Materials for Memories and Sensors

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Flash Memory

• **Flash memory** is a non-volatile computer storage chip that can be electrically erased and reprogrammed.

• Field-effect transistor (FET)-based memory devices have the advantages of nondestructive read-out and integrated circuit compatibility.

Example applications of both types of flash memory include personal computers, PDAs, digital audio players, digital cameras, mobile phones, synthesizers, video games, scientific instrumentation, industrial robotics, medical electronics, and so on.
Common structure

Out coupling of light from transistor structure

Emission from the edges

Waveguiding properties

V. A. L. Roy et. al. on semiconductors

ADVANCED MATERIALS 2005, 17 (10) 1258
ADVANCED MATERIALS 2008, 20 (7) 1258
ADVANCED MATERIALS 2008, 20 (11) 2120
ANGEWANDTE CHEMIE 2008, 47 (51) 9895
ANGEWANDTE CHEMIE 2009, 48 (41) 7621

13.56 MHz RFID tag
• **Particles instead of a thin film layer**
• A transistor with memory properties due to reversible charge trapping/detrapping at the gate dielectric layer.
• Optimum size of 15 nm particles for charge trapping

AFM image of PVP on Au NPs – impact on morphology due to the size of Au NPs

Heterostructure films in memory structure

Advanced Materials 2012, 24 (9), 1247-1251.

- To demonstrate the trapping of both electrons and holes
- The device work at both electron and hole enhancement mode
  
  With the heterostructure
  
  $Si/SiO_2/C_{60}/Pentacene/Au$

•

$V_{DS} = -40 \text{ V}$

$V_{DS} = 40 \text{ V}$
P/E endurance

Retention

Advanced Materials 2012, 24 (9), 1247-1251.
**Floating Gate memory device**

Two major issues
- Memory window (storage capacity)
- Retention time

Retention time is influenced by
- Lateral leakage of charges
- Vertical leakage (charges moving back to the semiconductor)
Microcontact printed nanoparticle array

Microcontact printing method

Advanced Materials 2012, 24 (26), 3556-3561.
Flexibility and endurance test for the memory device
Double Floating Gate Structure

To improve the retention time

Tunneling oxide

FROM

$E_F$

HOMO

Au NPs FG

Pentacene

Introduce a barrier!

68 % at $10^5$ s
Layer-by-Layer Assembled Reduced Graphene Oxide-Gold Nanoparticle Hybrid Double Floating Gate Structure

Reduced graphene oxide sheet

Enhanced memory window

Adv. Mater. 2013, 25, 872
Tunable Memory Characteristics through Controlled Doping of Reduced Graphene Oxide

- Energy band engineering to achieve larger memory window and controlled threshold voltage shifts.
- Be applicable to both p-type and n-type memories.

*ACS NANO* 2014, 8(2), 1923-1931.
**rGO**

**5 s**

**25 s**

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**P-type**

**N-type**

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**ACS NANO** 2014, 8(2), 1923-1931.

**TABLE 1.** Threshold Voltages of Programmed State and Erased States and Memory Windows with Respect to the Various Doping Concentration of AuCl$_3$ in rGO

<table>
<thead>
<tr>
<th>Doping</th>
<th>$V_{th}$ (P)</th>
<th>$V_{th}$ (E)</th>
<th>Memory window</th>
</tr>
</thead>
<tbody>
<tr>
<td>rGO</td>
<td>$-2.3 \ V$</td>
<td>$-1.6 \ V$</td>
<td>$0.7 \ V$</td>
</tr>
<tr>
<td>5 s</td>
<td>$-2.7 \ V$</td>
<td>$-1.7 \ V$</td>
<td>$1 \ V$</td>
</tr>
<tr>
<td>25 s</td>
<td>$-2.5 \ V$</td>
<td>$0.2 \ V$</td>
<td>$2.7 \ V$</td>
</tr>
</tbody>
</table>

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Floating gate

Semiconductor

$\Phi_{\text{rGO}}, 4.44 \ eV$

$\Phi_{\text{FcFePc}}, 4.9 \ eV$

$\Phi_{\text{Fc}}, 5.05 \ eV$

$\Phi_{\text{HOMO}}, 5.2 \ eV$

$\Phi_{\text{LUMO}}, 3.1 \ eV$

---
Nanocomposite charge trapping layer

Memory window with respect to Au NPs concentration

AFM image of the Au NP/PMMA film

Nanotechnology 2012, 23 (34), 344014.
# Device comparison

<table>
<thead>
<tr>
<th></th>
<th>APTES device</th>
<th>rGO-Au NP device</th>
<th>PMMA/Au NP device</th>
<th>AuCl₃ doped rGO</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Memory window</strong></td>
<td>~1 V @ ±5 V</td>
<td>~2 V @ ±5 V</td>
<td>~2 V @ ±5 V</td>
<td>~2.7 V @ ±5 V</td>
</tr>
<tr>
<td></td>
<td>for 1s</td>
<td>for 1s</td>
<td>for 1s</td>
<td>for 1s</td>
</tr>
<tr>
<td><strong>Retention</strong></td>
<td>68 % at 10⁵ s</td>
<td>95 % at 10⁵ s</td>
<td>84 % at 10⁵ s</td>
<td>71 % at 10⁵ s</td>
</tr>
<tr>
<td><strong>Endurance</strong></td>
<td>&gt;1000</td>
<td>&gt;1000</td>
<td>&gt;1000</td>
<td>&gt;800</td>
</tr>
</tbody>
</table>
Solution processed molecular floating gate - no metal particles

Fabrication procedure

Atomic layer deposition of $\text{Al}_2\text{O}_3$

Spin-coating $\text{C}_{60}$

Spin-coating PVP

Deposition of semiconductor layer and electrodes

AFM image of C60 layer

SCIENTIFIC REPORTS, 3, 3093 | DOI: 10.1038/srep03093
Ambipolar polymer flash memory

Au NP monolayer
Ambipolar trapping

SCIENTIFIC REPORTS 2013, 3, 2319.
Reversible Conversion of Dominant Polarity in Ambipolar Polymer/Graphene Oxide Hybrids

Control the hole/electron transport with pre-applied gate bias. The yellow region identifies hole trapping state and dark region corresponds to electron trapping state.
Ambipolar inverters

- Resonable signal gain
- Sharp switching
- Rail-to-rail output swings

**Improved static performance**

*SCIENTIFIC REPORTS 5, 9446, 2015*
Tunable Memory Characteristics based on functionalized rGO

ACS Appl. Mater. Interfaces, 2015, 7 (3), pp 1699–1708
An upconverted photonic nonvolatile memory

- Nonvolatile memory for data encryption
- Infrared light as a 4th terminal
- Multilevel data storage with infrared light

Nature Communications, 2014, 5, 4720
Memory characteristics

Data retention > $10^5$ s

Multilevel storage

Ultra flexible device

Nature Communications, 2014, 5, 4720
**CdSe/ZnS** core–shell quantum dots charge trapping layer for flexible photonic memory

- The CdSe/ZnS QDs act as either holes or electrons trapping elements in p-channel and n-channel flash memory respectively.
- The flash memory displays UV-controllable multi-states memory properties.
- The electrically programmed flash memory has even been erased by a low intense UV light without additional external electric field within 1 s which is superior to the traditional silicon-based erasable programmable read only memory EPROM.

*Journal of Materials Chemistry C 2015, 3, 3173-3180*
Plasmonic flash memory based on Au@Ag structure

- The plasmon resonance bands of Au@Ag core-shell NRs can be synthetically manipulated by varying the Au-core size or the Ag-shell thickness.
- The Au@Ag nanorods can support longitudinal and transverse dipolar plasmon modes with comparable intensities, so their photon response efficiency is relatively high.

Schematic diagram of the memory device; UV-vis spectrum of Au NRs and Au@Ag NRs in aqueous solution. TEM image of Au NRs and Au@Ag NRs.
MoS2 with metal NPs array as floating gate in flash memory

**Tunable Memory Characteristics**

The work function difference between metal and MoS2 causes a built-in electric field that directs from metal to MoS2 or MoS2 to metal (depend on the work function of metal). This barrier height and the corresponding electric field are responsible for collection of different type of charge carriers (holes or electrons), and a control over the charge trapping behavior could be achieved.

- Controlled charge trapping and long data retention have been achieved in a metal (Ag, Au, Pt) NPs–MoS2 floating gate flash memory.
- This controlled charge trapping is hypothesized to be attributed to band bending and a built-in electric field $\xi_{bi}$ between the interface of the metal NPs and MoS2.

V. A. L. Roy et al. *Nanoscale* 2015, 7, 17496-17503
A novel hybrid architecture to achieve programmable transistor nodes that are analogies to flash memory by incorporating a RRAM device as a resistive switch gate for FET on flexible substrate. Controlled well-defined memory window, long retention time and fast access speed of this novel hybrid device may open up new possibilities of realizing fully functional nonvolatile memory for high-performance flexible electronics.

Core-shell floating gate for enhanced retention time

Printed core-shell nanoparticle array on flexible PET substrate
- To avoid charges leaking back to the semiconductor
Characterized for multi-bit memory.

Optical image of the PET substrate with printed particle array

Patent:
United States Patent Application No. 14/528,044 Filed on 30th October 2014
Title: An Electronic Device for Data Storage and a Method of Producing an Electronic Device for Data Storage.
Density of the particle layer

Au NP
Density: $4 \times 10^{11}$ per cm$^2$

Ag NP
Density: $3.6 \times 10^{11}$ per cm$^2$

Au core-Ag shell NP
Density: $3 \times 10^{11}$ per cm$^2$

Ag core-Au shell NP
Density: $5 \times 10^{11}$ per cm$^2$

Optical image of the fabricated memory device
Memory window comparison of the memory transistors based on various core-shell particles

Single memory transistor:
- Retention time over $10^8$ seconds
- P/E cycles over $10^6$

Date retention property of the memory transistor.

P/E endurance property of the memory transistor.
Summary (1st part):
1. Fundamental charge trapping properties at the dielectric/semiconductor interface of thin film transistors have been used as storage element
2. Various floating gate architectures have been discussed
3. Finally, light tunable optoelectronic memories have been demonstrated.
SPIE - Printed Memory and Circuits II (yearly in summer)

Chair Emil J. W. List Kratochvil, Humboldt-Univ. zu Berlin (Germany)

• Program Committee
  • Dago M. de Leeuw, Max-Planck-Institut für Polymerforschung (Germany)
  • Jan Genoe, IMEC (Belgium)
  • Norbert Koch, Humboldt-Univ. zu Berlin (Germany)
  • Tae-Woo Lee, Pohang Univ. of Science and Technology (Korea, Republic of)
  • Ronald Österbacka, Åbo Akademi Univ. (Finland)
  • Wen-Chang Chen, National Taiwan Univ. (Taiwan)
  • Tsuyoshi Sekitani, Osaka Univ. (Japan)
  • Barbara Stadlober, JOANNEUM RESEARCH Forschungsgesellschaft mbH (Austria)
  • A L Roy Vellaisamy, City Univ. of Hong Kong (Hong Kong)
Detection of ions and molecules in aqueous and vapor phase
Real time monitoring - Internet of things (IoT)

- food toxins
- drug trafficking
- organic pollutants/contaminants in water or air

http://en.wikipedia.org/wiki/Water_pollution
Sources of chemical contamination in drinking water

Pre-Treatment (Water Source Contamination)
- Nitrates (pesticides)
- Heavy Metal (Industry, Landfill)
- Hydrocarbons
- Sulphates (Acid rain)

Post Treatment Contamination
- Chlorine, Fluoride (Disinfectants)

Heavy Metals (Plumbing)
Water chemistry analysis

Water Chemistry analysis - Determine the chemical component and quantify its quantity

Techniques Used:
- Ion Chromatography – dissolved ions, pH
- Titration analysis
- Spectroscopy (UV-Vis & IR) - Organic carbon
- Gas Chromatography/Mass Spectroscopy - Trace elements & Isotopes
FET based water chemistry analysis

Based on ISFET (Ion-Sensitive Field Effect Transistor)

- Ion Receptor is mobilized on the gate dielectric (or semiconducting channel)
- Upon attachment of target ion, a charge is formed
- V_{threshold} changes (or channel conductivity)
Advantages of FET based water chemistry analysis

- Cheap
- Fast
- Sampling not required
- Real-time monitoring possible (can be placed directly in contact with water supply systems)
- Training required is minimized
- Basic layout is very versatile – can be modified easily towards various targets

------------- Mainly for pre-screening purpose-------------
FET sensors

- Electrical component is separated
- Sensor is disposable
- Non-reversible reactions between the receptor and analyte

Pb (II) Sensor

Selectivity

$\frac{(I_{\text{sample}} - I_{\text{diwater}})}{I_{\text{diwater}}}$

- DI Water
- K: 100 ppm
- Na: 100 ppm
- Ca: 100 ppm
- Al: 100 ppm
- Pb: 1 ppm
Drain Current (A)

Time (s)

Mixed Solution with Na

- 100 ppm Na
- 1 ppb Pb - 100 ppm Na
- 10 ppb Pb - 100 ppm Na
- 1000 ppb Pb - 100 ppm Na

Sensitivity down to 10 ppb as required by WHO
A Multi-functional Selective Bonding Interaction based Electronic nose

Capable of detecting different application targets simultaneously
Able to deal with liquid and/or gas phase detection targets
High selectivity and sensitivity
Use of ink jet printing and low cost materials for receptors
  Making overall equipment and production costs low
  Enabling one-off detection application such as on spot drug detection
Range of Applications

- Drugs
- Explosives
- CO$_2$
- VOCs
- Food safety
The outlook

Electronic skin for selective and sensitive detection (eg. Ketamine)

Data

Tag integrated with sensors

ppb Level detection
<table>
<thead>
<tr>
<th>The Sensor</th>
<th>Characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td>Product Form</td>
<td>Portable/handheld</td>
</tr>
<tr>
<td>Detection Form</td>
<td>Vapor/liquid sampling</td>
</tr>
<tr>
<td>Detection Selectivity</td>
<td>Specific to application</td>
</tr>
<tr>
<td>Detection Range</td>
<td>Variable</td>
</tr>
<tr>
<td>Sensitivity</td>
<td>ppb</td>
</tr>
<tr>
<td>Detection time</td>
<td>&lt;5s</td>
</tr>
<tr>
<td>Product Form</td>
<td>Plastic sensor head with handheld electronics</td>
</tr>
<tr>
<td>Power Requirement</td>
<td>Low operating power</td>
</tr>
<tr>
<td>Material cost (HK$)</td>
<td>&lt;0.5 (excluding electronics)</td>
</tr>
<tr>
<td>Drug group</td>
<td>Ketamine</td>
</tr>
<tr>
<td>Service time (year)</td>
<td>Sensor is lifetime of the electronics; sensing head is for one-time use</td>
</tr>
</tbody>
</table>
Ketamine sensor
Common Types of Illicit Drugs

Heroin

Ketamine

Methamphetamine

Triazolam

Cocaine

Midazolam

Zopiclone
Why the use of Ketamine as the First Drug Detection Application?
Common type of drugs abused in HK

All reported persons in all age

<table>
<thead>
<tr>
<th>Age group / common type of drugs abused</th>
<th>2011</th>
<th>2012</th>
<th>2013</th>
<th>2013 first quarter</th>
<th>2014 first quarter</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>No.</td>
<td>% *</td>
<td>No.</td>
<td>% *</td>
<td>No.</td>
</tr>
<tr>
<td>Heroin</td>
<td>5 951</td>
<td>51.7</td>
<td>5 847</td>
<td>52.9</td>
<td>5 113</td>
</tr>
<tr>
<td>Psychotropic substances</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ketamine</td>
<td>3 642</td>
<td>31.7</td>
<td>3 301</td>
<td>29.9</td>
<td>2 814</td>
</tr>
<tr>
<td>Methylamphetamine(Ice)</td>
<td>1 549</td>
<td>13.5</td>
<td>1 681</td>
<td>15.2</td>
<td>1 822</td>
</tr>
<tr>
<td>Triazolam / Midazolam / Zopiclone</td>
<td>1 220</td>
<td>10.6</td>
<td>1 263</td>
<td>11.4</td>
<td>1 123</td>
</tr>
<tr>
<td>Cocaine</td>
<td>868</td>
<td>7.5</td>
<td>848</td>
<td>7.7</td>
<td>855</td>
</tr>
<tr>
<td>Cough Medicine</td>
<td>530</td>
<td>4.6</td>
<td>482</td>
<td>4.4</td>
<td>399</td>
</tr>
<tr>
<td>Cannabis</td>
<td>401</td>
<td>3.5</td>
<td>350</td>
<td>3.2</td>
<td>296</td>
</tr>
<tr>
<td>MDMA(Ecstasy)</td>
<td>118</td>
<td>1.0</td>
<td>69</td>
<td>0.6</td>
<td>50</td>
</tr>
<tr>
<td>Nimetazepam</td>
<td>110</td>
<td>1.0</td>
<td>85</td>
<td>0.8</td>
<td>24</td>
</tr>
</tbody>
</table>

Current Drug Detection Technology

1. Ion Mobility Spectrometry (IMS) and its products
2. Surface Acoustic Wave (SAW) sensing technology and its products
3. Cantilever based sensing technology
4. Surface Enhanced Raman Scattering (SERS) technology
5. Protein microarray chip
6. Aptamer-based biosensor
7. Molecularly imprinted polymer sensing technology
8. Electronic sensor with selective bonding interaction detection

This has the potential as being a low cost solution
Hidden in a travel pouch

- Use selective non-covalent interaction for ketamine vapor detection
Potential Customers

• Government
  – Reduce the reliance on sniffer dog
  – Higher screening availability and lower operational cost allow screening to be more frequent

• School
  – Low cost (handheld unit);
  – Easy operate
  – Better detection against drug penetration

• Security company
  – Low cost;
  – Easy to operate
  – Additional means for detection

• Private enterprises (hotel, casino...)
  – Low cost (handheld unit)
  – Easy to operate
  – Better detection against drug penetration
Electronic sensor array with sensitive and selective detection of amines for food safety

ITS/284/14FP
# Product Specifications

<table>
<thead>
<tr>
<th>The Sensor</th>
<th>Characteristics</th>
</tr>
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<tbody>
<tr>
<td><strong>Product Form</strong></td>
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<tr>
<td><strong>Detection Form</strong></td>
<td>Vapor sampling</td>
</tr>
<tr>
<td><strong>Detection Selectivity</strong></td>
<td>Specific to Bio-genic amines</td>
</tr>
<tr>
<td><strong>Detection Range</strong></td>
<td>1 cm</td>
</tr>
<tr>
<td><strong>Sensitivity</strong></td>
<td>100 ppb</td>
</tr>
<tr>
<td><strong>Detection time</strong></td>
<td>Real time</td>
</tr>
<tr>
<td><strong>Product Form</strong></td>
<td>flexible</td>
</tr>
<tr>
<td><strong>Power Requirement</strong></td>
<td>Battery operating power</td>
</tr>
<tr>
<td><strong>Material cost (HK$)</strong></td>
<td>&lt;0.5 (excluding electronics)</td>
</tr>
<tr>
<td><strong>Target group</strong></td>
<td>Histamine</td>
</tr>
<tr>
<td><strong>Target shelf Life time</strong></td>
<td>1 year</td>
</tr>
</tbody>
</table>
Food safety market size

Target customers:
- Government
- Private Enterprise
- Restaurant Chain
- Supermarket chain
- General public
Outlook of the handheld electronics with sensor head

Display to indicate ppm/ppb levels

Sensor head position
Ultra-Flexible High Densified UV-Sensitive Pressure Sensor Array for the Application in Artificial Intelligence Machine

- Electronic skin controls the behavior of the robot by employing pressure/UV light
- In normal state, the pressure sensors are in OFF state
- In abnormal state, state changes by applying force/pressure (sensitive to 100 Pa force/pressure)
- A safe current can be set for the sensor arrays, and when the current overloads, the power supply will be cut off. Unexpected behaviors can be subsequently avoided.
Summary (2nd part):
1. Extended gate FET for the sensitive & selective detection of various vapor phase elements
2. Simple fabrication techniques for building an inexpensive sensor for food safety applications
3. Electronic tongue for the sensitive & selective detection of various aqueous phase elements.

Thank you for your attention

QUT, Australia
P. Sonar (Polymer)
CityU
Michael Lam
Vincent KO
(Sensory molecules)