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Drs. Alan J. Heeger, Fred Wudl and Paul Smith

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OFFICE OF NAVAL RESEARCH
PUBLICATIONS/PATENTS/PRESENTATIONS/HONORS REPORT

R&T Number: 4132012
Contract/Grant Number: N00014-91-J-1235
Contract/Grant Title: Program for Research in Conducting Polymers
Principal Investigators:

Alan J. Heeger, Dept. of Physics and Materials Dept., Univ. of Calif., Santa Barbara
Paul Smith, Materials Dept., University of California, Santa Barbara
Fred Wudl, Dept. of Physics and Dept. of Chemistry, Univ. of Calif., Santa Barbara
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a. Number of papers submitted to refereed journals, but not published 8

b. Number of papers published in refereed journals (list attached): 11

c. Number of books or chapters submitted, but not yet published: 0

d. Number of books or chapters published (list attached): 0

e. Number of printed technical reports and non-refereed papers (list attached): 7

f. Number of patents filed: 1

g. Number of patents granted (list attached): 0

h. Number of invited presentations at workshops or professional society meetings: 24

i. Number of presentations at workshops or professional society meetings: 24

j. Honors, Awards, Prizes for contract/grant employees: 0
(this might include Scientific Society Awards/Offices/
Promotions, Faculty Awards/Offices)

k. Total number of Graduate Students and Post-Doctoral associates supported by at least 25% during the period under this R&T project number:

Graduate Students: 4
Post-Doctoral Associates: 5

including the number of,
Female graduate students 0
Female Post-doctoral Associates: 0

the number of
Minority Graduate Students: 0
Minority Post-Doctoral Associates: 0

and, the number of
Asian Graduate Students: 2
Asian Post-Doctoral Associates: 3

l. Other funding - list agency, grant title, amount received this year, total amount, and period of performance (see attached list)

Part I

b. Papers published in Refereed Journals

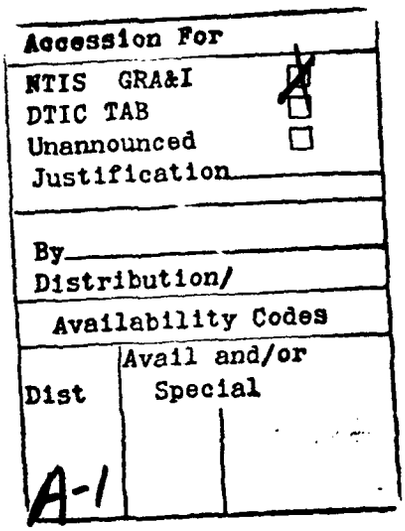
d. Books (and sections thereof) Published

e. Printed Technical Reports Published and Non-Refereed Papers

g. Patents Granted

j. Honors/Awards/ Prizes

l. Other funding



b. Papers published in refereed journals:

Poly(ketene), K. C. Khemani and F. Wudl, Amer. J. Chem. Soc., 111, 9124 (1989).

Photogenerated Carriers in La_2CuO_4, $YBa_2Cu_3O_{7-\delta}$ and $Tl_2Ba_2Ca_{(1-x)}Gd_xCu_2O_8$: Polarizability-Induced Pairing of Polarons, C. M. Foster, A. J. Heeger, Y. H. Kim and G. Stucky, Synth. Metals 33, 171 (1989).

Spectroscopic Studies of Polyaniline in Solution and in Spin-Cast Films, Y. Cao, P. Smith and A. J. Heeger, Synth. Metals 32, 263 (1989).

Electroabsorption of Polyacetylene, S. D. Phillips, R. Worland, G. Yu, T. Hagler, R. Freedman, Y. Cao, V. Yoon, J. Chiang, W. C. Walker and A. J. Heeger, Phys. Rev. B 40 (14), 9751 (1989).

Transient Photoinduced Conductivity in Semiconducting Single Crystals of $YBa_2Cu_3O_{6.3}$: Search for Photoinduced Metallic State and for Photoinduced Superconductivity, G. Yu, A. J. Heeger, G. Stucky, N. Herron and E. M. McCarron, Solid State Commun. 72 4, 345 (1989).

Synthesis and Characterization of Two Regiochemically Defined Poly(dialkylbithiophenes): A Comparative Study, R. M. Souto Maior, K. Hinkelmann, H. Eckert and F. Wudl, Macromol. 23 1268 (1990).

Photoexcited Polarons in High Temperature Superconducting Oxides: Structural Distortion and Low Frequency Polarizability, C. M. Foster, Structural and Low Frequency Polarizability, C. M. Foster, A. J. Heeger, Y. H. Kim and G. Stucky and N. Herron, Reviews of Solid State Science 4 (2&3), 601 (1990).

High Performance Fibers of Conducting Polymers, A. Andreatta, S. Tokito, P. Smith and A. J. Heeger, Mol. Cryst. Liq. Cryst. 189, 169 (1990).

Pyroelectric & Piezoelectric Effects in Single Crystals of $YBa_2Cu_3O_{7-\delta}$, D. Mihailovic and A. J. Heeger, Solid State Commun. 75 (4), 319 (1990).

Mechanical and Electrical Properties of Poly(2,5-Thienylene Vinylene) Fibers, Shizuo Tokito, Paul Smith and Alan J. Heeger, Synth. Metals 36, 183 (1990).

Substitution Effects on Bipolarons in Alkoxy Derivates of Poly(1-4-phenylene-vinylene), K. F. Voss, C. M. Foster, L. Smilowitz, D. Mihailovic, S. Askari, G. Srdanov, Z. Ni, S. Shi, A. J. Heeger and F. Wudl, Phys. Rev. B 43 (6) (1991).

e. Printed technical reports and non-refereed papers:

"Conducting Polymers: The Route from Fundamental Science to Technology," Alan J. Heeger, Science and Applications of Conducting Polymers, edited by W. R. Salaneck, D. T. Clark and E. J. Samuelsen (Proceedings of the Sixth Europhysics Industrial Workshop, Lofthus, Norway, May 1990).

"Polyaniline Processed from Sulfuric Acid and in Solution in Sulfuric Acid: Electrical, Optical, and Magnetic Properties, Y. Cao, P. Smith and A. J. Heeger, Conjugated Polymeric Materials: Opportunities in Electronics, Optoelectronics, and Molecular Electronics, edited by J. L. Brédas and R. R. Chance (NATO ASI Series).

"Synthesis and Characterization of a Water Soluble Polyparaphenylene Vinylene Derivative", S. Shi and F. Wudl, Conjugated Polymeric Materials: Opportunities in Electronics, Optoelectronics and Molecular Electronics, edited by J. L. Brédas and R. R. Chance (NATO ASI Series).

Recent Progress in Conducting Polymers: Opportunities for Science and Opportunities for Technology, International Conference on Science and Technology of Synthetic Metals (ICSM '90), September 1990, Tübingen, Germany.

Mechanical and Electrical Properties of Highly Oriented Polyacetylene Films, International Conference on Science and Technology of Synthetic Metals (ICSM '90), September 1990, Tübingen, Germany.

The Cation Radical Salts of the Oxygen-Substituted Donor, BEDO-TTF, H. Yamochi, T. Nakamura and G. Saito, Intertnational Confernce on Science and Technology of Synthetic Metals (ICSM '90), September 1990, Tübingen, Germany.

Polymers and an Unusual Molecular Crystal with Nonlinear Optical Properties, F. Wudl, P. M. Allemand, G. Srdanov, Z. Ni and D. McBranch, ACS Symposium Series No. 455, Materials for Nonlinear Optics: Chemical Perspectives, edited by Seth R. Marder, John E. Sohn and Galen D. Stucky.

CURRENT AND PENDING SUPPORT

Principal Investigator	Source of Support	Project Title	Award Amount	Period Covered by Award	% Effort Committed	Location Research	Co-PI
Current Support A.J. Heeger	AFOSR	"Oriented Electro/Optical Polymers Through In-Situ Chemistry During Gel Processing: A Research Opportunity"	$115,000[a]	9/15/90-9/14/91	10	UCSB	P. Smith F. Wudl
	AFOSR	Mesoepitaxy: A "Universal" Route to Oriented Materials"	$ 96,389[b]	6/15/90 6/14/91	5	UCSB	P. Smith
	NSF	"Conducting Polymers as Macromolecular Systems: Comprehensive Studies in Solution, In the Melt, and in the Solid State"	$ 78,000	5/1/91 4/30/92	5	UCSB	
	NSF-MRG	"Oriented Conducting Polymers: Solution Processing and Characterization" Renewal pending: $650,000/year over 7 P.I.s	$ 90,000[c]	3/1/90-2/28/91	10	UCSB	P. Pincus P. Smith F.Wudl D. Pearson
	Showa Denko	"Cooperative Program in Polymers and Organic Solids"	$ 50,000[d]	10/1/89-9/30/90	5	UCSB	F. Wudl
	EPRI	"Toward Improvements in the Current Carrying Capability of Conducting Polymers"	$112,384	1/1/91-5/15/92	5	UCSB	
	NSF	"Program of Cooperative Research on Conjugated Polymers With Prof. J.-L. Brédas (Chemistry, University of Mons, Belgium)"	$ 1,500[e]	11/1/90-10/31/91	1	UCSB	Wudl
	NSF	"Acquisition of a Sub-Picosecond Electro-Optic Sampling Facility"	$304,240	1 Year funding	5	UCSB	
	NSF	"Time-Resolved Optical Wavequide Experiments with Conjugated Polymers: Direct Measurement of the Magnitude and Sign of $\chi^{(3)}(\omega_1; \omega_1, \omega_2, -\omega_2)$"	$ 68,000	11/1/90-10/31/91	5	UCSB	

1. Other Funding

CURRENT AND PENDING SUPPORT

Principal Investigator	Source of Support	Project Title	Award Amount	Period Covered by Award	% Effort Committed	Location Research	Co-PI
Current Support (cont.)							
A.J. Heeger							
	NSF (SGER)	"Photogenerated Polarons in High-T_c Superconducting Oxides: Infrared Excitation Spectroscopy and Transient Photoinduced Conductivity in Semiconducting $YBa_2Cu_3O_{7-\partial}$	$ 49,000	2/15/91-1/31/92	1	UCSB	
	ONR	"Program for Research in Conducting Polymers"	$ 90,000[f]	10/1/90-9/30/91	10	UCSB	F. Wudl P. Smith
	INCOR	"Search for Photoinduced Metallic State and for Photoinduced Superconductivity: Transient Photoinduced Conductivity in Semiconducting Single Crystals of $YBA_2Cu_3O_{6.3}$"	$ 16,000	8/1/90-6/30/91	1	UCSB	
Pending Support							
	NSF	"Transport and Optical/IR Properties of Oriented Conducting Polymers Exhibiting High Conductivity and Excellent Mechanical Properties"	$91,428	First Year Funding Funding requested for three years	5	UCSB	
	NSF	"High Performance Oriented Conducting Polymers: High Conductivity in Combination with Excellent Mechanical Properties	$ 97,841	First Year Funding Funding requested for three years	5	UCSB	

a. Total award for this period is $345,000, shared by Heeger, Wudl and Smith. This is the final year.
b. Total award for this period is $175,002, shared by Heeger and Smith. This project will be funded for two more years beyond the current period at the same level.
c. The total NSF MRG award is for $441,000 for this third and final year. Renewal pending for $650,000/year, shared with F. Wudl, P. Smith, P. Pincus, D. Pearson, G. Fredrickson, and H.-W. Schmidt
d. The total award for this period is $102,305, shared by Wudl and Heeger.
e. Total award is $9,250 for three years, shared by Wudl and Heeger.
f. Total award for this period is $265,000, shared by Heeger, Wudl and Smith. This project will be funded for two more years beyond the current period, at the same level.

CURRENT AND PENDING SUPPORT

Principal Investigator	Source of Support	Project Title	Award Amount	Period Covered by Award	% of Effort Committed	Location Research	Co-PI
Current Support **Paul Smith**	AFOSR	"Oriented Electro/Optical Polymers Through In-Situ Chemistry During Gel Processing: A Research Opportunity"	$115,000[a]	09/15/90-09/14/91	10	UCSB	A.J. Heeger F. Wudl
	NSF-MRG	"Oriented Conducting Polymers: Solution Processing and Characterization"	$ 90,000[b]	03/15/90-03/14/91 FINAL YEAR	10	UCSB	P. Pincus D. Pearson F. Wudl A.J. Heeger
	AFOSR	Mesoepitaxy: A "Universal" Route to Oriented Materials"	$ 96,389[c]	6/15/90 6/14/91	5	UCSB	A.J. Heeger
	ONR	"Program for Research on Conductive Polymers"	$ 70,000[d]	10/01/89-09/30/90	5	UCSB	F. Wudl A.J. Heeger
	DSM	Research Gift	$ 50,000	1988-present			
Pending Support	None						

a. Total award for this period is $345,000, shared by Heeger, Wudl and Smith. This is the final year.
b. The total NSF MRG award is for $441,000, shared by Smith, Heeger, Pearson, Pincus & Wudl; this is the final year.
c. Total award for this period is $175,002, shared by Heeger and Smith. This project will be funded for two more years beyond the current period at the same level.
d. The total award for this period is $265,000, shared by Smith, Wudl and Heeger; final year: applying for renewal.

1. Other Funding

CURRENT AND PENDING SUPPORT

Principal Investigator	Source of Support	Project Title	Award Amount	Period Covered by Award	% of Effort Committed to Project	Location Research	Co-PI
Current Support Fred Wudl	NSF	"Oriented Conducting Polymers: Solution Processing and Characterization"	$ 35,000[a]	3/15/90-3/14/91 Renewal pending	3	UCSB	P. Pincus P. Smith A.J. Heeger D. Pearson
	Showa Denko	"Cooperative Program in Polymers and Organic Solids"	$ 52,000[b]	10/1/90-9/30/91	5	UCSB	A.J. Heeger
	AFOSR	"Oriented/Optical Polymers Through In Situ Chemistry During Gel Processing..."	$115,000[c]	9/15/90-9/14/91	2	UCSB	P. Smith A. J. Heeger
	NSF	"Synthesis of New Organic Materials: Ferromagnetic Organic Metals, Cyanovinyl Acceptors and Oxydonors"	$96,000[d]	4/1/91 3/31/92	15	UCSB	
	NSF	"High Strength Materials, Polymers for Nonlinear Optics and New Electrically Conducting Polymers"	$ 87,200	8/1/90-7/31/91	15	UCSB	
	NSF	"Molecular Atoms (Heterospherophanes)"	$157,000	9/1/89 8/31/91	10	UCSB	P. Pincus
	NSF	"Program of Cooperative Research on Conjugated Polymers With Prof. J.-L. Brédas (Chemistry, University of Mons, Belgium)"	$ 1,500[e]	11/1/90-10/31/91	1	UCSB	Heeger
	ONR	"Program for Research in Conducting Polymers"	$90,000[f]	10/1/90-9/30/91	5	UCSB	A. J. Heeger P. Smith

1. Other Funding

CURRENT AND PENDING SUPPORT (CONTINUED)

Principal Investigator	Source of Support	Project Title	Award Amount	Period Covered by Award	% of Effort Committed to Project	Location Research	Co-PI
Fred Wudl Page 2							
Proposals Pending	DOE	"High Temperature Organic Superconductors"	$ 90,000	First Year Funding Funding requested for Three years	5	UCSB	
	DOE	"Polyketenes and Polymers from Polyketal and Polyacetal Precursors"	$ 74,203	First Year Funding Funding requested for Three years	5	UCSB	
	NSF	SGER: "Functionalized Fullerenes: Unprecedented Materials Based on The New Carbon Allotrope"	$ 50,000	One Year Funding	1	UCSB	

a. The Total MRG renewal pending is $650,000, shared by Wudl, Heeger, Smith, Pincus, Pearson, Fredrickson, and Schmidt. Renewal is for three years..
b. Total award for this period is $104,658, shared by Wudl and Heeger.
c. Total award for this period is 345,000, shared by Wudl, Heeger and Smith. This is the final year.
d. This project will be funded for one year beyond the current period, at the same level.
e. The total award is $9250, for three years, shared by Wudl and Heeger.
f. Total award for this period is $265,000, shared by Wudl, Heeger and Smith. This project will be funded for two years beyond the current period, at the same level.

5/91

1. Other Funding

Part II

a. Principal Investigators

Alan J. Heeger
Paul Smith
Fred Wudl

b. Current Telephone Numbers

Alan J. Heeger	(805) 893-3184;	FAX: (805) 961-4755
Paul Smith	(805) 893-8104;	FAX: (805) 961-4755
Fred Wudl	(805) 893-3755;	FAX: (805) 961-4755

c. Dr. Kenneth J. Wynne (ONR-Chemistry)

d. Brief (100-200 words) description of project

This is an interdisciplinary project focused on the fundamental chemistry, physics and materials science of conducting polymers in the context of novel electronic phenomena associated with this emerging class of materials. The research draws upon and utilizes a broad base: synthesis and characterization of new conducting polymers, processing directed toward the achievement of chain oriented and chain extended materials with a goal of achieving the intrinsic electronic and optical properties, and physical measurements directed at characterizing these electronic and optical properties and of identifying the basic physical mechanisms involved in these phenomena.

e. Significant Results During Past Year

We reported visible light emission from Schottky diodes made from semiconducting polymers. Our results demonstrated that light emitting diodes can be fabricated by casting the polymer film from solution with no subsequent processing or heat treatment required. Electrical characterization reveals diode behavior with rectification ratios of 100,000. Electroluminescence quantum efficiencies (photons out per electrons in) of 1% have been achieved. The discovery of conducting polymer LEDs expands the possible applications for conducting polymers into the area of active light sources. Controlling the energy gap of the polymer, either through the judicious choice of the conjugated backbone structure or through side-chain functionalization, should make possible a variety of colors. Moreover, because of the processing advantages of of semiconductors cast from solution, large active areas can be envisioned.

f. Brief (100-200 words) summary of plans for next years work

Our recent success with light emitting diodes fabricated from semiconducting polymers has opened an entirely new direction for our research --- with many new questions. Specific areas of importance for next year's research include optimization of luminescence efficiency (how to minimize non-radiative recombination), the achievement of stable conjugated polymers which emit blue light, and the achievement of highly oriented thin films which emit polarized luminescence (the latter can then be used to fabricate LEDs emitting *polarized* light).
In the area of electrical properties, we have made significant progress in improving the quality of the materials (through orientation by means of polymer processing). To proceed to take advantage of this important progress, we initiated the re-construction of our transport laboratory to extend our measurement capabilities. The experimental capabilities within our electrical transport laboratory now include the following:

(i) Electrical conductivity as a function of temperature from 1K to 300°C. Measurements above room temperature are intended primarily for evaluation of thermal stability.
(ii) High pressure capability (up to 20kbar).
(iii) Magneto-resistance (as a function of temperature and pressure) in magnetic fields up to 60 kgauss.
(iv) Hall effect (vs temperature and vs pressure)
(v) Thermopower (vs temperature) as a function of magnetic field and as a function of pressure
(vi) AC complex conductivity over the extended frequency range from dc to 1 GHz.

The purpose of the focus on the addition of the high pressure capability is to increase the interchain electronic transfer interaction. As a result of our work in the past few years, we know that interchain delocalization to form anisotropic three-dimensional metals is of major importance. "Three-dimensionality" is essential for the achievement of high conductivities (for otherwise the mean free paths are limited by the tendency of the electronic states in quasi-one-dimensional systems to be localized by disorder).

g. List of names of graduate students and post-doctorals currently working on project

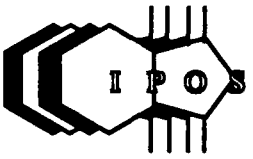
Graduate students: D. Braun, Kwanghee Lee

Postdoctoral Researchers: D. Moses, K. J. Ihn, Y. Cao, C. Zhang

Part III. Research Highlight

Viewgraphs and explanatory text on following pages:

Part III. Research Highlight

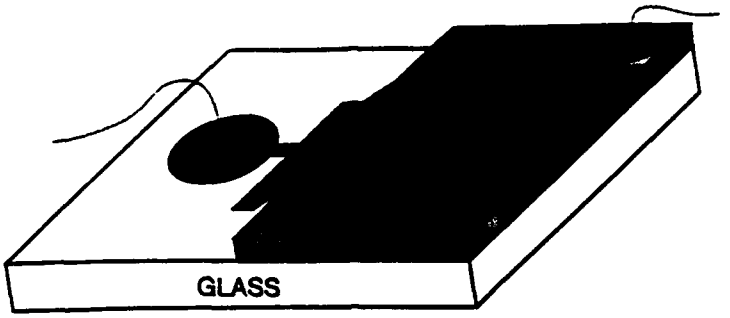


Visible Light Emission from Semiconducting Polymer Diodes

- We have reported visible light emission from Schottky diodes made from semiconducting polymers.
- Our results demonstrated that light emitting diodes can be fabricated by casting the polymer film from solution with no subsequent processing or heat treatment required.
- Electrical characterization reveals diode behavior with rectification ratios of 100,000.
- Electroluminescence quantum efficiencies (photons out per electrons in) of 1% have been achieved; the light emitted from these devices is bright and easily seen in a fully lighted room.
- Turn-on below 5 Volts; compatible with digital electronics.

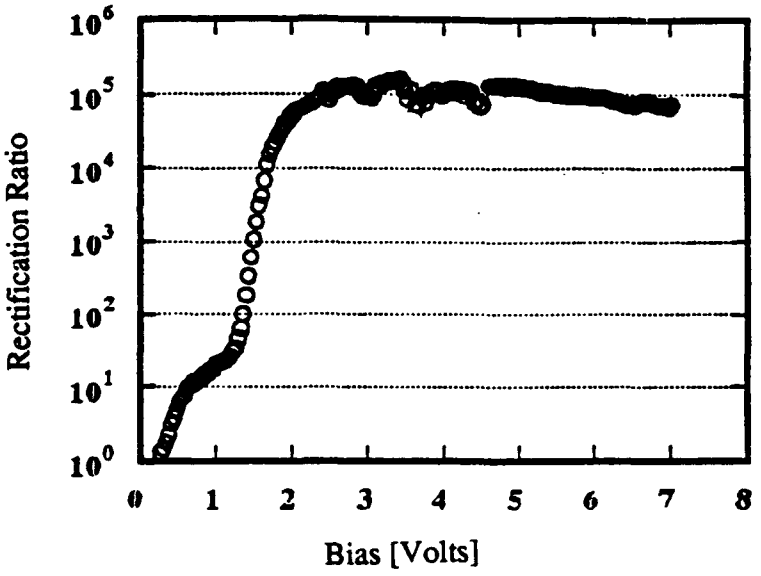
Principal Investigators:
Prof. Alan J. Heeger
Prof. Paul Smith
Prof. Fred Wudl

Structure of Polymer LED Device

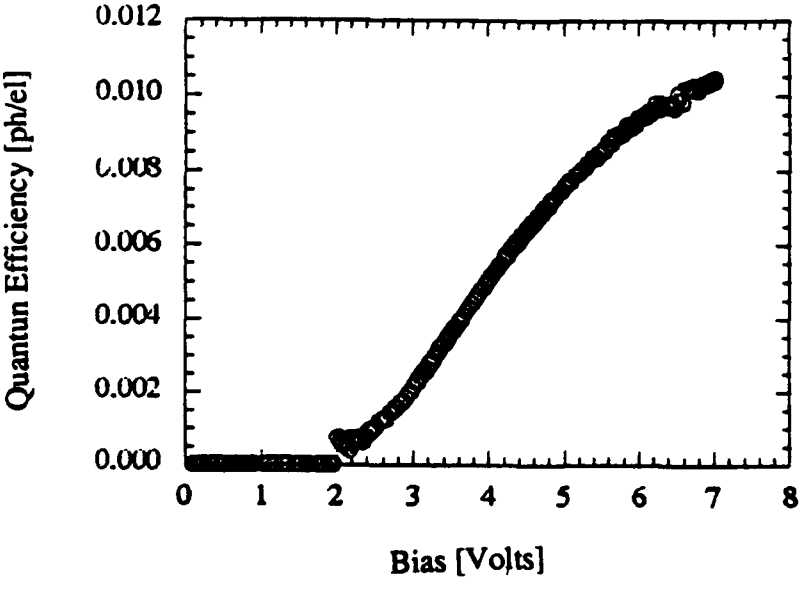


Light Out

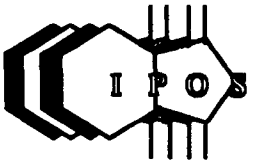
Polymer LED Rectification Ratio vs Bias Voltage



Polymer LED Quantum Efficiency vs Bias Voltage



Part III. Research Highlight:



- The discovery of conducting polymer LEDs expands the possible applications for conducting polymers into the area of active light sources.

- Controlling the energy gap of the polymer, either through the judicious choice of the conjugated backbone structure or through side-chain functionalization, should make possible a variety of colors.

- Because of the processing advantages of of semiconductors cast from solution, large active areas can be envisioned.

- LEDs fabricated from conducting polymers offer a number of potential advantages to future technology.

Part III. Research Highlight

Paragraph of explanatory text

The light emitting diodes, LEDs, consist of a rectifying Indium contact on the front surface of a semiconducting polymer (MEH-PPV) film which is deposited by spin-casting onto a glass substrate, partially coated with a layer of indium/tin-oxide (ITO), the "ohmic" contact. The MEH-PPV films are prepared by spin-casting from tetrahydrofuran (THF) solution containing 1% MEH-PPV by weight. The resulting MEH-PPV films have uniform surfaces with thicknesses near 1200Å. Rectifying metal contacts are deposited on top of the polymer films by vacuum evaporation. The fabrication steps are shown schematically in the Figure.

Using these remarkably simple structure, diodes with rectification ratios of 10^5 have been achieved. Using low work function metals (such as Calcium) as the rectifying contact, LEDs with quantum efficiency (photons out to electrons in) of 1% have been achieved.