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13. ABSTRACT (Maximum 200 words) The project sought to implement a new technology for a novel solid state optical shutter obtained from interfacing inorganic semiconductors to conducting polymers, which then switch on activation by a high intensity radiation source in the ultrafast regime. Se/P(DPA) interfaces were prepared and yielded switching efficiencies at 532 nm, calculated as $\Delta OD = OD(\text{laser}) - OD(\text{rest})$, of between 0.3 and 0.6 at pulse energies as low as 0.1-1.0 mJ/pulse (7 mm beam). Tests with CdSe, AlSb yielded similar ΔOD values. Tests with single crystal CdSe did not yield promising results. The conclusion appears to be that much additional work is needed, especially on a scientific level probing the physical aspects of the phenomenon, before practical devices can become feasible.			
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INTRODUCTION

This project seeks to implement a new technology for a novel solid state optical shutter, which involves interfacing inorganic semiconductor and electrodes made therefrom to conducting polymers in a solid state assemblage. The well-known electrochromic switching properties of the conducting polymers are utilized in this technology in a novel manner. The inorganic semiconductors, activated by a laser or other high intensity radiation, transfer charge to or from the conducting polymers, causing them to switch. Since the semiconductor activation and charge transfer and thus assemblage switching occur in the sub-ns or ns time region. The present project sought to practically implement previous, initially positive results.

OBJECTIVES OF THE RESEARCH EFFORT

- 1) Evaluate existing conducting polymers (CPs) synthesized earlier in these laboratories as well as selected, limited new CPs for incorporation into SC/CP optical shutters. Improve processibility of CPs if necessary. Evaluate selected semiconductor (SC) materials for matching to CPs.
- 2) Fabricate prototype SC/CP devices with components selected from objective 1), and evaluate under pulsed laser radiation. Evaluate switching rise and fall times, thresholds, efficiencies. Visible and NIR laser frequencies will be used.
- 3) Test prototype devices for switching under CW laser and high-intensity, non-laser optical radiation. Visible and NIR frequencies will be used.

In accordance with the above objectives, the following tasks were initially formulated for the work:

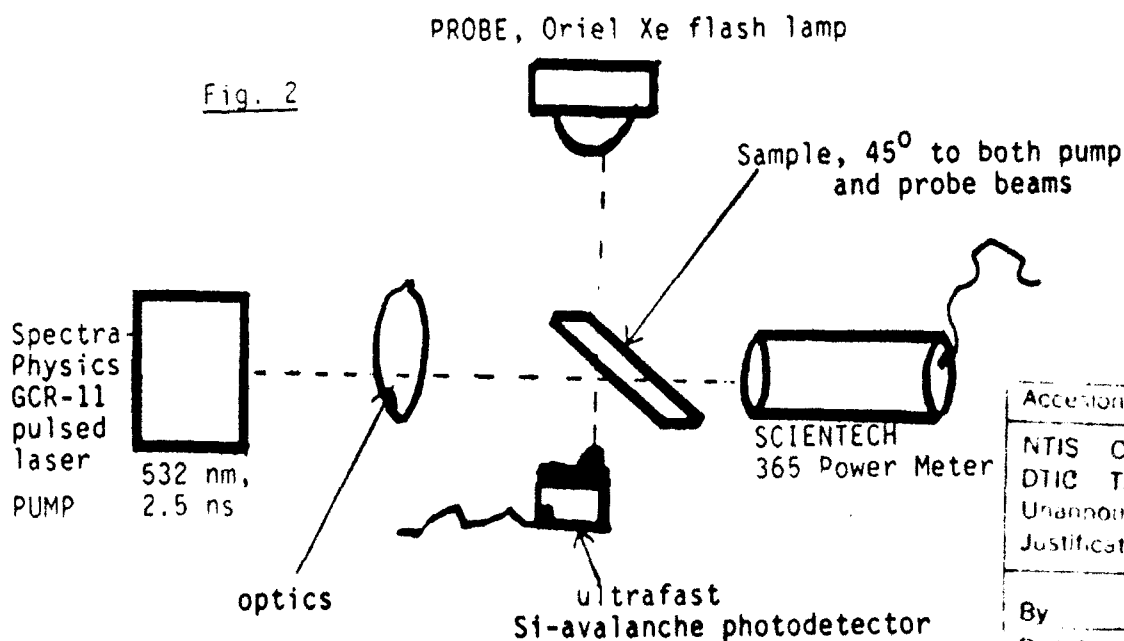
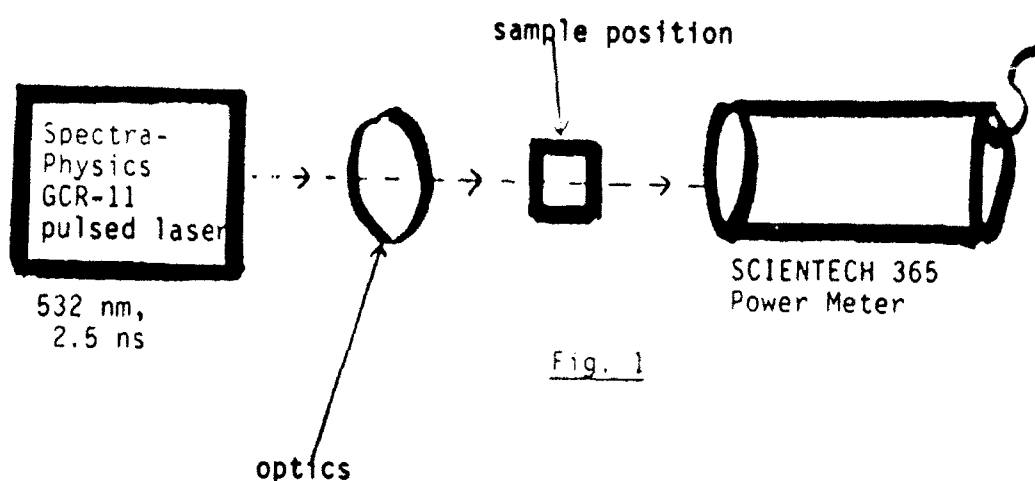
- Task 1: Electrosynthesis, Characterization, Evaluation of CPs, SCs
- Task 2: Testing, Characterization of Prototype SC/CP Optical Shutters Under Pulsed Laser Radiation
- Task 3: Testing, Characterization of Prototype SC/CP Optical Shutters Under CW Laser and High-Intensity Optical Radiation
- Task 4: Final Report.

WORK CARRIED OUT AND RESULTS

Work was carried out with the conducting polymer (CP) poly(diphenyl amine) (P(DPA)), shown in initial tests to be very effective in laser activated switching, and the semiconductor (SC) selenium (Se). Electrosynthesis of new batches of P(DPA) to specifications required in SC/CP interfaces has been completed. In this, several new procedures were used. In one such procedure, a ca. 0.2 M electrolyte concentration and 0.4 M monomer (DPA) concentration was used with pyrolytic graphite electrodes set at +4.95 V under strict deoxygenation over a 3 hr period to obtain highly soluble conducting polymer. The polymer was then reprocessed by ballmilling with glass beads in toluene for a ca. 3-hr period, dried at 65 °C for 2 hrs. The polymer's conductivity could in this manner

be adjusted from very small to ca. 165 S/cm. Its redox cyclability also improved, making it highly amenable to incorporation into SC/CP interfaces.

We also further enhanced the stability and adjustable conductivity of the conducting polymer via doping with Br^- ion using elemental bromine directly. The semiconductor Se used during this period was prepared in the form of thin films deposited on glass or quartz substrates of microscope-slide dimensions. Se has a bandgap suitable for activation at 532 nm (doubled Nd:YAG). The deposition was effected by thermal vacuum evaporation in our Denton Vacuum, Inc. Model 502-A deposition apparatus.



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SC/CP devices were prepared by spin coating of the P(DPA) from its ball milled preparation as described above. These devices were then tested for optical switching efficiency employing the apparatus shown in Fig. 1. In the procedure used, the rest-state optical density (OD) of the device was first measured at 532 nm. The incident laser energy, I_0 , was then set to a prescribed level at the power meter, without any sample introduced. The sample was then introduced, and the transmitted energy, I , at the power meter measured. From these, the OD under laser activation, OD_{laser} , was calculated. The optical switching efficiency is then calculated as:

$$\Delta OD = OD_{laser} - OD_{rest} \quad (1)$$

A number of Se/P(DPA) SC/CP samples were tested. At an $I_0 = 0.5$ mJ/pulse a ca. 100 nm P(DPA)/25 nm Se sample yielded a ΔOD of 0.48, while the same sample yielded a ΔOD of 0.30 at $I_0 = 1.0$ mJ/pulse, indicating possible sample ablation at the higher laser intensity. A similar sample with nearly identical Se/P(DPA) thicknesses but treated with electrolyte beforehand yielded corresponding ΔOD 's of 0.18 at $I_0 = 0.5$ mJ/pulse and 0.20 at $I_0 = 1.0$ mJ/pulse, indicating that sample ablation could be partially avoided by pre-treatment with electrolyte.

Additionally, we set up a more accurate testing apparatus, as shown in Fig. 2. In this pump-and-probe setup, the sample OD at any specific wavelength from 400 - ca. 900 nm was monitored by a Xe-flash lamp before and after pumping by the laser at 532 nm. This setup and its actual use will be described in more detail in subsequent reports.

We also carried out very promising studies with the previously electrosynthesized conducting polymer poly(diphenyl amine) (P(DPA)) and the semiconductor Se. The latter is deposited via thermal vacuum evaporation as a thin film (ca. 100 nm or less) on a glass slide substrate. The polymer, doped with either Br^- or BF_4^- , was deposited on the semiconductor via spin coating. Initial studies with single crystal CdSe were also carried out.

The testing of these samples was carried out with the apparatus shown in Fig. 2. In this pump-and-probe setup, the sample OD at any specific wavelength from 400 - ca. 900 nm is monitored by a Xe-flash lamp before and after pumping by the laser at 532 nm. The laser-attenuation efficiency is then characterized, as described above (Eq. 1).

Salient results from these tests are tabulated in Table I below:

All samples listed in the table showed excellent ablation resistance. However, some damage was observed at the highest energy used, 1.0 mJ, evidenced via an increase in the Rest OD from 0.456 to 0.476.

We also completed initial studies with the semiconductor single-crystal Si, procured in the form of commercial cells, tested with all usable conducting polymers, which showed promise.

Studies with single crystal CdSe were not promising primarily due to the large thickness of the CdSe hampering signal received. Additionally, several other SC/CP systems were studied. Results from these are summarized in Table II:

TABLE I: Salient results from laser-attenuation testing of the samples listed, employing the apparatus shown in Fig. 1. Laser: 532 nm, Q-switched, pulsewidth 2.5 ns, 10 Hz. Probe (monitoring) wavelength- 650 nm.

<u>Sample</u>	<u>Laser intensity, mJ/pulse</u>	<u>ΔOD</u>
P(DPA)-Br ⁻ /Se, Rest OD= 0.456	0.1 mJ	0.3
	0.25	0.6
	0.50	1.05
	1.0	1.1
P(DPA)-BF ₄ ⁻ /Se Rest OD= 0.234	0.1	0.2
	0.25	0.3
	0.50	0.41
	1.0	0.51
P(DPA)-Tos ⁻ /CdSe	0.1	0.25
	0.25	0.35
	1.0	0.62

TABLE II: Additional SC/CP systems tested. Pulsed laser energy at 532 nm = 1.3 mJ/cm² per pulse, 10 Hz, other parameters as before. *C= chemically polymerized, *EC= electrochemically polymerized. P= poly.

<u>Sample</u>	<u>ΔOD</u>
8 mg AlSb + 5.6 mg *C P(DPA)	0.56
8 mg AlSb + 5 mg *EC P(DPA)	0.99
8 mg AlSb + 3.2 mg P(ANI), redcd.	1.06
CdSe + 2 mg P(diphenyl benzidine)	0.42

Laser pump-and-probe transient absorption data obtained in our related, prior work on the systems in Table II showed broad band transient absorptions across the 400 - 900 nm region with fall times of ca. 100 ns (sub-ns risetimes).

LIST OF PUBLICATIONS

The following are the only directly related publications:

- o Chandrasekhar, P., "Conducting Polymers in Novel Interfaces with Inorganic Semiconductors for Ultrafast, Passive, Broad-Band, Laser-Activated Polymer Switching", *Polymer Prepr.* 33, 1, 1206 (1992).

LIST OF PROFESSIONAL PERSONNEL ASSOCIATED WITH THE RESEARCH EFFORT

PRASANNA CHANDRA SEKHAR (CHANDRASEKHAR)

EDUCATION: Ph.D.: Electroanalytical Chemistry, State University of New York at Buffalo, Buffalo, NY, 1984
Thesis Title: "Theoretical and Experimental Treatment of Square Wave Voltammetry at the Thin Film Mercury Electrode"
M.S.: Inorganic Chemistry/Crystallography, Concordia University, Montreal, Canada, 1980
B.Sc. (Honors): Chemistry, University of Delhi, India, 1978

EXPERIENCE: 10/1987 to present: Manager, Electrochemical Programs, Gumbs Associates, Inc., East Brunswick, NJ, supervising 3 Ph.D. scientists, 2 postdocs.
6/1987 to 10/1987: Visiting Research Scientist, Dept. of Chemistry, Drexel University, Philadelphia, PA.
6/1985 to 6/1987: Senior Research Scientist, Honeywell, Inc. (Physical Sci. Ctr (now Sensors & Signals Res. Ctr.), Bloomington, MN to 12/86, Defense Syst. Divn. (now Antech), Horsham, PA, -6/87).
1984-5: Postdoctoral Associate, Dept. of Chemistry and Materials Science Center, Cornell University, Ithaca, N.Y.

Electroanalytical Chemistry: All pulse techniques, classical methods, rotating, semiconductor electrodes, ultramicro electrodes, instrumentation (incl. computer control), conducting polymer, nonaqueous electrochemistry. Good knowledge of theory (kinetics, reaction mech.) applicable to problem solving.

Materials Science, Energy Devices/Sensors: Extensive experience at Cornell MSC and at Honeywell. PVD, thin film methods, lithogr.; batteries, e.chem. sensors.

Conducting Polymers: Syntheses, electrosyntheses, charactzn., electrochemistry, spectroelectrochemistry, processing, 3rd order NLO measurements.

Synthetic Inorganic, Theoretical Chemistry: Schlenk/Dry Box techniques (designed, set up lines, schlenkware). Theor. Chem. (Cornell). Extensive syntheses for M.S..

Computers: Fluent in Fortran 77, Basic, assemblers, UNIX (Ultrix), MS-DOS, CMS. Familiar with mainframes (IBM 3090, CDC), Prime, DEC VAX, HP 3000, IBM PS/2, PC, Apple MacIntosh II machines/systems. Laboratory interfacing.

X-Ray Crystallography/EXAFS: M.S., 1-1/2 yrs Ph.D. work in Crystallogr. Solved 5 structures incl. metalloporphyrin, used Picker, CAD4 automated diffractometers, Some exp. w/ high-resol. (multipolar ref. low temp.) e-density techniques. Extensive EXAFS exp. at CHESS (Cornell synchrotron).

Foreign Lang.: French, Ger., Hindi, Marathi, Sanskrit (fluent spok./writ./lit.). Some Spanish. 2 yrs. tech. transl. French/Ger/Span w/ INSDOC. Sev. oth. lang.

PUBLICATIONS: List attached/available. PERSONAL: Born 10/17/1957.

PUBLICATIONS- P. CHANDRASEKHAR (SEKHAR)

1. Chandrasekhar, P.; Bird, P.H., "Synthesis and Characterization of an Oxygen-Bridged Vanadium(III) Dimer", *Inorg. Chem.*, (1984), 23, 3677.
2. Chandrasekhar, P.; Osteryoung, J.G., "Square Wave Stripping Voltammetry at the Thin Film Mercury Electrode", Paper No. 251 presented by P. Chandrasekhar at the ACS Pittsburgh Conference and Exposition on Analytical Chemistry and Applied Spectroscopy, Atlantic City, NJ, published in Abstracts (1984).
3. Chandrasekhar, P.; Bird, P.H., "Synthesis and Characterization of $[V(NCCH_3)_4-ZnCl_4]$, a Low Valence Vanadium Complex", *Inorg. Chim. Acta*, (1985), 97, L31.
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7. Chandrasekhar, P., "Dioxygen Activation by Metalloporphyrins: O-O Bond Scission Through Sigma Antibonding Orbital Population in u-Peroxo Dinuclear Dimers", Paper No. 216 presented at the Annual Meeting of the American Association for the Advancement of Science (AAAS), Chicago, IL (USA), (1987).
8. Chandrasekhar, P.; Wheeler, R.A.; Hoffmann, Roald, "Sigma Bond Cleavage in Coordinated Dioxygen: The Case of the u-Peroxo Complex $[(THF)_3Cl_2V(III)(O_2^{2-})-V(III)Cl_2(THF)_3]$ and Vanadyl Formation in Solution", *Inorg. Chim. Acta*, (1987), 59, 386.
9. Chandrasekhar, P., "Electro-optic Switches Based on Novel Conducting Polymer Technology: Enhancing Optical Switching Times", *Electrochem. Soc. Ext. Abstr.*, (1988), 88-2 (479), 703.
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11. Chandrasekhar, P.; Masulaitis, A.M.; Gumbs, R.W., "Novel Synthesis, Spectroelectrochemical, Electrochemical and Chronovoltabsorptometric Characterization of Poly(Isothianaphthene)" *Synth. Met.*, (1990), 36 (3), 303-326.
12. Chandrasekhar, P.; Gumbs, R.W., "Novel Synthesis, Spectroelectrochemical, Electrochemical and Chronovoltabsorptometric Characterization of Family of Poly(Aromatic Amines), Novel Processible Conducting Polymers. I. Poly(benzidines)", *J. Electrochem. Soc.*, (1991), 138, 1337-1346.
13. Chandrasekhar, P.; Thorne, J.R.G.; Hochstrasser, R.M., "Third-order Nonlinear Optical Properties of Poly(diphenyl Amine) and Poly(4-Amino Biphenyl), Novel Processible Conducting Polymers", *Appl. Phys. Lett.*, (1991), 59, 1661-3.

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18. Chandrasekhar, P., "Novel Semiconductor/Conducting Polymer Interfaces as Ultrafast, Passive, Broad-Band, Laser-Activated Optical Switching Interfaces", Paper No. 144, Physical Chemistry Division, A.C.S. National Meeting, San Francisco, CA (April 1992).
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21. Chandrasekhar, P.; Thorne, J.R.G.; Hochstrasser, R.M., "Structure Property Relationships in Off-Resonant Third Order Nonlinearities of Conducting Polymers. 1. Poly(aromatic Amines) and Ring-S-heteroatom-containing Polymers", *Synth. Met.* **53** (2), 175 (1993) (*In press*).

INTERACTIONS (COUPLING ACTIVITIES)

a) Papers presented: paper listed under publications above presented at ACS Spring 1992 San Francisco meeting by P. Chandrasekhar.

b) Consultative and advisory functions - none.

NEW DISCOVERIES, INVENTIONS

New discoveries- The SC/CP phenomenon described above is a new discovery, but is not patentable in its present form.

SUMMARY

The overall conclusion for the work appears to be that much additional work is needed, especially on a scientific level probing the physical aspects of the phenomenon, before practical devices can become feasible.