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13. ABSTRACT (Maximum 200 words)  
Our multidisciplinary research efforts over the last few years have been focused on the preparation and characterization of high quality, thermally stable thin films that exhibit high nonlinear optical properties using vacuum vapor deposition and in-situ poling (ionized cluster beam/partially ionized beam (PIB) deposition) techniques. The project's primary accomplishments are the vapor deposition of oriented organic thin films and polymer-chromophore complexes, and the development of novel nonlinear optical materials systems, such as side-chain polymers and particle-polymer complexes. Highlights of the research are as follows: 1. Organic crystals called DAST with the highest known nonlinearity have been grown and characterized. 2. PIB deposited highly transparent MNA films on PTFE substrates demonstrate a large second harmonic generation (SHG) signal; 3. Vapor deposited chromophore-polymer composite thin films show large EO effect (several pm/V); 4. Seven synthetic diol and triol chromophores developed have been copolymerized into polyurethane cross-linked EO polymer; 5. Vapor deposited polyurethane based side-chain polymeric thin films demonstrate large EO effects with  $r_{33} = 5.6$  pm/V; 6. Spin-coated BaTiO<sub>3</sub>/PMMA composite thin films show large electrooptical effect. 7. Two novel techniques, electro-optical characterization and subpicosecond optical rectification, have been implemented.

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# Ionized-Cluster Beam/Partially Ionized Beam Deposition of Electro-Optical and Nonlinear Optical Organic Materials and Device Development

Final report

T.-M. Lu, J. F. McDonald, N. Vlannes, and G. E. Wnek

August 29, 1993

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## Foreword

The development of passive and active electro-optic organic and polymeric materials opens new possibilities for the implementation of photonic interconnection. Our multidisciplinary expertise, coupled with the superior facilities and key discoveries made possible by the ARO support, provides a unique opportunity to design, fabricate and characterize organic materials with superior EO properties. While we have made extensive progress on the conventional evaporation and partially ionized beam (PIB) deposition of organic and polymeric EO thin films, our research efforts have also diversified rapidly into other areas, such as crystal growth and cross-linking in polymers, in order to take advantage of the latest developments in materials and techniques. The basic accomplishments achieved in this project range from vapor deposition of oriented organic thin films and polymer-chromophore complexes, to the development of some novel nonlinear optical materials systems, such as side-chain polymers and particle-polymer complexes. We have been rigorously continuing our research on the vapor deposition polymerization of linear and cross-linked polymers in high vacuum chamber, with an emphasis on polyurethane-based systems. Novel EO thin films of BaTiO<sub>3</sub> nanocrystals in PMMA matrix are being fabricated, poled and characterized. The material systems which we develop should aid in accelerating the applicability of EO thin films in high density photonic interconnections.

The excellent research facilities available at RPI have afforded us extensive experience and subsequent success in many projects. Thus, efforts continue to improve the nonlinear optical effect in organic crystals, polyurethane based polymers, and new crystallite-doped polymer thin films.

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## I. Statement of problems studied

Organic and polymeric materials containing conjugated electronic systems coupled with donor/acceptor interactions exhibit extraordinary nonlinear optical (NLO) and electro-optic (EO) properties [1, 2, 3]. These materials maintain significant advantages over conventional inorganic crystals, such as LiNbO<sub>3</sub> and GaAs, in that they offer a larger nonlinear optical effect with ultrafast response, easy processability, and manufacturing compatibility with the current electronic technology. They also possess very low dielectric constants, which is critical to their use in high frequency modulation applications. The development of passive and active electro-optic organic and polymeric materials opens new possibilities for the implementation of photonic interconnection, which has been proposed to replace metallic lines for chip-to-chip communication[4].

The research program at Rensselaer is aimed at developing new materials and techniques for electrooptical modulation to be used in photonic interconnections, which are expected to play a pivotal role in the advancement of IC packaging technology[4]. Over the last three years, our research has been centered around vapor deposition of organic preferred oriented organic thin films and novel characterization techniques. The basic problems that we have studied are summarized in Table 1.

Our research was initiated with conventional evaporation and partially ionized beam (PIB) deposition of commonly used organic MNA thin films. Using vapor deposition to make organic thin films is a recently developed concept that holds many advantages over the commonly used spin-on technique. We have shown that PIB deposition can give preferred oriented MNA thin films[5]. After fully studying the feasibility and limitations of vapor deposition of MNA thin films, we expanded our research to include other organic molecules with large molecular hyperpolarizability, especially DANS and MMONS. However, with the discovery of the centrosymmetrical structure of DANS crystalline thin films and the amorphous feature of MMONS films, we found that it may be possible to make composite organic thin films comprised of oriented polar chromophores in an amorphous matrix. We thus turned our attention to the codeposition of several combinations of organic nonlinear optical materials.

Table 1. The problems studied in our research projects

<b>Time Period</b>	<b>Problem Studied</b>	<b>Purpose</b>
April 1990- Nov. 1991	Vapor deposition of organic thin films, namely MNA, p-NA, and DANS.	Fabricate single crystalline (or at least preferred oriented) thin films.
Fall 1991 - Dec. 1991	Codeposition of organic thin films.	Break the anti-pair effect in highly polar organic molecules by providing a matrix.
Fall 1991 -Spring 1992	Vapor deposition of Teflon AF thin films.	Develop the deposition techniques required to make low dielectric polymer matrix NLO thin films.
June 1992- Present	Vapor deposition of polymer-chromophore thin films.	Increase the thermal stability of composite organic- polymer thin films.
1990 - Present	Synthesis of diol and triol chromophores.	Prepare new organic chromophores to be used in polymeric EO materials.
January 1993 - Present	Vapor deposition polymerization of polyurethane based polymers.	Increase thermal stability.
May 1993 - Present	Spin coating of BaTiO <sub>3</sub> /PMMA thin films.	Develop particle-polymer systems as high EO materials.
Jan. 1992 - June 1992	DAST crystal growth.	Study the growth conditions, characterization, and applications.
Fall 1992 - Present	Spin coating of DAST and DAST particle doped polymer films.	Incorporate the large $\beta$ of DAST into polymeric thin films.
Spring 1991 - Present	Find electrooptical characterization techniques.	Easily characterize EO thin films.
Spring 1992 - Present	Subpicosecond optical rectification, theory, technique and application.	Develop a novel NLO characterization technique.

Our successful vapor deposition of Teflon AF and other polymers[6], such as parylene, demonstrates a promising new technique for the fabrication of nonlinear optical polymeric thin films. We have therefore studied vapor deposition of polymer-chromophore complexes and polyurethane based side-chain polymers.

The vapor deposition of polymer-chromophore complexes yields high EO thin films, where the polymer serves as a matrix and the organic chromophore acts as a nonlinear optical moiety. While the use of polymeric electrooptical thin films in electrooptical devices is limited by their lack of stability, cross-linking and vapor deposition have nonetheless been demonstrated separately as two promising approaches to increase stability [7, 8]. We have combined these two approaches to fabricate polymers with large electrooptical coefficients and very high stability.

In addition to studying thin film technology, we have also investigated the growth and characterization of a highly nonlinear organic crystal [9], dimethyl amino 4-N-methylstilbazolium tosylate (DAST). The crystals have an extremely large nonlinear optical effect. DAST provides the largest second order nonlinearity among all current materials.

Barium titanate ( $\text{BaTiO}_3$ ) is a very common ferroelectric with very high optical nonlinearity. However, due to its high dielectric constant,  $\text{BaTiO}_3$  demonstrates a very low figure of merit, which renders it quite unpromising for electrooptic application. The difficulty of making single crystalline thin films has also limited its practical applications. We propose and demonstrate new materials systems to retain the high optical nonlinearity of  $\text{BaTiO}_3$ , but to possess a reasonably low dielectric constant. Thus,  $\text{BaTiO}_3$  nanocrystallites in an amorphous  $\text{BaTiO}_3$  matrix, which can be fabricated by our PIB deposition [10], and in a polymer matrix, which can be easily made by the spin-on technique, have been investigated.

At the same time, we have implemented two novel characterization techniques for evaluating newly developed electrooptical and nonlinear optical thin films. For organic and polymeric thin films, a simple reflection technique [11] has proven to be a very good method to obtain the EO coefficient. To determine the optical coefficient or the ratios between the nonlinear optical coefficients of organic crystal with a low symmetry, we have developed a new technique known as subpicosecond optical rectification [12, 13].

## II. Summary of Significant Findings

Our strategies over the last few years have focused on the preparation of high quality, thermally stable thin films by vacuum vapor deposition which exhibit high nonlinear optical activities. Our work is centered around the vapor deposition of single crystalline or preferentially oriented thin films [5], chromophore-polymer composite thin films [14], and the development and use of some novel characterization techniques [12]. Our main contributions are listed in Table 2.

Table 2. Main contributions from prior support

- Vapor deposited many organic EO and NLO thin films. Highly transparent MNA films deposited on a PTFE substrate by PIB demonstrate large second harmonic generation (SHG) signal.
- Vapor deposited chromophore-polymer composite thin films show large EO effect (several pm/V) and comparable Figure of Merit (FOM) with current LiNbO<sub>3</sub> EO crystals.
- Seven synthetic diol and triol chromophores developed can copolymerize into polyurethane cross-linked EO polymer.
- Vapor deposited polyurethane based side-chain polymeric thin films demonstrate large EO effects with  $r_{33} = 5.6$  pm/V.
- DAST crystals grown from solutions generate the largest second order rectifying effect and THz radiation known to date.
- The spin-coated BaTiO<sub>3</sub>/PMMA composite thin films show large electrooptical effect.
- Two novel characterization techniques: reflection measurement of electro-optic coefficients and subpicosecond optical rectification have been implemented.

### II.1 Vapor deposition of preferred oriented organic thin films

Conventional evaporation and partially ionized beam (PIB) deposition have been used in our laboratory to make novel organic EO materials into preferentially oriented or single crystalline



thin films. Several promising nonlinear optical materials, such as DANS, MNA, p-NA, MMONS, and DAST, have been investigated. (See Appendix A and Appendix C for their full names and specific properties.) We have found that PIB deposition can increase the preferred orientation of MNA thin films [5]. A strong SHC signal has been observed in these MNA thin films. However, the nontransparency of these thin films may cause some problems in device applications. Nevertheless, we have also discovered that using a PTFE substrate can increase the transparency of the thin films.

Vapor deposition of thin films of DANS, MMONS, and p-NA has also been investigated. DANS gives very clear and transparent thin films, but we do not observe any second order nonlinearity from the films. We believe this is due to the tendency of DANS to form centrosymmetric structures with null electro-optic effects. Vapor deposition of MMONS does not afford uniform and transparent thin films. The thin films even show amorphous structures. However, we have observed a peculiar growth behavior which merits further attention.

## **II.2 Vapor deposition of chromophore-polymer composite thin films**

In order to produce denser and cleaner electro-optic thin films with high thermal stability, chromophore-polymer composites have been deposited by the vacuum evaporation technique. The chromophores employed were DANS, MNA, p-NA, DR1, MMONS, and ANDS. The host polymers were PMMA, Teflon AF and Parylene-N. (See Appendix A and Appendix B for details.) Single crucible co-evaporation is used to deposit the films. The two materials, DANS and Teflon AF 1600, are mixed by the ratio of their volumes and put in a single graphite crucible with a nozzle of 2-3 mm diameter. The crucible temperature is slowly increased to and maintained at 300°C - 320°C for 5 minutes in order to get the source materials well mixed. The deposition takes place at the source temperature of about 400°C to 420°C at a deposition rate of 5 -30 Å/s. The thin films thus produced are usually 0.5 μm to 2 μm thick. These thin films are then poled using a corona poling scheme. After poling, electro-optic effects are observed in most of the films. The figures of merit (FOM's) of these thin films are reasonably large compared to those of currently used inorganic materials such as LiNbO<sub>3</sub> and GaAs. Selected EO results are shown in Table 3.

While host polymers are selected by their glass transition temperatures and their vapor depositability, the choices of the organic chromophores are primarily dictated by their high  $\mu\beta$  values (the product of the molecular dipole moment and second order hyperpolarizability). As

an example, DANS + Teflon AF thin films show a pronounced electro-optic effect ( $r_{33} = 2.4$  pm/V) [14]. The organic chromophore, DANS, has a high  $\mu\beta$  of about  $3.34 \times 10^{-29}$  esu (see appendix A), and the host polymer, Teflon AF 1600 from Dupont, is a novel evaporable copolymer [6] with a glass transition temperature of about 160°C.

Table 3. Selected EO results for chromophore-polymer composite thin films

	Electro-optic coefficient (pm/V)	FOM = $n^3 r/\epsilon$ (pm/V)
Teflon AF + DANS	2.4	3.80
Teflon AF + MMONS	1.6	2.55
Teflon AF + ANDS	2.1	3.35
PA-N + DANS	0.1	0.16

These studies have demonstrated the potential of vacuum evaporation in the fabrication of EO thin films and EO devices. It should be noted that the EO coefficients and FOM listed in Table 3 *are not* optimized. Future work will be directed toward improving deposition and poling conditions, as well as toward the search for more promising organic chromophores and host polymers.

### II.3. Synthesis of diol and triol chromophores and the fabrication of cross-linked polyurethane thin films

Crosslinked EO polymers possess the best resistance to thermal depolarization of aligned chromophores. Currently, crosslinked EO polymers are mainly epoxy and polyurethane based polymers. Some polyurethane thin films have demonstrated a high EO effect (up to 39 pm/V) with high thermal stability [7]. Our research work in crosslinked polymeric EO and NLO materials has been centered around the synthesis of diol and triol chromophores and the fabrication of poled polyurethanes [15]. Seven polymerizable chromophores which we have prepared are listed in FIG. 1. The diol and triol chromophores have the capability to copolymerize with isocyanate to form side-chain and crosslinked polyurethanes, respectively. These polyurethane films have demonstrated a large nonlinearity, and high thermal stability. The second harmonic generation coefficients ( $d_{33}$ 's) have been found to be as high as  $27 \times 10^{-29}$  esu. with no observable relaxations in 10 days.

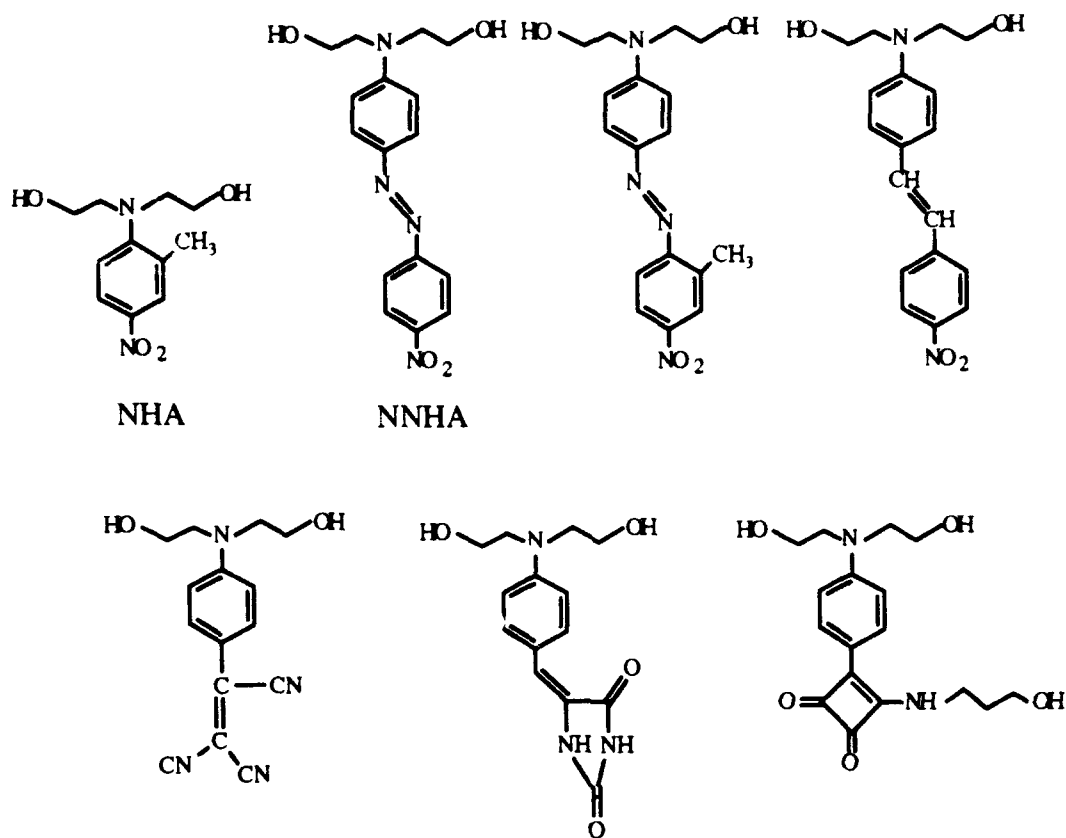


FIG. 1 Seven polymerizable chromophores

#### II.4 Vapor deposition of side-chain polymeric EO thin films

Most of the diol chromophores in FIG. 1 are evaporable. While liquid 2,4-tolylene diisocyanate (TDI) has been used as the monomer in spin-coated polyurethane thin films, 2-methylene diphenylisocyanate (MDI) is preferred for the vapor deposited polyurethane thin films. The first side-chain polyurethane thin film that we investigated is MDI-MNHA (DR19) copolymer. The resulting polymer has a polyurethane backbone and an NLO active chromophore as a side-chain group. When the substrate temperature is at  $-10^{\circ}\text{C}$ , there is no polymerization, but if the substrate temperature is at room temperature, a reasonable degree of polymerization is possible. The glass transition temperature was determined to be around  $65^{\circ}\text{C}$ . In these thin films, a pronounced electro-optic effect has been observed and the electro-optic coefficients are found to be about  $5.6 \text{ pm/V}$ . We find that polyurethane thin films have a temporal response significantly better than many other side-chain polymers due

to hydrogen bonding between urethane groups [15]. It is interesting that these thin films also show a pronounced electro-acoustic effect.

### **II.5 DAST crystal growth**

DAST crystals [9] were grown from methanol and dimethyl formamide (DMF) solutions. The largest crystal plates we achieved were about  $6 \times 8 \times 1.5 \text{ mm}^3$ . Typical DAST crystallites are about  $4 \times 5 \text{ mm}^2$  with a thickness varying from 0.2 to 1.7 mm. DAST belongs to the monoclinic point group with class *m* standard orientation. In this crystal, highly nonlinear chromophores align along a polar axis. The combination of molecular structure and the noncentrosymmetric environment is responsible for DAST's large second order susceptibility. The second harmonic generation efficiency from its powder is reported to be roughly 1,000 times that of the urea reference standard at a fundamental wavelength of  $1.9 \mu\text{m}$  [9]. With these DAST crystals, we recently demonstrated the largest THz generation known to date, which is two orders of magnitude larger than that from  $\text{LiTaO}_3$  [13]. Even though we have grown reasonably large and high quality crystals, we are still more interested in exploring a method to incorporate these highly nonlinear materials into thin films. Fabrication of nanocrystal-polymer composite thin films may be a promising approach.

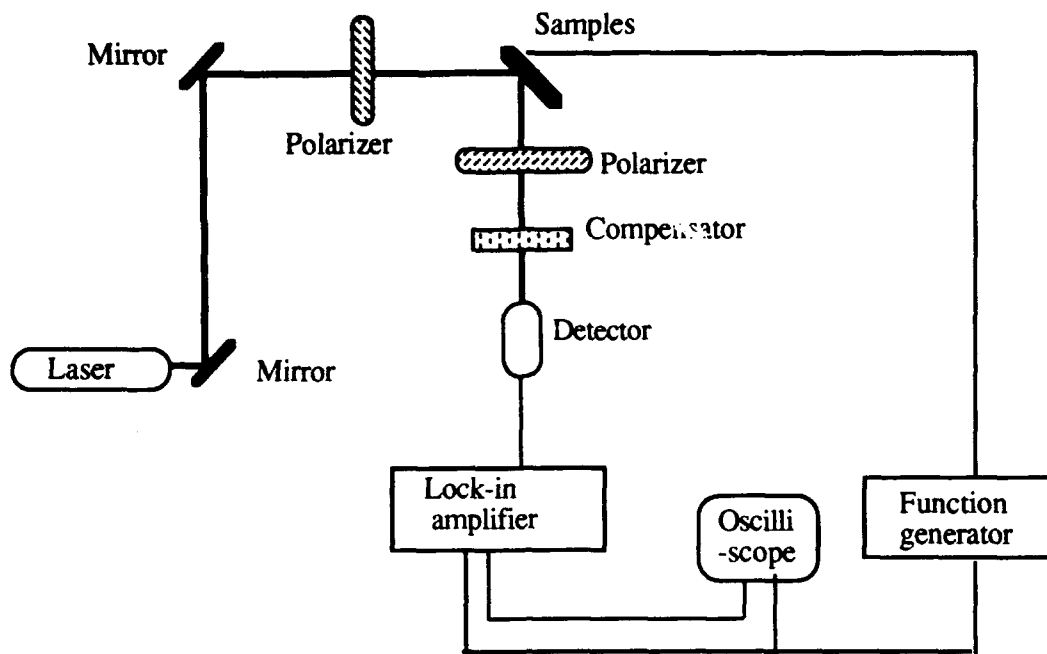
### **II.6 BaTiO<sub>3</sub>/PMMA thin films**

$\text{BaTiO}_3$  nanocrystallites in an amorphous  $\text{BaTiO}_3$  matrix or polymer matrix is expected to possess a high electrooptic coefficient and a reasonably low dielectric constant. In particular, we have studied thin films with  $\text{BaTiO}_3$  crystallites in an amorphous PMMA matrix.

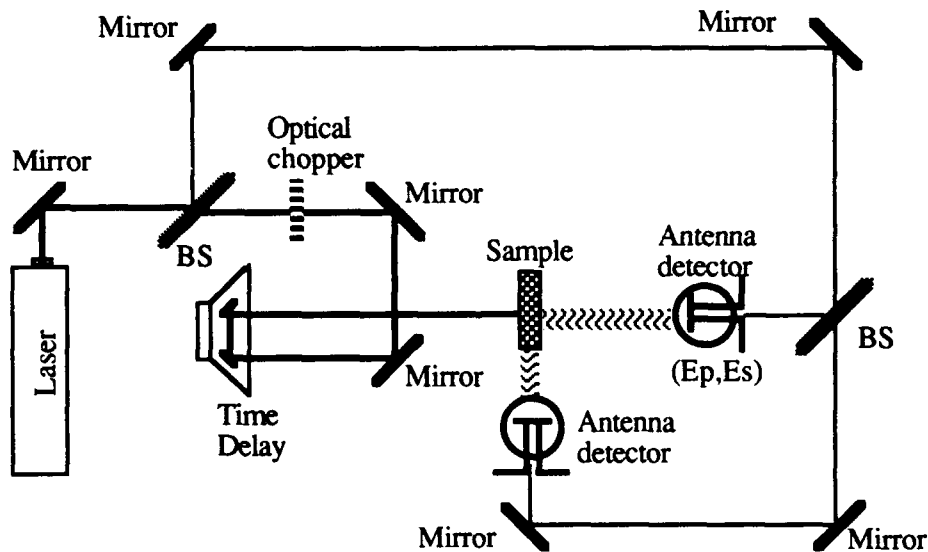
The  $\text{BaTiO}_3$  powder is ground mechanically and dispersed in an acetone solvent. After the large particles settle out, the clear liquid, which holds some  $\text{BaTiO}_3$  particles, is used to dissolve PMMA polymer at  $50^\circ\text{C}$ .  $\text{BaTiO}_3$ /PMMA thin films up to several  $\mu\text{m}$  thick are spin-coated by a common spinner and are then corona poled at about  $115^\circ\text{C}$  for about 30 minutes. After poling, the thin films demonstrate a large EO modulation signal.

### **II.7 Development of characterization techniques**

Over the last few years, we have designed and equipped a laboratory with a complete set of NLO and EO characterization techniques, such as electro-optic measurement, second



(a) Reflection technique



(b) Subpicosecond optical rectification

FIG. 2 Experimental setup of reflection technique of EO measurement and subpicosecond optical rectification

harmonic generation measurement. We have even developed a novel technique, subpicosecond optical rectification. The EO coefficients have been measured by a simple reflection technique [11]. The schematic diagrams of electro-optic coefficient measurement setups are shown in FIG.2(a). The reflection technique has the capability of in-situ measurement during the poling process, which can give us great opportunity to study the thermal dynamic properties during poling.

Second harmonic generation and subpicosecond optical rectification experimental setups have been implemented in our Ultrafast Photonics Lab. While second harmonic generation (SHG) is a commonly used technique, subpicosecond optical rectification (SOR), as shown in Fig 3(b), is a brand-new and powerful technique developed at Rensselaer [12, 13]. Subpicosecond optical rectification is induced by an intense pulsed light beam. When a pulsed light beam, containing a broad frequency spectrum determined by the shape and duration of the pulse, is incident on a nonlinear optical sample, the nonlinear interaction between any two frequency components will create a polarization and radiate electromagnetic waves at their beat frequency. This radiation has a continuous spectrum with frequencies from a few GHz to several THz. A coherent detector, which is a specially designed antenna, can acquire the information about amplitude, phase, and polarization of the radiated electric field. This novel detection method enables us to determine the ratios between any two nonlinear optical coefficients in a nonlinear optical crystal by simply evaluating the angular dependence of the radiation. Subpicosecond optical rectification, with very few sample requirements and without special electrodes, provides an alternative noncontact technique in characterizing nonlinear optical materials.

With these facilities, we have characterized our thin films and bulk crystals. We can also study the most important issues in detail, namely the films' second order optical nonlinearity and thermal stability. The reflection technique for EO measurement provides an in-situ evaluation of the thin films during poling and relaxation. The simultaneous combination of second harmonic generation and subpicosecond optical rectification measurements can provide a complete picture of the second order nonlinearity of our novel thin films.

### III. The list of the publication and technical reports

#### Publications

- [1] "Photonic Multichip Packaging (PMP) using Electro-optic Organic Materials and Devices", J. F. McDonald, N. P. Vlannes, T.-M. Lu, G. E. Wnek, T. C. Nason, and L. You, in International Conference on Advances in Interconnection and Packaging, *SPIE*, Vol. **1390**, 274(1990).
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- [3] N. P. Vlannes, J. F. McDonald, T.-M. Lu, "Organic Photonics, A materials and Devices Strategy for Computational and Communication Systems", *Proc. of the 1992 National Telesystems Conference*, Page 9-7, George Washington University, Va. IEEE Catalog 92-CH3120-3.
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- [10] G.-R. Yang, X.-F. Ma, W. Chen, L. You, P. Wu, J. F. McDonald, and T.-M. Lu, "Vacuum Deposition of Nonlinear Chromophore-polymer Composite Thin Films", submitted to *Appl. Phys. Lett.*

#### **Technical reports**

- [1] Technical report April 1990-December 1990
- [2] Technical report January 1991-June 1991
- [3] Technical report July 1991-December 1991
- [4] Technical report February 1991-February 1992
- [5] Technical report January 1992-June 1992
- [6] Technical report July 1992-December 1992



#### **IV. The Rensselaer personnel participated in this project**

##### **Faculty investigators**

T.-M. Lu, Professor and Chair, Department of Physics. Supervise and direct the project.

J. F. McDonald, Professor, Electrical, Computer, and System Engineering Department.

G. Wnek, Professor and Chair, Department of Chemistry.

N. Vlannes, Assistant Professor, Electrical, Computer, and System Engineering  
Department.

##### **Research associate**

G.-R. Yang, June 1992 - Present, vapor deposition of chromophore-polymer complex,  
and polyurethane based side-chain polymer.

##### **Visiting Scientist**

Professor W. Chen, March 1992 -February 1993. United Nation Fellowship. The  
synthesis of diol and triol organic chromophores.

##### **Graduate students**

X. F. Ma, Spring 1991 - Present. Development of electrooptical and subpicosecond optical  
rectification characterization; DAST crystal growth; Spin-coating guest-host polymer,  
especially, DAST doped polymer and BaTiO<sub>3</sub> thin films.

T Nason, April 1990 - April 1992, Vapor deposition and codeposition of organic  
preferentially oriented thin films.

##### **Undergraduate student**

Alex Cocozziello, September 1992 - July 1993, Poling and EO characterization of  
electrooptical thin films.

##### **Collaborators**

Professors X.-C. Zhang (Physics), G. M. Korenowski (Chemistry) and their students.

## V. Bibliography

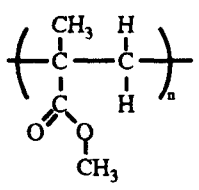
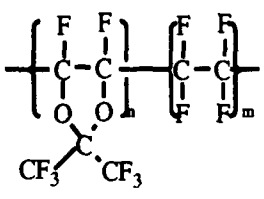
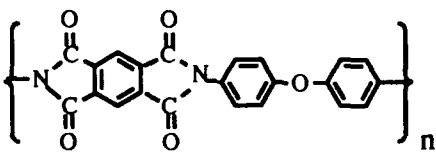
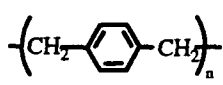
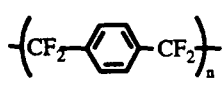
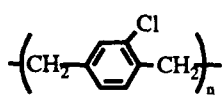
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## VI. Appendixes

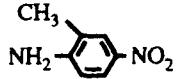
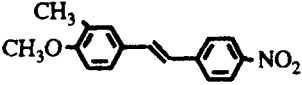
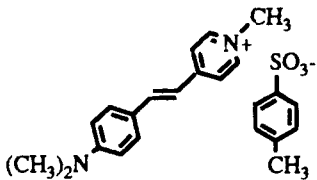
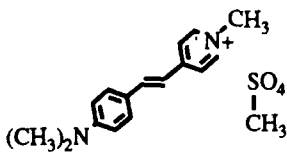
Appendix A Molecular structure of selected organic electro-optic materials

Chemical name (short name)	Molecular structure	Dipole moment $\mu$ (debye)	$\mu\beta$ ( $\times 10^{-28}$ debye-esu)
p-NA		6.2	2.9(1.89 $\mu$ m)
m-NA			
MNA		7.0	2.94(1.064 $\mu$ m)
ANS		7.54	19.6(1.064 $\mu$ m)
DANS		7.42	33.4(1.064 $\mu$ m)
ANDS			
NHA			
MNHA(DR19)			
DR1		8.7	10.6(1.356 $\mu$ m)
MMONS			
DCV		8.2	26.5(1.890 $\mu$ m)
TCV		10.5	41.1(1.580 $\mu$ m)

**Appendix B Molecular structure of selected host polymers  
for electro-optic thin films**

Chemical name	Molecular structure	Melting temperature (°C)	Glass transition temp.(°C)
Poly(methyl acrylate) (PMMA)		180	110
Teflon AF 1600 and Teflon AF 2400		320 -360	160 240
Kapton			>250
Parylene-N		430	60-70
Paralene-F		530	110
Parylene-C		290	80-100

**Appendix C Molecular structure of selected organic electro-optic crystals**

Chemical name (Short name)	Molecular structure	EO coefficient (pm/V)	$n^3r$ (pm/V)	FOM= $n^3r/e^{1/2}$ (pm/V)
2-methyl 4-nitroaniline (MNA)		67	460	145
3-methyl-4-methoxy-4'-nitrostilbene (MMONS)		40	--	--
4'-dimethylamino -N-4-stylbazolium tosylate (DAST)		200	3125	1000
Styrylpyridinium cyanine dye (SPCD)		400	1490	470