optical output gain in decibels[(22)], given as

$$OR(f) = 20\log\frac{|\Delta\phi(f,t)|}{|\Delta\phi(0,t)|} \quad . \tag{1.9}$$

When OR(f) = 3dB, the corresponding frequency f is the bandwidth of the modulator. Many factors affect bandwidth including impedance mismatch between the electrical field and optical field, coupling between the two arms of MZI modulator, interaction length L, capacitance between electrodes, and modulator configuration, And there is a trade off between V_π and OR(f), in that increasing electrode length L reduces V_π, although bandwidth is also decreased. The other important properties of modulators

are losses, including the reflection loss at the interface, propagation loss of the waveguide and loss due to mode mismatch.

1.3 Objectives of this research and dissertation

The goal of my research is to develop new electro-optic materials and use them to form improved performance of next generation electro-optic modulators. As reviewed above, semiconductor nano-crystals and electro-optic polymers are two kinds of novel electro-optic materials, and they have potentially very useful properties. For optical modulators and switches, with a view toward devices, the amplitude of the electro-optic response (in terms of power-length product) and the response time (in terms of switching

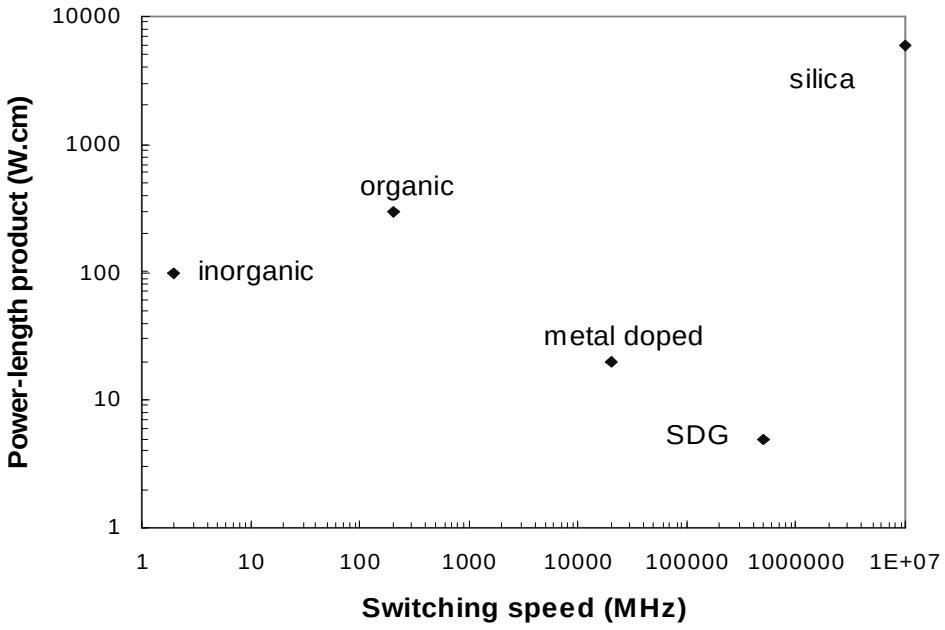

Fig. 1-2. Power-length product as function of switching speed of some electro-optic and nonlinear optical materials.

speed) of electro-optic materials are two critical parameters. Electro-optic polymers with r_{33} larger than 100 (pm/V) have been reported [23] and the response speed is also high due to its low dielectric constant (10 times lower than that of some ferroelectric crystals). Semiconductor nano-crystals promise even higher response speed due to the unique quantum confinement mechanism, as discussed above, and they also show very high EO response. Nano-semiconductor particle doped glass (SDG) can achieve a nonlinear refractive index of 1000 times higher than pure silica glass with a doping concentration only 1—2%[24]. Fig.1-2 shows the power-length product as function of switching speed of some materials. Of these materials, SDGs possess both high switching speed and low power-length product. Silica is the extreme of both high switching speed and power-length product. The switch speed of organic materials is less than that of SDGs, but organic EO materials have higher power-length products than those of SDGs.

We have investigated these two materials and good preliminary results have been achieved. Besides this, we also have developed the electrostatic self-assembly (ESA) technique for thin film fabrication. By using this technique, films have been made from II-VI semiconductor nano-crystals (CdSe, CdS) and EO polymers having remarkable EO coefficients (r_{33} and r_{13}) compared with the same materials but made by traditional processes such as spin coating. For the first time, periodically arraying of semiconductor nano-clusters has been achieved in this way, using these new materials and new film making technique in optical device fabrication to open a new way to make high performance optical devices.

Many investigative efforts have been made in the area of semiconductor nano-clusters. These efforts mainly focus on synthesizing high quality particles (monodisperse, low defect concentration), and their physical and chemistry properties (luminescence spectra, nonlinear optical, and other effects), but their electro-optic properties and potential uses in devices have not been fully investigated, so there is still much work to

do in this aspect. Commercial polymeric electro-optic modulators are now available from some companies such as TACAN Inc. but still there is a possibility to improve device performances remarkably if better materials can be made.

This dissertation will include a materials section and a device section, mainly focusing on materials and some on devices. In the materials section, the overriding objective will be to design and synthesize good EO materials, and to characterize them. For semiconductor nano-crystals based EO materials, I have synthesized CdS nano-particles and dispersed CdSe and CdS in several kinds of polymer hosts by ESA and spin coating, electro-optic and absorption properties have been measured, and the preliminary results are encouraging. I have performed proper measurements in order to understand the structural differences between spin coated and ESA films and to know the reason why ESA films have EO and other properties which are quite different from those of spin coated films. Finally I have studied on the stability of these films, which are important for modulator fabrication.

For EO polymers, I fabricated some samples by the ESA technique and measured their r_{33} and r_{13} coefficients. I have been mainly concerned about how and why the EO properties of the films may vary with thickness and in the presence of an external electric field during the process of ESA so film properties can be further improved by this electrophoresis approach. Besides this, our group is now working on how proton irradiation affects the EO properties of films by means of r_{33}, and r_{13} measurements and FT-IR measurement of irradiated and non-irradiated films. These analysis are included. As a result of the above work, we can fully understand these two types of materials, and how to analytically compare them.

Another important issue is measurement and characterization of materials (films), and I have dedicated much time to it. Various spectra (such as UV-vis absorbance, photo lumiescene, FT-IR) can be measured in our lab, but for electro-optic (Pockel and Kerr) coefficients, we have to establish measurement setups, there two choices, one is an ellipsometric type, the other is a standard MZI type. They are the most important setup of my experiment, so this will be discussed in detail below.

In the application section, I mainly focus on the basic aspects of modulator design. But those materials are also good to make other optical devices, and those conclusions are also valuable to other optical devices. Discussions include the following aspects.

Wave-guide of optical modulators Wave-guide analysis, such as single mode conditions, cut-off conditions, in order to determine the basic dimensions of modulator, such as minimum films, waveguide width and etching depth. These results are also useable to other devices, such as optical switches, and variable optical attenuators.

Considerations for high speed operation Issues regarding high speed operation are also discussed. Refractive index, impedance and speed matching between the optical field and the rf-electric field, and how bandwidth and V_π and bandwidth vary with modulator structure, dimension and material properties, will be considered. Based on those, optimum modulator architecture (electrode configuration, cladding layer, active layer and electrode dimensions) will be determined.

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