出國報告（出國類別：國際會議）

參加第五屆國際表面科學與技術會議心得報告

服務機關：國立雲林科技大學
姓名職稱：林智汶 教授
派赴國家：日本
報告日期：97.11.25
出國時間：97.11.08 ~ 97.11.14

參加第五屆國際表面科學與技術會議心得報告

本屆大會 11/09~11/13 在日本東京早稻田大學 Waseda University 的 International Conference Center 舉行, 大會主席由 Prof. I. Ohdomari 主持，Vice-Chair 分別爲 K. Yoshihara (ULVAC PHI)，K. Takayanagi (Tokyo Inst. Technol.)擔任。ISSS-5 係由日本表面科學會所主辦之第五屆國際會議，該會議每三年舉行一次。 本會議主要在探討最新的奈米科技相關的表面科技。主要的主題包括： Theory and dynamics, fabrication and application of nano-structures and nano-materials, novel characterization methods, and chemical and biological applications. 並且鼓勵針對未來發展發向進行研習與討論。其中

Theory and dynamics 部份包括：

- Theoretical approaches to surface/interface and nano-structures and properties
- Surface structures: atomic and electronic structures, and surface vibrations
- Surface dynamics: adsorption, desorption, reaction and diffusion

Fabrication and physical properties 部份包括：

- Atomic-scale controlled surface/interfaces and self-organized nanostructures

- Nano-materials: nanotubes, nanowires, nanoparticles and nanodots
- Fabrication processes: epitaxy, deposition, etching, cleaning and thin-film growth
- Device applications of metal, ceramics, organic and hybrid films

Characterization methods 部份包括：
- Characterization of surfaces, interfaces and nanostructures
- Tools and standards for micro/nano-analysis
- Scanning probe microscopy

Surface chemistry 部份包括：
- Colloid chemistry and soft materials: supramolecules, macromolecules and liquid crystal
- Electrochemistry, photochemistry and catalysis
- Self-assembly and self-organization for nanostructure formation and characterization

Biological applications of surface science and nanotechnology 部份包括：
- Nanobio-processes, biosurfaces and biointerfaces
- Bio-diagnostics, bioassays and biosensors

會議的議程如下：

November, 2008

9 (Sun) 3:00pm-6:00pm.....Registration and Get-Together

10 (Mon) 9:00am-8:00pm.....Scientific Sessions

11 (Tue) 9:00am-5:45pm.....Scientific Sessions

6:00pm-8:30pm.....Banquet (RIHGA ROYAL HOTEL)

12 (Wed) 9:00am-8:00pm.....Scientific Sessions

13 (Thu) 9:00am-６:30pm.....Scientific Sessions

議程密集又冗長是本會議的特色，每天都開到晚上，不過像１１月１１日大會特地安排在 RIHGA ROYAL HOTEL 進行大會晚宴，讓大夥在辛苦開會學習與討論之餘，也能進行國際交流，相互輕鬆交談。

大會安排的 Plenary 演講包括：

- **Patrick Soukiassian** (Univ. de Paris-Sud/Orsay)
  Engineering and Understanding Surface, Interfaces and Nanostructures Properties at the Atomic Scale
- **Yasuhiro Iwasawa** (Univ. of Tokyo)
  In-situ Surface Science of Dynamic Catalysis: Active Organized Structure and Reaction Genesis at Surfaces
- **Wolfgang Knoll** (Max-Planck-Institute for Polymer Research)
  Interfacial Architectures for Bio-Sensing

大會邀請的演講包括：

Theory, structure and dynamics

- (A) Theoretical approaches to surface/interface- and nano-structures and properties

- Mads Brandbyge (Tech. Univ. of Denmark)
  Theoretical studies of electron transport in nano-scale systems
- Alessandro De Vita (King's College London)
  Modelling the self-assembly of supported supramolecular nanostructures
- Mineo Saito (Kanazawa Univ.)
  Half-metallicity of Carrier-doped Armchair Graphene Nanoribbon

- (B) Surface structures: atomic and electronic structures, and surface vibrations

- Ulrich Heiz (Tech. Univ. of Munich)
  Size-dependent chemistry of supported clusters
- Natarajan Chandrasekhar （Nat'l Univ. of Singapore）
  BEEM - probing technologically important interfaces with nanometer spatial resolution
- Kota Tomatsu （Univ. of Tokyo）
  Scattering potentials of Si and Sn atoms embedded into Ge (001) studied by STM and ab-initio calculations

- (C) Surface Dynamics: adsorption, desorption, reaction, and diffusion

- Andrew Hodgson (Liverpool Univ.)
  The Structure and Reactions of Water and OH at Metal Surfaces
- Hiroshi Morikawa （Kyoto Univ.）
  Tunneling dynamics of single-molecule tautomerization

Fabrication and physical properties

- (D) Atomic-scale controlled surfaces/interfaces, and self-organized nanostructures

- Sebastian Loth (Andreas Heinrich) (IBM)
  Quantum magnetism and spin coupling at the atomic scale
- Richard Berndt (Univ. of Kiel)
  Conductance of controlled single atom and single molecule contacts

- (E) Nano-materials: nanotubes, nanowires, nanoparticles, and nanodots

- Chuan Liang Feng (Max Plank Inst.)
  Quantum-Dot/Dendrimer Based Functional Nanotubes for Sensitive Detection of DNA Hybridization
- Kenji Hata (AIST, Japan)
  Super-Growth CVD for Mass production of Carbon nanotubes and its applications
- Nan Wang (Univ. of Cambridge)
  Direct measurement of charge transport through single conducting polymer molecule
  wired into gaps in single walled carbon nanotubes
- Takami Muto (Tohoku Univ.)
  The Formation Mechanism of Aluminum Nanodots by Inhomogeneous Anodization
  as a Self-Alignment Technique for a Room-Temperature Operating Single-Electron Transistor

- (F) Fabrication processes: epitaxy, deposition, etching, cleaning, thin-film growth

- Masaharu Oshima (Univ. of Tokyo)
  In-situ photoelectron spectroscopy and photoemission electron microscopy for local electronic and magnetic structures of transition metal oxide thin films
- Kenji Shiraishi (Univ. of Tsukuba)
  What happens at nano-scale interfaces?
- Wei-Chuan Fang (Industrial Tech. Research Inst., Taiwan)
  Low-Temperature Synthesis and Characterization of ITO Thin Films

- (G) Device application of metal, ceramics, organic, and hybrid films

- Masakazu Nakamura (Chiba Univ.)
  Limiting Factors of Carrier Transport in Organic TFTs with Polycrystalline Active Layer

Characterization methods

- (H) Characterization of novel surfaces, interfaces and nanostructures

- Michel A. Van Hove (City Univ. of Hong Kong)
  Nanostructure from Scanning Tunneling Microscopy and Low-Energy Electron Diffraction
- Shirley Chiang (Univ. of California-Davis)
  High Resolution Surface Microscopy of Nucleation, Growth, and Phase Transitions
- Taku Suzuki (NIMS, Japan)
  Element selective spin state analysis at surfaces and interfaces by spin-polarized ion scattering

- (I) Tools and standards for micro/nano-analysis

- Thomas Schmidt (Fritz-Haber-Institute in Berlin)
  SMART: using an aberration corrected photoemission electron microscope as a nano-analytic tool
- Hiroshi Daimon (NAIST, Japan)
  Two-dimensional photoelectron spectroscopy by a conventional and newly-developed display analyzer

- (J) Scanning probe microscopy

- Hirofumi Yamada (Kyoto Univ.)
  Subnanometer-resolution Imaging of Biomolecules and Hydration Force Measurements
  by Frequency Modulation Atomic Force Microscopy
- Holger Schönherr (Univ. of Twente)
  Chemical and Optical Probing of Nanoscale Soft Materials by AFM Approaches: Challenges, Hopes and Opportunities

Surface chemistry

- (K) Colloid chemistry and soft materials: supramolecules, macromolecules, and liquid crystal

- Satomi Onishi (Univ. of South Australia)
  Friction and capillary forces at the nanometer scale
- Masatsugu Shimomura (Tohoku Univ.)
  A Novel Nano Bio-interface Prepared by Self-organization

- (L) Electrochemistry, photochemistry and catalysis

- Charles T. Campbell (Univ. of Washington)
  Thermodynamics and Kinetics of Elementary Steps in Catalysis

- (M) Self-assembly and self-organization for nanostructure formation, and characterization

- Atsushi Takahara (Kyushu Univ.)
  Molecular Design and Characterization of Soft Interfaces
- Li-Jun Wan (Chinese Academy of Sciences)
  Surface Molecular Engineering: From Single Molecule to Self-assembly

Biological applications of surface science and nanotechnology

- (N) Nanobio-process, biosurfaces and biointerfaces

- Robert Hamers (Univ. of Wisconsin-Madison)
  Ultra-stable Molecular and Biomolecular Interfaces via Covalent Grafting

- (O) Bio-diagnostics, bioassays and biosensors

- Andreas Offenhäusser (Research Center Jülich)
  Connecting DNA, Protein and Neurons with Electronics
- Hiroshi Kawarada (Waseda Univ.)
  Mechanism of DNA and RNA sensing by diamond surface channel devices

本職此次參予口頭報告，被安排在１１月１０日星期一的下午５：４５～６：００，

報告的題目是：Surface thermodynamics of the chemically synthesized polypyrrole and polyaniline nanofibers and their gassensing responses to BTEX compounds

內容如下：

Surface thermodynamics of the chemically synthesized polypyrrole films and their gas-sensing responses to BTEX compounds

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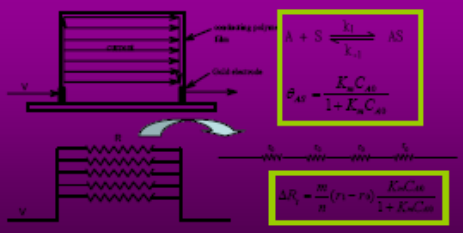
Background

- Considerable quantities of volatile organic compounds (VOCs) are produced from industrial sources such as printing and coating facilities, foundries, electronics and paint manufacturing units.
- A group of VOCs, including aromatic hydrocarbons such as benzene, ethylbenzene, toluene, and xylene (commonly referred to BTEX), are widely used in industry and poses serious adverse effects on the quality of air.
- The utilization of conducting polymers as gas sensors for detecting these highly health-threatening VOCs may be a promising approach.

Microscopic Gas-Sensing Model based on Langmuir isotherm



The overall resistance of the sensing film can be regarded as the paralleling of several pseudo-monolayers and each layer is composed of several resistors in series.

$$\frac{1}{\Delta R_t} = \frac{n}{m(r_1 - r_0)} + \frac{n}{m(r_1 - r_0)K_m}\frac{1}{C_{A0}}$$

m: number of active site per monolayer

n: thickness of the thin film

ΔR: resistance change before and after gas sorption

K_m: Adsorption Equilibrium Constant

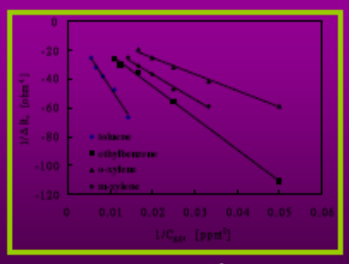
C_{A0}: Concentration of the detected gas

r_1, r_0: site resistance as the site is occupied and vacant

To plot (1/ΔR) vs. ($1/C_{A0}$)

- The value of $[m(r_1-r_0)]/n$ (regarded as secondary doping efficiency) can be determined from the reciprocal of the intercept and K_m can be obtained by dividing the intercept by the slope.

Chemically-polymerized PPyCl sensors exposed to BTEX compounds



- The effect of adsorption affinity (K_m) and the doping efficiency ($[m(r_1-r_0)]/n$) could be distinguished and calculated in terms of adsorption equilibrium constant.

The values of sensitivity, K_m, and $m(r_1-r_0)/n$ for BTEX vapors detected by PPyCl sensor

Vapors	Sensitivity (Ω/ppm)	K_m	$m(r_1 - r_0)/n$ (Ω)
Benzene	8×10^{-5}	1.72×10^{-4}	−0.44
Toluene	2×10^{-4}	2.50×10^{-4}	−0.91
Ethylbenzene	4×10^{-4}	6.50×10^{-4}	−0.70
o-Xylene	8×10^{-4}	1.97×10^{-3}	−0.44
m-Xylene	6×10^{-4}	1.07×10^{-3}	−0.54
p-Xylene	6×10^{-4}	7.45×10^{-4}	−0.71

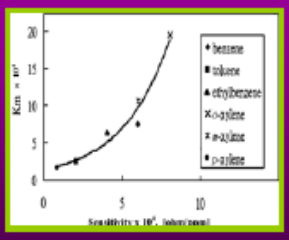
➢ K_m:

o-xylene > m-xylene > p-xylene > ethylbenzene > toluene > benzene

➢ *Sensitivity:*

o-xylene > m-xylene > p-xylene > ethylbenzene > toluene > benzene

K_m vs. sensitivity for BTEX vapors to *PPyCl* sensors



➢ The sensing ability of PPyCl polymer film is dominated by the affinity of the compound to the sensing material rather than the secondary doping level by the detected compound.

- Is it possible to have a directly experimental proof to the remark obtained from the resistance measurements that the affinity of the detected vapor to the sensing material dominates the sensitivity of the gas sensor?

Surface Properties of Conducting Polymers

- Inverse Gas Chromatography (IGC) have been used to investigate surfaces of conducting materials. It appears to be particularly useful for determining the sorption properties of molecules on surface.
- We are intending to present some preliminary results obtained by using IGC technique subjected to the relationship of the surface interaction force and the sensing response.

Measurements of IGC data

➢ In IGC, measurements were carried out at infinite probe dilution, i.e approximately zero sorbent surface coverage, ensure that the results obtained from the experiments apply exclusively to adsorbate-adsorbent interactions.

➢ The retention time of the probe, t_r, the time it takes the probe to travel through the column, can be converted to the net retention volume V_N, by

$$V_N = JF(t_r - t_0) = JFt_n$$

where *F* is the carrier gas flow rate and t_n is the net retention time. *J* is the correction factor of pressure gradient for mobile phase

Relation of ΔG_a and V_N

- The net retention volume, V_N is related to the free energy of adsorption, ΔG_a (J mol^{-1}) by :

$$\Delta G_a = -RT\ln(V_N) + C$$

where *R* is the gas constant, *T* is the column temperature, and *C* is a constant which takes into account the weight and specific surface area of the packing material and the standard states of the probes in the mobile and the adsorbed states.

- Manipulation of ΔG_a (or $RT\ln V_N$) data for the various probes leads to the evaluation of γ_s^d, the dispersive contribution to the surface energy of the materials.
- A standard method to evaluate the dispersive component of the surface energy relies on the retention data of the n-alkane series.

Dispersion component of surface energy for *PPy* determined at three temperatures

	Temperature (K)		
	443	433	423
γ_s^d (mJ/m^2)	69.96	72.10	74.73

➢ Increase in the kinetic energy of the absorbed molecules on the surface would cause decrease in the surface energy

➢ *PPyCl* is a high surface-energy material compared to conventional polymers, advantageously to be used to fabricate sensors with better sensitivity

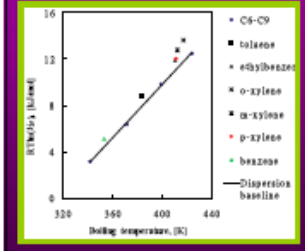
Specific Interactions

- If both dispersive and specific interactions are operative at the gas/solid interface, it is assumed that they contribute to the total ΔG_a in an additive manner:

$$\Delta G_a = \Delta G_a^d + \Delta G_a^s$$

where *d* and *s* are referred to dispersive and specific interactions, respectively. Several approaches were proposed to distinguish between ΔG_a^d and ΔG_a^s

Plot of $RT\ln(V_N)$ vs. boiling point for alkanes and BTEX probes adsorbed onto *PPyCl*



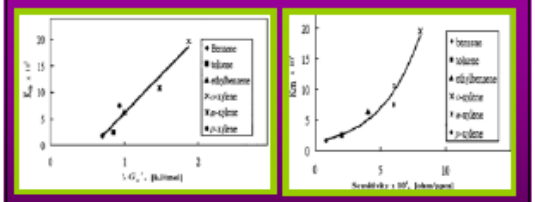
- We use the traditional approach : ΔG_a values are related to the boiling point of the injected probes.
- The n-alkane series lead to a linear plot which constitutes a reference for London dispersive interactions
- The marker corresponding to the BTEX compounds are located off the baseline, from which the specific interaction ΔG_a^s can be determined.

Values of ΔG_v, ΔG^d_v and ΔG^s_v for BTEX adsorbed on to PPyCl

ΔG [kJ/mol]	Benzene	Toluene	Ethylbenzene	o-Xylene	m-Xylene	p-Xylene
ΔG_v	5.12	8.79	11.93	13.61	12.68	12.02
ΔG_v^d	4.42	7.94	10.94	11.75	11.21	11.06
ΔG_v^s	0.70	0.85	0.99	1.86	1.47	0.94

- Surface free energy ΔG_v^s shows an order of
  o-xylene > m-xylene > p-xylene ≒ ethylbenzene > toluene > benzene

Adsorption free energy ΔG_a^s vs. K_m



- An excellent correlation between K_m and ΔG_a^s(specific interaction between the BTEX compounds and *PPy*Cl surface. 【 Left-hand plot 】
- This observation is an experimental proof to our earlier conclusion from the resistance measurements 【 Right-hand plot 】 that the affinity of the detected vapor to the sensing material dominates the sensitivity of the gas sensor.

Conclusions(I)

- The sensing responses of the *Cl*-doped *PPy* sensors towards BTEX compounds were investigated by measuring the resistance change of the film.
- The adsorption equilibrium constant, K_m, according to the adsorption theory were in a magnitude order of *o*-xylene > *m*-xylene > *p*-xylene > ethylbenzene > toluene > benzene. A good correlation between the sensitivity and K_m values was obtained.

Conclusions(II)

- A good correlation between the adsorption equilibrium constants, K_m, and specific component of adsorption free energy, ΔG_a^s, substantiate the fact that the affinity (i.e. the coverage) of the detected BTEX vapor to the sensing material dominated the sensitivity of the gas sensor in the present work.

Thank you for your attention

報告完畢後，得到很好的迴響，主持人評爲相當出色的報告（Excellent presentation），個人也認爲報告得相當成功，也在一次爲我國學術界爭取高度曝光的機會。

日本東京早稻田大學 International Conference Center

總結本次參加在日本東京稻田大學舉辦之 ISSS-5 國際會議，對於日本人組織的能力相當讚賞，就如日本人發明的產品一般，小巧精緻非凡，雖然不若歐美國家動輒十幾個演講廳同時舉行的規模，非但沒有炫麗的大會佈置 而且還樸儉的令人驚訝，如下圖的海報夠樸實了吧!

但大會將心思花在研討內容的品質提昇，反而更能凸顯焦點及引發參與者的興趣，發現絕大多數台灣來的與會者都全神貫注地參加，相信大家再短短五天的會議都有不錯的收穫,也做了互動良好的學術交流。