From ref. 1

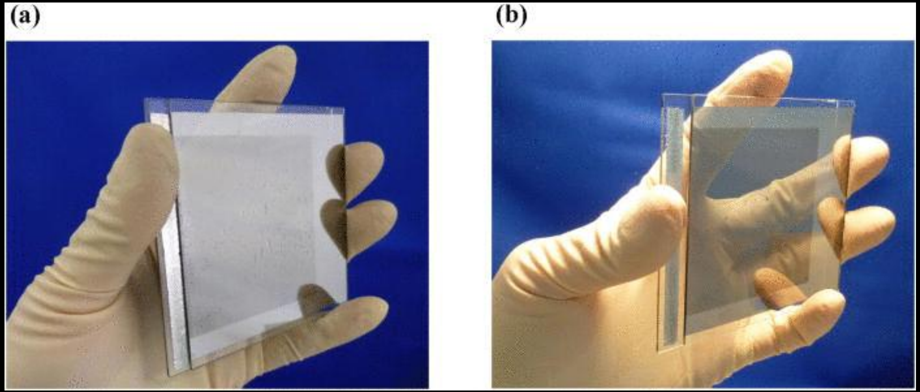
# INCORPORATING POLYMERS FOR REDUCED COST OF SMART WINDOWS

A presentation by Team Smart Cicada

May 14, 2014

# Motivation and Purpose

- Low eco-impact buildings
- Smart Window - a solid state device that changes based on applied voltage
- Switchable Mirror - goes from reflective to transparent for enhanced efficiency
- Replace ITO and tungsten oxide with PEDOT:PSS and PANI

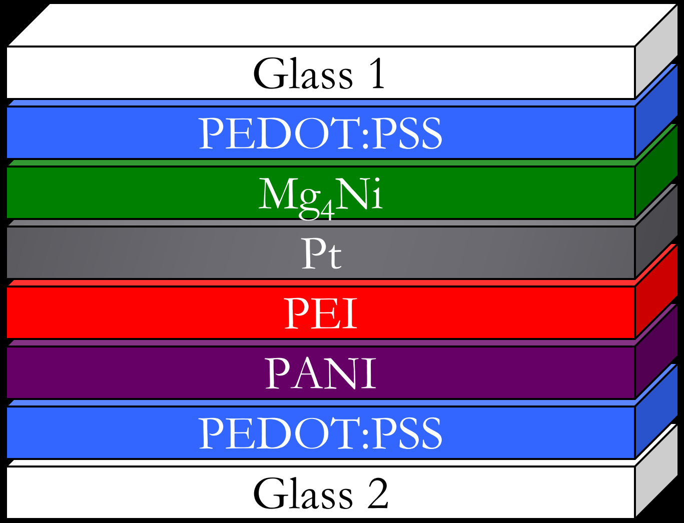



[2]

- COMSOL simulation of optical transmittance

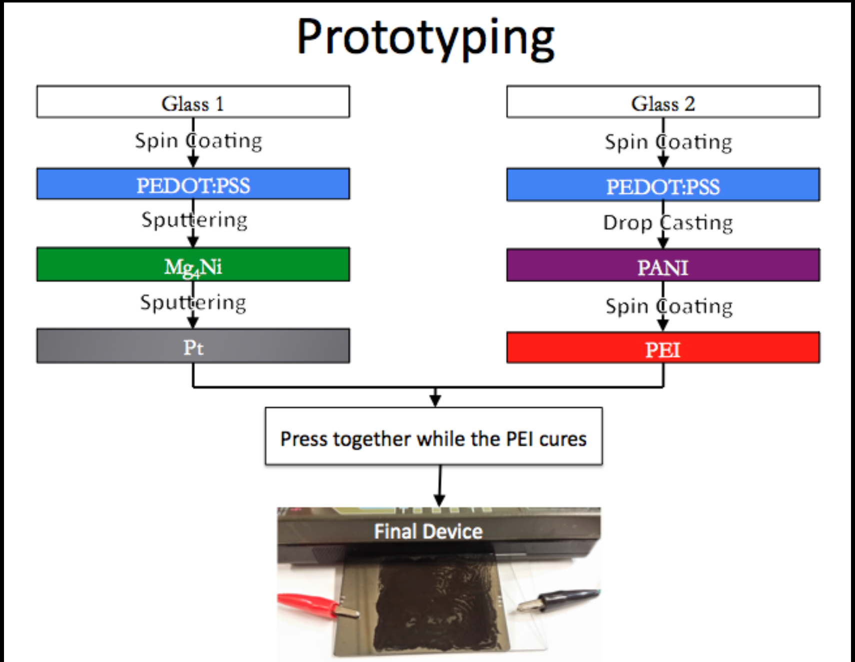
# Design and Goals

- Switchable Mirror - Move hydrogen into and out of an active layer to cause changes in optical properties
- Electrode/Ion storage/Electrolyte/Active Layer/Electrode
- Tajima's group device had a layering of:
  - ITO/$WO_3$/PEI/Pt-$Mg_4Ni$/ITO
  - Our device replaces ITO with PEDOT:PSS as a conductive transparent electrode and $WO_3$ with PANI as the ion storage layer:
  - PEDOT:PSS/PANI/PEI/Pt-$Mg_4Ni$/PEDOT:PSS
- **GOALS**



# Technical Approach - Polymer Processing

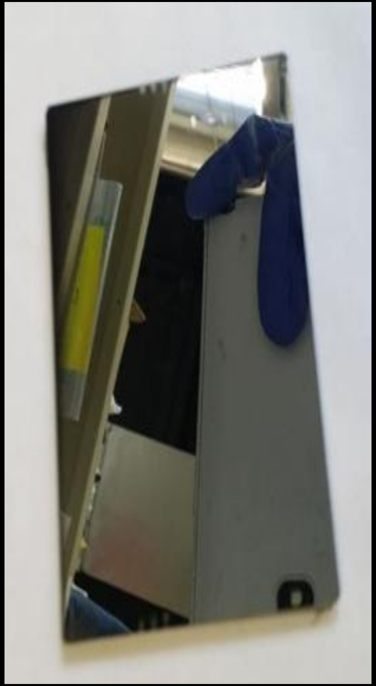
- Shape, thickness, and structure of each layer is dependent on processing conditions
  - Polymer Synthesis
    - PANI
    - PEI
    - PEDOT:PSS
  - Deposition Methods
    - Spin Coating
    - Meyer Rod Coating



# Technical Approach - Sputtering Processing

- Sputtering - Mg4Ni & Pt
  - Mg4Ni layer on PEDOT:PSS
    - Goal of 70nm of Mg4Ni
    - Power ratio of 1.88 : 1 for Mg : Ni
    - Absorbing and desorbing hydrogen
  - Pt layer on Mg4Ni layer
    - Goal of 4nm of Pt
    - Shiny and like mirror

AJA Sputtering unit



# Technical Approach - Electrical Analysis

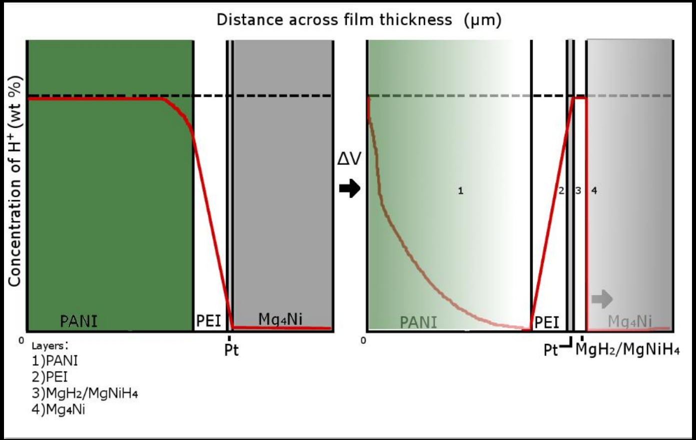
- Modelling through hydrogen diffusion: Fick's First Law

$$J_i = -D_i \frac{\partial v}{\partial x} = D_i \cdot E_i$$

$$J_i = \frac{\sigma_i \cdot V_{app} \cdot \varepsilon_{r,i}}{d_{total} \cdot \delta}$$

$$t_i = \frac{d_i \cdot \rho_i \cdot n_i}{J_i m_{w,i}}$$

$$t_{swtiching} = \frac{d_{total} \cdot \delta}{V_{app}} \sum_{i=1}^{n_{layers}} \frac{d_i \cdot \rho_i \cdot n_i}{\sigma_i \cdot \varepsilon_{r,i} \cdot m_{w,i}}$$



# Technical Approach - Electrical Analysis

- Mass balancing to determine PANI thickness

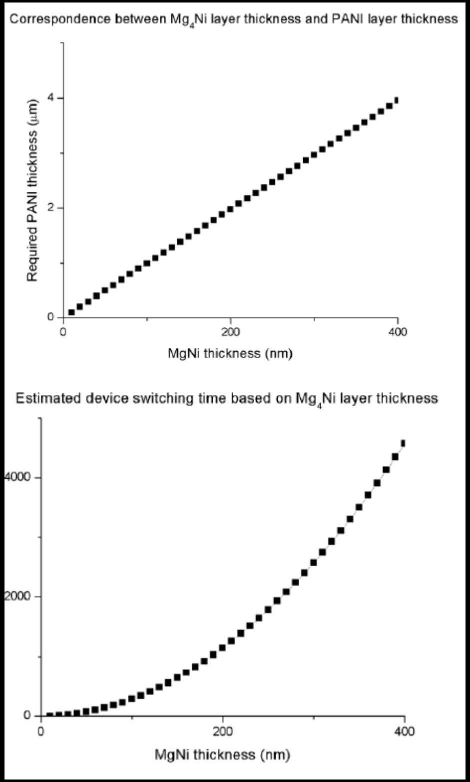
$$N_{H,MgH_2/MgNiH_4} = \frac{d_{MgH_2/MgNiH_4} \cdot A_{device} \cdot \rho_{MgH_2/MgNiH_4} \cdot n_{MgH_2/MgNiH_4} \cdot N_A}{m_{w,MgH_2/MgNiH_4}}$$

$$N_{H,PANI} = \frac{d_{PANI} \cdot A_{device} \cdot \rho_{PANI} \cdot n_{PANI} \cdot N_A}{m_{w,PANI}}$$

$$d_{PANI} = \frac{1.31 \cdot d_{Mg_4Ni} \cdot \rho_{MgH_2/MgNiH_4} \cdot n_{MgH_2/MgNiH_4} \cdot m_{w,PANI}}{m_{w,MgH_2/MgNiH_4} \cdot \rho_{PANI} \cdot n_{PANI}}$$

# Electrical Predictions

- Make assumptions:
  - One layer is rate limiting
  - Most likely MgH2/MgNiH4 or PANI
  - Assume dimensions for our prototype and dielectric
  - Use data from literature to assess conductivity
- MgH2/MgNiH4 conductivity: ~1.32*10^-8 /ohm-m
- PANI conductivity: ~3.8*10^-8 /ohm-m



# Technical Approach - COMSOL 4.4

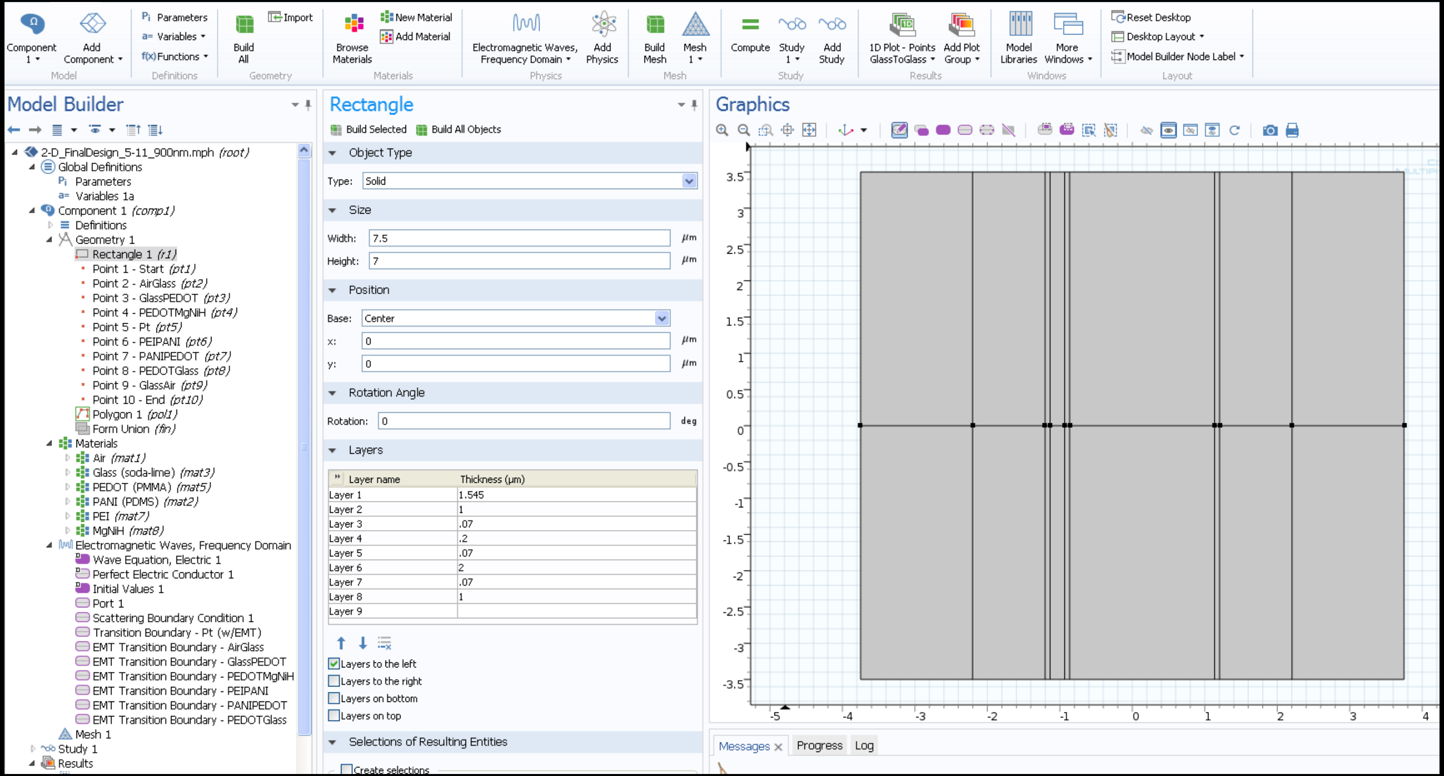
- Aimed to model the optical properties of our device through COMSOL Multiphysics 4.4
- Obtained a floating license through Dr. Phaneuf
  - Included Wave Optics Module
- Original Plan - Fresnel Equations
  - Model transmittance and reflectance vs. wavelength/frequency
  - Could do this for a simple 2-layer, 3-D model
    - More advanced models proved to be difficult
    - Computing issues / Frequency sweep issues
- Final Simulations - Maxwell’s equations
  - Model transmitted light beam intensity through our device
  - Simple 2-D model with accurate layer thicknesses
  - Frequency Domain, time independent, FEM

# Technical Approach - COMSOL 4.4

- Performed multiple thought-experiments to test the validity of our assumptions and choices in COMSOL.
- Needed to estimate multiple material layers since we could not get sufficient experimental constants
- Applied necessary boundary conditions - (transition, scattering)
- Modelled roughness at each interface with effective medium theory:.

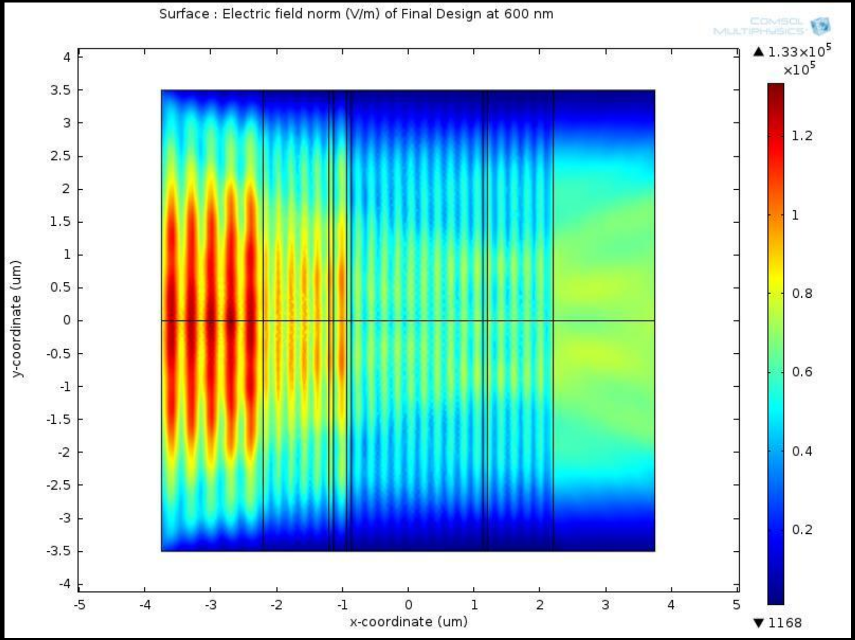
| Effective Medium Approximation | Equation |
|---|---|
| Drude | $n_{eff}^2 = (1-\phi)n_c^2 + \phi n_d^2$ |

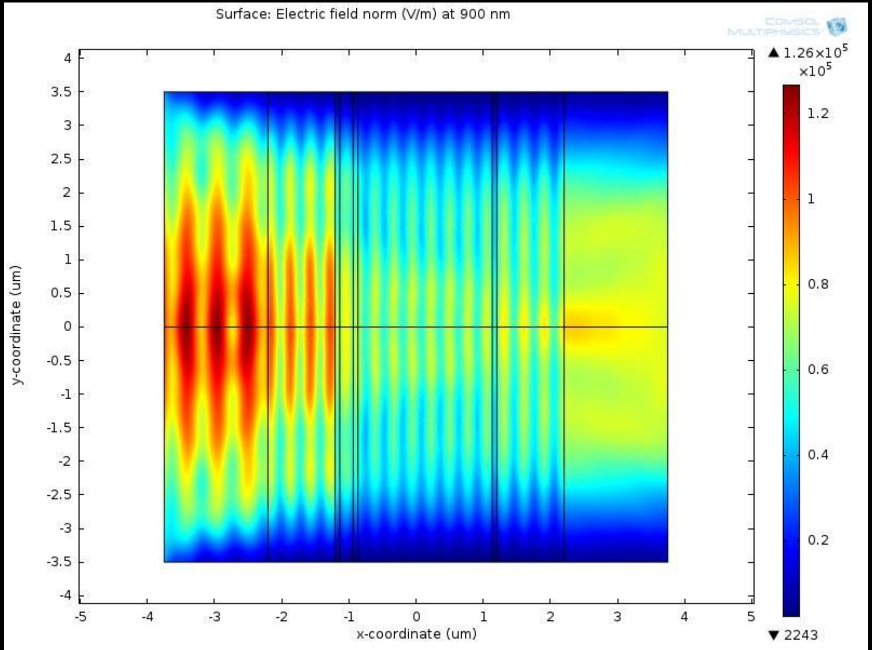
# COMSOL 4.4 RESULTS



# COMSOL 4.4 RESULTS

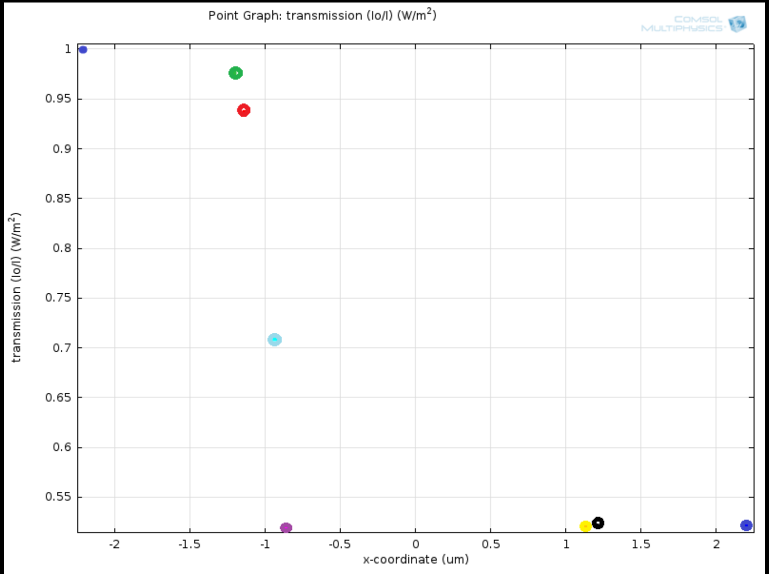
- Electric field of final design at 600 nm (left) and 900 nm (right).

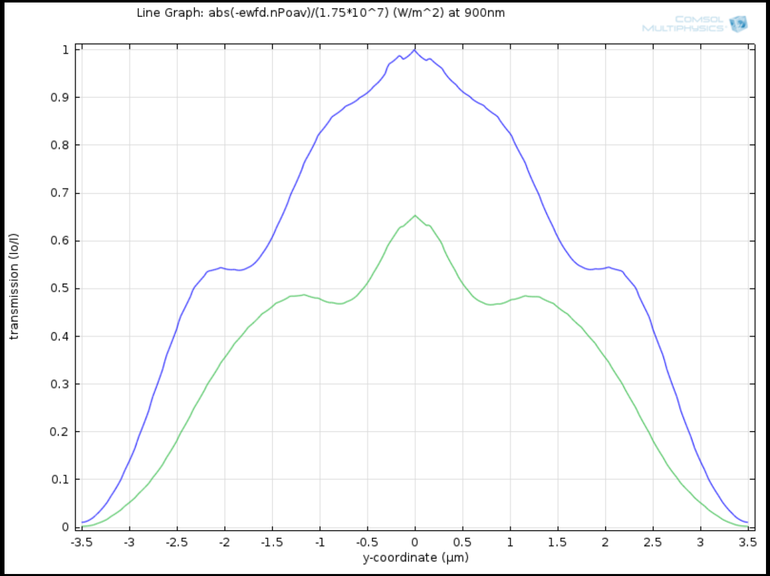


# COMSOL 4.4 RESULTS

- Power out/in curve of our final design at 900 nm (right).
- Point plot of power out of each interface along the using a 600 nm plane wave (left).



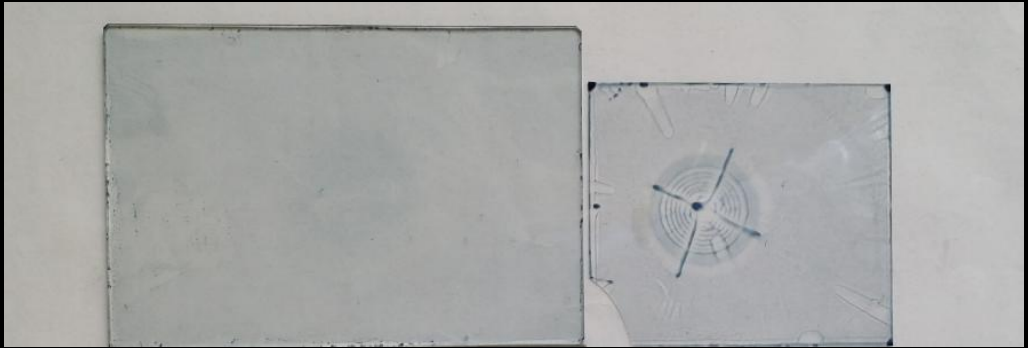



# POLYMER SYNTHESIS


From left to right: concentrated PANI, PEDOT:PSS, and PEI solutions

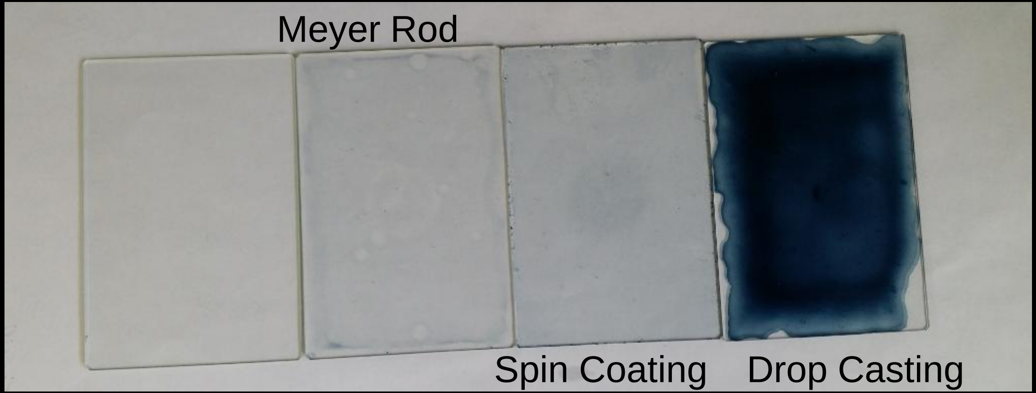
# PEDOT:PSS

Preliminary Spin Coating Attempts



Uneven Coating

Final Deposition Techniques




Delicate Film

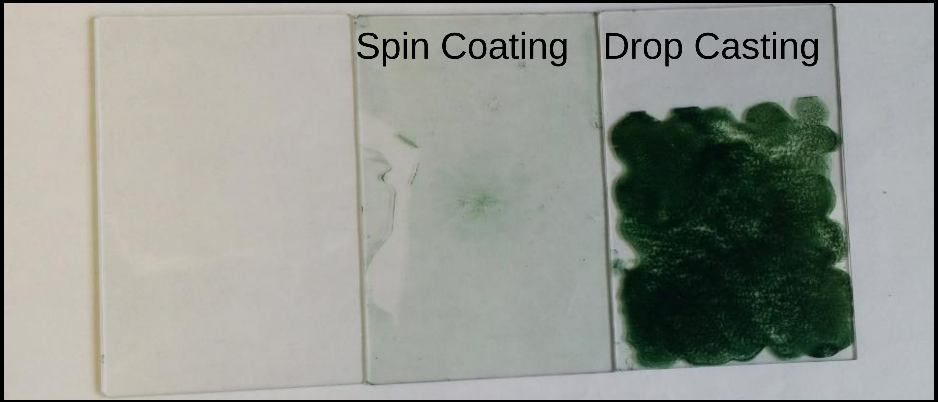
Multiple Layers Split

# PANI

Preliminary Spin Coating Attempts

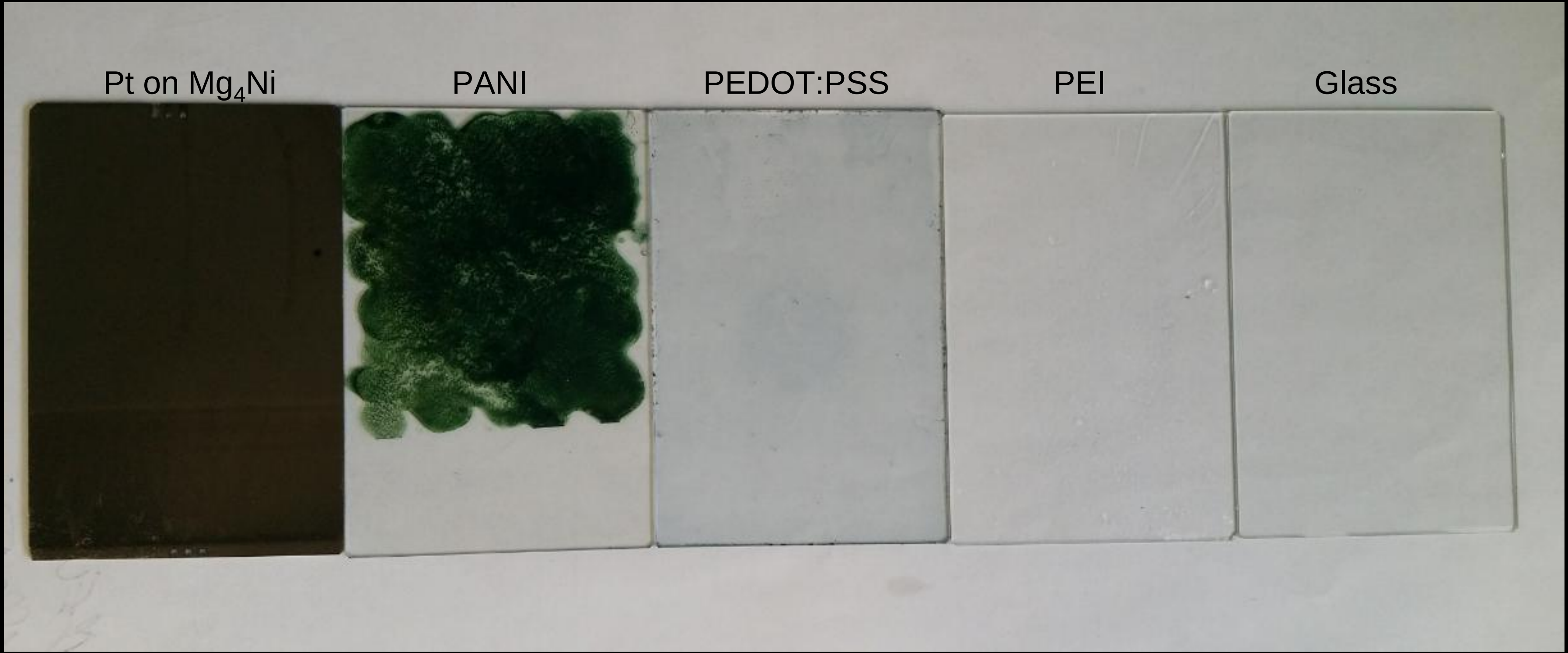
Rough,
Uneven Coating,
Agglomerations

Final Deposition Techniques




Too thin vs.
Too rough,
too thick

# Thin Film Results



# Characterization - Profilometer

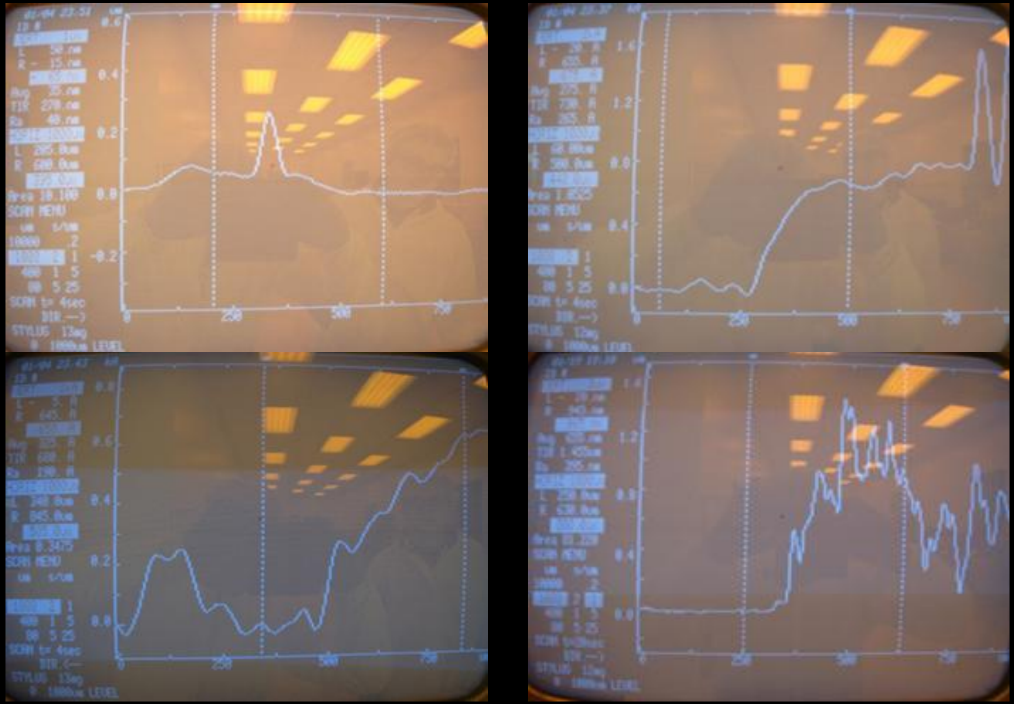
- Measuring thickness of layers.

  - PANI layer by spin-coating - 70nm
  - PANI layer by drop-casting - 4um
  - PEDOT layer - 70 nm
  - PEI layer - 70nm
  - Mg4Ni layer & Pt layer - 200nm

Profilometer Tenco Alpha Step 200

# Characterization - Profilometer

- Measuring thickness of layers:
  - PANI layer by spin-coating - 70nm
  - PANI layer by drop-casting - 4um
  - PEDOT:PSS layer - 70 nm
  - PEI layer - 70nm
  - Mg4Ni layer & Pt layer - 200nm



Clockwise from top left, PANI by spin-coating, PEDOT:PSS, PANI by drop-casting, and PEI.

# Characterization - N&K spectrophometer

- Measuring refractive index and reflectivity of layers.
  - PEDOT:PSS layer
    - 1.68 as refractive index
    - About 94% as reflectivity @ 900nm
  - PEI layer
    - 1.62 as refractive index
    - About 92% as reflectivity @ 900nm

N&K spectrophotometer

# Characterization - N&K spectrophometer

- Measuring refractive index and reflectivity of layers.
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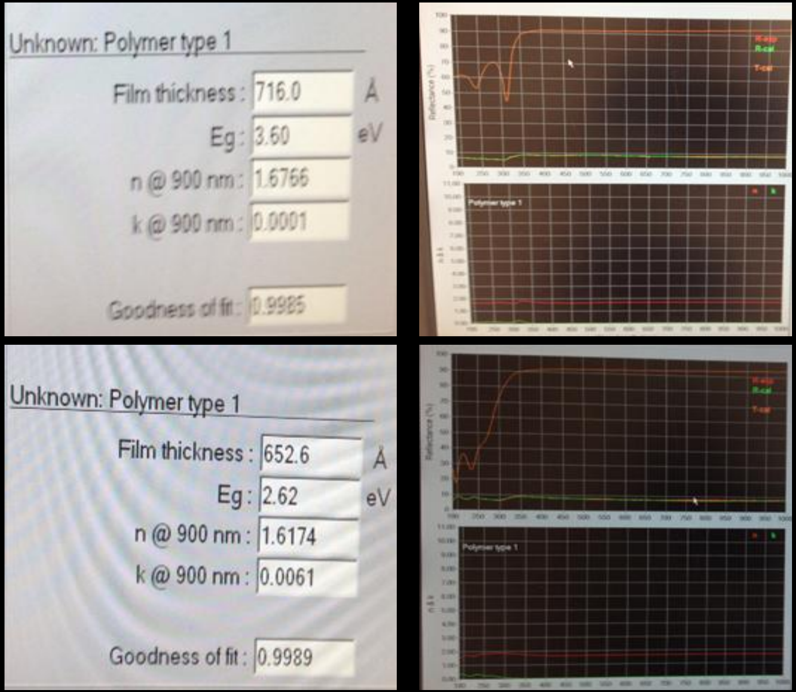
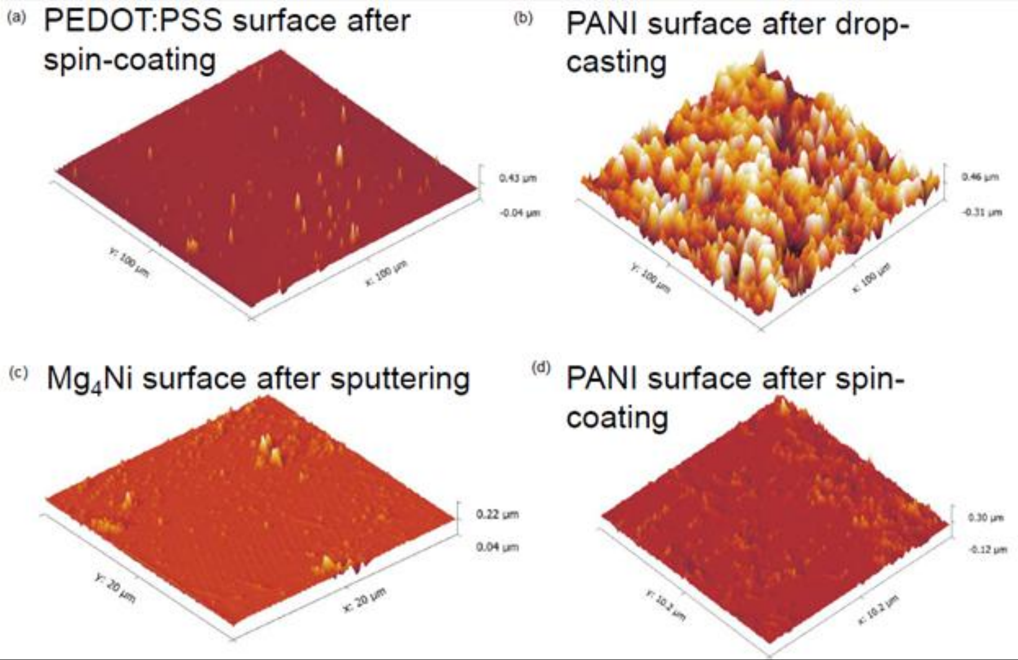


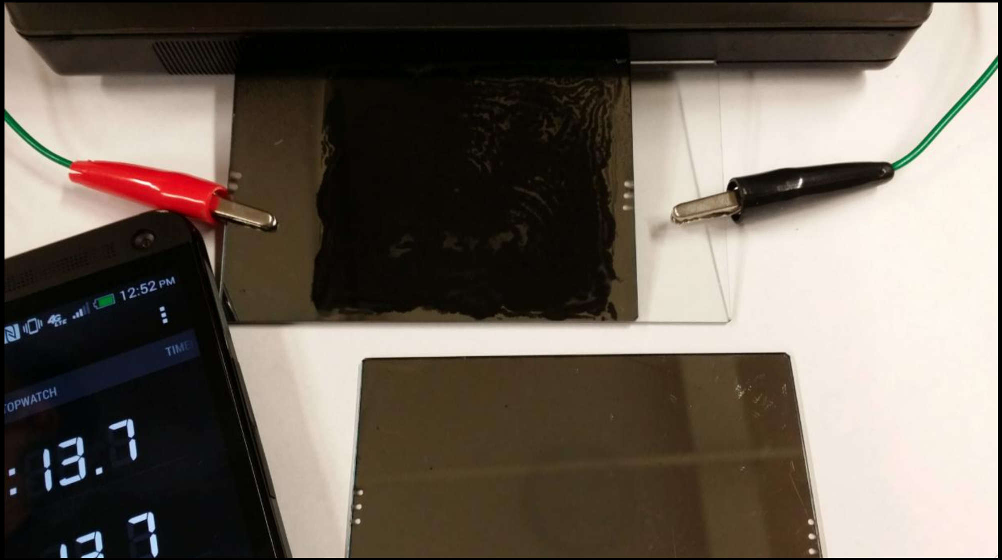

Clockwise from top left, index of refraction and reflectivity of PEDOT:PSS and reflectivity and index of refraction of PEI layer.

# CHARACTERIZATION - AFM

| Material | Thickness | RMS Roughness (nm) |
|---|---|---|
| PEDOT:PSS spin-coat | ~70 nm | 7.59 |
| PEI spin-coat | ~70 nm | Equal to PANI |
| PANI spin-coat | ~70 nm | 12.36 |
| PANI drop-cast | ~4 µm | 130.16 |
| Mg4Ni/Pt sputtered | 200 nm | 4.67 |
| Glass | 1.5 mm | 5.27 |



# Results and Looking Forward




Final prototype showing hydrogenated $Mg_4Ni$ (above) compared to its reflective state (below)

- Further Characterization
  - optical properties for modelling
  - N-and-K Spectrometry
  - More techniques and equations
  - Mechanism of hydrogen diffusion for electrical modelling
- Prototype Next Steps
  - Deposit thicker PEI
  - Thinner $Mg_4Ni$
  - Smoother PANI
- Scale-up Considerations

# Roles

## Executive Committee

- Project Leader - Jake Steiner
- Secretary & Cinematographer - Kari McPartland
- Treasurer - Glenn Pastel

## Prototype Committee

- Eshwari Murty
- Kari McPartland

## Design Committees

Optical Analysis

- Glenn Pastel
- Soo-Hwan Jang
- Ryan Tillman

Electrical Analysis

- Jake Steiner

# Acknowledgments

Dr. Ray Phaneuf
Dr. Rob Briber
Dr. Ichiro Takeuchi
Xin Zhang
Sean Fackler
Dr. Aldo Ponce
Dr. Richard Kaner
the Fablab staff
the rest of the Materials Science Department faculty and staff
and YOU, our supporters :D

# References

1. Baetens R, Jelle BP, and A Gustaven. “Properties, requirements and possibilities of smart windows for dynamic daylight and solar energy control in buildings: A state-of-the-art review.” Solar Energy Materials and Solar Cells, vol. 94; pp.87-105. 2010.
2. Tajima K, Hotta H et al. “Electrochromic switchable mirror glass fabricated using adhesive electrolyte layer.” Applied Physics Letters, vol. 101. 2012.
3. Kirchmeyer S and K Reuter. “Scientific importance, properties, and growing applications of poly(3,4-ethylenedioxythiophene).” Journal of Materials Chemistry, vol. 15; pp. 2077-88. 2005.
4. Deepa M, Ahmad S, et al. “Electrochromic properties of polyaniline thin film nanostructures derived from solutions of ionic liquid/polyethylene glycol.” Electrochimica Acta, vol. 52; pp. 7453-63. 2007.

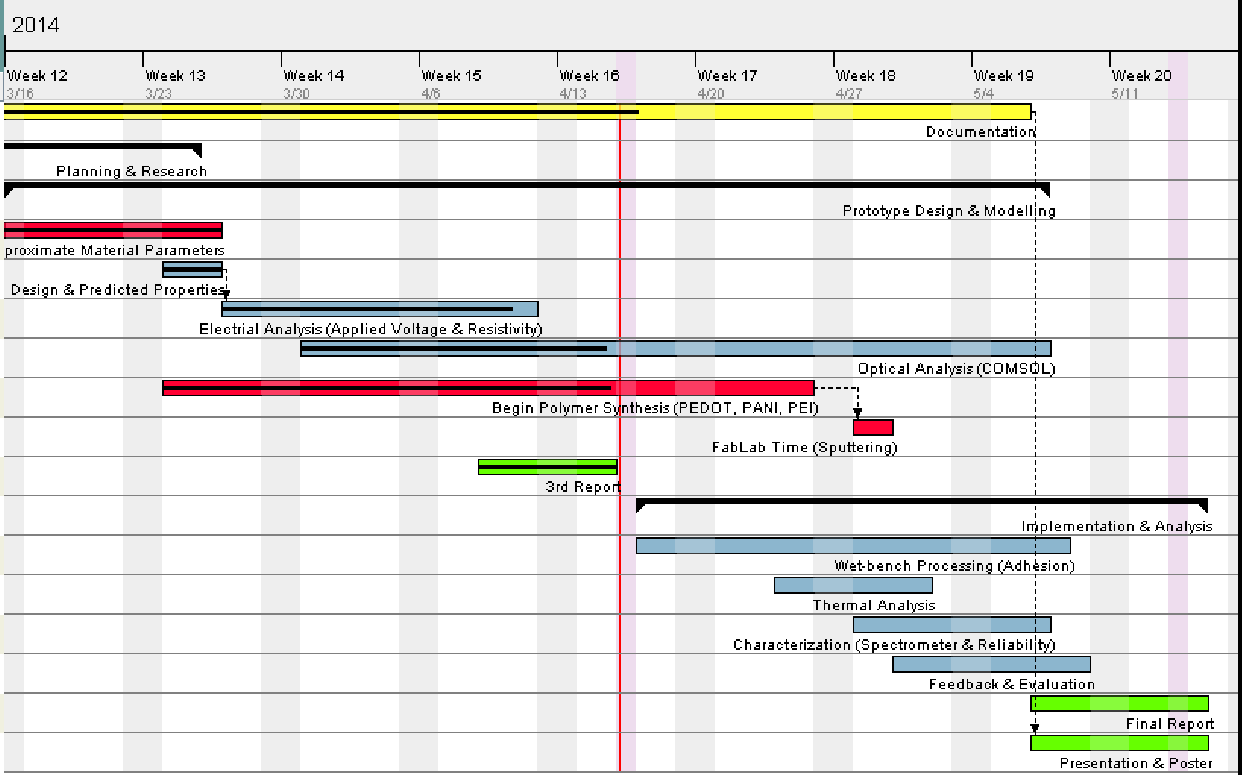
# old slides...

# FACILITIES

- Dr. Briber's lab - to use stuffs such as glasswares and a spin-coater machine to synthesize polymer.
- Dr. Hu's lab - To use the Meyer Rod deposition equipment.
- Sputter deposition machine in Fablab - To fabricate the $Mg_4Ni/Pt$.
- Dr. Takeuchi's lab - To use EDS analyze the layer of Mg4Ni/Pt.
- Fablab in IREAP building - To utilize an ellipsometer to measure indices of refraction for each layer.
- Fablab in KIM building - To utilize a profilometer to characterize to find out the thickness of each layer exactly.
- Fablab in KIM building - To utilize a spectrometer to characterize under various applied voltages.
- Dr. Phaneuf's lab - To use COMSOL Multiphysics 4.4 to set proper models up.
- Dr Wuttig's lab - Getting information of electrical properties requires a variety of machines.

# WORK PLAN

| Name | Begin date | End date |
|---|---|---|
| Documentation | 2/10 | 5/6 |
| Planning & Research | 2/10 | 3/25 |
| Prototype Design & Modelling | 3/13 | 5/7 |
| Approximate Material Parameters | 3/13 | 3/26 |
| Confirm Design & Predicted Prope... | 3/24 | 3/26 |
| Electrial Analysis (Applied Voltage ... | 3/27 | 4/11 |
| Optical Analysis (COMSOL) | 3/31 | 5/7 |
| Begin Polymer Synthesis (PEDOT, ... | 3/24 | 4/25 |
| FabLab Time (Sputtering) | 4/28 | 4/29 |
| 3rd Report | 4/9 | 4/15 |
| Implementation & Analysis | 4/17 | 5/15 |
| Wet-bench Processing (Adhesion) | 4/17 | 5/8 |
| Thermal Analysis | 4/24 | 5/1 |
| Characterization (Spectrometer & ... | 4/28 | 5/7 |
| Feedback & Evaluation | 4/30 | 5/9 |
| Final Report | 5/7 | 5/15 |
| Presentation & Poster | 5/7 | 5/15 |



# Budget

| Item | Purpose/Details | Provider | Rate | Shipping | Allocation |
|---|---|---|---|---|---|
| Mg Sputtering Target 3" x 1/4" | $Mg_4Ni$ film (1.88:1 ratio Mg:Ni) | AJA International | $185 | Yes | $ 185.00 |
| E-Beam Deposition onto PEDOT | Using FabLab for deposition | FabLab | $70/hr | - | $ 210.00 |
| Use of Ni target | $Mg_4Ni$ film | FabLab | $70/1000Å | - | $ 70.00 |
| Use of Pt target | 4nm Pt film | FabLab | $70/1000Å | - | $ 10.00 |
| Optical Borosilicate Slides 43 x 50mm | Samples | Tedpella | $26.95/35 pcs | Yes/$10 | $ 41.95 |
| Clevios PEDOT (PH 1000 grade) | PEDOT layer | Herceaus (PA) | $155/100g | Yes/$35 | $ 190.00 |
| Ammonium Peroxydisulfate (98%) | PANI processing | Sigma Aldrich | $35.60/100G | Yes/67.18 | $ 102.78 |
| Polyvinyl Butyral (Butvar B-98?) | 0.5g other adhesive in GBL | Sigma Aldrich | $22.40/100G | Yes/67.18 | $ 22.40 |
| Poly(ethyleneimine) solution | PEI aka 0.1ml adhesive electrolyte | Sigma Aldrich | $38.50/100ML | Yes/67.18 | $ 38.50 |
| Gamma-butyrolactone (GBL) | 10ml. Tajima used PVB in GBL | Sigma Aldrich | $19/25G | Yes/67.18 | $ 19.00 |
| Aniline (ACS reagent >99.5%) | Material Processing? PANI? | TedPella | $30/100ML | Yes/~**$15?** | $ 45.00 |
| Hydrochloric Acid | PEI processing | UMD | $8.91/1L | - | $ 8.91 |
| DMSO methyl sulfoxide | CM138 - PEDOT processing | UMD | $13.70/500ML | - | $ 13.70 |
| Dialysis cassettes | for PANI processing | Dr. Briber - free | $150/10pk | - | $ - |
| Wet-Bench Lab Space/Fume Hood | Need to provide details of use | Dr. Briber - free | $0 for use | - | $ - |
| Ellipsometer and Spectometer | For Unknown Mat. Properties | UMD | - | - | $ - |
| COMSOL Multiphysics - Wave Optics | Optical Modelling and Analysis | Dr. Phaneuf's Lab | MSE Dep. | - | $ - |
| | | | | **Sum:** | $ 957.24 |
| | | | | **Remaining:** | $ 42.76 |

# Motivation

- Smart windows change optical properties from transparent to absorbing under stimulus
- By minimizing heat loss and gain they can thereby maximize building energy efficiency
- Japanese group led by Tajima created reflective smart window, better for deterring radiative heating
- ITO and $WO_3$ used in the original configuration limit financial viability
- We propose organic substitutes to reduce costs while maintaining effectiveness of the switchable mirror

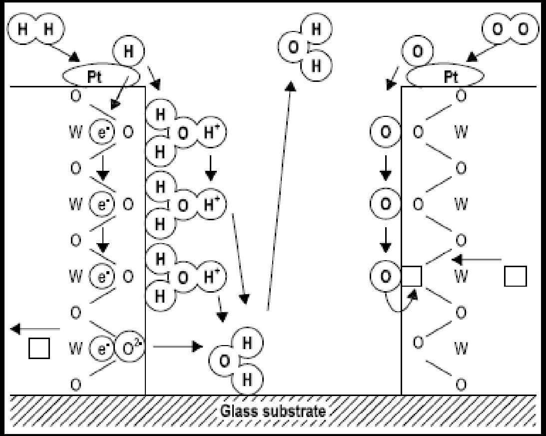
From SwitchLite website:
http://www.switchlite.com/home.html#

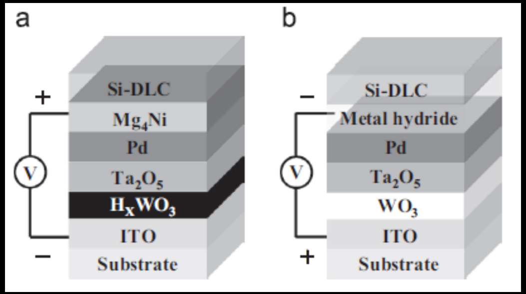
# Feasibility

- Hard to estimate due to novel combination of layers
- PANI/ PEDOT:PSS interface could be problematic
- Affordability could be an issue if a Pt or Pd target cannot be found
- Potential for failure/frustration in both properly

# BACKGROUND

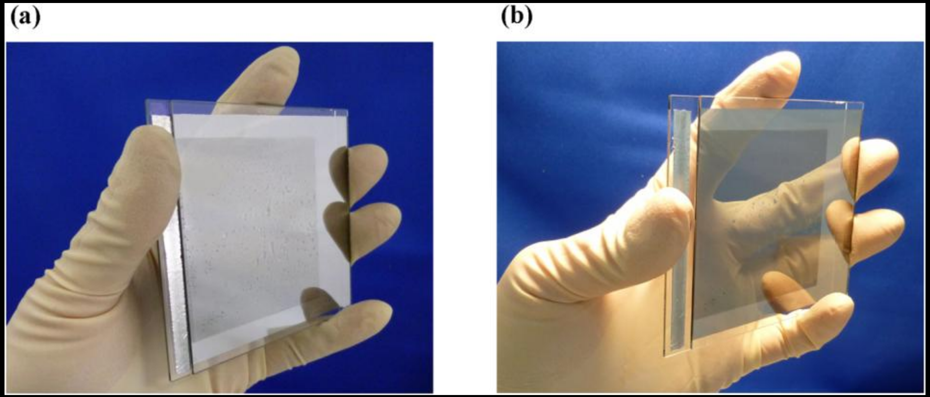
- Most smart windows employ solid-state reactions via cation transport
- Cations diffuse in and out of materials like $WO_3$ causing structural changes and thus changes in optical properties
- Electrical potential induces diffusion of cations
- Devices need electrode/active layer/electrolyte/charge storage/electrode structure



# Previous Work

- The Baetens review specifies minimum performance criteria for commercialization
- $WO_3$ and ITO meet these requirements, but are expensive and hard to scale up
- Nb- Ni- and Ir- oxides have similar expense drawbacks
- PEDOT:PSS and PANI are electrochromatic polymers but may be UV sensitive
- Tajima’s device uses $Mg_4Ni$, which turns reflective when it takes in hydrogen, and PEI



# Intellectual merit

- Incorporating PEDOT:PSS and PANI into the switchable mirror is a novel approach
- Opportunity to observe polymer interfaces
- New processing approaches
- Sputtering of $Mg_4Ni$/Pt on polymer substrate
- Hydrogen diffusion modeling across $Mg_4Ni$, PEI, and PANI
- Stress analysis in order to improve device lifetime despite thermal cycling

# Broader impact

- Windows are some of the least efficient building components
- Reduce dependence on rare earth elements like indium in ITO
- Smart windows are in response to stricter building energy regulations and a refocus on sustainability
- Lowering energy costs of buildings also reduces their environmental impact
- Anywhere windows are used: houses, factories, cars, planes

# Ethical Issues

- Actual device materials are non-toxic, no human health concern
- Chemicals in synthesis must be handled properly
- Magnesium reacts violently to $H_2O$ at room temperature
- HCl and aniline in PANI synthesis are also dangerous
- Potential success could lead to improvement of sustainable building design