Electrospun a-Si using Liquid Silane/Polymer Inks

Douglas L. Schulz, Justin M. Hoey, Jeremiah Smith,
John Lovaasen, Chris Braun, Xuliang Dai,
Kenneth Anderson, Arumugasamy Elangovan, Xiangfa Wu,
Scott Payne, Konstantin Pokhodnya, Iskander Akhatov,
Larry Pederson and Philip Boudjouk

Center for Nanoscale Science and Engineering, North Dakota State University
1805 NDSU Research Park Drive, Fargo, ND USA

IDW '10 Presentation FMC5 - 2:
Fukuoka, Japan

CNSE NDSU Center for Nanoscale Science and Engineering

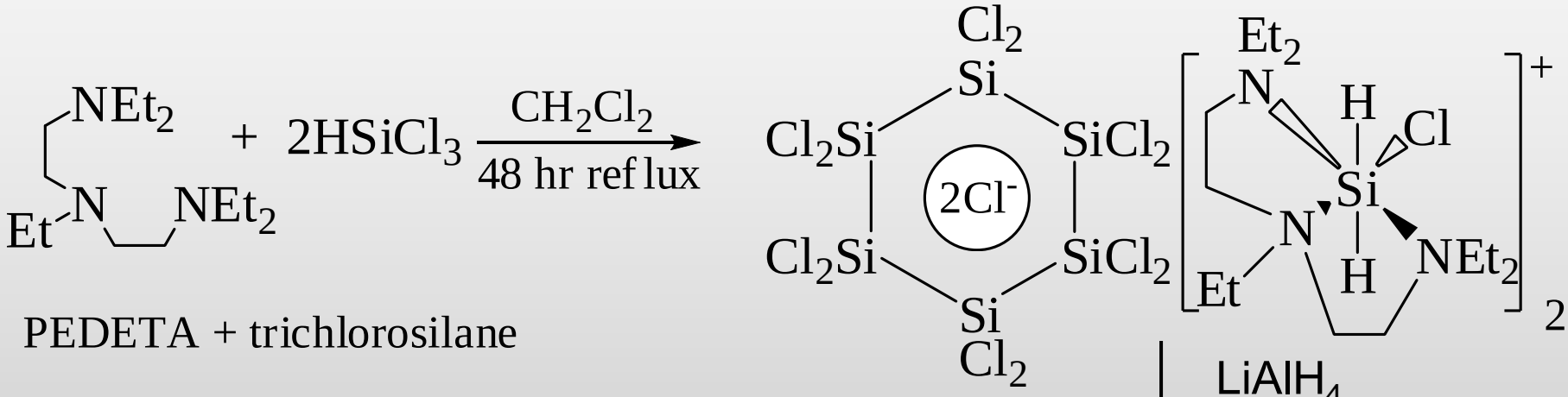
NDSU Old Main

Research 2 – Home of NDSU-CNSE

My 2nd home at NDSU

Cyclohexasilane Si_6H_{12} Chemisty

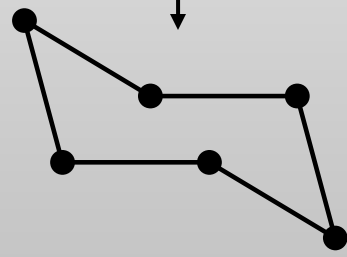
Amine-promoted disproportionation and redistribution: Si-Si bond formation



PEDETA + trichlorosilane

pyrophoric, translucent liquid

$LiAlH_4$ reduction



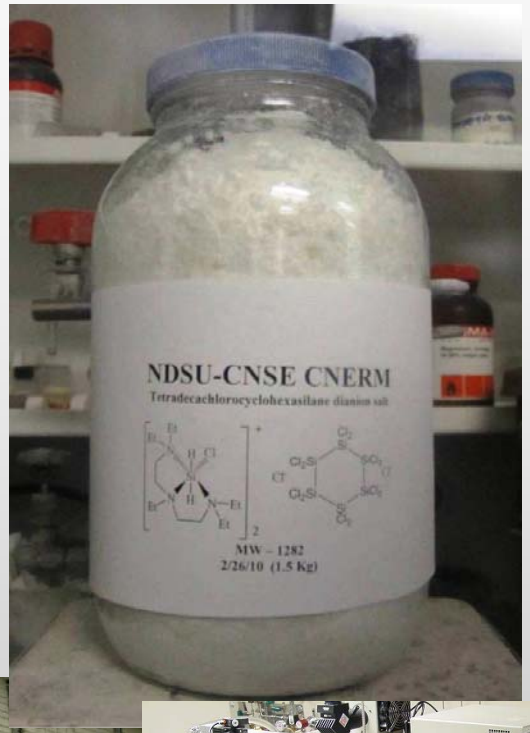
≡ Si_6H_{12}

bp. ~ 80 °C/1.3Pa
mp. ~18 °C
ρ 0.97 g/mL

P. Boudjouk et al.
J. Am. Chem. Soc. **2001,** *123,* 8117-8

Si_6H_{12} Production at NDSU

- Scaleup to 10 g/week
- 2 kg/day facility envisioned
- Discussions with several manufacturers of fine chemicals for the semiconductor industry ongoing

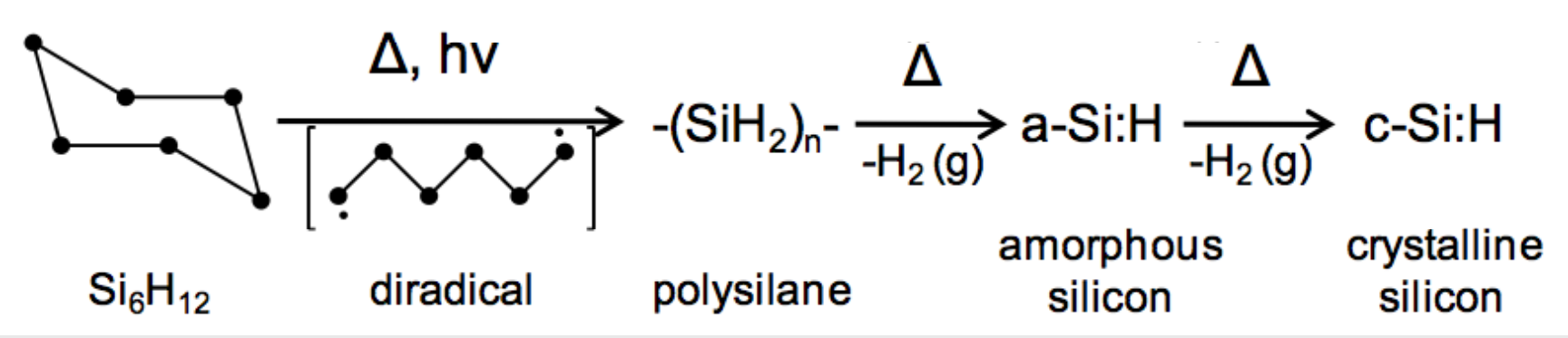


3L reactor

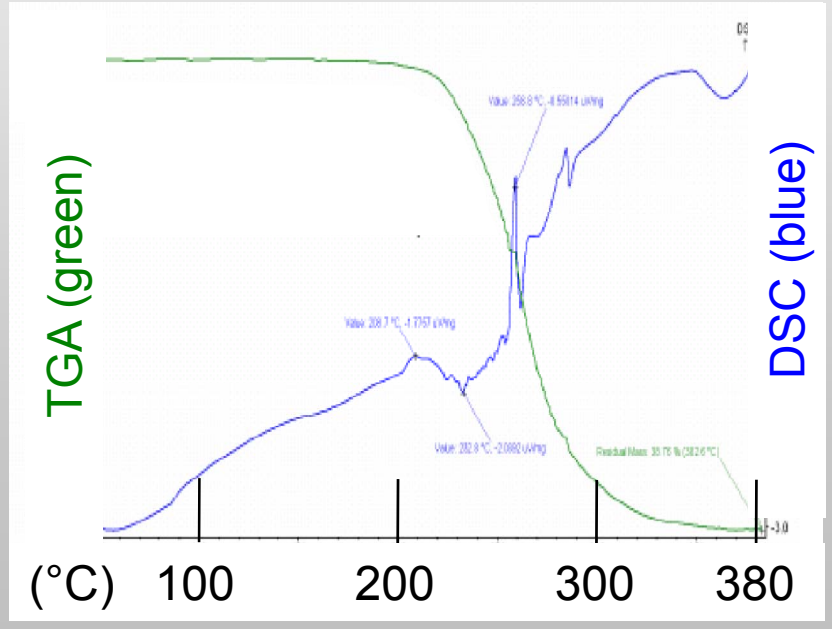
Si_6H_{12} Distillation

✳ Dr. Xuliang Dai

Si_6H_{12} Precursor to Si-based Electronic Materials

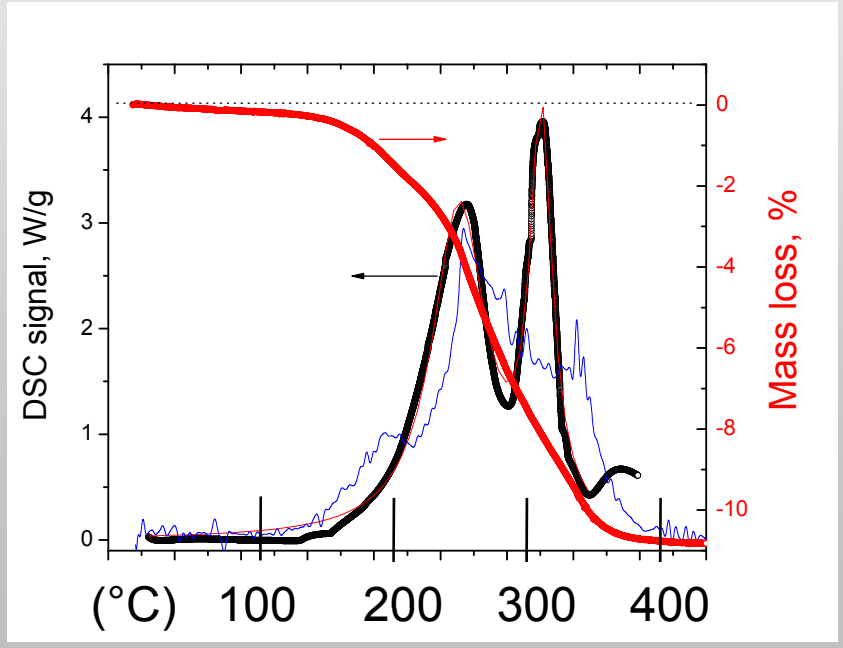


Thermal Stability



Isothermal TGA at 100 ºC shows no weight change after 12 h

Thermolytic Behavior of Si_6LSM



Results similar to Shimoda et al. *Nature*, **2006,** *440*, 783-6.

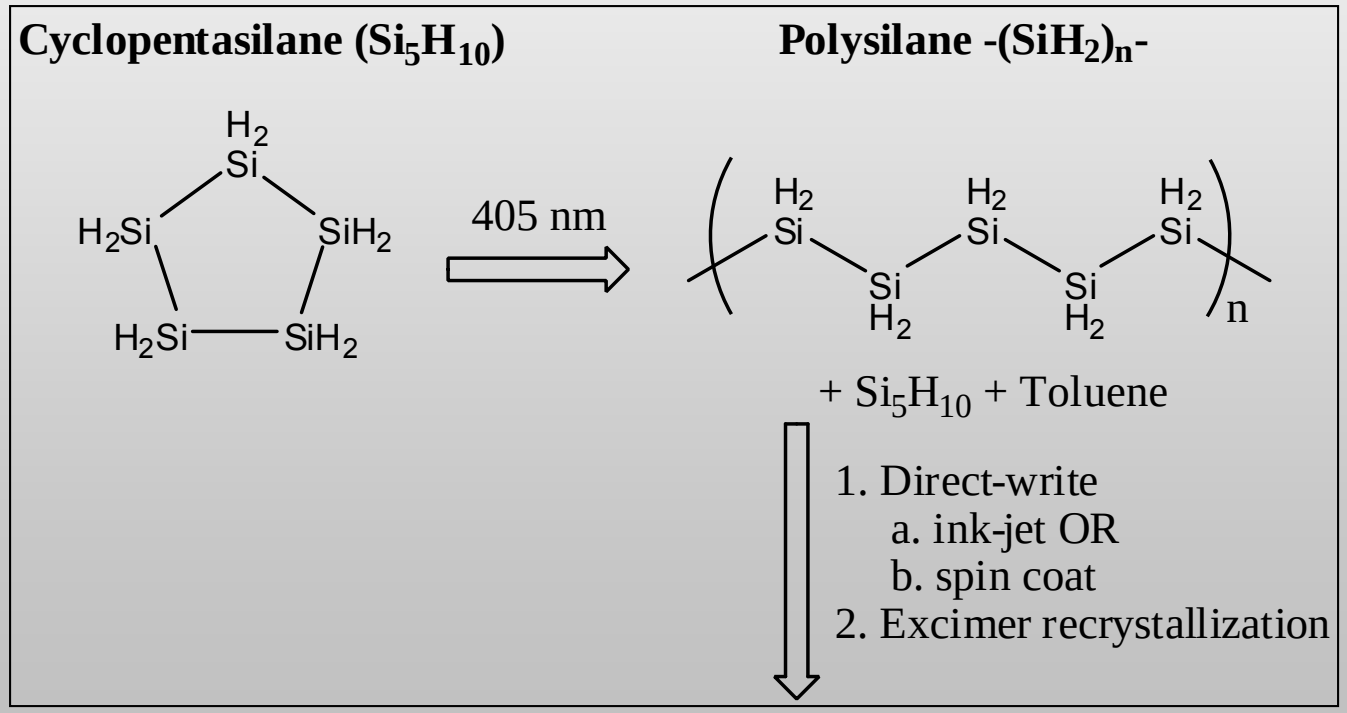
Initial Approach - Reproduce Seiko-Epson/JSR

Si_6LSM Ink Formulation and Method

10 mL laser-treated Si_6H_{12} + 10 mL Si_6H_{12} + 130 mL toluene

Spin coat

Thermal treatment (e.g., 40 min ramp to 350 °C / 20 min soak)



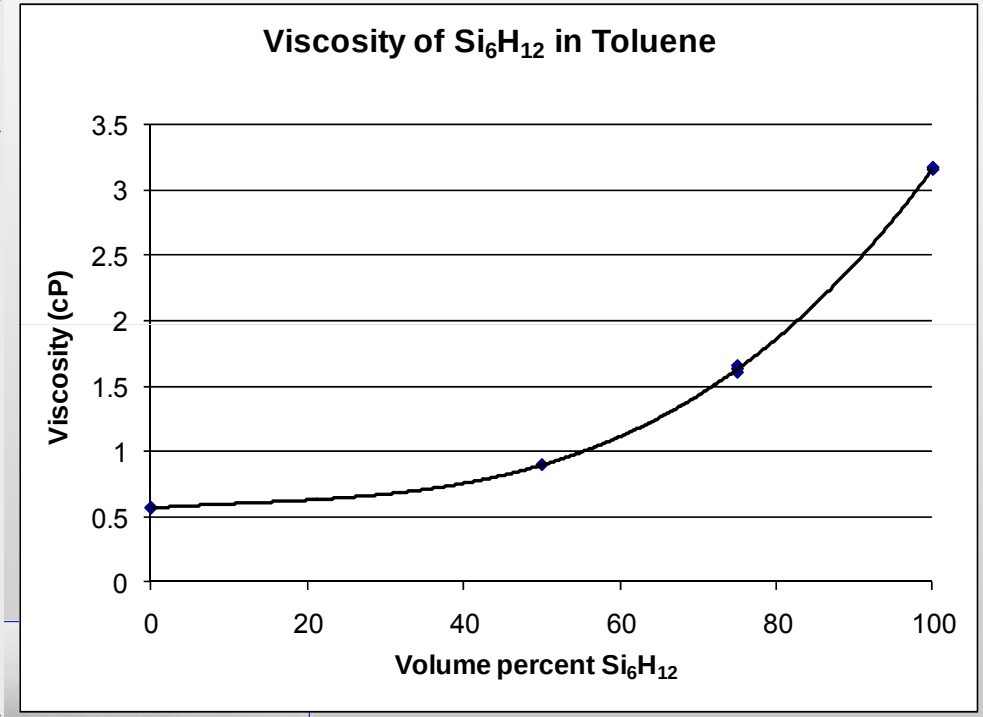
Recipe according to Shimoda et al. *Nature,* **2006,** *440*, 783-6.

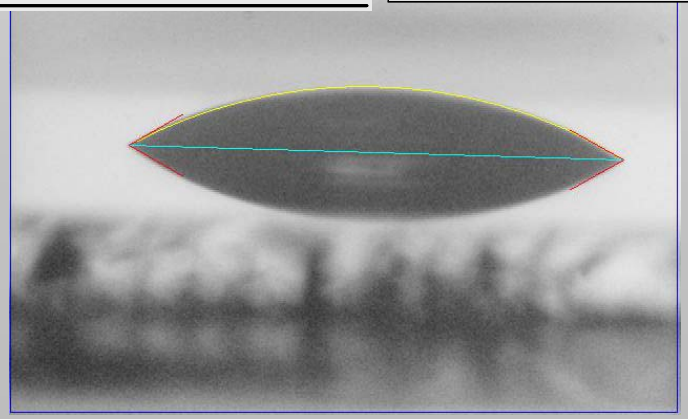
Characteristics of Si_6H_{12} and Si_6LSMs

Contact Angle

Substrate and Treatment [a]	Liquid (µL)	Contact angle (°)
Glass (stnd)	10 µL Si_6H_{12}	25.3±1.4
Glass (Pirahna)	10 µL Si_6H_{12}	19.2±1.7
Si wafer (HF)	10 µL Si_6H_{12}	18.6±1.7
Stainless (stnd)	10 µL Si_6H_{12}	13.7±1.4
Glass (stnd & HMDS)	10 µL Si_6H_{12}	30.0
Glass (stnd)	2 µL Si_6H_{12}	26.3
Glass (stnd)	2 µL Si_6LSM	3.8

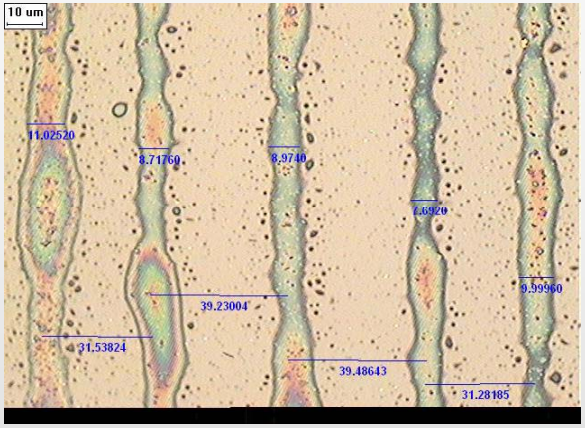
Viscosity





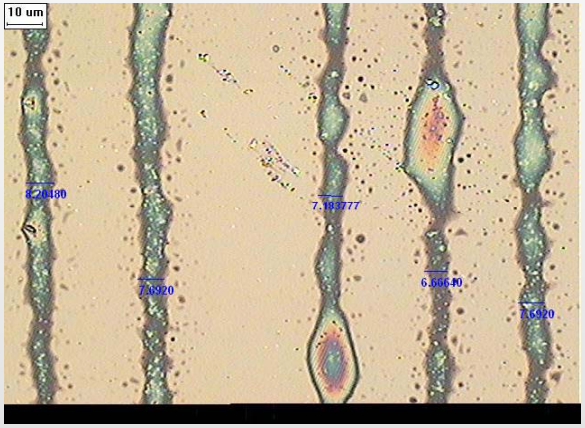
Liquid Silane Precursors to Printed Silicon

After UV

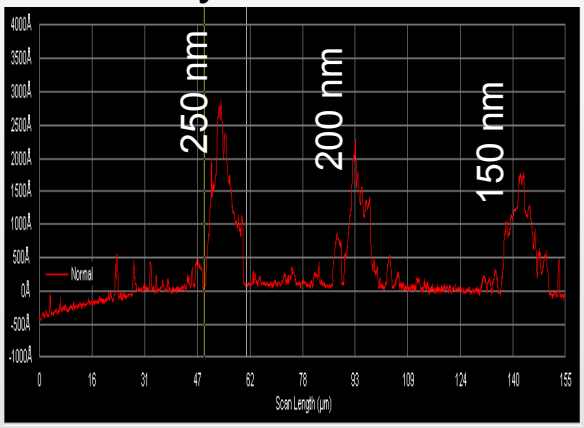


50 X mag

After UV + 350 °C

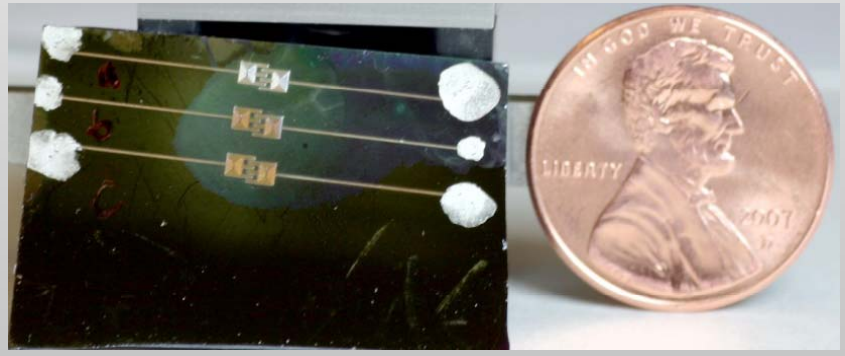


Stylus Profile



First Diode

First Transistor



Film thickness < 200 nm

Preliminary Studies: Limited to T < 400 °C; Focused Mainly on Low-Temperature Dopants

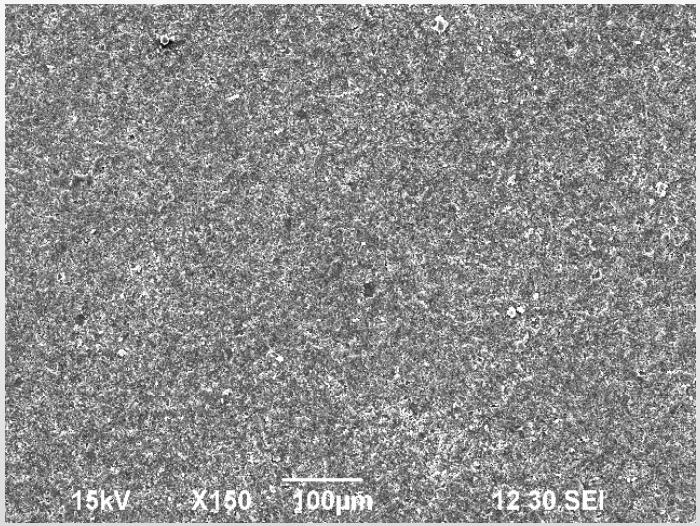
NDSU-CNSE Si_6ers *J. Non-Cryst. Solids*, **2008**, *354*, 2623-2626

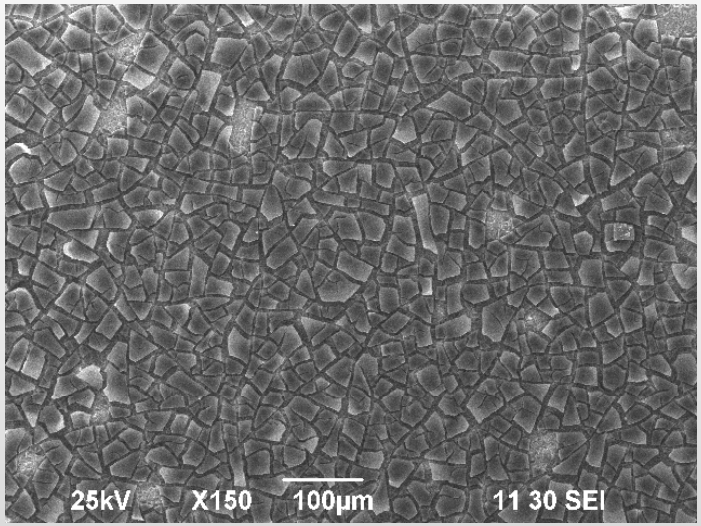
Printed Silicon – Thicker Films Crack

~1 µm

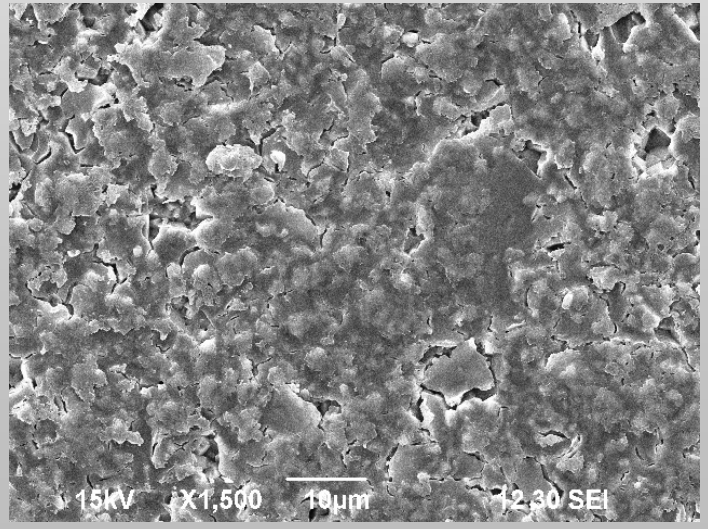
~3 µm

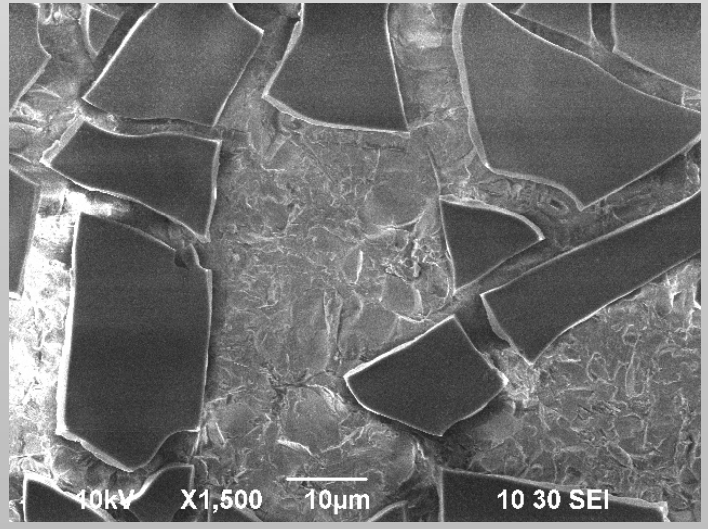
Low Magnification



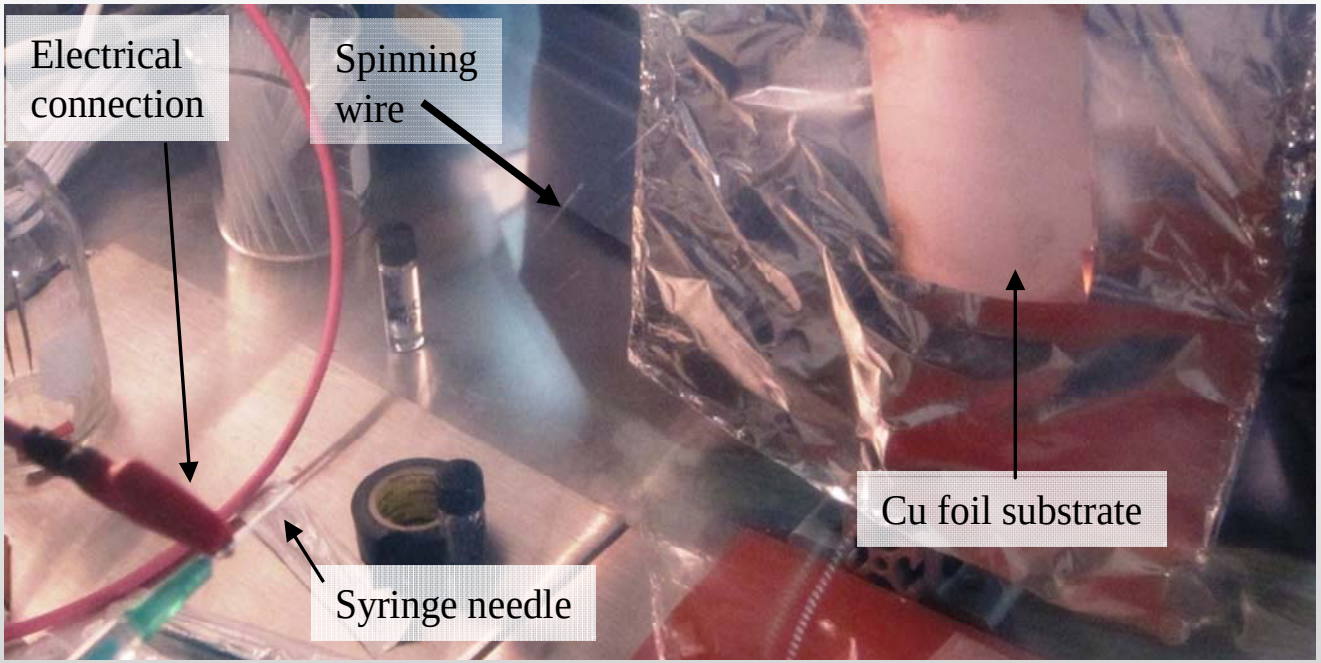


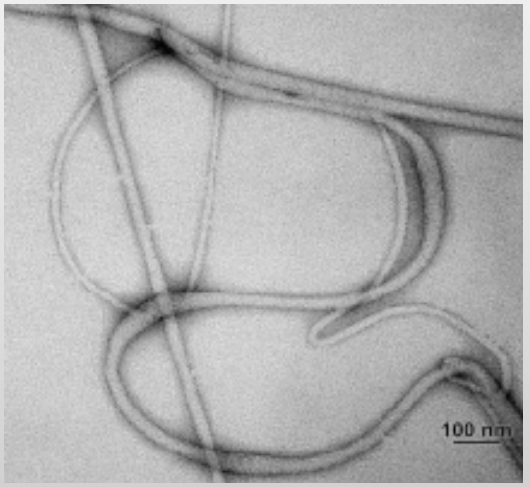
High Magnification



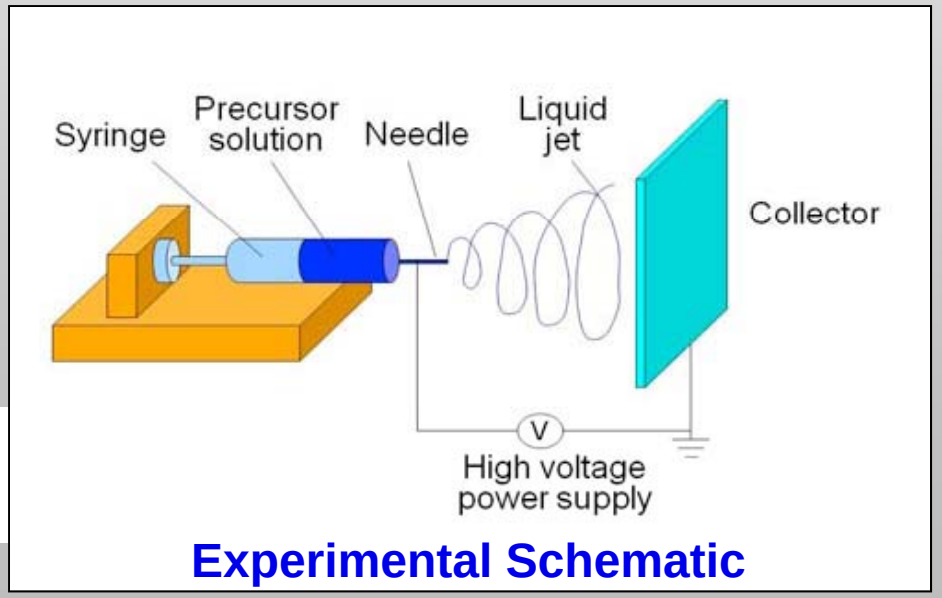


Electrospinning SiNWs from Si_6H_{12}-based Inks





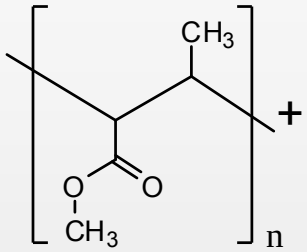
SEM of 1st Nanowires



Experimental Schematic

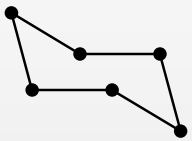
Located inside inert glovebox

1st Gen Ink. PMMA in Toluene, Add Si_6H_{12}, Electrospin, Thermolysis



PMMA in toluene
MW= 996,000

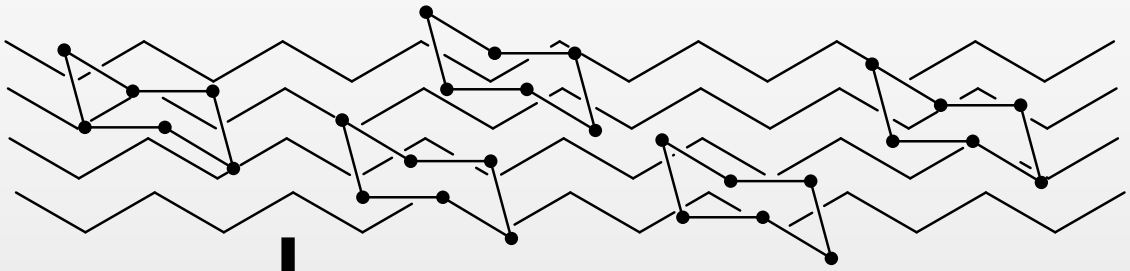
+



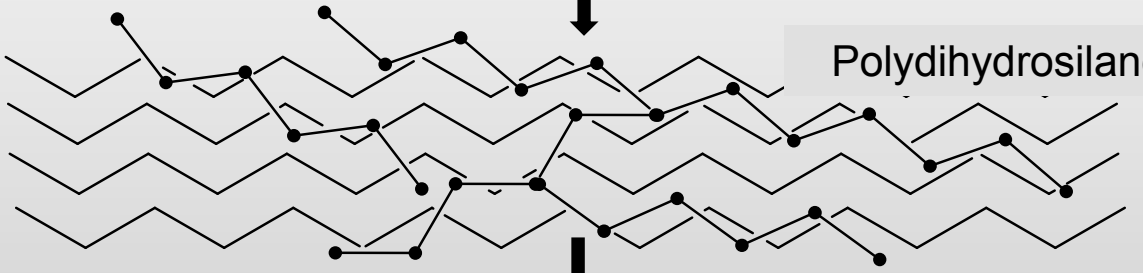
Si_6H_{12}

Electrospin

-toluene (g)

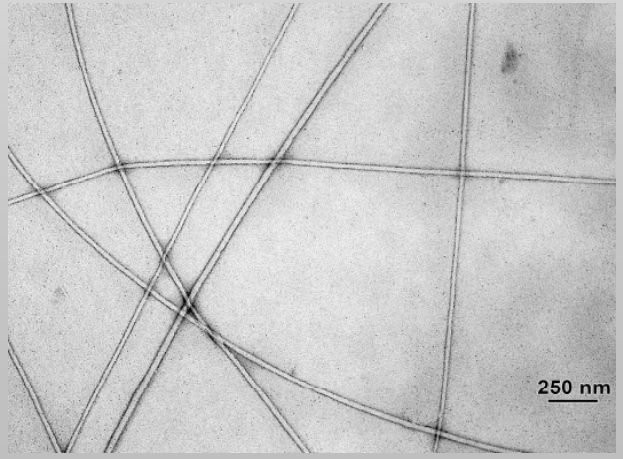


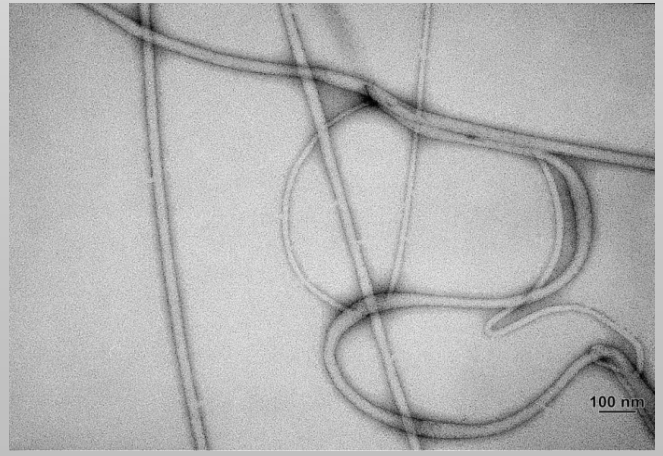
Heat



Polydihydrosilane / PMMA

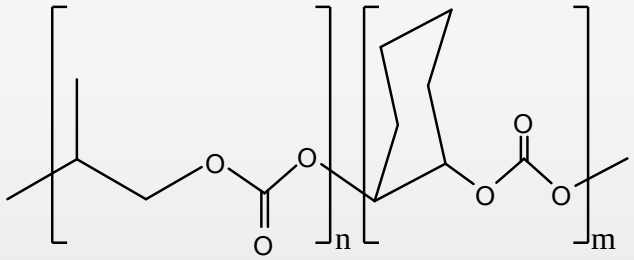
Heat (350 °C)





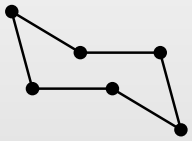
TEM micrographs

2nd Ink'. QPAC100®/Toluene/Si_6H_{12}, E-spin, Laser Treatment, Thermolysis



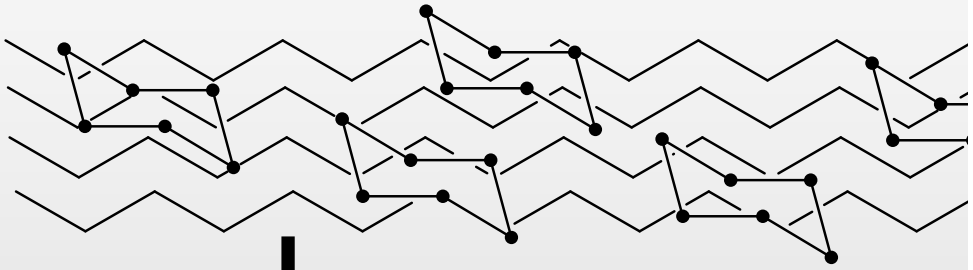
QPAC100®
polypropylene carbonate/
polycyclohexene carbonate
in toluene MW = 660,000

+



Electrospin

-toluene (g)



Laser (355 nm @ ~250mW/cm²)

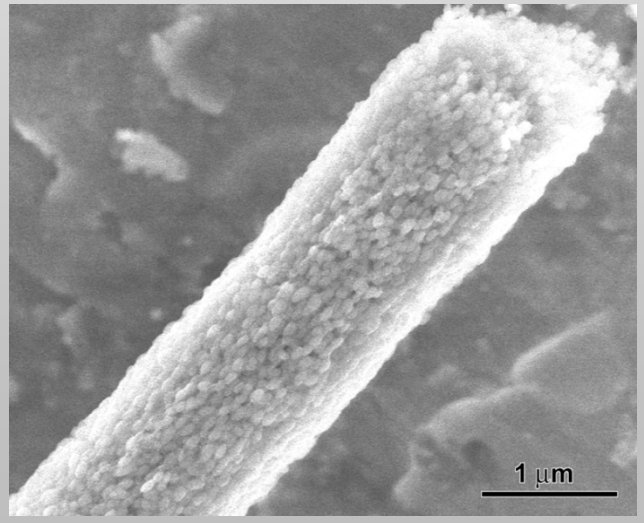
1) Si_6H_{12} transformed to $-(SiH_2)_n-$

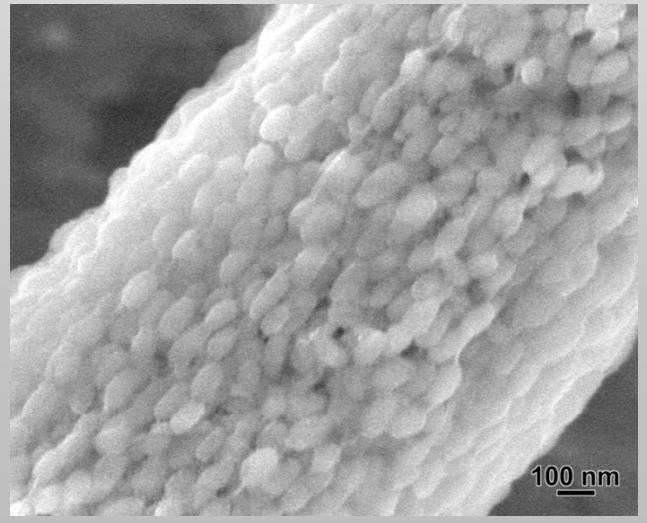
Heat (350 °C/20 min)

2) QPAC 100® volatizes

3) $-(SiH_2)_n-$ transformed to a-Si

Porous a-Si NWs

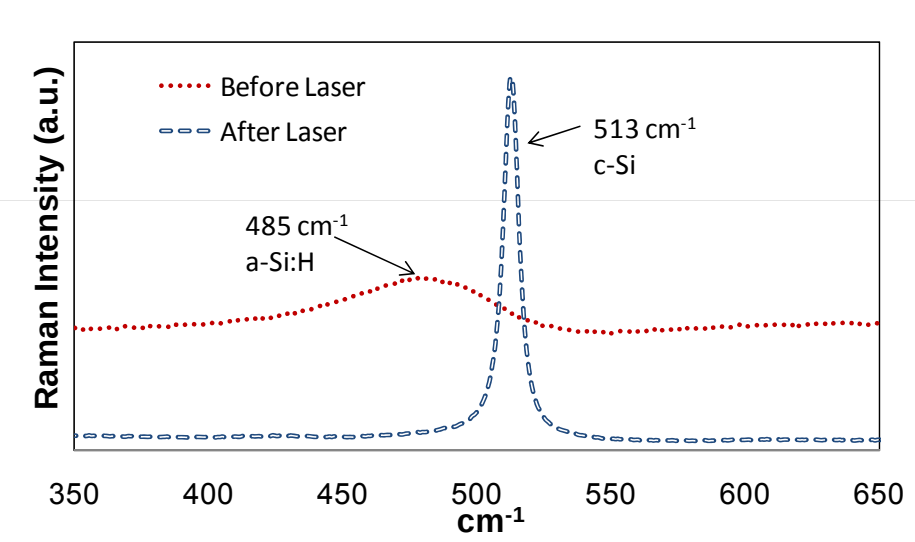




HRSEM micrographs

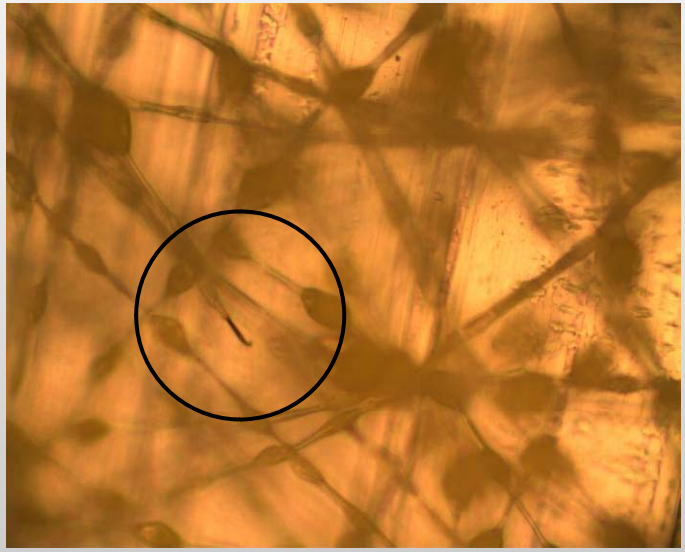
Characterization – Electrospun Si NWs from PMMA

Raman Spectra



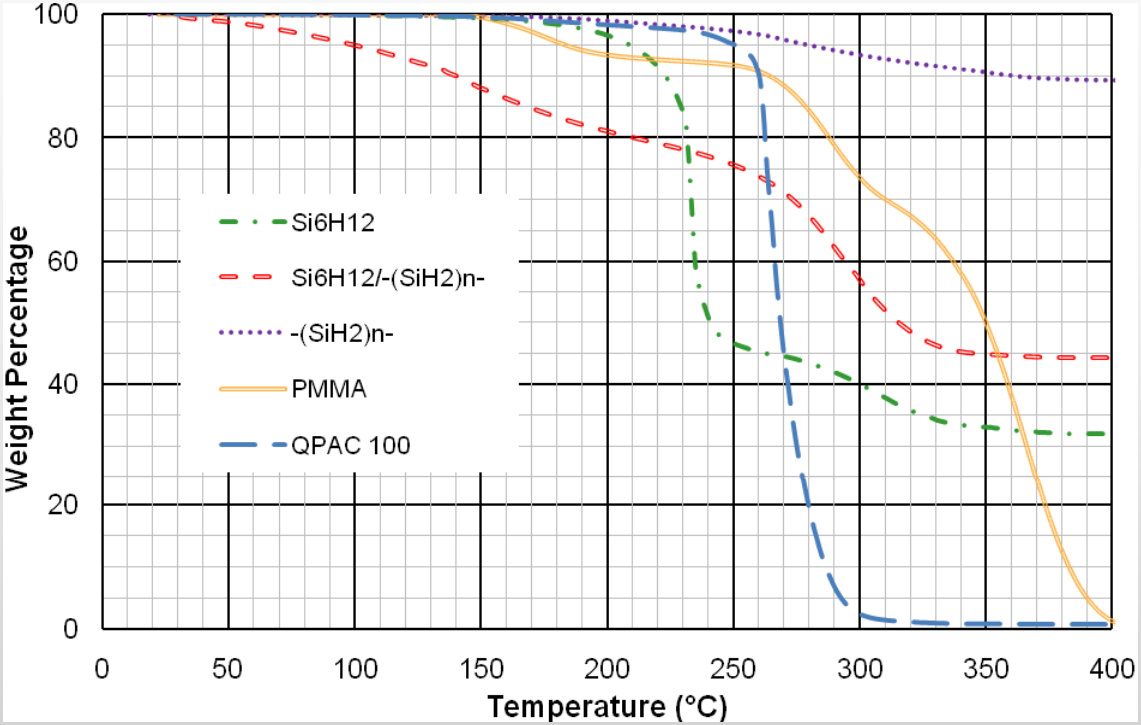
before (red) and after (blue) melting

Optical Micrograph

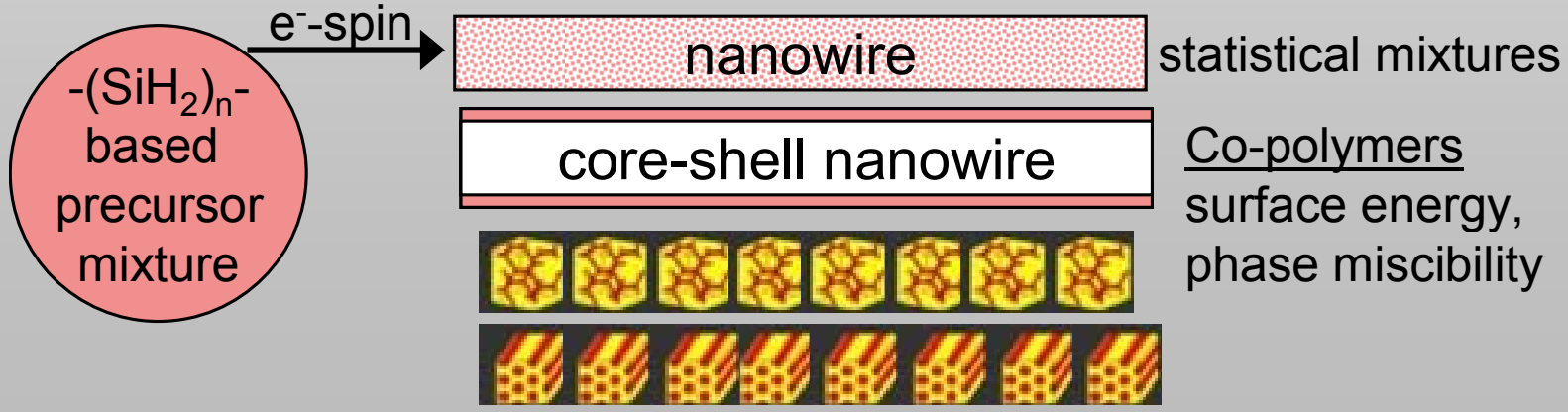


melted Si after focused beam

Electrospinning Polysilane-based Mixtures



Potential for New Copolymer Physical Chemistry



Future Plans

"Metallosilane" Solution Route to Metal Silicides (MSi_x)

Si_6H_{12} + metal reagent + solvent → viscous MSi_x inks

MSi_x inks → spin coating / electrospinning → thin films / nanowires

Applications of Si and MSi_x Films and Nanowires

Electroluminescence

Field emission

Lithium ion battery anode

Photovoltaics

Sensors

Transistors

Thermoelectrics

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Prof. Masafumi Unno - Director (Gunma University, Kiryu).

JustinH KennyA

Sumo wrestling with
"John" Masuda in Kusastu

Masafumi Ogawa

Nikko-San Chuzen-Ji Temple

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