

Aalto University



Indium Replacement by Single-Walled Carbon Nanotube Thin Films



Japan Science and Technology Agency

IRENA project: Indium replacement by singlewalled carbon nanotube thin films

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Content

- The need to replace Indium and Gallium in transparent conductors (TCF) and thin film transistor (TFT): carbon nanotubes as novel materials for flexible, transparent and stretchable electronics ?
- Project objectives: meet ITO (indium-tin oxide) TCF and IGZO (indoum-zinc-gallium oxide) TFT specs with flexible SWNT thin films
- **Partners**: 3 from EU and 3 from Japan
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- Future plans how to use the results



REPORT ON CRITICAL RAW MATERIALS FOR THE EU

Report of the Ad hoc Working Group on defining critical raw materials

May 2014



Economic importance

Antimony	Beryllium	Borates	Chromium	Cobalt	Coking coal	Fluorspar
Gallium	Germanium	Indium	Magnesite	Magnesium	Natural Graphite	Niobium
PGMs	Phosphate Rock	REEs (Heavy)	REEs (Light)	Silicon Metal	Tungsten	



Commission



EIT Raw Materials was designated as an EIT Knowledge and Innovation Community (KIC) by the EIT Governing Board on 09 December 2014. The below provides some information about the challenges the KIC will address in the field of raw materials (sustainable exploration, extraction, processing, recycling and substitution) and the impact it will generate.



Indium in touch sensors

- Touch technology is increasingly applied to all types of electronic devices used daily.
- With projected capacitive touch sensors being applied as almost a standard to smartphones and other consumer electronics, capacitive touch technology is replacing other technologies used in almost every touch-sensor application.





Dverall touch panel market forecast (\$ million)								
	2012	2013	2014	2015	2016	2017	CAGR	
Revenue	18,054	20,125	23,282	25,586	27,591	27,960	9.1%	
Y/Y Growth	47.3%	11.5%	15.7%	9.9%	7.8%	1.3%		







Touch panel market share by major application (%)





Capacitive touch panel market forecast by layer structure (Ksqm) Capac

Capacitive touch panel market forecast by layer structure (%)







Overall transparent conductive film market forecast (Ksqm)



(-1) M

- The market initially started with glass types (GG, DITO) and film types (GFF), but currently there are more than 10 types of touch panels with different layer structures.
 - Each method has its pros and cons according to the technology, production cost, client preference, and each developer's situation.

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GG - cover glass+ ITO glass sensor GFF - cover glass + two ITO film sensors







History and forecast: Projected capacitive layers by application

Advantages of one layer type solution over two layer type: Simpler process and lower cost



Single layer touch patterns (Without a via hole and with a via hole)







Single Layer with Multi-touch (w/o a via hole)

(with a via hole)







ITO-on-glass (fragile) and ITO-on-PET (a bit pendable) transmittance vs. sheet resistance - NOT flexible and vacuum-processed REFLECTION and HAZE IMPORTANT ISSUES, not only sheet resistance



LCD

Emerging materials: metal mesh and nanowires, conducting polymers, CNT, graphene

Aalto Univ./ Canatu CNT film: below 100 ohm/sq @ 90 % T





-16 -16

Metal-based transparent conductive film types – Overall							
	Ag Nanowire	Ag Halide	Cu Mesh	Ag (Direct Printing)	ITO		
Resistance(Ω)	30~50Ω	60Ω	0.1~0.5Ω	60Ω	80Ω or higher		
Transmittance(%)	More than 90%	89% ~ 91%	≈ 85%	More than 90%	89% (Based on 150Ω)		
Merit	Able to use existing touch panel production lines	Micro patterning Double side patterning	Strong against static electricity Able to use existing PDP mesh infrastructure	Bezel wiring can be formed at once	Superior pattern visibility Proven for mass production Secured ample capacity		
Demerit	Limited makers, milky color, weak chemical resistance	Moiré Limited width in production lines	Moiré, corrosion	Moiré, haze	Instability in indium supply		
Flexibility	Good	Good	Good	Good	Bad		
Method of securing pattern visibility	Partial etching, half etching	Partial etching, half etching	Introduce blackened layer	Process separate layer that controls light reflection	Introduce index matching layer		
Layer Type	GFF / GF	GF2	GFF / GF	GFF / GF	GFF / GF / GF2		
Price (ITO sensor: 1)	x1.2	x0.8~1	x0.8~1	x1	x1		
Target Application	Large laptop~AIO PC	Smartphone~AIO PC	Large laptop~electronic board	Large laptop~AIO PC	Smartphone~laptop		
Major Supplier	LGE, E&H, Toray, Okura, Nitto, Hyosung, Cheil Industry, Iljin Display, O- film, Carestream	Fujifilm, Mitsubishi Paper, Kodak	LG Chem, Toppan, DNP, Toray, Atmel, Panasonic, Fujikura	Mirae Nanotech, O-film, LGI	Nitto, LG Chem, Oike, Sekisui, Gunze, MAX film, LG Hausys, Miraestech, O-film		



Requirements to material and devices for flexible, transparent and stretchable electronics Silicon and ITO: Hard, Fragile Plastic: Flexible, Elastic

Fabrication on plastic substrate

Low-cost fabrication

Low temperature process



Hewlett-Packard

Atmospheric pressure process High-speed printing method Roll-to-roll manufacturization



Deflection in the market 1: Flexible Products Finally Coming of Age

Flexible and curved display revenue forecast (\$ million)



Source: Touch Display Research, Flexible and Curved Display Technologies and Market Forecast Report, September 2013

Deflection in the market 2: ITO Replacements Finally Coming of Age

Touch Display Research forecasts the non-ITO transparent conductor market will grow from \$206 million in 2013 to \$8 billion by 2021.



Source: Touch Display Research, ITO-replacement report, Nov, 2014



Traditional thin film transistors materials

Material	Mobility (cm²/Vs)	Method (Process temp.)	Flexibility	Large area	Cost	Stability
Poly-Si	30~300	Vac. CVD (500°C)	Bad	Fair	High	Very good
Amorphous-Si	0.5~1	Vac. CVD (> 200°C)	Bad	Fair	High	Very good
Oxide (InGaZnO)	1~10	Vac. Sputter (R.T.~200°C)	Good	Fair	Moderate	Very good
Organic	0.01~10	Solution, Sublimation (R.T.)	Good	Very good	Low	Bad

Additional important parameter: on/off ratio is larger than 1 000 000 = 10⁶ (needed for display and digital (IC) applications) Manufacturing yield very important for real applications

Allotropes of carbon – CNT and graphene -NOVEL NANOCARBONs for electronics ?









diamond



2D



Graphene – NO band gap







SWCNT and graphene show extremely high carrier mobility for flexible electronics applications = fast large devices -> Ideal material for printed electronics ?

Material	Mobility (cm²/Vs)	On/off ratio	Manuf. method (Process temp.)	Flexibility	Cost	Stability
Individual SWCNT on the subtrate	10 000 – 200 000	10 ⁸	CVD (600-900°C)	Very good	High	Very good
SWCNT thin film on the subtrate	5 - 2000	10 ⁴ - 10 ⁸	Depositon from solution or gas phase (ambient)	Very good	Low	Very good
Free-standing graphene single crystal	100 000 - 1 000 000	2-100	Exfoliation (not an industrial manufacturing process)	Very good	Very High	Very good
Graphene thin film on the Si subtrate	1 000 – 5 000	2-100	CVD (900-1050°C)	Very good	High	Very good

On/off ratio: For digital electronics and display backplane >10⁶ New 2-D materials –lower mobility, on-off OK, high cost

SWNT challenge is the material control: not only (n,m), but also *bundling, length, orientation*



Rolling in different directions makes different kinds of tubes

We like to show *individual tubes*

BUT mainly tubes are *in bundles*

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GOALS

GOALS

Fig. 4. SWCNT TFTs and ICs on flexible substrate. a) Photograph of fabricated devices on a flexible and transparent PEN substrate. b) Schematic cross section of a bottom gate TFT on PEN substrate with Al_2O_3 gate insulator. c) Transfer characteristics of a typical TFT with $L_c=100 \ \mu\text{m}$ at $V_{DS}=-0.5 \ V$, $W_c=100 \ \mu\text{m}$. d) Input-output and gain characteristics of an inverter. Insets show the optical micrograph, circuit diagram and symbol of the inverter. e, f) Optical micrograph and circuit diagram of a 21-stage ring oscillator. g) Output characteristics of the ring oscillator with oscillation frequency of 2.0 kHz at $V_{DD}=-4 \ V$. h) Mobility and on/off ratio. Comparison between our SWCNT TFTs with other representative TFTs based on SWCNT network^[6] amorphous-Si. polycrystalline Si. In-Ga-Zn-O semiconductors and organic materials

Provide Technology for Future Flexible, Bendable and Stretchable Devices

Fig. 1. A few examples of future concepts based on transparent, flexible and conductive materials: a) Nokia concept Morph; b) Smartphone Booklet Device; c) Curved Tablet Design - a flexible smartphone; d) Pen-sized rollup display. <u>http://www.concept-phones.com/?s=flexible</u>

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FP7-NMP-2013-EU-Japan

IRENA <604472>

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Fig.2. The structure of the project work packaged: 5 Work Packages (in the circle), 8 objectives around the Work Packages, divided into 16 subtasks. Subtasks of WP5 and WP6 are not shown. The illustration includes also the work carried out by the Japanese coordinated project.

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Aalto University novel dry, direct CNT film deposition method: <u>DPP</u> – <u>Direct Dry Printing</u> Industrial manufacturing – Canatu Oy **Synthesis** Thin Films Deposition SWCNTs in the reactor gas **Control of SWCNT** Patterned/nonproperties patterned HUT NanoMaterials Group 5 m NanoMaterials Grou

Heterojuction Solar Cell

n-type Si $(7.5-12.5 \Omega \text{cm}, \sim 10^{15} \text{ cm}^{-3})$ With 100 nm SiO₂ 5 M NaOH at 90 °C for 30min RCA 2 Cleaning

Fundamentals of particles in gas dynamics – how catalyst particles and nanotubes behave during the floating catalyst CVD synthesis

Processes tacking place in an elemental volume in the general dynamic equation. Gas flow produce particle transport across the element boundaries. In addition to gravitation, other force field can drive the fluxes, i.e. electrical potential, temperature gradient.

Basic dynamical processes in aerosol systems

Aerosol are physically unstable systems experiencing the continual influence of various dynamic processes. These processes change the aerosol properties, such as particle size and charge distribution, particle morphology, and so on. $N = number \ concentration \ in \ the \ FC-CVD \ gas$

General dynamics equations:

$$\frac{dN_{k}}{dt} = J(t)\delta_{i,k} + \frac{1}{2}\rho_{g}\sum_{i=1}^{k-1}\beta_{k-j,j}N_{k-j}N_{j} - \rho_{g}\beta_{k}N_{k}\sum_{i=1}^{\infty}N_{j} +$$
Nucleation
of Catalyst
particles
$$+ \rho_{g}\left(\beta_{1,k-1}^{'}N_{1}^{'}(t)N_{k-1} - \beta_{1,k}^{'}N_{1}^{'}(t)N_{k}\right)$$
Condensation of catalyst metal vapour on SWNTs
and on non-active catalyst particles

 β – the coagulation kernel (coefficient) if two colliding particles, $\delta_{i,k}$ – Kroneker delta ($\delta_{i,k}$ =1 for i=k, $\delta_{i,k}$ =0 otherwise), ρ_g – the carrier gas density, N'₁- number concentration of condensing monomers. β – the collision frequency of monomers and particles,

Catalyst concentration Controlled FC-CVD with Concentration Monitoring – New Reactor

- CO as carrier gas and carbon source with ferrocene and CO₂
- Particle formation by thermal decomposition of ferrocene
- SWCNTs grown in the gas flow via Bouduard reaction

 $CO + CO \stackrel{Fe}{=} C(s) + CO_2$

- Controlled concentration
 - 1e4 1e6 #/cm^3
 - High individual SWCNT fraction
- Substantially improved
 - Stability
 - Performance
 - A. Kaskela et al. (2015)To be submitted

Jiang, H., Kaskela A. et al. (2015) In preparation

Optical Absorption Spectra of as-produced SWNT Thin Films

Bundle Diameter Distribution from AFM

ON N

Micropatterned SWNT TCFs – 67 ohms/sq @ 97 % T

N. Fukaya, D. Y. Kim, S. Kishimoto, S. Noda, and Y. Ohno, "One-Step Sub-10 µm Patterning of Carbon-Nanotube Thin Films for Transparent Conductor Applications," ACS Nano, Apr. 2014.

With micropattern: <u>67 ohm/sq @ 97 %T -</u> collaboration with Prof. Yutaka Ohno Record performance level of SWCNT-based transparent electrodes (1.7 nm tubes)

Novel spark discharge FC-CVD SWNT technology – separate catalyst formation and SWNT nucleation - bundling control

TCF with Individual tubes – length 4 microns – 60 ohms/sq @ 90 % T (HNO₃ doped)

SWNT bundling in the laminar flow reactor – 0 to 360 s delay time.

Spark discharge Fe catalyst in N_2 - H_2 -CO FC-CVD – low and high SWNT number concentration

The effect of bundling on sheet resistance vs. transmittance – non-doped films

TFT-FETs Spark FC- CVD SWNT random network via filter transfer

- Excellent SWCNT network uniformity
 - High device yield and controlled transfer characteristics
- The charge carrier mobility ~100cm²/Vs and typical ON/OFF ratios >10⁵
- Small ON current spread
- ON/OFF ratios scaling as function of channel length
 - SWCNT network uniformity approaches ideal random network with 1/3 metallic and 2/3 semiconductive SWCNT

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Companies following IRENA From EU:

- Osram
- Nokia Oy
- Canatu Oy
- Fortum Oy
- Sefar AG
- Beneq Oy
- Amcor
- Eight19 Ltd

From Japan:

- Showa Denko K.K.
- Toray

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PRINTED TOUCH SENSORS USING CARBON NANOBUD[®] MATERIAL

Anton S. Anisimov*, David P. Brown*, Bjørn F. Mikladal*, Liam Ó Súilleabháin*, Kunjal Parikh**, <u>Erkki Soininen</u>*, Martti Sonninen*, Dewei Tian*, Ilkka Varjos*, Risto Vuohelainen*

* Canatu Oy, Finland ** Intel Corporation, USA

www.canatu.com

Canatu's production facility

NOIN

- In Helsinki, Finland
- Roll-to-roll 600mm wide CNB[™] Films
- STSTEM CERI 1200 m² production space
- 400 m² clean room
- Canatu is ISO 9001:2008 certified

DNV.GL

ISO 9001

Commercially available by Canatu Oy: High transparency nanotube film meeting ITO stability and uniformity specs

Haze comparison in touch modules Intel measurements from 13.3" Ultrabooks

Touch Module	Туре	Sensor	Haze (%)	
Carbon NanoBud	CNB	GFF	0.6	
ITO OGS (no index matching)	ITO	OGS	3.3	
Silver nanowires Metal Mesh	Mesh	GFF	1.4	
Silver Metal Mesh #1	Mesh	GFF	2.0	
Copper Metal Mesh #1	Mesh	GF2	1.6	
Copper Metal Mesh #2	Mesh	GF2	2.0	
Silver Metal Mesh #2	Mesh	GF2	1.3	
IPAD 4 (Air)	ITO	GF2	1.0	

CNB has the lowest haze in the industry

CNB Film lifetime bending test – touch sensors for *flexible devices*

Gray lines are raw values and orange lines are fittet values.

7% resistivity change at 2 mm bending radius over 140 k bending cycles.

CNB survives a lifetime of a foldable device.

CNB™ films can be stretched

- Using Industry-standard forming and injection moulding processes: Pressure forming, Film Insert Molding (FIM)
- Locally streched as much as 120%, bending radius 1 mm
 - CNB[™] still remained conductive in the tested challenging forms

Bayer MaterialScience

* Aalto MIDE and AEF programs

Indium **Re**placement by Single-Walled Carbon **Na**notube Thin Films

The Canatu Team

Dr. Erkki Soininen

