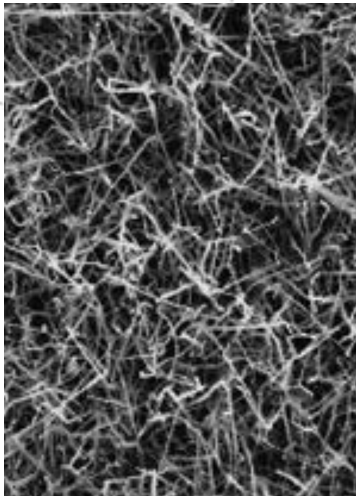
NTNU
Norwegian University of Science and Technology

TMT4320 Nanomaterials
October 31st, 2016

- TNN-Chapter 6-Quantum dots and GaN nanowires



Wikipedia

Quantum Dots (QDs)-Definition

Research in microelectronic materials → need to tailor electronic and optical properties

Progress in epitaxial growth, advances in patterning and other processing techniques → Fabricate «artificial» dedicated materials for microelectronics.

Electronic structure tailored by changing local material composition and by confining the electrons in nanometric size foils or grains → quantization of electron energies → quantum structures

Quantum Dots (QDs)-Definition

If electrons confined by a potential in 3D the nanocrystals are called quantum dots (QDs)

QDs unique properties between bulk semiconductors and individual molecules.

Applications in transistors, solar cells, LEDs, diode lasers, medical imaging or even «qubits».

Quantum Dots (QDs)-Fabrication

Promising QD technologies include:

-Semiconductor Nanocrystal QDs (NCQD)

-Lithographically made QDs (LGQD)

-Field effect quantum dots (FEQD)

-Self-assembled quantum dots (SAQD)

Quantum Dots (QDs)-Fabrication

-Semiconductor Nanocrystal QDs (NCQD)

Nanocrystal (NC(is a single crstal with a diameter of few nanometers

A NCQD is a nanocrystal which has a smaller band gap than the sourranding material

Attractive for optical applications because their color determined by their dimensions

Size can be controlled by filtering NCQDs or tunning parameters of the chemical process

Quantum Dots (QDs)-Fabrication

-Semiconductor Nanocrystal QDs (NCQD)

CdSe nanocrystals.

Spherical crystallites: 1-10 nm diameter

Cd(CH3)2+ Se in TBP + TOPO (360 ^{o}C in Ar) → CdSe NCQDs

Photo stability and quantum yield can be improved by covering with CdS.

Quantum Dots (QDs)-Fabrication

-Semiconductor Nanocrystal QDs (NCQD)

CdSe nanocrystals.

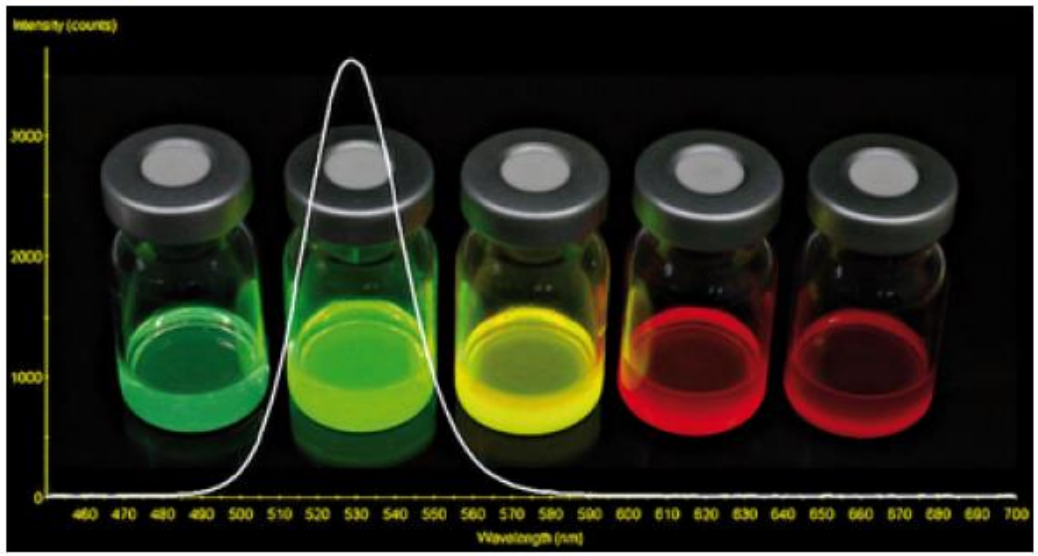


Fig. 6.2 *(see page 178)* CdSe NCQDs that fluoresce into different colours depending on their size. (*Source:* http://commons.wikimedia.org/wiki/File:CdSeqdots.jpg).

Quantum Dots (QDs)-Fabrication

-Semiconductor Nanocrystal QDs (NCQD)

Silicon nanocrystals.

Si/SiO_2 NCQDs → Si clusters embedded in insulating SiO_2

Fabricated by ion-implanting Si atoms into either ultapure quartz or thermally grown SiO_2

Structure unknown with 3nm diameters and NCQD density of $2x10^{-19}$ cm^{-3}

Quantum Dots (QDs)-Fabrication

-Lithographically made QDs (LGQD)

Vertical QD (VQD) is formed by etching out a pillar from a quantum wall (QW) or a double barrier heterostructure (DBH)

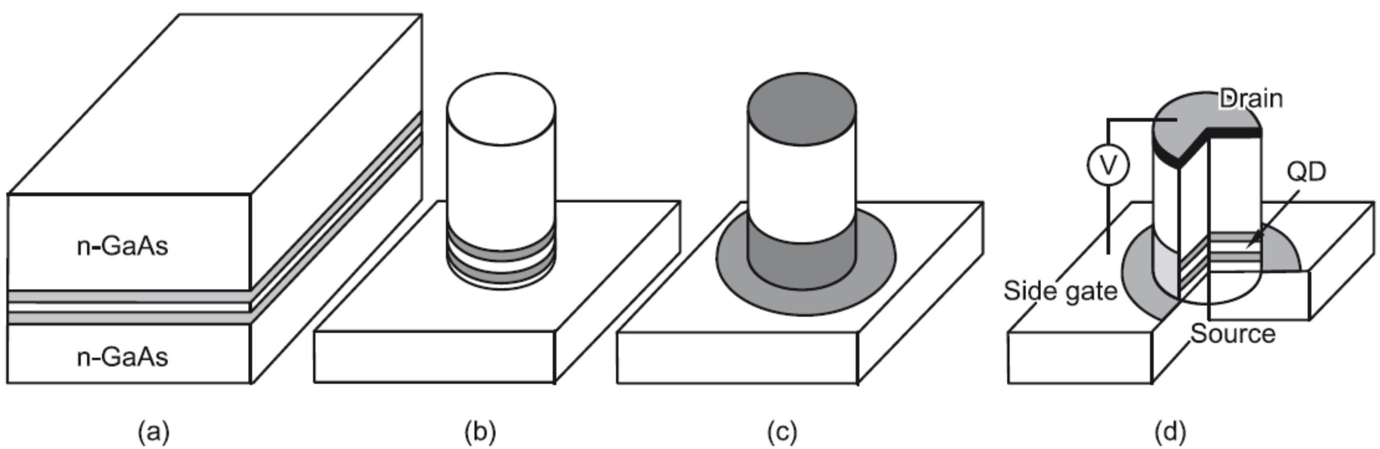


Fig. 6.3 Schematic representation of the fabrication process of a VQD. (a) Epitaxial growth of a DBH, (b) etching of a pillar through the DBH and (c) the metallization.

Quantum Dots (QDs)-Fabrication

-Lithographically made QDs (LGQD)

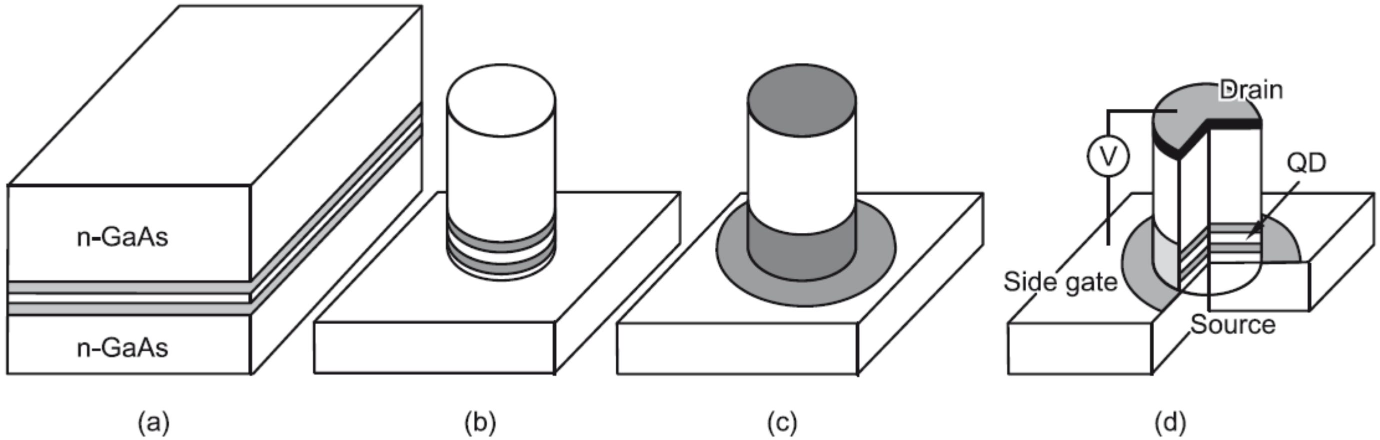


Fig. 6.3 Schematic representation of the fabrication process of a VQD. (a) Epitaxial growth of a DBH, (b) etching of a pillar through the DBH and (c) the metallization.

Al-GaAs/InGaAs/AlGaAs DBH was grown epitaxially after which a cylindrical pillar was etched trough the DBH.
Finally, metallic contacts
Diameter of about 500 nm and thickness of about 50 nm
Attractive for electrical devices

Quantum Dots (QDs)-Fabrication

-Field effect quantum dots (FEQD)

In a FEQD the charge carries are confined into a 2D electron gas (2DEG) by a modulation-doped heterojunction.

Within the 2DEG plane, the charges are electrostatically confined by external gates.

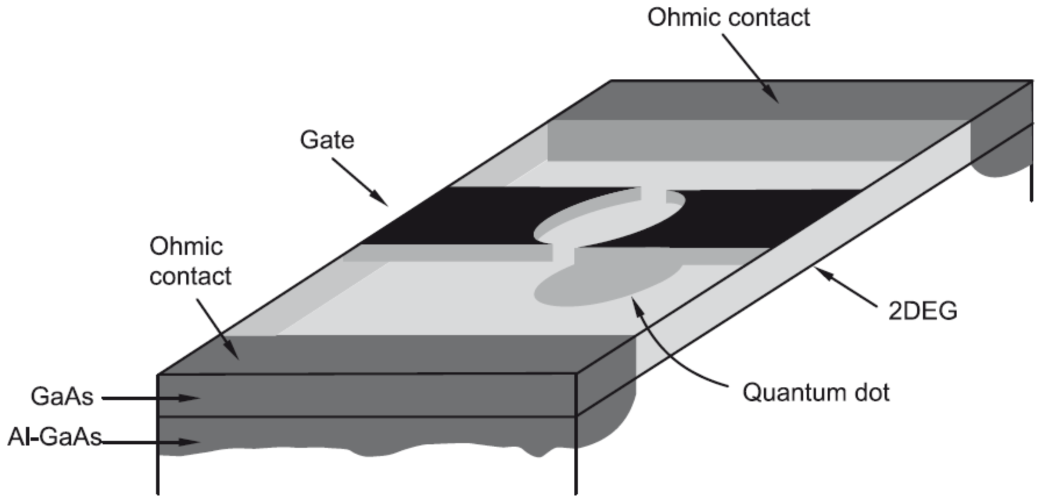


Fig. 6.4 A schematic drawing of an FEQD in a 2DEG at the material interface between Al-GaAs and GaAs.

Quantum Dots (QDs)-Fabrication

-Field effect quantum dots (FEQD)

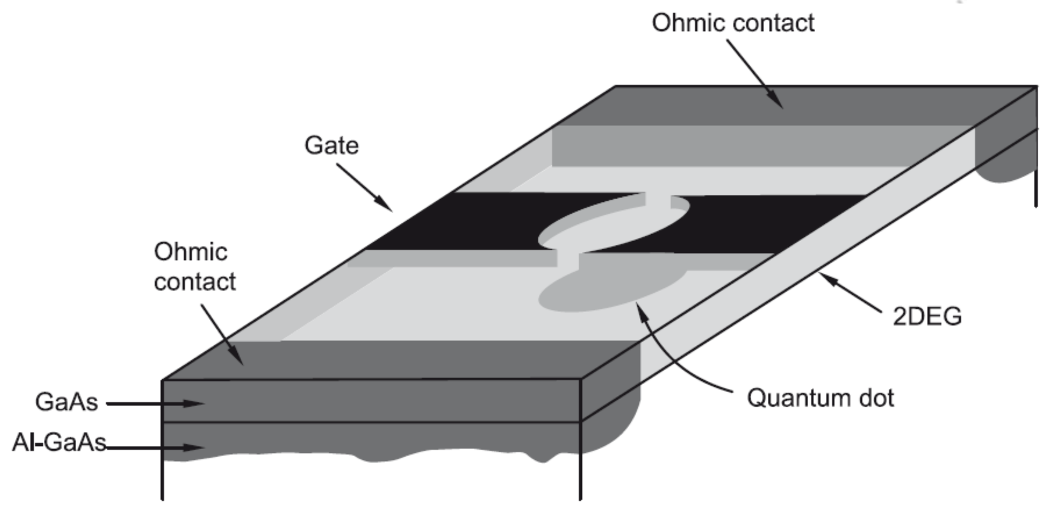


Fig. 6.4 A schematic drawing of an FEQD in a 2DEG at the material interface between Al-GaAs and GaAs.

FEQD with a diameter of 200 nm → spacing of energy level is typically tens of µeV.

Attractive for low temperature infrared light detectors → very smooth gate-induced potential and high-quality heterostructures interfaces.

Quantum Dots (QDs)-Fabrication

-Self-assembled quantum dots (SAQD)

In SAQD → use of an island formation in epitaxial growth

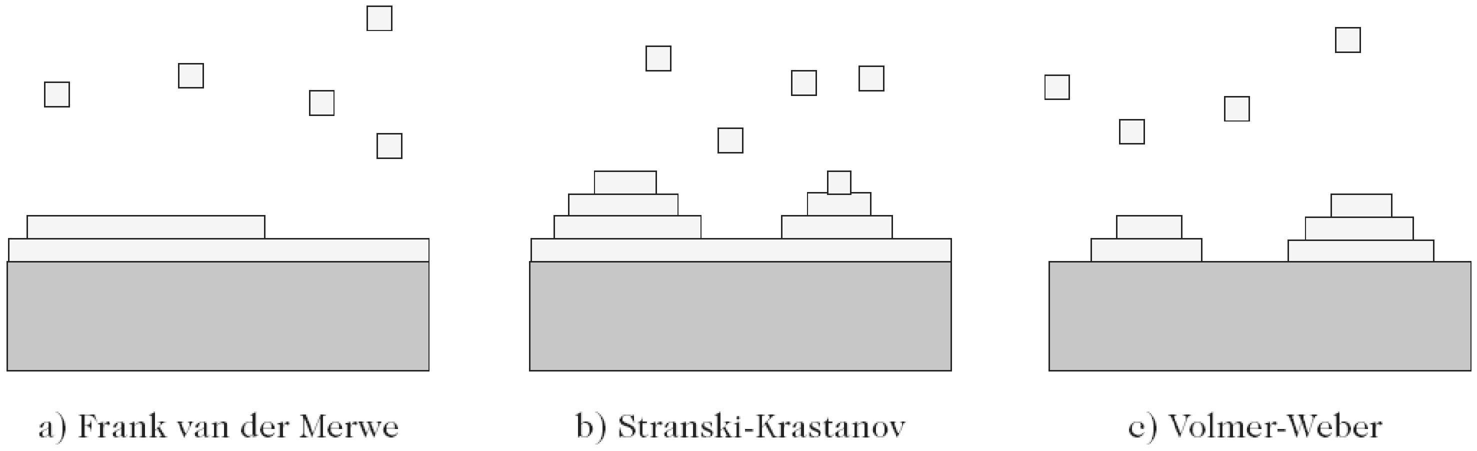
Major self-assembly growth techniques are vapour phase epitaxy (VPE) and molecular beam epitaxy (MBE)

Layered growth of atoms:

- Layer by layer mode
- Island mode
- Intermediate mode

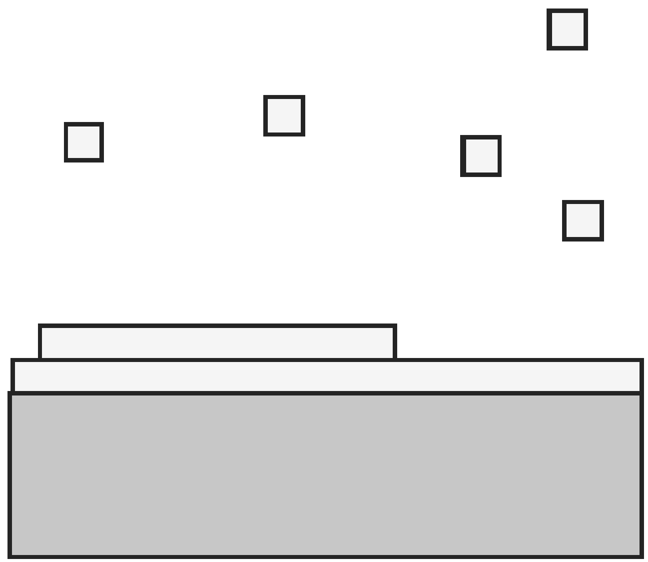
Growth modes

- The equilibrium shape of the adsorbate deposited on the surface of the substrate depends on the energy balance between the surface free energies of adsorbate and substrate and that created at their interface
- Three growth modes are accessible:



Frank-van der Merwe (layer-by-layer)

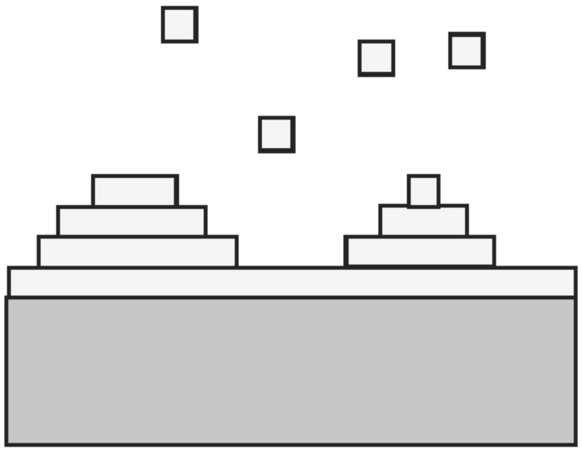
- A new layer only begins when the previous one has been completed, and the successive layers tend to spread out
- If $\gamma_{substrate} > \gamma_{adsorbate} + \gamma_{interface}$, the first layer will tend to wet the substrate



a) Frank van der Merwe

Stranski-Krastanov

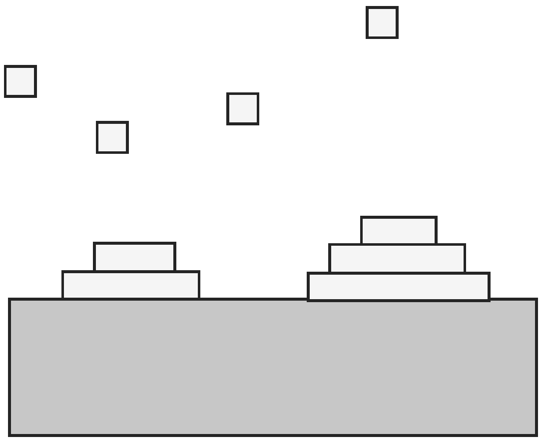
- Intermediate growth mode that begins with two-dimensional growth and then continues by three-dimensional growth
- Overall interaction energy between the adsorbed atoms and the film varies significantly with the thickness of the deposited film



b) Stranski-Krastanov

Volmer-Weber (island)

- Atoms tend to bind to each other rather than to the substrate → small clusters nucleate directly on the surface of the substrate
- If $\gamma_{substrate} < \gamma_{adsorbate} + \gamma_{interface}$, the adsorbate will form 3D islands directly

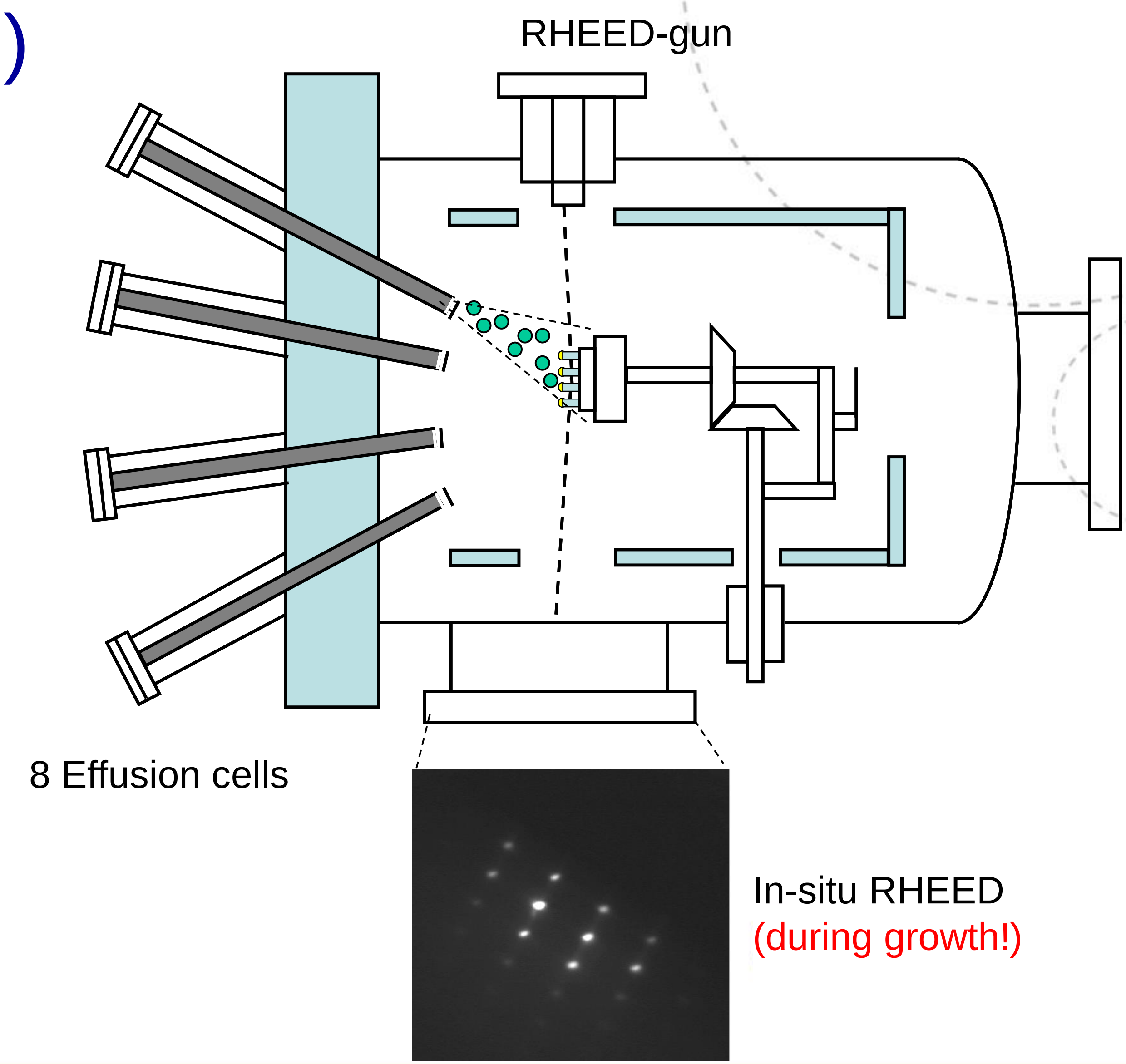


c) Volmer-Weber

Molecular Beam Epitaxy (MBE) system (Varian Gen II)

- III: Ga, In, Al
- V: As, Sb
- Dopants: Si, Be, Te

- High vacuum → high purity
- Heterostructures with abrupt interfaces
- Growth rate can be accurately controlled
- In-situ characterization



Quantum Dots (QDs)-Applications

Computing

-Quantum calculations

Biology

-Replace organic dyes. Better brightness and stability

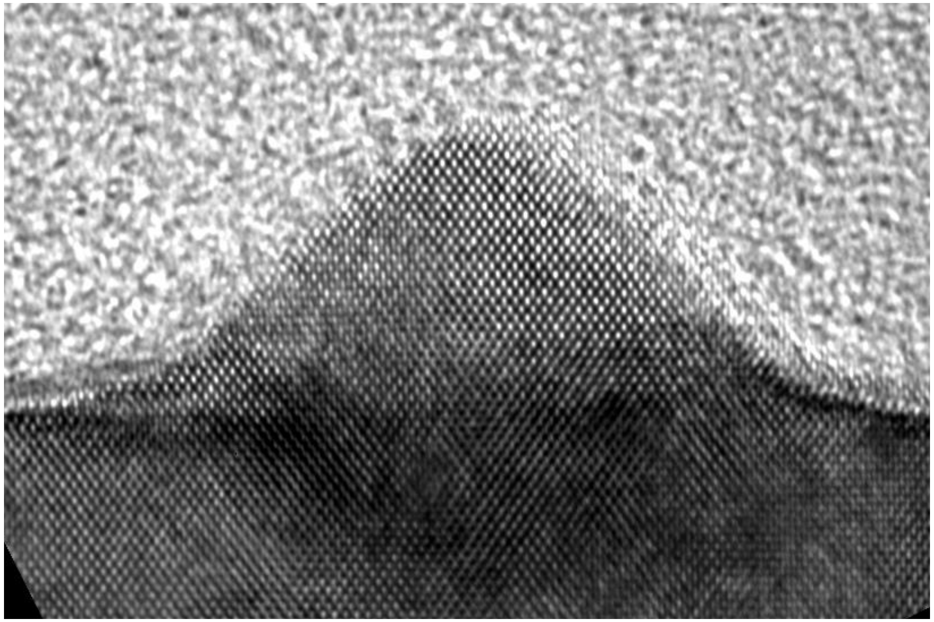
Light emitting devices

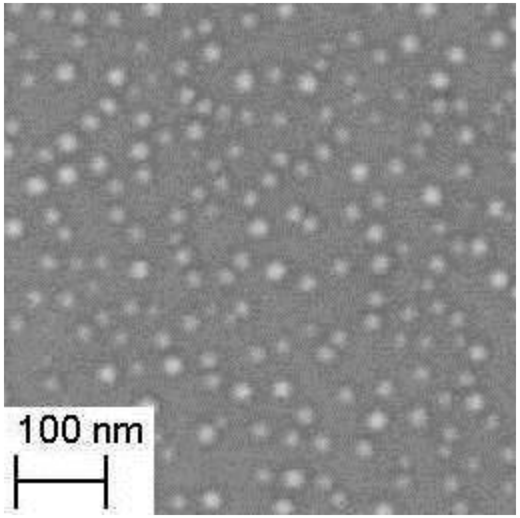
-QDs emit light in very specific Gaussian distribution

Photovoltaic devices

NTNU research: Quantum dot intermediate band solar cell materials

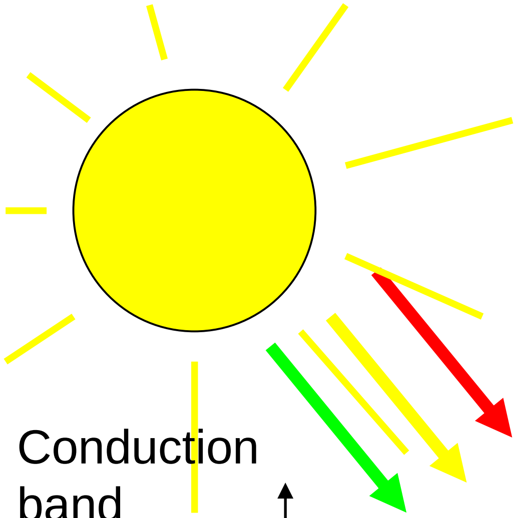
- Associate professor Turid Worren Reenaas and co-workers, Department of Physics

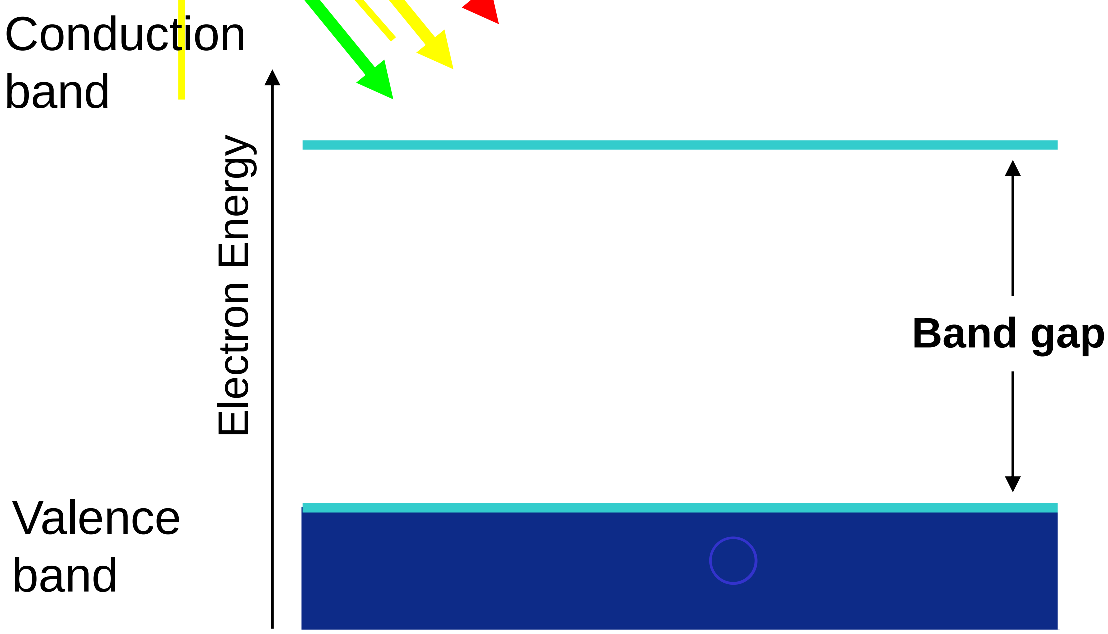




InAs QDs on GaAs

Energy diagram of a conventional solar cell*

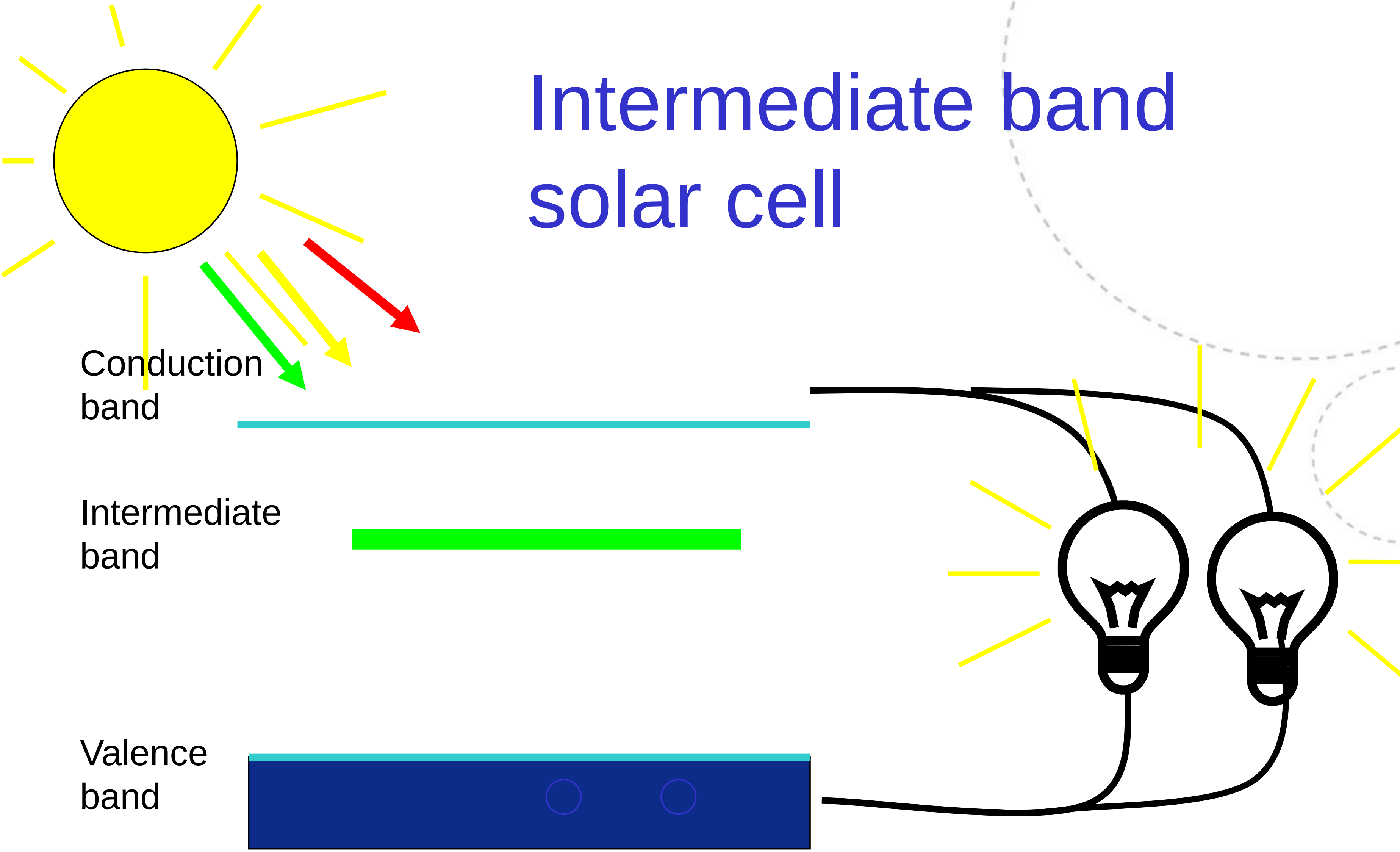




A smaller bandgap would result in a larger photo-generated current, but the voltage delivered by the solar cell is always smaller than the bandgap (divided by the electron charge).

*Omitting the pn-junction and contacts

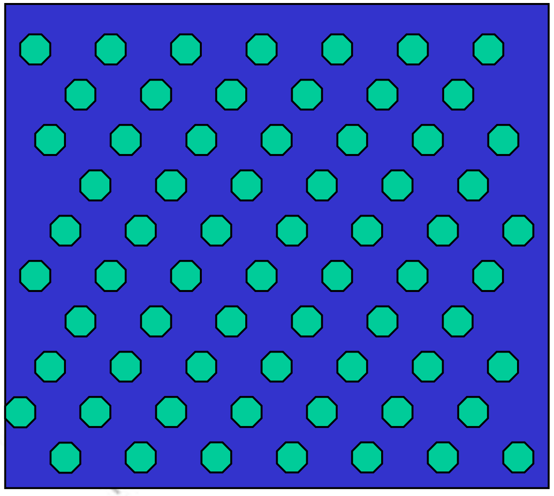
Intermediate band solar cell

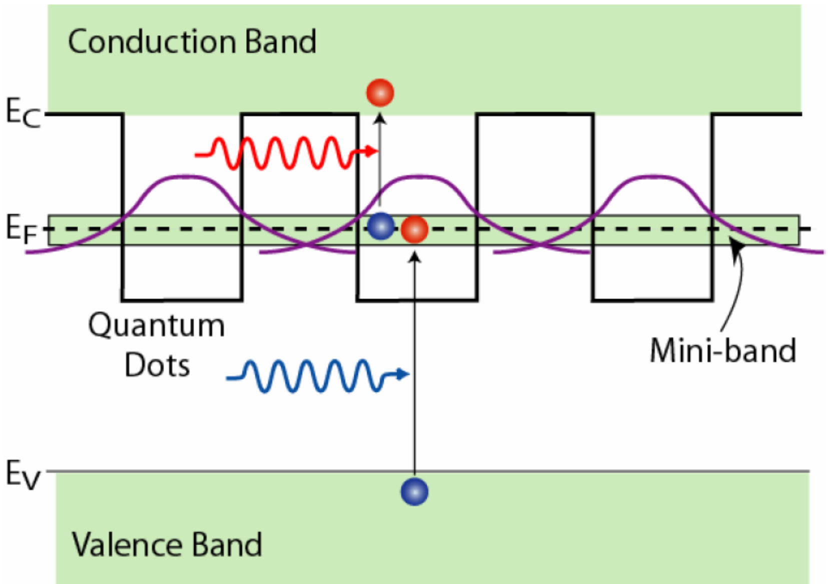


Increase the photo-generated current without reducing the bandgap and thus the voltage.

Quantum dot-based IBSC

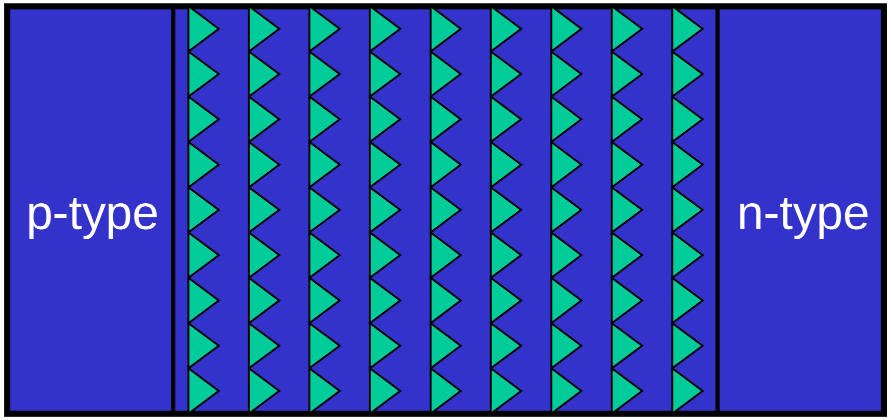
- Quantum dot (QD) is a nanometer sized particle of a low band gap material surrounded by a material with larger band gap:
  - Energy levels depend on dot size and on the bandgap difference.
  - Many quantum dots placed closed to each other in a lattice can form one or more intermediate bands
- The intermediate band arise from confined electronic states of the electrons in the potential wells of the conduction band
- High density of QDs → electron wave functions overlap → electrons in the intermediate band become delocalized





Quantum dot IBSC

The quantum dots are placed in the pn-junction of the conventional solar cell, to form a pin-junction.



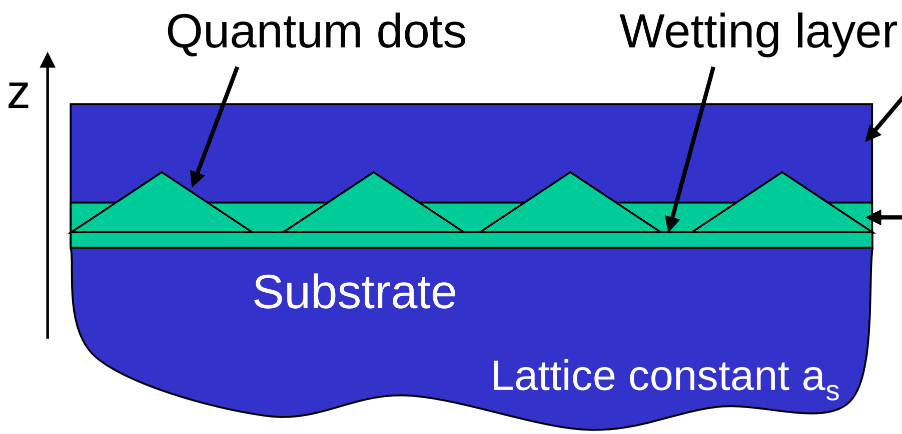
Challenge: Grow many (50-100 or more) layers of QDs without creating defects)

Solution:
Strain balancing

A single dot absorbs little solar radiation:

A high layer density of quantum dots and many layers stacked on top of each other are needed.

Self-organized growth of quantum dots



Finally grow a layer of barrier (large bandgap) material

Deposit a few atomic layers of quantum dot material, with lattice constant $a_d > a_s$.

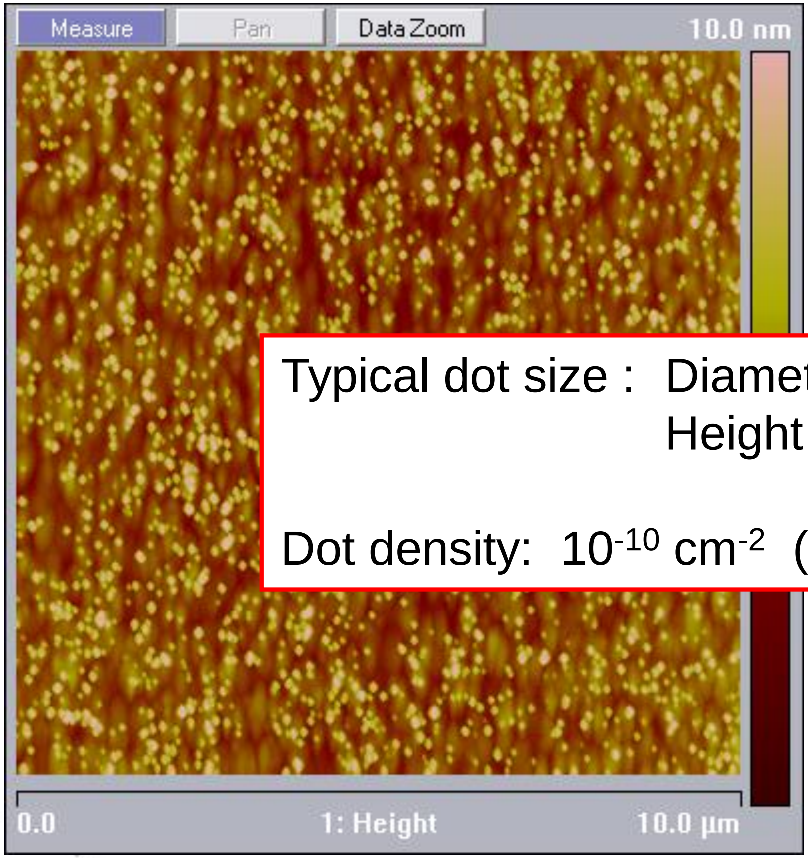
Difference in lattice constants ($a_d > a_s$) compresses the deposited layer in-plane. The deposited material relaxes (<u>self-organizes</u>) to form pyramidal shaped islands when the deposited layer is <u>thicker than a critical thickness</u>.

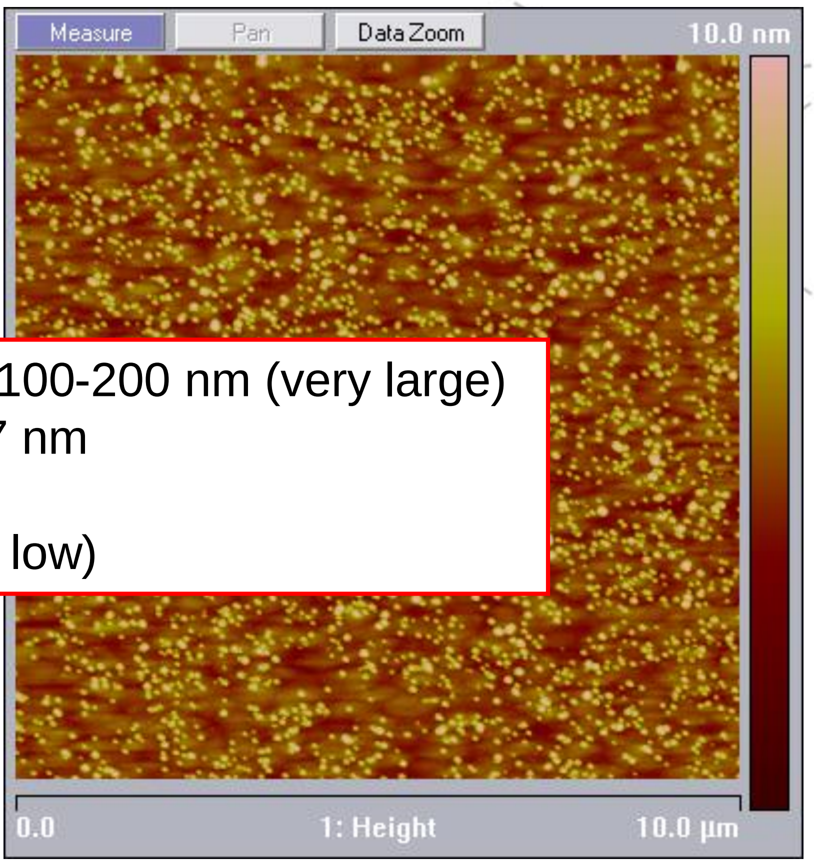
Atomic Force Microscopy (AFM)

1 QD layer

GaAs/AlAs/InAs

GaAs/AlAs/GaAs/InAs





Typical dot size : Diameter 100-200 nm (very large)
Height 2-7 nm

Dot density: 10^{-10} cm^{-2} (too low)

GaN nanowires

GaN: Wide-band gap semiconductor for electronic and opto-electronic devices.

Simplest method for GaN nanowires: thermal evaporation of GaN powders at temperatures of 1200 ^{o}C in Ar.

Diameter of 30 nm and length of several microns. Dielectric constant much larger for nanowires explained by space charge polarization and rotation direction polarization.

GaN nanowires

Other synthesis methods include Laser ablation or Hot Filament Chemical Vapor Deposition (HFCVD)

Synthesis method with experimental parameters	**Resulting wire or tube features**
Laser ablation: GaN/Fe target, 250 torr, 900°C	~10 nm diameter, >1 µm long, [1 0 0] growth direction
HFCVD: Ga_2O_3/C powder, NH_3, 200 torr, 900°C,1 hour	5–12 nm diameter, >1 µm long, single crystalline.
Direct reaction of Ga with NH_3: 825–925°C, 15 torr, 3–4 hours	20–150 nm diameter, 500 µm long

GaN nanowires

Laser ablation

Available online at www.sciencedirect.com
ScienceDirect
Applied Surface Science 254 (2008) 1947–1952
applied surface science
www.elsevier.com/locate/apsusc

Synthesis of GaN nanowires on gold-coated SiC substrates by novel pulsed electron deposition technique

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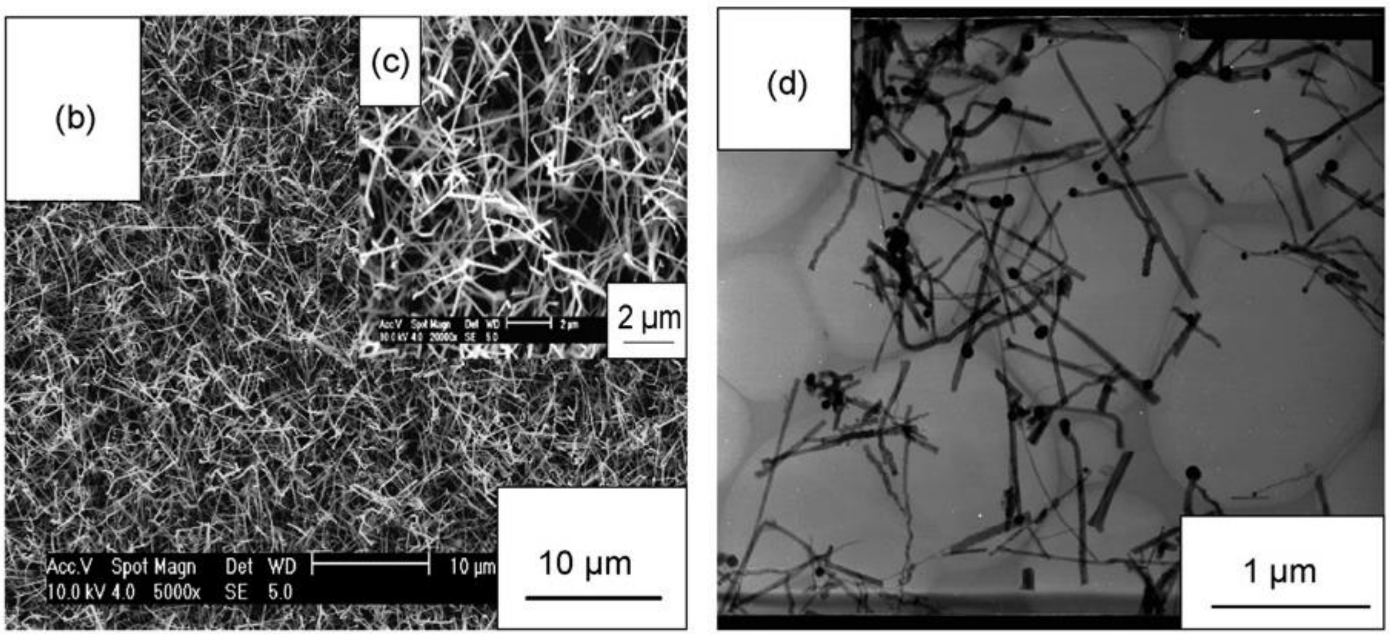

GaN nanowires

Other synthesis methods include Laser ablation or Hot Filament Chemical Vapor Deposition (HFCVD)

Journal of Physics and Chemistry of Solids 74 (2013) 862–866

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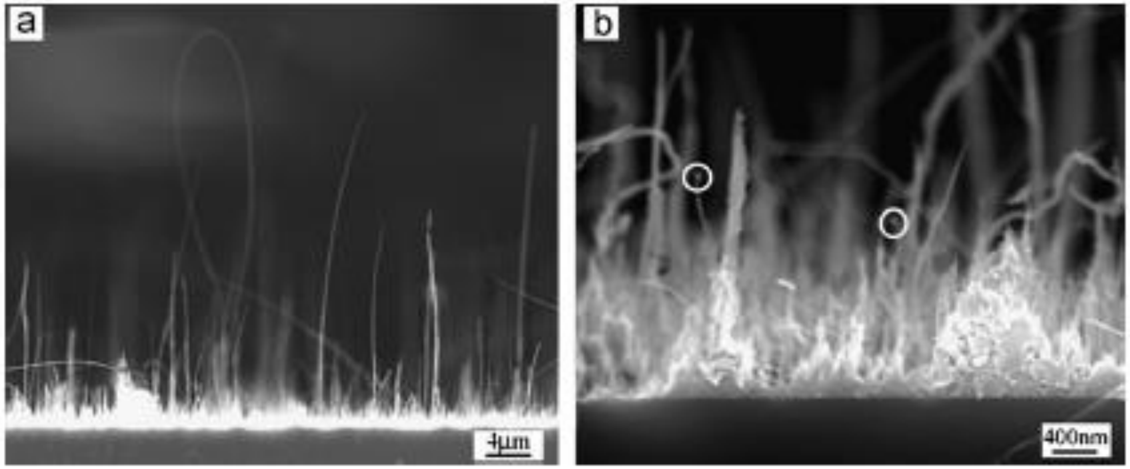

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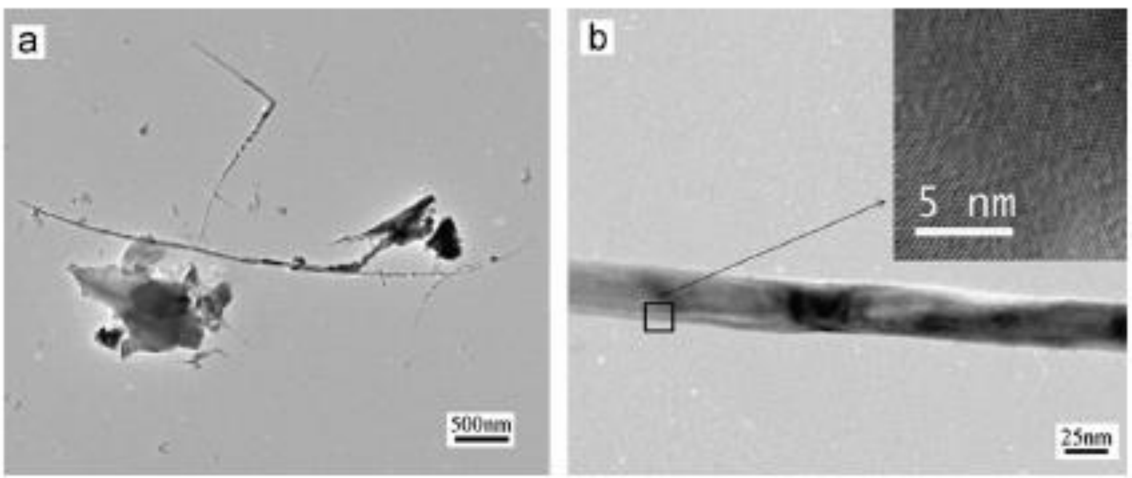

Fig. 4. TEM images of (a) GaN NWs and (b) single GaN NW. The inset in Fig. 4(b) is the high resolution TEM of GaN NW.

GaN nanowires-applications

Ultraviolet-blue laser

Shuji Nakamura → developed blue LED

Nobel prize in Physics in 2014.

In Trondheim last September as

http://ssleec.ucsb.edu/nakamura

https://www.youtube.com/watch?v=vp9z9r2kJUI

Nanowire fabrication

Few methods of nanowire fabrication:

- Template assisted synthesis
- Electrochemical deposition
- High-pressure injection
- Chemical vapour deposition
- Laser assisted techniques
- VLS method

Next lecture-Nanowire fabrication

Few methods of nanowire fabrication:

- Template assisted synthesis
- VLS method