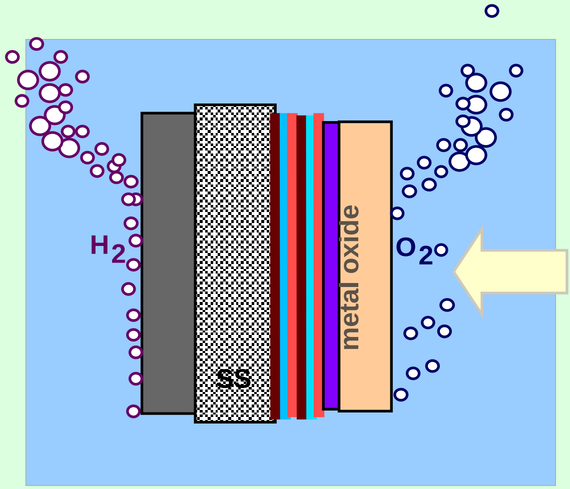
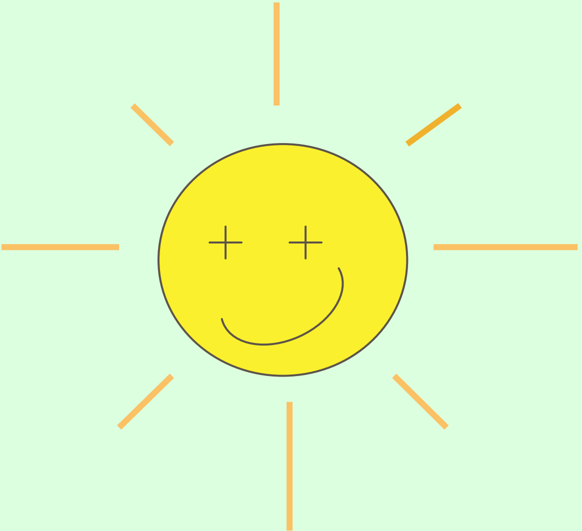
Goal

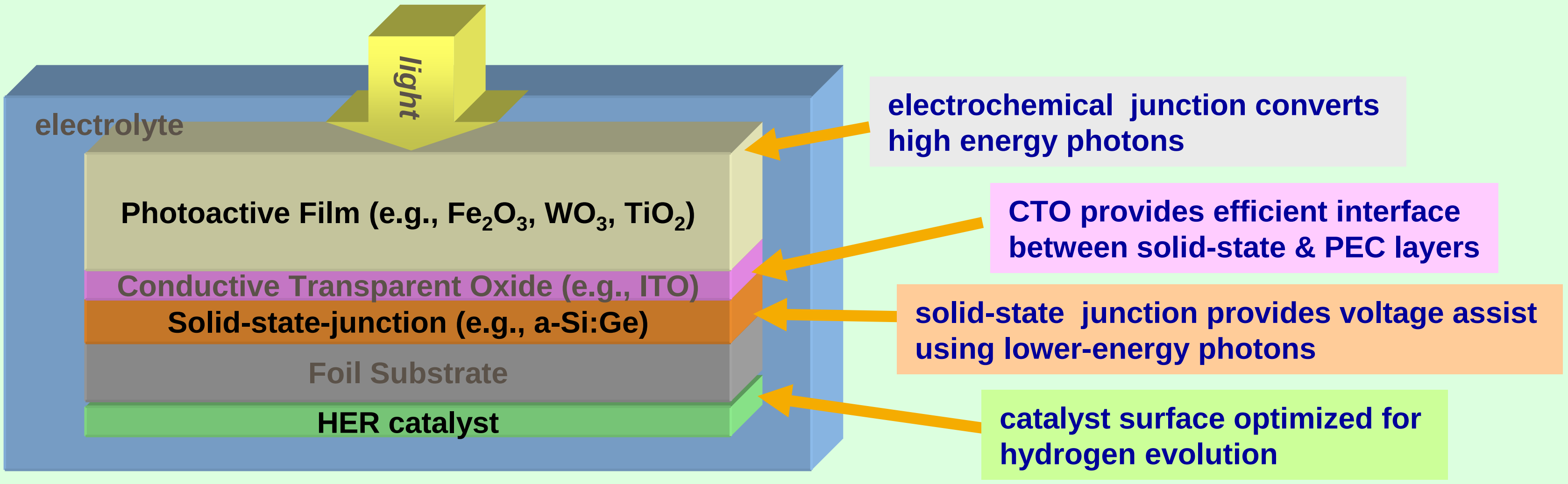
To build a photoelectrochemical (PEC) system that produces hydrogen fuel directly from water using sunlight as the energy source.





Approach: development of a multi-junction monolithic photoelectrode using low cost thin films materials

The Hybrid Photoelectrode



UH-developed integrated multijunction electrochemical device to provide sufficient photo-generated current & voltage for efficient water splitting

Oxide layer is photoactive and corrosion resistance

Metal Oxides Candidates

tungsten and titanium oxides are photoactive, but their high bandgap limits photocurrent

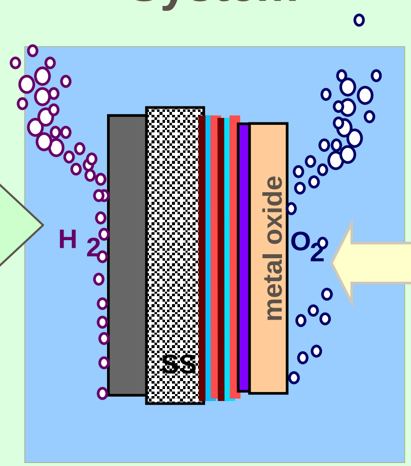
WO_3 or TiO_2 with reduced bandgap
(doping, surface mod, etc)

iron oxide has near-optimal bandgap, but recombination losses limit photocurrents

Fe_2O_3 with improved electronic properties
(doping, surface mod, etc)

Integration with optimized solid state materials/devices

Viable PEC System



Other materials may arise through combinatorial discovery, etc….

Why WO_3 ?

- Conduction band minimum well aligned with H^+/H_2 level
- Bandgap wide enough to produce photoelectrolysis of water
- Good chemical stability demonstrated in 1 Normal H_3PO_4
- Low cost material, environmentally friendly

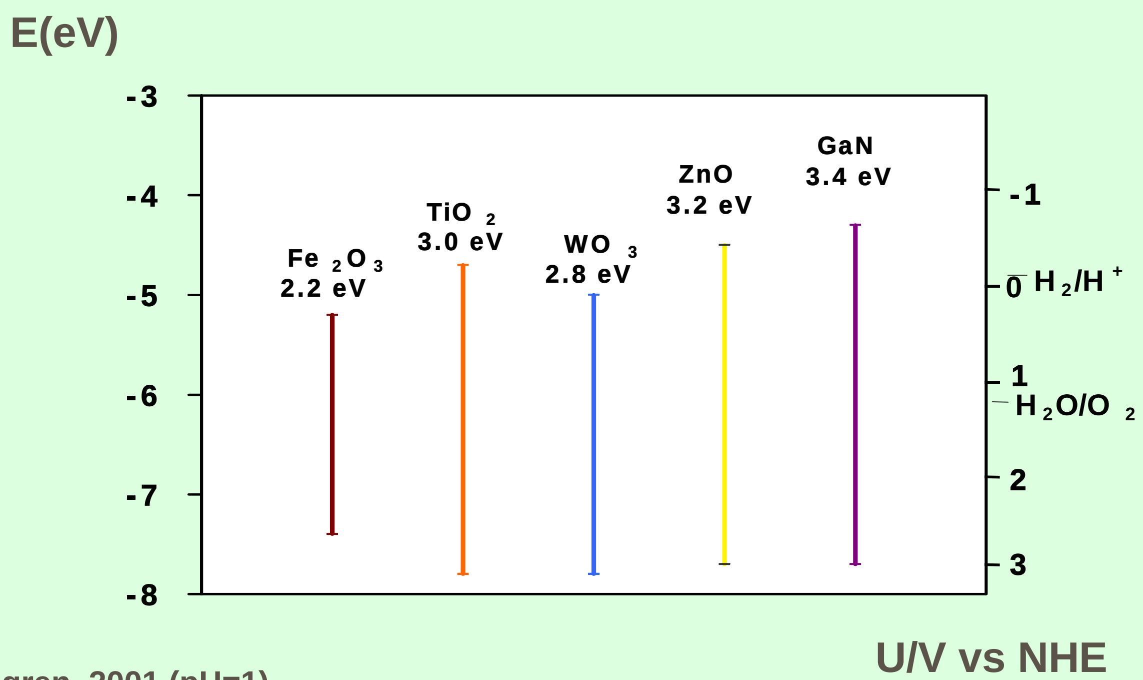
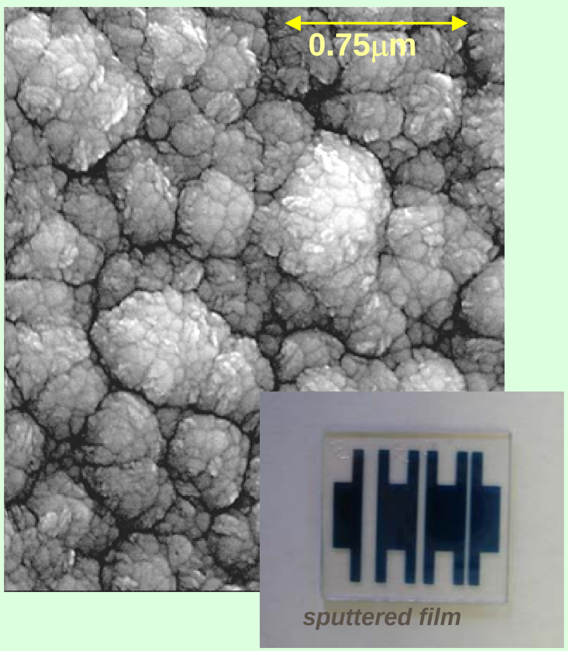
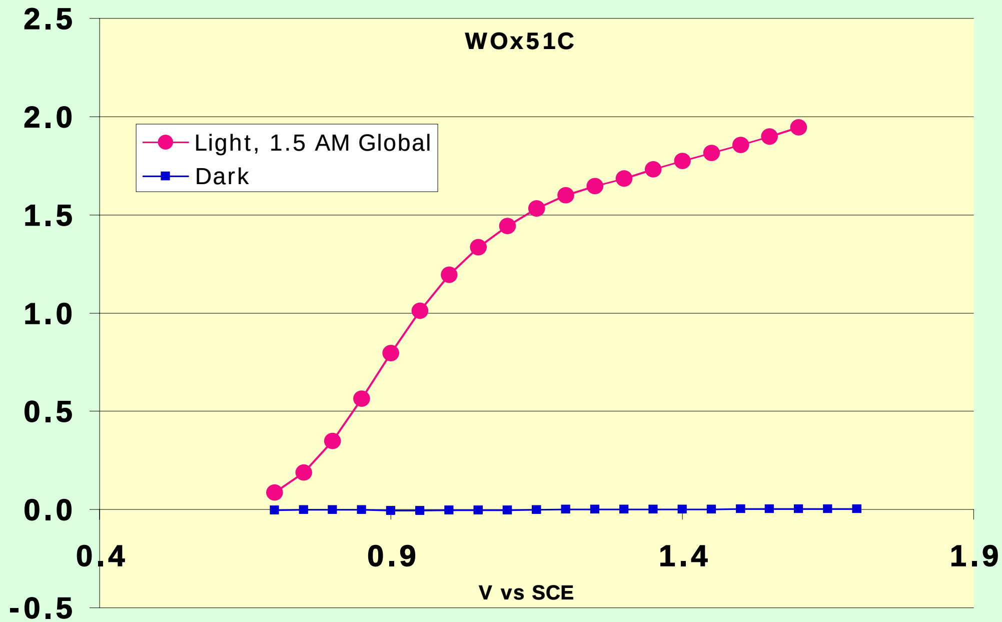


Table from T. Lindgren, 2001 (pH=1)

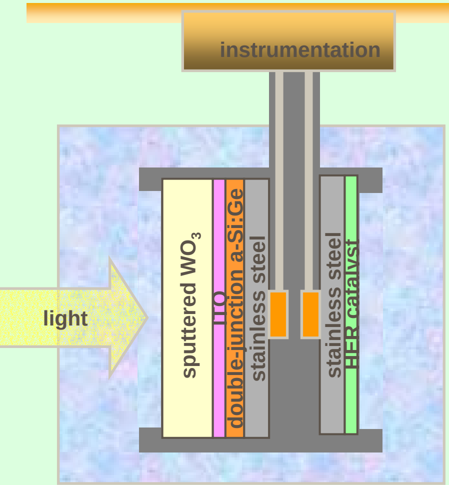
WO_3 Film Research at HNEI

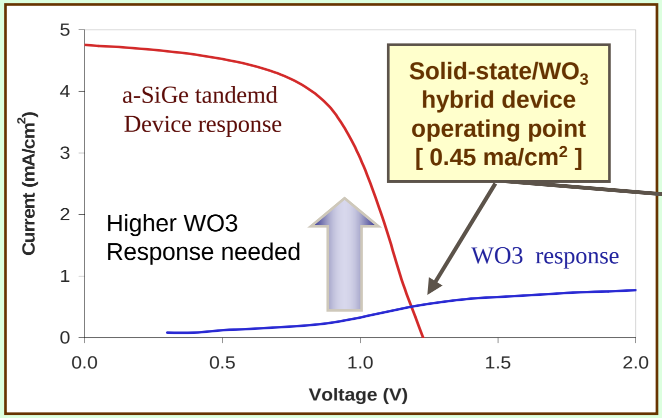
- WO_3 thin films are produced via reactive sputtering from a tungsten target
- To date, films deposited at low temperature (200°C) with photocurrents up to 2 mA/cm^2 under 1 sun illumination in phosphoric acid

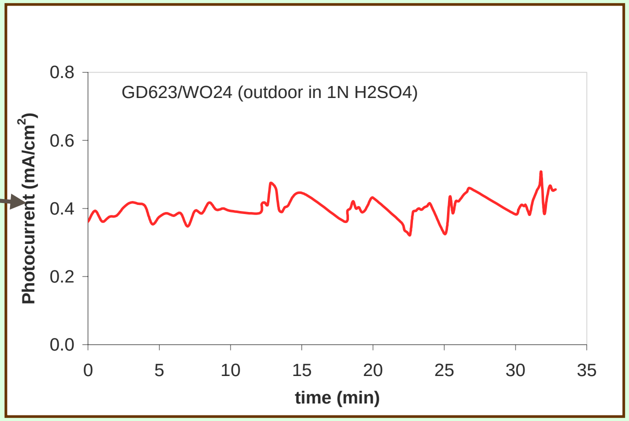




Early Prototype Photoelectrodes







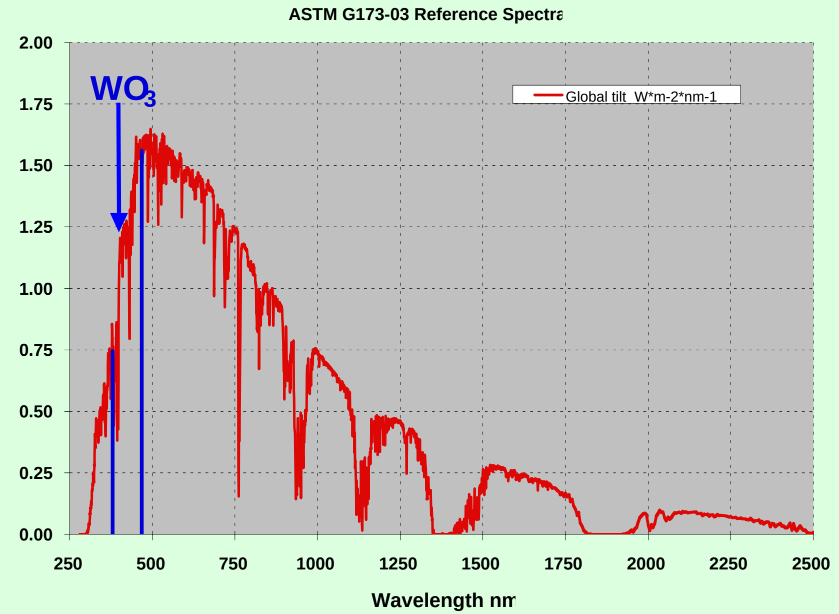
outdoor hydrogen production current

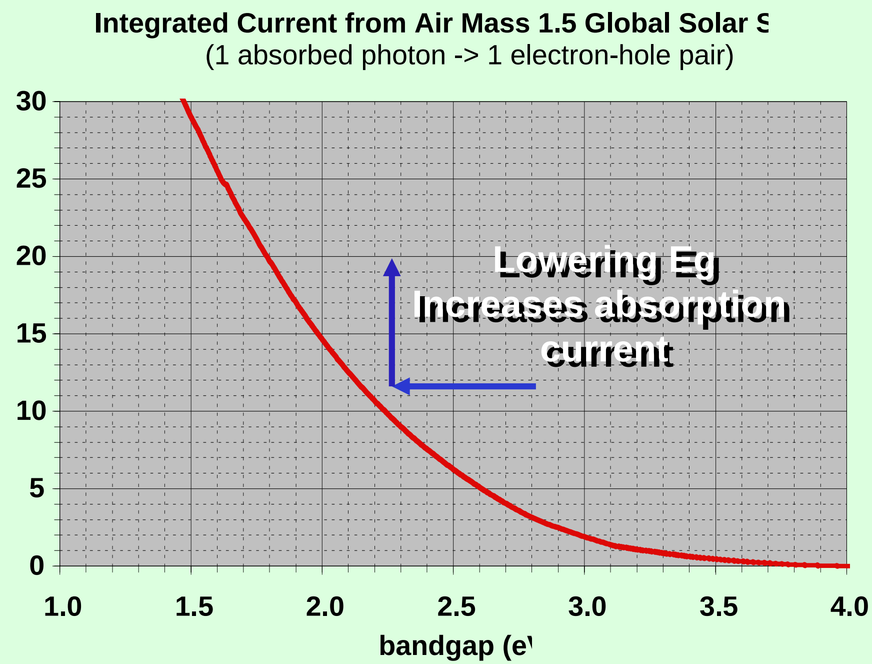
- Currents up to 0.5mA/cm^2 in 1-sun outdoor tests were achieved in unbiased conditions (0.7% Solar to Hydrogen Efficiency)
- Stable operation in 1N H_2SO_4 was measured up to ten hours

Improved metal-oxide properties are necessary to enhance STH efficiency conversion

WO_3 Bandgap versus Current Absorption

Because of its high bandgap (Eg ~2.6-3.2 eV) WO_3 mainly absorbs in the near ultraviolet and blue region of the spectrum (~470-380 nm).





To include a wider region of the solar spectrum, and therefore increase PEC performance, the WO_3 bandgap must be lowered.

Doping as one of the pathways for bandgap reduction

Why Nitrogen Doping

The VB of WO_3 is mainly produced by the O 2p electrons and the CB is mainly generated by the W 5d electrons (Detraux et al. 1997, etc…).

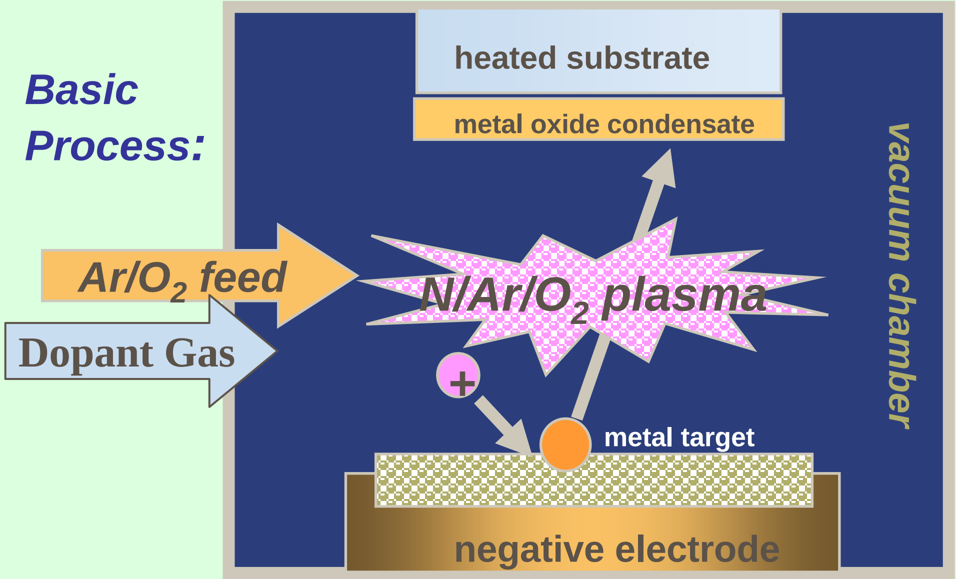
- Anion impurities substituting on O sites will introduce purity defects bands above the VB of WO_3
- Cation impurities substituting W may introduce impurity bands below the CB.

Impurities that can be considered for bandgap reduction include N, S, C, P, As, Cu…

Asahi et al., 2001 (on N-doped TiO_2): “Substitutional doping of N was the most effective because its p states contribute to the bandgap narrowing by mixing with the O 2p states”

Fabrication Technique: Reactive Sputtering

Basic Process:



- Un-doped WO_3 films are produced via 'low-temperature' reactive r.f. sputter from a metallic target, using Argon and Oxygen gas.
- Nitrogen containing gas (N_2 or NH_3)are introduced along with Argon and Oxygen, to produce nitrogen doped tungsten trioxide films.

Important process parameters influencing film properties are: ambient pressure, oxygen partial pressure, substrate temperature, r.f. power, geometry, substrate material.

support

Sputtering Parameters

Standard baseline

Ambient Pressure: 10 mTorr.
Oxygen partial pressure: 12%
Substrate Temperature: 200C
r.f. Power: 300W

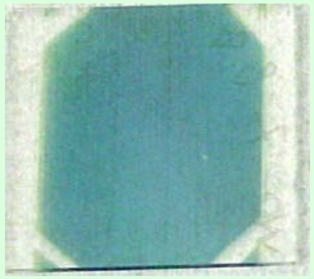
N_2 Doping

Nitrogen partial pressure → 3.5%, 1.8%

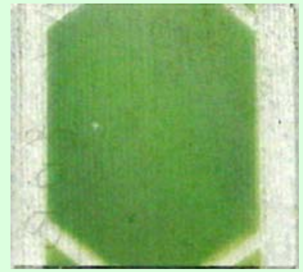
NH_3 Doping

Ammonia partial pressure → 2.3%, 1.8%

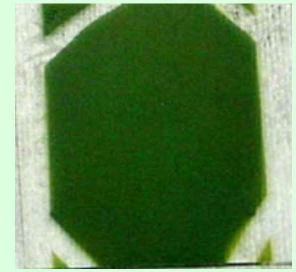
N_2 Doping: Optical & Electronic Properties



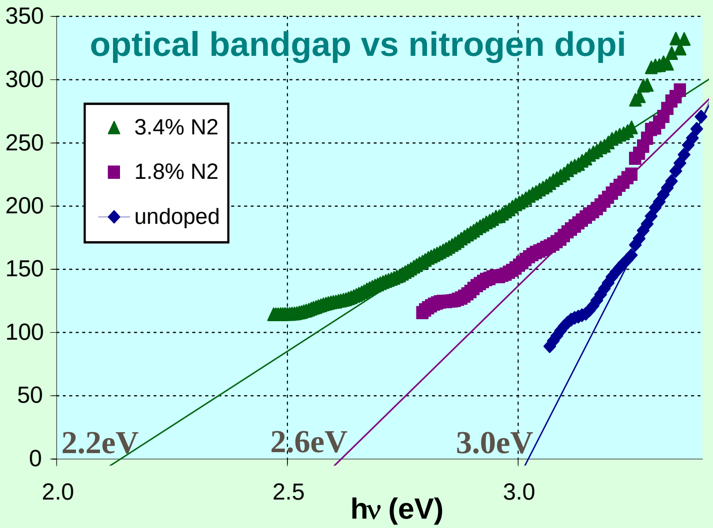
N_2 : 0%

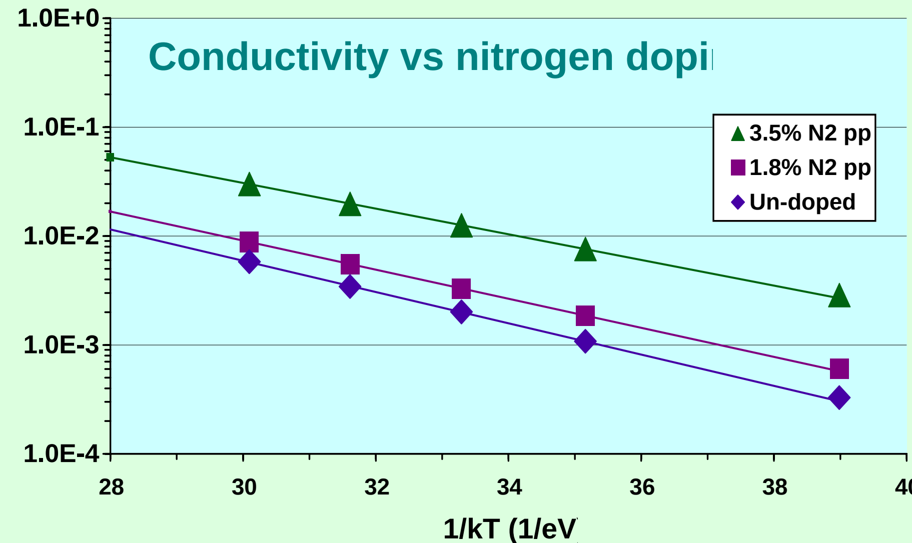


N_2 : 1.8%



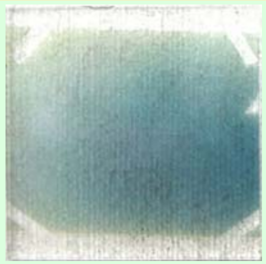
N_2 : 3.5%



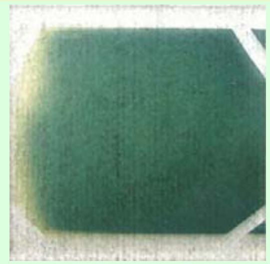


As N_2 doping ↑ => the bandgap ↓ , the conductivity (σ) ↑ , and the activation energy (slope) ↓

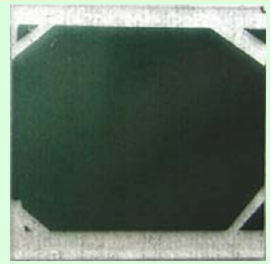
NH_3 Doping: Optical & Electronic Properties



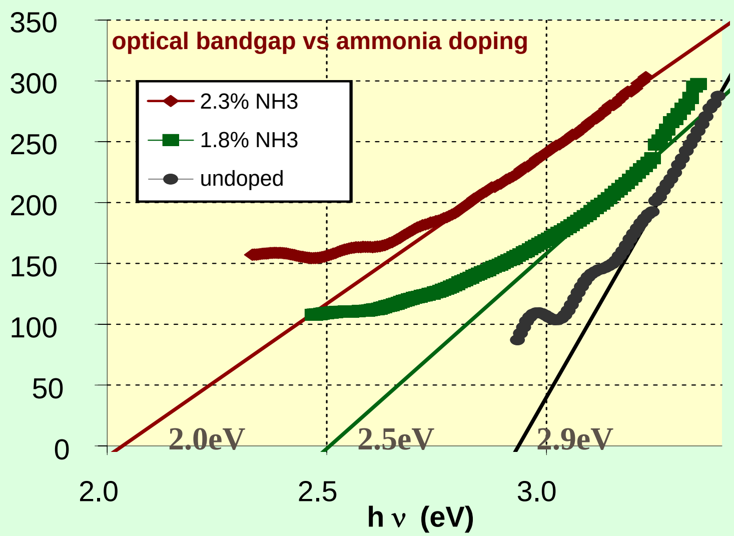
NH_3 : 0%

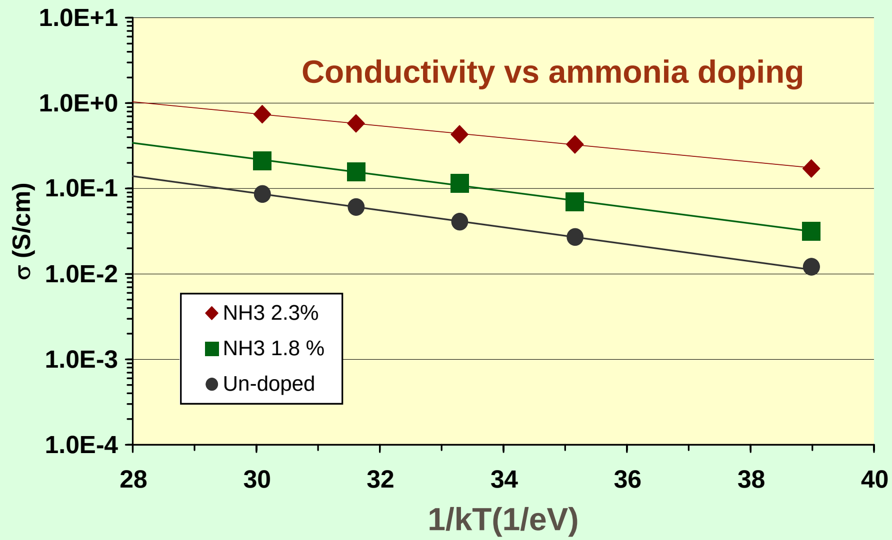


NH_3: 1.8%



NH_3 : 2.3%





As NH_3 doping ↑ => the bandgap ↓ , the conductivity (σ) ↑ , and the activation energy (slope) ↓

Summary

• Improved metal oxides properties are necessary to enhance STH conversion efficiency in multijunction photoelectrodes (such as the UH Hybrid Photoelectrode)

• Tungsten trioxide is a good candidate but it only absorbs high energy photons. Its bandgap must be reduced.

• Doping via nitrogen or ammonia has proved to decrease the bandgap of reactively-sputtered tungsten trioxide films.

• Doping also enhances electronic properties of the film by increasing conductivity.

• This indicates that nitrogen doping (via NH_3 or N_2) increases the n-type characteristics of the film, introducing energy levels closer to the conduction band than to the valence band.

Conclusions

- The optical and electronic properties of the present hybrid-compatible metal oxides are key limiting factors to efficiency. This clearly defines the primary focus for continued research effort.

- By lowering the bandgap, doping of metal oxides might provide a pathway to enhance efficiency.

- Further study and film characterizations are necessary to understand the nature of the introduced states, and their effect on photoelectrochemical activity.

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