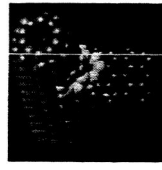


Carbon Nanotube Sensors For Gas and Vapor Detection In Space and Terrestrial Applications

Jing Li, Ph.D.
Center for Nanotechnology
NASA Ames Research Center



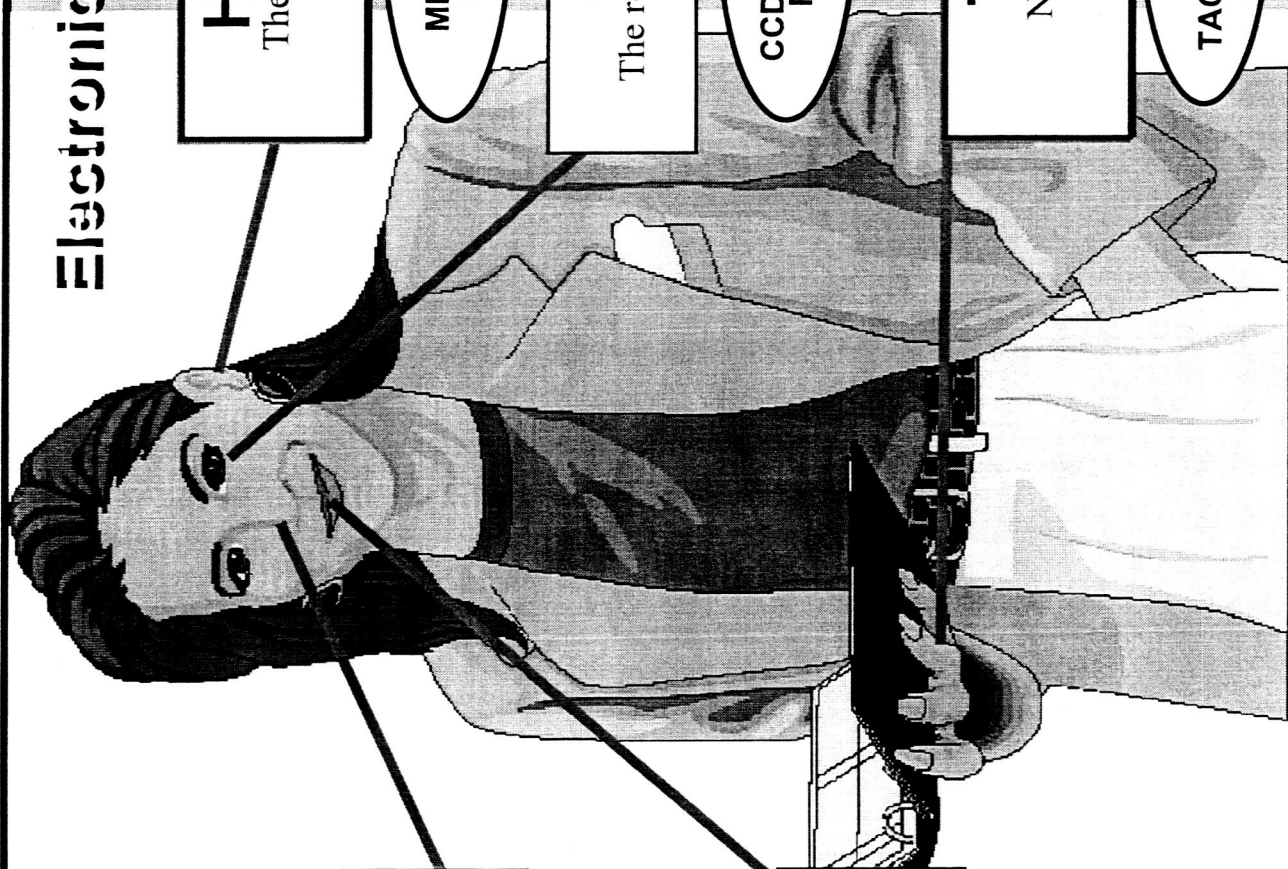
Outline



NACNT

- Applications and Requirements
- Nanotechnology Advantages
- Current Studies on Nano Chemical Sensors
- Our Research Status and Results

Electronically Mature



Hearing
The cochlea of the inner ear

MICROPHONES
SPEAKERS

Sight
The retina at the back of the eye

CCD/CMOS IMAGERS
FIBER OPTICS

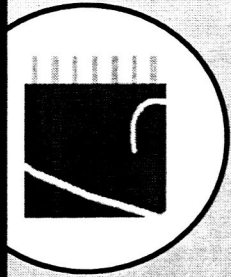
Touch
Nerve endings in the skin

TACTILE ARRAYS

Smell
Olfactory nerves inside the nose

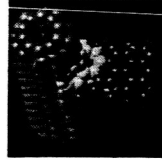


Taste
Taste buds on the tongue



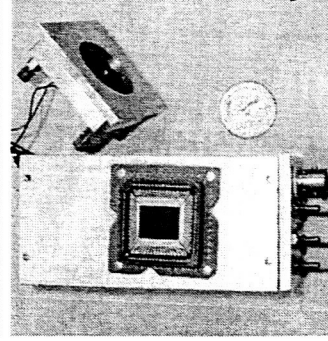


Nano Chemical Sensors for NASA Mission



NACNT

Uninhabited Aircraft



ESE
nanotech gas
sensors
sensors

Existing NO₂ detector

Demonstration of gas detectors 100 times lighter and 10 times smaller than those in use today, matching current capability.

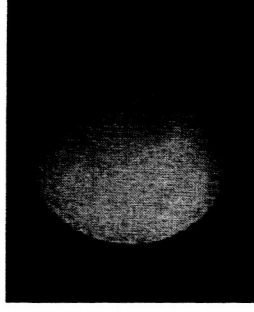
Objectives

- Greatly increased science measurement capability - less mass and power requirements for electronics and sensors. Lightweight (Kg or so)
- Demonstrate capabilities nanotechnology can provide for composition measurements of Earth's atmosphere.
- Highly miniaturized gas detectors enabling Earth Science Enterprise Plans for in situ measurements to validate satellite observations.
- Cosmochemistry: Volatiles: NO₂, H₂O, NH₃, CH₄, SO₂, CO₂, H₂S



Here:

Earth



There:

Space

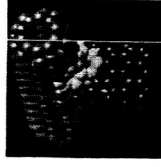


Beyond:

Outer Space



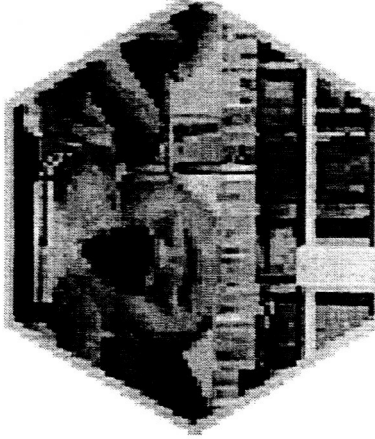
Nano Chemsensors for Terrestrial Applications



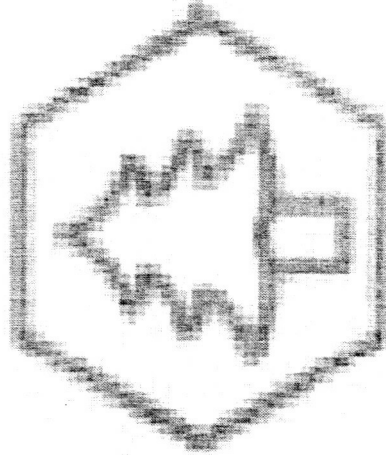
NACNT



Defense &
Homeland
security



Process
control



Environment
monitoring

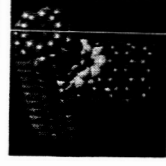


Medical
diagnoses

Requirements:

high sensitivity and selectivity,
fast response,
low power consumption,
small size,
high discrimination power.

Nanotechnology Advantages



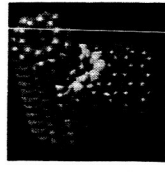
NACNT

- High surface area to volume ratio ($1587 \text{ m}^2/\text{g}$)
- Low energy barrier (Room temperature sensing)
- Small size with nanoscale manipulation of materials
- Low power consumption (1 mW/sensor)
- Easy integration (2-terminal I/V measurement)

Nanomaterial + Chip (micro) $\longrightarrow$ Macro sensing system

Nano-Micro-Macro Hierarchy

Single-Walled Carbon Nanotubes



NACNT

Basic Properties:

Mechanical:

Tough and strong, $Y \sim 1 \text{ TPa}$

Structural:

1-2 nm in radius;

Micron in length;

Every atom in a single-walled nanotube is on the surface and exposed environment

Thermal:

Sustain 400°C in air, 2000°C in vacuum

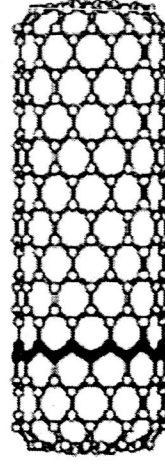
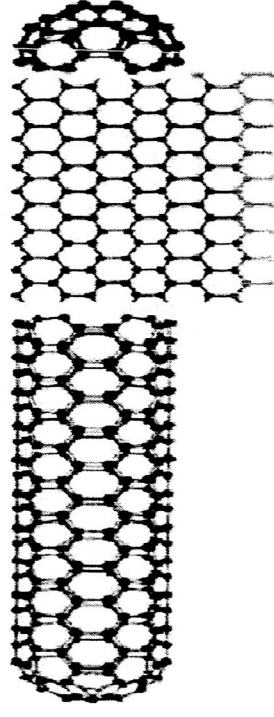
Electronic:

Ballistic charge transport at room temperature,

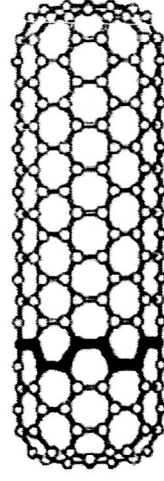
Semiconducting $E_{\text{gap}} \sim 1/d$

Small changes in the charge-environment of a nanotube can cause drastic changes to its electrical properties

Single Wall Carbon Nanotube: A slice of graphene sheet rolled into a nm-diameter tube

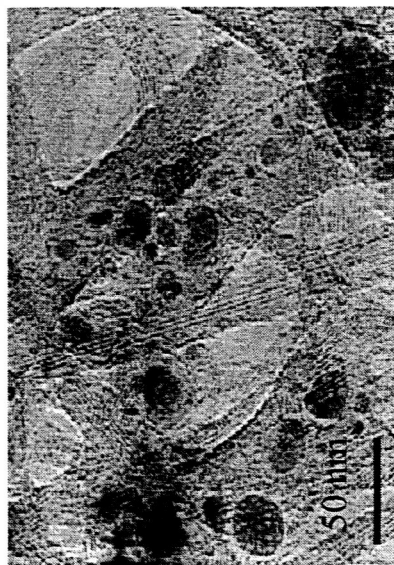


'zigzag'



'armchair'

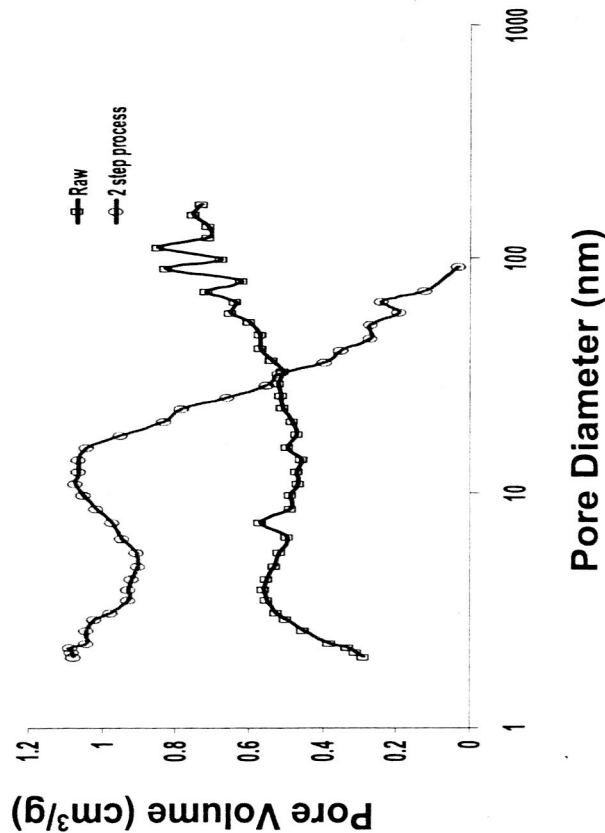
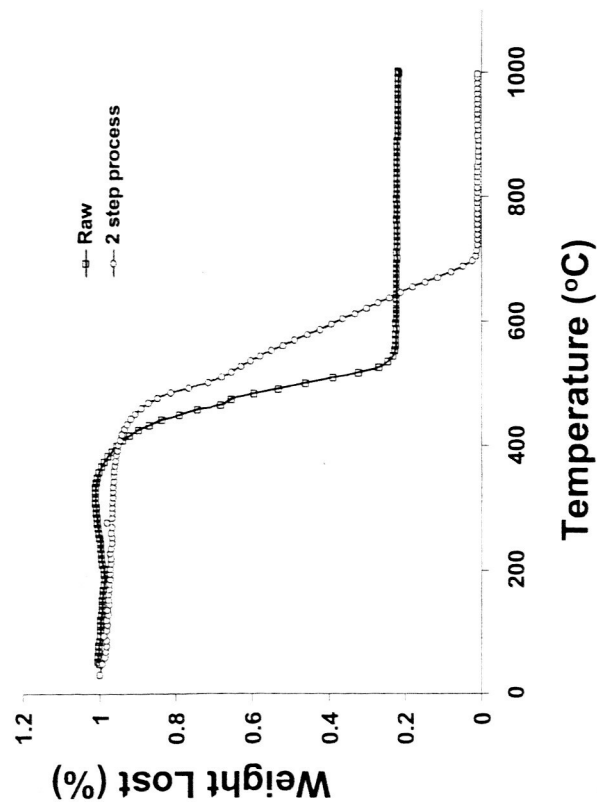
Characterization of SWNTs



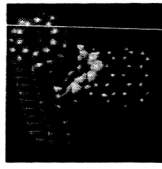
Raw: Impurity: 22%
Surface area: 577 m²/g



Purified: Impurity: 0.4%
Surface area: 1587 m²/g



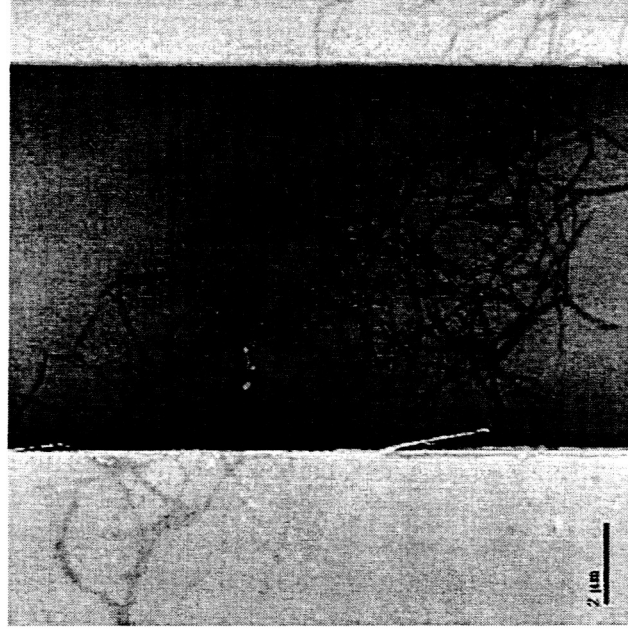
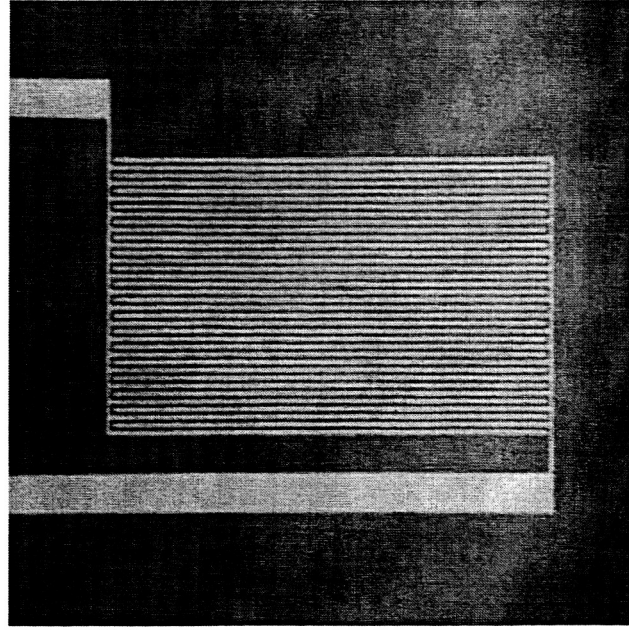
SWCNT Chemiresistor:



NACNT

Sensor fabrication:

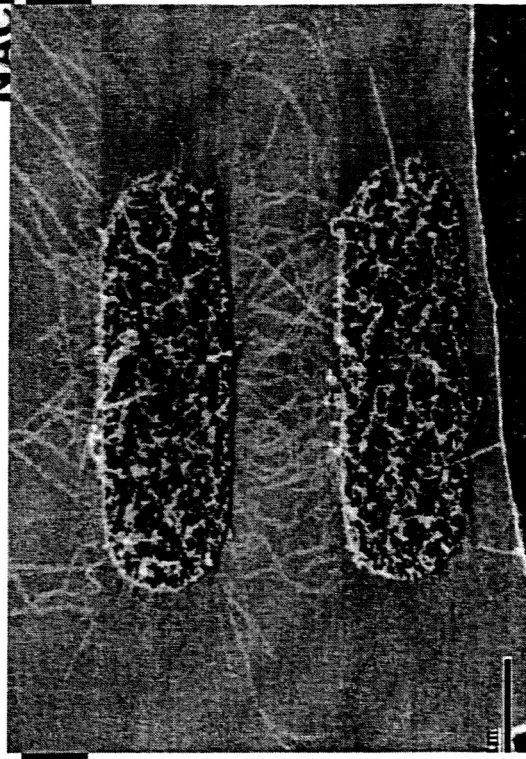
1. SWCNT dispersions--Nice dispersion of CNT in DMF/H₂O
2. Device fabrication--(see the interdigitated electrodes below)
3. SWCNT deposition—Casting, or in-situ growth



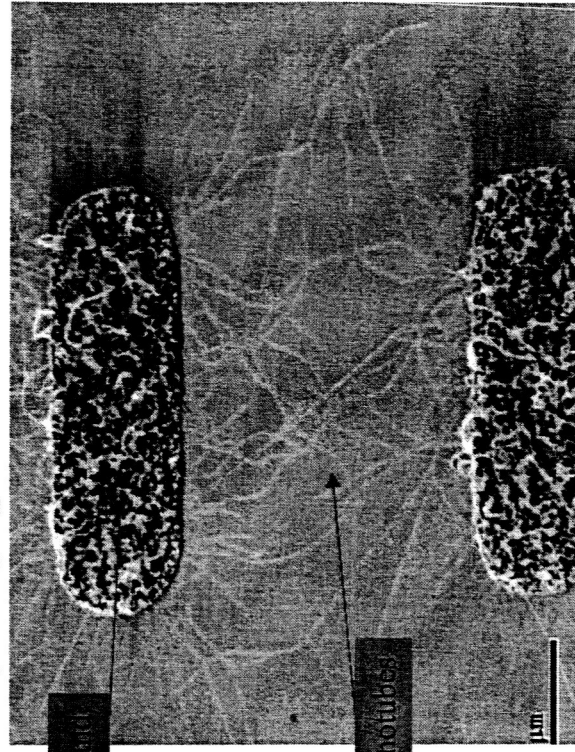
Nanodevice fabrication:

1. Patterned the catalyst for Nanotube growth
2. Grow SWNTs between two catalyst islands
See SEM images on the right.
3. Build contact pads (20nm Ti/40nm Au)

4 μm gap

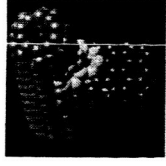


8 μm gap

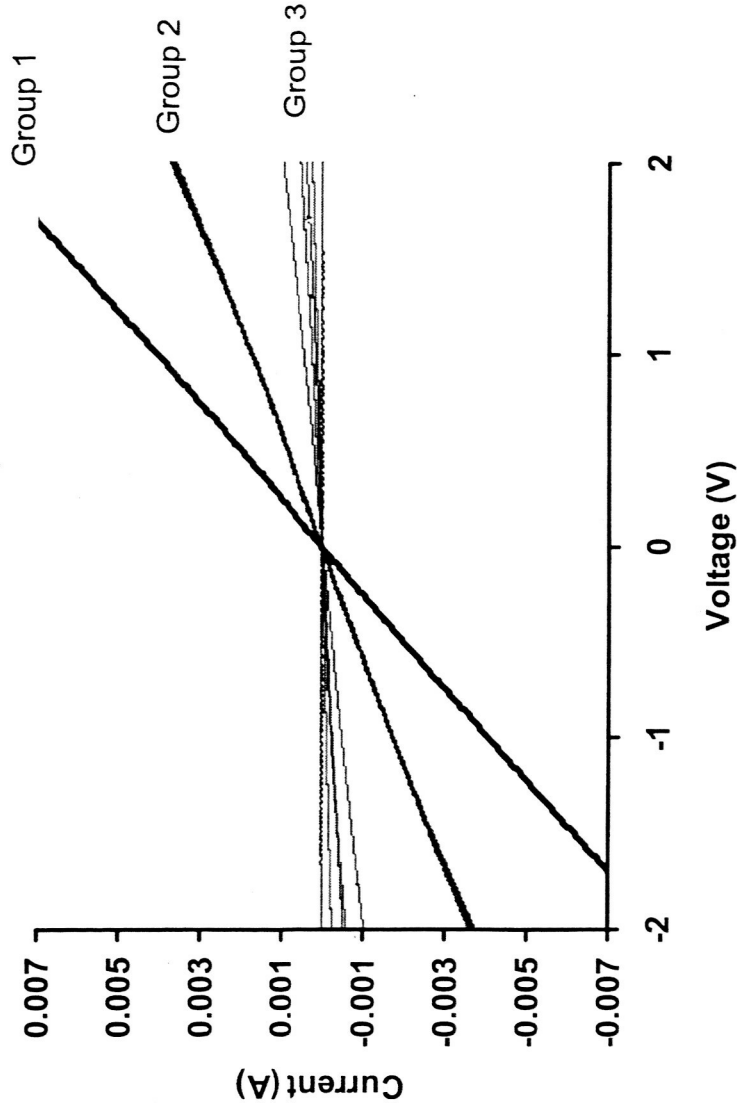




SWNT Casting

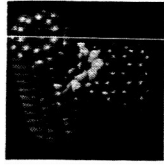


NACNT



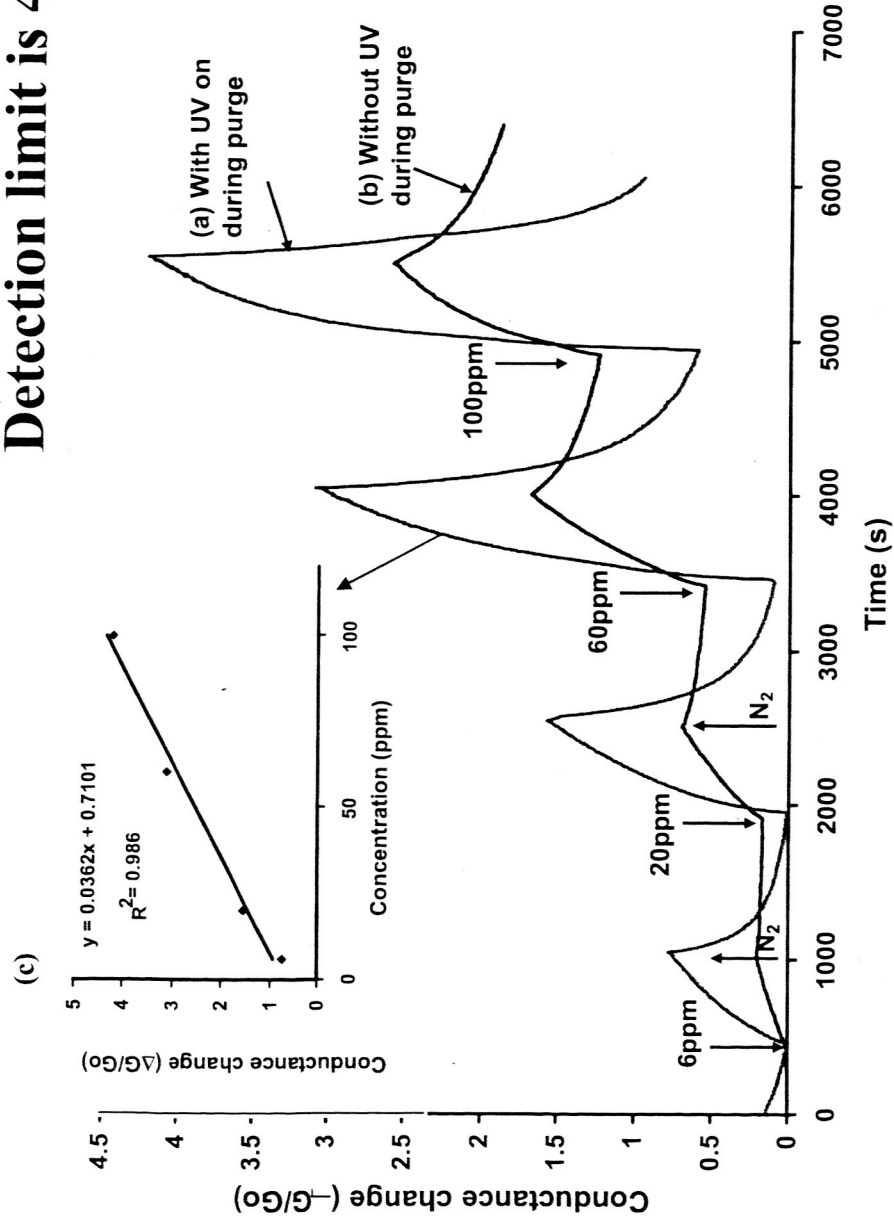
Group 1: with denser SWNTs
Group 2: with medium density
Group 3: with looser SWNTs (Sensors start to show variation and the extreme case is the single tube device.)

SWNT Sensor to NO₂

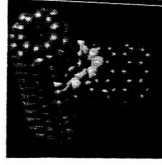


NACNT

Detection limit is 44ppb.

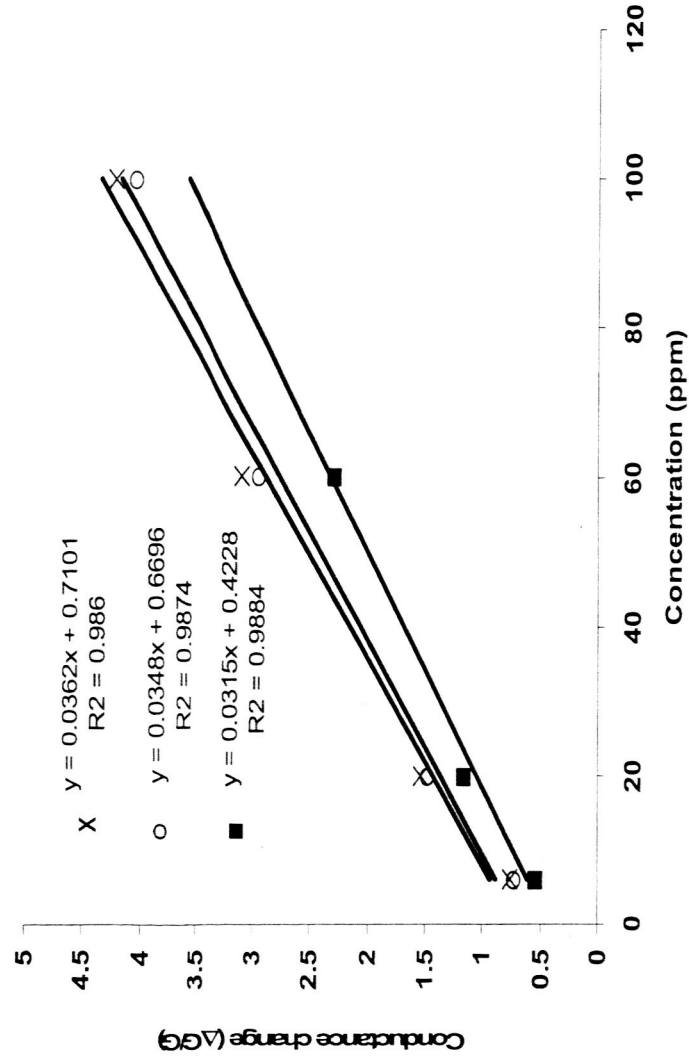


SWNT Sensors' Reproducibility



NACNT

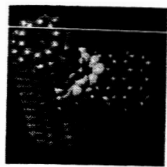
(3 sensors to NO₂)



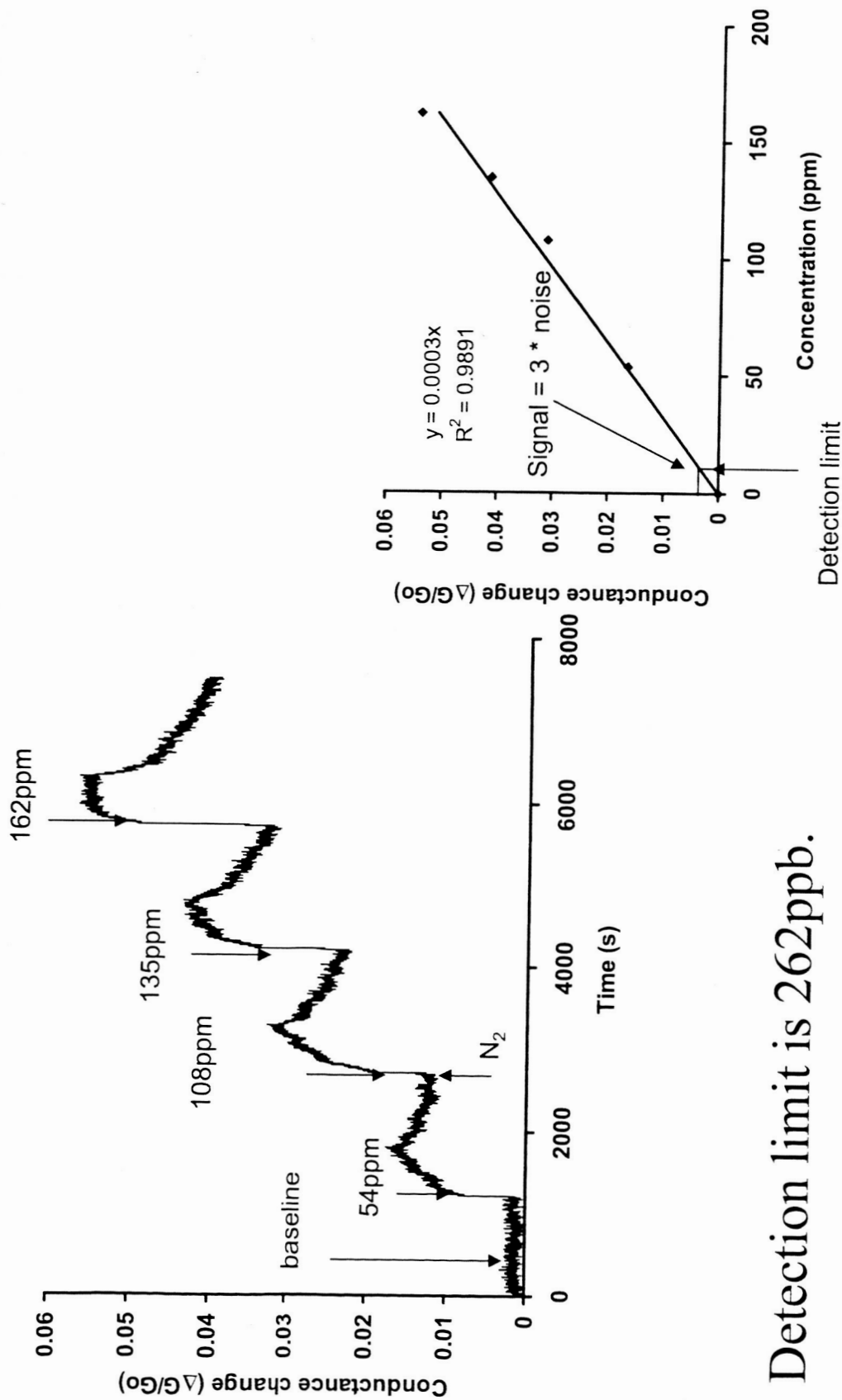
Sensitivity is the slope of the calibration curves.
The average slope is 0.034 ± 0.002 .



SWNT Sensor to Nitrotoluene

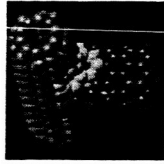


NACNT



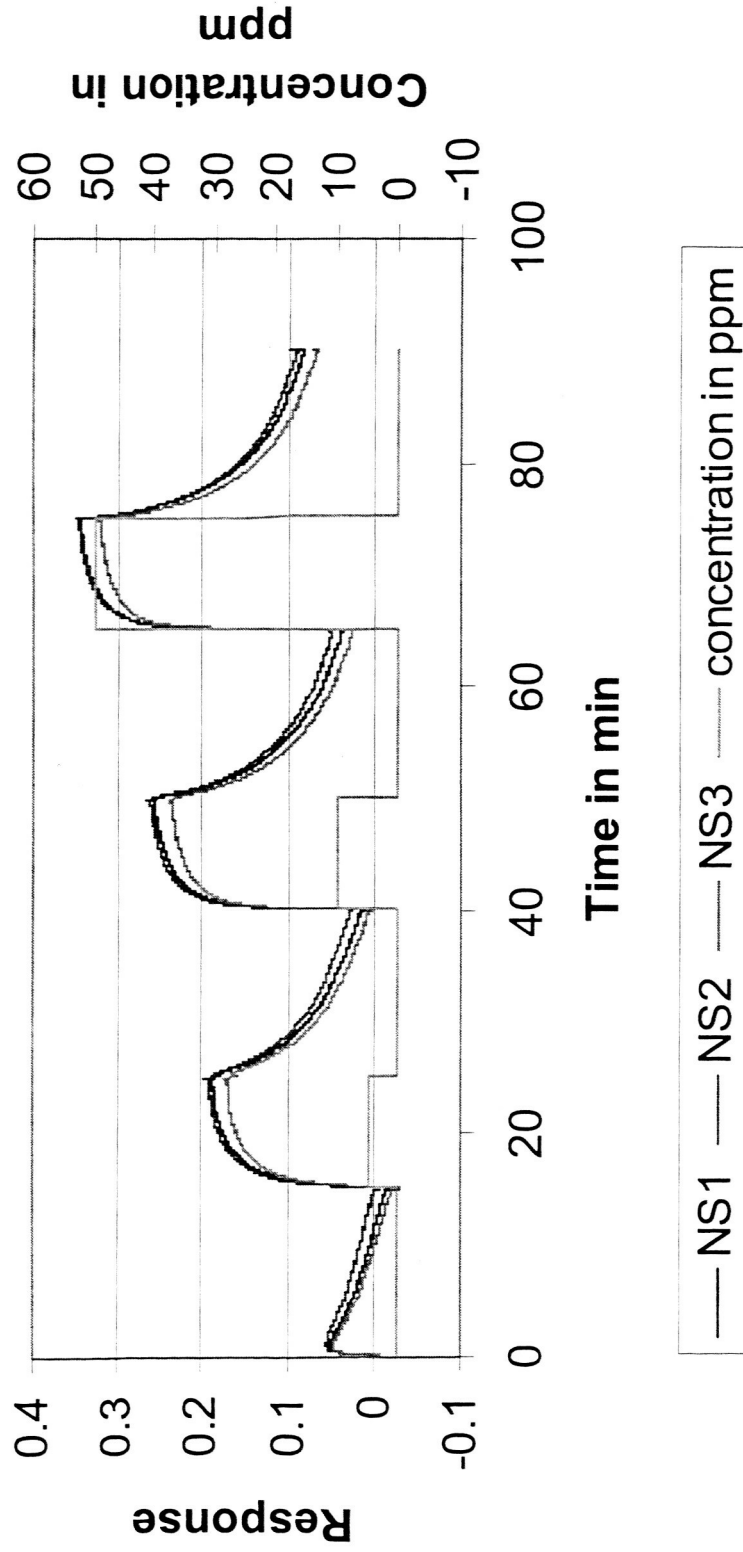
Detection limit is 262ppb.

CNT sensors to Ammonia

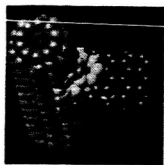


NACNT

Ammonia test on 50 IDE with UV recovery

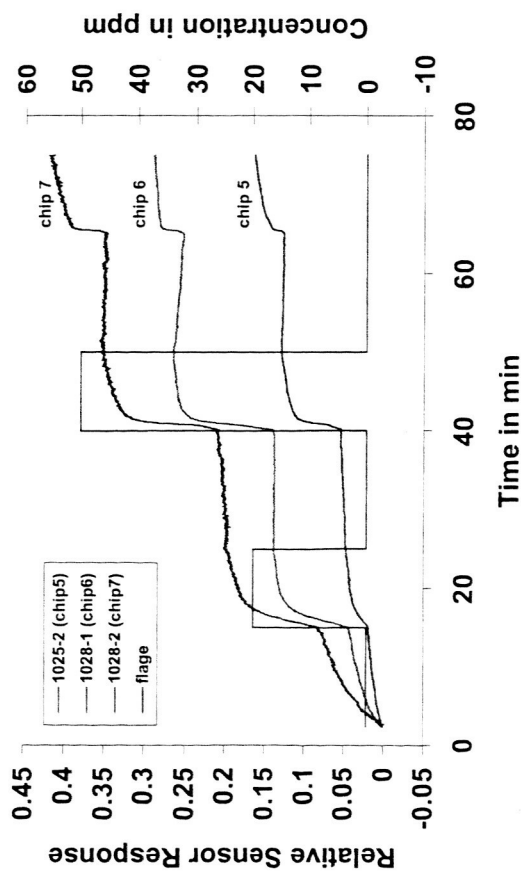


Other Gases and Vapors

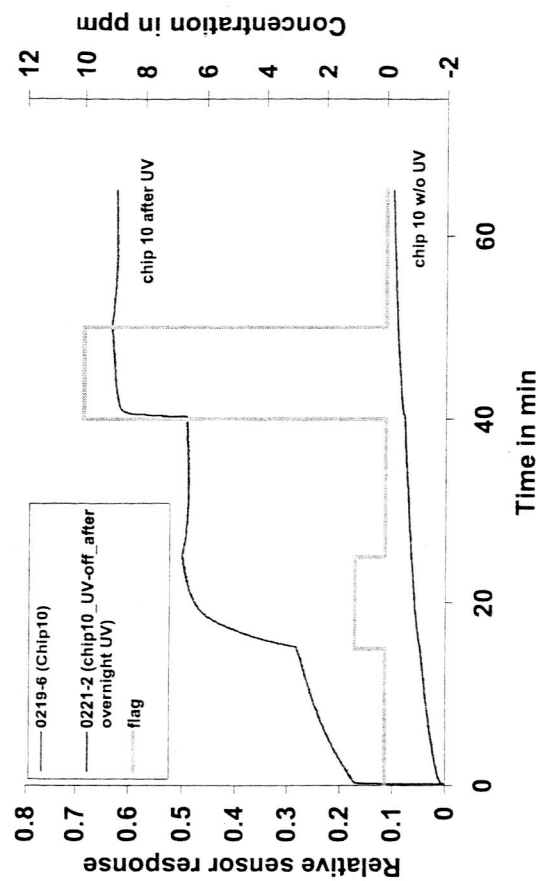


NACNT

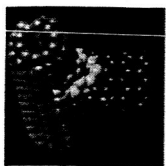
Benzene



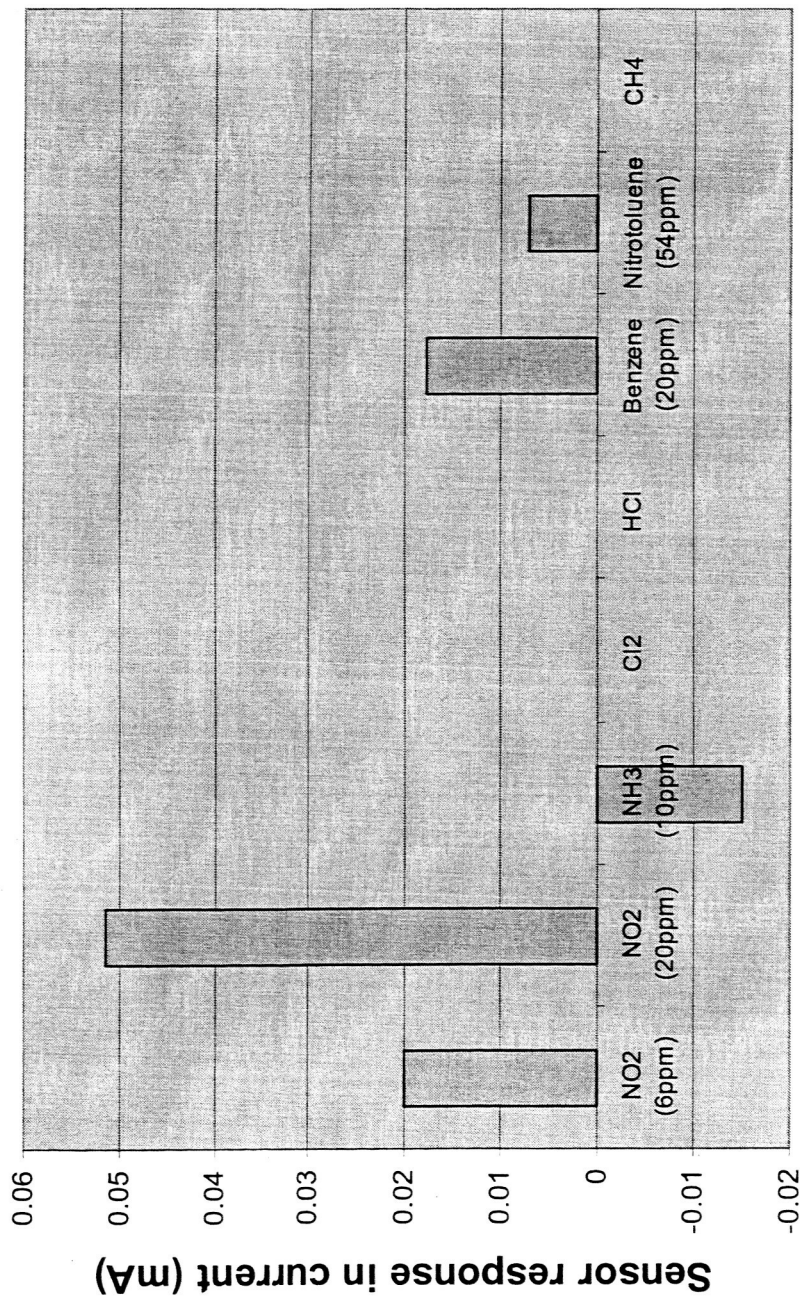
Acetone



Comparison of CNT sensors to different gases and vapors



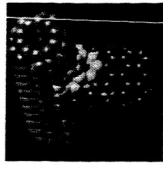
NACNT



Different gases with concentration in ppm



How to Ensure Selectivity



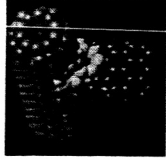
NACNT

Major approaches:

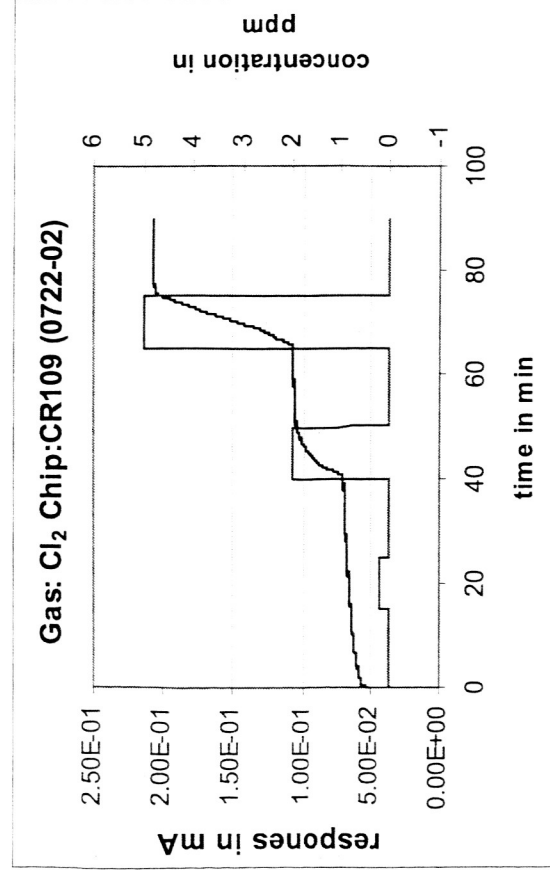
- Functionalization of CNTs
- CNT + polymer composites
- Doping: catalytic metal clusters
- Field effect: gate bias for selective detection
- Programmed temperature control
- Sensor array with pattern recognition: electronic nose



Polymer coated CNT Composite Sensors

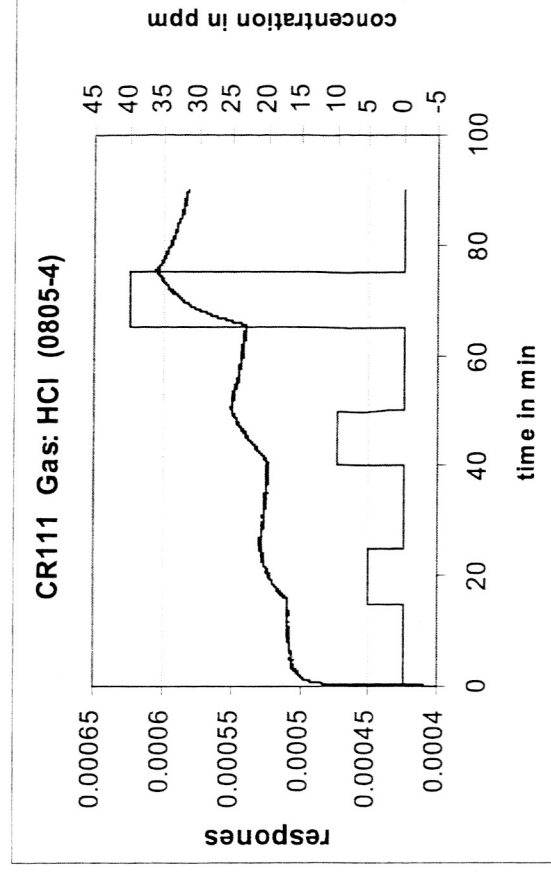


NACNT



CNT + polyethylene chlorosulfonated

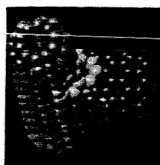
- Good response to 5ppm Cl₂ gas in N₂
- Very small response to 5ppm NO₂ in N₂



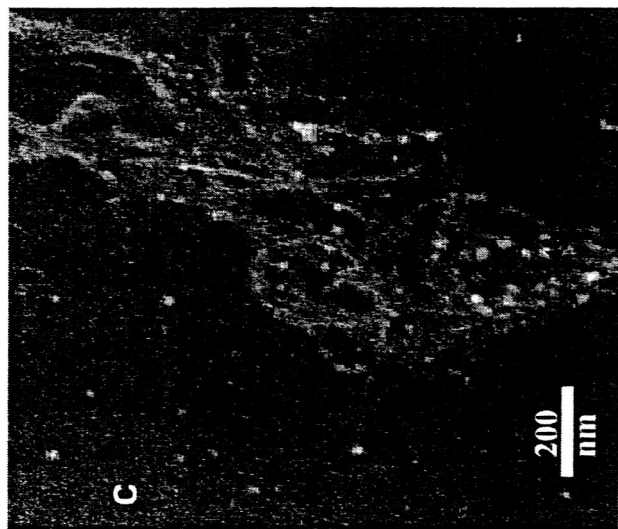
CNT + Hydroxypropyl cellulose

- Fairly good response to 35ppm HCl in N₂
- Large response to 5ppm NO₂ in N₂

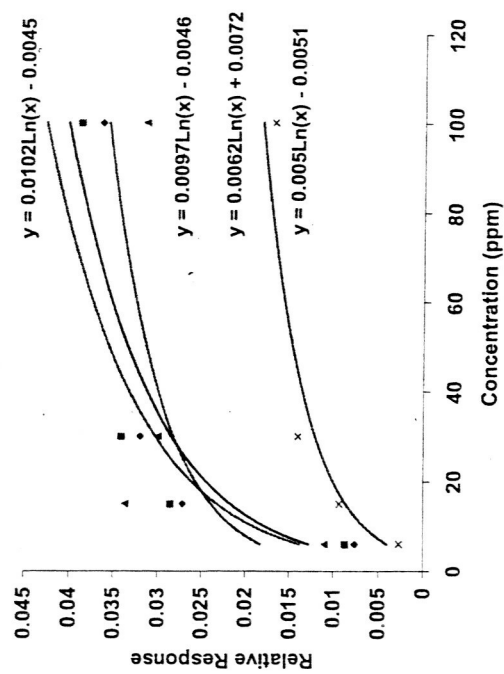
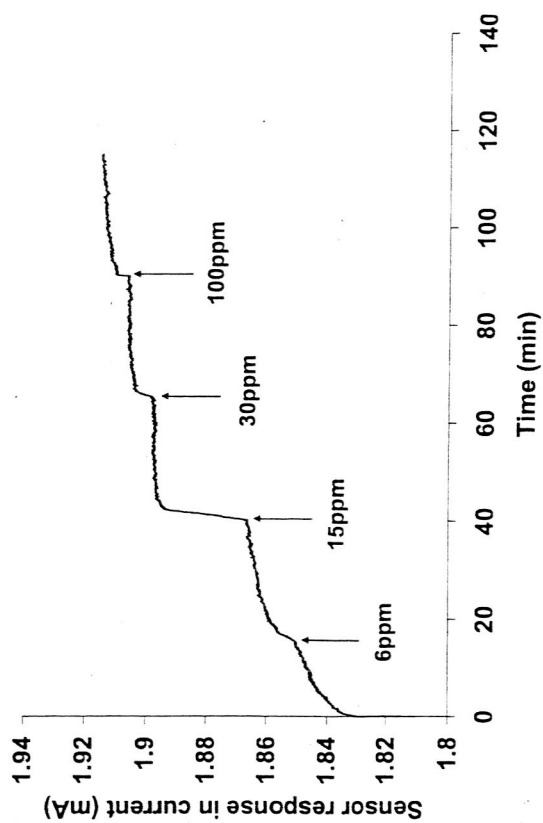
SWNT-Pd Sensor to Methane



NACNT

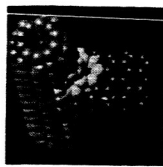


Pd particle
SWNTs



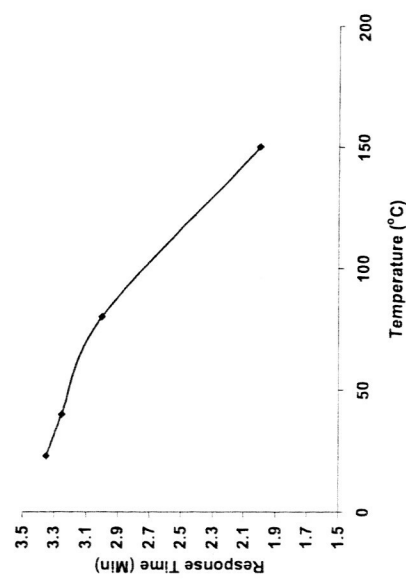
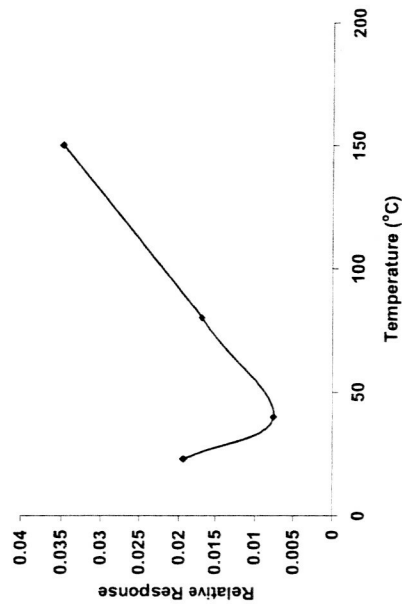
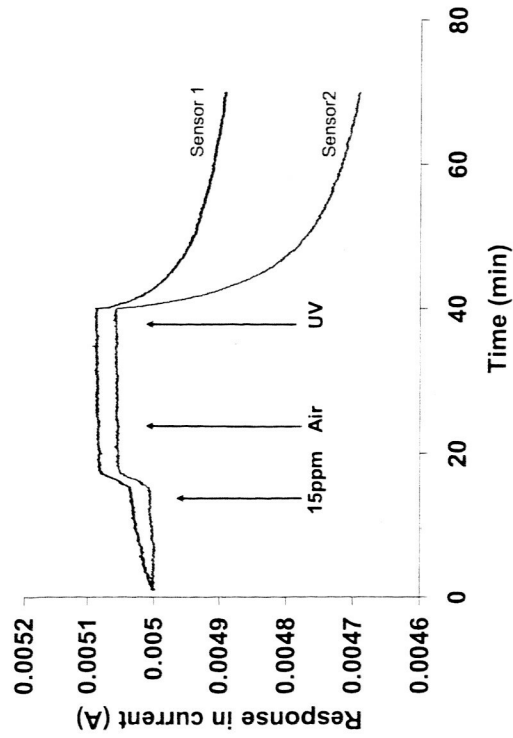


Pd doped SWNT Sensor for Methane Detection



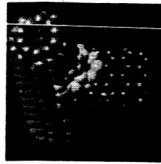
NACNT

UV light enhances the recovery.
Temperature effect





Comparison of CNT with different mixing materials for gases

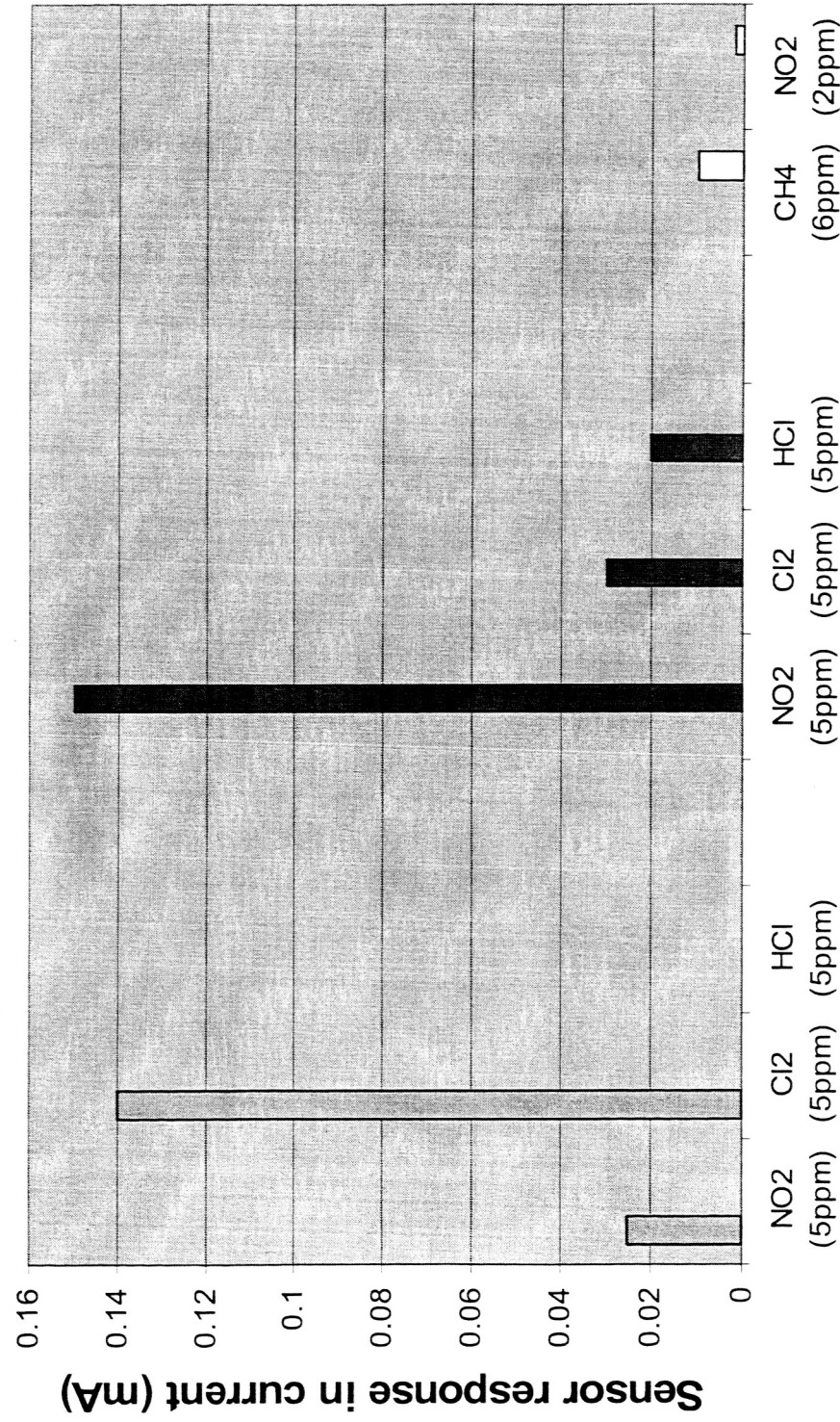


NACNT

CNT + Polyethylene
chlorosulfonated

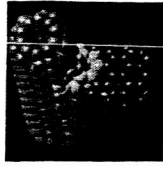
CNT + Hydroxypropyl
cellulose

CNT + Pd



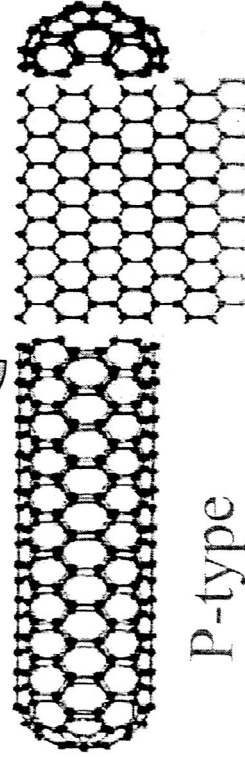
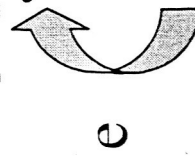
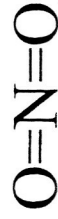
Gases with concentration in ppm

Sensing Mechanisms



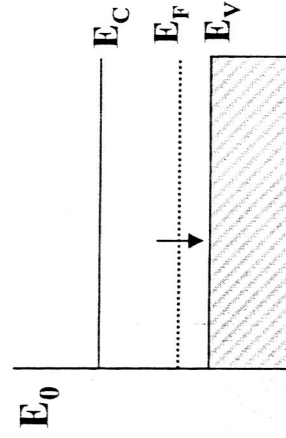
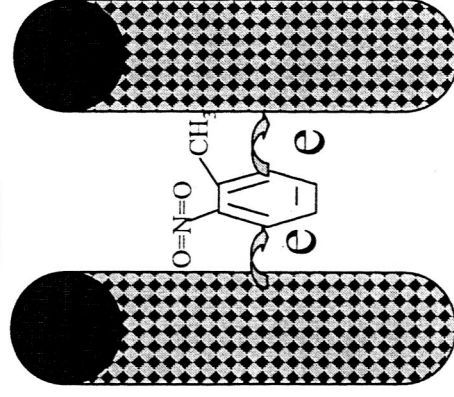
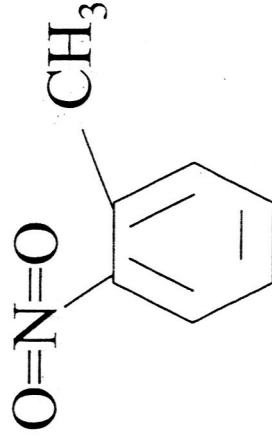
NACNT

NO₂



P-type

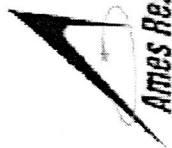
Nitrotoluene



SWNT

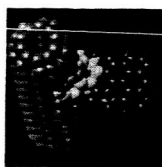
Intratube Modulation

Intertube Modulation

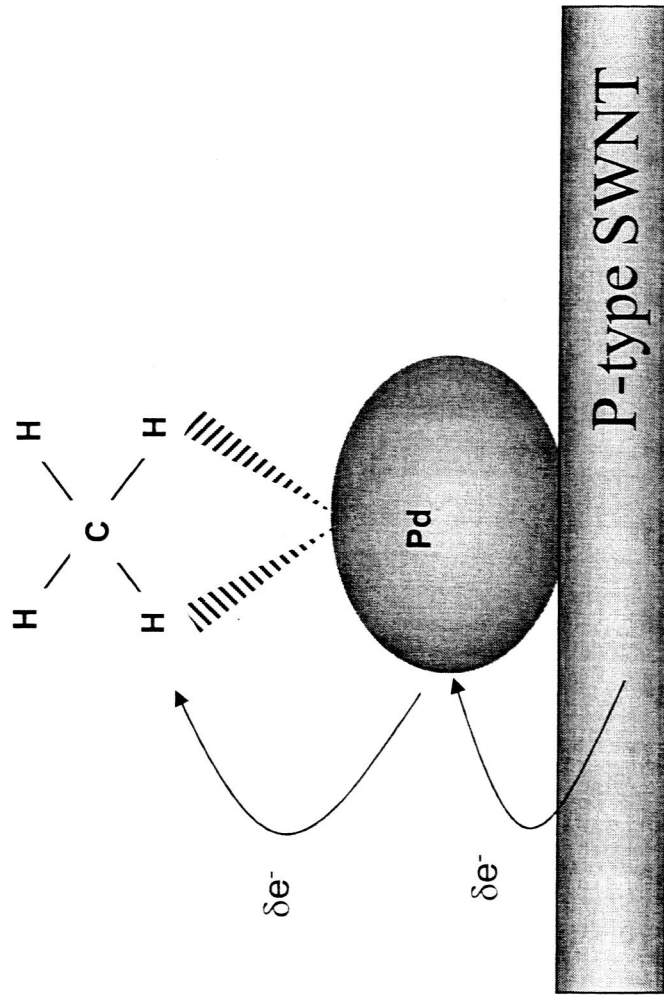


Ames Research Center

Sensing Mechanism of Pd-SWNTs to Methane

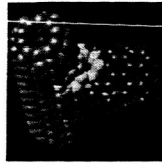


NACNT

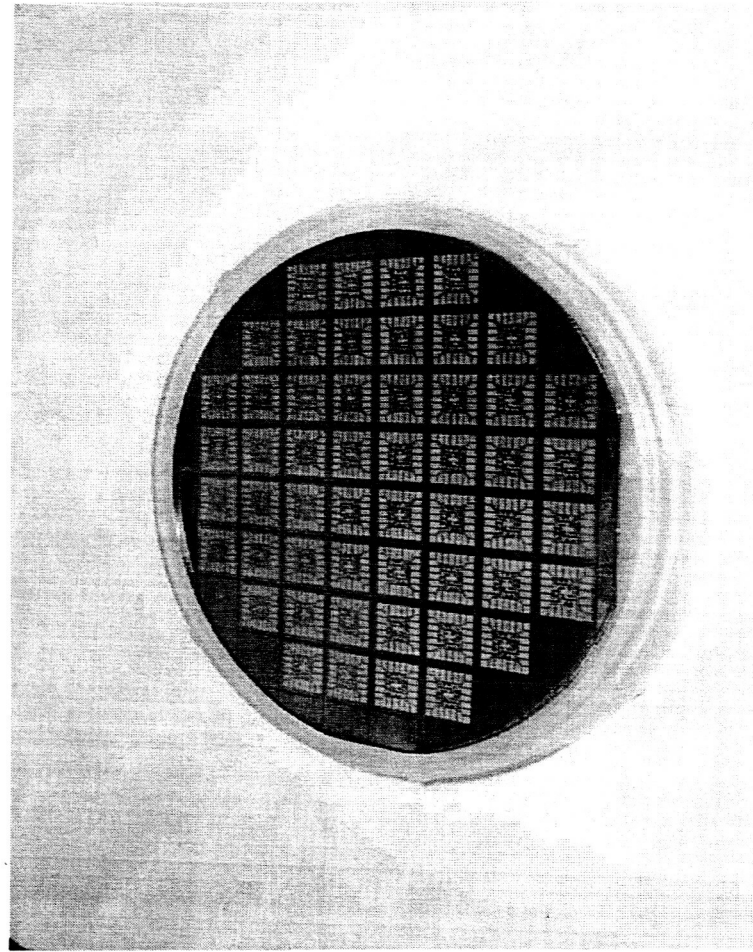
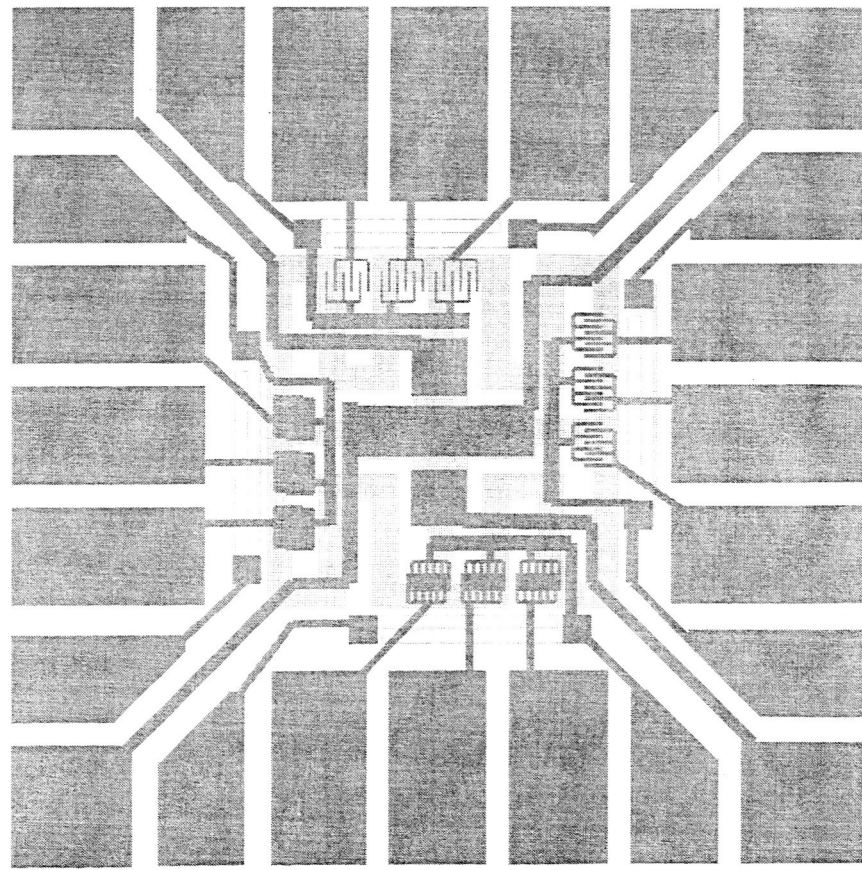




Array Approach

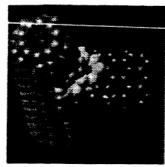


NACNT

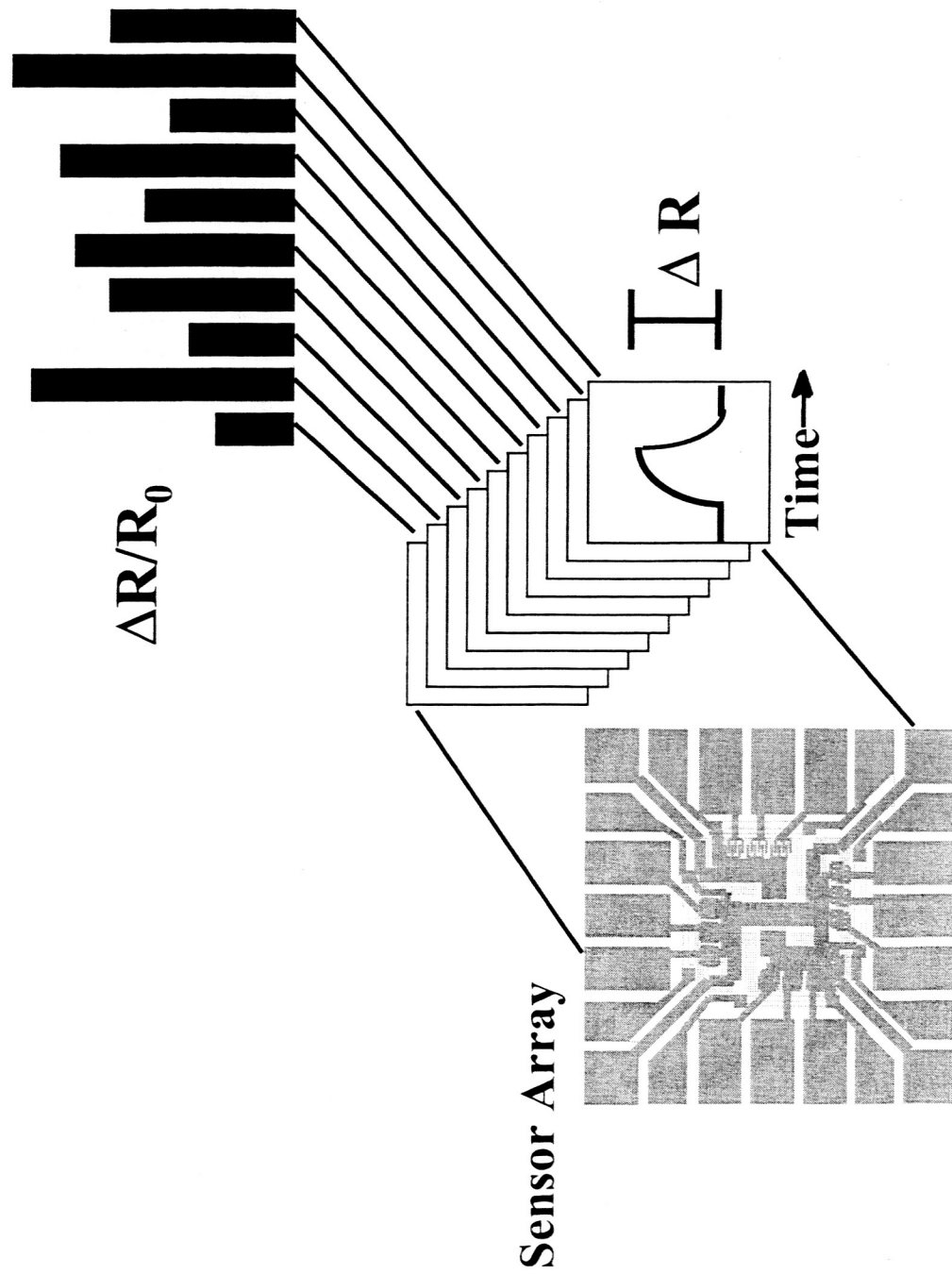


Twelve sensing elements are on a chip (1cm x 1cm) with heaters and thermistors.

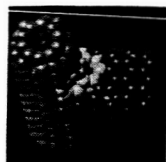
Data Manipulation



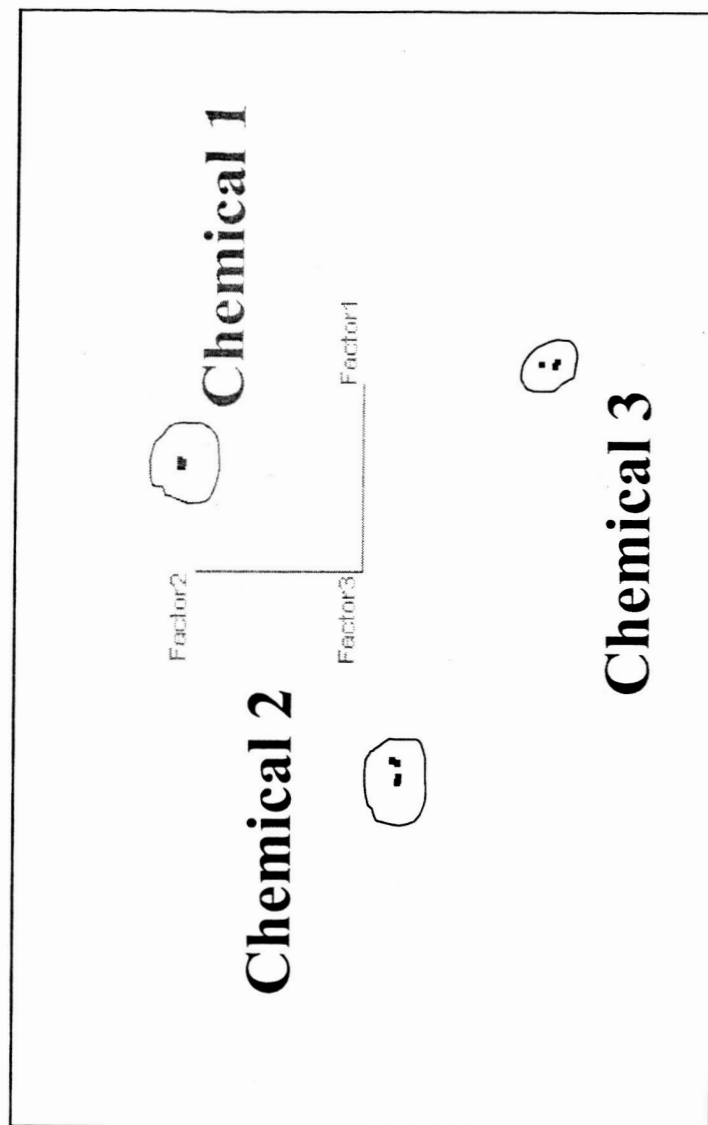
NACNT



Discrimination of Chemicals



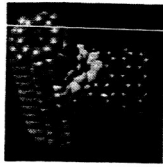
NACNT



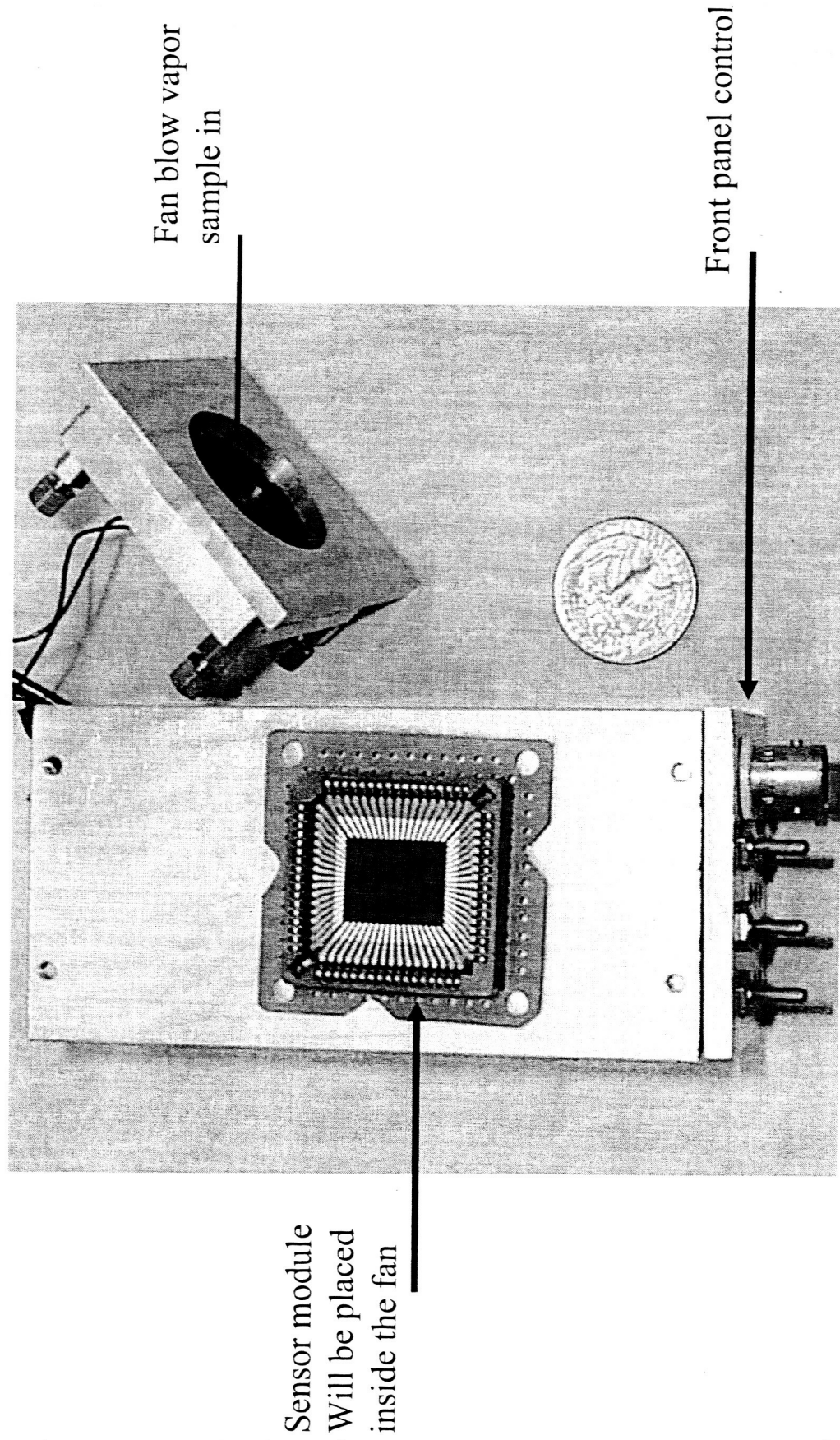


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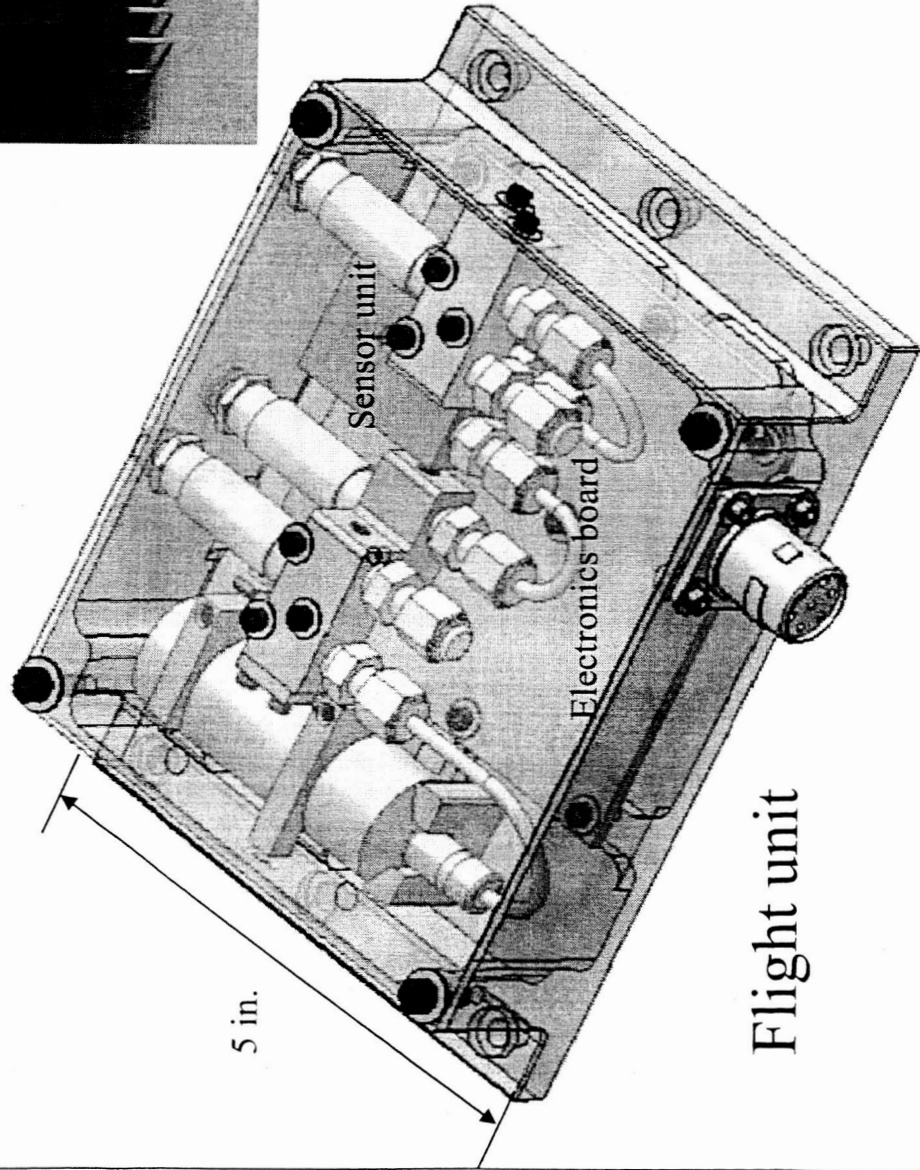
Handheld Device for in-situ Explosive Detection



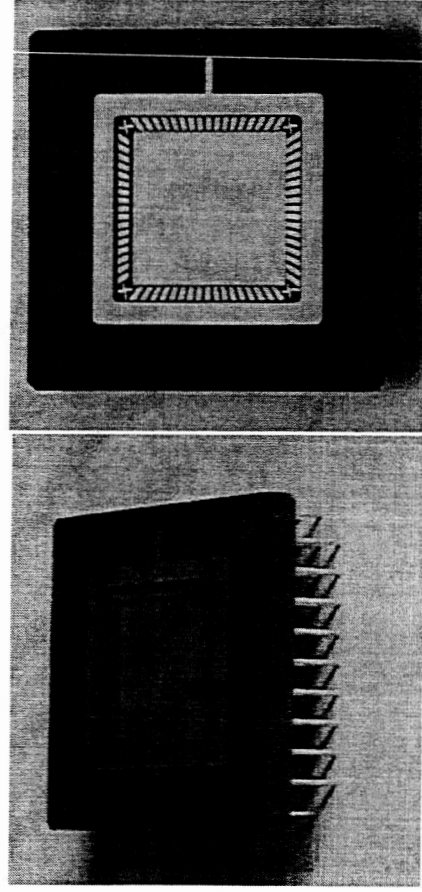
NACNT



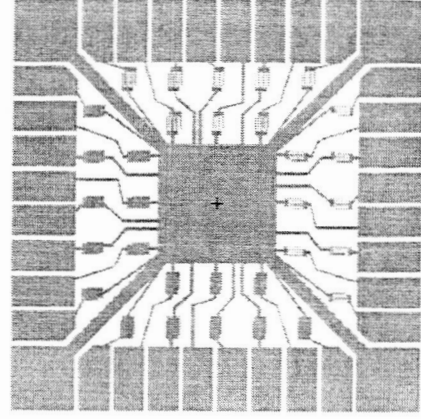
Flight Demo Unit for Satellite



Flight unit



Ceramic chip carrier

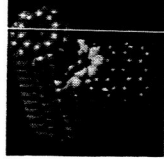


32-channel sensor chip



Ames Research Center

Summary



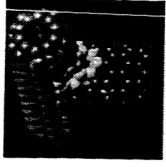
NACNT

- We have worked on the development of portable, low cost, low power consumption and room temperature operated, nanostructure engineered chemical sensors.
- CNT semiconductor sensors have potential of being used for NASA mission due to the unique physiochemical properties.
- This sensing platform can be utilized to the applications in homeland security, environmental monitoring, industry process control, and medical diagnostics.
- Final products will be sensor modules, handheld devices, badge type detectors, sensor chips for wireless and networking.



Ames Research Center

Acknowledgments



NACNT

- The nanotube sensor work is, in part, sponsored by an Interagency Agreement with FAA and Richard Laraeu is acknowledged for his support.
- Professor R. Smalley and his HiPCo team are acknowledged for providing SWNTs.