Production of Hydrogen for Clean and Renewable Sources of Energy for Fuel Cell Vehicles

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Project ID #
PDP-35

Overview

Timeline

- Project start date: June, 2005
- Project end date: June, 2007
- Percent complete: 10%

Budget

- Total project funding
  - DOE share: $992,000
  - UT share: $451,000
  - ODOD share: $204,000
- Funding received in FY05 to date: $992,000 ($100,000 spent)
- Funding for FY06: $0

Overview

Barriers Addressed

- DOE MYPP Objective for Photoelectrochemical Production of Hydrogen
  - By 2015, demonstrate direct PEC water splitting with a plant-gate hydrogen production cost of $5/kg projected to commercial scale.
- Technical Targets:
  - 2010: STH Eff >9%; Durability >10,000 hours; Cost < $22/kg
  - 2015: STH Eff >14%; Durability >20,000 hours; Cost < $5/kg
- PEC Hydrogen Generation Barriers -- MYPP 3.1.4.2.3
  - M. Materials Durability
  - N. Materials and Systems Engineering
  - O. PEC efficiency

Partners

- Bowling Green State University
- Ohio Department of Development
- Midwest Optoelectronics, LLC

Objectives

- To expand a research program directed to the development of clean and renewable domestic methods of producing hydrogen. This program will provide industry with ways to produce hydrogen in an environmentally sound manner to support the use of fuel cells in vehicles and at stationary locations.

Approach - Tasks

Task 1: Integrated hydrogen facility

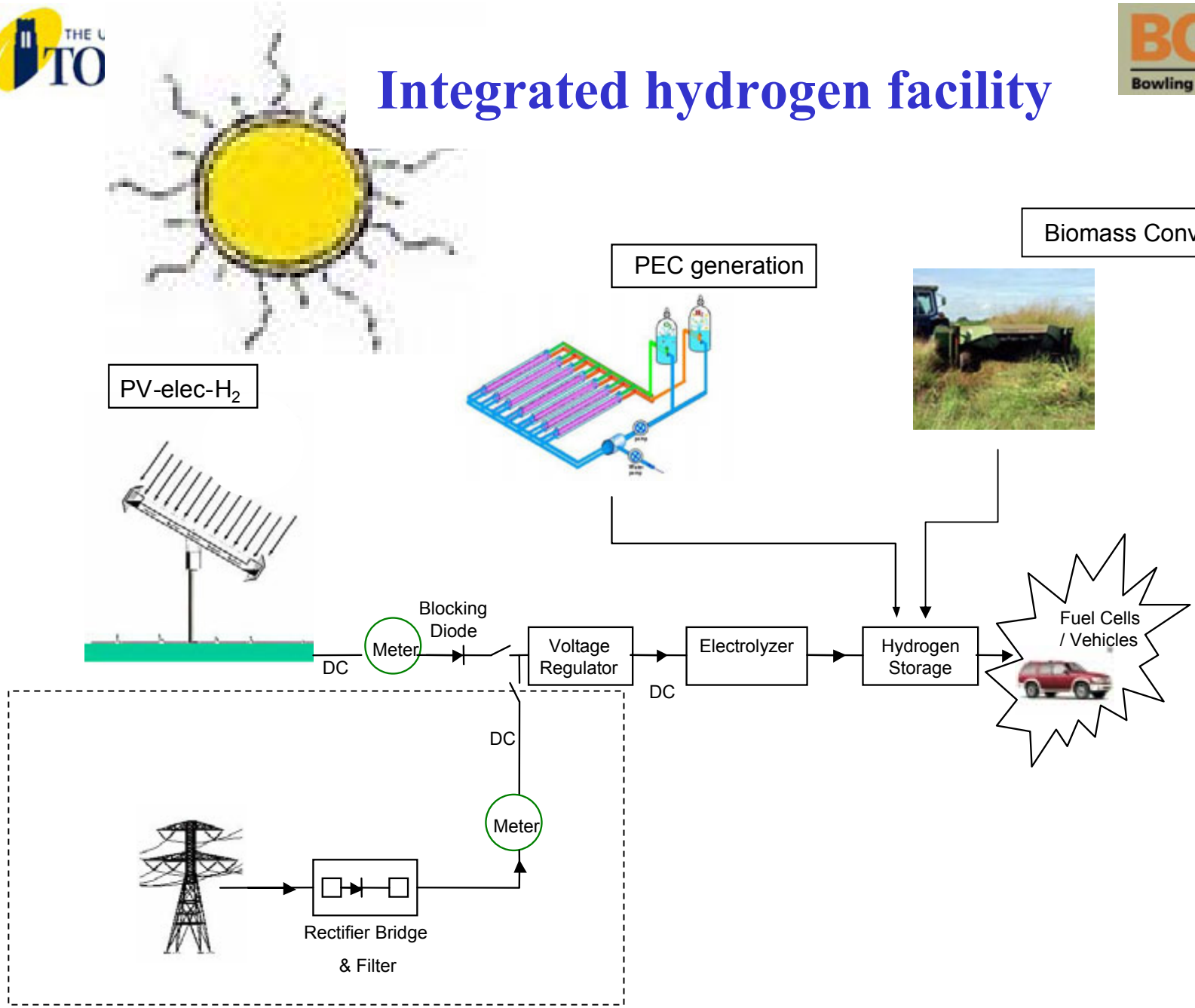
Task 2: Development of substrate-type PEC cells

Task 3: Development of advanced materials for immersion-type PEC cells

Task 4: Hydrogen production through conversion of biomass-derived wastes

Task 5: Economic analysis of integrated system

Integrated hydrogen facility



Task 1: Integrated hydrogen facility

Demonstration of a solar-powered fuel cell vehicle. While this task involves some research elements, this is largely a demonstration of technologies. The task includes

- 12 kW PV array installation (First Solar thin-film CdTe on glass modules)
- Integration of the solar array with a pressurized electrolyzer (or an integrated electrolyzer plus compressor)
- DC voltage regulation system for direct PV-to-electrolyzer power feed
- Hydrogen storage options include storage in carbon fiber cylinders or nickel metal hydride
- Retrofit of an electric vehicle, envisioned to be of a GEM-style, with a Ballard 5 kW liquid-cooled fuel cell, including all balance of plant components

This task is to be cost shared with funds from Ohio Department of Development and from University of Toledo.

Task 2: Development of substrate-type photoelectrochemical cells

To develop and improve a substrate-type photoelectrochemical cell for hydrogen generation. In such a PEC cell, a triple-junction amorphous silicon photoelectrode deposited on a conducting substrate is integrated in a PEC cell, in which the hydrogen and oxygen compartments are both behind the photoelectrode and are separated by a membrane. Specific research activities include:

- Development of improved encapsulation materials and process
- Optimization of grid configuration and installation process
- Investigation of effect of various cell dimensions in the oxidation and reduction compartments
- Design of improved membrane holder to prevent hydrogen and oxygen from intermixing, and
- Study of various electrolyte inlet and gas/electrolyte outlet configurations

Task 3: Development of advanced materials for immersion-type photoelectrochemical cells

- Deposition of a transparent, conducting and corrosion resistant coating for PEC photoelectrode.
- Deposition of photoactive semiconductor as the top component cell absorber layer in a multi-junction PEC photoelectrode
- Characterization and modeling of PEC materials and photoelectrodes

Deposition of a transparent, conducting and corrosion resistant coating for PEC photoelectrode

The objective of this subtask is to develop a transparent, conducting and corrosion resistant (TCCR) material that can be made at low temperature (below 250°C) using a low-cost thin-film deposition technique, and in addition has the following properties: high optical transmission in the visible wavelength range, high electrochemical stability in the electrolyte, and sufficient conductivity for transport of charge carriers, such that an ohmic contact is formed with both the electrolyte and the topmost layer of the a-Si solar cell.

Materials to be studied under this task will include:

- p-type a-SiC TCCR layer
- fluorine-doped tin oxide (SnO_2:F)
- TiO_2 based alloys
- polymer nanocomposite

Deposition of photoactive semiconductor as the top component cell absorber layer in a multi-junction PEC photoelectrode

The objective of the task is to develop a photoactive semiconductor material that

1) is stable in electrolyte both in dark and under illumination,
2) forms a high-quality rectifying junction with electrolyte and an ohmic contact with the tf-Si layer underneath;
3) generates at least 7.5 mA/cm^2 current so that it can be matched with the middle and bottom component solar cells in an a-Si based triple-junction stack, and
4) is deposited at low temperature (< 250°C) using a low-cost deposition method.

Materials to be studied under this task will include:

- polycrystalline CdS based II-VI compounds
- TiO_2 based materials such as $SrTiO_3$

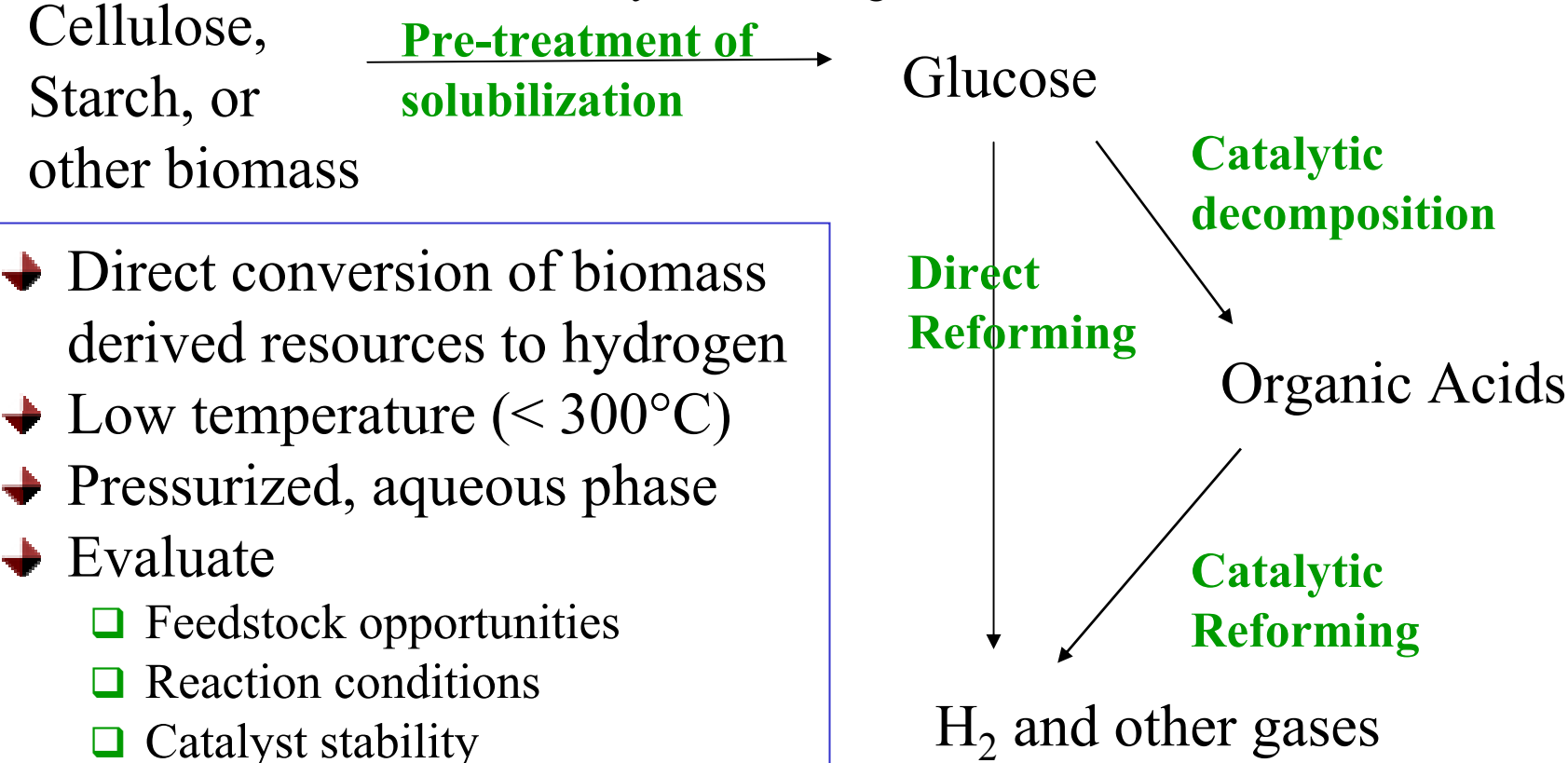
Characterization and modeling of PEC materials and photoelectrodes

- Real time characterization of corrosion resistance using Mueller matrix ellipsometry
- Modeling of PEC photoelectrode

Task 4: Hydrogen production through conversion of biomass-derived wastes

Task 4a: Identify the products of fermentation

Task 4b: Catalytic reforming



- Direct conversion of biomass derived resources to hydrogen
- Low temperature (< 300°C)
- Pressurized, aqueous phase
- Evaluate
  - Feedstock opportunities
  - Reaction conditions
  - Catalyst stability

Task 5: Economic Analysis of Integrated System

- Cost analysis:
  - Economic analysis of different types of PEC cells
  - Operating and equipment cost at each step
  - Cost projections considering
    - Economies of scale
    - Technology advancements
- Efficiency: energy loss at each step and across the system
- System Reliability

DC Magnetron Sputter Deposition for Photoelectrode Materials

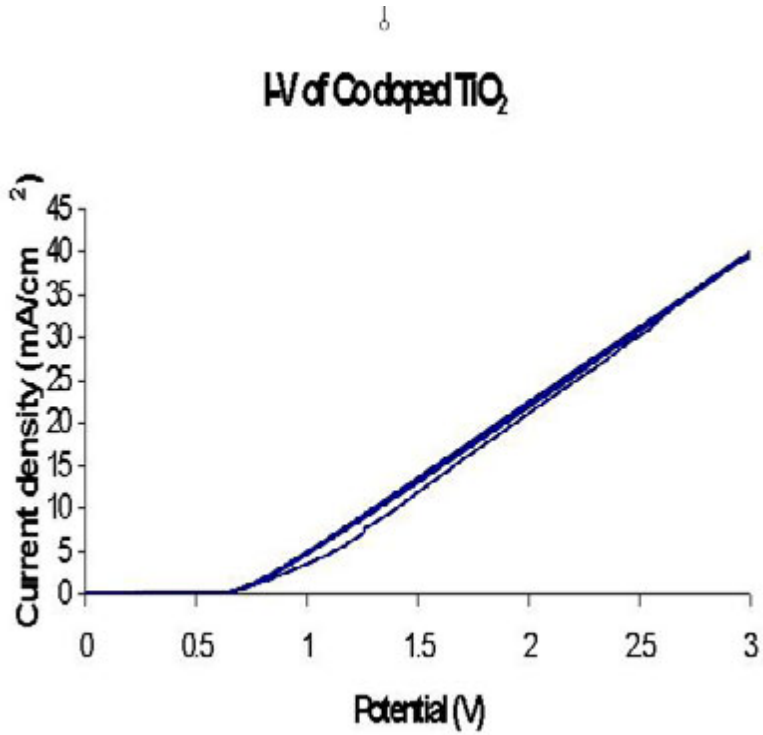
- Argon sputtering
- 3-gun chamber, so up to 3 targets can be sputtered at once (i.e., TiO_2 and In targets for $TiO_{2-x}In_x$)
- 2 mass flow controllers to mix gases during sputtering

Highlights – TiO_2

- TiO_2 film doped with Co showed increased current density, and high stability.
- Reactive sputtering of Ti to make TiO_2 shows better control and reproducibility.
- Zr doped TiO_2 and TiO_2 deposited on ZrO_2 seed layer showed good stability.

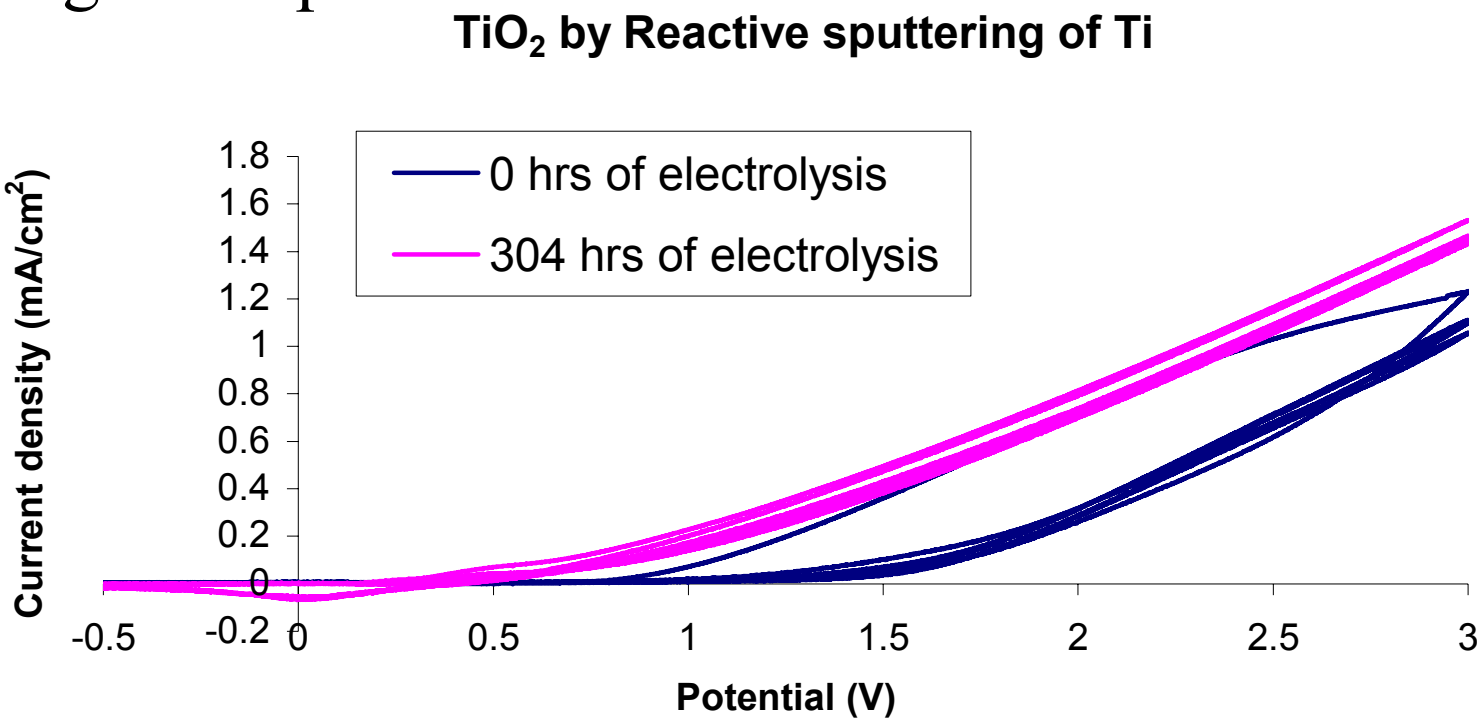
I-V Measurements – $TiO_{2-x}Co_x$

- Addition of small amounts cobalt with O_2 stabilized the films
- However, addition of Co increases the light absorption.



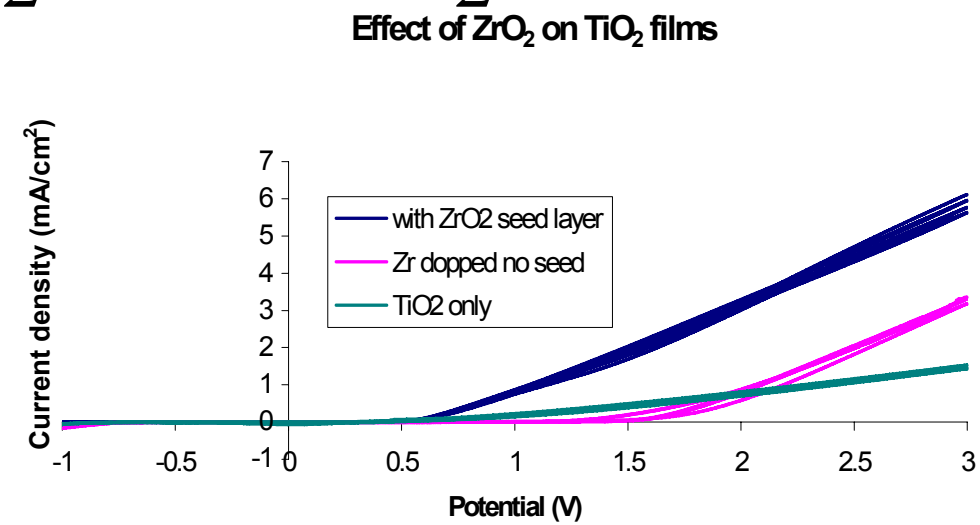
Reactive Sputtering of TiO_2

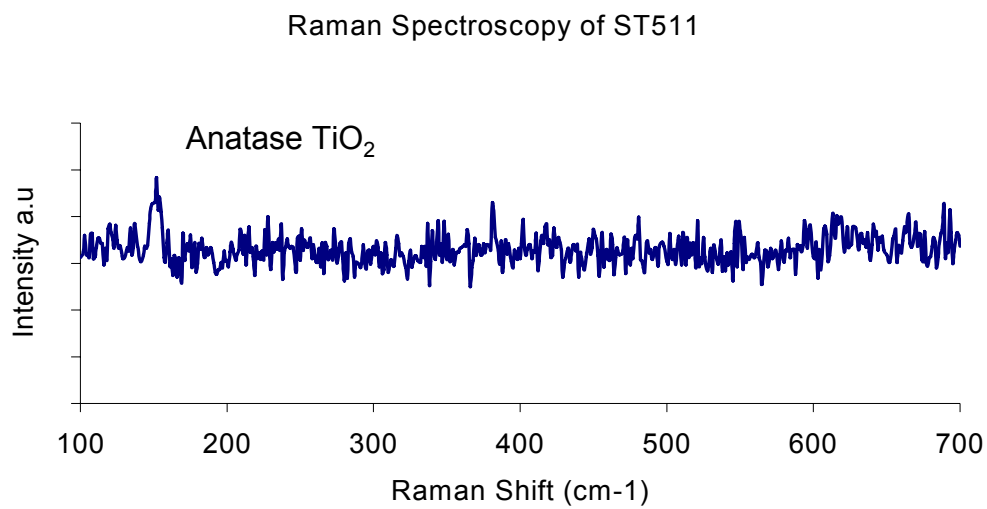
- Reactive sputtering of Ti in O_2/Ar gas mixture gives reproducible stable films.



TiO_2 and ZrO_2

- Addition of a little amount of Zr stabilizes the TiO_2 electrode.
- Use of ZrO_2 as the seed layer produces anatase TiO_2.

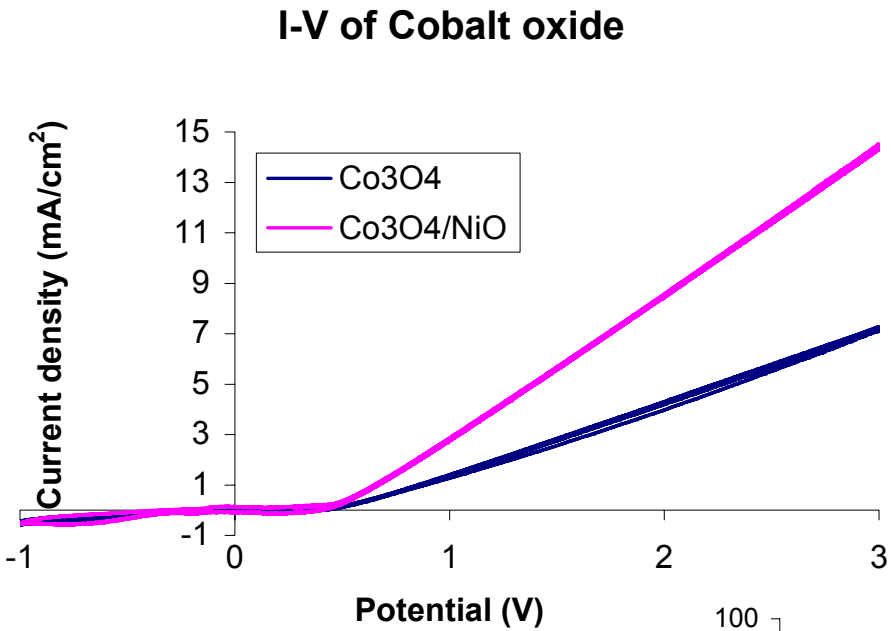


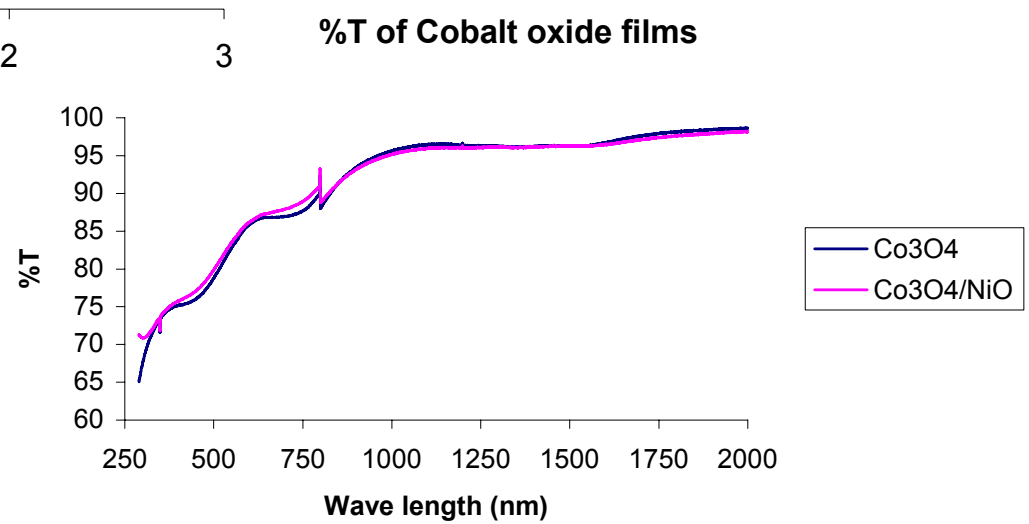


Co_3O_4 as a TCCR

- Co_3O_4 formed by reactive sputtering of Co provides very stable films.
- Addition of NiO further increases the conductivity.
- Thicker layer of Co_3O_4 makes the films dark.

I-V and transmission of Co_3O_4 films



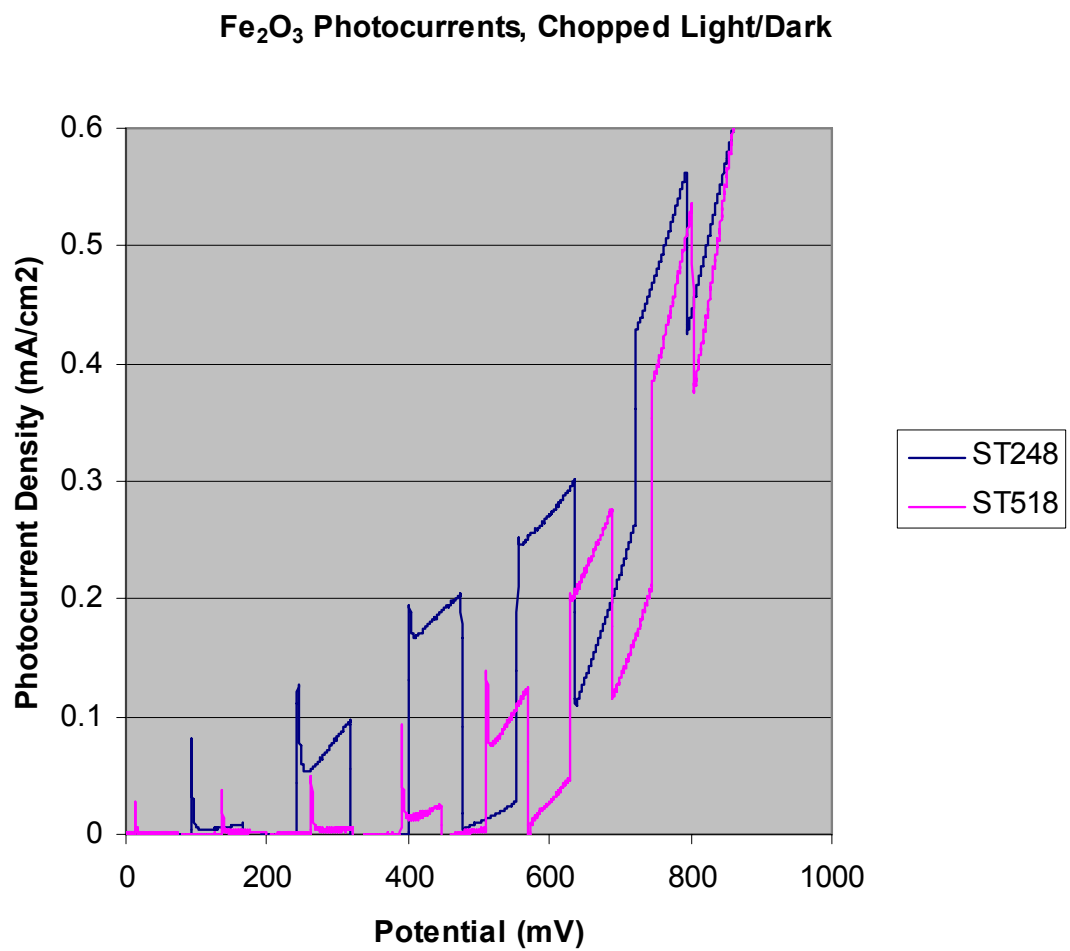


Highlights – Fe_2O_3

- RF sputter deposited with Ar and Ar-O_2 mixture
- Stable in 33% KOH standard solution
- Best films produced at temperatures near 400°C at 100 W for 120 minutes; 2% oxygen in the deposition chamber atmosphere
- Currently, films generating photocurrents near 0.2 mA/cm^2 have been consistently produced
- 70-80% Transparent
- 200-300nm film thickness
- Band gap of 2 eV

Photocurrent – Fe_2O_3

- Measured photocurrent densities near 0.2 mA/cm^2
- Currently working on reducing the onset potential

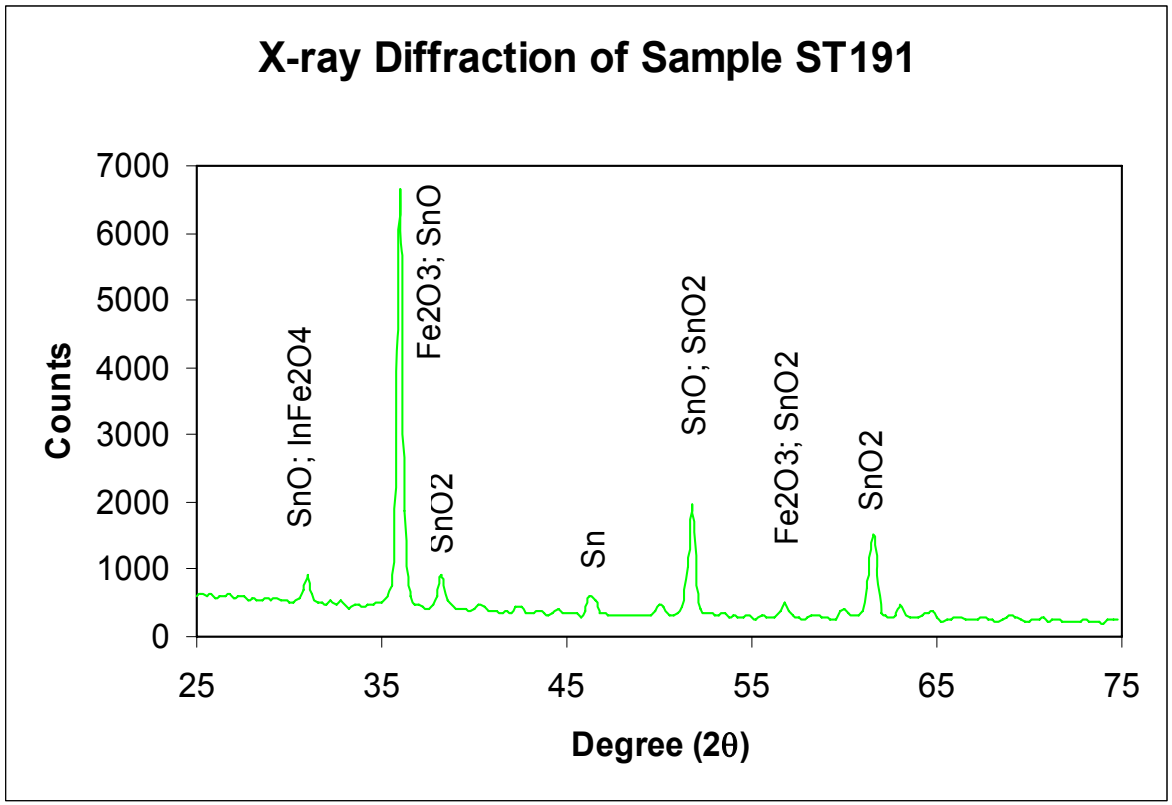


Highlights – $Fe_2O_{3-x}In_x$

- Relatively stable in 33% KOH, though not so much as Fe_2O_3
- Best film made at 200°C at 100 W / 20 W (Fe2O3 / In) for 120 minutes with 5% oxygen
- Measured photocurrents near 0.03 mA/cm^2

X-ray Diffraction – $Fe_2O_{3-x}In_x$

- Scans indicate the presence of Fe_2O_3, SnO, SnO_2, and $InFe_2O_4$



Highlights – WO_3

- WO_3 prepared using RF magnetron sputtering
- Sputtered in 20% O_2/Ar mixture using Tungsten target
- Films produced at different pressures and gas flow rates

Optimization

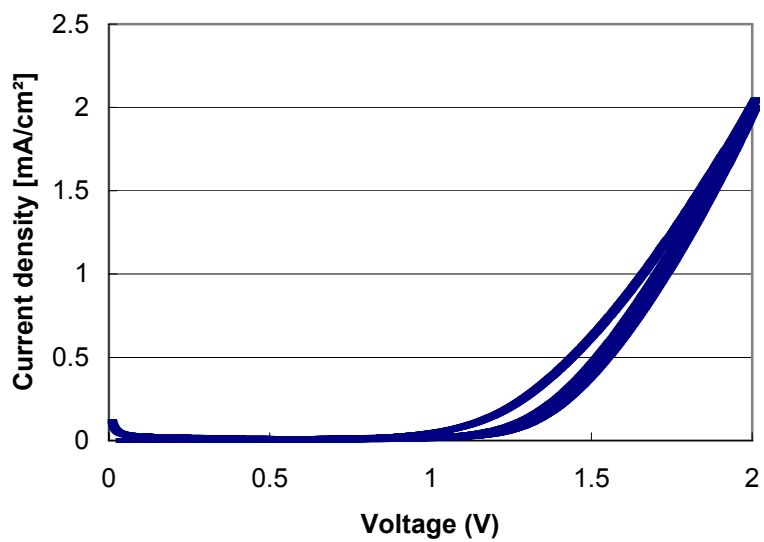
- WO_3 films deposited on ITO as well TEC15 (commercial ITO)
- Stability as well as current density good for
  - Temperature - 250 ^oC
  - Pressure - 20 mtorr
  - Gas flow rate - 20 sccm
  - Time - 2 hrs

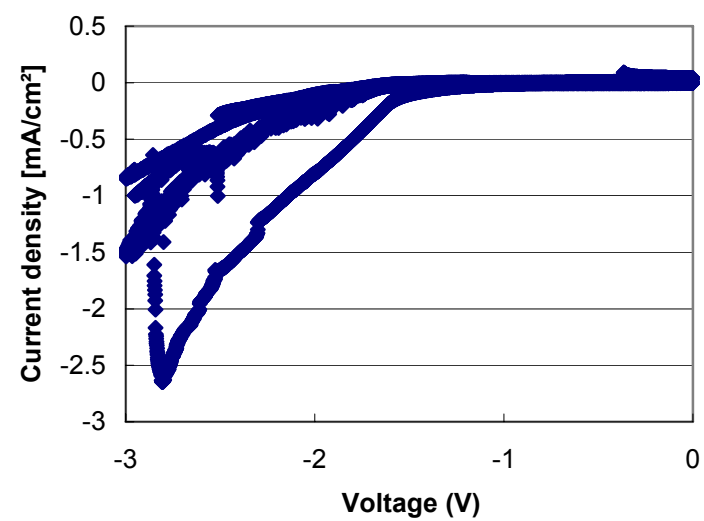
Highest current density of 50 mA/cm^2 obtained on TEC15 at V_{oc}= 3.0 V (Results reproduced).

Current density of 3.5 mA/cm^2 obtained on ITO at 3.0 V

I-V Measurements – Flexbond-ATO composite film in 33% KOH

- Flexbond-Antimony tin oxide (ATO) (30V%) composite film coated on ITO-glass shows good stability as anode side
- Flexbond-ATO (30V%) composite film coated on ITO-glass shows bad stability as cathode side





The Optimum Spin-Coating Condition For Film Fabrication

Properties of Flexbond-ATO (30V%)-Carbon Nanofiber (0.01wt%) Composite Films coated on glass cast by different conditions

Sample	Speed (rpm)	Time Before Spin (s)	Resistance (KΩ)	Transmittance (%)
# 1	167	5	30.8	83
# 2	167	1	31.7	90
# 3	167	0	36.1	91
# 4	200	1	70.5	91

- Higher spin speed, lower electrical conductivity while transmittance
- Longer interval time between casting solution and spin, higher electrical conductivity while lower transmittance
- Addition of carbon nanofiber appears to increase electrical conductivity, which should be further confirmed later.
- Transmittance measurement was performed using silica detector

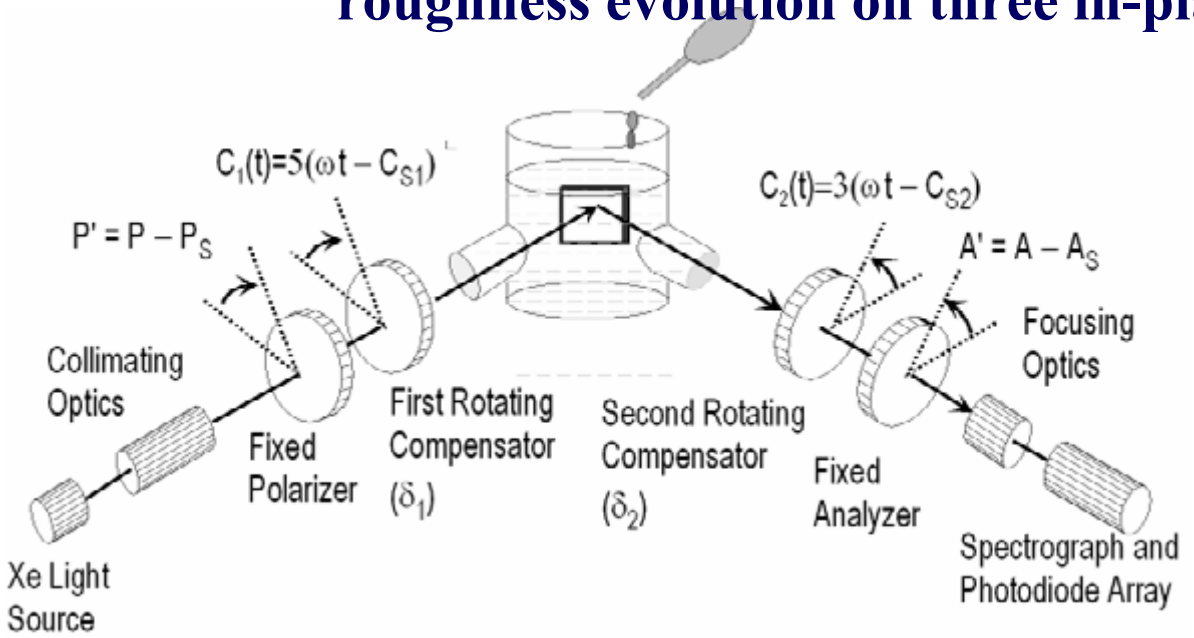
Gas Generation by triple junction solar cell coated with Flexbond-ATO (30V%) composite film

- 3 minutes after solar cell was immersed, bubbles started being generated around good ITO circles
- Thin polymer film resulted in a small decrease in voltage of the solar cell (around 8~20%)
- However, different from the stability results shown in the first slide, the polymer film started peeling off from solar cell after about 2 hours and 1 hour running for 1N and 2 N KOH, respectively.
- The adhesion between polymer film and solar cell was poor, which should be focused on later.

Advanced optical analysis of transparent conducting electrodes for PV-H_2

- Optical instrumentation development
- Illustrative application: modification of ZnO electrodes
  - Analysis of microscopic surface roughness
    with in-plane scale L given by $L << \lambda$ where λ is wavelength:
    apply effective medium theory to analyze $r_{pp}/r_{ss} = \tan\psi_{pp}\exp(i\Delta_{pp})$
  - Analysis of "macroscopic" surface roughness
    with in-plane scale L given by $L \sim \lambda$:
    apply scalar random diffraction theory to analyze R(unpolarized)
  - Analysis of "geometric optics scale" surface roughness
    with in-plane scale L given by $L >> \lambda$; $L>L_c$, lateral coherence
    apply incoherent superposition to analyze degree of polarization
  - Correlations with atomic force microscopy on different scales
    and profilometry

Real time Mueller matrix spectro-ellipsometry (MM-SE) for modification of ZnO electrodes as a model system Analysis of roughness evolution on three in-plane scales



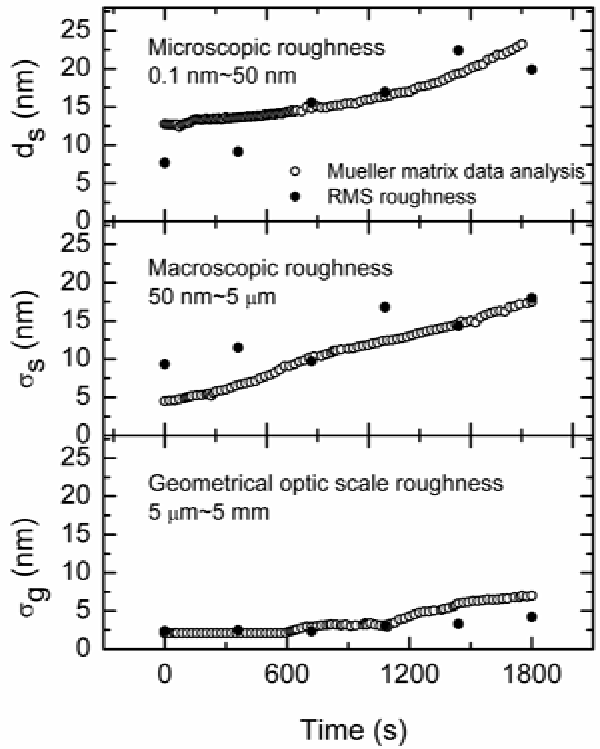
- ~ 8200 Å thick sputtered ZnO on glass used as model system
- ZnO film immersed in 20 ppm HCl in H_2O
- Surface rough- ness evolution tracked in real time by MM-SE

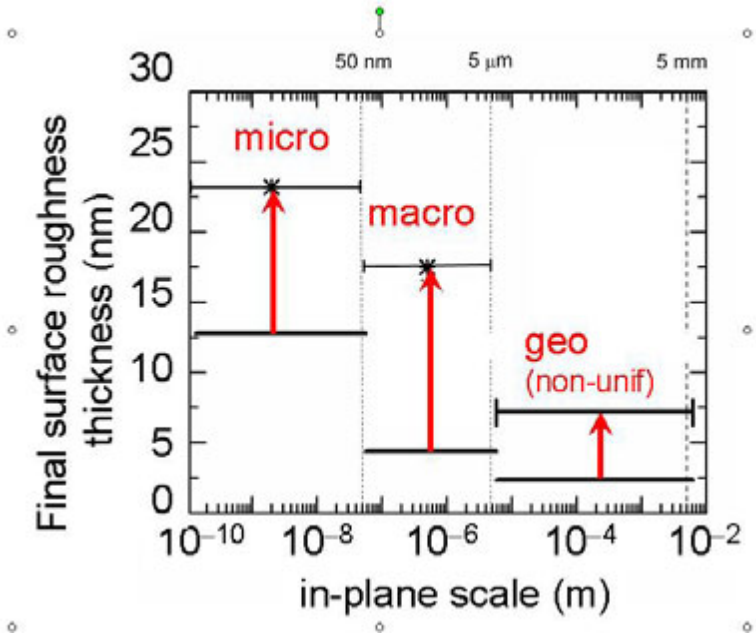
Strategy [Chen, An, Collins, Phys. Rev. Lett (2003)]

- Use {Re(ρ_{pp}), Im(ρ_{pp})} [(real, imaginary) parts of p→p/s→s complex amplitude reflection ratio] to extract microscopic roughness thickness via an EMT.
- Use M_{11} [reflectance for unpolarized light] to extract macroscopic roughness via scalar diffraction theory.
- Use D [depolarization parameter] to extract geometric scale roughness using incoherent superposition of irradiance waveforms.

Summary: evolution of surface roughness on three different in-plane scales for ZnO during modification

The dominant increase in roughness occurs on the macroscopic scale, so leads to "texture-etching" of surface; however, microroughness development is also significant.

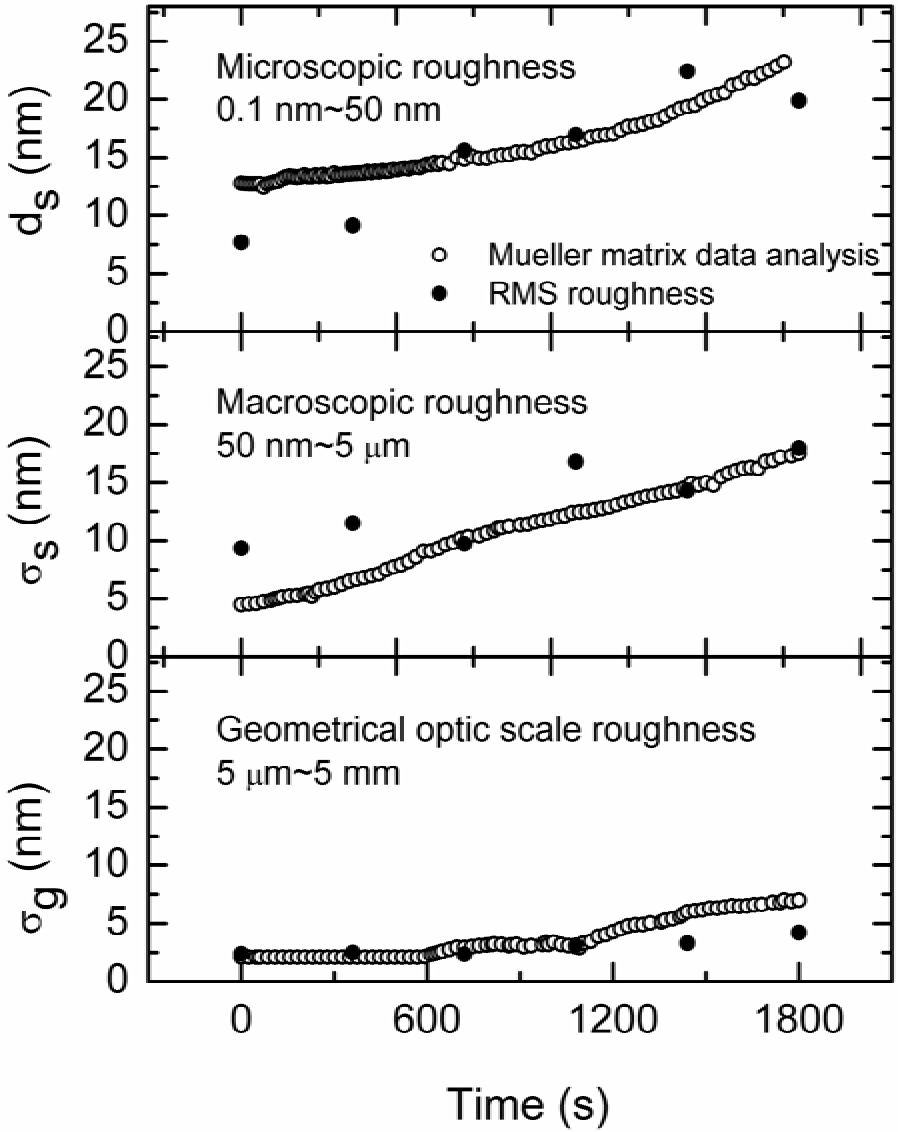




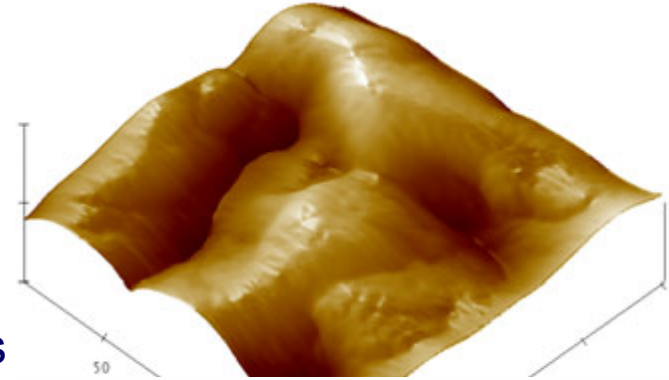
The dominant increase in roughness occurs on the macroscopic scale, so leads to "texture-etching" of surface; however, microroughness development is also significant.

Solid symbols: root mean square roughness from AFM and profilometry (next).

Correlation of roughness by MM-SE with that by AFM and profilometry

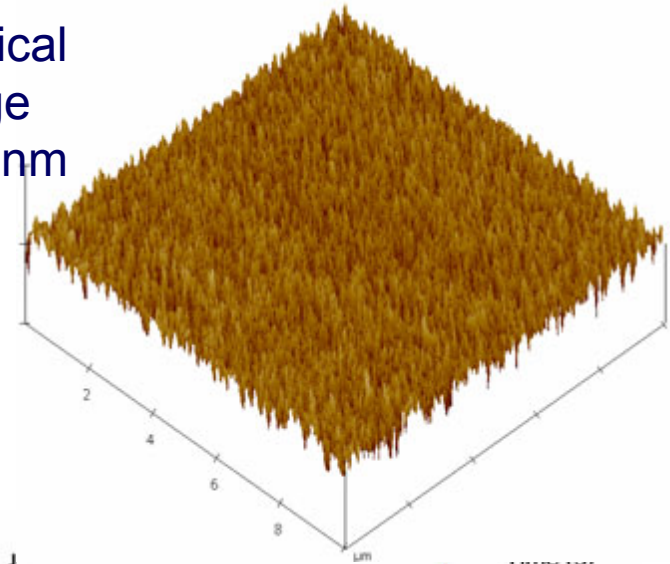


200 nm x 200 nm AFM image t = 1800 s

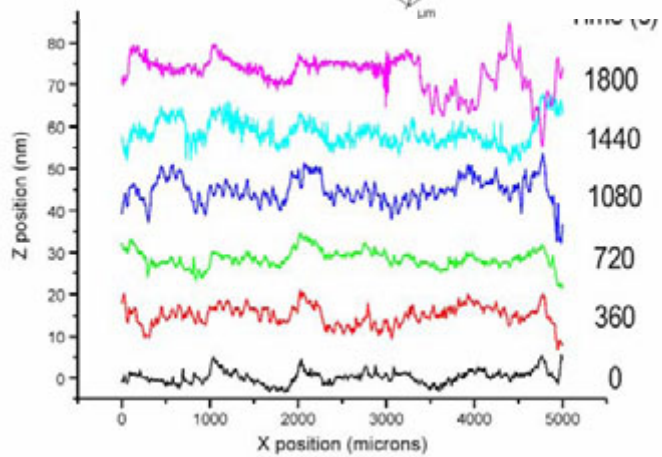


Vertical range 150 nm

10 μm x 10 μm AFM image t = 1800 s



5 mm profilo-meter scans



Summary for Ellipsometer Characterization

- **By using a newly-developed multichannel ellipsometer based on the dual rotating-compensator principle, small changes in optical properties can be extracted as well as surface roughness thickness over a wide range of in-plane scales for analysis of transparent conducting electrode modification by dissolution.**

- **Analysis involves determination of:**
  (i) dielectric functions from the polarization change; (this is done most accurately in the initial stage of processing when the surface is the smoothest);
  (ii) microscopic scale roughness evolution from the polarization change;
  (iii) macroscopic scale roughness evolution from the unpolarized reflectance; and
  (iv) geometric optics scale roughness evolution from the depolarization.

Hydrogen Safety

The most significant hydrogen hazard associated with this project is:

- Hydrogen generated from PV/electrolyzer and PEC panels needs to be appropriately handled.

Our approach to deal with this hazard is:

- Follow related federal and state guidelines for handling the hydrogen generated in our PEC panels
- Provide safety training to all personals handling hydrogen

Other significant hazard related to this research is the handling of hazard gases such as PH_3, GeH_4, SiH_4, BF_3, H_2 during the deposition of semiconductor layers for the photoelectrodes

Have installed comprehensive safety measures for the handling of toxic gasses including

- toxic gas monitors probing various areas of deposition machines.
- gas monitor that can be accessed remotely and is monitored by police department.
- 24-hour training course provided to system operator.
- Visit by Toledo Fire department to discuss various safety issues and preventive measures.

UT Key Participants

Office of Research

- Frank Calzonetti, Vice Provost for Research, Graduate Education and Economic Development

College of Arts and Sciences

Department of Physics and Astronom

- Xunming Deng, Professor
- Alvin Compaan, Professor and Chair
- Robert Collins, Professor

Department of Chemistry

- Dean Giolando, Professor

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Department of Chemical and Environmental Engineering

- Martin Abraham, Professor
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Collaborators

- Bowling Green State University
- Ohio Department of Development
- Midwest Optoelectronics, LLC