

AD-A284 471



Dist: A

ANNUAL 01 Apr 93 TO 31 Mar 94

1

SINGLE CRYSTAL FILMS AND WAVEGUIDES OF ORGANIC MATERIALS;
PREPARATION AND NONLINEAR OPTICAL PROPERTIES

F49620-93-1-0216

61102F

2303/CS

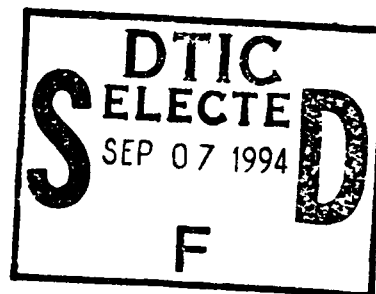
Dr Mrinal Thakur

Dept of Materials Engineering
Auburn University
202 Samford Hall
Auburn AL 36849

AEOSR-JR- 94 0506

AFOSR/NL
110 Duncan Ave Suite B115
Bolling AFB DC 20332-0001

Dr Lee



Approved for public release;
distribution unlimited.

A

The objective of this program is to establish a generic method for the growth of thin single crystal films of important organic nonlinear optical materials and measurement of their nonlinear optical properties. Through the last year's effort we have successfully prepared single crystal films of three organic materials which are: i) (N-4-Nitrophenyl)-L-prolinol) abbreviated as NPP, ii) 2-cyclooctylamino-5-nitropyridine, abbreviated as COANP, iii) 4'-N,N-dimethylamino-4-N-methylstilbazolium toluene-p-sulfonate, abbreviated as DAST. These materials have very large second order susceptibilities. Both NPP and COANP have an amphiphillic molecular structure, while DAST is an organic molecular salt. The single crystal films were prepared by a method called the "shear method", with appropriate choice of the growth conditions. The shear method involves crystal growth at an interface and was originally applied to the growth of polydiacetylene films. Our results show that using the principles involved in the shear method, if the growth conditions are properly optimized for each compound, then molecules other than diacetylene are possible to organize as single crystal films. The only major condition that needs to be satisfied for this method to be applicable is that the molecule must be of an elongated shape with polar chemical groups at one or both ends.

DTIC QUALITY INSPECTED 3

(U)

(U)

(U)

(U)

GENERAL INSTRUCTIONS FOR COMPLETING SF 298

The Report Documentation Page (RDP) is used in announcing and cataloging reports. It is important that this information be consistent with the rest of the report, particularly the cover and title page. Instructions for filling in each block of the form follow. It is important to **stay within the lines to meet optical scanning requirements.**

Block 1. Agency Use Only (Leave Blank)

Block 2. Report Date. Full publication date including day, month, and year, if available (e.g. 1 Jan 88). Must cite at least the year.

Block 3. Type of Report and Dates Covered. State whether report is interim, final, etc. If applicable, enter inclusive report dates (e.g. 10 Jun 87 - 30 Jun 88).

Block 4. Title and Subtitle. A title is taken from the part of the report that provides the most meaningful and complete information. When a report is prepared in more than one volume, repeat the primary title, add volume number, and include subtitle for the specific volume. On classified documents enter the title classification in parentheses.

Block 5. Funding Numbers. To include contract and grant numbers; may include program element number(s), project number(s), task number(s), and work unit number(s). Use the following labels:

C - Contract	PR - Project
G - Grant	TA - Task
PE - Program Element	WU - Work Unit Accession No.

Block 6. Author(s). Name(s) of person(s) responsible for writing the report, performing the research, or credited with the content of the report. If editor or compiler, this should follow the name(s).

Block 7. Performing Organization Name(s) and Address(es). Self-explanatory.

Block 8. Performing Organization Report Number. Enter the unique alphanumeric report number(s) assigned by the organization performing the report.

Block 9. Sponsoring/Monitoring Agency Name(s) and Address(es). Self-explanatory.

Block 10. Sponsoring/Monitoring Agency Report Number. (If known)

Block 11. Supplementary Notes. Enter information not included elsewhere such as: Prepared in cooperation with...; Trans. of ..., To be published in When a report is revised, include a statement whether the new report supersedes or supplements the older report.

Block 12a. Distribution/Availability Statement. Denote public availability or limitation. Cite any availability to the public. Enter additional limitations or special markings in all capitals (e.g. NOFORN, REL, ITAR)

DOD - See DoDD 5230.24, "Distribution Statements on Technical Documents."

DOE - See authorities

NASA - See Handbook NHB 2200.2.

NTIS - Leave blank.

Block 12b. Distribution Code.

DOD - DOD - Leave blank

DOE - DOE - Enter DOE distribution categories from the Standard Distribution for Unclassified Scientific and Technical Reports

NASA - NASA - Leave blank

NTIS - NTIS - Leave blank.

Block 13. Abstract. Include a brief (Maximum 200 words) factual summary of the most significant information contained in the report.

Block 14. Subject Terms. Keywords or phrases identifying major subjects in the report.

Block 15. Number of Pages. Enter the total number of pages.

Block 16. Price Code. Enter appropriate price code (NTIS only).

Blocks 17. - 19. Security Classifications. Self-explanatory. Enter U.S. Security Classification in accordance with U.S. Security Regulations (i.e., UNCLASSIFIED). If form contains classified information, stamp classification on the top and bottom of the page.

Block 20. Limitation of Abstract. This block must be completed to assign a limitation to the abstract. Enter either UL (unlimited) or SAR (same as report). An entry in this block is necessary if the abstract is to be limited. If blank, the abstract is assumed to be unlimited.

512

94-28988

SINGLE CRYSTAL FILMS AND WAVEGUIDES OF ORGANIC MATERIALS;
PREPARATION AND NONLINEAR OPTICAL PROPERTIES

(F49620-93-1-0216)

M. Thakur, Auburn University

Annual Report

The objective of this program is to establish a generic method for the growth of this single crystal film: of important organic nonlinear optical materials and measurement of their nonlinear optical properties. Through the last year's effort we have successfully prepared single crystal films of three organic materials which are: i) (N-(4-Nitrophenyl)-L-prolinol) abbreviated as NPP, ii) 2-cyclooctylamino-5-nitropyridine, abbreviated as COANP, iii) 4'-N,N-dimethylamino-4-N-methylstilbazolium toluene-p-sulfonate, abbreviated as DAST. These materials have very large second order susceptibilities. Both NPP and COANP have an amphiphilic molecular structure, while DAST is an organic molecular salt. The single crystal films were prepared by a method called the "shear method", with appropriate choice of the growth conditions. The shear method involves crystal growth at an interface and was originally applied to the growth of polydiacetylene films. Our results show that using the principles involved in the shear method, if the growth conditions are properly optimized for each compound, then molecules other than diacetylene are possible to organize as single crystal films. The only major condition that needs to be satisfied for this method to be applicable is that the molecule must be of an elongated shape with polar chemical groups at one or both ends.

The films that we obtained for COANP and NPP were more than 1cm^2 in area and about $3\mu\text{m}$ in thickness. The surface orientations of these films as determined by x-ray diffraction, were (100) and (101) respectively. For DAST we obtained films that were about $5\text{mm} \times 5\text{mm}$ in area with a surface orientation of (101). Polarized optical microscopic studies have shown that these films have excellent optical quality. This is the first time that single crystal thin films of organic second order optical materials have been prepared. The second order optical susceptibilities of these films were measured by second harmonic generation (SHG) using a Nd:YAG laser. Since the thickness of these films was less than the typical coherence length ($\sim 20\mu\text{m}$), phase-matching was not necessary to consider in analyzing the SHG data.

The second harmonic generation measurements were made under various polarization conditions while the film was rotated in a plane perpendicular to the beam. Both the signs and magnitudes of the second order optical tensor elements of the films were measured. The calculated and observed SHG data for COANP and NPP are shown in Figs.1&2. The maximum effective d-coefficients for NPP and COANP are 97pm/V and 56pm/V respectively. Thus NPP

94 9 06 050

DTIC QUALITY INSPECTED 3

has a phase-matchable d-coefficient that is 18 times larger than that of LiNbO_3 .

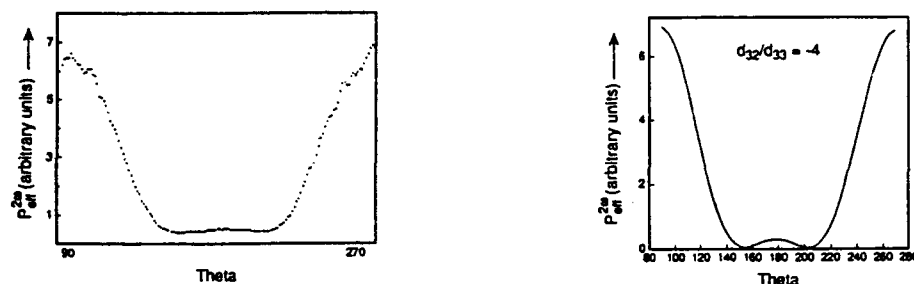


Fig.1 a) The measured SH power of COANP b) The calculated SH power of COANP

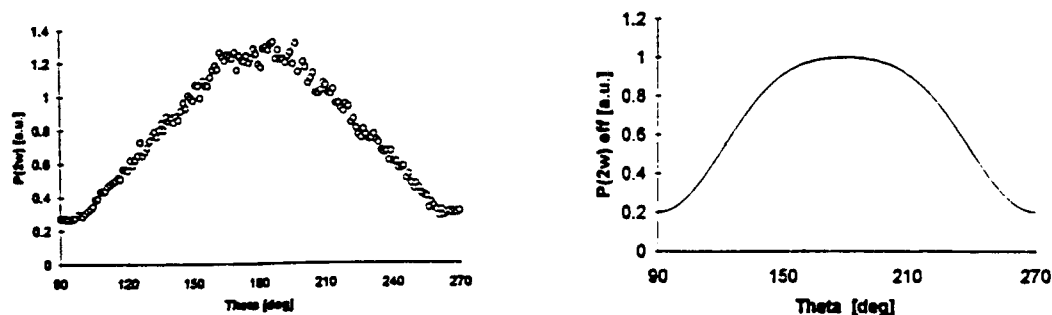


Fig.2 a) The measured SH power of NPP b) The calculated SH power of NPP

Since DAST is not transparent at 532nm wavelength (second harmonic for fundamental at 1.06 μm) SHG is not the best way to measure the nonlinearities. Therefore we used electrooptic measurements for nonlinear optical characterization of DAST films. This measurement was made using lock-in detection while applying an ac voltage across a single crystal film. The electrooptic coefficient that we measured was about 365pm/V.

In addition to the second order optical materials, we have studied specific organic third order optical materials such as polydiacetylene crystals which have very large off-resonant nonlinearities. The bulk crystals were prepared by conventional solvent evaporation method while the single crystal films were prepared by the "shear method". Two important optical experiments were performed on these crystals and films. The first one was the z-scan technique which provided information about the sign and magnitudes of the nonlinear refractive index in the off-resonant domain. The magnitude was found to be $1 \times 10^5 \text{cm}^2/\text{MW}$ and the sign was negative at 1.06 μm wavelength. Using z-scan two photon absorption coefficient was also measured and found to be 65cm/GW at 1.06 μm . The other important experiment that was performed involved

Dist	Avail. or Special
A-1	

a picosecond time resolved measurement in a Fabry-Perot cavity containing a PTS polydiacetylene. This measurement has shown intensity modulation (upto 50%) at a picosecond time scale, under a specific device configuration. This is the first time that a picosecond all-optical device has been demonstrated for an organic material.

Very recently we have been successful in fabrication of waveguide structures using the single crystal films of organic second order optical materials. Since molecular crystals are usually soluble in common organic solvents, an appropriate polymeric film is required as a protective barrier for photolithographic processing. We have used poly(vinyl alcohol) as a protective layer on COANP and NPP to fabricate channel waveguides. Poly(vinyl alcohol) was chosen because it can be cast as a film from a water solution leaving the molecular crystal film unaffected. These preliminary results of success in waveguide fabrication clearly show that various device microstructures can be fabricated using single crystal films. While significant progress has been made in device fabrication of electrooptic polymeric films, the major advantage of using single crystal films is that they have significantly larger and stable electrooptic and nonlinear optical coefficients. The selected materials also offer high temperature stability (melting point $> 115^{\circ}\text{C}$).

The future work will include optimization of the crystal growth conditions to produce significantly larger (> 1 square inch) single crystal films of a variety of novel organic molecules. Various waveguide microstructures including directional coupler, Mach-Zehnder interferometer and other device geometries such as Fabry-Perot interferometer will be fabricated using those films. Detailed understanding of the molecular organization depending on the nature of the substrate surface, will be gained via studies using polarized FTIR microscopy and x-ray diffraction. The films and device microstructures will be characterized by detailed linear and nonlinear optical measurements. This research may lead to many novel and unique devices based on single crystal films of novel organic materials.

PUBLICATIONS:

1. "Second Harmonic Generation in Single Crystal Films of an Organic Material", R. Quintero -Torres and M. Thakur, Opt. Lett., **19** 87 (1994).
2. "Second Harmonic Generation in Single Crystal Films of NPP", R. Quintero-Torres, Jianjun Xu and M. Thakur, Technical Digest IQEC, **9** 110 (1994), Anaheim, CA, May .
3. "Time-resolved Nonlinear Optical Studies of a Fabry-Perot Cavity Containing PTS-polydiacetylene", R. Quintero-Torres, Z. Han and M. Thakur, Tech. Digest IQEC, **9** 106 (1994), Anaheim, CA, May.
4. "The sign and magnitudes of the off-resonant nonlinearities of polydiacetylene measured by Z-scan", R. Quintero-Torres and M. Thakur, Mol. Cryst. Liq. Cryst., accepted.