# Chemical Interference of Quantum Size Controlled Photoelectrochemical Fabrication

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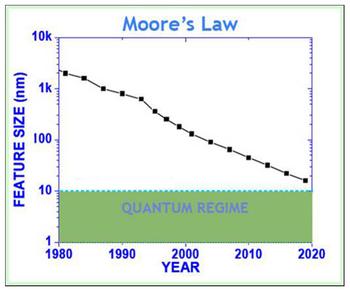
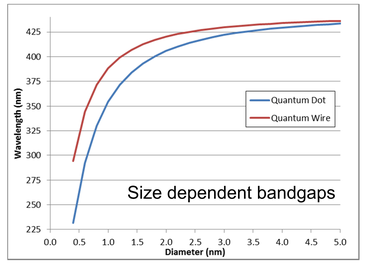
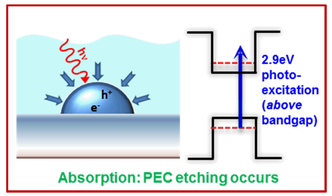
## Quantum confinement

**Properties ⟵ Size, shape and composition ⟶ Bandgap**




## Size-dependent photoelectrochemistry




$2GaN + 6h^+ \longrightarrow 2Ga^{3+} + N_2$

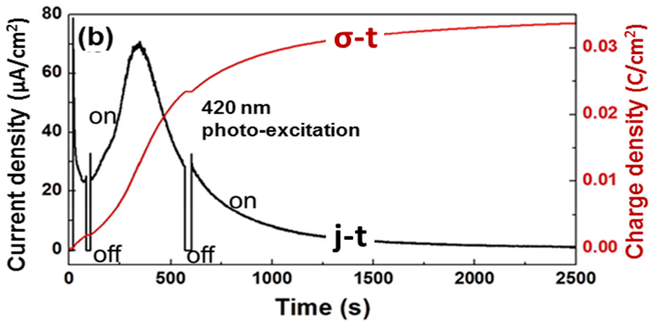
$2Ga^{3+} + 6OH^- \longrightarrow Ga_2O_3 + 3H_2O$

$2H_2O + 4h^+ \longrightarrow 4H^+ + O_2$

$4H_2O + 4e \longrightarrow 2H_2 + 4OH^-$

- Carrier generation depends on light absorption which is bandgap selective
- Electrochemical reactions cause oxidation at the semiconductor surface: etching

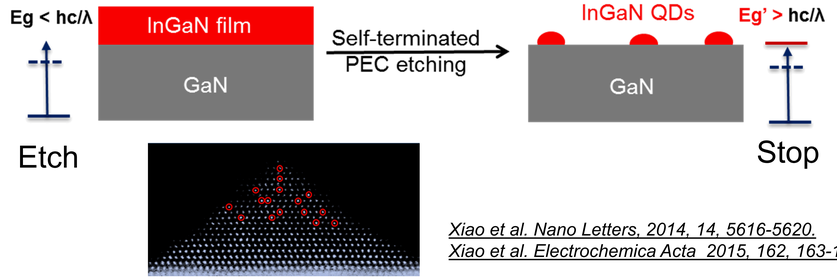
## PEC characteristics and critical requirements




**Chemistries at the semiconductor solid/liquid interface must be optimized**

- No dark etch reactions
- No electrochemical striping
- Size controlled self-termination
- Minimized formation of intermediates that will inhibit or interfere the PEC reactions

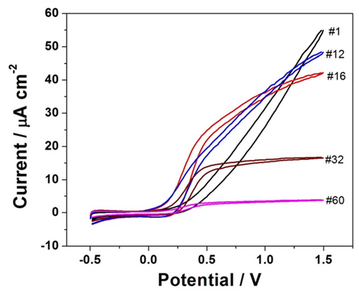
## Quantum size self-terminated PEC

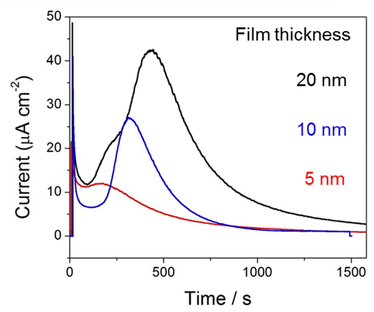



*Xiao et al. Nano Letters, 2014, 14, 5616-5620.*
*Xiao et al. Electrochemica Acta 2015, 162, 163-168.*

- Etch is slowed when the bandgap is substantially increased near the laser energy
- Laser wavelength essentially controls the size of quantum dots

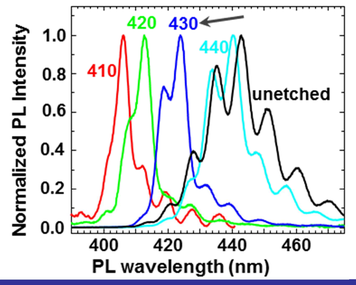
## Self-limited etch process




- Morphology transition from continuous films to nanostructures: s-shape and peak current
- Etch rate becomes negligible at a long time

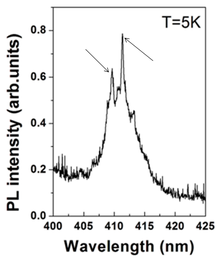
## Photoluminescence




Multiple dots (Left)

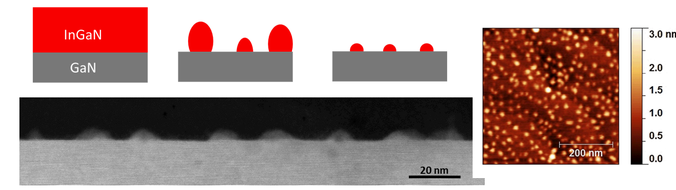
vs.

**Single dots** (Right)

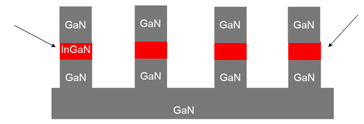


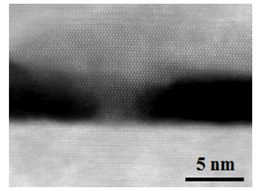

## Quantum structures

**Random QDs from etching of thin films: epitaxial dots**

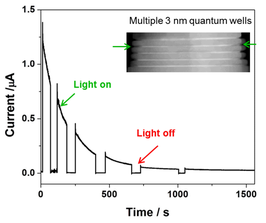


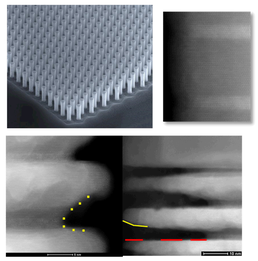

**Capped QD arrays: deterministic single dots and stronger PL**



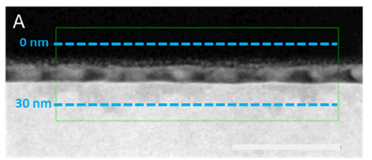




**Multiple QDs from microfabricated nanowire arrays**

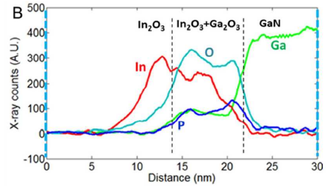


## Chemical interferences: pH effects




*Xiao et al. JPCC, 2015, 119, 28194−28198*




**Quantum size controlled etching is not preserved by:**

- pH induced oxide formation due to insolubility of In and Ga
- Anion intercalation which may occur

## Acknowledgements

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