

ITRI

Industrial Technology
Research Institute

Labeling Nanotech-enabled Products to Advance Social Responsibility



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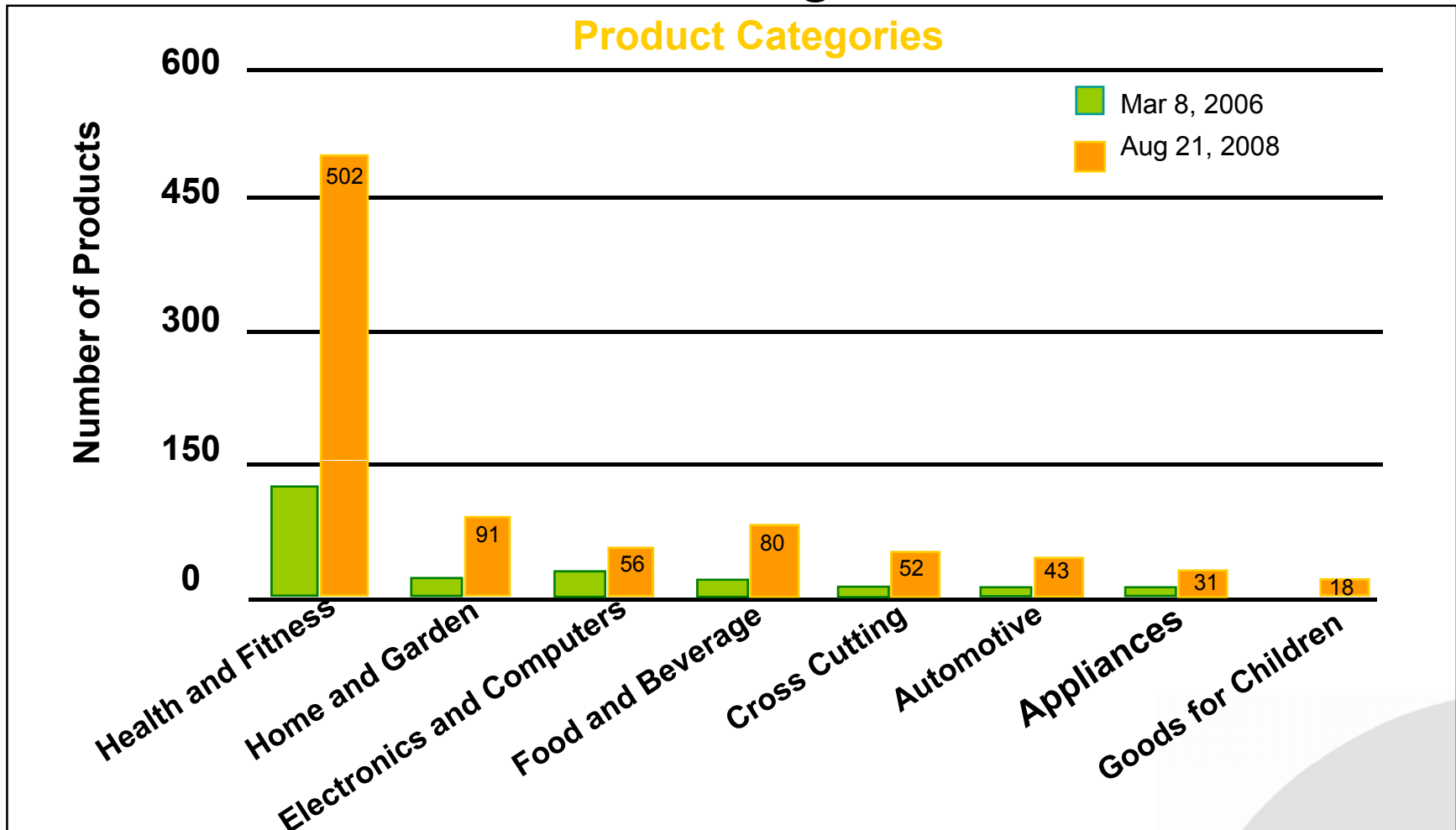
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2008 OCT, 22-24, CENAM Symposium of Metrology, Queretaro, Mexico

Outline

- Why Labeling
- Taiwan nanoMark System
- APEC Collaboration on Nano Measurement
- International & Regional Activities on Nano Metrology

More & More Nanotech-enabled Products Entering the Market



Number of products from 21 countries : 212 (2006/03/08) → 803 (2008/08/21)

- Paint is a sub-category under Home and Garden
- Display is a sub-category under Electronics and Computers
- Cross Cutting is a grouping of multi-functional products, e.g. coating

Why Labeling



With Nano, product price could be skyrocketed by more than ten times!

Are They Real Nano-enabled Products?

Why Labeling

- **Protect Consumers** : **Avoid waste money**
- **Protect Good Companies** : **Eliminate unfair competitions between good and bad products**
- **Increase Public Trust** : **Facilitate healthy development of nanotechnology**
- **Facilitate Trade** : **Stimulate economic growth**

Advance Social Responsibility

Approaches : Focus on Consumer Products

How to Choose which Products to Have nanoMark ?

◆ Impossible to certify all commercial nanoproducts

⇒ Specification / Testing Methods are not all ready

◆ How to choose ?

- Product Commercialized ? Capable Testing Labs ? Testing Methods ?
- Prudent with Risk Potential Products, e.g. cosmetics
- Producers could suggest items provided enough information is ready

Requirements

- **Basic Requirements**
 - **Nano Scale (in principle, < 100nm)**
 - **Unique Properties**
- **Quality System Installed**
- **Safety Issues being taken care / Traceable Products**
- **Contract to use “ nanoMark”**

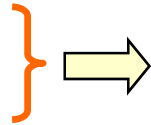
Example

— photocatalyst (UV & Visible light) Anti-bacterial Tiles

- How many bacteria have to be tested ?

- ◇ Representative

- ◇ Safe / easy to handle



Staphylococcus aureus : ATCC 65389, BCRC 10451

Escherichia Coli : ATCC 8739, BCRC 11634

- How effective anti-bacterial tiles should be ?

- ◇ achievable

- ◇ Testing Protocol (conditions, raw materials and/or final products)

- ◇ Top 50% Companies

} ⇒ > 90%

- What should be specified on the product package ?

- ◇ How to use

- ◆ where

- ◆ who

- ◆ how (application methods, maintenance, etc.)

- ◇ Reliability

Example

— photocatalyst (UV & Visible light) Anti-bacterial Tiles

Tiles : N041 (900mm x 1800mm) (CERABO)

N04590 (450mm x 900mm) (Ohayo)

Who : Construction Companies, General Publics

Where : Indoor (e.g.. toilet), Outdoor

How : • Adhesion to fix on the substrate

• Wet cloth to wipe if dirty

Reliability : real case (> 3 years)

Wall Tile (45 x 90 cm)



Floor Tile (90 x 90 cm)



Test :

Nano Scale : raw material, 40nm

Product, confirmed to have TiO₂

Anti-bacteria : *S. aureus* 99.99%

E. Coli 99.99%

S. aureus 99.99%

E. Coli 97.83%

365nm UV, 0.2mW/cm² / 24 hrs

543nm, 1000 lx / 24 hrs

Quality System : ISO9001 (Certification : 4XBY008-04)

Safety Issue : CNS 3298

| Nano-enabled Products | Criteria | | | | |
|--|---------------------------|--|--|---------------|--|
| | Nanoscale | Unique Properties | | Safety Issues | Others |
| | | Specified Properties | Reliability | | |
| Photocatalyst Products <ul style="list-style-type: none"> • anti-bacterial tiles | Photocatalysts & Products | <ul style="list-style-type: none"> • anti-bacteria >90% | | | |
| <ul style="list-style-type: none"> • anti-smudgy tiles | | <ul style="list-style-type: none"> • CA <10°; CA (dark/48hr)<30 ° • methylene blue de-color <1hr | <ul style="list-style-type: none"> • 3% salt water, 96hr • 5% H₂SO₄/24hr • 5% Na₂CO₃/24hr | | |
| <ul style="list-style-type: none"> • deodorized paints | | <ul style="list-style-type: none"> • de-odor (acetaldehyde >70%) | | | |
| <ul style="list-style-type: none"> • anti-smudgy paints | | <ul style="list-style-type: none"> • CA : 30°(<5hr) ; CA (dark/48hr)<30° • methylene blue >70%, 6hr | | | <ul style="list-style-type: none"> • meet national standards • equal or better than the industrial standards |
| <ul style="list-style-type: none"> • anti-bacterial light tubes | | <ul style="list-style-type: none"> • anti-bacteria >90% | | | |
| <ul style="list-style-type: none"> • air cleaning light tubes | | <ul style="list-style-type: none"> • acetaldehyde \geq 2mmol/kW·h • toluene \geq 0.05mmol/kW·h | | | |
| <ul style="list-style-type: none"> • air purifiers and filters | | <ul style="list-style-type: none"> • purifier : de-NO>60% filter : de-acetaldehyde >70% | | | |

| Nano-enabled Products | Criteria | | | | |
|---|---------------------------|---|--|---------------|--|
| | Nanoscale | Unique Properties | | Safety Issues | Others |
| | | Specified Properties | Reliability | | |
| <p>Hydrophobic Surface</p> <ul style="list-style-type: none"> • anti-smudgy sanitary facilities • anti-smudgy metal partition • anti-smudgy household exhaust hood • hydrophobic car wax | Product Surface Structure | <ul style="list-style-type: none"> • CA >100 ° • simulated dirt <1% | <ul style="list-style-type: none"> • anti-brush (2000 times) | | <ul style="list-style-type: none"> • meet national standards • equal or better than the industrial standards |
| | | <ul style="list-style-type: none"> • CA >100 ° • vegetable & animal oil adhesion <90% | <ul style="list-style-type: none"> • anti-brush (500 times) • heat resistance (100°C/8hrs) | | |
| | | <ul style="list-style-type: none"> • CA >100 ° • water roll angle <30° • water blot <10% | <ul style="list-style-type: none"> • anti-soap wash (1000 times) | | |
| <p>Anti-abrasive Products</p> <ul style="list-style-type: none"> • anti-abrasive PU resins & synthetic leathers • anti-abrasive bicycle seat | Nanoparticle & products | <ul style="list-style-type: none"> • anti-abrasion 50% higher than the originals (Taber test) | | | |
| | | (under developing) | (under developing) | | |
| <p>Nano-silver Products</p> <ul style="list-style-type: none"> • anti-bacterial marble • anti-bacterial household textile • anti-bacterial socks | Nanosilver & products | <ul style="list-style-type: none"> • anti-bacteria >90% • hardness maintain • glossness $\geq \pm 1.5GS$ | <ul style="list-style-type: none"> anti-abrasion (5000 times) anti-brush (520 times) | | <ul style="list-style-type: none"> • skin irritation test <2 • oral acute toxicity test |
| | | <ul style="list-style-type: none"> • anti-bacteria >90% | anti-wash 10 times | | |
| | | <ul style="list-style-type: none"> • anti-bacteria >90% | anti-wash 20 times | | |

Some Observations of nanoMark Impact to Industry

- **With nanoMark, Less Advertisement Expenses**
- **Second-tier Companies ⇒ First-tier**

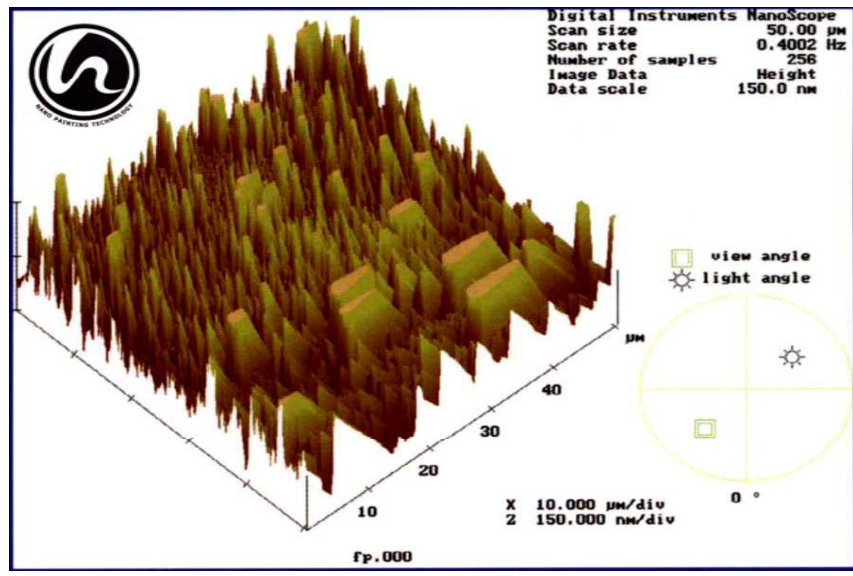
| Anti-smudgy paints | Nano Scale | Decomposed Rate (methylene blue) | Hydrophilic Test | |
|--------------------|--|-------------------------------------|------------------|----------------------------------|
| | | | CA30° (Time) | Contact Angle (48hrs in Dark) |
| Company A | TiO ₂ , Anatase 5.3nm (XRD) | 61%/6 hrs | 2 hr | 46 |
| Company B | TiO ₂ , Anatase 5.6nm (XRD) | 75%/6 hrs | 2 hr | 20 |

- **Accelerate Infrastructure-establishing**
- **Test Methods**
- **Test Labs ⇒ Service Sector**
- **Initiate Self-regulated Marks**



nano coating

Self-clean Coating



Notebook



APEC Collaboration on Nano Measurement

Regional Activities

— Nano Measurement on Particles Size & Film Thickness

APEC ISTWG Project

“Technological Cooperation Framework on Nanoscale Analytical and Measurement Methods”

Host economy : Chinese Taipei

**Co-sponsors : Australia, Canada, Indonesia, Japan, Korea, Malaysia,
Philippines, Singapore, Thailand, United States,
Vietnam**

Why Cooperation

❖ Characterization Tools:

- Many ⇒ How to choose
- Expensive ⇒ Can't get all

❖ Nanoscale Analytical and Measurement Technique:

- ⇒ need experienced people

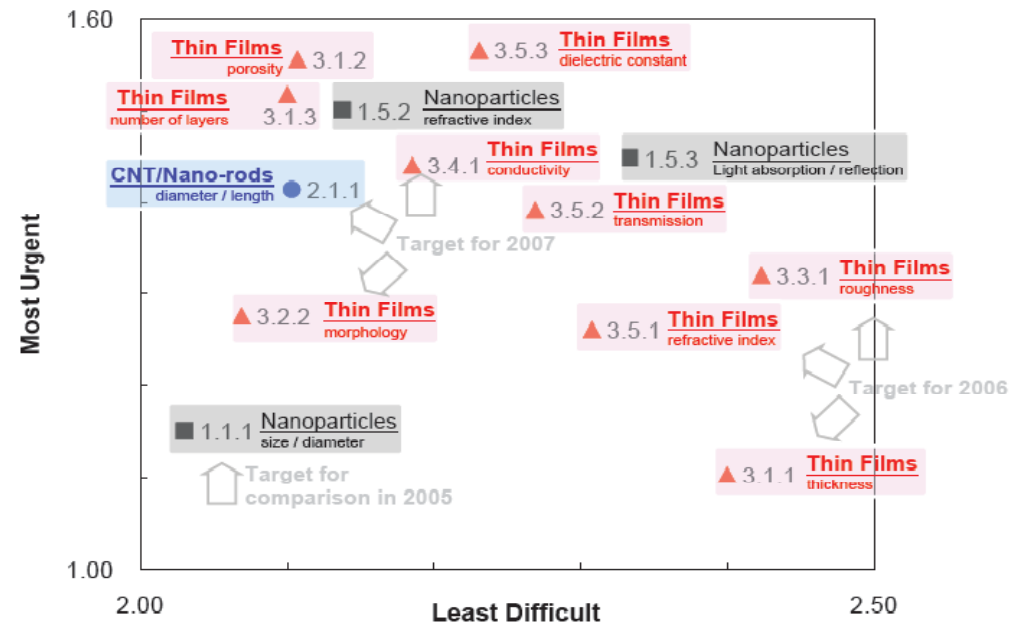
❖ For Trade:

- ⇒ International trade agreements demand demonstrated equivalence between the measurement standards of buyer and seller nations.

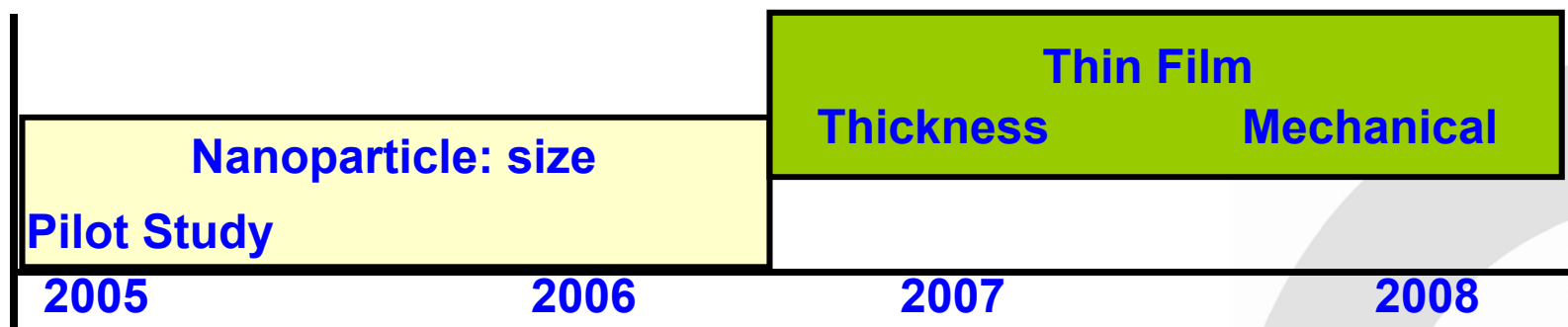


- ◆ Shorten developing time
- ◆ Develop human capability
- ◆ Base for mutual recognition among Economies

2005 : Three-year Roadmap (Urgency vs. Difficulties)



Considering Availability of Measurement Samples → Nanoparticle, Thin film



Objectives and Methodology

❖ Establish a Technological Cooperative Framework

- Interlab Comparison

❖ Provide a Unique Avenue to Share Most Recent Advances on Nanometrology

- Nanoscale Technological Forum, Hand-on Workshop



● Identify and Promote the Best Available Technologies in Nanometrology

● Contribute to strengthen the free trading system in APEC region

What Have Been Done

Sample : 2005 : PS Latex CRM (100, 20nm) , Nano-silver (20nm)

2006 : PS Latex CRM (100, 50, 30nm)

2007 : SiO₂ reference thickness (2,5,10nm)

2008 : Fused Silica and Polycarbonate

Instruments

- Diameter measurement : DLS, SPM, SEM, TEM, DMA
- Thin film thickness : SE, TEM, XPS, XRR, XRF
- Mechanical properties : Nano-indentation
(MTS, Hysitron, UMIS, CSM, MICRO MATERIALS)

Participants : 2005 : 10 labs (w/o 2 withdrawals)/ 6 Economies (Australia, China, Japan, Mexico, Chinese Taipei, USA)

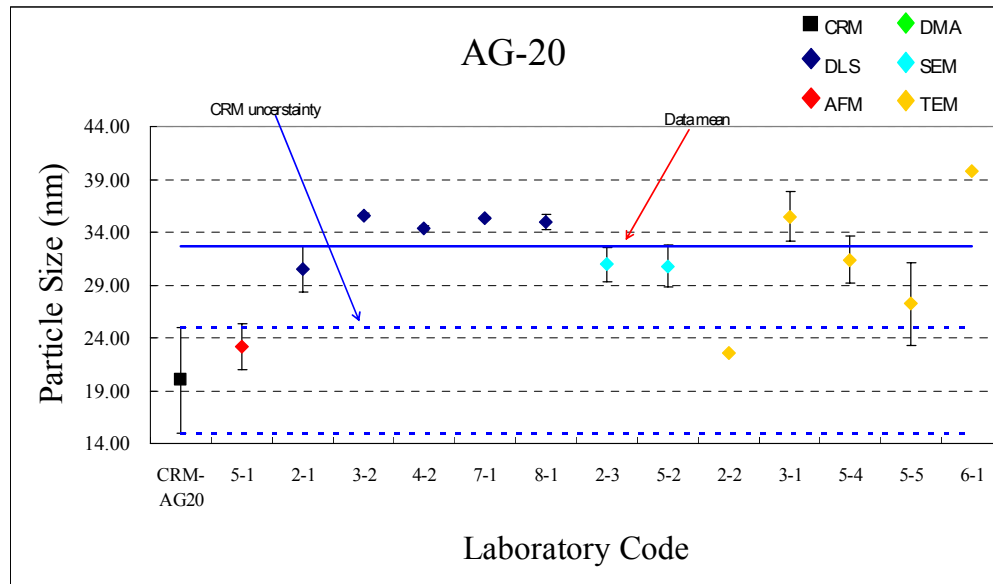
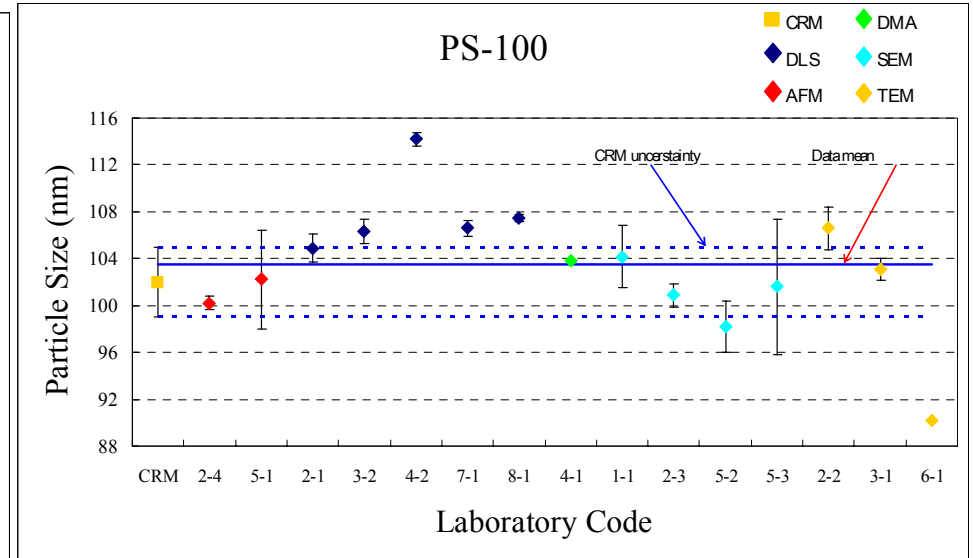
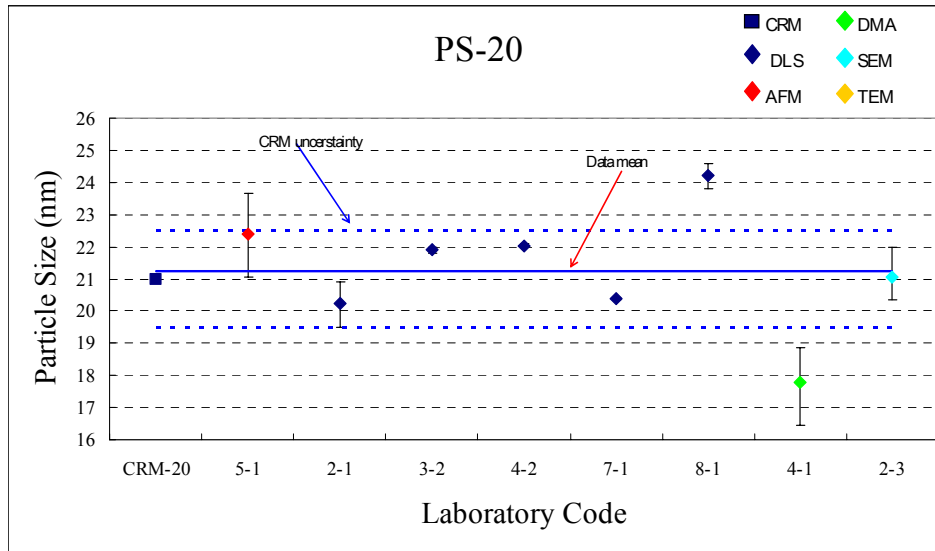
2006 : 16 labs (w/o 4 withdrawals)/ 10 Economies (Australia, Canada, China, Hong Kong, Japan, Mexico, Philippines, (South Africa), Chinese Taipei, Thailand)

2007 : 15 labs/ 11 Economies (Australia, Canada, China, Hong Kong, Japan, Mexico, Philippines, Chinese, Taipei, Thailand, US, Italy)

2008 : 16 labs/ 8 Economies (Australia, China, Korea, Malaysia, Mexico, Philippines, Thailand, Chinese Taipei)

What Have We Learned

2005 : • The Smaller the Size, The Larger Scattering the Measurement
• Shape Matters

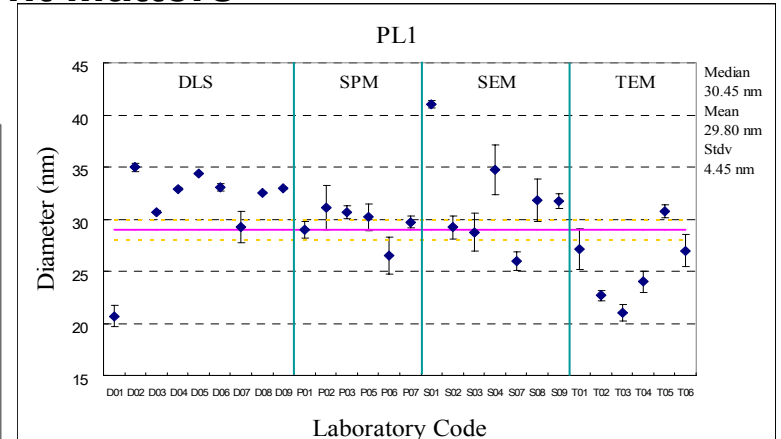
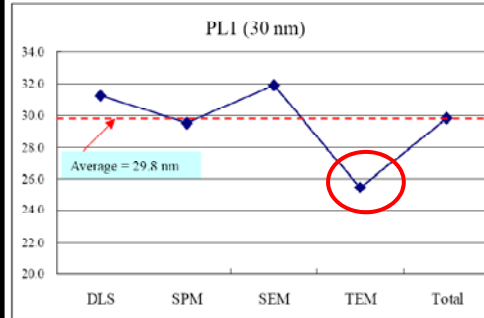


What Have We Learned

2006 : Instrument Matters

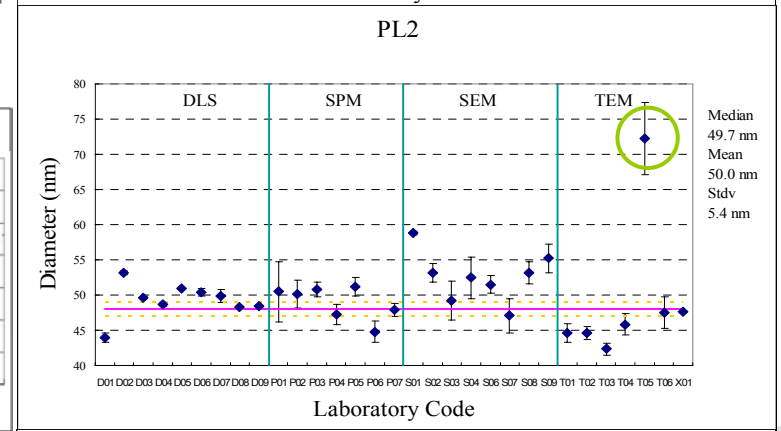
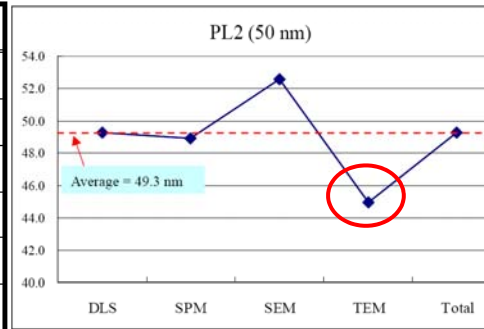
PL 1 (30 nm)-- Certified Value: 29 ± 1 nm

| PL1 | DLS | SPM | SEM | TEM | Total |
|---------|------|------|------|------|-------|
| Mean | 31.3 | 29.5 | 31.9 | 25.4 | 29.8 |
| Stdev | 4.3 | 1.7 | 4.9 | 3.5 | 4.5 |
| Minimum | 20.7 | 26.5 | 26.0 | 21.1 | 20.7 |
| Median | 32.9 | 30.0 | 31.7 | 25.5 | 30.4 |
| Maximum | 35.0 | 31.1 | 41.0 | 30.8 | 41.0 |
| Range | 14.3 | 4.6 | 15.0 | 9.7 | 20.3 |



PL2 (50 nm)-- Certified Value: 48 ± 1 nm

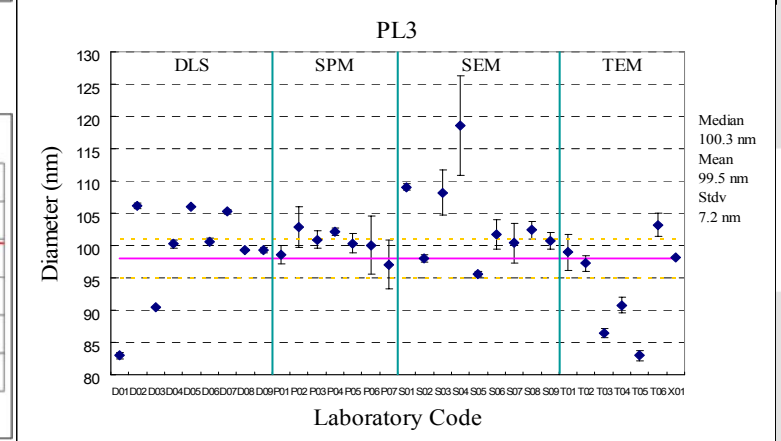
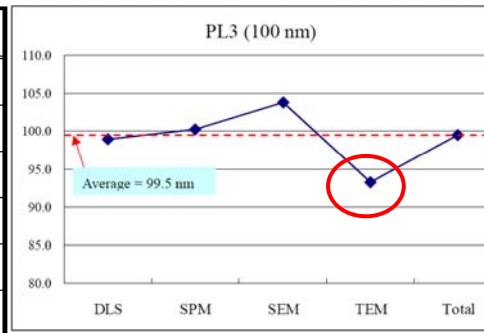
| PL2 | DLS | SPM | SEM | TEM | Total |
|---------|------|------|------|------|-------|
| Mean | 49.3 | 48.9 | 52.6 | 45.0 | 49.3 |
| Stdev | 2.5 | 2.4 | 3.6 | 1.9 | 3.6 |
| Minimum | 43.9 | 44.8 | 47.1 | 42.3 | 42.3 |
| Median | 49.7 | 50.2 | 52.8 | 44.7 | 49.4 |
| Maximum | 53.2 | 51.2 | 58.8 | 47.5 | 58.8 |
| Range | 9.2 | 6.4 | 11.7 | 5.2 | 16.5 |



Calculated Results excluding outlier

PL3 (100 nm)-- Certified Value: 100 ± 3 nm

| PL3 | DLS | SPM | SEM | TEM | Total |
|---------|-------|-------|-------|-------|-------|
| Mean | 98.9 | 100.3 | 103.9 | 93.3 | 99.5 |
| Stdev | 7.7 | 2.0 | 7.0 | 7.8 | 7.2 |
| Minimum | 83.0 | 97.1 | 95.6 | 82.9 | 82.9 |
| Median | 100.3 | 100.3 | 101.8 | 94.0 | 100.3 |
| Maximum | 106.2 | 102.9 | 118.6 | 103.2 | 118.6 |
| Range | 23.2 | 5.8 | 23.1 | 20.3 | 35.7 |

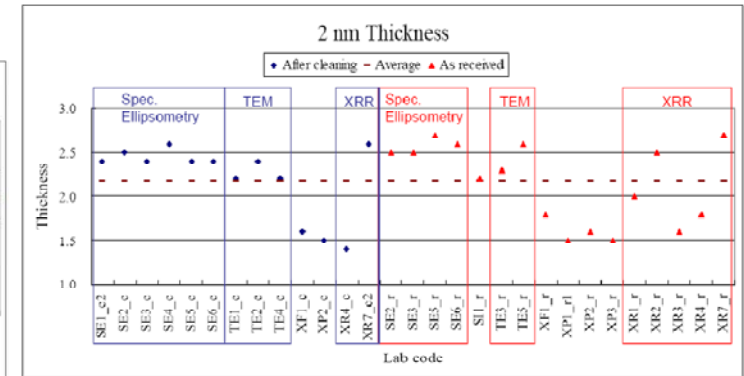
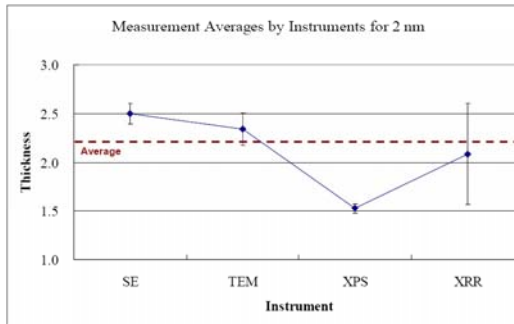


What Have We Learned

- 2007 : • Cleaning Method Makes Difference
• Instrument Matters

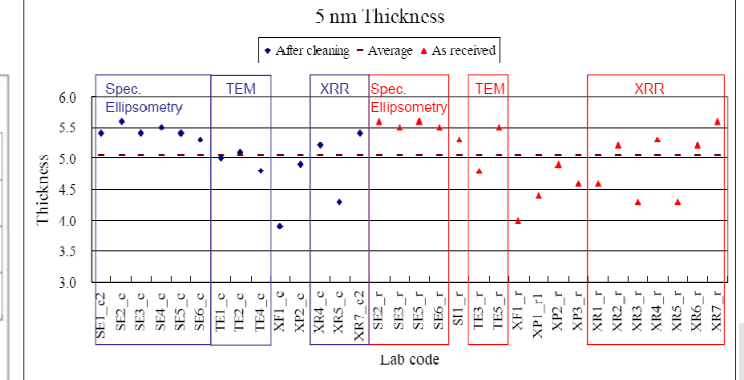
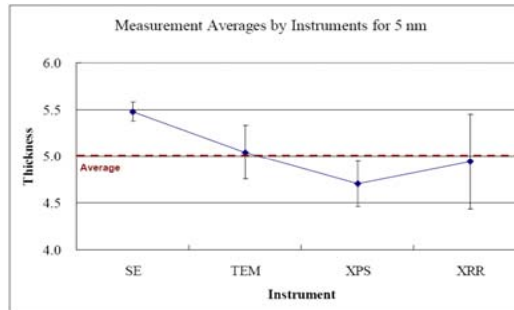
TK02 Series- 2 nm SiO₂ Thickness

| TK02 Series | SE | TEM | XPS | XRR |
|-------------------|-----|-----|-----|-----|
| Mean | 2.5 | 2.3 | 1.5 | 2.1 |
| Stdv | 0.1 | 0.2 | 0.1 | 0.5 |
| Minimum | 2.4 | 2.2 | 1.5 | 1.4 |
| Median | 2.5 | 2.3 | 1.5 | 2.0 |
| Maximum | 2.7 | 2.6 | 1.6 | 2.7 |
| Range | 0.3 | 0.4 | 0.1 | 1.3 |
| Number of samples | 10 | 5 | 4 | 7 |



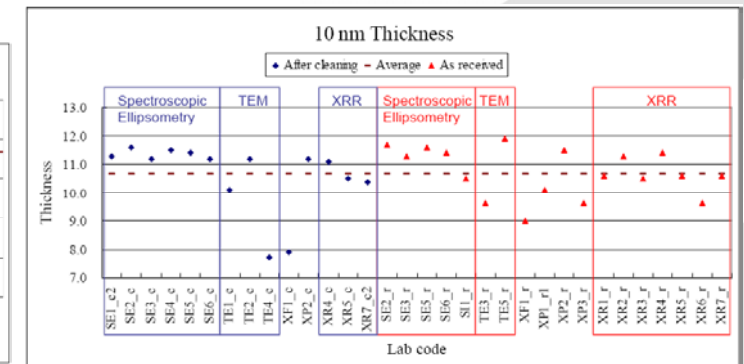
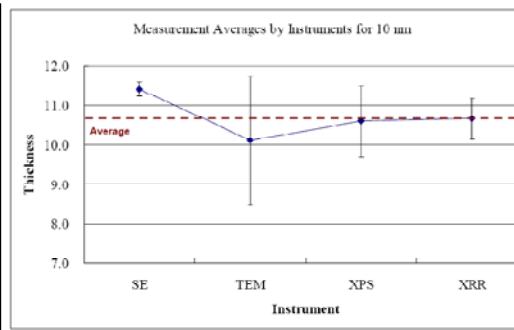
TK05 Series- 5 nm SiO₂ Thickness

| TK05 Series | SE | TEM | XPS | XRR |
|-------------------|-----|-----|-----|-----|
| Mean | 5.5 | 5.0 | 4.7 | 4.9 |
| Stdv | 0.1 | 0.3 | 0.2 | 0.5 |
| Minimum | 5.3 | 4.8 | 4.4 | 4.3 |
| Median | 5.5 | 5.0 | 4.8 | 5.2 |
| Maximum | 5.6 | 5.5 | 4.9 | 5.6 |
| Range | 0.3 | 0.7 | 0.5 | 1.3 |
| Number of samples | 10 | 5 | 4 | 10 |



TK10 Series- 10 nm SiO₂ Thickness

| TK10 Series | SE | TEM | XPS | XRR |
|-------------------|------|------|------|------|
| Mean | 11.4 | 10.1 | 10.6 | 10.7 |
| Stdv | 0.2 | 1.6 | 0.9 | 0.5 |
| Minimum | 11.2 | 7.7 | 9.6 | 9.6 |
| Median | 11.4 | 10.1 | 10.7 | 10.6 |
| Maximum | 11.7 | 11.9 | 11.5 | 11.4 |
| Range | 0.5 | 4.2 | 1.9 | 1.8 |
| Number of samples | 10 | 5 | 4 | 10 |



| | Global Organizations | | | Regional Organizations | | | U.S. Organizations | | | Other ISO |
|---|----------------------|-----------|------|------------------------|------|-----|--------------------|----------|----------|------------------------------|
| | ISO TC229 | IEC TC113 | OECD | CEN TC 352 | APEC | ANF | IEEE | ANSI-NSP | ASTM E56 | ISO TC 24, 35, 164, 201, 213 |
| Terminology | X | X | X | X | | X | | X | X | X |
| Basic metrology | X | X | | | X | X | | X | | X |
| Instruments test methods, characterizations | X | X | | | | X | | X | | X |
| Particle measurements, characterizations | | | | | X | X | | | X | X |
| Dimension measurements, characterizations | X | | | | X | X | | | X | X |
| Physical characterization | X | | | | X | X | | X | X | X |
| Chemical characterization | X | | | | | X | | | | |
| Environmental, health and safety | X | | X | X | | X | | X | X | |
| Test methods for toxicity | X | | X | X | | X | | X | X | |
| Risk evaluation | X | | X | X | | X | | X | X | |
| Societal impacts, Regulatory frameworks | | | X | | | | | | | |
| Materials or Products | X | X | | | X | X | X | X | X | |
| Materials specifications (CNT & others) | X | X | | | | X | X | X | X | |
| Materials specifications (reference standards) | | | | | | X | | | | |
| Manufacture processes | | | | | | | | | | |
| Certification, performance assessment | | X | | | | X | | | | |