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A Summary Report on the Flat-Plate Solar Array Project Workshop on Transparent Conducting Polymers

January 11 and 12, 1985

Ram Kachare
Jovan Moacanin

August 1, 1985

Prepared for
U.S. Department of Energy
Through an Agreement with
National Aeronautics and Space Administration
by
Jet Propulsion Laboratory
California Institute of Technology
Pasadena, California

JPL Publication 85-60
This report describes the proceedings and technical discussions of a workshop on Transparent Conducting Polymers (TCP) for solar cell applications, held in support of the Device Research Task of the Flat-Plate Solar Array Project. The workshop was held on January 11 and 12, 1985, in Santa Barbara, California. Participants included university and industry researchers. The discussions focused on the electronic and optical properties of TCP, and on experimental issues and problems that should be addressed for high-efficiency solar cell application.
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ABSTRACT

This report describes the proceedings and technical discussions of a workshop on Transparent Conducting Polymers (TCP) for solar cell applications, held in support of the Device Research Task of the Flat-Plate Solar Array Project. The workshop was held on January 11 and 12, 1985, in Santa Barbara, California. Participants included university and industry researchers. The discussions focused on the electronic and optical properties of TCP, and on experimental issues and problems that should be addressed for high-efficiency solar cell application.
SECTION I
INTRODUCTION

A Flat-Plate Solar Array Project (FSA) Workshop on Transparent Conducting Polymers (TCP) was held on January 11 and 12, 1985, in Santa Barbara, California. Jovan Moacanin of the Jet Propulsion Laboratory (JPL) arranged the workshop and was its chairman; the format was informal. The attendance, by invitation, was 23, including eight university and two industry researchers.

The objective of the workshop was to assess the status of the electronic and optical properties of TCP and related technological developments and to define theoretical and experimental issues and problems that should be addressed for high-efficiency solar cell applications. Needs for optical transparency and electrical conductivity are self-evident, but other properties are also important. These include surface passivation to minimize surface recombination velocity, matching the refractive index of silicon, and virtually zero surface reflectivity for antireflection (AR) coating. Other solar cell applications include replacement of front-surface and back-surface metal contacts of silicon solar cells.

Some of the important questions that were addressed during the workshop were:

(1) Is a transparent highly conductive polymer theoretically and experimentally possible?

(2) How will a candidate TCP and its processing affect solar cell surface properties, such as interface density of states and recombination velocity?

(3) If we understand the mechanisms of polymer conduction and optical absorption, will it be possible to design structures that optimize optical, electrical, and passivating properties?

Answers to these questions would help in planning research activities. For example, although not much is known about the electrical characteristics of the polymer-semiconductor interface, one may expect that by judiciously matching a conducting polymer and a semiconductor (e.g., p-doped polymer on p-type silicon), electrical contact approaching ohmic characteristics should be obtained; theory indicates that this should be the case.
Jovan Moacanin of JPL noted, after opening and introductory remarks, that the objective of TCP research is to prove concept feasibility of using TCP as an electroactive solar cell component. Research activities include studies of representative systems [e.g., Si/poly(pyrrrole)], conductivity mechanisms, and new TCP materials.

The key requirements that TCP should meet for various applications to develop high-efficiency silicon solar cells are:

- **Spectral range**: 0.4 - 1.0 µm
- **Transparency**: 95%
- **Refractive index**: >1.5 - 2.0
- **Surface recombination velocity**: <10³ cm/sec
- **Interface density of states**: <10¹¹/eV
- **Conductivity**: >10⁵ ohm⁻¹ cm⁻¹
- **Contact resistivity**: 10⁻³ - 10⁻⁷ ohm/cm²

Table 1 shows optical absorption for TCP layers versus sheet resistance.

Kris Koliwad, JPL, discussed the focus of high-efficiency research in FSA in the context of the Department of Energy five-year Plan. He described an n/p/p⁺ silicon solar cell structure and discussed the various causes of carrier losses that contribute to the conversion efficiency degradation. He pointed out that a polymer can be used as front-surface and back-surface metal contacts if it has metal-like electrical conductivity. It would be advantageous if it reduced recombination bases where the contacts formed an

<table>
<thead>
<tr>
<th>Absorption coefficient, cm⁻¹</th>
<th>Thickness for 90% Transmission, µm</th>
<th>Conductivity (σ), 10,000 ohm⁻¹ cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>10.54</td>
<td>0.095</td>
</tr>
<tr>
<td>1000</td>
<td>1.054</td>
<td>0.95</td>
</tr>
<tr>
<td>1 x 10⁴</td>
<td>0.1054</td>
<td>9.50</td>
</tr>
<tr>
<td>1 x 10⁵</td>
<td>0.01054</td>
<td>95.00</td>
</tr>
</tbody>
</table>
interface with the semiconductor. It was also suggested that if a polymer has
suitable refractive index and good optical transparency, as well as excellent
surface passivation properties, then it can be employed as AR coating and
surface passivator. Thus, if a polymer possesses suitable electrical, optical,
and surface passivation properties, then it can simultaneously serve as front-
surface and back-surface metal contacts, AR coating, and surface passivation.

S. Di Stefano, JPL, reviewed available conducting polymers that may be
of interest for solar cell applications. Though the electrical properties of
poly(acetylene), poly(pyrrole), and poly(paraphenylene) are known, not much is
known about their optical and interfacial properties on semiconductors. The
primary concerns expressed to obtain good film quality include adhesion,
chemical stability, morphology and density variations.

Initial results of a study on poly(pyrrole) were discussed. An
electrochemical method was used to deposit poly(pyrrole) on a silicon surface
from an acetonitrile solution containing 0.1 mol tetra-butyl ammonium
perchlorate and 1.0 mol pyrrole. A setup to measure quantum yield was
described and preliminary absolute quantum yield data that were obtained in
the 500- to 1040-nm wavelength region on n-Si/polypyrrole/MeOH for various
polypyrrole thicknesses (100, 1000, 2000 and 4000 Å) were presented. The
purpose of this study was to prove the feasibility of assessing TCP
performance using a liquid semiconductor interface configuration.

Professor Nathan Lewis, Stanford University, presented his extensive
results from a quantitative investigation of the open-circuit photovoltage
(Voc) at the interface between a semiconductor and liquid electrolyte. In
particular, he discussed the treatment of the energetics at semiconductor/
liquid interfaces as a means of evaluating the intrinsic properties of the
semiconductor (e.g., bulk carrier transport, Fermi level pinning by surface
states, etc.). Experimentally, the open-circuit voltage of a semiconductor/liquid
junction is determined directly by measuring the voltage between a
semiconductor electrode under illumination and a platinum control electrode in
a two-electrode cell configuration. Lower than ideal Voc values were
observed; this may reflect poor diffusion length in bulk semiconductor,
classical tunneling over the barrier, or the effects of surface states. The
same technique can be used to evaluate the properties of semiconductor/polymer
interfaces. Preliminary quantum yield measurements on n-silicon/poly(pyrrole)
indicate that for thin layers of the polymer, absorption of light by the
polymer obeys Beer's law.

Professor A. Heeger, University of California at Santa Barbara, addressed
the issue of the feasibility of achieving good conductivity with acceptable
transparency. He applied the theory of free electrons in metals to conducting
polymers. This approach was used for the first time to interpret the optical
properties of polyisothionaphthene (PIIN), which is a highly transparent
conducting polymer (σ = 50 Ω⁻¹·cm⁻¹). The polymer has the smallest band
gap of any known conducting polymer: E_g = 1 eV.

If one can treat the heavily doped polymer (doped to 20% to 50%) as a
metal with free electrons, the absorption of such a polymer is determined by
the frequency-dependent conductivity (σ). In the simple free electron model

\[ \sigma(\omega) = \sigma_0 \left(1 + \omega^2 \gamma^2\right) \]  

(1)
where $\sigma_0 = Ne^2\gamma/m$ is the dc conductivity arising from $N$ electrons (mass $m$) per unit volume with a mean scattering time $\gamma$. The corresponding absorption coefficient can be expressed as

$$\alpha = 2^{1/2}(\omega/e) \left[ \sqrt{\varepsilon_1^2 + \varepsilon_2^2 - \Sigma} \right]^{1/2}$$ (2)

where

$$\varepsilon_1 = \varepsilon_c - 4\pi\sigma(\omega)$$

$$\varepsilon_2 = 4\pi/\omega$$

and $\varepsilon_c$ is the core (high frequency) dielectric constant. Equations 2 and 3 imply that for the free carrier absorption to be weak, $\omega\gamma >> 1$ in the frequency range of interest. For PITN, the data of Figures 1 and 2 imply $\omega\gamma$ at $h\omega = 1$ eV; i.e., $\gamma \approx 10^{-15}$ seconds. With this magnitude for the scattering time (surprisingly long for a disordered polymer such as PITN), the observed transparency after doping can be understood. Undoubtedly, the underlying physics is more complex than this simple model. Nevertheless, these ideas provide a sound basis for more detailed analysis of the polymer problem.

In the long wavelength limit ($\omega\gamma < 1$), the absorption coefficient is given by the classical skin-depth expression

$$\alpha = \frac{2}{c}(2\pi\omega)^{1/2}$$ (4)

Using Equation 4 and the data of Figures 1 and 2, the expected change in dc conductivity upon doping can be estimated. The long-wavelength data for the as-grown and the heavily doped films imply an increase in $\alpha$ by much more than an order of magnitude on doping. These infrared data, therefore, would imply an increase in dc conductivity by more than two orders of magnitude, to values $>10^3\Omega^{-1} - \text{cm}^{-1}$ in the heavily doped samples.

After the above noted theoretical discussion, Professor F. Wudl, University of California at Santa Barbara, described various approaches to the synthesis and characterization of poly(isothionaphthene), PITN. PITN is prepared from the monomer, isothionaphthene, by means of oxidative polymerization from an electrolyte solution containing tetraphenylphosphonium chloride. The p-type doping of the polymer was found to be electrochemically reversible (13,000 cycles, no measurable change), but it cannot be reversibly doped using n-type dopant. The polymer exhibits excellent thermal stability as shown by DSC and TGA measurements. Also, the polymer is stable to electrochemical cycling as evidenced by the unchanged shape of the cyclic voltammograms after 13,000 cycles.

A most interesting feature of undoped PITN is that its electronic spectrum consists of an intense intraband absorption with a maximum at 880 nm. A weak second absorption band at 1,350 nm was also observed. The
Figure 1. Absorption Spectrum of PITN As-Grown (Solid Curve) and After In-Situ Electrochemical Doping (Dashed Curve)
Figure 2. Absorption Spectrum of PTN As-Grown (Solid Curve) and After Chemical Doping With AsF₅ (Dashed Curve)
880 nm intense band of the undoped polymer disappears after doping. Significant decrease in absorption of the heavily doped PITH polymer was observed in the visible region. Also, after doping, there was no indication of an energy-gap variation over the spectral range studied, indicating that PITH is metallic in this respect. The observed spectral changes are reversible. These observations should be compared with other doped polymers, including polyacetylene and polythiophene, for which the absorption coefficient remains large throughout the visible range of the spectrum. Although oxidative polymerization by electrochemical means is a method of choice for the synthesis of PITH, it can also be synthesized by a chemical cationic polymerization method.

Professor R.H. Grubbs, California Institute of Technology (Caltech), described a novel synthetic approach for TCP and provided a few examples of a new class of conducting polymers based on a polyacetylene skeleton. This process yields high polymers that are transparent and that can be characterized by various spectroscopic techniques, including NMR, IR, Raman, UV and visible as well as ESCA. These polymers have been doped with the usual dopants, including AsF₅ and I₂, to produce high-conductivity metal-like polymers. The unique feature of the approach is that the synthesis results in a polymer that is amenable to extensive characterization of the bulk molecular structure. Another advantage of this approach is that subsequent to synthesis, the undoped polymer can be stored indefinitely and can be deposited on a surface by spinning technique, then doped to the required level. None of the other techniques currently used in TCP synthesis provide purified, characterizable polymers; hence, establishment of fundamental relationships have not been possible until now between molecular structure and physical properties, including optical and electrical. It is intended to exploit this capability for controlled synthesis for development of a molecular modeling approach. Initially, ionization potentials (IPs) of small oligomers will be calculated and then validated by experimental studies of their IPs as well as their optical and electrical properties. If successful, this modeling will be extended to polymers. This close coordination of theoretical model development with the synthesis and characterization studies will help to provide direction to the synthesis approaches in selecting the polymer with the best combination of properties.
SECTION III
CONCLUSIONS AND RECOMMENDATIONS

The workshop discussions focused on identifying key issues that must be addressed to develop a useful TCP for solar cell applications. The consensus was that, overall, the prospects for a successful outcome are bright. This optimistic viewpoint is based on developments during the last few years. The theoretical analysis (Heeger) based on the free-electron Drude model makes the crucial prediction that the absorption band may shift as conductivity increases, increasing dopant concentration. Recent results on the newly developed P3HT polymer (Wudl) provide experimental support for this prediction. This is an important result, because virtually all known conductive polymers are dark. Advances in controlled synthesis of substituted acetylenes (Grubbs) provide realistic expectations that preparation of conducting polymers of well defined structures is at hand. Furthermore, known oligomer and polymer structures (Grubbs) will provide a unique tool for the experimental validation of theoretical predictions of polymer work function (Mckoy) which are currently being carried out.

Electrochemical experimental techniques for investigating the energetics of the liquid-electrolyte/semiconductor interface are well understood (Lewis). Preliminary results showed that these techniques are applicable to the TCP/semiconductor interface (Nagasubramanian and Di Stefano). These results show that interface characterization can be carried out. This area needs a great deal of attention. There is virtually no published work on electrochemical interface studies, although research on conducting polymers has been done for the last 10 years or so. A related issue is surface passivation of both the front and back surfaces of a solar cell. TCP may have potential as a surface passivant because only low temperature processes are required for their application, and considerable latitude is available for controlling interface chemistry; this can range from controlling surface energetics for Van der Waals bonding to covalent bonding (silane coupling agents?) for chemical interactions with surface states.

The stability and long-term durability of TCP will have to be studied on solar cells or at least on test configurations that simulate one or more cell functions. Work in this area and in those related to manufacturing processes are essential to the successful development of a practical TCP technology. But the first priority should be given to synthesizing new TCP systems that are better than those currently available, and evaluating their performance in a way that is meaningful to solar cell performance.

Based on the above conclusions, the following recommended actions for the next 18 months were developed during the concluding session of the workshop:

1. The Jet Propulsion Laboratory should set up capabilities for evaluating TCP on solar cells and in test configurations that characterize the TCP/semiconductor interface. JPL should carry out evaluation and characterization of TCP for all the participants in the program, to ensure a meaningful comparison of the various TCP systems as they are developed.
(2) Studies on polyprrole as a representative system should be continued, but PITN should be considered as the next candidate material because of its promising properties.

(3) The feasibility of predicting theoretically the TCP work function should be assessed.

(4) Process of the TCP task should be reviewed by JPL in six to eight months; informal discussions will be carried out with the participants in the program. One of the purposes of the review will be to decide on the suitability of planning a research forum on TCP in the second half of 1987. Recommendation was made to seek joint sponsorship with another government agency.
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AGENDA

FSA Workshop

on

Transparent Conducting Polymers

a.m. 10:00 - 10:30 .......... Coffee

10:30 - 10:45 .............. J. Moscanin: Introduction

10:45 - 11:30 .............. Z. Koliwač: Approaches to High-Efficiency Solar Cells

11:30 - 12:30 .............. G. Nagasubramanian: Conducting Polymers

p.m. 12:30 - 1:30 .......... Lunch

1:30 - 2:30 .............. Electrical versus Optical Properties

3:00 ...................... Coffee

2:30 - 4:00 .............. Polymer/Semiconductor Interface

4:00 - 5:00 .............. Synthesis

5:00 - 5:30 .............. Processing and Durability

5:30 - 6:00 .............. Research Issues and Priorities
INTRODUCTION
JET PROPULSION LABORATORY
Jovan Moacanin
FY 1985-FY 1986

Objective:
Prove concept feasibility of using TCP as solar-cell electroactive component

Research Activities:
- Representative systems (e.g., Si/polypyrrole)
  - Deposition on Si
  - TCP structure
  - Interface characterization
- Conductivity mechanisms
  - Theory
  - Representative model systems characterization
- New TCP materials

Requirements

- Spectral range: 0.4 - 1.0 µm
- Transparency: > 95%
- Refractive index: 1.5 - 2
- Surface recombination velocity: < 10^4 cm/s
- Surface states density: < 10^{11} eV
- Conductivity: 10^5 ohm^{-1}cm^{-1}
- Contact resistivity: 10^3 - 10^{-7} ohm/cm^2
- Ohmic contact
Synthesis

Representative systems: controlled conditions, known structures, stable
Model structures: support theory and mechanisms
Candidate materials: guided by electrical-optical-interface models

Key Milestones

Workshop January 1985
Progress Report July-September 1985
Research Forum May 1986
Research Agenda July-September 1986
TECHNICAL ISSUES OF HIGH-EFFICIENCY SILICON SOLAR CELLS
JET PROPULSION LABORATORY
Kris Koliwad
DOE Goal

"The five-year goal of flat-plate collector research is to establish the technologies by 1988 which industry can apply to the production of 15%-efficient crystalline silicon modules..."

National Photovoltaics Program Five Year Research Plan 1984 - 1988

Introduction

• Module efficiency of 15% (NOCT) requires solar cells of efficiencies in the range of 18% to 20% (AM1.5)

• Attainment of such levels of solar cell efficiencies using large-area and low-cost silicon sheet is beyond the state of the art

• Inadequate quality of the low-cost silicon sheets and the inherent limitations of the state-of-the-art cell structures are the primary barriers

• Extensive research is required toward improving the quality of low-cost silicon sheet and extending the understanding of device physics, design and processing
Efficiency Limits

- Based on fundamental physical mechanisms, the absolute efficiency limit for silicon solar cells is above 30%.

- The best efficiency reported to date is 19% (AM1)
  - Float-zone silicon sheet
  - 2 x 2 cm cell area
  - MINP cell structure using tunneling contacts

- The best efficiency achieved to date on low-cost silicon sheet is 16% (AM1)
  - Dendritic web ribbon
  - 2 x 2 cm cell area
  - n⁺p⁺ cell structure

- Carrier recombination losses within the bulk and at surfaces of the cell largely account for the difference.
Primary Causes of Losses

1. Light-generated current:
   A. Optical surface properties (reflection)
   B. Contact coverage
   C. Incomplete absorption (thickness)
   D. Recombination outside depletion region (bulk and surface, including contacts)
   E. "Dead layers"

2. Open-circuit voltage:
   A. Recombination outside depletion region (bulk and surface, including contacts)
   B. Band-gap narrowing
   C. "Current leakage"

3. Fill factor:
   A. Same as open-circuit voltage
   B. Recombination in depletion region
   C. Series resistance

<table>
<thead>
<tr>
<th>Conversion Efficiency</th>
<th>20%</th>
<th>12%</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>1. Light Generated Current:</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fundamental Limit (AM1)</td>
<td>44 mA cm(^{-2})</td>
<td></td>
</tr>
<tr>
<td>A. Optical surface properties (reflection)</td>
<td>0.97</td>
<td>0.95 (± 0.02)</td>
</tr>
<tr>
<td>B. Contact coverage</td>
<td>0.966</td>
<td>0.97</td>
</tr>
<tr>
<td>C. Incomplete absorption (thickness)</td>
<td>0.92</td>
<td>0.88 (Distribution Assumed)</td>
</tr>
<tr>
<td>D. Recombination outside depletion region (bulk and surface, including contacts)</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>E. &quot;Dead layers&quot;</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>Overall collection efficiency</td>
<td>0.86</td>
<td>0.81</td>
</tr>
<tr>
<td>Light generated current (AM1)</td>
<td>37.9 mA cm(^{-2})</td>
<td>25.5 mA cm(^{-2})</td>
</tr>
</tbody>
</table>

| **2. Open Circuit Voltage:** |     |     |
| Fundamental Limit: | 0.836 V |     |
| A. Recombination outside depletion region (bulk and surface, including contacts) | 0.60 | 0.54 |
| B. Band-gap narrowing | 1.0 | 1.0 |
| C. "Current leakage" | 1.0 | 1.0 |
| Open circuit voltage | 0.661 V | 0.594 V |

| **3. Fill Factor:** |     |     |
| Fundamental Limit: | 0.96 |     |
| A. Same as open circuit voltage | 0.84 | 0.84 |
| B. Same as open circuit voltage | 1.0 | 1.0 |
| C. Same as open circuit voltage | 0.97 | 0.975 |
| D. Recombination in depletion region | 0.98 | 0.975 |
| E. Series resistance | 0.80 | 0.80 |

Fill factor | 0.80 | 0.80 |
Research Approaches

• Bulk loss control
  • High-quality sheet growth (high $\tau$)
  • Bulk defect passivation
  • Carrier lifetime measurement techniques in heavily doped thin layers

• Surface loss control
  • Fundamental understanding of the origin and nature of surface-interface states and surface recombination mechanisms
  • Surface recombination velocity measurement techniques
  • Surface passivation

• Process
  • Heavy doping effects
  • Innovative current collection designs (e.g., tunneling contacts, chargeable transparent conductors, polymers)

• Modeling
  • Better phenomena simulation
  • Process sensitivity analysis
  • Designs for effective loss reduction

Summary

• Achievement of 20% efficient large-area solar cells using low-cost silicon sheet is a difficult task and it requires:
  • Understanding of all aspects of carrier recombination losses
  • Innovative designs and processes based on sound modeling

• Research is showing promising results
MATERIAL, CHEMICAL AND ELECTRICAL PROPERTIES (THICKNESS, DEFECTS, GB, IMPURITIES, RESISTIVITY, CARRIER LIFE-TIME, ETC)

DOPANT, DOPING METHOD, DOPING CONCENTRATION, DOPING PROFILE (GRADED VS UNIFORM), LOCALIZED EFFECTS AT GBs, DEFECTS.

GROWTH, METHODS (CVD), EVAPORATION, OXIDATION, REFLECTANCE, REFRACTIVE INDEX, LATTICE STRAIN, SURFACE PASSIVATION (SiO₅, Ta₂O₅, Si₃N₄)

THICKNESS AND QUALITY OF BASE, MINORITY CARRIER RECOMBINATION, SURFACE PREPARATION, SHARP VS GRADUAL (A₂, B) CONCENTRATION DEPTH

TOP METAL CONTACT, METALS (Ti, Pd, Ag; Ni, Cu, A₂, Ag), METHODS (EVAPORATED, SCREEN PRINTED), CONTACT AND GRID RESISTANCE, STABILITY WITH TEMPERATURE

AREA COVERAGE, METALS (Ti, Pd, Ag, A₂, Ni, Ag, Cu) EVAPORATION, SCREEN PRINTING, SINTERING
CONDUCTING POLYMERS FOR SOLAR-CELL APPLICATIONS
JET PROPULSION LABORATORY

G. Nagasubramanian
S. Di Stefano

p/n Junction Cell

- Effects of metallization
  - Surface loss
  - Introduction of surface state (increase recombination velocity)
  - Diffusion of metal into bulk
- Polymers are known to passivate surface states
Desirable Criteria

- Transparent to light with $E \gg 1.1 \text{ eV}$
- Should form an ideal interface with Si
- Persistent adhesion to the surface
- Protection of the surface from degradation
- Good electronic conductor
- Refractive index less than or equal to that of Si
- Easily processible
- Mechanically robust
- Electrochemical and chemical stability
- Large electronegativity

Well-Known Conducting Polymers

- Polymers that form highly conducting compositions

<table>
<thead>
<tr>
<th>POLYMER</th>
<th>DOPANT</th>
<th>CONDUCTIVITY</th>
<th>STABILITY</th>
</tr>
</thead>
<tbody>
<tr>
<td>POLYACETYLENE</td>
<td>Li, C$_2$O$_4$</td>
<td>$= 100 - 1000 \ \Omega^{-1} \ cm^{-1}$</td>
<td>?</td>
</tr>
<tr>
<td>POLYACETYLENE</td>
<td>$\text{BF}_4$</td>
<td>$= 100 \ \Omega^{-1} \ cm^{-1}$</td>
<td>?</td>
</tr>
<tr>
<td>POLYPARAPHENYLENE</td>
<td>AsF$_5$</td>
<td>$= 500 \ \Omega^{-1} \ cm^{-1}$</td>
<td>?</td>
</tr>
</tbody>
</table>

- Not much is known about optical properties—absorption coeff $\sim 10^5 \ \text{cm}^{-1}$
- Much less is known about interfacial properties of these materials on semiconductors
Primary Concerns for Obtaining Good Film Quality

- Morphology and processability
- Density variations
- Effect of counterion or solvent
- Chemical and electrochemical stability
- Adhesion

Oxidation Reduction Potentials of Polymeric Species in Solutions

\[ \text{Oxidation: } \text{PPP} + \text{H}_2\text{O} \rightarrow \text{PMeT} \rightarrow \text{PA} \]

\[ \text{Reduction: } \text{PMeT} + \text{PA} \rightarrow \text{PPP} \]

\[ V \text{ vs SCE} \]

1.6 1.2 0.8 0.4 0.0 -0.4 -0.8 -1.2 -1.6 -2.0
Covalent Surface Modification

\[ \text{N-\text{[3-(TRIMETHOXY Silyl)-propyl] Pyrrole}} \]

\[ \text{OH} \quad \xrightarrow{+ 1} \quad 95\% \text{ EtOH (pH 5, HOAc)} \quad 24-72 \text{ h, } 25^\circ\text{C} \]

\[ \text{OH} \]

\[ \text{POSITIVE POTENTIAL, 0.3 M (Et}_{4}\text{N}) \text{BF}_4 \text{, MeCN} \]

\[ \text{Me} \quad \text{Me} \quad \text{H-N} \quad \text{Me} \quad \text{Me} \quad \text{H-N} \]

\[ \text{Me} \quad \text{Me} \quad \text{Me} \quad \text{H-N} \quad \text{Me} \quad \text{Me} \quad \text{H-N} \]
Electrochemical Synthesis of Poly(pyrrole)

**SOLUTION:** 1 M PYRROLE
0-1 M TBAP/MeCN
BIAS = +0.7 V vs SCE

**OXIDATIVE POLYMERIZATION OF PYRROLE: MECHANISM**

\[
\text{Pyrrrole} \quad h^+ \rightarrow \text{Pyrrrole} \rightarrow \text{Polymer} \quad -2H^+ \quad h^+
\]

\[
\text{Polymer} \quad n \text{ClO}_4^-
\]

\[
\text{Polymer} \quad h^+ \rightarrow \text{Pyrrrole} \rightarrow \text{Polymer} \quad -2H^+ \quad h^+
\]
Quantum Yield Measurements: Experimental Setup

- Deposit polypyrrole on silicon
- Measurement of \( I_{\text{photo}} \) vs \( \lambda \)

Quantum Yield Measurements

![Graph showing quantum yield measurements for different films of polypyrrole on silicon.](image-url)
THE POLYMER/SEMICONDUCTOR INTERFACE
STANFORD UNIVERSITY

N. Lewis

Figure 1. Interfacial energetics for an n-type semiconductor-liquid junction. At left: the situation at the flat-band condition, before charge transfer equilibration has taken place between the semiconductor and the liquid. Right: energetics after charge transfer equilibration with the redox species $A^+/A$. 

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Figure 2. Schematic of photoelectrochemical cell, based on a semiconductor/liquid junction, for the conversion of light into electricity. Left: irradiation of the photoanode results in current flow, but no net change in chemical composition of the cell. Right: the electrical parameters of such devices and the relationships of the open-circuit voltage, short-circuit current, fill factor and cell efficiency.
n-Si/Poly(pyrrole)/MeOH

![Graph showing the relationship between wavelength and absolute quantum yield. The graph has a y-axis labeled 'Absolute Quantum Yield' ranging from 0 to 1.0, and an x-axis labeled 'Wavelength, nm' ranging from 400 to 1000. There are multiple curves representing different concentrations of pyrrole. Each curve peaks at a different wavelength, indicating variation in quantum yield with wavelength. The curves are labeled with concentration values: 0.6%w, 0.8%w, 1.0%w, and 1.2%w. The graph shows that at higher concentrations, the quantum yield is higher at shorter wavelengths and decreases at longer wavelengths.]
n-Type Si/MeOH

![Graph showing quantum yield vs wavelength for n-Type Si/MeOH]
Open-circuit photovoltage vs solution redox potential for n-Si and p-Si photoelectrodes in 1.0 M KCl/CH₃OH solution. The redox couples used were: (a) cobaltocene +7⁰, (b) N,N'-dimethyl-4,4'-bipyridinium dichloride 2+/+, (c) N,N'-dibenzyl-4,4'-bipyridinium dibromide 2+/+, (d) decamethylferrocene+7⁰, (e) N,N',N'-tetramethylphenylenediamine+7⁰, (f) dimethylferrocene+7⁰, (g) ferrocene +7⁰ and (h) acetylferrocene+7⁰. A tungsten-halogen bulb was used to provide light intensities that yielded short-circuit photocurrent densities of 25 to 30 mA/cm².
For a metal (free electron)

\[ \varepsilon(\omega) = \varepsilon_\infty - \frac{4\pi N e^2}{m^* \omega^2} \]

\[ \varepsilon(\omega) = \varepsilon_\infty - \frac{\varepsilon_p^2}{\omega^2} \]

where

\[ \omega_p^2 = \frac{4\pi N e^2}{m^*} = \text{plasma frequency} \]

Put in damping

\[ \varepsilon(\omega) = \varepsilon_\infty - \frac{\omega_p^2}{\omega(\omega + i/\tau)} \]
For conductive polymers:

After doping to "metallic" levels

N is relatively small (low-density materials, high molecular wt. of monomer
doped to 20% - 50%

\[ \left\{ \begin{array}{l}
\varepsilon > 0 \\
\text{Intramolecular absorptions}
\end{array} \right. \]

For \( \omega > \omega_p \)

\[ \varepsilon = n^2 = \varepsilon_c \]

\[ R = \left( \frac{n - 1}{n + 1} \right)^2 \]

For \( \omega < \omega_p \)

\[ \varepsilon < 0 \]

\( n \longrightarrow \) pure imaginary

Perfect reflection

Numbers:

\[ \omega_p^2 = \frac{4 \pi N e^2}{m^*} \]

\[ \approx 2 \times 10^9 N \]

Thus for

<table>
<thead>
<tr>
<th>N</th>
<th>h\omega_p</th>
</tr>
</thead>
<tbody>
<tr>
<td>10^{23}</td>
<td>0.1 eV</td>
</tr>
<tr>
<td>10^{20}</td>
<td>0.3 eV</td>
</tr>
<tr>
<td>10^{18}</td>
<td>0.03 eV</td>
</tr>
</tbody>
</table>
\[ \varepsilon'(\omega) = \varepsilon_1(\omega) + i \varepsilon_2(\omega) \]

\[ = \varepsilon_1(\omega) + i \frac{4\pi}{\omega} \sigma(\omega) \]

\[ \varepsilon(\omega) = \varepsilon_c - \frac{\omega_p^2}{\omega(\omega + 1/\tau)} \]

For a metal

\[ \varepsilon(\omega) = \varepsilon_c - \frac{\omega_p^2\tau^2}{1 + \omega^2\tau^2} + i \frac{4\pi}{\omega} \frac{1}{1 + \frac{\omega p^2 \tau}{\tau}} \frac{\omega p^2 \tau}{\sigma(\omega)} \]

\[ \sigma(\omega) = \frac{4\pi^1 \omega_p^2 \tau}{1 + \omega^2\tau^2} = \frac{N\varepsilon^2 \tau/m^2}{1 + \omega^2\tau^2} \]

Criteria for a transparent conductor

\[ h\omega_p < \text{visible (1.5 eV) (low carrier density)} \]

\[ \omega_p \tau >> 1 \text{ (little absorption at higher frequencies)} \]

No intramolecular transitions \( (\text{e.g.} \sigma - \sigma^0) \)

Note: for \( \omega_p \tau > 1 \), conductivity is high.
Trans-(CH)$_x$: Chemically Doped Na$^+$ Naphth$^-$
NEUTRAL POINT COMPATIBLE WITH POLYACETYLENE

L: REFERENCE ELECTRODE
The title polymer was prepared by several different approaches. Electrochemical polymerization of isothianaphthene is strongly electrolyte-dependent; non-nucleophilic anions produce poly(dihydroisothianaphthene), whereas nucleophilic anions ($\text{Br}^-$, $\text{Cl}^-$) allow formation of the title compound. The latter, either in a Bronsted acid ($\text{HSO}_4\cdot\text{nH}_2\text{O}$-doped form or chloride-doped form is a better conductor than polythiophene by one order of magnitude and about as good a conductor as poly(3-methylthiophene).

1. $\text{HSO}_4\cdot\text{nH}_2\text{O}$
2. $\text{HSO}_4$-doped form
3. $\text{Cl}-$-doped form

$\text{a} = \text{Al}_2\text{O}_3$
$\text{b} = \text{H}_2\text{SO}_4$
Absorption Spectrum of PITN As-Grown (solid curve) and After In-Situ Electrochemical Doping (dashed curve)
SOME PROCESSING AND DURABILITY ISSUES
MASSACHUSETTS INSTITUTE OF TECHNOLOGY

G. Wnek

Processing

1. Direct synthesis (chemical, electromechanical, photochemical)
   - Films
   - Fibers
   - Gels
   - Foams
   - Powders
   - Composites (blends)

2. Synthesis of processable precursors
   Examples: "Durham" (CH)$_x$

\[ \text{Chemical Reaction Diagram} \]
Solubilization of Doped Polymers (Polyelectrolytes)

1. Allied

\[
\text{[Chemical Structure]} \xrightarrow{1. \text{AsF}_3} \text{BLUE SOLUTION} \xrightarrow{2. \text{AsF}_5} -\text{AsF}_3 \xrightarrow{\rightarrow} \text{CONDUCTIVE FILM}
\]

2. U. of Minn.

\[
(\text{Chemical Structure}) \xrightarrow{I_2 (\text{Liq})} -I_2 \xrightarrow{\rightarrow} \text{CONDUCTIVE FILM}
\]

3. MIT

\[
(\text{CH}_4) \xrightarrow{\text{HSO}_3\text{CF}} \text{BLUE SOLUTION}
\]
Solubilization of Pristine Polymers

a. Grafts (MIT, Bell Labs)

i. \[ \text{PMMA} \]

ii. \[ \text{(CH}_2\text{CH} - \text{CH}_2\text{CH})_m\text{CH} - \text{CH} - \text{CH}_2 \]
   \[ \xrightarrow{1 + 3 + 5} \]
   \[ \text{Ti-CH - CH} \]
   \[ \xrightarrow{\text{P} \text{OLYBUTADIENE}} \]
   \[ (\text{CH})_x \]

b. Blocks (MIT, Bell Labs)

i. \[ \text{CH}_2 \text{CH Li}^+ \]
   \[ \xrightarrow{\text{Ti(OBu)}_4} \]
   \[ \text{C}_2\text{H}_2 \]

ii. \[ \text{CH}_2 \text{CH Li}^+ + \text{MeC C} \]
   \[ \xrightarrow{\text{Ti-(CH} - \text{CH})_n} \]
   \[ \text{CH}_2 \text{CH CMe} \]

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Absorption Spectrum of PITN As-Grown (solid curve) and After Chemical Doping With AsF₅ (dashed curve)