Pivotal Role of MBE in Nanostructure Fabrication

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Illustration of 3-temperature method

$T_1 =$ high temperature $T_S =$ intermediate (substrate) temperature $T_3 =$ low temperature


First application to grow polycrystalline InSb and InAs films on glass substrates under high vacuum conditions for Hall sensors  >> *Compound Semiconductors*
Real-time analysis of crystal growth

Line-of-sight quadrupole mass spectroscopy (QMS)

Reflection high-energy electron diffraction (RHEED)
It all began with ....

W. Shockley
"Transistor electronics"
Proc. IRE 40, 1289 (1952)

H. Kroemer
"Wide-gap emitter for transistors"
Proc. IRE 45, 1535 (1957)

K. G. Günther
"Three-temperature method"
Z. Naturforsch. 13a, 1081 (1958)

J. R. Arthur
"Interaction of Ga and As, molecular beams with GaAs surfaces"
J. Appl. Phys. 39, 4032 (1968)

H. Kroemer
"Heterojunction injection lasers"
Proc. IRE 51, 1782 (1963)

A. Y. Cho
"Epitaxial growth of GaAs by molecular beam epitaxy"

L. V. Keldish
"Artificial periodic potential through ultrasonic-wave deformation"
Fiz. Tverd. Tela 4, 2265 (1962)

L. Esaki and R. Tsu
"Artificial semiconductor superlattices"

BAND-GAP ENGINEERING
(WAVE FUNCTION ENGINEERING)

SUBNANOMETER (ATOMIC)
CONTROL OF CRYSTAL GROWTH

ARTIFICIAL (MAN-MADE) MATERIALS
VERTICAL TRANSPORT (TUNNELING)
-----> BLOCH OSCILLATOR
On bare surface numerous dangling bonds exist

Therefore this surface is energetically **not** stable >>> **Reconstruction** required
Idealized crystals and their diffraction patterns

bulk crystal
truncated crystal lattice
reconstructed surface
epitaxial layer
epitaxial layer

Bragg peaks \( hkl \)
crystal truncation rods (CTRs) \( hkL \)
Surface reconstruction and morphology monitored by RHEED
Typical RHEED patterns of (2x4) reconstruction on GaAs(001)

Bulk diffraction features are indicated by top-down arrows
RHEED intensity oscillations indicate layer-by-layer growth mode

Damping of intensity oscillations is caused by surface roughening, i.e. loss of specularity

Phase difference between layers

$\Phi = \pi(1+L)$
What are Compound Semiconductors?

III-V, II-VI, IV-VI,..... Compound semiconductors

III-Phosphides, -Arsenides, III-Antimonides and alloys

III-Nitrides and alloys, ZnO.....

Octet Rule: Outer orbitals are filled with 8 electrons

H. Welker, Z. Naturforschg. 7a (1952) 744
Re-evaporation of ad-atoms and molecules from growing surface monitored by QMS

This method was used by Foxon et al. to establish the first valid model for epitaxial growth of GaAs from gallium and arsenic molecular beams.

Experimental data for epitaxial growth of Ge-Sb-Te phase-change material on GaSb substrate.

Note the onset of a GeTe desorption from the growing surface already at 180°C substrate temperature.
Ga effusion cells generate Ga atoms (unity sticking coefficient on As-stable surface)

As effusion cells generate tetrameric As$_4$ molecules (sticking coefficient < 0.5)

As$_2$ molecules can be generated by cracking of As$_4$ molecules or by heating of GaAs.
Early model for MBE growth of III-V semiconductors

- Thermal-energy neutral beams of constituent elements (atoms or molecules) arrive and react on the substrate surface to form the single-crystal film

- Growth rate and alloy composition is determined by flux of group-III elements impinging on the growing surface

- Stoichiometry secured by excess group-V flux impinging on the growing surface

- Group-V rich surfaces provide stable growth conditions

  >> layer-by-layer growth

- Incorporation of n- and p-type dopants depends on flux of impurity species

  >> unity sticking coefficient
Characteristics of molecular beam epitaxy

- Low growth rate of 1 monolayer (lattice plane) per second
- Low growth temperature (550°C for GaAs)
- Smooth growth surface with steps of atomic height and flat terraces
- Precise control of surface composition and morphology
- Abrupt variation of chemical composition at interfaces
- In-situ control of crystal growth at the atomic level

Note that low growth rates require highest purity around the growing crystal
Ultra-high vacuum (UHV) conditions for MBE growth

UHV chamber with effusion cells, substrate heater, and RHEED equipment. LN$_2$ cryopanels around substrate and effusion cells reduce background impurity level ($10^{-11}$ mbar).
Continuous improvements of MBE equipment

- Load-lock and preparation chamber added to maintain UHV conditions

- Liquid-nitrogen cryopanel around substrate in growth chamber

- Continuously rotating substrate holder and homogeneous substrate heating for improved homogeneity of epilayer thickness and composition

- Effusion cells with low outgassing characteristics and improved design for stable flux distribution

- Linear shutter operation and valved effusion cells for abrupt flux control

- Precise growth control by appropriate hard- and software
Layer-by-layer growth mode in MBE

**Ideal Picture**
- Atoms impinging on the surface diffuse and nucleate 2D islands
- Islands grow by attaching further atoms until the layer is completed
- Process repeats for subsequent layer

**Real Picture**
- Subsequent layer is nucleated before previous one is completed
- Number of incomplete layers, i.e. surface roughness, increases with growth time

- Upon interruption of growth, the surface starts to recover. The roughness decreases and it returns to the initial flat state.
Different types of effusion cells

(a) Crucible
Heater
Ta shields for thermal isolation
Thermocouple: W / Re 3 - W / Re 25
Cryoshroud
UHV flange
Electrical and water cooling feedthroughs

(b) High T zone (cracking zone)
Cracking filament
Crucible

(c) Evaporant
Auxiliary filament for evaporant conditioning
Shutter
Water-cooled electrical connections
Mechanical or pneumatic actuator
View of advanced MBE system for growth of oxide films

Bosevic et al., Brookhaven National Laboratory
Stimulation of layer-by-layer growth mode by flux modulation

Continuous flux leads to damping of intensity oscillations


Flux modulation in monolayer sequence (Migration Enhanced Epitaxy) promotes layer-by-layer growth


Pulsed beams also promote layer-by-layer growth mode

Oscillations are used to precisely determine the epilayer thickness
Dependence of RHEED pattern on GaAs(001) surface morphology

(a) Flat surface                          (b) Island formation                      (c) Corrugated stripes

AFM

RHEED

Flat surface                          Island formation                          Corrugated stripes
As-stabilized (2x4) surface reconstruction on GaAs(001)

(2x4) reconstructed terraces on vicinal GaAs(001) with straight As$_2$ dimer and missing dimer rows, holes and islands. B-type steps are more ragged than A-type steps.

(2x4) surface reconstruction is stable over a wide range of substrate temperatures and of As$_4$ to Ga flux ratios. The growing GaAs(001) surface is atomically flat.
As-rich (2×4) reconstruction reflects the most stable growth conditions of GaAs(001) with smooth surface morphology.

Ga-rich reconstructions lead to unstable growth conditions with Ga-droplet formation on GaAs(001).

L. Däweritz and R. Hey,
Cross-section TEM image of GaAs/AlAs multilayer structure

Note that interface abruptness is different depending on growth sequence
More subtle problems in MBE growth

- **Flux drift**
  - >> temporal stability of atomic fluxes (e.g. Ga cell, because Ga does wet p-BN cell)
  - >> random flux instabilities (e.g. Al cell, because Al does not wet p-BN crucible)

- **Flux uniformity** (accuracy of layer thickness and composition across substrate area)
  - >> angle between cell axis and normal to substrate wafer (optimize angle and distance)
  - >> substrate rotation-induced layer non-uniformity (synchronize rotation with ML deposition rate)

- **Flux transients**
  - >> opening and closing the shutter changes thermal environment of the effusion cell
Why has MBE attracted so much attention?

MBE provides unique capability to study crystal growth in real-time and on a sub-nanometer scale
- Reflection high-energy electron diffraction (RHEED)
- In-situ X-ray diffraction
- Line-of-sight quadrupole mass spectroscopy (QMS)
- Reflectance difference spectroscopy (RDS)

Growth of artificial layered crystals of various complexity with high degree of control and reproducibility
- In low-dimensional structures the experimental physics based on quantum phenomena is brought to the classroom
- Improved performance and new functionalities in heterojunction devices
- Materials engineering at the atomic level despite lattice and symmetry mismatch, chemical incompatibility, structural dissimilarity and/or thermal-expansion difference
**Abrupt material interfaces required for functionality of devices**

Most functions in semiconductor devices rely on band discontinuities or band offsets.

** Confinement of carriers (charge and spin)**

** Confinement of photons (energy and spin)**

** Confinement of phonons

Energy quantization („quantum size effects“)
Need of perfect material interface (1)
Modulation-doped heterostructures with 2DEG

Arrangement of conduction and valence bands of GaAs and (Al,Ga)As before (left) and after (right) interface formation. Band bending due to carrier depletion and ionized impurities leads to 2DEG formation.
Improvement of electron mobilities in modulation-doped heterostructures

- The high-mobility 2DEG system has served as a favorite playground for extensive research in the field of quantum transport and mesoscopic physics.

- Correlations between the classical transport properties (electron mobility and low-field quantum scattering times) and the disorder landscape which governs the appearance of fragile quantum Hall states were established.

- Main scattering mechanisms governing the mobility are (i) unintentional charged background impurities in the channel and (ii) remote ionized dopants in the modulation-doped layers.

- Further progress in mobility enhancement, i.e. >35x10^6 cm^2/Vsec, required new design of heterostructure and new growth procedures.

Heterostructures with different doping profiles for mobility enhancement

Conduction band profiles for different doping schemes

Electron mobilities measured in the dark
Inequality of AlAs/GaAs(001) interfaces

- **Normal interface**, i.e. AlAs grown on GaAs(001), has superior electronic properties. However, the metallurgical abruptness is poor due to Ga segregation into the growing AlAs layer.

- **Inverted interface**, i.e. GaAs grown on AlAs(001), has superior metallurgical abruptness (within 1 ML). However, the electronic properties are poor due to high kink density on the AlAs(001) surface.

- **Note that** GaAs(001) exhibits ordered (2x4) reconstruction, while AlAs(001) shows disordered (2x3) reconstruction with high kink density.

- **Differences in electronic properties arise from fundamental differences in surface kinetics during interface formation**.
Need of perfect material interfaces (2)
Intersubband emitter (quantum cascade laser)

Comparison of interband (bipolar) and intraband (unipolar) transitions in conventional laser and QCL

Emission wavelength of QCL can be tuned by band offset and subband energy, i.e. layer thickness
Intersubband Laser (QCL):

Proposal by Kazarinov/Suris

Interband Laser:

GaAs/(Al,Ga)As double heterostructure laser (cw, 300 K)

GaAs/(Al,Ga)As quantum well laser

vertical cavity surface emitting laser (pulsed, 77 K)

Lead salt laser (cw, 80 K)

GaAs/(Al,Ga)As QCL (pulsed, low temperature)

(In,Ga)N/GaN blue laser diode (cw, 300 K)

Each cascade consists of about 20 layers, a few ML thick, which requires precise thickness control.

At least 25 cascades amounting to more than 500 individual layers constitute the final QCL structure.
Application of QCL for sensing toxic gases

Upper panel shows transmission spectrum of air with two distinct transparency windows.

Lower panel shows temperature tuning range of DFB QCL designed to operate in selected window regions where many common gases have absorption fingerprints.

Spintronic devices require the ability to
* generate
* maintain/manipulate
* propagate
* detect

long-lived spins in semiconductors

To combine spin and charge and to use the spin for new functionalities, we must inject spins electrically into semiconductor heterostructures at room temperature.

**Spin injector:** Metal, half-metal (Heusler alloy or ferromagnetic semiconductor)
Azimuthal RHEED scans of different stages of Fe growth on GaAs(001) at 100C. Starting surface is either As-rich (left column) or Ga-rich (right column).

*J. Herfort et al., Int. J. Mat. Res. 97, 7(2006)*
Structural and magnetic properties of bcc Fe films on GaAs(001)

Cross-section HRTEM Image of 140 ML Fe grown on As-terminated GaAs(001) at 50 C

Remanent magnetization of Fe-on-GaAs films of different thickness as function of thickness. Inset shows saturation magnetization at 10K.

*J. Herfort et al., Int.J.Mat.Res. 97, 7 (2006)*
Epitaxial Fe$_3$Si layer on GaAs

Three different Fe lattice sites in cubic D0$_3$ structure. Very good lattice match to GaAs.

Comparison of measured and simulated XRD curves shows excellent long-range order in epitaxial film
Effect of growth temperature on structure of Fe$_3$Si

- $T_g = 275$ °C
  - homogenous epitaxial layer
  - sharp

- $T_g = 200$ °C
  - epitaxial layer with 90° domain boundaries
  - sharp

- $T_g = 400$ °C
  - polycrystalline & multiphase layer?
  - structurally rough

J. Herfort et al., Int.J.Mat.Res. 97, 7 (2006)
Heusler alloy Co$_2$FeSi on GaAs(001)

Fourier-filtered cross-section HRTEM image of film grown at 300K. Simulated model shown in inset uses 1 ML intermixing at interface.


L2$_1$ structure model

Full Heusler alloy
Only 0.08% lattice mismatch to GaAs
$T_c = 980$ K
Large magnetic moment
How abrupt can interfaces between different materials be made?

The universal sigmoidal profile (left) quantifies chemical interfaces by the interface width $L$. The profile originates from a model of cooperative growth, mediated by 2D island formation. The cooperative effects are described by a specific functional dependence of the sticking coefficient on the surface coverage. The actual profile is dominated by either nucleation (sharp) or island (broad) mediated growth or in-between. The island-mediated growth proceeds via Eden cluster formation.

Achievements of MBE in quantum dot and nanowire fabrication (bottom-up)

Motivation
Reduced dimensionality changes density of states and hence threshold current density of lasers
Self-organized island formation by Stranski-Krastanov growth mode

In 2D Frank-van der Merwe mode, lattice-matched materials grow layer-by-layer.

In Volmer-Weber mode, separate 3D islands of lattice-mismatched material form on the substrate.

Classification based on energetical considerations introduced by E. Bauer, Z. Kristallogr. 110, 372-394 (1958)

In Stranski-Krastanow mode, first one or two monolayers (wetting layer) of lattice-mismatched material form, followed by individual islands. To a critical size, the islands are coherently strained and free of misfit dislocations.
Details of Stranski-Krastanov growth of InAs quantum dots

For InAs on GaAs(001), this mechanism is valid only for this orientation under As-stable conditions. For other orientations and under In-stable conditions, 2D strained InAs layers beyond the critical thickness are formed.
**Catalyst-induced nucleation**

Any vapor-phase deposition technique can be used to supply the gaseous species which form the Au eutectic. At supersaturation, the wire constituents precipitate and the wire grows at constant wire diameter.

**Important question:**

Is the material of the catalyst (or seed) incorporated into the semiconductor quantum wire as unintentional dopant?
Ga atoms diffuse on the SiO$_2$ surface and accumulate into droplets in the pinholes of the thin SiO$_2$ layer. The Ga droplets act as sinks, where As$_4$ molecules from the vapor precipitate and diffuse towards the solid-liquid interface → growth of nanowires.

Ga droplet at the tip is constantly enriched with Ga atoms diffusing on SiO$_2$ surface and along wall of nanowire growing in /111/ direction.

Prismatic heterostructures grown by tuning the MBE conditions to form quantum heterostructures on the side facets. Depending on the inclination angle of the nanowires the thickness can vary gradually.

Transition from droplet-driven to droplet-free nanowire growth induced by facet formation

As$_4$ flux dependent transition from VLS to noncatalytic droplet-free nanowire growth driven by facet formation monitored by RHEED. Note low vertical growth rate of facet-driven selective area growth.

Numerous planar defects in vicinity of Ga droplet at tip. Pyramidal shape of short nanowires formed by /110/ planes, random layer stacking with many planar defects.

*G. Abstreiter et al., Nano Lett. 11, 3848 (2011)*
Catalyst-free GaN nanowire growth on AlN template

HRTEM images of nucleation of dislocation-free coherent GaN islands and pyramids and distinct shape transitions at different stages of nanowire growth.


Intensity evolution of RHEED features at six distinct stages of GaN nanowire growth indicating different shapes of the GaN nano-objects.
Catalyst-free GaN nanowire growth on amorphous template

HRTEM images and RHEED intensity evolution of GaN nucleation as spherical cap-shaped islands which then coarsen and undergo a shape transition during four distinct stages of GaN nanowire growth.

Bottom-up versus top-down approach for fabrication of nano-objects

- Can **bottom-up approach**, i.e. direct growth of nano-objects, compete with **top-down approach**, i.e. lithographic patterning and etching of epitaxial layer, concerning
  - Homogeneity of feature size and composition
  - Accurate number and position/location of nano-objects
  - over large wafer areas?
- **Growth is a stochastic process and statistical aspects are important for nucleation and crystal formation**

Stranski-Krastanow growth of InAs islands on GaAs(001) indicating the poor uniformity of shape, size, and placement
Future prospects and challenges of MBE

- Control of material interfaces on atomic scale (design and growth)
  - InAs/GaSb interfaces and superlattices
  - Ferromagnetic metals and Heusler alloys on semiconductors
- Synthesis of crystalline films of new and metastable compounds
  - Cubic GaN on GaAs
  - M-plane hexagonal GaN on LiAlO$_2$
- Combination of dissimilar materials by engineered interfaces
  - Crystalline high-k materials on Si and other semiconductors
  - Fabrication of interfaces formed by transition-metal oxide materials
- Interface and composition control over large wafer size on atomic scale
Sb-based heterostructures

Energy gap versus lattice constant of III-V compounds

Materials with smaller gap for high-frequency and low-power operation

GaSb/InAs type-II-superlattices for mid-IR detectors

InAs/GaSb heterostructures for topological insulators

Configuration of InAs/GaSb interface

X-STM image of InAs/GaSb interface with InSb interfacial bonds. Bottom: Line profile for simulated image in inset


X-STM image of GaSb/InAs interface with GaAs interfacial bonds. Bottom: Line profile for simulated image in inset
Strain balance in InAs/GaSb superlattice by inserting 1 ML InSb

Cross-section TEM image of type-II InAs/GaSb SL for mid-IR detectors with 1 ML InSb inserted at each interface for strain balancing

Regular satellite peaks in XRD show perfect superlattice which is almost strain balanced to GaSb substrate

Substrate stabilization of meta-stable phase: *Cubic GaN on GaAs*

- *Cubic III-Nitrides* are not affected by intrinsic piezo-electric fields as compared to hexagonal III-Nitrides along c-direction.
- *Cubic III-Nitrides* are metastable phases that require suitable substrates for nucleation and low growth temperatures for stabilization.
- Large lattice mismatch between GaN and GaAs (16%).
- Low growth temperatures can generate additional point and extended defects.
- Residual arsenic in growth chamber can form deep impurity defects in GaN.

Coincidence lattice in cubic-GaN/GaAs accounts for 16% lattice mismatch

Substrate stabilization of metastable growth direction: *m*-plane GaN on LAO

Along non-polar directions intrinsic piezo-electric fields in hexagonal III-Nitrides are absent

*J.S. Speck and S.F. Chichibu, MRS Bull.** **34**, 304ff (2009)
M-plane GaN on LiAlO$_2$:
Interface structure

Coherent regions indicate perfect matching of GaN(11-20) planes and LiAlO$_2$ planes
> Agreement between HRTEM image and interface mode
> No abrupt change in stacking of atom planes despite break in symmetry
Semi-coherent interface with high residual strain

Identification of polarity for growth of m-plane GaN on LiAlO$_2$

Identification of polarity by HRTEM and image simulations

>>> Contrast is consistent with Ga-O and N-Al bonds at interface

>>> Coherent tetrahedral coordination, low misfit of 0.3%, chemically favorable
High-$k$ crystalline oxides on Si for energy-constrained CMOS scaling

Proper scaling of CMOS requires also a reduction of the gate-oxide thickness. **However**, leakage current in amorphous SiO$_2$ gate dielectrics increases drastically.

**Replace SiO$_2$ by high-$k$ dielectric material**

D.G. Schlom et al., MRS Bull. 27, 198 (2002) and MRS Bull. 33, 1006ff (2008)
G. Niu et al., in *Molecular Beam Epitaxy* (Elsevier 2012) Chapter 18, p.451

High-$k$ dielectrics provide an equivalent oxide thickness that is thinner than the original SiO$_2$ but keeping the gate-leakage current low

- permittivity higher than SiO$_2$, but <60
- band gap >5eV, band offsets >1eV
- thermodynamically stable up to 1000 C
- low density of traps at Si/high-$k$ interface
Strain-compensated all-binary RE oxide superlattice on Si(111)

Ternary LaLuO$_3$ with distorted perovskite structure is grown as all-binary short-period superlattice composed of 2 ML of La$_2$O$_3$ and 2 ML of Lu$_2$O$_3$.

Accurate control of layer thickness by RHEED intensity oscillations and growth interruptions.

Using special high-temperature thermal effusion cells provides stable fluxes of constituent binaries

Crystal structures of complex oxides important for "Oxide Electronics"

R. Ramesh and D. G. Schlom, MRS Bull. 33, 1006 (2008)
Formation of suitable interface compounds is secret of perfect heteroepitaxy
Monolayer (delta) doping by replacing 3% of Cu with isovalent Zn in a cuprate insulator serves as variable marker near the interface to experimentally demonstrate high-Tc superconductivity in a single copper-oxygen plane.

Zn substitution suppresses superconductivity.

I = insulator
M= non-superconducting metal

Each LSCO and LCO layer is three unit cells thick, each bilayer film contains 12 CuO$_2$ planes.

I. Bosovic et al., Science 326, 699 (2009)
RHEED pattern during growth of high-Tc cuprate superconductor

Colour-coded RHEED pattern during growth of La$_2$CuO$_4$ layer. Spacing between major streaks indicates in-plane lattice spacing of 0.38 nm. Surface reconstruction with 5x larger lattice spacing is shown by four weak satellites in-between.

I. Bosovic et al., Science 326, 699 (2009)
Perovskites and related layered compounds have broad spectrum of functional properties.

Functional properties arise from a variety of orderings of their charge, orbital, spin, and lattice degrees of freedom.

At oxide interfaces these interactions can be modified through the effects of symmetry breaking, charge transfer, electrostatic coupling, strain, and frustration, leading to exciting new phenomena in these heterostructures.
Outlook

New achievements in MBE require

- Excellent laboratory skills
- Patience
- Creativity
- Dedication
- Continuous funding

Further reading:
M. Henini, Ed., „Molecular Beam Epitaxy“, Elsevier (Amsterdam 2012)