"Application of Room Temperature Ionic Liquids to the electrodeposition of semiconducting nanowires"

Gordon Research Conferences on Electrodeposition
August 3rd, 2010

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LMEN: overview of research on semiconducting nanowires

Synthesis: Electrodeposition

Physical characterization

Near field microscopy and spectroscopy techniques

Semiconducting Nanowires

Low cost technique: Ink jet printing

Applications

Organic transistors

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Electrodeposition using Room Temperature Ionic Liquids (RTILs): Introduction and perspectives

Why working on Si/Ge Nanowires (NWs): Recent perspectives and usual growth processes

Electrodeposition of GeNWs and SiNWs:

Characterization of SiNWs

Conclusion: Recent progresses and perspectives
## A brief introduction to Ionic Liquids

### What is an Ionic Liquid (IL)?

- An ionic material being liquid below 100°C
- Fine tunable properties by changing cations and anions (millions of Ionic Liquids)

### Some History:

- The first one: ethylammonium nitrate \([\text{EtNH}_3^-][\text{NO}_3^-]\) (Walden in 1914)
- First generation of Ionic Liquids based on AlCl\(_3\) (Hurley and Wier, 1951)
- Third generation: air- and water-stable Ionic Liquids (John Wilkes and coworkers, 1992)

### Important ILs properties

- Wide temperature range for liquid phase (300°C)
- Low volatility
- High chemical and thermal stability
- High intrinsic ion conductivity
New expectations with Room Temperature Ionic Liquids

Aqueous solvent

The main limitation of aqueous solvent: the electrochemical window: voltage range between which the substance doesn't get oxidized nor reduced

N.B. Outside solvent window, materials are thermodynamically unstable
New expectations with Room Temperature Ionic Liquids

Ionic liquids

Wide electrochemical windows

⇒ Many materials (which couldn’t be electrodeposited with water) can thermodynamically be electrodeposited with ionic liquid

exple: Al, Si, Ge, Ti and so on

Same easy protocol as aqueous electrodeposition

Almost no oxydation of electrodeposited material (no H₂O nor O in ionic liquid)

Cheap and easy way of elaborating many materials
Current drawbacks using RTILs

Physical properties strongly dependant of **water content** ⇒ inert atmosphere needed

*solution*: glove box and purification of solvent

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**Viscosity** at room temperature 10 to 100 times **higher than that of water or organic solvent**

⇒ quite low ionic conductivity
⇒ quite low diffusion coefficients

*solution*: working at higher temperature
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Introduction: few recent perspectives for Si/Ge nanowires

Transport of Ge/Si nanowire heterostructures

NWs FET: Improvement of transconductance and hole mobility compare to the best MOSFET


Conductance of Si nanowires (SiNWs)

ab initio simulations ⇒ a preserved transport quasiballistic in Si nanowires

whereas

functionalization strongly affect the conductance of carbon nanotubes (CNT)

Introduction: few recent perspectives for Si/Ge nanowires

High capacity anode for Li batteries

Si : highest known theoretical charge capacity
Advantage of SiNWs : large strain without pulverization when cycling

Growth of Si nanowires (SiNWs): VLS

Advantages

- Single-crystalline NWs
- Little or no visible amorphous oxide

Drawbacks

- Diameter of SiNWs determined by that of starting nanoclusters
- High temperature and high vacuum process
- Possible diffusion of gold inside SiNWs


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Basics of Electrodeposition applied to nanowires growth

Electrodeposition of nanowires:

⇒ polarization of the Au layer

(a) Electrodeposition cell for NWs
(b) Top view of a nanoporous PolyCarbonate (PC) membrane (200 nm)
(c) Cross section view of a nanoporous Al$_2$O$_3$ membrane supported on Si (80 nm)
RTIL for deposition of Si and Ge NWs: \([\text{BMP}]\text{Tf}_2\text{N}\)

Ionic liquid \([\text{BMP}]\text{Tf}_2\text{N}\) \(\{1\text{-butyl-1-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide}\}\)

Structure

\[
\begin{align*}
\text{Cation} & : 1\text{-Butyl-1-methylpyrrolidinium} \\
\text{Anion} & : \text{bis(trifluoromethanesulfonyl)imide}
\end{align*}
\]

Physical properties* (at 20°C)

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\eta) (m P a s)</td>
<td>89</td>
</tr>
<tr>
<td>(\kappa) (m S cm(^{-1}))</td>
<td>2.2</td>
</tr>
<tr>
<td>(\rho) (g cm(^{-1}))</td>
<td>1.40</td>
</tr>
<tr>
<td>(\text{decomp}) (K)</td>
<td>583</td>
</tr>
</tbody>
</table>

Electrodeposition of Ge (1D)

Voltammogram of GeCl$_4$ + [BMP]Tf$_2$N in a M90 PC membrane

- Ge oxidation
- Ge + Au oxidation
- Ge deposition
- OCP
- [Py$_{1,4}$]$^+$ breakdown

$I$ / mA

$E$ / V vs. Ag
Electrodeposition of Si (1D)

Voltammogram of SiCl$_4$ + [BMP]Tf$_2$N in a M90 PC membrane
SEM images of Si and Ge nanowires

Si and Ge nanowires after dissolution of the PC membrane

Deposition potential: -2500 mV/Pt

Average diameter: **400nm**

Deposition potential: -2300 mV/Pt

Average diameter: **90nm**

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SEM images of Ge nanowires

Ge nanowires after dissolution of AAO membrane

Average diameter: 200nm

High density of nanowires

Good size homogeneity
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Characterization of as-deposited Si nanowires

**Bright field TEM image of isolated 15 nm SiNWs**

Inset: Corresponding diffraction pattern

**Preliminary conclusion:**

- SiNWs and Ge NWs can be electrodeposited
- Size: 15 à 400 nm
- Crystallographic aspect homogeneous for all nanowires dimension
- High density of NWs

**However:**

- As-deposited amorphous
Characterization of as-deposited Si nanowires

Raman Spectrum on a bunch of 110 nm SiNWs

150 and 480 cm$^{-1}$ bands correlated to amorphous Si
Characterization of as-deposited Si nanowires

IR absorption on a bunch of 400 nm SiNWs

Without HF etching:

1020 cm\(^{-1}\): asymmetric vibration of Si-O bonds (stretching)

460 cm\(^{-1}\): Si-O bonds rocking vibration

After etching:

630 cm\(^{-1}\): vibration of Si-H bonds (bending)

2000 cm\(^{-1}\): asymmetric vibration of Si-H bonds (stretching)

* Etching done with 5% fluoridric acid (HF)
Characterization of as-deposited Si nanowires

EELS measurements on a single 400nm NW

Energy loss peaks for SiO₂
105.5eV, 108eV, 115eV

Energy loss peak for Si
100eV (L edge)

Top view of a single 400nm NW
Crystallized Si nanowires

Bright field TEM image of isolated 15 nm SiNWs annealed at 650°C

Inset: Corresponding diffraction pattern

Grazing incidence X-ray Diffraction (GIXD) of a bunch of 110 nm SiNWs annealed at 650°C

Amorphous SiNWs $\Rightarrow$ Crystallized SiNWs

Annealing
Emission properties of the SiNWs

Photoluminescence experiments

As-deposited Si NWs

No confinement effect for such diameters
  • peak at 480nm related to the oxide shell??
  • peak at 780nm related to the amorphous silicon?

Si NWs after 5 min in 5% HF

Disappearance of the low energy band after removing of the oxide

Spectrum at room temperature of 40nm Si NWs
Conclusion on electrodeposited SiNWs

* **High density** of wires for the whole range of diameter (15 à 400 nm)

* Dimension and crystallographic aspect **homogeneous** for all nanowires

* **No** observation of any **impurities** in SiNWs (Au or else…)

* As-deposited **amorphous, polycrystalline** after quick thermal annealing

* **Strong photoluminescence at RT** for Si NWs


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Electrodeposition of Si nanotubes (SiNTs)

SEM images of a bunch of 400 nm Si Nanotubes

Bright field TEM pictures confirm homogeneity of SiNTs along their whole length

SiNTs reproducibly obtained between 400 nm to 90 nm
Electrodeposition of Si nanotubes (SiNTs)

- Possibility of having nanotubes with different shell thicknesses

- High density of nanotubes

- Good size homogeneity

To be published (2010)
First preliminary result:

SEM image of SiGe dot of 400 nm
Thank you very much for your attention

Thanks to all Group members working on Si, Ge nanowires:

Graduate students:
F. Martineau
K. Namur

Research Professors, Lecturers and research scientists
J. Mallet
M. Molinari
M. Troyon
RTIL for deposition of Si and Ge NWs: [BMP]Tf2N

Purification of solvent [BMP]Tf2N {1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide}

**Electrochemical window > 4V**

- Dried under vacuum during **12 hours**
- Dried under vacuum during **3 days**
- Dried under vacuum during **7 days**

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