

# Aluminium en chroom depositie in ionische vloeistoffen

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**TNO | Knowledge for business**



Al en Cr depositie in ionische vloeistoffen

D05

# Elektrodepositie in ionische vloeistoffen

- wat zijn ionic liquids
- “unieke” elektrochemische mogelijkheden
- chroom depositie met Cr(III)-zouten
- depositie van aluminium
  - DC
  - DC-pulse
- samenvatting



# Ionic Liquids (IL) low temperature molten salts

Defined as materials containing only ionic species without any neutral molecules and having a low melting point (usually less than 100 °C)

## Room Temperature Ionic liquids (RTIL)

I.L. which are already liquid below room temperature



# I.L. Properties:

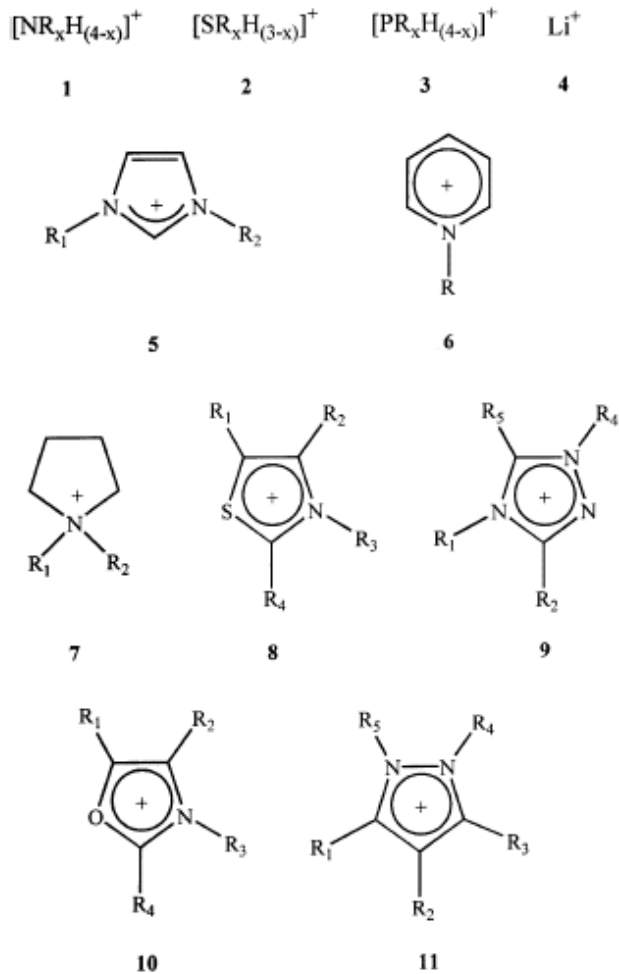
- Liquid over a wide temperature range
- Negligible vapor pressure (non-volatile) —————> Green Chemistry
- Non-flammable
- High thermal and chemical stability
- Act as acids, bases or ligands
- Dissolution of many organic and inorganic compounds
  
- Intrinsic conductive
- Very large electrochemical window (4-7V)

**Physical and chemical properties tuneable by composition**



# Ionic Liquids: cations

## control the physical properties



Ammonium **1**  
 Sulfonium **2**  
 Phosphonium **3**  
 Lithium **4**  
 Imidazolium **5**  
 Pyridinium **6**  
 Pyrrolidinium **7**  
 Thiazolium **8**  
 Triazolium **9**  
 Oxazolium **10**  
 Pyrazolium **11**  
 differently substituted

# Ionic Liquids: anions

Control the chemical properties and the reactivity

## Inorganic anions

- $[\text{AlCl}_4]^-$  tuneable Lewis Acid/Base
- $[\text{PF}_6]^-$  moisture stable, water immiscible IL
- $[\text{BF}_4]^- / \text{Cl}^-$  moisture stable, but water miscible IL

Organic anions moisture stable, water immiscible

- Triflate [Tf]  $\text{CF}_3\text{SO}_2^-$
- Bis(trifluoromethylsulfonylimide)  $[\text{NTf}_2] (\text{CF}_3\text{SO}_2)_2\text{N}^-$

# Melting point of I.L.

## Various cations:

Salt	M.p. [°C]
NaCl	803
KCl	772
[MMIm]Cl	125
[EMIm]Cl	87
[BMIm]Cl	65

## cations effect:

- Low symmetry
- Weak intermolecular interactions
- Good distribution of charge

## Different anions:

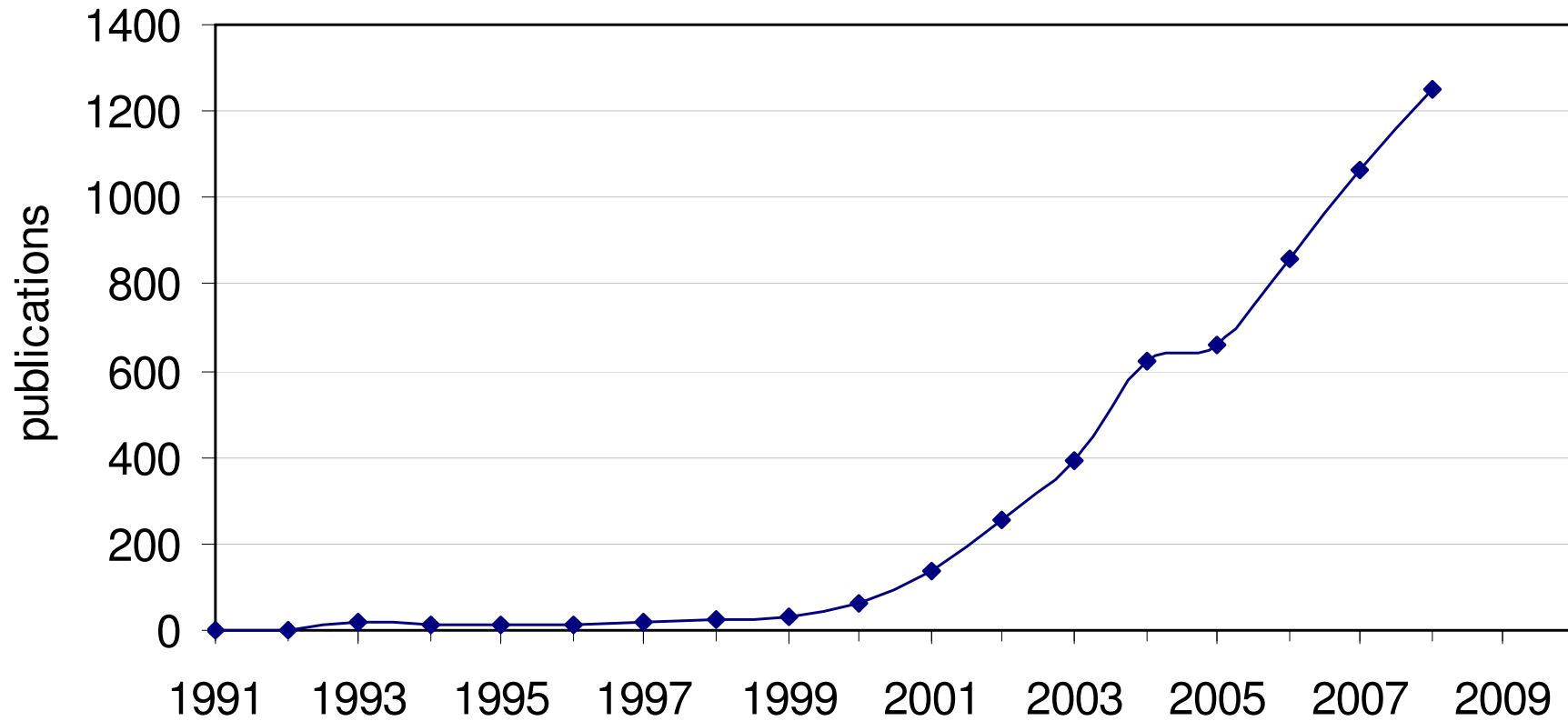
Salt	M.p. [°C]
[EMIm]Cl	87
[EMIm]NO <sub>3</sub>	38
[EMIm]CF <sub>3</sub> SO <sub>3</sub>	-9
[EMIm]CF <sub>3</sub> CO <sub>2</sub>	-14

## anion effect:

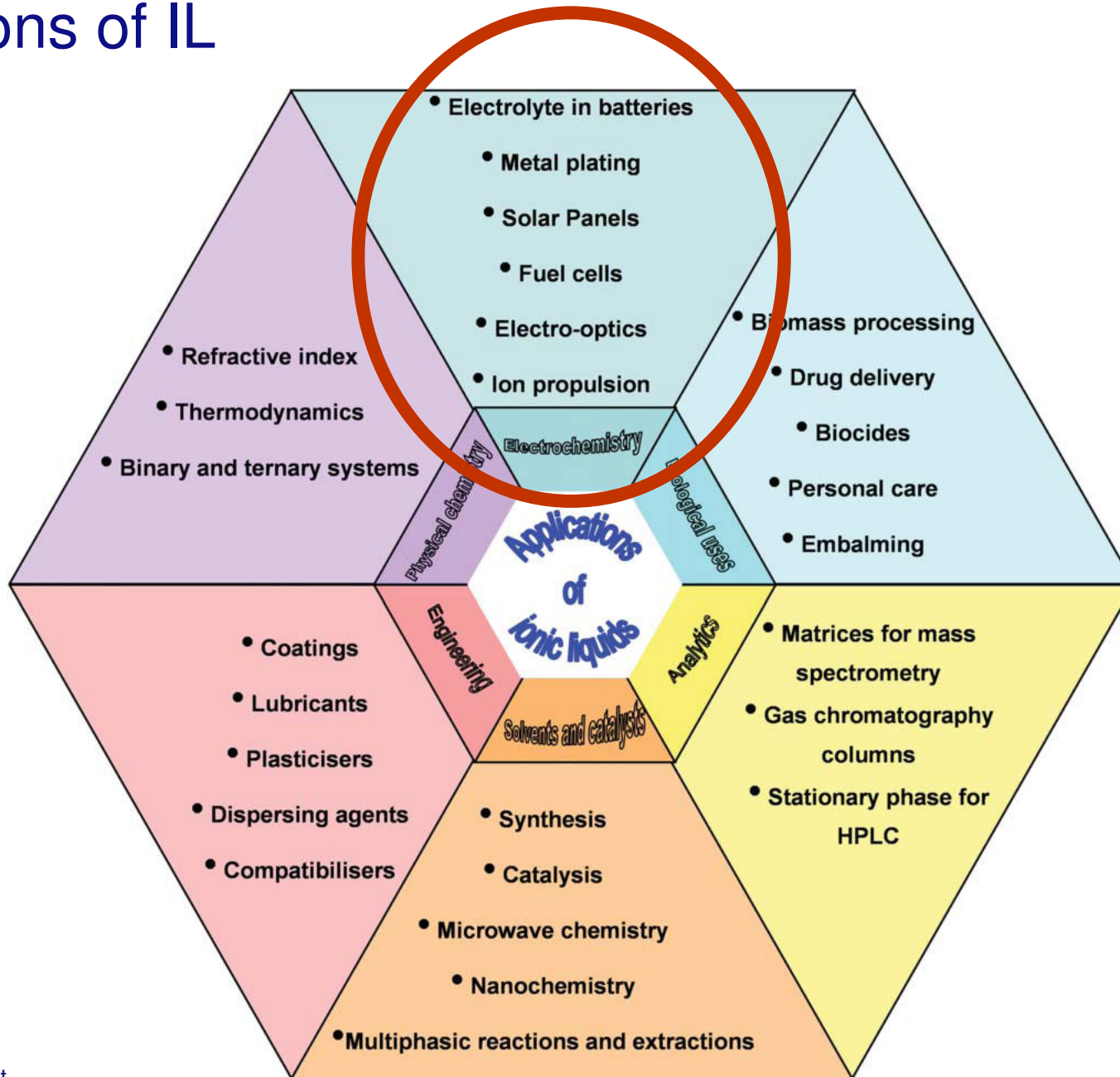
increasing size → decrease in melting point.

Philippe Hapiot, Corine Lagrost, Chem.Rev. Vol.108, 2008, p.2238-2264

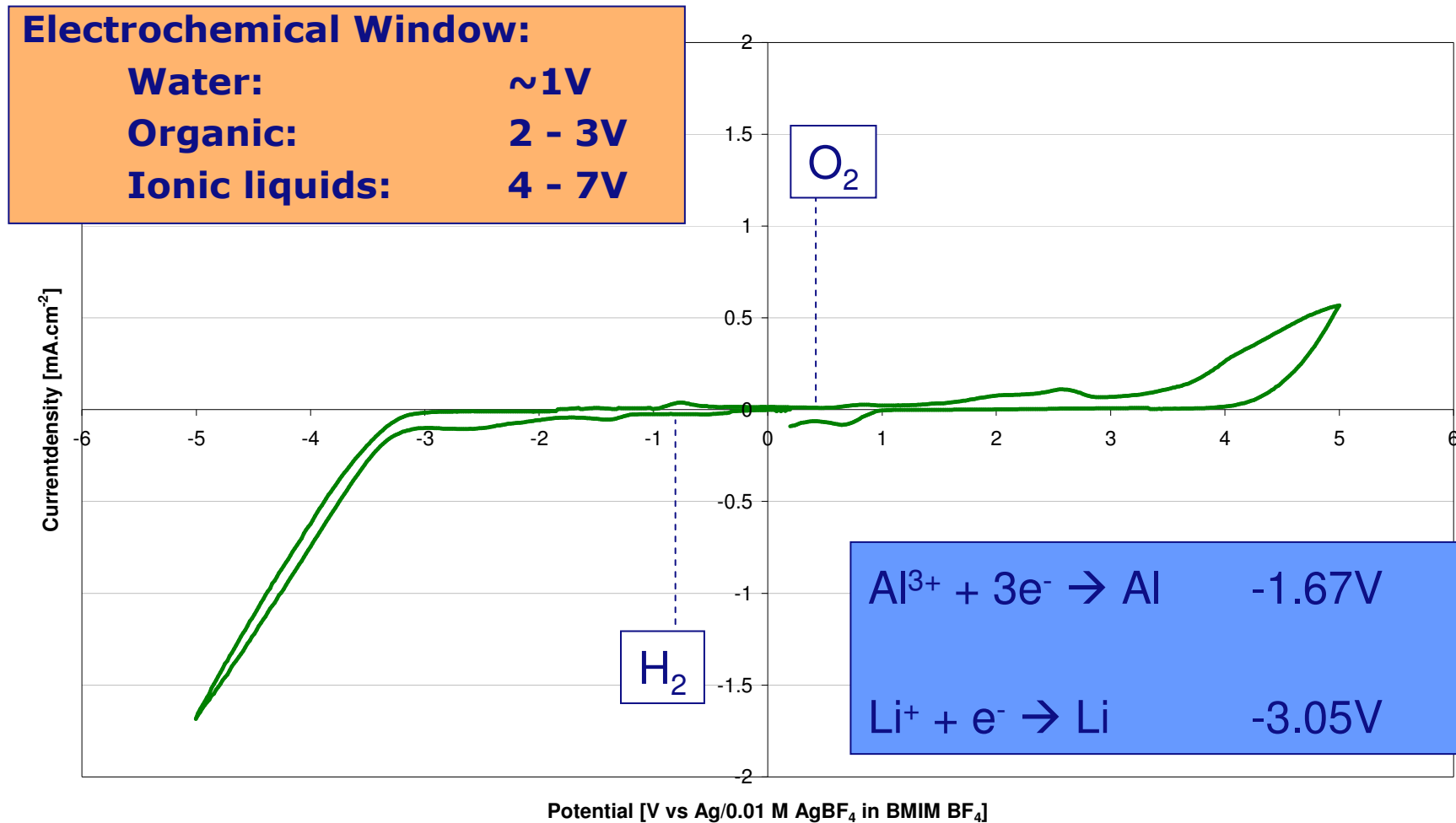
# Publicaties



# Applications of IL



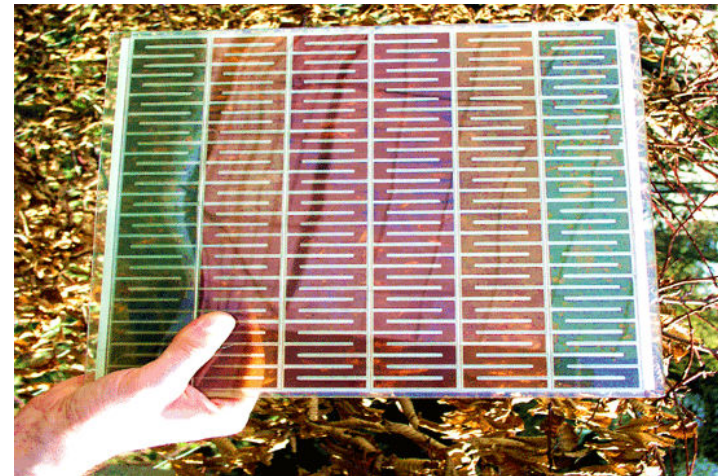
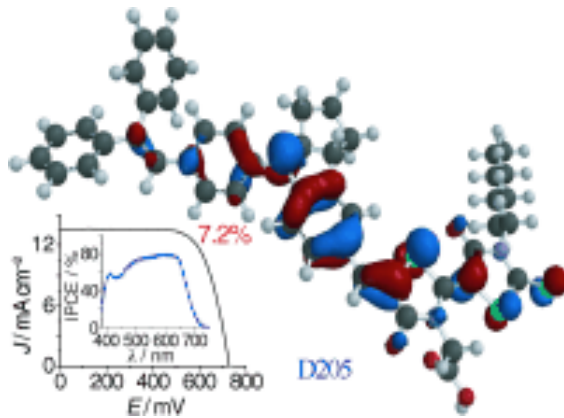
# Ionic liquids: electrochemical stability



# Ionic liquids in electrochemistry

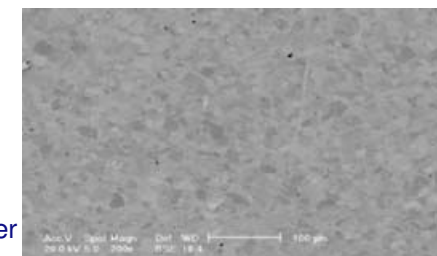
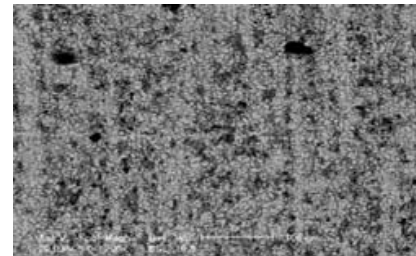
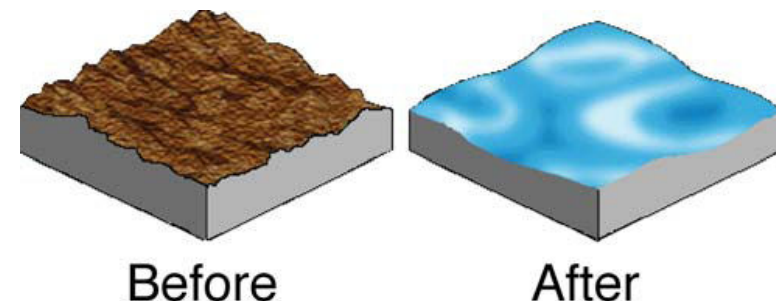
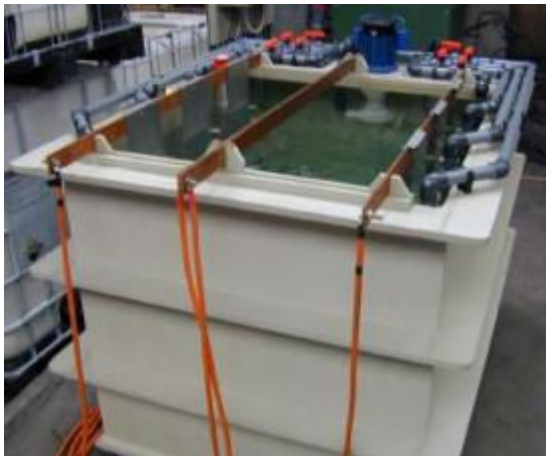
## Electrolytes

- Li-ion batteries
  - Super capacitors (EDLC)
  - Fuel Cells
  - Organic solar cells (Grätzel cell)
    - Non-volatile
    - Large temperature range
- > more robust



# Electropolishing of Stainless Steel (Scionix)

- Glycol:Choline Cl
- Improved current efficiency (>80%)
- Better surface finish on many types of steel
- Non-corrosive, non acid
- Less gas evolution
- Metal recoverable



# Electrodeposition from Ionic Liquids:

- Semi-conductors: Si, Ge
- Metals: Pt, Au, Ag, Pd, Ir, Al, Li, Mg, Ta, Cr
- Alloy deposition: Sn/Ni, Pt/Ru, Al/Mn, Ge/Si, Li/Al
- Electroless deposition: Ag, Cu
- Morphology:
  - nano particles
  - sponge-like layers
  - closed layers



# Chroom plating from Cr(III) in Ionic Liquids

- Alternative for Cr(VI) plating from aqueous solutions
  - Due to Health, Safety and Environmental pressures, a search for alternatives to hexavalent hard chrome plating has been in progress for many years
  - Cr(III) salts are not classified as hazardous and are ideal alternatives
  - A direct hard chrome replacement using trivalent chemistry is the Holy Grail of many designers
- FP6 EU-project IONMET



# IONMET: $\text{CholineCl}:\text{Cr(III)Cl}_3 + 20\%\text{H}_2\text{O}$

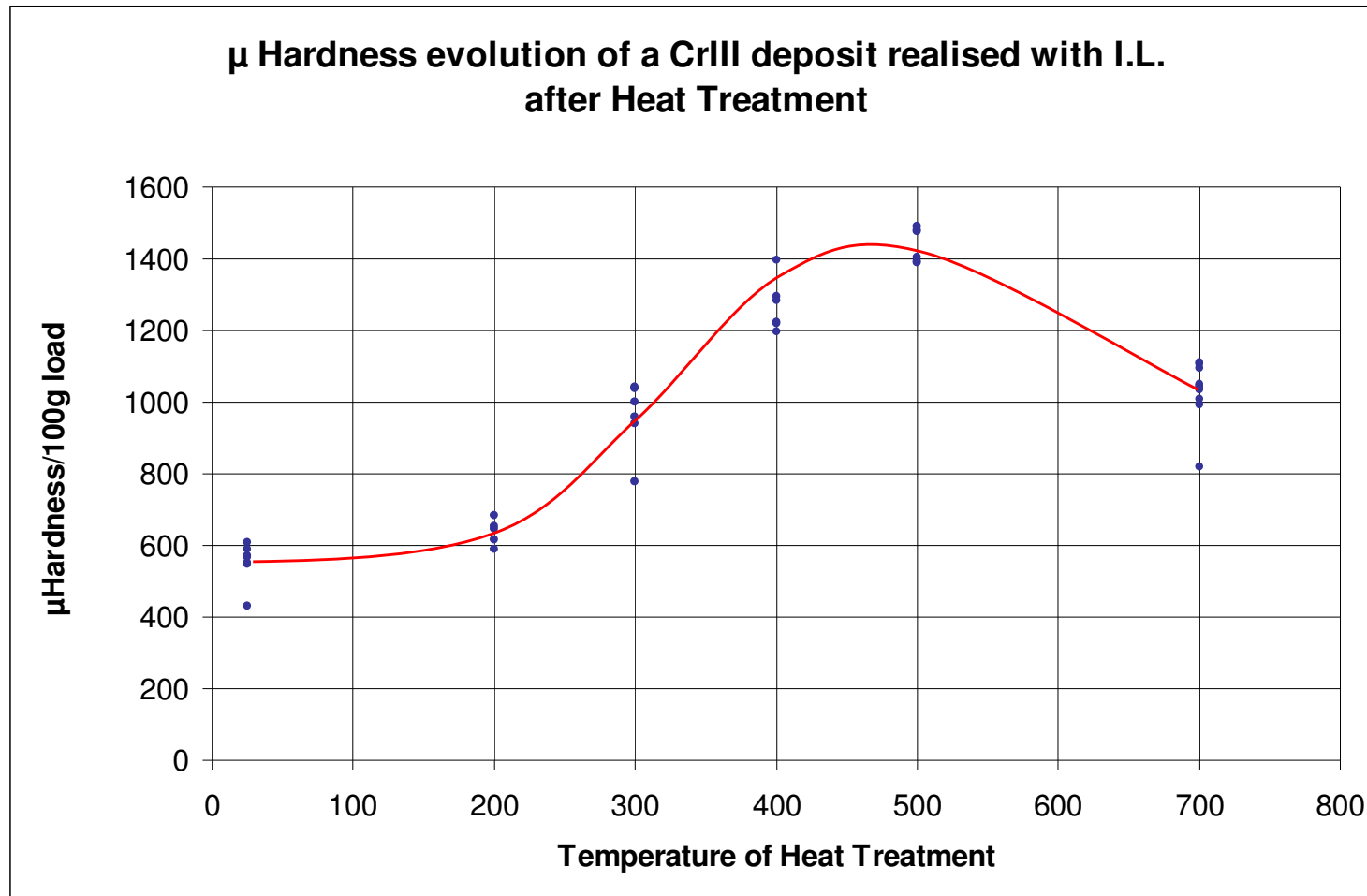


## Main results:

- Metallic and bright homogeneous (darker)
- Good reproducibility
- Efficiency ~ 30 – 40 %
- Deposition rate ~  $0,7 \mu\text{m}\cdot\text{min}^{-1}$  ( $15 \text{ A}\cdot\text{dm}^{-2}$ )
- Hardness ~ 600 to 700 Hv
- Adhesion: to be improved
- Deposit: 25 to 50  $\mu\text{m}$



# Effect of post thermal treatment



# Aluminium deposition from ionic liquids

## Aim:

Low temperature atmospheric pressure deposition of dense pin-hole free aluminium layers from ionic liquid solutions

- New possibilities, alternative technology to vacuum deposition
- Pin-hole free layers
- Using well-known established technology
- High dissolution of Al salts → high deposition rates



# Aluminium deposition from ionic liquids

## Experimental:

Potentiostat: Eco Chemie Autolab PGStat 12

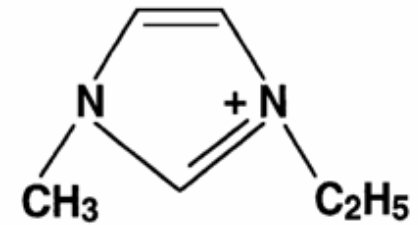
- Substrate: Si/Au  
RVS  
Al
- Reference: Al (99.99%)
- Counter: Al (99.99%)

Argon glove box: < 1ppm H<sub>2</sub>O, O<sub>2</sub>

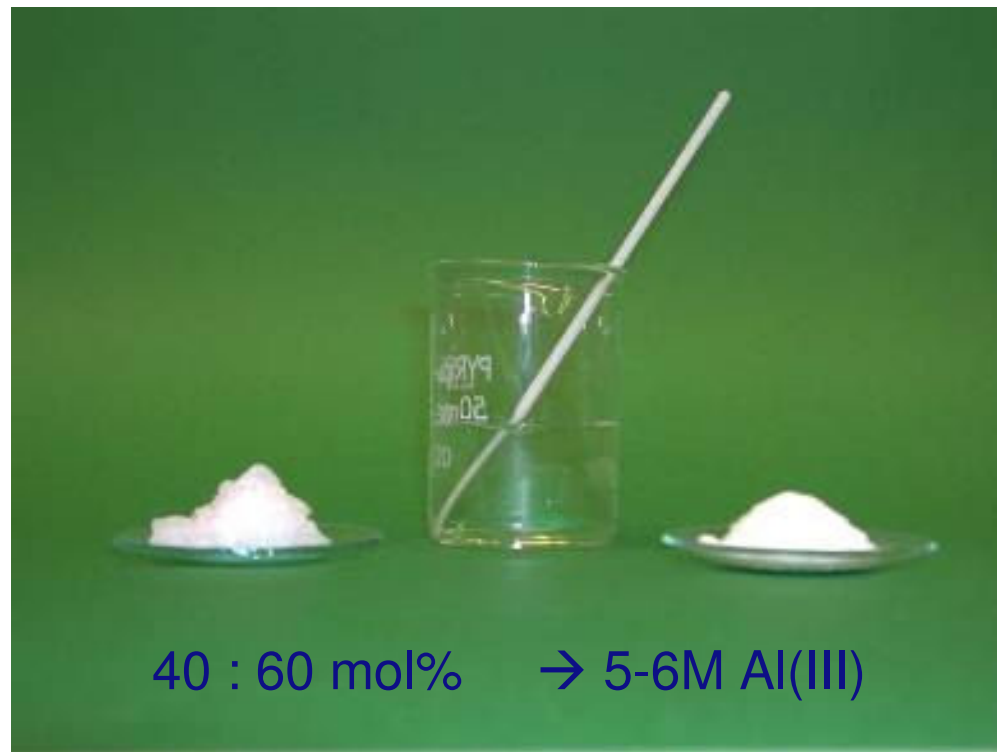


# Ionic liquid system

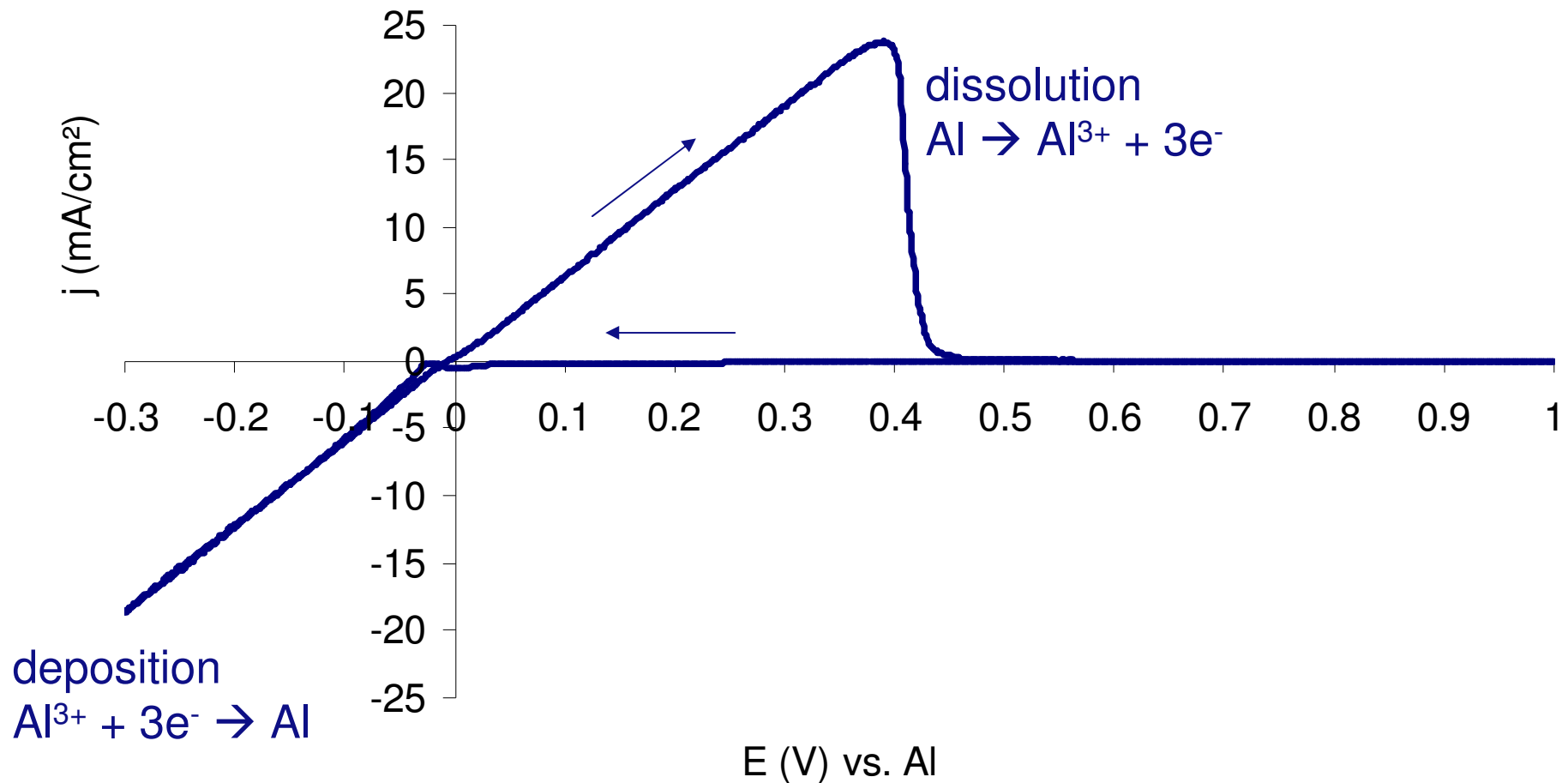
- EMImCl : AlCl<sub>3</sub>
- M.p. EMImCl 78 °C
- M.p. AlCl<sub>3</sub> sublimes



1-Ethyl-3-methylimidazolium

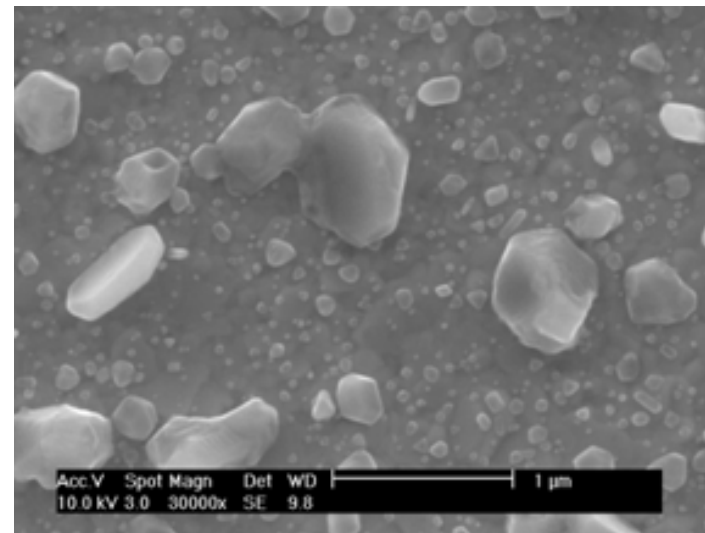
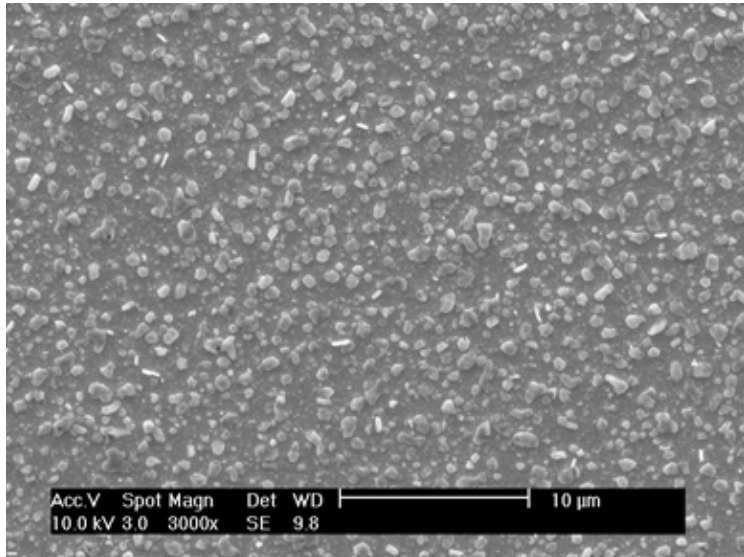


# Electrochemical characterisation

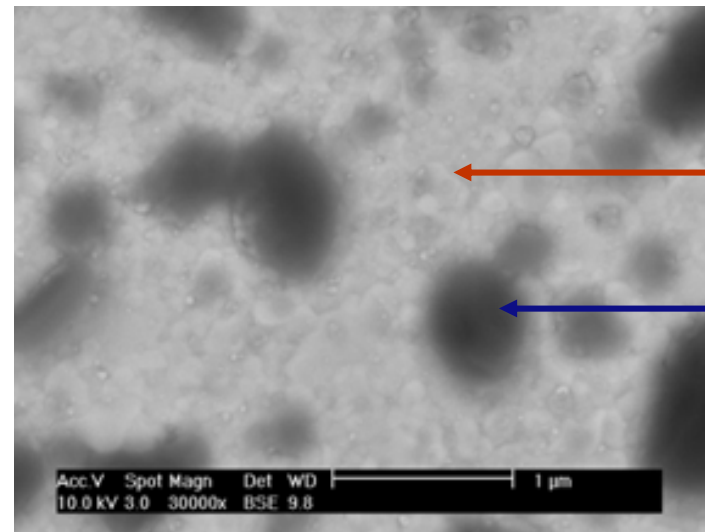
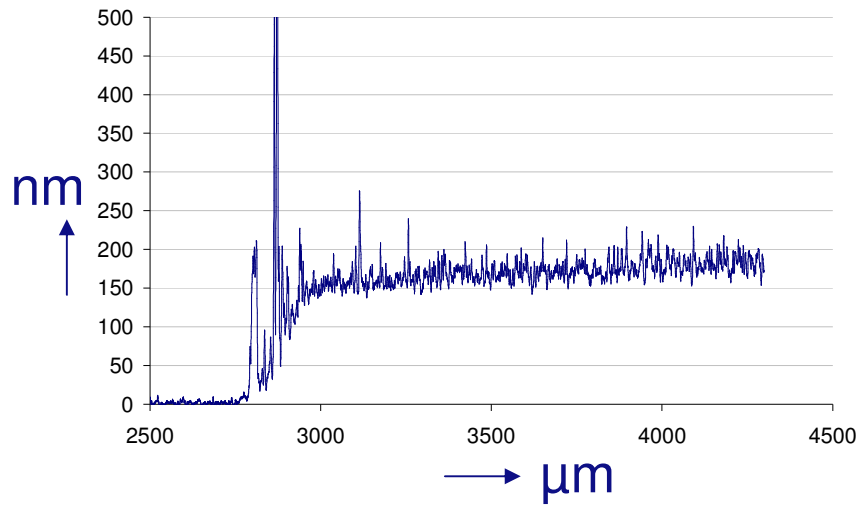


# HR-SEM

# DC deposition



SE



BSE

Au

Al

# DC-Pulse deposition

- Incr. homogeneity
- Incr. layer density, elimination of defects
- Reduction of additives
- Improved layer properties
- Acceleration of deposition process

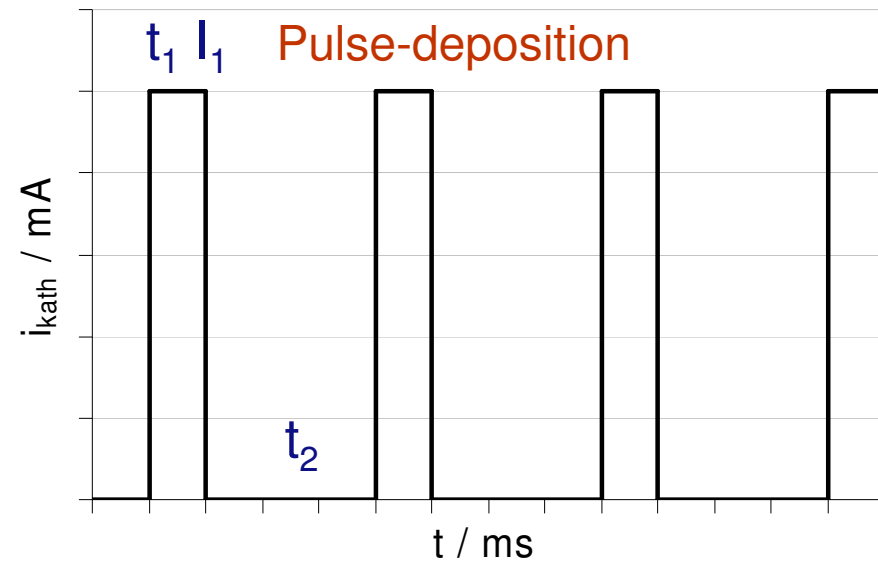
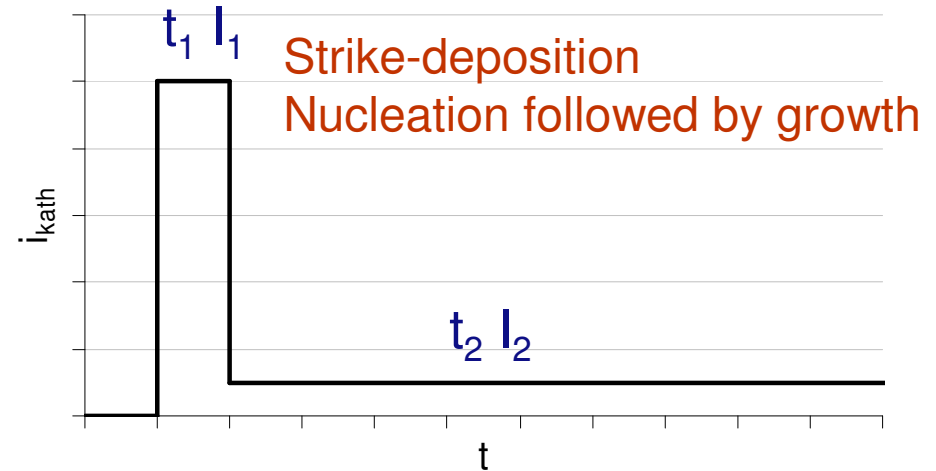
## Results

- Homogeneous deposition
- High reflection 75 → 95%

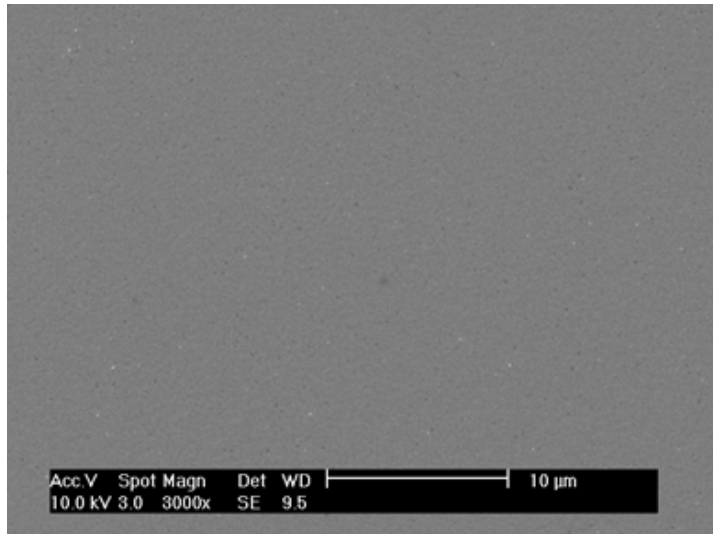


**Au**

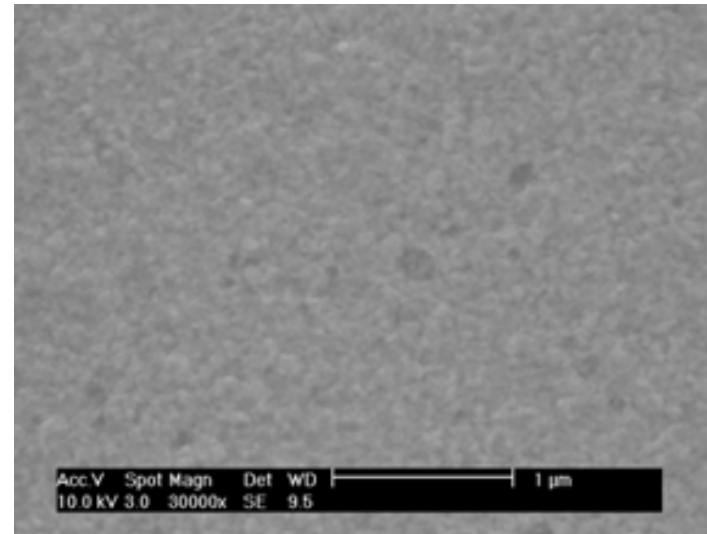
**Al**



# HR-SEM

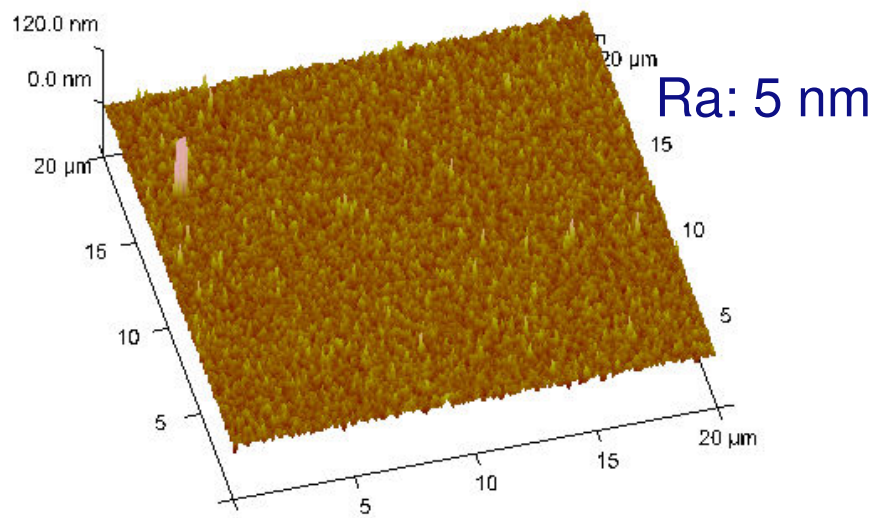


# DC-pulse deposition

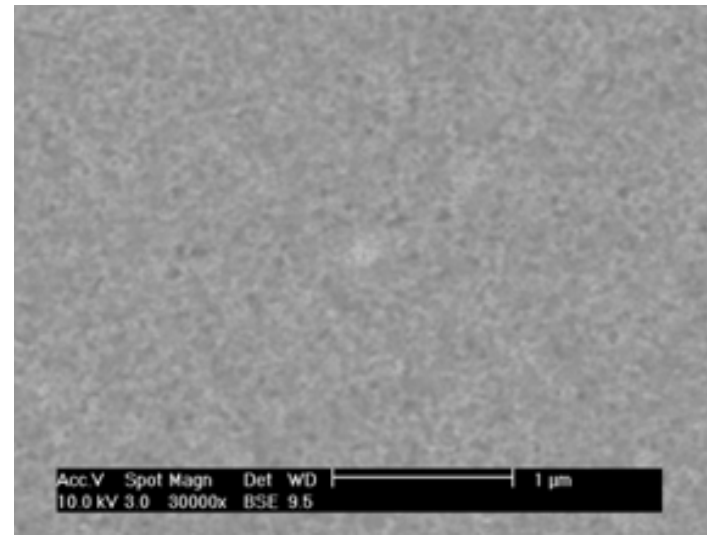


SE

# AFM



**No pinholes observed**



BSE

# Conclusions:

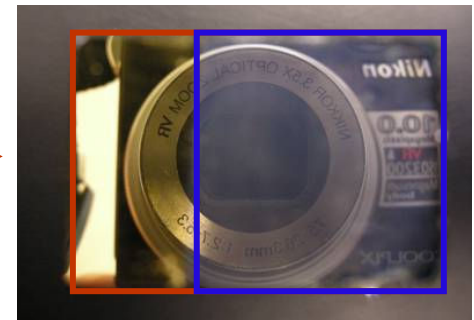
## Aluminium deposition from ionic liquids

- Room temperature process at atmospheric pressure
- Deposition on Au, TCO, Steel-foil ... →
- Stable process / high reproducibility
- Electrochemical efficiency ~ 100%
- Good adherence →

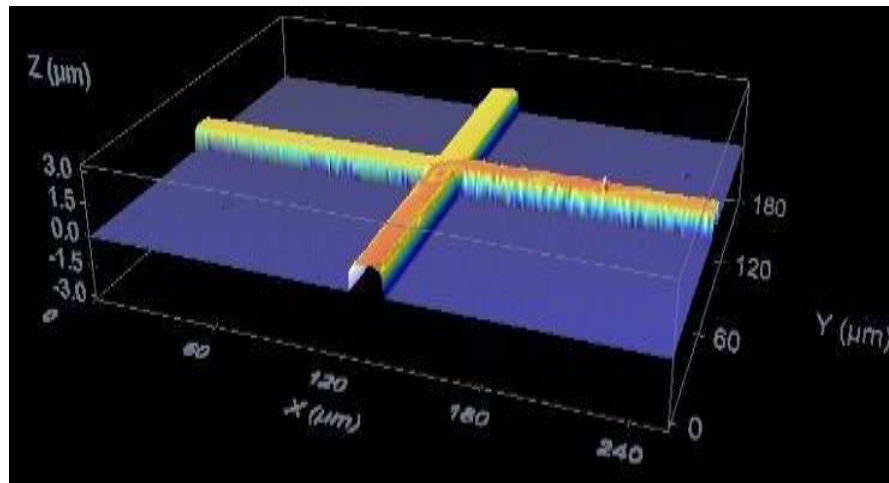
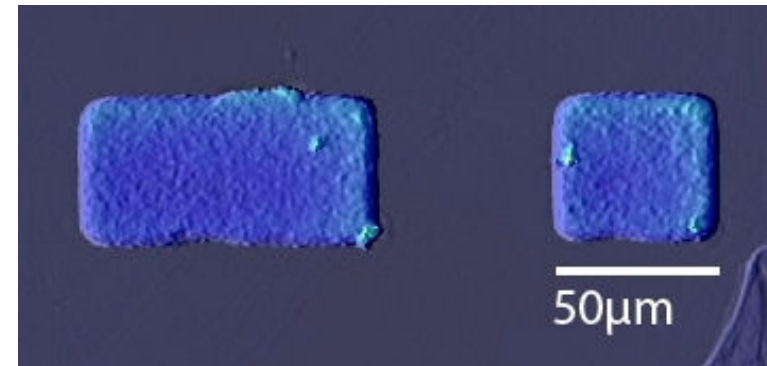
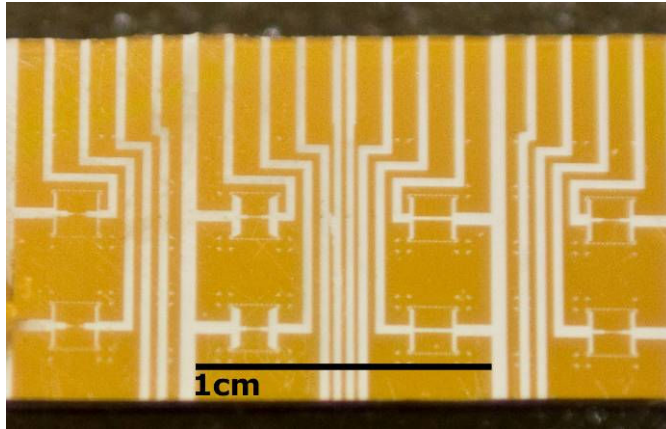


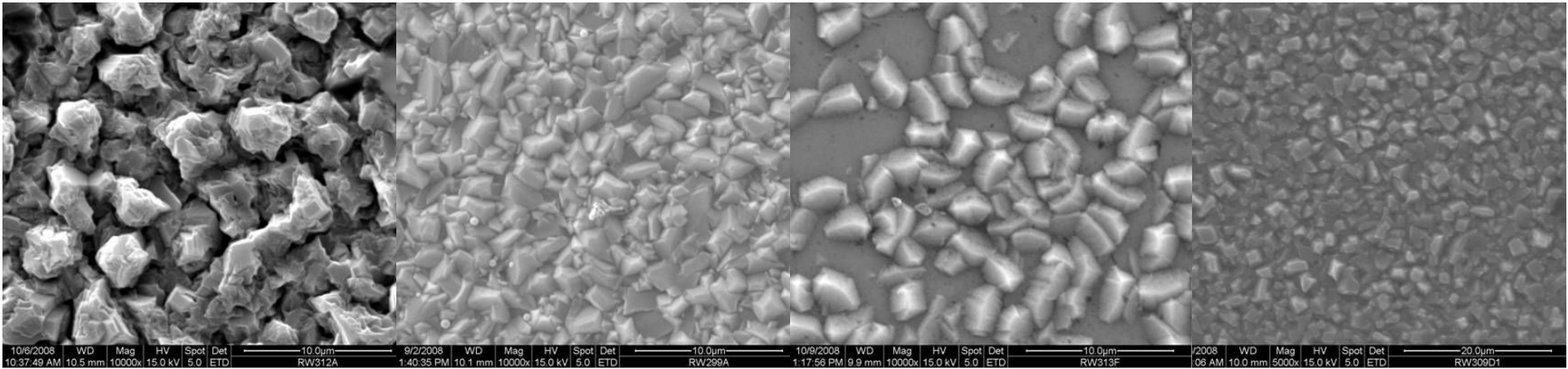
## Advantages Pulse Plating

- Homogeneous layers → closed Al layers (XPS)
- Low surface roughness (high optical reflection) →
- Fast process



# Patterned Al deposition





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