

Vékonyrétegek előállítása és alkalmazásai

2010. október 19.

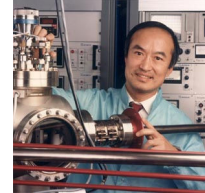
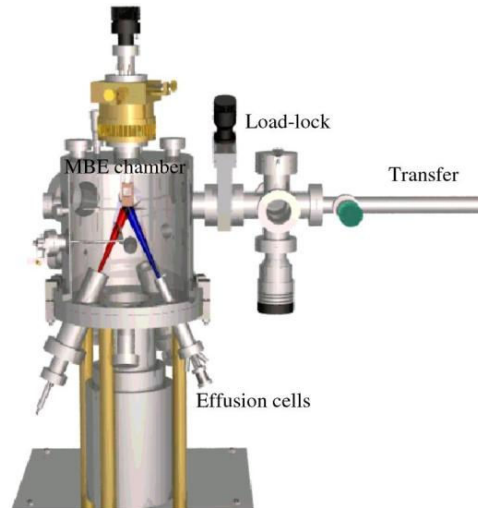
Dr. Geretovszky Zsolt

Kiselőadás témák

- 1) Mi az a „tilted layer epitaxy”? Hogyan keletkezik egy ilyen réteg? Mutasson be egy példát az epitaxiális illeszkedésre!
- 2) A párolgási sebességet leíró Hertz egyenlet levezetése és alkalmazása elemek szilárd, illetve olvadék fázisainak párolgására. (Az összefüggésben szereplő egyensúlyi nyomás, illetve hidrosztatikai nyomás magyarázata.)
- 3) A vékonyrétegépítés szelektív módszerei. Elv(ek) és lehetséges módszerek rövid bemutatása.
- 4) Ismertesse a pszeudomorf rétegépülés Nix modelljét, különös tekintettel arra, hogy az epitaxiális vékonyrétegépítés során milyen kritikus rétegvastagságnál jelennek meg az épülő rétegben diszlokációk.
- 5) A tangens szabály. Kísérleti tapasztalatok és azok modellezése.
- 6) Vékonyrétegek textúrája. A textúra leírása, meghatározásának módszerei vékonyrétegek esetén. Milyen módon lehet kontrollálni az épülő réteg textúráját?

Molecular Beam Epitaxy, MBE

This conceptually simple single-crystal film-growth technique is the state-of-the-art in vapor phase deposition. MBE involves highly controlled evaporation in an ultra-high vacuum ($\sim 10^{-10}$ torr) system.



Alfred Yi CHO
1937-

MBE was invented in 1968 at Bell Laboratories by Al Cho and J.R. Arthur Jr.

J.R. Arthur Jr., *J. Appl. Phys.* **39**, pp. 4032-4034 (1968)

W.P. McCray, *Nature Nanotechnology* **2**, pp. 259-261 (2007)

Molecular Beam Epitaxy, MBE

MBE takes place in a reactor/growth chamber in which source materials are introduced in the form of molecular beams.

Molecular beams are usually created by heating solid source materials, which are placed inside crucibles within containers known as effusion cells, until they vaporize. A gas source may be used instead of a solid source, in which case the source material is introduced into the reactor through a gas injector nozzle.

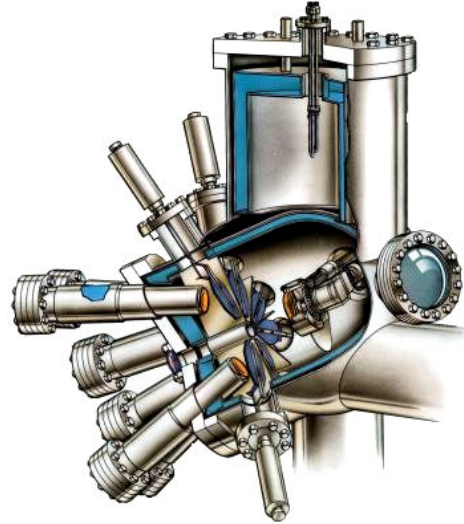
Due to the *UHV environment* of the reactor, when the source materials escape from the crucibles their molecules form a series of directed beams that are able to travel *without collision* until they make impact with the substrate's surface. As the molecular beams collide with the surface of the substrate, their molecules decompose into the constituent atoms of the source materials. Because the *substrate is heated* during the process, there is sufficient kinetic energy for the atoms to rearrange themselves into a *single crystal structure* replicating the crystal structure of the underlying substrate.

Molecular Beam Epitaxy, MBE

MBE is a versatile technique for growing thin epitaxial structures made of semiconductors, metals or insulators. In MBE thin films crystallize via reactions between molecular or atomic beams of the constituent elements and a substrate surface which is maintained at an elevated temperature in ultra high vacuum.

The composition of the grown epilayer and its doping level depend on the relative arrival rates of the constituent elements and dopants, which in turn depend on the evaporation rates of the corresponding sources.

Simple mechanical shutters in front of the beam sources are used to interrupt the beam fluxes, i.e. to start and to stop the deposition or doping. Changes in composition and doping can thus be abrupt on an atomic scale.



MBE has a unique advantage: being realised in UHV, it may be controlled in-situ by a multitude of surface sensitive diagnostic methods such as reflection high energy electron diffraction (RHEED) or reflection anisotropy spectroscopy (RAS).

Types of MBE

Solid-Source MBE (SS-MBE)

group-III and -V molecular beams (mainly arsenides and antimonides)

The Gas-Source MBE (GS-MBE, or Chemical Beam Epitaxy)

III-V semiconductors,

group-V materials are hydrides such as arsine (AsH_3) or phosphine (PH_3)

high-temperature cells, good for P-containing layers

Metalorganic MBE (MO-MBE)

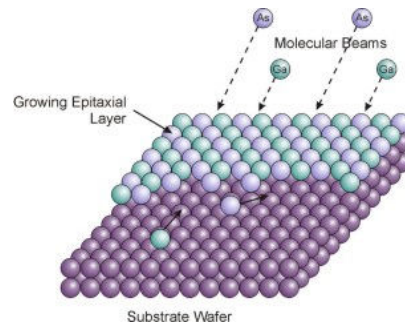
group-III materials are metalorganic compounds, e.g. tetra-ethyl-gallium (TEGa) or tetra-methyl-indium (TMIn)

low-temperature cells

MBE techniques using gas or a combination of gas and solid sources are capable to produce devices with enhanced performance capabilities through

- the use of lower epitaxial process temperatures,
- to increase the possibilities of higher epitaxial growth rates than currently possible with MBE using solid source materials, and
- to make epiwafers for the production of high quality compound semiconductors made up of four elements, such as GaInAsP.

MBE growth mechanism



Atoms arriving at the substrate surface may undergo

- adsorption to the surface,
- surface migration,
- incorporation into the crystal lattice,
- thermal desorption.

All process depends strongly on the temperature of the substrate.

Epitaxial growth is ensured by

- very low rates of impinging atoms,
- migration on the surface and
- subsequent surface reactions

MBE is almost exclusively used for growing semiconducting materials like:

- group IV elemental semiconductors like Si, Ge, and C
- III-V-semiconductors: arsenides (GaAs, AlAs, InAs), antimonides like GaSb and phosphides like InP
- II-VI- semiconductors: ZnSe, CdS, and HgTe

	IIIA	IVA	VA	VIA
	BORON B	CARBON C	NITROGEN N	OXYGEN O
	ALUMINUM Al	SILICON Si	PHOSPHORUS P	SULFUR S
IIB	ZINC Zn	GALLIUM Ga	GERMANIUM Ge	ARSENIC As
	CADMIUM Cd	INDIUM In	TIN Sn	ANTIMONY Sb
	MERCURY Hg	THALLIUM Tl	LEAD Pb	BISMUTH Bi
				POLONIUM Po

MBE is a key enabling technology of the semiconductor industry. The first R&D machine was introduced in 1975, while MBE systems have been employed in manufacturing since 1984.

Precursors for (SS-)MBE

Element	Application
Al	III-V
As	III-V
Be	dopant
C	dopant
Cd	CMT
Ga	III-V
In	III-V
Mg	dopant
P	III-V
S	II-VI
Sb	III-V
Se	II-VI
Si	dopant
Te	CMT
Zn	II-VI

<http://www.riber.com/en2/public/solidcells.htm>

Precursors for MO-MBE and CBE

Gasous precursors are introduced to the deposition chamber via gas injectors. Depending on the nature of the precursor and its thermal stability relative to the growth temperature, the gas injector will be operated either at a low temperature (<100°C) for preventing condensation and dissociation of compounds before on-substrate cracking, or at a higher temperature (>600°C) to thermally decompose the molecular species before impinging on the substrate.

Element	Application	Precursor
Al	III-V and GaN	DMEAl
As	main III-V	AsH ₃ or TBAs
As	n-doping SiGe	AsH ₃ in H ₂
B	p-doping SiGe	B ₂ H ₆ in H ₂
C	p-dopant III-V	CBr ₄
C	main SiC	SiH ₃ CH ₃ in H ₂
Ga	III-V and GaN	TMGa or TEGa
Ge	main SiGe	GeH ₄ in H ₂
In	III-V and GaN	TMIIn
Mg	p-doping III-V	Cp ₂ Mg
N	main GaN	NH ₃
P	main III-V	PH ₃ or TBP
P	n-doping SiGe	PH ₃ in H ₂
Si	main SiGe	SiH ₄ or Si ₂ H ₆
Si	n-doping III-V	SiBr ₄

<http://www.riber.com/en2/public/gassys3.htm>

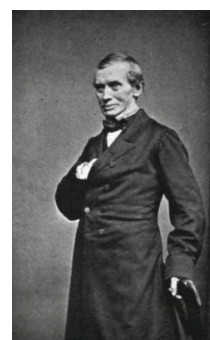
Effusion

Effusion is the process in which individual molecules flow through a hole without collisions between molecules. This occurs if the diameter of the hole is considerably smaller than the mean free path of the molecules. (**Diffusion** is the process of a substance spreading out to evenly fill its container or environment. If the hole is large enough, the process may be considered diffusion instead of effusion.)

Graham's law or **Graham's law of effusion**: Graham found experimentally that the rate of effusion of a gas is inversely proportional to the square root of the mass of its particles.

$$\frac{Rate_1}{Rate_2} = \sqrt{\frac{M_2}{M_1}}$$

It is most accurate for molecular effusion which involves the movement of one gas at a time through a hole. It is only approximate for diffusion of one gas in another, as these processes involve the movement of more than one gas.



Thomas GRAHAM
1805-1869

Effusion cells

Knudsen cells or K-cells:

heated sources to evaporate solid – mainly elemental – materials



A special heating system attached to the top of the Low-Temperature-Effusion cell cracks certain molecules (e.g. As, S, Sb or Se) at temperatures much higher than the evaporation temperature.



Crackers:

Cells for gaseous media



Different crucibles for K-cells

- made of Ta, Mo, and pyrolytic boron nitride (PBN)
- do not decompose or outgas impurities even when heated to 1400°C.

Cylindrical crucible



offers good charge material capacity, but uniformity decreases as charge material is depleted. It offers excellent long-term flux stability, but permits large shutter flux transients

Conical crucible



offers reduced charge material capacity, excellent uniformity, and poor long-term flux stability, and permits large shutter flux transients

SUMO crucible



offers excellent charge material capacity, excellent uniformity, excellent long-term flux stability, and minimal shutter-related flux transients

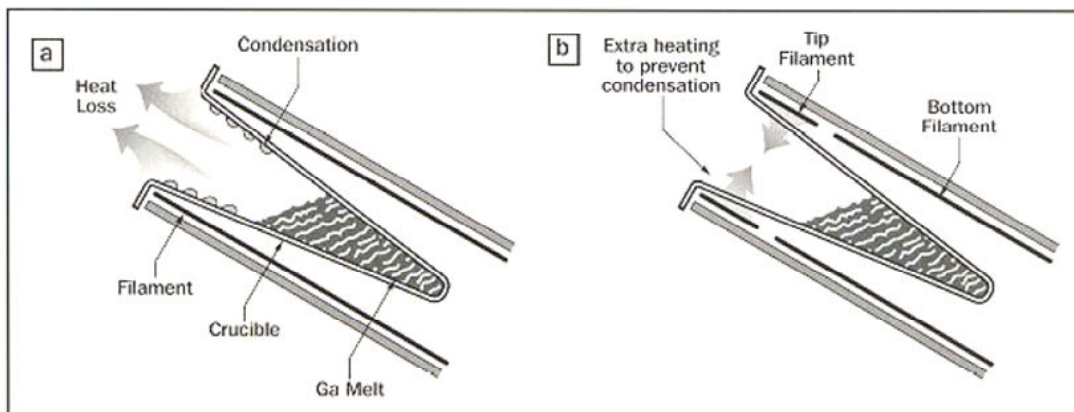


Figure Two: Principle of operation, Dual Filament Cell. In the conventional cell (a), a single filament uniformly heats the entire length of the crucible. The crucible orifice area is cooled by radiated heat loss, causing the evaporant to condense and form droplets. In the Dual Filament Cell (b), the crucible orifice area is independently heated by the second filament, to create a "hot-tip", thereby eliminating condensation and reducing oval defect densities.

Cracker effusion cell

- combines the evaporation and cracking of elements like P, S, As, Se, Te etc.

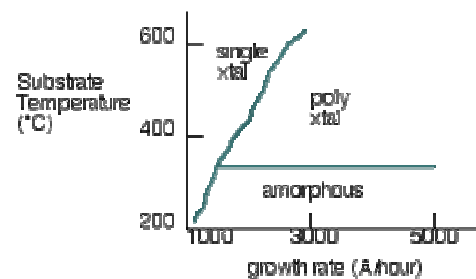
Technical Data

Heating System	Radiation heating, tantalum wires with PBN insulators
Temperature range	100 °C ...800 °C bulk zone 100 °C ...1000 °C cracker
Temperature stability	≤ 0.1 K depending on the PID controller
Bake out temperature	250 °C

Features of MBE

1. Works typically in ultra-high vacuum
2. Produces films of good crystalline structure
3. Uses high purity elemental charge materials
4. Often use multiple sources to grow alloy films
5. Very low deposition rates typically $1\mu\text{m/hr}$ or $1\text{\AA}/\text{sec}$
6. Very well controlled growth
7. Deposition rate is so low that substrate temperature does not need to be high.

High quality films can only be grown if the surface-diffusion-incorporation time, τ_{di} is less than the characteristic time of monolayer formation. Since atom incorporation is a thermally activated process, a low growth temperature limit is implied for good epitaxy. If τ_{di} is the larger unincorporated atoms will be buried by the faster growing ML (i.e. a defective layer is formed).



Deposition rate:

$$\dot{R} \leq (\text{constant}) e^{-E_d / kT}$$

Key advantages of MBE

compared to other epi process technologies

Precise control

MBE allows to grow epilayers with different chemical compositions to atomic layer accuracy (with the thickness of each surface layer being as thin as one or two atoms) AND

ensure that uniformity across the wafer surface is maintained (up to 95% of the epiwafer material can be processed). The ability of MBE to produce abrupt transitions between layers of different semiconductor crystals also reduces electronic noise and distortion and increases power efficiency in devices.

Monitoring of epitaxial process

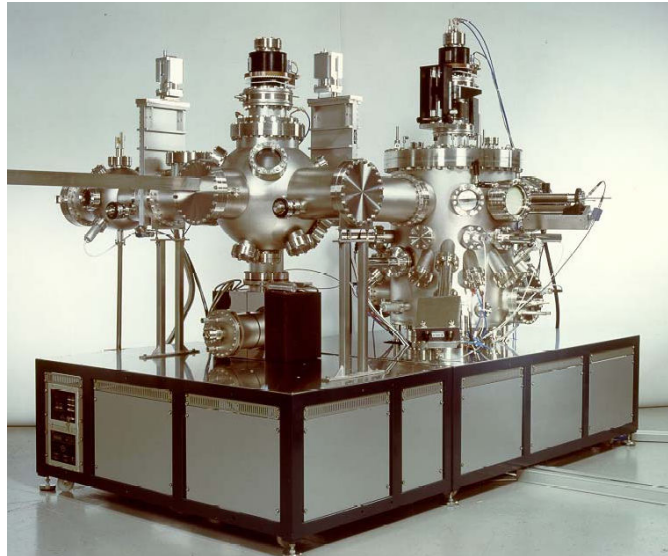
The UHV environment makes it possible to use electrons and light particles as probes to monitor the wafer's surface and epilayer quality during epitaxial growth. These monitoring processes facilitate the real-time control of the deposition and thereby provide a highly accurate quality control tool.

Manufacturing flexibility

The UHV conditions within the MBE reactor allow for the rapid removal of unused source materials upon completion of a growing cycle, thereby decreasing the amount of time between growing cycles.

Safety and ease of maintenance

The MBE process does not use high volumes of toxic gases, typical of several competing epi processes (e.g. MOVPE), resulting in greater safety and ease of maintenance.



Riber's MBE 32
an R&D apparatus



Riber's MBE 49
a production tool

Application of MBE films

The primary application for MBE-grown layers is the fabrication of electronic devices.

But it was the technique used to make the first GMR layers in 1986.

Other possible meanings of MBE

Mega-Buck Evaporator

Mostly Broken Equipment

Mind Boggling Experiment

Medieval Brain Extractor

Money Buys Everything

Management Bullshits Everyone