STRAW – A Hydrogen-Specific Pressure Gauge for XHV

Gregory Mulhollan
Saxet Surface Science
3913 Todd Lane, Suite 303
Austin, TX 78744

Work funded by Department of Energy SBIR Grant DE-SC0004437

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Sorbing UHV/XHV Vacuum Gauge Development
Up Front Summary

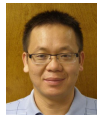
- Sensor
  - Relative H_2 pressure
  - No heat or charged particle generation
- Status
  - Operation at UHV shown; XHV soon
  - Sensitivity boost using optically pumped shallow traps
- Technology
  - Titania nanotube arrays
- To Do List
  - Regeneration method for post-bake use
  - Catalog other gas sensitivities
  - Enhance vacuum sensitivity, temperature stability, reduce noise, etc.
- Commercialization
  - Vacuum gauge manufacturers have interest in beta testing prototype

About Saxet

- Organization
  - Sole Proprietorship
  - Founded in 2002

- Staff
  - Principal Scientist: Gregory Mulhollan
  - Senior Scientist: Robert Kirby (CA)
  - Research Scientist: Pingheng Zhou
  - Senior Research Associate: John Bierman
  - Recent Research Assistants
  - Travis Hutchins (Graduate school in physics)
  - Steven Bierman (EE undergraduate)



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- Location

– 1,982 ft^2 in the Pecan Business Park in south Austin

– Texas is the 28th state and was a republic prior to statehood

– Austin is home to the Texas state capital, the University of Texas and many high-tech companies including Samsung (flash memory chips & mobile device processors)

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- Capabilities
  - Four loadlocked photocathode test systems
  - RF PECVD system for amorphous SiGe photoemitter growth
  - High vacuum and UHV/XHV chambers for STRAW gauge research
  - Sputter deposition system for metal growth
  - Auger system for surface compositional analysis
  - Clean (class 100) assembly area
  - Chemical work area
  - Optical spectroscopy bench
  - + more

John Bierman (left) and Jeff Hurst (right, now at Samsung, Austin) working on the Auger analysis system

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- Research Partners

SLAC NATIONAL ACCELERATOR LABORATORY

SSRL

PENN STATE

RTI INTERNATIONAL

UNIVERSITY of HOUSTON

- Funding Agencies/Sales

  – Government

U.S. DEPARTMENT OF ENERGY

ARMY SBIR SMALL BUSINESS INNOVATION RESEARCH

NAVY

  – Private

ITT

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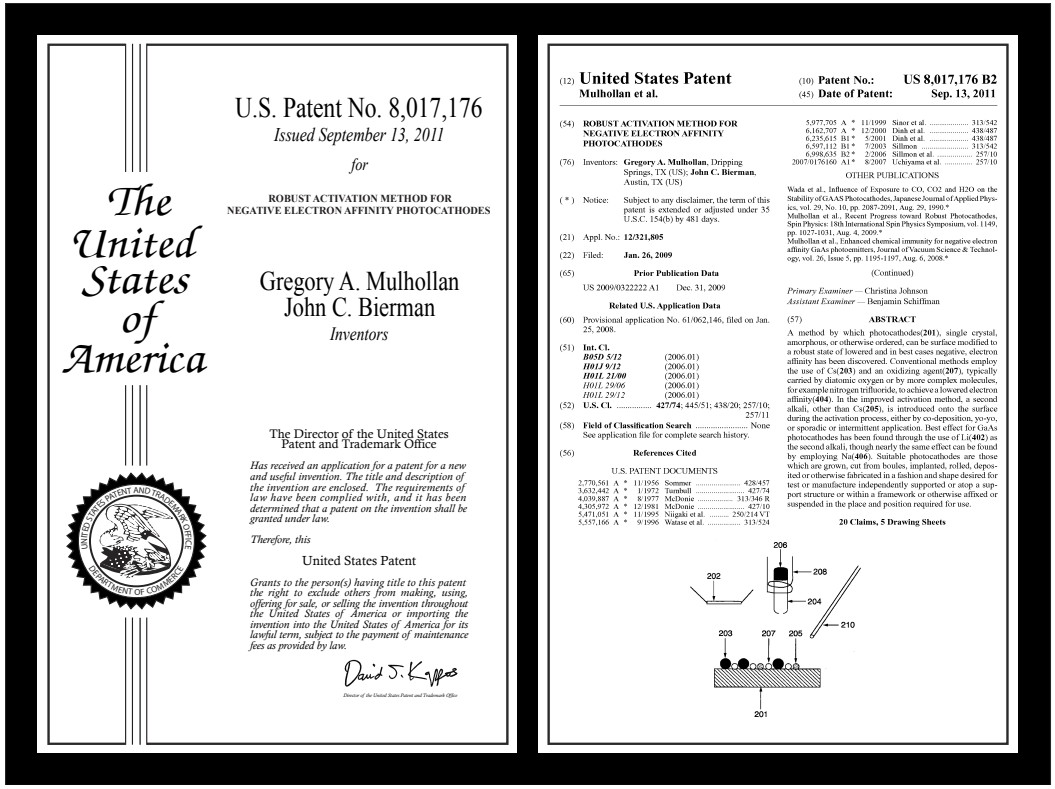
- Intellectual Property
  - – One issued patent
  - – One allowed patent (issuing soon)➤➤➤➤➤➤➤
  - – One patent application

Method for Employing Titania Nanotube Sensors as Vacuum Gauges 04/09/2012



U.S. Patent No. 8,017,176
Issued September 13, 2011
for

ROBUST ACTIVATION METHOD FOR NEGATIVE ELECTRON AFFINITY PHOTOCATHODES

The United States of America

Gregory A. Mulhollan
John C. Bierman
Inventors

The Director of the United States Patent and Trademark Office

Has received an application for a patent for a new and useful invention. The title and description of the invention are enclosed. The requirements of law have been complied with, and it has been determined that a patent on the invention shall be granted under law.

Therefore, this

United States Patent

Grants to the person(s) having title to this patent the right to exclude others from making, using, offering for sale, or selling the invention throughout the United States of America or importing the invention into the United States of America for its lawful term, subject to the payment of maintenance fees as provided by law.

(12) **United States Patent**
Mulhollan et al.

(10) **Patent No.: US 8,017,176 B2**
(45) **Date of Patent: Sep. 13, 2011**

(54) **ROBUST ACTIVATION METHOD FOR NEGATIVE ELECTRON AFFINITY PHOTOCATHODES**

(76) Inventors: **Gregory A. Mulhollan**, Dripping Springs, TX (US); **John C. Bierman**, Austin, TX (US)

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 481 days.

(21) Appl. No.: **12/321,805**

(22) Filed: **Jan. 26, 2009**

(65) **Prior Publication Data**

US 2009/0322222 A1 Dec. 31, 2009

Related U.S. Application Data

(60) Provisional application No. 61/062,146, filed on Jan. 25, 2008.

(51) **Int. Cl.**
B05D 5/12 (2006.01)
H01J 9/12 (2006.01)
H01L 21/00 (2006.01)
H01L 29/06 (2006.01)
H01L 29/12 (2006.01)

(52) **U.S. Cl.** **427/74**; 445/51; 438/20; 257/10; 257/11

(58) **Field of Classification Search** ..... None
See application file for complete search history.

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(Continued)

Primary Examiner — Christina Johnson
Assistant Examiner — Benjamin Schiffman

(57) **ABSTRACT**

A method by which photocathodes(**201**), single crystal, amorphous, or otherwise ordered, can be surface modified to a robust state of lowered and in best cases negative, electron affinity has been discovered. Conventional methods employ the use of Cs(**203**) and an oxidizing agent(**207**), typically carried by diatomic oxygen or by more complex molecules, for example nitrogen trifluoride, to achieve a lowered electron affinity(**404**). In the improved activation method, a second alkali, other than Cs(**205**), is introduced onto the surface during the activation process, either by co-deposition, yo-yo, or sporadic or intermittent application. Best effect for GaAs photocathodes has been found through the use of Li(**402**) as the second alkali, though nearly the same effect can be found by employing Na(**406**). Suitable photocathodes are those which are grown, cut from boules, implanted, rolled, deposited or otherwise fabricated in a fashion and shape desired for test or manufacture independently supported or atop a support structure or within a framework or otherwise affixed or suspended in the place and position required for use.

20 Claims, 5 Drawing Sheets

US 20110201244A1

(19) **United States**
(12) **Patent Application Publication**
Mulhollan et al.

(10) **Pub. No.: US 2011/0201244 A1**
(43) **Pub. Date: Aug. 18, 2011**

(54) **METHOD FOR RESURRECTING NEGATIVE ELECTRON AFFINITY PHOTOCATHODES AFTER EXPOSURE TO AN OXIDIZING GAS**

(76) Inventors: **Gregory A. Mulhollan**, Austin, TX (US); **John C. Bierman**, Austin, TX (US)

(21) Appl. No.: **12/931,839**

(22) Filed: **Feb. 11, 2011**

Related U.S. Application Data

(60) Provisional application No. 61/338,085, filed on Feb. 16, 2010.

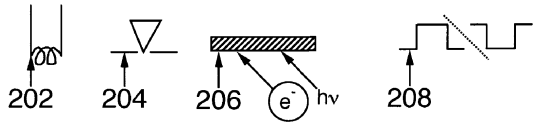
Publication Classification

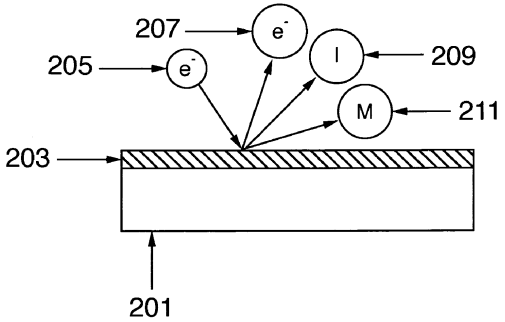
(51) **Int. Cl.**
H01J 9/50 (2006.01)

(52) **U.S. Cl.** **445/2**

(57) **ABSTRACT**

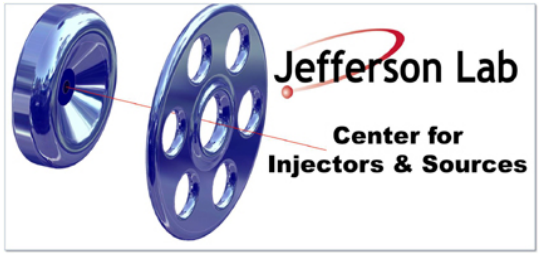
A method by which negative electron affinity photocathodes (**201**), single crystal, amorphous, or otherwise ordered, can be made to recover their quantum yield following exposure to an oxidizing gas has been discovered. Conventional recovery methods employ the use of cesium as a positive acting agent (**104**). In the improved recovery method, an electron beam (**205**), sufficiently energetic to generate a secondary electron cloud (**207**), is applied to the photocathode in need of recovery. The energetic beam, through the high secondary electron yield of the negative electron affinity surface (**203**), creates sufficient numbers of low energy electrons which act on the reduced-yield surface so as to negate the effects of absorbed oxidizing atoms thereby recovering the quantum yield to a pre-decay value.



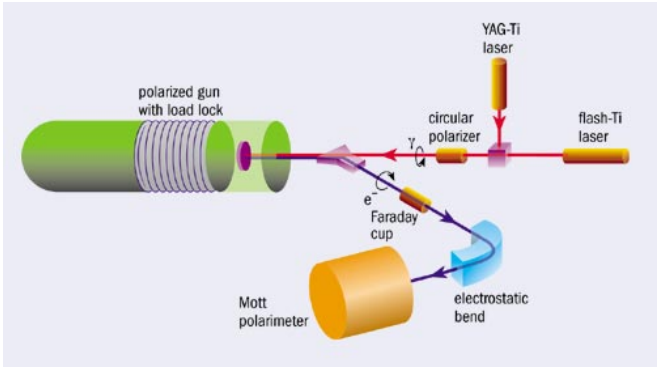


Motivation

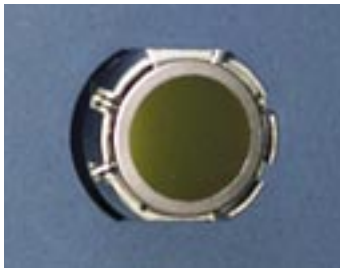
- What do vacuum gauges have to do with nuclear physics?
  - Photocathode e^- sources for accelerators ➛➛➛➛➛➛
    need excellent vacuum for longevity…how to measure?



- Why photocathodes as particle sources?
  - Fast time response
  - Low emittance
  - Spin-polarization



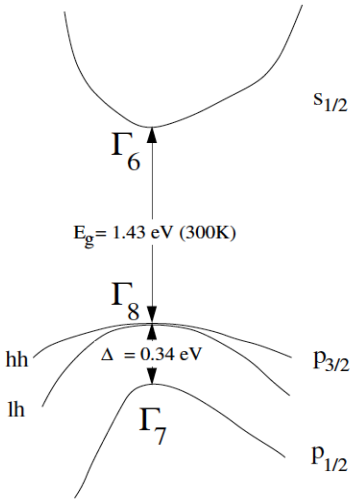
- Where are they used for nuclear physics?
  - JLab, BNL, SLAC, etc.



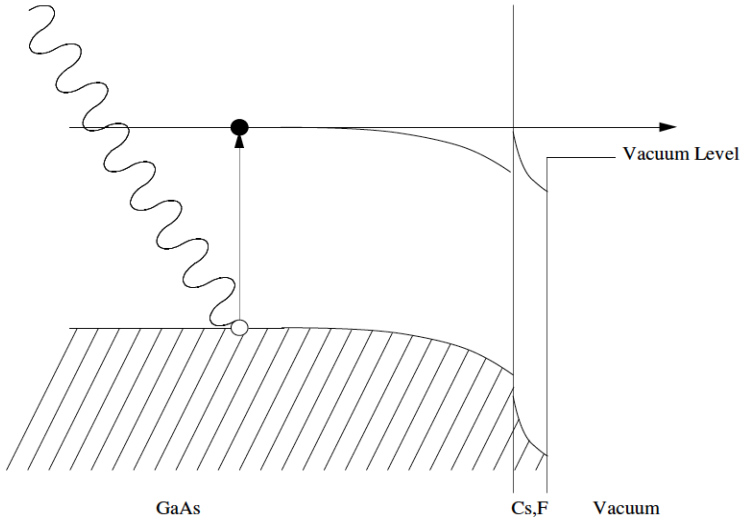
- What types of photocathodes are employed?
  - Metal, semiconductor and amorphous

- What is a photocathode?
  - Source of free electrons
  - Electrons ejected upon photon absorption
  - Anything with sufficiently high *hv*

- Semiconductor (NEA GaAs)
  - Activation allows bandgap energy excitation to generate free electrons



GaAs band structure in vicinity of Γ point



NEA Surface

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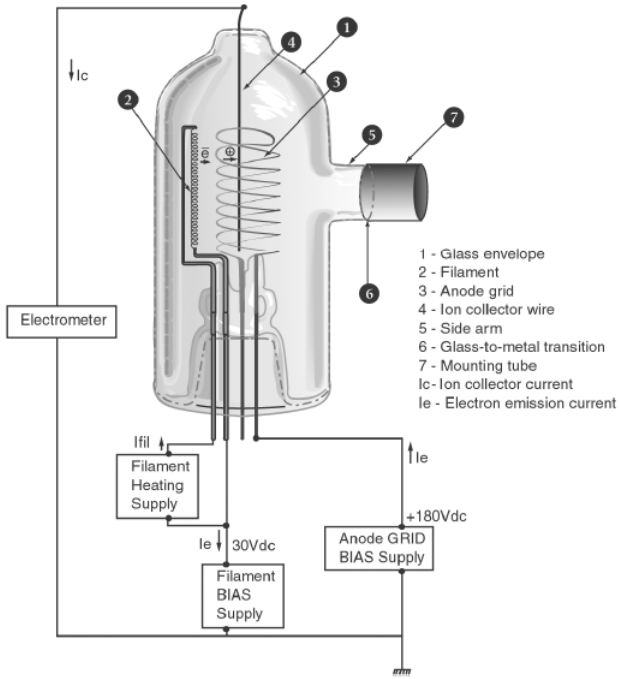
- Pressure ranges of interest: lower pressure = longer photocathode lifetimes
  - UHV (Ultra-high vacuum)

    $1x10^{-12}$ Torr < P < $1x10^{-9}$ Torr
  - XHV (Extreme-high vacuum)

    P < $1x10^{-12}$ Torr

- Ion gauge: particle and heat generation
  - Standard (Bayard-Alpert, $1x10^{-11}$ Torr, x-ray limit)
  - Extractor (Redhead 1960s, extends to $1x10^{-12}$, Leybold, Ulvac)
  - Radioisotope powered (no heater)

SRS Ion gauge diagram (IGC100 manual)



- Cold cathode gauge: particle generation
  - Commercial UHV (Balzers, $7.5x10^{-12}$ Torr)
  - Ion pump (Very low current monitoring: leakage currents, pump 'sleep')

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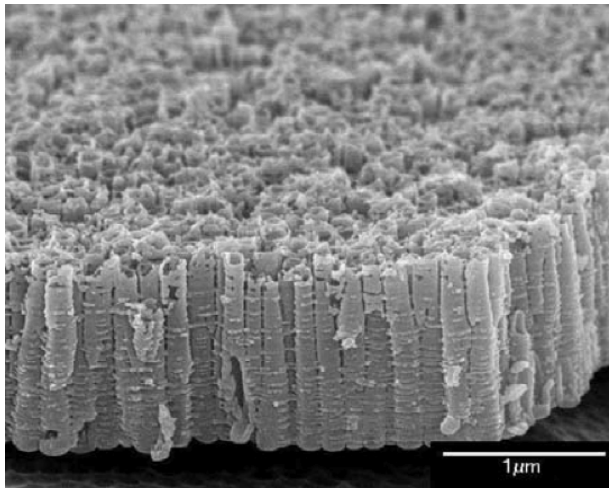
- Sensor possibilities considered
  - LEED pattern shift on H_2 sensitive surface ⇒
  - Optical excitation of H_2 characteristic lines
  - Evanescent field coupling
  - Cryogenic absorption of H_2 on an oscillator
  - Higher sensitivity capacitance vacuum gauge
  - IR detection of H_2 adsorbate vibrational modes
  - Adapt atmospheric level H_2 sensor for vacuum

    Titania nanotube arrays

⇓



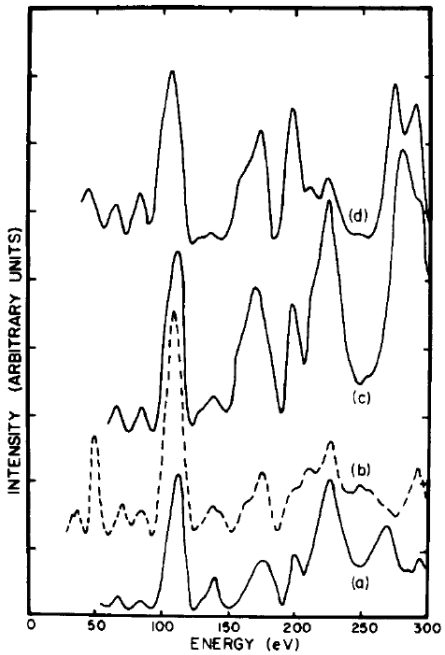
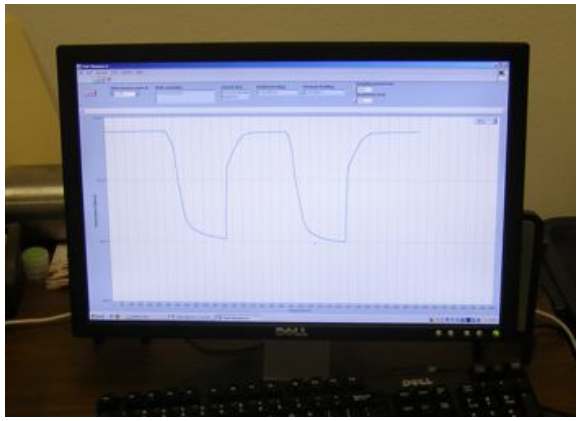


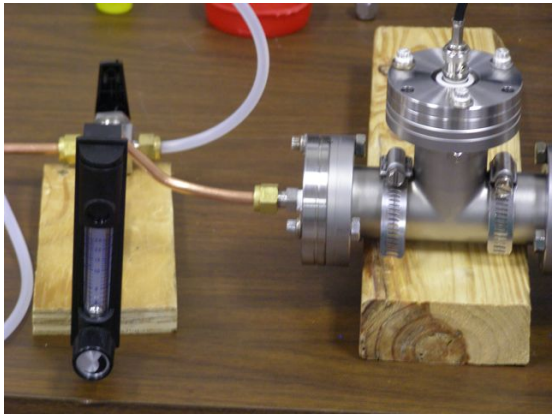
FIG. 7. Comparison of our experimental I–V curves, for the 10 beam at normal incidence with various degrees of hydrogen exposure, to the 10 beam I–V curve reported by Wei.[2] Note the tendency of Wei's curve toward hydrogen contamination (see text). Curve (a) clean; curve (b) Wei; curve (c) hydrogen covered $\theta = 0.25$; curve (d) hydrogen covered $\theta = 1.0$.

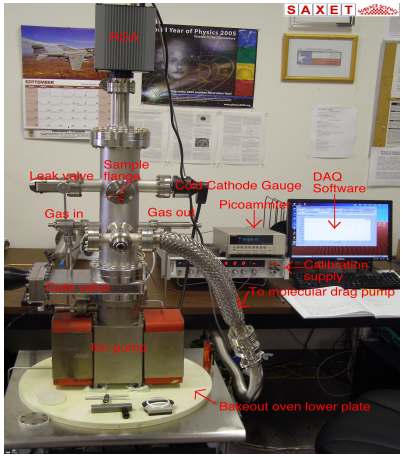
Contraction of the Clean W(001)Face, B. W. Lee, A. Ignatiev, S. Y. Tong and M. VanHove, *J. Vac. Sci. Technol.* **14,** 291 (1977).

Phase I

- Goal
  - Demonstrate that devices can show adequate hydrogen sensitivity in vacuum
    - * Atmospheric response; transition to vacuum







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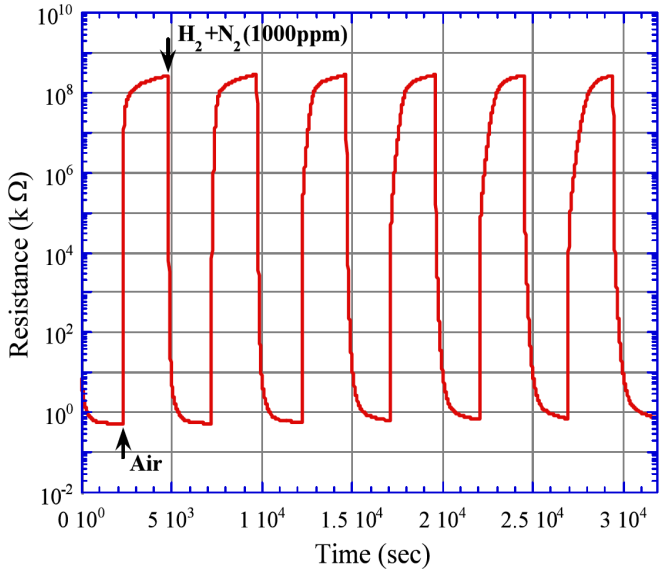
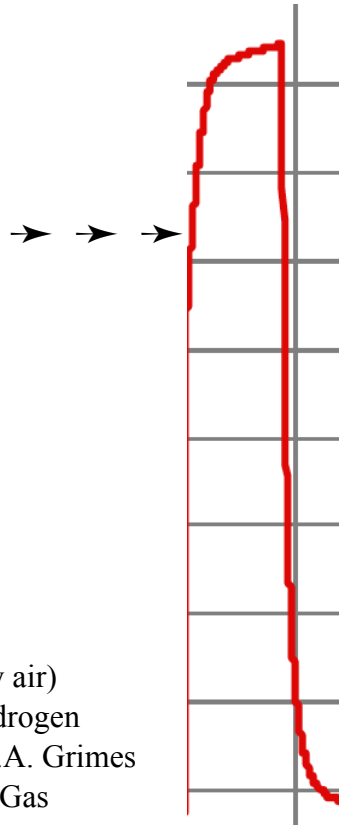
•Extrapolate vacuum sensitivity from atmospheric level response (risky!)





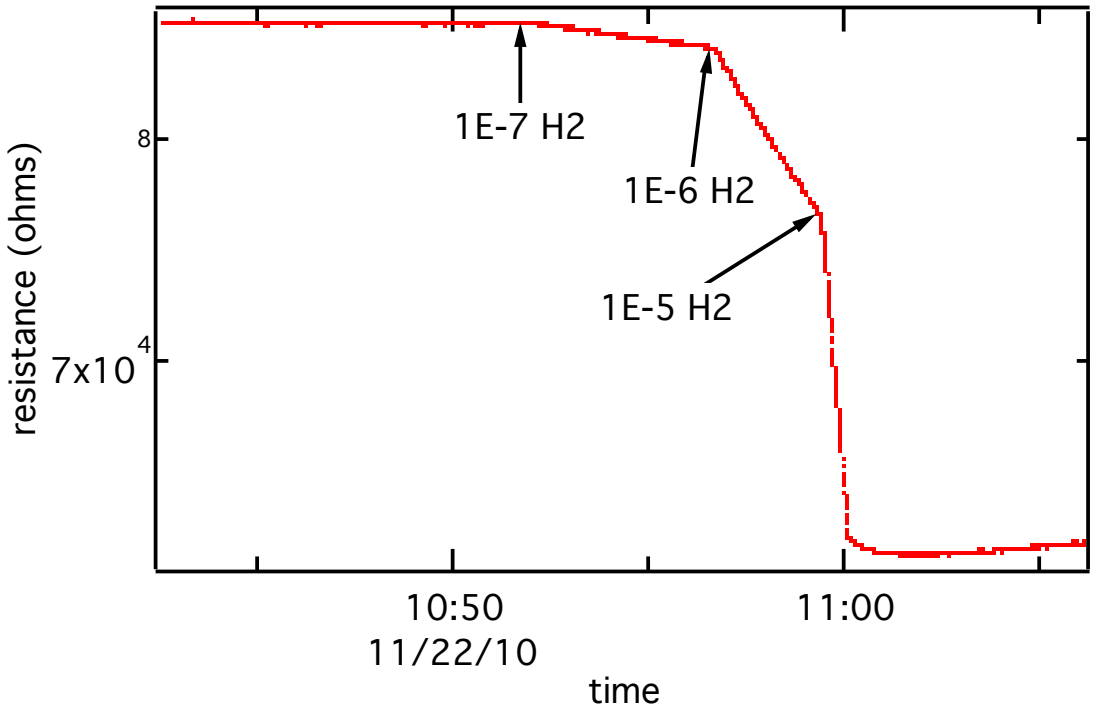
Time response of resistance for hydrogen purged (dry air) and hydrogen dosed (H_2 + N_2) using 1000 ppm of hydrogen [figure 3 of M. Paulose, O.K. Varghese, G.K. Mor, C.A. Grimes and K.G. Ong, Unprecedented Ultra-High Hydrogen Gas Sensitivity in Undoped Titania Nanotubes, Nanotechnology **17**, 398(2006)].

Atmosphere = 760 Torr

– 1 milliTorr (6) ---> 1 s
– 1x10^{-6} Torr (7) ---> 1.7 min.
– 1x10^{-9} Torr (8) ---> 28 hrs.
(X) = digit showing change

'Slice' of atmospheric response data used for calculating response function parameters. Time requirement for extrapolated sensitivity (Keithley 2001 DMM, for example).

– Vacuum response ?



Device "A" vacuum sensitivity to pure hydrogen. Total (H_2) pressure was as indicated.

– Why so much larger than atmosphere response extrapolated value?

* Molecular flow vs viscous flow
* Water vapor removed from surface

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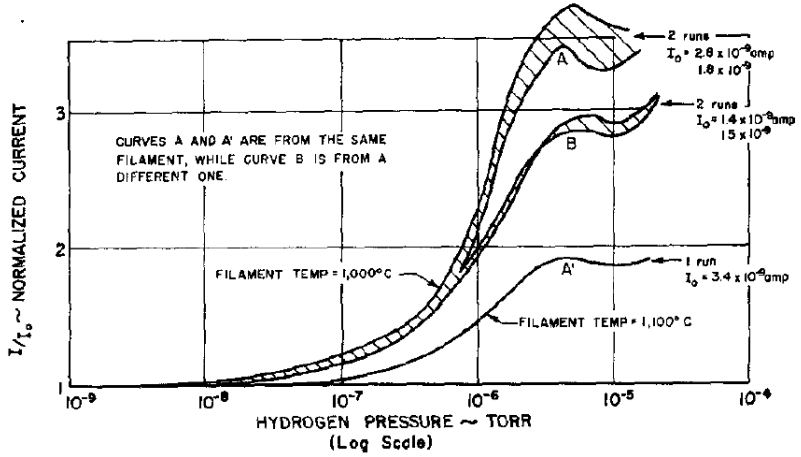
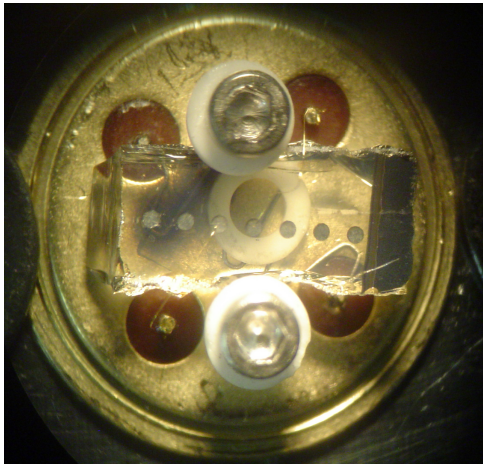
- How it works
  - Sensor structure
    - * Titania (TiO_2) nanotubes anodically grown from Ti film
    - * Wall thickness comparable to space charge length (all surface, no bulk)
    - * Conduction along nanotubes dependent on surface chemistry
    - * Absorption of hydrogen facilitated by Pd nanoparticles + Pt contacts
    - * Resistance change proportional to hydrogen absorption
  - Analogous to hot Pd wire H_2 sensor

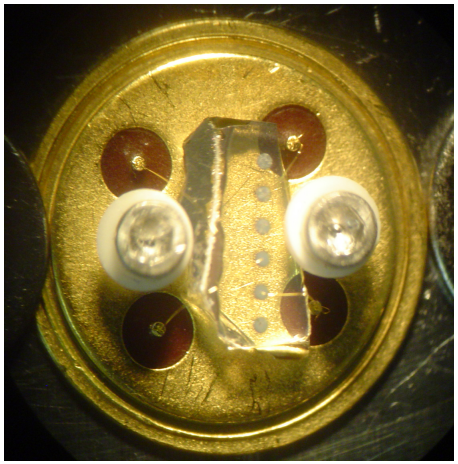


Hydrogen sensitivity of hot Pd (T ≥ 1,000°C). Sensitivity limits to high vacuum use. Electron emission change due to work function shift. Oxygen reverses effect from H_2, same as for titania nanotubes. [M. M. EisenStadt and S. A. Hoenig, Chemisorption Detector for Hydrogen, *Rev. Sci. Instrum.* **36,** 66 (1965)]

– Physical appearance

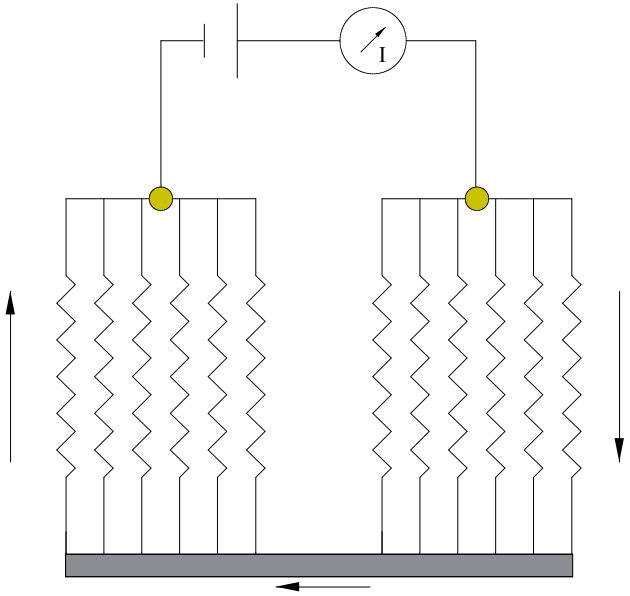
* Glass substrate clamp mounted on TO8-550 header (Kovar, Au, glass)
* Anodized films are ~transparent
* Pt contact pads Au wire bonded to header pins





– Electrical characteristics

* Signal conversion very simple! V = IR
* Operational parameters: Bias = 0.40 V, I ≤ 20 μA
* Tolerant device, but best if handled as ESD sensitive
* Single point grounding used to eliminate ground loop noise
* Most other electrical noise eliminated by simple signal averaging (100x)
* Stability of high quality off-the-shelf measurement instruments sufficient, e.g, Keithley 2401 source meter



Simplified 1D diagram of nanotube array electrical circuit. Each parallel cluster is made up of the nanotubes under the individual Pt contact pads.

Phase II

- Goals Y1
  - Tune devices for best vacuum operation
    Status: Ongoing through year 2.
  - Demonstrate XHV operation
    Status: Ongoing through year 2.
  - Environmental characterization/immunization
    Status: Ongoing through year 2: Initiated early in year 1.
  - Measurement optimization
    Status: Year 2 activity: Initiated early.
  - Communicate availability to potential users
    Status: Year 2 activity: Initiated early

- Goals Y2
  - Quantify and eliminate false signal sources
  - Rejuvenation method development
  - Establish cross-calibration procedure
  - Control system prototype

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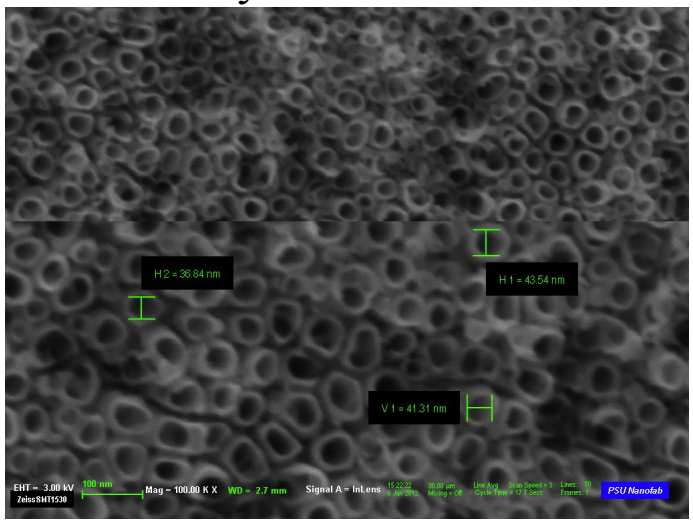
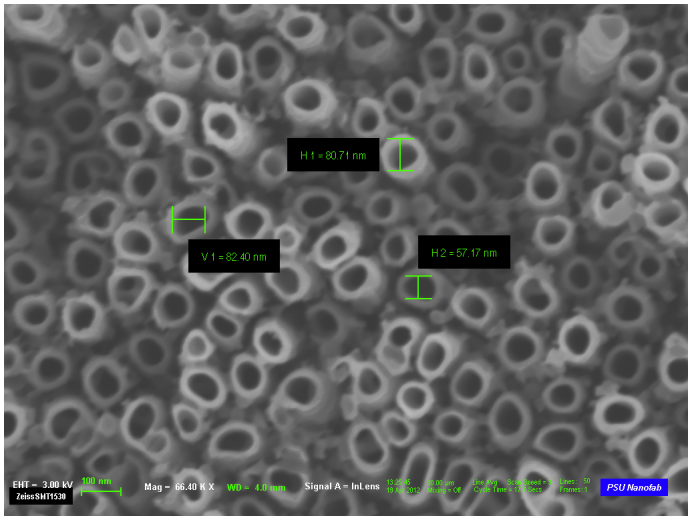
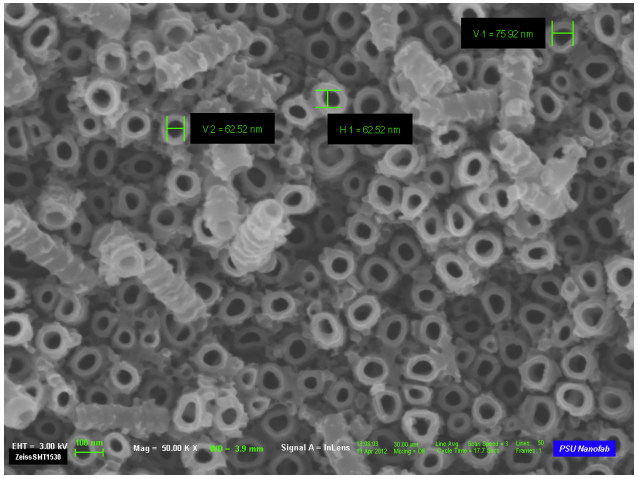
- Vacuum sensitivity enhancement







SEM photographs of the titania nanotubes end-on from the devices with average sized 45 nm pores (top left), 70 nm pores (top right) and 65 nm pores (bottom). Better response is obtained from the devices with the smaller pore sizes.

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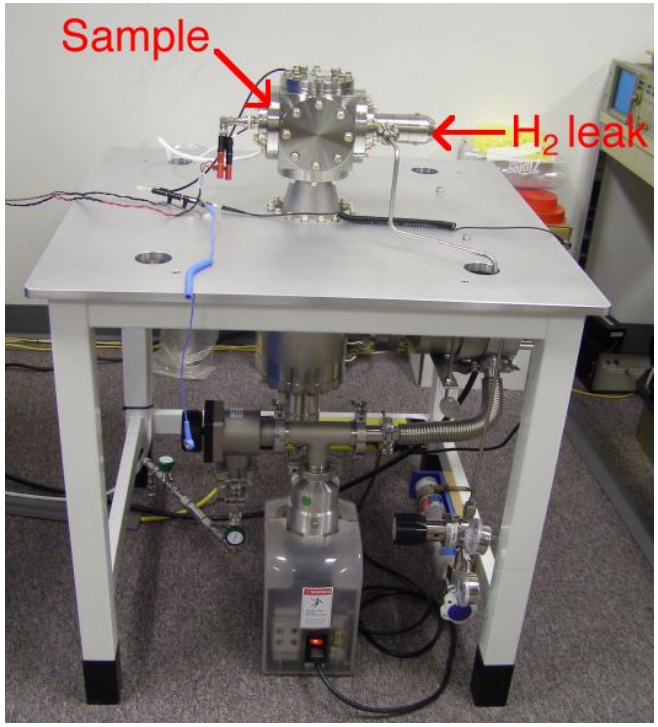
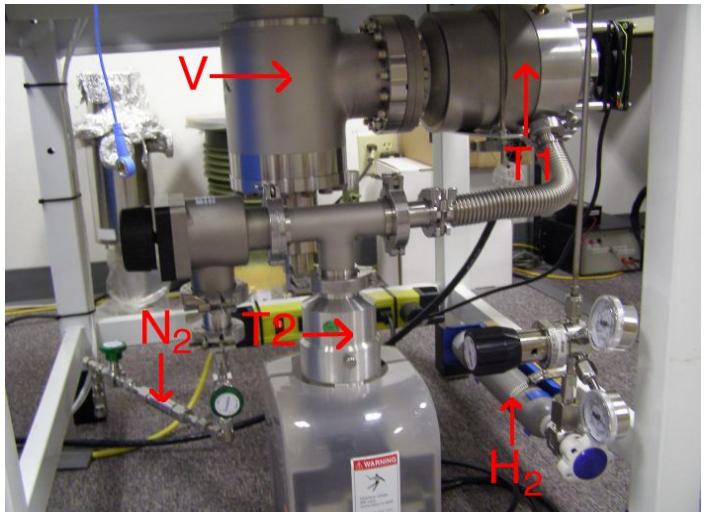
- UHV/XHV test system
  - Vacuum cube to minimize volume/surface area
  - Series turbos allows UHV in ~2 days without baking
  - Extractor gauge (not shown) for cross calibration
  - System holds two samples; each on own flange

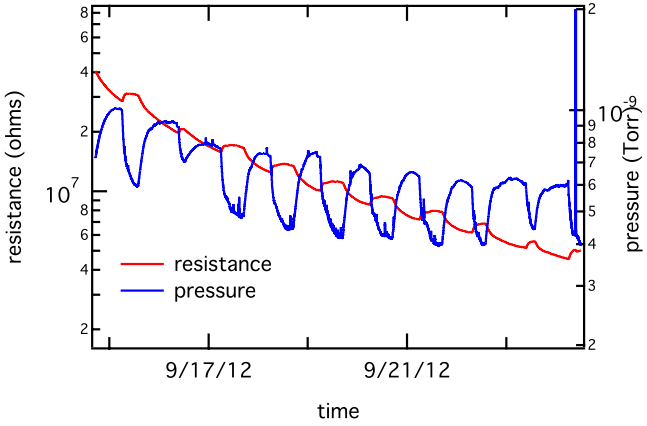




• Operation at UHV

– Pressure achieved by pumping speed only (no baking)

Leybold extractor gauge (IE514 sensor, IM540 controller) showing UHV achieved with tandem turbo pumps.

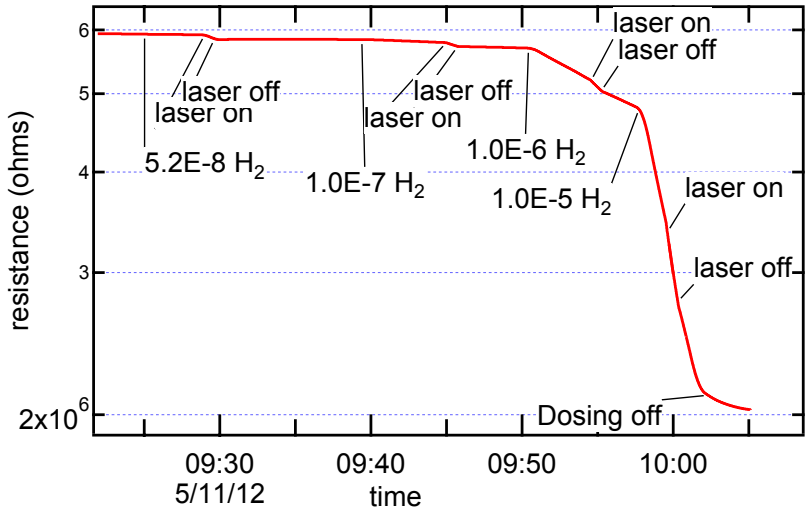


UHV pressure and resistance versus time (no laser). <P> = 6×10^{-10} Torr, R_1 = 400 MΩ, R_2 = 40 MΩ, in 10 days, corresponding to 625 ppm resistance change per 10 minutes.

Easy to measure!

SAXET SURFACE SCIENCE

- Performance needed for XHV sensitivity
  - Best performance (extrapolated via H_2 dosing at $1x10^{-7}$,$1x10^{-6}$,$1x10^{-5}$ Torr)
    Time for measurable change, T_{sense}, at $1x10^{-12}$ Torr = 500 minutes (F1)
  - Boost response rate by optically pumping shallow traps
    Huge increase in sensitivity

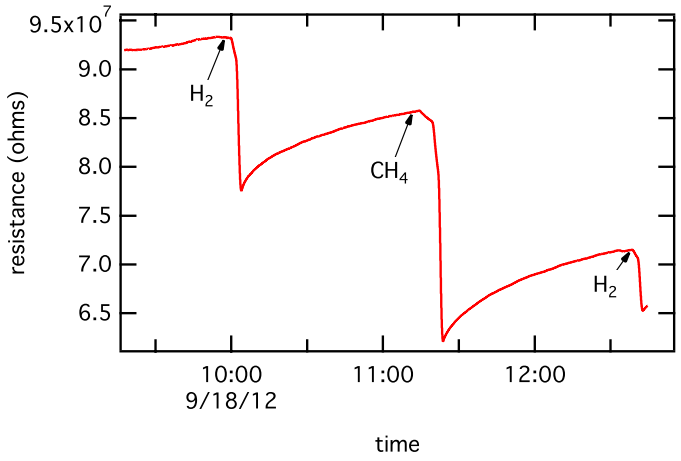


Interleaved measurement of illumination enhanced sensitivity

  - Example: Modest performing device (G1)
    No laser: T_{sense} = 3,400 minutes
    With laser: T_{sense} = 4 min

SAXET SURFACE SCIENCE

- False Signals (gasses not normally found in XHV)
  - Example: CH_4 (methane)

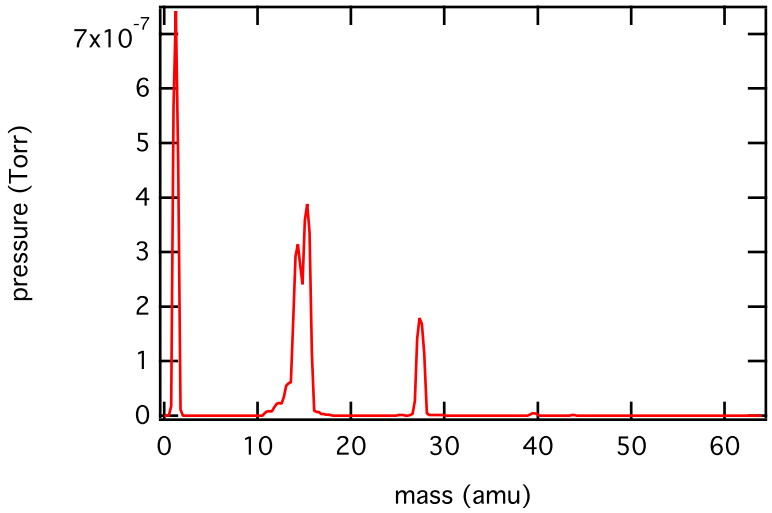


* Standard gas dosing: 5 minutes at $1x10^{-7}$ Torr, 2 minutes at $1x10^{-6}$ Torr, 1 minute at $1x10^{-5}$ Torr

Gas	R_0 (MΩ)	ΔR (MΩ)	Change (%)
H_2	93	16	17
CH_4	86	24	28
H_2	72	6	8

* Relative resistance drop compared to value immediately prior to dosing

* Not the full story!

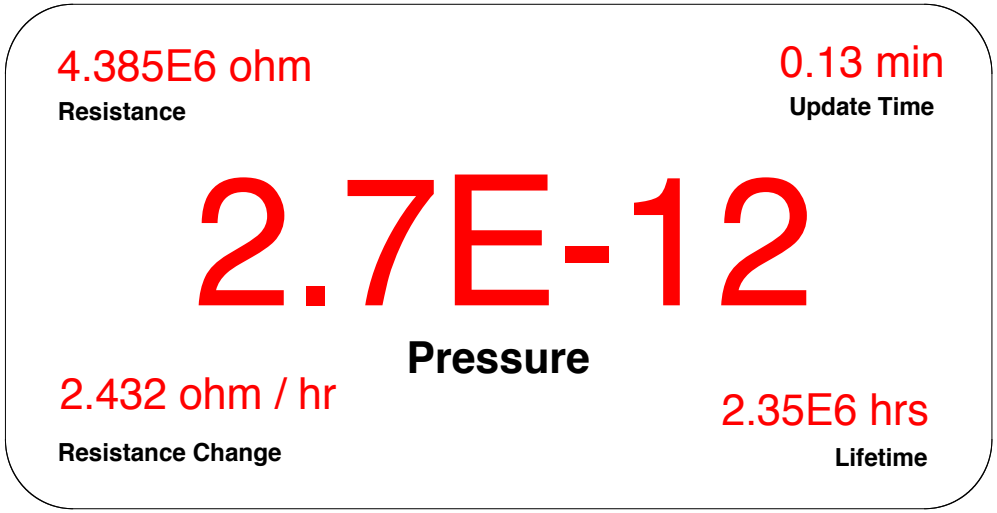


* Hydrogen also increases with the addition of methane
* Carbon monoxide also present
* Interactions with ion pump
* Interactions with hot filament in RGA
* Requires careful analysis of RGA data: ionization, transport and detection
* Gasses to be tested (ongoing now)

    -- CO, CO_2, CH_4, O_2, Ne

SAXET SURFACE SCIENCE

- Form of vacuum gauge + controller (**Deliverables**)
  - Sensor on 2-3/4” CF with local control box, like most modern RGAs
  - Control software resident on remote computer
  - Display with pressure and sensor parameters
  - Software incorporates cross calibration at UHV using standard gauge



Prototype control system display of operating titania nanotube sensor at XHV pressures.

SAXET SURFACE SCIENCE

- Commercialization activities
  - Dawnbreaker services enlisted

    * Primary Market Research Report :Interest expressed by major vacuum gauge manufacturers

    * Potential beta testers found (volunteers!)
      -- Gerardo Brucker, Chief Technologist Brooks Automation (Granville-Phillips)
      -- James Fedchak, NIST Pressure and Vacuum Group
      -- Marcy Stuztman, JLab

    * Size of market is not large, but will expand with time

SAXET SURFACE SCIENCE

Ending Summary

- Sensor
  - Relative H_2 pressure
  - No heat or charged particle generation
- Status
  - Operation at UHV shown; XHV soon
  - Sensitivity boost using optically pumped shallow traps
- Technology
  - Titania nanotube arrays
- To Do List
  - Regeneration method for post-bake use
  - Catalog other gas sensitivities
  - Enhance vacuum sensitivity, temperature stability, reduce noise, etc.
- Commercialization
  - Vacuum gauge manufacturers have interest in beta testing prototype