Progress Report

for

"Photomodulation Spectroscopy of Photocarrier Dynamics,
Electronic Defects and Morphology of Conducting Polymers"

by

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to

U.S. Department of Energy
Division of Material Science

Grant No.: DE-FG02-89ER45409

October 8, 1991

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COMPREHENSIVE REPORT
for
GRANT NO.: DE-FG02-89ER45409-2

I. INTRODUCTION

This is a progress report on the second period of activities associated with the DOE grant to the Physics Department of the University of Utah, starting on April 1st, 1991, on photocarrier dynamics, electronic defects and morphology of conducting polymers using the photomodulation spectroscopy. During the second period of this grant we have achieved impressive results and have started new studies, to be completed during the grant continuation period of the third year. We will describe our progress according to the material studied, since this is the best method to summarize our accomplishments. We have used a variety of techniques in our studies such as: CW photomodulation, photomodulation in the femtosecond and picosecond time ranges, CW resonant Raman scattering, transient photoinduced Raman scattering, electro-absorption, degenerate four-wave mixing and the newly technique of spin dependent photomodulation. These techniques have been used to obtain the transient electronic response of the studied conducting polymers.

II. ACCOMPLISHMENTS

(1) Polythiophene and Soluble Derivatives:

We have measured the nonlinear optical response $\chi^{(3)}$ of this material with 60 femtoseconds resolution (Refs. A8 and A15). We discovered a very fast electronic process (200 fs) which is probably associated with free-carrier renormalization (Ref. A10). We have also studied the longer electronic relaxation (up to 3ns) and measured the transient PA spectrum for the first time (Ref. A10). We have also studied the film morphology by the picosecond ultrasonics technique (Refs. A4 and A13) and found a linear dispersion relation for the LA mode for frequencies up to 100 GHz.

(2) Polydiacetylene - 4BCMU

We have studied the resonant Raman scattering (RRS) dispersion with the laser frequency ω_L in a solution cast polydiacetylene film. The data were analyzed (Refs. A3 and A7) using the amplitude mode formalism. We have conjectured that the disorder in the film affects the exciton bands in the same way as is affects the excited energy levels in $(CH)_x$. We have started a thorough study of transient photoinduced RRS in 4BCMU films. Preliminary results show dynamic spectral hole burning in the RRS of the C=C stretching phonon (Refs. A13, A20 and B10). We have studied the RRS dispersion and the picosecond transient response

of photoexcitations in 4BCMU at high pressures, up to 80 kbars. We found that the photoinduced excitons dramatically change their dynamics at high pressure, due to fewer 3D chain defects; the results were published in Phys. Rev. Lett. (Ref. A17).

(3) Polydiethynylsilanes

In collaboration with Tom Barton's group at Ames Laboratories we have undertaken a through study on a new type of π conjugated conducting polymers incorporating group IV elements such as Si and Ge. The new polymers are polydiethynylsilanes (PDES) - $(C_4H_2SiBu_2)_x$ or $(C_4H_2GeBu_2)_x$. First we have measured the ground state properties (Ref. A11) using standard optical techniques such as RRS, optical absorption, ESR and photoluminescence. We followed this by measuring some properties of the electronic excitations revealed in doping and photomodulation (Ref. B12). Then we measured the optical nonlinear properties using the DFM technique (Ref. A16). PDES prove to have very interesting NLO properties. PDES have high values of $\chi^{(3)}$, with ultrafast response without long time tails; these properties are very promising for device application in nonlinear-optics and we would like to pursue this avenue.

(4) Polysilane Alloys

With the PI background in a-Si:H (solar-cells) we became interested in novel materials involving σ conjugated polymers: the polysilanes alloys: These are polysilanes $(SiH_2)_n$ embedded in an a-Si:H matrix. We have measured the ultrashort electronic response in the visible spectral range (Refs. A1 and A2) and concluded that it is due to geminate recombination of photocarriers in small clusters of a-Si:H which are surrounded by the polysilane polymers. We have also measured the CW PM spectra and LESR and conjectured that the observed features are due to trapped photocarriers at dangling bonds; the results were submitted to publication (Ref. B3).

(5) Fullerenes

We have recently measured some optical properties of the ground state and photoexcitations in undoped Fullerenes C_{60} and C_{70} . By RRS and electroabsorption (EA) spectroscopies in thin C_{60} films (Refs. B17 and B18) we found that the weak absorption band at 2eV has a very strong response in both RRS and EA spectra. We speculate that the weak band is caused by a forbidden transition, which however is associate with strong e-p coupling. We have also measured the photoexcitation properties using the PM spectroscopy: we have found that triplet excitons dominate the photophysics of undoped Fullerenes.

III. PUBLICATIONS WHICH RESULTED FROM THIS PROJECT

(A) In print

1. "Picosecond and CW Photomodulation Spectroscopy of Polysilane Alloys" (with S. Han, B. Hess, X. Wei and S. Nitta), Jour. Non-Cryst. Solids 14, 588 (1989).
2. "Studies of Picosecond Carrier Dynamics in Polysilane Alloys; Evidence for Geminate Recombination in Small a-Si:H Clusters" (with S.G. Han, B.C. Hess, G.S. Kanner and S. Nitta), Appl. Phys. Lett. 57, 1215 (1990).
3. "Resonant Raman Scattering Study of Polydiacetylene Films" (with L.X. Zheng, R.E. Benner and G.L. Baker), Phys. Rev. B42 (Rapid Commun.), 3235 (1990).
4. "Picosecond Acoustics in Polythiophene Thin Films" (with G.S. Kanner and B.C. Hess), Phys. Rev. B42 (Rapid Commun.), 5403 (1990)
5. "Femtosecond Optical detection of Quasi-Particle Dynamics in $\text{HT}_c\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ Superconducting Thin Films" (with S.G. Han, O.G. Symko and G. Koren), Phys. Rev. Lett. 65, 2709 (1990).
6. "Electric Field Effects in the Picosecond Dynamics of Carriers in a-Si:H" (with R.I. Devlen, Jan Tauc, G.S. Kanner and E.A. Schiff), Proc. of 20th Int. Conf. of Semiconductor Physics, Tesaloniki, August 1990, page 2039.
7. "Studies of Resonant Raman Scattering in Polydiacetylene Films" (with L.X. Zheng, R.E. Benner and G.L. Baker), Jour. Synth. Metals 41, 235 (1991).
8. "Femtosecond Degenerate Four Wave Mixing Studies of $\chi^{(3)}$ in Conjugated Polymers" (with S.G. Han and K.S. Wong), Jour. Synth. Metals 43, 3209 (1991).
9. "Optical Studies of BaBiO_3 ; a Charge Density Wave Insulator" (with G. Ruani et al.), Jour. Synth. Metals 41, 3977 (1991).
10. "Picosecond Photomodulation Spectroscopy of Conducting Polymers with a Nondegenerate Ground State" (with G.S. Kanner), Jour. Synth. Metals 41, 1291 (1991).

11. "Optical Properties of polydiethynylsilanes; A Quasi (AB)_x Polymer" (with X. Wei et al.), Jour. Synth. Metals 42, 1561 (1991).
12. "High Pressure Effects in Picosecond and CW Spectroscopy of Conjugated Polymers" (with B.C. Hess, G.S. Kanner and G.L. Baker), Jour. Synth. Metals 41, 1285 (1991).
13. "Picosecond Lattice Dynamics in Conducting Polymer Thin Films" (with G.S. Kanner, B.C. Hess, L.X. Zheng and R.E. Benner), Jour. Synth. Metals 41, 1393 (1991).
14. "Picosecond Photomodulation Spectra of a-Si:H in the Small Signal Limit; Evidence for Transient Photoinduced Electroabsorption" (with R.I. Devlen, G.S. Kanner and J. Tauc), Solid State Commun., 78, 665 (1991).
15. "Studies of Resonant and Preresonant Femtosecond Degenerate Four-wave Mixing in Unoriented Conducting Polymers", (with K.S. Wong, and S.G. Han) Jour. of Appl. Phys. 70, 1896 (1991).
16. "Femtosecond Dynamics of the Nonlinear Optical Response in Polydiethynylsilane" (with K.S. Wong et al.), Appl. Phys. Lett. 58, 1695 (1991).
17. "High Pressure Effects on Ultrafast relaxation Kinetics of Excitons in Polydiacetylene 4BCMU (with B.C. Hess, G.S. Kanner and G.L. Baker), Phys. Rev. Lett. 66, 2364 (1991).
18. "Quasiparticle Relaxations in HT_c Superconductor" (with S.G. Han, O.G. Symko and G. Koren), Phys. Rev. Lett. 67, 1053 (1991).
19. "Picosecond Spectroscopy in Conducting Polymers", G.S. Kanner, Ph.D. Thesis University of Utah, 1991, unpublished.
20. "CW and Transient RRS in Polydiacetylene 4BCMU Films", L.X. Zheng, Ph.D. Thesis University of Utah, 1991, unpublished.

B. Submitted

1. "Photoexcitation Dynamics in Polyacetylene Probed by Transient Photoinduced Resonant Raman Scattering" (with G. Lanzani et al.) submitted to Phys. Rev. Lett.
2. "CDW Suppression and Photoinduced Gap States in BaBiO₃" (with X. Wei et al.) Solid State Commun. (in press).
3. "Studies of Photocarrier Relaxation Processes in Polysilane Alloys from Subpicosecond to Metastability" (with X. Wei, B.C. Hess, S.G. Han and S. Nitta), Jour. Non Crystal. Solids (in press).
4. "Optical Studies of Photoexcitations in trans-(CH)_x", proceedings of the Nobel Symposium on Conducting Polymers, NS-81, Loulea Sweden, June 1991, (in press).
5. "Anomalous Optical and ESR Properties of Doped PDES" (with Q.-X. Ni et al.), Phys. Rev. B (Rapid Commun.) in press.
6. "Studies of Photoexcited States in Polyacetylene and Poly(paraphenylene-vinylene) by Spin Dependent Photomodulation; the case of neutral photoexcitations" (with X. Wei, B. Hess and F. Wudl), Phys. Rev. Lett. (in press).
7. "Picosecond Transient Spectroscopy Techniques and Application to (CH)_x", Proceedings of the Summer School on "Photonics in Conducting polymers", Bolzano, Italy, June 1991, in press.
8. "Measurements of $\chi^{(3)}$ in Conducting Polymers at $\lambda = 620$ nm" (with K.S. Wong), Jour. of Synth. Metals (in press).
9. "Theoretical Study of PDES Polymers for Nonlinear Optical Applications" (with S. Grigoros, J. Shinar and T.J. Barton) Jour of Synth. Metals (in press).
10. "Studies of CW and Picosecond Transient Resonant Raman Scattering in Polydiacetylene Films" (with L.X. Zheng, R.E. Benner and G.L. Baker), Jour. of Synth. Metals (in press).
11. "Picosecond Photoinduced RRS in cis-rich (CH)_x" (with G. Lanzani, R.E. Benner and L.X. Zheng), Jour. of Synth. Metals (in press).

12. "Optical Probes of Polydiethynsilanes" (with X. Wei et al.), Synth Metals (in press).
13. "Photoinduced Absorption in Soluble Trans Polyacetylene" (with G. Lanzani, G.S. Kanner and S. Jeglinski) Jour. of Synth. Metals (in press).
14. "Charge Conjugation Symmetry in Conducting Polymers: an ODMR Study" (with L.S. Swanson et al.), Jour. of Synth. Metals (in press).
15. "Doping-Induced Optical Absorption and ESR of PDES Films and Solutions (with Z.-X. Ni et al.), Jour. of Synth. Metals (in press).
16. "Electroabsorption Spectroscopy of Conducting Polymers" (with S. Jeglinski), Jour. of Synth. Metals (in press).
17. "Resonant Raman Scattering Studies of Undoped Fullerenes" (with D. Dick et al.), Jour. of Synth Metals (in press).
18. "Electro-absorption of Undoped Fullerenes" (with S. Jeglinski et al.), Jour. of Synth. Metals (in press).
19. "Optical Characterization of Excited States in Undoped Fullerene Thin Films" (with X. Wei et al.), Jour. of Synth. Metals (in press).
20. "Picosecond and CW Optical Probes of Polydiacetylene at High pressure" (with B.C. Hess et al.), Jour. of Synth. Metals (in press).
21. "Picosecond Transient PA spectra of Conducting Polymers" (with G.S. Kanner), Jour. of Synth. Metals (in press).
22. "Studies of Spin States of Photoexcitations in Conducting Polymers by the SDPM Technique" (with X. Wei and B.C. Hess), Jour. of Synth. Metals (in press).

IV. GRADUATE STUDENTS AND POSTDOC TRAINING

S.G. Han	1988 - 1991	PhD 10/1991
L.X. Zheng	1988 - 1991	PhD 9/1991
G.S. Kanner	1988 - 1991	PhD 6/1991
X. Wei	1988 - 1991	PhD expected in 1992
S. Jeglinski	1990 - 1991	PhD expected in 1993
G. Lanzani	1989 - 1991	visitor from Italy Ph.D. expected 12/1991
D. Dick	1991 -	PhD expected in 1994
Dr. B.C. Hess	1989 - 1990	Postdoctoral Fellow now at Fresno, California State University
Dr. K.S. Wong	1989 - 1991	Postdoctoral Fellow now at Hong Kong Technical University

V. PROPOSED RESEARCH FOR PERIOD 4/1/92 TO 3/31/93

The research will continue in the directions outlined in the original proposal while taking into account the results achieved in the first two research periods of this grant.

It has become clear that the high optical non-linearity in π conjugated polymers is quite different from that of 2D and 3D materials. The excitons in polymers are strongly coupled to the backbone phonons and the study of the excited vibrational modes in various polymers can, in principle, reveal the nonlinear electronic response of the excitons. We plan to continue our study of transient photoinduced RRS in polydiacetylene 4BCMU with the aim to find the reason for the observed spectral hole burning in RRS when excited in the polymer absorption Urbach - edge (Ref. A20). Also we would apply the transient RRS technique to trans-in cis $(CH)_x$ to see whether we can observe intersystem crossing from trans- $(CH)_x$ segments into segments of cis- $(CH)_x$ (Ref. A11).

Another major effort in this period will be the application of the newly developed technique of spin-dependent photomodulation (SDPM) (Ref. B22) to various conducting polymers. The SDPM technique is capable, in principle, to separate various photoexcitations in the PM spectra using spin-dependent recombination. We will try to identify various photoexcitations such as charged and neutral solitons in $(CH)_x$, polarons, bipolarons and triplet excitons in other, nondegenerate polymers such as polythiophene and poly(paraphenylene-vinylene). A major advance in material science of polymers is that we can now investigate stretched oriented blended films in which the chains are isolated and semioriented (only along one axis). Applying the SDPM technique in such films is going to give us more precise information about the photoexcitation microscopic parameters such as the spin-spin matrices D and E for triplet excitons and the hyperfine interaction tensor for spin $1/2$ particles.

We will continue our studies of the novel polymer PDES and other supplied by Ames Laboratories. We will measure the doping properties and the magnetic properties of the photoexcitations together with basic properties such as the PL yield and the singlet to triplet intersystem crossing process.

VI. SUMMARY OF OTHER SUPPORT

Currently Active Support

Office of Naval Research, division of material research, within the University of Utah Laser Institute. Annual support \$400,000 for 11 PIs. This program has supported two graduate students (L.X. Zheng and K.S. Kanner) and has provided me a one-month summer salary. The effort I put in it is 10% of my time during the academic year and 33% during the summer.

Pending Proposals

NSF in collaboration with Tom Barton and Joe Shinar from Ames Laboratories, on device oriented studies of novel nonlinear optical polymers. Annual level of proposed support \$50,000.

END

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01 / 22 / 92