

summary – vacuum science

The kinetic theory of gases is all that is needed to adequately describe isolated reduced-pressure environments and the behavior of gases within them.

Molecular velocities and their statistical spread, collision rates between gas molecules, and impingement rates at surfaces are all readily calculable in terms of the system temperature and molecular weights and sizes and thus pressure.

Summation of these microscopic events over all molecules leads to the perfect gas law and gives significance to the primary measurable variable in a vacuum chamber, namely its pressure.

In the low-pressure molecular-flow regime the situation is little changed from that of an isolated chamber where the perfect gas law applies. Even though pressure differences develop across components, conductances are calculable from the kinetic theory of gases.

However, at the higher pressures in the viscous-flow regime, gas flow is governed by the laws of compressible fluid dynamics. Conductances, throughputs, and pumping speeds are now complicated functions of pressure, which is important for CVD processes.

Attaining low system pressures is largely a matter of connecting a high vacuum-backing pump combination to the chamber via high-conductance.

Oil diffusion, turbomolecular, cryo-, and ion pumps produce the low pressures, while rotary, Roots, and sorption pumps are necessary to provide the necessary forepressure for operation of the former.

Assorted valves, cold traps, and gauges round out the complement of required vacuum hardware.



Q & A vacuum science

- 1) Assuming a sticking coefficient of 1, how long does it take to form a monolayer on a surface as a function of pressure? Give examples of orders of magnitude for low and high vacuum regions.

$$t_c = \frac{3.80 \cdot 10^{-8}}{P} (MT)^{1/2} \text{ s} ; P \text{ in mbar}$$

In air $3.6 \cdot 10^{-9}$ s means around ns, at 10^{-5} mbar 0.36s, at 10^{-10} mbar 36000s=10h,

- 2) Calculate the mean speed of He, Ar and Xe atoms in high vacuum at room temperature and at 1000 C.

$$\bar{v} = \sqrt{3RT/M} \quad \text{for H at RT: } \bar{v} = (3 \cdot 8.31 \text{ kgm}^2/\text{s}^2\text{molK} \cdot 300\text{K} / 0.002\text{Kg/mol})^{0.5} = 1,9 \cdot 10^5 \text{ cm/s}$$

- 3) Write down the equation of the mean free path. For which pressure range the mean free path exceeds the dimension of max. meter sized vacuum chambers. Explain the Knudsen Number.

$$\lambda_{mfp} = \frac{k_B T}{\sqrt{2} \pi P d_c^2} ; \text{ At pressures below } 10^{-5} \text{ mbar, } \lambda_{mfp} \text{ is So large (6.15m in the example)} ; \quad K_n = \lambda_{mfp} / D_p$$

- 4) How does mean free path and surface impingement rate scale with pressure?

$\sim 1/p$ resulting a slope of -1 in log/log plot

- 5) Which type of flow should dominate at high pressures? Which should dominate at low pressures? Which will evacuate a chamber faster?

Viscous at high p (trending faster due to high conductance), molecular at low p (slower) -

- 6) What determines the pumping speed of a system at a given pressure?

The conductances of the viscous and molecular flow regimes above 10^{-5} mbar, surface desorption & diffusion & permeation below 10^{-5} mbar which can be influence by chamber surface temperature (baking)

Q & A vacuum science

7) Why should gloves be worn when taking materials in and out of the vacuum chamber?

Organic contaminants from the finger tips have a high vapor pressure and increase pumping time and may contaminate the chamber for long time (bad purity of deposits)

8) Discuss possible chamber designs, pump and flange types to maintain a base pressure below 10^{-10} mbar. Which gases and modes of transport are of key consideration?

High conductance; bake out possibilities; Combination of rotary, turbo and ion pump, Cu gaskets, Gases: Water is nasty, all molecular flow

9) For a cubic vacuum chamber with a side length of 0.5 m, at what pressure does the mean free path exceed the chamber dimensions?

10^{-6} mbar, see question above

10) Assuming only argon in the above chamber, calculate the number of atoms confined at 10^{-6} mbar and room temperature.

$1\text{ mol} = 22.4 \text{ l}$, chamber size is 125l $\rightarrow 125\text{l}/22.4 = 5.58 \text{ mol} = 5.58 * 6.034 \text{ } 10^{23} = 33.6 * 10^{23}$ at ambient p
 \rightarrow at 10^{-6} mbar follows $33.6 * 10^{14}$

11) The equilibrium vapor pressure of oil is around 50 kPa at room temperature. How is the presence of oil contamination expected to behave in high vacuum chambers? How can we get rid of it?

Will evaporate below 10^{-5} mbar (high vac) as evaporation pressure is higher with 5 mbar. We need bake out or plasma etching or getter sputtering (sputter Ti as cleaning step)

12) Could a turbomolecular pump operate without a backing pump? Can it be started at atmosphere? What are the risks?

Turbomolecular pumps only work in molecular flow conditions, a pure turbomolecular pump will require in most cases a backing pump to work effectively. Risks without backing or a male function: heat overload

Q & A vacuum science

13) What limits the peak temperature of a chamber bakeout?

Desorption of water, hardware components have T limits

14) Name 3 pressure measurement devices, explain their operation principle and give ranges of operation pressure

Capacitive → bulging membrane, atm to 10-5mbar

Pirani → heated filament which T depends on gas flow: 10-4 to 1 atm

Hot cathode gauges (Bayard Alpert) → gas is ionized and ion current is measured: 10-5 to 10-13 mbar

15) Is the cold or the hot cathode vacuum gauge more sensitive to contamination?

The hot one is more sensitive as molecules may decompose and deposit on electrode

The cold one has plasma and sputters itself and keeps it clean

summary - evaporation

Evaporation methods are perhaps the simplest means of producing thin films and coatings comprised of sequentially deposited atoms.

Thermodynamics, particularly source temperature-vapor pressure relationships, govern rates of evaporation and the nature of the vapor stream.

Film thickness uniformity is governed by the geometric placement of source and substrate. As long as the substrates are planar, the film thickness distribution can usually be modeled in terms of the laws of emission from point or surface sources, and substrate reception based on the inverse square separation distance between the two.

Film uniformity and coverage become more problematical over substrates that are stepped or contain trenches and other complex topographies.

The vacuum space and partial pressures of residual gases within it have an influence on film purity and properties such as resistivity, reflectivity, and hardness.

Evaporation techniques for thin-film deposition have been superseded in many instances by sputtering and CVD methods; difficulties in maintaining stoichiometry and achieving conformal coverage are among the reasons for this. Paradoxically, however, pulsed-laser deposition enables excellent stoichiometry to be attained in complex oxide films.

Despite shortcomings, evaporation methods are readily scalable to large operations such as web coating. However, in addition to conventional applications, the versatility of evaporation techniques is exploited in molecular beam epitaxy as well as other hybrid deposition processes. Arc evaporation is used for deposition of hard coatings.

Q & A evaporation

- 1) What are the different methods for melting the charge, and their advantages and disadvantages?
Thermal boat (low cost, compounds difficult, bad adhesion), ebeam (high cost, local melting but pure materials, refractory metals), laser (very high cost but stoichiometric oxides), arc (difficult control spot location, melt droplets, but high ionization degree)
- 2) Explain how e-beam evaporation works
KV ebeam is 270° bent and melts local target
- 3) How is film thickness controlled in evaporation systems?
Calibrate evaporation rate (SEM cross-sectional thickness after deposition), Quartz microbalance, understand cosine*cosine-law
- 4) How can we control the mean free path of the vapor?
Via pressure
- 5) Explain the view factor, $1/r^2$ deposition rate dependence, and their impact on across wafer uniformity
$$\text{deposition rate} \sim \frac{\cos\Phi \cos\theta}{r^2}$$
- 6) Why is shadowing/step coverage a problem, and what can we do about it?
Not a problem in photolithography! To avoid: more sources, substrate rotation, higher pressure (more scattering of atoms)
- 7) Explain the advantages and disadvantages of evaporation
advantage: direct line of sight, low cost,
disadvantage: impurities, limited no of materials, bad uniformity, low density, bad adhesion
- 8) How can tungsten be evaporated?
By sublimation in thermal but high T, better ebeam evaporation

Q & A evaporation

9) State the similarity and difference of arc evaporation with that of vacuum evaporation. How is the cathode spot characterised? How does the cathode spot split? What is meant by steered arc? State the challenges with arc evaporation deposition

similar: melt, vacuum level difference: small spot, high ionization degree and melt drops in arc, arc is magnetically or mechanically steered (target movement) to avoid inhomogeneous target use, after ignition with a striker the spot self-extinguishes due to melt & vapour locally and reignites at multiple other places.

10) State the similarity and difference of arc evaporation with that of vacuum evaporation.

Dito

11) How is the cathode spot characterized in cathodic arc evaporation?

Local high current density (10^5 A/cm 2) leads to 15000°C and related melting and ejection of vapourized jet (10km/s) which includes melt droplets

12) Discuss possible interactions between the target material and the evaporation crucible. Propose solutions for circumventing these problems.

Alloying and prob. low melting eutectic; diffusion interlayer formation; impurities -> check phase diagrams; use inert materials such as oxides, or rely entirely on ebeam/laser/arc that melt only locally

13) Let's assume a standard chamber design where the evaporation source and the substrate are centered on the same axis and facing each other. Propose modifications in chamber geometry that can improve coating uniformity.

Multiple sources, 3D rotating samples

14) Zinc has a melting point of 420 C and a vapor pressure of 0.1 mbar at this temperature. To deposit a film by evaporation, is a melt necessary or would it also sublime?

We are above 10^{-3} mbar -> no melt needed

Q & A evaporation

15) An Al film was deposited at a rate of $\sim 1 \mu\text{m}/\text{min}$ in vacuum at 25°C and it was estimated that the oxygen content of the film was 10^{-3} . What was the partial pressure of oxygen in the system?
 Impurity concentration C_i scales as gas impurity concentration C_i in film as function of partial pressure (O_2 for instance) and film deposition rate d :

$$C_i \sim \frac{P}{d}$$

exact equation:

$$C_i = \frac{7.76 \times 10^{-2} P M_a}{\sqrt{M_g T} \rho d}$$

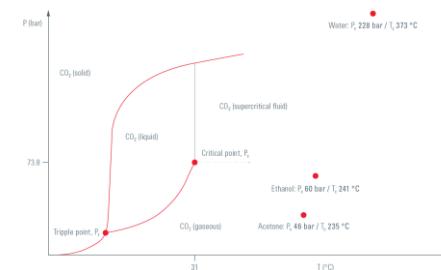
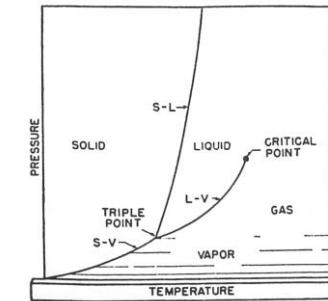
16) A critical point dryer is used to remove liquid from delicate samples. It is sometimes necessary to circumvent damage caused by surface tension during drying. Discuss possible process flows that can achieve this and mark them on the PVT diagram.

We should not cross the L-V, but go through the critical or above. This is impractical with water, therefore we take exchange liquids such as CO_2 via alcohol

From Leica homepage:

To preserve sample morphology, critical point drying is the state of the art method (see "[Pressure/temperature phase diagram for \$\text{CO}_2\$](#) "). At the critical point physical characteristics of liquid and gaseous are not distinguishable. Compounds which are in the critical point can be converted into the liquid or gaseous phase without crossing the interfaces between liquid and gaseous avoiding the damaging effects. The dehydration of the samples using the critical point of water is not feasible since it lies at 374°C and 229 bar where any biological sample would be destroyed. To overcome this problem, water can be replaced against liquid carbon dioxide (CO_2), whose critical point lies at 31°C and 74 bar and is more appropriate for all biological applications and technically relative easy to maintain.

However, CO_2 has one serious disadvantage as transitional fluid; it is not miscible with water. Therefore, water has to be replaced by exchange fluids like ethanol or acetone which are miscible in both water and liquid CO_2 .



Summary - Discharges & Plasma

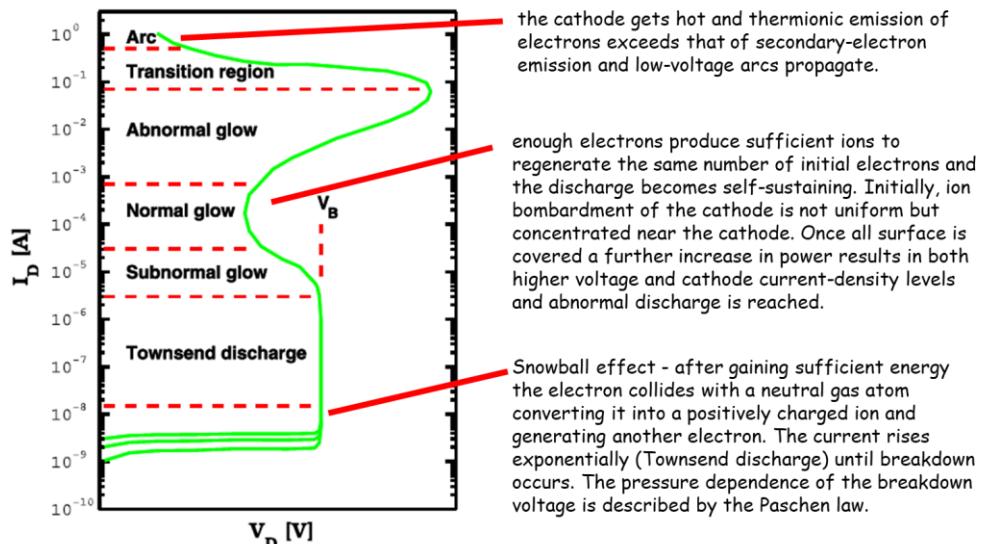
- electron collisions with reactive gases create metastable species that promote plasma-assisted chemical reactions.
- Confinement in crossed electric and magnetic fields prolongs the electron lifetime enhancing the ionizing efficiency near the cathode. A denser plasma and larger discharge currents result which is heavily exploited in Magnetron sputtering.
- Debye length is a measure of the mobility of the electron cloud and if system dimensions exceed the Debye length then the plasma is neutral
- AC effects: higher ionization degree, capacitive and inductive coupling from outside possible
- Electrode sheath: both electrodes are negatively charged with respect to the plasma potential with a voltage drop near the electrode surface because electrons are faster than ions
- Collisions: Due to huge mass differences very little energy is transferred in elastic collisions between electrons and atoms. Collision cross-sections describe the probability of inelastic interaction and vary with electron energy incl. the ionization threshold.
- Plasma chemistry: plasma generated reactions generally enhance chemical vapor deposition and film etching processes. Thus gas-phase chemical reactions will usually occur more rapidly and at lower temperatures with benefit of plasma assist.

Q & A - Discharges & Plasma

- 1) What happens microscopically in a DC plasma?

Positive gas ions strike the cathode and eject/ sputter target atoms and these atoms enter and pass through the discharge region to deposit on the growing film. Electrons and negatively charged ions toward the anode substrate where they impinge on the growing film and play a beneficial role, this time to modify the structure and composition of the growing films.

- 2) Describe a typical voltage - current curve of a discharge.



- 3) Explain the term "snowball effect" in a Townsend discharge

Snowball effect - after gaining sufficient energy the electron collides with a neutral gas atom converting it into a positively charged ion and generating another electron. The current rises exponentially (Townsend discharge) until breakdown occurs. The pressure dependence of the breakdown voltage is described by the Paschen law.

Q & A - Discharges & Plasma

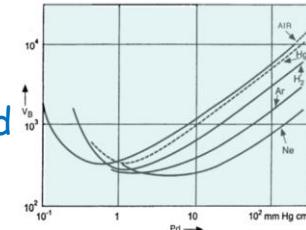
4) How is the breakdown voltage related to system pressure and inter electrode distance in DC discharge?

$$\text{Paschen law: } V_B = \frac{APd}{\ln(Pd) + B}$$

The Paschen curve: breakdown voltage V_B vs pressure P * electrode distance d
left: $P \cdot d$ too few electron-ion collisions \rightarrow secondary electron yield is too low to sustain ionization in the discharge.

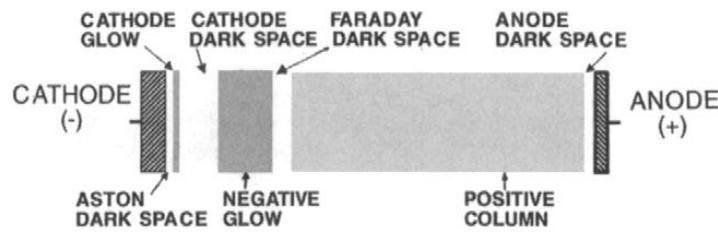
Right: at high pressures electrons do not acquire sufficient energy to ionize gas atoms, the discharge is quenched.

In between: at typically a few hundred to a thousand volts, the discharge is self-sustaining



5) Draw and denote the different dark and bright areas of a glow discharge.

Full:



Simple: cathode DS, negative glow,
Faraday DS, positive column

6) Why is the cathode dark space dark?

Because electrons don't have yet enough energy to excite carrier gas (Ar typically)

7) Why arc discharges form at high voltages? How do they compare in terms of voltage and current to normal glow discharges?

The cathode gets hot and thermionic emission of electrons exceeds secondary electron emission; low voltage and high currents compared to glow discharge

Q & A - Discharges & Plasma

8) Why is the target negatively biased compared to the plasma region? Explain the term plasma sheath.
both electrodes are negatively charged with respect to the plasma potential with a voltage drop near the electrode surface because electrons are faster than ions
Once electrons are mostly depleted from the boundary interface between plasma and electrodes or samples, a region with only positive ions and neutrals will be formed. This usually dark boundary region is called plasma sheath.

9) What are typical electron, ion and neutral temperatures in a glow discharge?
The electron temperature is around 23000K, ion temperature around 500K and neutral gas atoms are at room temperature

10) What is meant by $E \times B$ drift motion of a charged particle?
Charged particles within the dual field environment experience the well-known Lorentz force in addition to electric field force, which leads to spiral motion if E and B are perpendicular

11) Explain AC effects in plasmas as compared to DC variants.
Even smaller values of E can produce ionization if, after electron-gas collisions, the reversal in electron velocity coincides with the changing electric-field direction.

12) Explain the term collision cross-section.
collision cross-section σ_c reflects the probability of interaction or collision between particles.
Collisions are either elastic or inelastic depending on whether the internal energy of the colliding species is preserved or not. When $M_1 = M_2$ the moving projectile is brought to a halt and all of its energy is efficiently transferred to M_2 , which speeds away. When, however, $M_1 \ll M_2$ reflecting, say, a collision between a moving electron and a stationary nitrogen molecule, then the energy transfer ratio is approximately 10-4.

Summary - sputtering and film ion bombardment

- Sputtering: high energy particles eject target atoms through momentum transfer. These atoms travel to the substrate and form the film.
- Optimum pressure to sustain the plasma (too low then not enough collisions, too high not enough time to gain enough energy)
- Upon bombardment incoming ions may be reflected back, stick or adsorb, scatter, eject or sputter surface atoms, or get buried in subsurface layers (ion implantation). Surface heating, chemical reactions, atom mixing, and alteration of surface topography also happens.
- The ion beam energy is the critical parameter with < 5 eV : Adsorption or reflection; 5 - 10 eV : Surface damage and migration; 10eV - 3 keV : Sputtering; >10 keV : Ion implantation
- The sticking probability is lowest in the range 0.2eV and 20eV
- Ions sputter like billiard balls: maximum energy/momentum transfer at mass ratio=1
- Sputter yield varies 0.1-10
- The energy threshold energy is typically 4x heat of sublimation
- There are three different sputter regimes: single knock-on, linear collision cascade and spike regime
- Angular distribution of sputtered atoms follows a cosine law and number distribution the Boltzmann distribution
- Alloy targets are widely used as compared to evaporation as surface composition stays stable due to minimum surface diffusion in the solid.
- During ion bombardment of the growing film similar processes as at the target surface happen. Film topography, microstructure, density etc. is affected.
- Compared to evaporation the target surface stays cold, atoms exhibit higher energy. Evaporation yields higher deposition rates, operates at lower pressures and films are cleaner.

Q & A - sputtering and film ion bombardment

- 1) Explain why there is an optimum pressure to maintain the plasma.
Optimum pressure to sustain the plasma (too low then not enough collisions, too high not enough time to gain enough energy)
- 2) Name the processes that happen when the surface is hit with energetic particles from the plasma
Upon bombardment incoming ions may be reflected back, stick or adsorb, scatter, eject or sputter surface atoms, or get buried in subsurface layers (ion implantation). Surface heating, chemical reactions, atom mixing, and alteration of surface topography also happens.
- 3) Give ion beam energy ranges for Adsorption, surface damage/migration, Sputtering and ion implantation to happen
The ion beam energy is the critical parameter with <5eV: Adsorption or reflection; 5-10eV: Surface damage and migration; 10eV-3keV: Sputtering; >10keV : Ion implantation
- 4) For which mass ratio maximum energy transfer happens during sputtering
Ions sputter like billiard balls: maximum energy/momentum transfer at mass ratio=1
- 5) Define the term "sputter yield". What are typical numbers (range). Give a range of typical threshold energies for sputtering.
Sputter yield varies 0.1-10; The energy threshold energy is typically 4x heat of sublimation

Q & A - sputtering and film ion bombardment

6) Explain the sputter regimes as a function incident ion energy. Which laws follow angular and energy distribution?

There are three different sputter regimes: single knock-on, linear collision cascade and spike regime. Angular distribution of sputtered atoms follows a cosine law and number distribution the Boltzmann distribution

7) Why is the composition of the deposited film closer to the target in sputtering than in evaporation.

Evaporation: fractionation of alloy melts during evaporation, with subsequent loss of deposit stoichiometry. Greater disparity in vapor pressures compared to the difference in sputter yields under comparable deposition conditions. Melts homogenize readily because of rapid atomic diffusion and convection effects in the liquid phase;

Sputtering: minimal solid-state diffusion enables the maintenance of the required altered target surface composition.

8) How far do adatoms move when they arrive with thermal energies (KT)? Explain the term temperature spike at higher arrival energies.

For ion energies up to the sputtering threshold where $E/E_s \sim 30$, r is calculated to be only in the order of one atomic distance from maximum thermal-diffusion distance $r = 0.4a_r(E/E_s)^{1/3}$,

At much higher energies: spike regime \rightarrow high temperature bubble

9) How does ion bombardment affect the film microstructure?

Film topography, microstructure, density etc. is affected.

10) Compare plasma sputtering to evaporation. Point out at least 4 differences.

Sputtering: target surface stays cold, atoms exhibit higher energy.

Evaporation: higher deposition rates, lower pressures, films are cleaner

summary - plasma and ion beam processing

- All important classes of materials are available as target in a variety of shapes
- the basic configuration of two electrically powered electrodes separated by a plasma is common to a number of film deposition and etching processes. Problems: high pressures and related low film quality, low ionization degrees, low deposition rates irrespective of DC, AC, or RF powering, or whether reactive gases are present or not.
- A hollow cathode exhibits enhanced ionization degree and higher discharge currents compared to a planar diode configuration.
- Substrate bias of -50V to -300V lead to a broad energy distribution (collisions prior arrival) of ions bombarding the growing film that lead to improved adhesion, better step coverage, increased density and alternation of film morphology related to removal of contaminants, enhanced nucleation and renucleation and higher surface adatom mobility.
- RF sputtering at 13.56 MHz: electron bombard during negative and ions during positive cycle the target and therefore charge built-up for insulating targets is prevented. At RF frequencies essentially the electrons move. Sputtering occurs because a self-bias at the target establishes which leads to dc-like sputtering. Deposition rates are comparable low and non-conducting targets are susceptible to thermal stress.
- Magnetron sputtering processes relying on magnetic confinement of the plasma are now universally employed because they yield films of all materials at relatively high deposition rates, at lower pressures.
- Typical magnet arrangements are an outer annular magnet and an inner magnet of opposite polarity at the backside of the cathode target.

summary – plasma and ion beam processing

- Pulsed power magnetron sputtering exploit discharge pulses to the target at frequencies of several tens of kilohertz, where pulse magnitude, polarity, width, and off-time can all be varied. This prevents arcing and the formation of dielectrics such as oxides at the target surface.
- Unbalanced magnetron sputtering exhibit less confined plasmas that allows for extension of the plasma to the anode to promote ion bombardment at the substrate.
- Typical problems with magnetron sputtering are inhomogeneous target erosion, particulate contamination, and film uniformity.
- Sputter deposition of nonmetallic films, e.g., oxides or nitrides, can be done either employing cathodes of these materials as in RF sputtering, or more commonly now by reactive sputtering using metal targets. A mixture of inert and reactive gases used for sputtering leads to chemical reactions during film growth. Target poisoning and related compound formation can be prevented using pulsed plasmas.
- Ion plating combines evaporation with high energy ion bombardment/sputtering of the substrate (2-5KV). Deposition rates are between evaporation and sputtering.
- Ion beam assisted deposition aim at independent control of ions and energies of the ions. Inert gas ion beams are used for cleaning and target sputtering. In the second mode ions are directed at the substrate to modify film properties.
- Ion cluster beam exploit vapor cluster agglomeration and acceleration of clusters to the substrate
- Virtually any material can be deposited with Magnetron sputtering and is therefore used widely in industry
- Hybrid film-deposition systems combining two or more of the following features, i.e., evaporation, sputtering, low voltage-high current arcs, inertgas plasmas, chemically reactive plasmas, and ion beams, have been widely used. They include ion plating, cathodic arc, and ion-beam-assisted deposition processes.

Q & A - plasma and ion beam processing

- 1) Which target materials are available for sputtering?

All important classes of materials

- 2) Describe the basic components of a DC sputter system

two electrically powered electrodes separated by a plasma, vacuum chamber with pumps

Problems of simple DC system: high pressures and related low film quality, low ionization degrees, low deposition rates irrespective of DC, AC, or RF powering, or whether reactive gases are present or not.

- 3) Why is the optimal pressure around 0.1mbar so high in a DC sputtering system

It is around 0.1mbar (100mtorr). At lower pressures not enough collisions (we loose electrons at chamber walls) and at higher pressures not enough energy

- 4) Define "sputter yield"

number of sputtered atoms per incident ion

- 5) Why is a substrate bias used?

-50V to -300V lead to a broad energy distribution (collisions prior arrival) of ions bombarding the growing film -> improved adhesion, better step coverage, increased density, alternation of film morphology related to removal of contaminants, enhanced nucleation and renucleation and higher surface adatom mobility (->SZM).

Q & A - plasma and ion beam processing

6) Explain how a hollow cathode target works

"pendel-electron" effect: discharge cavity consists of a negative glow region separated from opposite cathode surfaces by two dark spaces. In a pendulum-like motion, electrons emitted from the cavity surface are accelerated toward the negative glow, penetrate the opposite dark space, turn around, and enter the negative glow again -> enhanced ionization degree and higher discharge currents compared to a planar diode configuration.

7) Explain the operation and effects of magnetron sputtering

magnetic confinement of the plasma with electrons hopping over target surface -> high deposition rates at lower pressures. Typical magnet arrangements are an outer annular magnet and an inner magnet of opposite polarity at the backside of the cathode target.

8) How is step coverage controlled in sputter deposition systems?

By pressure and substrate rotations

9) Sputtering: Why is the target negatively biased? How is the break down voltage related to system pressure and inter electrode distance in DC discharge?

Electron emission for plasma and accelerate ions towards cathode that sputter; Optimum pressure to sustain the plasma (too low then not enough collisions, too high then not enough time to gain enough energy),

$P \cdot d$ in Paschen equation/curve -> ((too small d then not enough collisions, too high d then we loose electrons to chamber wall))

Q & A - plasma and ion beam processing

10) Magnetron Sputtering: State the limitation of planar diode sputtering. What is meant by $E \times B$ drift motion of a charged particle? Show the drift motion near the surface of rectangular planar magnetron. Why the trajectory of the electron near the surface of cylindrical magnetron is that of a cycloid? How is the performance of a magnetron evaluated?

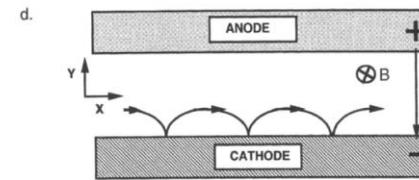
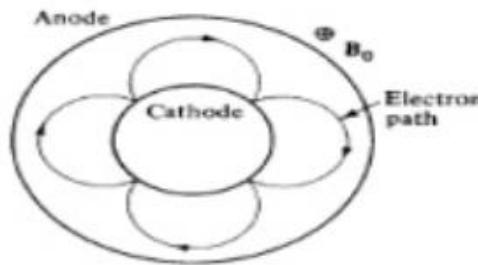
-Problems of simple DC system: high pressures and related low film quality, low ionization degrees, low deposition rates irrespective of DC, AC, or RF powering, or whether reactive gases are present or not.

-Charged particles within the dual field environment experience the well-known Lorentz force in addition to electric field force, which leads to spiral motion if E and B are perpendicular

- planar magnetron side view:

denote E , B fields!

- cylindrical:



- performance of magnetron: homogeneity of sputtering, sputter rate

11) State the limitation of balanced magnetron and specific advantage of unbalanced magnetron?

Limits magnetron sputtering: erosion tracks/poor efficiency, particle may form

Unbalanced magnetron \rightarrow less confined plasmas \rightarrow promote ion bombardment at the substrate.

Q & A - plasma and ion beam processing

12) Radio Frequency and Pulsed DC Sputtering

Why RF sputtering can be done at lower target voltage and process pressure than that required in DC sputtering? How does a negative bias develop on a non-conducting target? Can a conducting target be connected to RF power? How may the pulse-ON and OFF time be selected during pulse DC sputtering? Is there any advantage of providing pulse DC supply even to a conducting substrate?

- smaller values of E can produce ionization if, after electron-gas collisions, the reversal in electron velocity coincides with the changing electric-field direction. Paschen curve shifted to lower pressures (complicated)
- electron bombard during negative and ions during positive cycle the target and therefore charge built-up for insulating targets is prevented
- At RF frequencies essentially the electrons move. Sputtering occurs because a self-bias at the target establishes which leads to dc-like sputtering.
- Yes - also on conducting target but typically lower sputter rates than DC
- Pulsed power magnetron sputtering prevents arcing and the formation of dielectrics such as oxides at the target surface. Works on metal surfaces in particular. Speed of chem. reactions or arc melt forming process determines pulse length.

13) Sputter Deposition of Nitride Coating: State the advantage of reactive sputtering over direct sputtering of TiN. How may the partial pressure of N_2 affect Ti:N ratio in the coating higher rate of sputtering from conductive, N concentration determines exact composition of coating

14) Polymers are among the few materials that are not made by sputtering. Why? Start the discussion with atomistic processes at the sputter target.

Thermal load on target (spike) may melt, insulating material, polymer chains will break and will not be transported to the substrate

Summary - CVD

- Instead of the physical transfer of atoms from a condensed evaporation source or sputtering target to the substrate, CVD relies on gas phase and gas-solid chemical reactions to produce thin films.
- Fundamental steps at the surface are: Convective and diffusive transport of reactants, Chemical reactions in the gas phase, Transport to the substrate surface, Adsorption and diffusion, chemical reaction at surface, desorption of volatile by-products, Convective and diffusive transport of the reaction by-products away
- Reaction types are Pyrolysis, Reduction, Oxidation, Compound formation, Disproportionisation or reversible Transfer
- Thermal CVD of silicon exploits the silane reaction as silane is less stable as Chloride based precursors -> highest growth rate for all thermodynamic possible reactions
- Vapour supersaturation determines the grain size in CVD
- Nucleation rate on various surfaces: K, S, F faces; linear, exponential, and square dependence
- Diffusion involves motion of individual atoms, but viscous flow and convection moves the gas as a whole
- convection arises from the response to gravitational, centrifugal, electric, and magnetic forces
- Molecular flow vs viscous flow vs turbulent flow and its relation to boundary layer thickness
- Viscous flow happens above 0.01atm. A boundary layer establishes at tube/reactor where the the velocity drops to zero.
- The Reynolds number defines the boundary layer thickness and marks the transition from laminar to turbulent flow above $Re>2100$.
- Growth regimes are determined by pressure and the related mean free path of species (Knudsen number): atm-10mbar: kinetics and mass transport dominant, <1mbar surface reactions are important, < 10^{-4} mbar temperature of gas and surface and desorption of precursor fragments

Summary - CVD

- Turbulent flow happens at $Re > 2100$. Note role of pipe diameter or length of surface along gas flow
- Modelling mostly numerical, but dimensionless numbers such as Knudsen, Peclet, or Reynolds guide the process
- Thermal CVD: active surface sites are important, temperature drives vapor supersaturation. Growth regimes are reaction rate limited, diffusion/mass transport limited and desorption rate limited
- Batch processing ideally in surface reaction limited mode
- MOCVD precursors exhibit high volatility at moderately low temperatures which allows control of gas flow rates instead controlling vapour pressure of solids.
- PECVD exploits rf diode discharges to decompose gas molecules into a variety of reactive species enabling lower process temperatures
- Silicon nitride is stoichiometric with thermal CVD at 900° and amorphous & hydrogenated after PECVD at 300°.
- Example carbon: DLC as low-T PECVD and diamond as Thermal CVD
- CVD precursors and reaction products are typically toxic, flammable, pyrophoric, or corrosive substances and are therefore a health hazard to humans

In General because they are subject to thermodynamic and kinetic limitations and constrained by the flow of gaseous reactants and products, CVD processes are generally more complex than those involving PVD. An impressive number of different CVD materials (metals, elemental and compound semiconductors, oxides, nitrides, carbides, diamond, etc.) can be synthesized. These materials and applications needs have been fulfilled through a variety of CVD processes involving different reactor designs and operating conditions.

Q & A - CVD

1) Compare CVD, ALD and PVD and explain at least 3 fundamental differences

	Evaporation	Sputtering	CVD	ALD
Material Mobilisation	thermal	momentum transfer	thermal (Plasma)	thermal (Plasma)
Particle type	atoms	atoms, ions	molecules, ions, radicals	molecules
Particle Energy in eV	0.1-5	1 to 100, more with bias	1 to 10eV	1 to 10eV
popular Materials	metals	metals, dielectrics	metals, dielectrics	oxides
Pressure in mbar	Below 10 ⁻³	10 ⁻⁴ -10 ⁻¹	10 ⁻² - 1	10 ⁻² - 1
3D	no	no	yes	yes
Interface modifications	no	yes	no	no

2) What are the different steps governing the mechanisms of CVD?

Convective and diffusive transport of reactants, Chemical reactions in the gas phase, Transport to the substrate surface, Adsorption and diffusion, chemical reaction at surface, desorption of volatile by-products, Convective and diffusive transport of the reaction by-products away

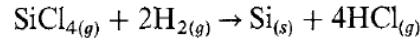
3) Give 3 examples of reaction types in CVD (chemical reaction formulas)

simples ones:

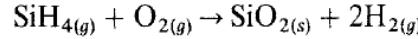
Pyrolysis:



Reduction:



Oxidation:



4) Why is silane preferred over chlorine based precursors in thermal CVD of silicon?

Silane is less stable as Chloride based precursors -> highest growth rate for all thermodynamic possible reactions

Q & A - CVD

- 5) Explain the relation between vapor supersaturation and grain size
higher supersaturation means smaller grain size, amorphous at very high supersaturations - example CVD of silicon
- 6) Explain the difference between diffusion, convection and viscous flow
 - diffusion: motion of individual atomic or molecular species
 - convection: gas flow due to gravity, centrifugal forces etc. Example cold wall reactor with convection downwards at chamber wall
 - viscous: gas transport in confined volumes at 10mbar and above with significant boundary layer
- 7) How does the pressure influence CVD processes. Use the Knudsen number for your arguments
 - if $MFP/D = Kn \ll 0.01$, then viscous and then laminar or turbulent according Re Number, molecule-molecule interactions important
 - $Kn > 1$, then molecular flow. Gas phase reactions less important and surface reactions more important, easy trajectory calculations
- 8) Explain laminar vers Turbulent flow. How can we estimate the transition. Use the Reynolds number equation to discuss strategies to avoid turbulent flow.
If $Re < 2100$, the boundary layer, and parabolic velocity profile, turbulent is chaotic for $Re > 2100$

The $Re = \frac{\rho x v_0}{\eta}$ and therefore we avoid high Reynolds numbers by low density and high viscosity gas combined with short tube length/diameter and low velocity of gas

Q & A - CVD

9) Explain surface /Reaction Rate vs mass transport limited reactions

Mass Transport Limited: Rate limiting step is the transport of gas molecules into the reactor and through the stagnant layer, nearly independent of temperature.

Reaction Rate Limited: ... chem reaction speed limits overall growth rate

10) Explain desorption rate limited Regime

Rate limiting step is the desorption of molecules at high temperatures. The growth rate decreases, and the surface mobility of the adsorbates increases.

11) How does pressure affect deposition rate?

See Q7

12) How does one switch between reaction controlled and diffusion-controlled regimes?

At very low T we are reaction rate limited compared to intermediate T where mass control is limiting

13) How does the regime (reaction- vs. diffusion controlled) affect CVD system design?

Batch reaction in RR-limited regime, single wafer type in mass transport/diffusion limited

14) Why is the Reaction Rate Limited Regime the Regime of choice for batch coating using hot wall CVD reactors

We'll deposit everywhere on cold substrates with equal thickness, chamber wall in different growth regime and therefore maybe lower rate.

15) Why is MOCVD so popular in terms of process control?

All precursors are in the gaseous state and pyrolysis reactions that are insensitive to temperature

Q & A - CVD

16) Explain the advantages and disadvantages of atmospheric CVD, LPCVD, and PECVD

Process	Advantages	Disadvantages	Applications	Remark	Pressure/ Temperature
APCVD	Simple, high deposition rate (700 Å/min for SiO_2), low temperature	Poorer step coverage, particle contamination	Doped and undoped, low temperature, thick oxides (mainly dielectrics)	Mass transport-controlled	100–10 kPa 250–450°C
LPCVD	Excellent purity and uniformity, conformable step coverage, large wafer capacity	High temperature and lower deposition rate	Doped and undoped, high-temperature oxides, silicon nitride, polysilicon, W, WSi_2	Surface reaction-controlled	100 Pa 550–650°C
VLPCVD			Single-crystalline Si and compound semiconductor superlattices	Surface reaction-controlled	1.3 Pa
MOCVD	Excellent for epi on large surface areas	Safety concerns (highly toxic), very expensive source material	Compound semiconductors for solar cells, laser, photocathodes, LEDs, HEMTs, and quantum wells; also W and Cu	High volume, large surface area production	
PECVD	Lower substrate temperatures, fast, good adhesion, good step coverage, low pinhole density	Chemical (e.g., hydrogen) and particulate contamination, plasma damage	Low-temperature insulators over metals, passivation (nitride)	Tends to have more pinholes than LPCVD	2–5 Torr (pressure higher than in sputter deposition, more gas-phase collisions, less ion bombardment on surface) more collision in gas phase, less ion bombardment on substrate –200–400°C
Atomic layer deposition (ALD)	ALD is the deposition method with the greatest potential for producing very thin, conformal films with control of the thickness and composition of the films possible at the atomic level.	A major limitation of ALD is its slowness; usually only a fraction of a monolayer is deposited in one cycle.	A major driving force for the interest in ALD is for scaling down microelectronic devices.	Many technologically important materials such as Si and Ge, several multi-component oxides and certain metals cannot currently be deposited by ALD in a cost-effective way.	RT to 400°C

summary diamond

- Carbon represents with its both crystalline modifications diamond and graphite two complementary features: superhard, insulating, transparent and soft, conductive, absorbing, respectively.
- By smart use of the **growth kinetics**, diamond as the high-pressure carbon modification can be prepared under low-pressure conditions
- The basic requirement is a **large excess of atomic hydrogen** (or comparable reactive species) in comparison to the impinging carbon species.
- The **role of atomic hydrogen** consists in the **transformation of the carbon containing molecules (usually CH₄) into reactive radicals** and in the **generation and temporary stabilization of active surface**. Oxygen may replace hydrogen around the CO line which enables low-T growth.
- The necessary kinetic works in a certain range of **substrate temperatures, typically around 900 °C**. and few at% of hydrocarbons. At lower temperatures or higher C concentrations nc diamond is formed. Bombardment of the surface with energetic ions leads to self-nucleation, allowing very high nucleation densities.
- The standard processes are the **hot filament CVD** (mechanical applications) and the **microwave CVD**. In the hot filament CVD, the atomic hydrogen is generated at the surface of tantalum or tungsten wires, heated to temperatures around 2000 °C. Deposition rate scales in principle with the gas Temperature for all methods.
- The diamond films grow homoepitaxially from tiny diamond clusters (**nuclei**) made by mechanical surface treatments with microsized diamond grains ("scratching"). Alternatively **bias enhanced implantation** of carbon atoms generated clusters that serve as nuclei.
- For substrate materials with high carbon solubility (e.g. iron metals), **interlayers as diffusion barriers** must hinder the fast drain of the deposited carbon atoms.
- Applications include tools for machining of non-ferrous materials, loadspeaker membranes, electrodes, heat spreader and electronic applications (large band gap)

Summary amorphous carbon based materials

- According to the various states (sp_1 , sp_2 , sp_3) with C-C and with C-H bonds, a-C:H films realize a very broad structural spectrum: polymerlike films (PLCH) with dominating linear C-C chains, diamondlike carbon (DLCH) with a strong carbon network of sp_2 and sp_3 C-C bonds, graphitelike films (GLCH) with dominating sp_2 C-C and C-H bonds and tetrahedrally bonded hydrogenated amorphous carbon (ta-C:H) with a very strong carbon network mainly of sp_3 C-C bonds (notwithstanding a certain hydrogen content).
- Deposition conditions use T and especially the assistance of energetic ions, films with very low electrical conductivity, high hardness and high optical transparency (at least in the infrared) can be produced.
- In the CVD from hydrocarbon precursors, the film structures change with decreasing temperature, increasing hydrocarbon concentration and increasing ion bombardment from (nearly perfect) diamond polycrystals to nanodiamonds (with increasing amounts of non-diamond phases) and finally to hydrogenated amorphous carbon a-C:H.
- The CVD of DLC high-temperature plasma chemistry in the diamond deposition is replaced by the combination of chemical reactions of excited radicals and ballistic effects of energetic ions.

Summary amorphous carbon based materials

- Higher temperatures, more intense ion bombardment and less hydrogen incorporation favor the formation of GLCH. Lower temperatures, less intense ion bombardment and plenty hydrogen promote the formation of PLCH.
- For industrial applications, the CVD with capacitively coupled glow discharge is mostly used. The oscillating field with rf frequencies in the MHz range avoids the charging of the more or less insulating coatings.
- The mean energies of the impacting ions are in the range of some ten electron volts. They increase proportional to the self-bias.
- The a-C:H films, prepared by PECVD, contain between 5 and 60% hydrogen.
- Nonmetals, especially silicon, nitrogen or fluorine, can be introduced into the amorphous carbon films by mixing the hydrocarbon precursor with corresponding reactive gases. Nitrogen favors the formation of GLCH, silicon the formation of DLCH and fluorine the formation of PLCH.
- The incorporation of metals into the growing amorphous carbon film is usually realized by reactive sputtering of metal or metal carbide targets in an argon-hydrocarbon discharge. At low metal concentrations below some percent, the metal atoms are dissolved, forming a solid solution in the carbon film. At higher concentrations they segregate to nearly spherical metal(carbide) crystallites from nanometers up to some ten nanometers embedded in the amorphous carbon matrix

Q & A - Carbon based materials

- 1) State the application of diamond coating in mechanical manufacturing
Hard coatings (Wood, dental), microengineering (components, Watch parts)
- 2) Explain the growth mechanism of diamond. State the CVD reactions for growth of diamond coating
Methane + Hydrogen radical \rightarrow Methyl radical + Hydrogen molecule
Diamond Surface + Hydrogen radical \rightarrow active surface site + hydrogen molecule
active surface site + Methyl radical \rightarrow bonded CH_3 group
- 3) Why is H_2 used in CVD of diamond? Which other element can replace it under which conditions?
As seen under 2 to generate radicals and active surface sites, also to etch sp2 type of material from surface, Oxygen works also around CO line
- 4) How does the grain size depend on temperature and hydrocarbon concentration?
Around 900°C and few at% hydrocarbon ideal; lower T or higher higher hydrocarbon leads to lower grain size
- 5) Which deposition techniques for diamond films you know?
Hot filament and Microwave CVD are most important
- 6) State the advantage of HFCVD process over other process of diamond CVD.
Inexpensive, large surfaces due to multifilament arrays
- 7) Explain the nucleation of diamond. How is nucleation enhanced in practice?
Seeding with Diamond nanoparticles (scratching, ultrasonic etc), bias enhanced alternative

Q & A - Carbon based materials

- 8) Why does cemented carbide substrate require special surface treatment before the CVD process?
Co binder is catalyst for graphite growth
- 9) Name at least 3 applications of diamond films
machining of wood, electrodes, implants, loadspeaker membranes
- 10) Explain the differences between PLCH, DLCH and GLCH and ta-C:H. Under which deposition conditions they form?
*polymerlike films (PLCH) with dominating linear C-C chains,
diamondlike carbon (DLCH) with a strong carbon network of sp² and sp³ C-C bonds,
graphitelike films (GLCH) with dominating sp² C-C and C-H bonds and
tetrahedrally bonded hydrogenated amorphous carbon (ta-C:H) with a very strong carbon network mainly of sp³ C-C bonds
From High T & low energy (PLCH) to low T and high energy (ta-C:H)*
- 11) What is the standard process for a-C:H deposition
PECVD
- 12) Compare briefly the growth mechanisms of diamond to PECVD of a-c:H in a few lines.
a-c:H growth understood as beyond nc diamond structures - amorphous due to lower substrate temperatures, higher carbon concentrations in the gas atmosphere and an intensified ion bombardment of the growing film

Q & A - Carbon based materials

13) What additional alloying elements are used for a-C:H and what is their effect on coating properties?

Nitrogen favors the formation of GLCH, silicon the formation of DLCH and fluorine the formation of PLCH with the related properties (lubricating, harder, low adhesion)

14) Rank diamond-Ta-C, a-c:H and graphite in terms of hardness, sp³ content, band gap and electrical resistivity

all decrease with diamond → Ta-C → a-c:H → graphite

8) Name 3 applications for amorphous carbon based materials

hard and lubricating any wear application

scratch resistant sun glasses

decorative black for watches

Summary - ALD

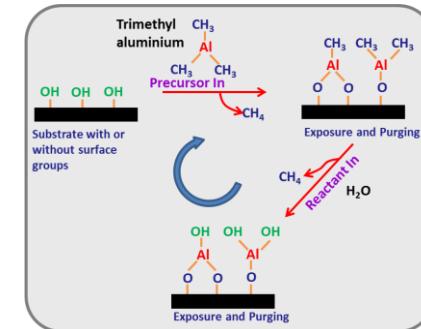
- In atomic layer deposition (ALD), the precursor vapors are introduced to the substrates alternately, one at a time, separated by purging periods with inert gas.
- Typical cycle times are from one second to several seconds. Most ALD processes operate between 200°C and 400°C
- ALD and MLD have unprecedented thickness control down to the ML (or atomistic) level with typically half a monolayer per cycle (incomplete coverage)
- Adsorption kinetics described by Langmuir equation, adsorption kinetics (over time) for physisorption and chemisorption
- Energies of physisorption ~0.1eV and Chemisorption 1-10eV,
- Growth rate and steric hindrance, H incorporation at low T
- MLD exploits short organic precursors with OH-group instead water
- The first reactant is either a halogen or an organometallic and the second water vapor or ozone for oxides/ammonia for Nitrides, HS for sulfides.
- Precursor requirements englobe Volatility at low T, ability to physisorb & chemisorb, ability to dissociate and finally non-toxic etc. The success of ALD is built on chemistry, and for each film material an appropriate combination of precursor molecules suited to the ALD process must be found. The requirements for the precursors are contradictory: they must be thermally stable and reactive.
- The ALD window is limited by low reaction rates and condensation at low temperatures and thermal desorption and thermal dissociation at higher temperatures. The reactions should be saturative and no precursor decomposition should take place. Only then is the film growth self-limiting, which is one of the attractive features of ALD
- Self-limiting surface reactions provide for conformal coatings even in high-aspect ratio structures
- Nanolaminate (multilayers) & hybrid organic - inorganic materials possible
- The main stream in ALD is thermal processing, where activation for the surface reaction is brought about by heat. Plasma ALD is increasingly used to provide radicals during the ALD process enabling low deposition temperatures.
- ALD reactor types, range from multilevel batch to flow reactors, PE-ALD reactors and spatial ALD reactors.
- ALD processes have been developed for oxides, nitrides, carbides, fluorides, certain metals, II-VI and III-V compounds, and polymers.
- Applications range from sub-10nm barrier layers or CMOS gate oxides to thick anti-corrosion layers.

Q & A ALD

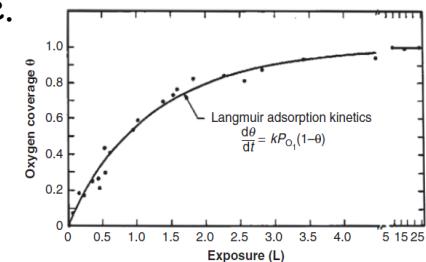
1) Explain the typical process steps of an ALD process of alumina. What are typical cycle times. Why is the film thickness not just the sum of deposited lattice planes in crystalline alumina?

Typical cycle times are seconds

Steric hindrance leads typically to half a monolayer



2) Draw the function for the adsorption kinetics at the substrate surface.



2. Adsorption kinetics of O_2 on Rh(111) [9].

3) Compare energies of chemisorption and physisorption

$E_{\text{chem}} \approx 1-10 \text{ eV} \approx 100-1000 \text{ kJ/mol}$

$E_{\text{phys}} \approx 0.1 \text{ eV}$ (approx. 10 kJ/mol)

4) Name typical precursors for the two separate ALD cycles

For Alumina: Trimethylaluminium and H_2O ; for MLD H_2O replaced e.g. Ethylenglycon; for sulfides H_2O replaced by H_2S

In general: the first reactant is either a halogen or an organometallic and the second reactant is water vapor or ozone for oxides, ammonia for Nitrides, and HS for sulfides

Ohring 2002

Q & A ALD

- 5) Which design rules for ALD precursors you know?
Volatility at low T, ability to physisorb & chemisorb, ability to dissociate, non-toxic
- 6) Explain the term ALD window. What happens when process temperatures are a) too high or b) too low at the substrate surface?
Only in the ALD window the film growth self-limiting. The reactions should be saturative and no precursor decomposition should take place.
a) thermal desorption and thermal dissociation at higher temperatures.
b) the ALD window is limited by low reaction rates and condensation at low temperatures
- 7) Why can ALD coatings be conformal despite aspect ratios of surface structures of 1:1000?
→ self limiting chemical reaction - just long enough exposure times needed to reach bottom of high aspect structure
- 8) What are typical pressures and temperatures for the ALD process?
Most ALD processes operate between 200°C and 400°C, Pressure 10⁻² - 1 mbar
- 9) What distinguishes ALD from CVD processes - note at least 3 differences
ALD no ions, mostly oxides, self-limiting, lower T
- 10) What are the benefits of PEALD compared to thermal ALD
radicals form during the PEALD process enabling low deposition temperatures, also some materials PEALD only
- 11) Explain the concept of spatial ALD
Wafer on rotating disk exposed partially to different chambers
- 12) Name at least 3 technological applications of ALD thin films
Barrier coatings, CMOS HfO₂ barrier coating, anti-reflection coatings solar cells

Summary - nucleation

- Sequence of events nucleation, growth and coalescence
- Island (Volmer-Weber), layer (Frank Van der Merwe), or Stranski-Krastanov nucleation mode
- Surface structure: atoms relax at the outer surface in a way to preserve in plane symmetry which leads to surface reconstruction
- 3 Surface energies: towards vapor phase around 1 J/m^2 , Metals have highest, organic close to 100 mJ/m^2
- Capillary theory: Gibb's free energy scales with r^3 and three interface contributions with r^2 . Mechanical equilibrium leads to Young's equation. The $\text{derivative}=0$ leads to critical radius of nucleus size r^* and the nucleation barrier ΔG^*
- wetting factor dependent on Θ which has the value of zero for $\Theta = 0^\circ$ and unity for $\Theta = 180^\circ$. When the film wets the substrate, there is no barrier to nucleation. At the other extreme of dewetting, ΔG^* is maximum and equal to that for homogeneous nucleation.
- If γ_{fs} is neglected island growth occurs when the surface tension of the film exceeds that of the substrate
- The strain energy is relaxed in a 3D island, Therefore transition from 2D to 3D occurs beyond critical thickness of 2D layer (Stranski Krastanov growth). Atomistically the strained lattice planes can relax outwards in a 3D island.
- Higher substrate temperatures lead to increase in size of critical nucleus. Increasing the deposition rate leads to smaller islands
- Nucleation rate describes how many nuclei of critical size form per unit area and unit time. The rate at which critical nuclei grow depends on the rate at which adsorbed monomers (adatoms) attach, which is more likely at cleavage steps or ledges and depends strongly on ΔG^* .
- Ostwald ripening means larger islands grow or "ripen" at the expense of the smaller ones
- Sintering is a coalescence mechanism involving islands in contact.
- Cluster migration has been observed experimentally
- Dewetting might happen during annealing driven by minimization of surface energies at elevated temperatures

Q & A - nucleation

- 1) What are the three basic growth modes?

Island (Volmer-Weber), layer (Frank Van der Merwe), or Stranski-Krastanov nucleation mode

- 2) What is a reconstructed surface?

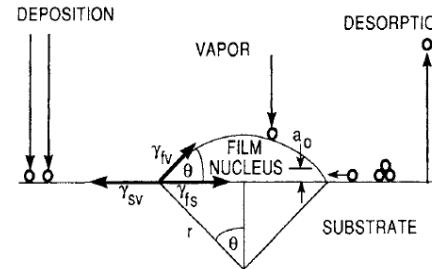
atoms relax at the outer surface in a way to preserve in plane symmetry

- 3) Derive the Young's equation. Start with a cross-section through a nucleus in form of a hemispherical cap. Explain the total wetting case.

Force equilibrium:

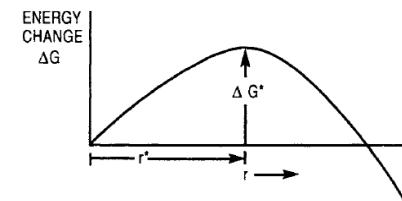
$$\gamma_{sv} = \gamma_{fs} + \gamma_{fv} \cos \theta$$

Total wetting for theta=0 if γ_{sv} larger than sum of others



- 4) Explain the terms critical nucleus size and activation energy for nucleation. Denote both quantities in a free energy change vs nucleus radius plot.

radius less than r^* , the cluster is unstable and will shrink
 ΔG^* represents an energy barrier to the nucleation process.



Q & A - nucleation

5) How does Stranski Krastanov Growth can be explained.

The strain energy is relaxed in a 3D island, Therefore transition from 2D to 3D occurs beyond critical thickness of 2D layer (Stranski Krastanov growth). Atomistically the strained lattice planes can relax outwards in a 3D island.

6) Explain the term nucleation rate.

describes how many nuclei of critical size form per unit area and unit time.
is more likely at cleavage steps or ledges and depends strongly on ΔG^* .

7) Explain the difference between Ostwald ripening and sintering

Ostwald ripening means larger islands grow or "ripen" at the expense of the smaller ones
Sintering is a coalescence mechanism involving islands in contact.

summary epitaxy

- But, by nature, heteroepitaxial thin films have proven a greater challenge to grow and exploit than bulk crystals.
- Notation: The indices of the overgrowth plane are written as (HKL) while those of the parallel substrate plane at the common interface are taken as (hkl). Note: (HKL)//(hkl); [UVW]//[uvw],
- Pseudomorphic growth with $f < 9\%$.
- Elastic strain energy scales with Elastic modulus * film thickness * strain²
- Strain is relieved by b/S with S dislocation distance and b Burgervector
- For film thickness larger than the critical thickness dislocations appear
- Surface ripples may relax strain energy elastically
- Defects in epitaxial films are dislocations, stacking faults, twin, growth hillocks, etc.
- Misfit dislocations propagate through threading segments through the crystal during the relaxation process
- Epitaxy of compound semiconductors: bandgap engineering through alloying and epitaxial growth on lattice mismatched substrate for defect free growth.
- Liquid phase epitaxy allows to choice of composition along the liquidus line of the phase diagram
- Epitaxial overgrowth limits dislocations to epitaxial window through SiO₂ mask
- MOCVD and MBE: A collection of epitaxial vapor-phase deposition processes based on chemical (CVD, MOCVD) and physical (MBE) methods as well as hybrid combinations (MOMBE, high-vacuum CVD) have been developed.
- An MBE system features semiconductor and dopant atom heating sources consisting of either effusion cells or electron-beam guns. An effusion cell is essentially an isothermal cavity containing a hole through which the evaporant exits. These have enabled extraordinary compositional, structural, and film-thickness control of layered heteroepitaxial structures, resulting in an impressive array of GaAs and InP-based LEDs and lasers for display, recording, and optical communications applications. Ge_xSi_{1-x} materials have also been exploited in high-speed transistors used for assorted computer and communications purposes.

Q & A - epitaxy

- 1) Note the indices of the overgrowth planes and directions of Ni/Cu and PbTe//MgAl₂O₄ system.
(001)Ni//(001)Cu; [100]Ni//[100]Cu they are both fcc and have close lattice constants
(III)PbTe//(III)MgAl₂O₄ ;[211]PbTe//[101]MgAl₂O₄
- 2) How is the film elastic strain calculated in the presence of misfit dislocations.
$$\varepsilon = f - b / S$$
- 3) What happens if the critical thickness is reached during epitaxial film growth.
It is energetically favored that misfit dislocations form to relax elastic strain
- 4) An epitaxial film is deposited with a lattice mismatch of 2% relative to a substrate whose diameter is 10 cm. The epilayer grown at elevated temperature is thick enough that the residual strain is zero. (a) If the Burgers vector is 0.2nm, what is the interfacial misfit-dislocation spacing? (b) A misfit dislocation grid covers the entire film/substrate interface. What is the total length of dislocation line? (c) Estimate the dislocation density.
a) $f=0.02; \varepsilon=0 \rightarrow S=b/f=0.2\text{nm}/0.02=10\text{nm}$
b) 10nm spacing over 10cm square (instead circular for simplicity) $\rightarrow 2 \cdot 10^7$ lines of 10cm length = $2 \cdot 10^6\text{m}$
c) needs some thinking: dislocation threading density is like classic etch pits/ area = density in cm^{-2} , for the square network in plane we discuss better a dislocation interdistance S

Q & A - epitaxy

5) Physically explain the ordinate intercepts and curve shapes that lead to E vs b/S variations for $d < d_c$ and $d > d_c$. Plot qualitatively the expected equilibrium misfit dislocation spacing S vs film thickness. In general the experimental misfit dislocation spacing is larger than the equilibrium spacing. Why?

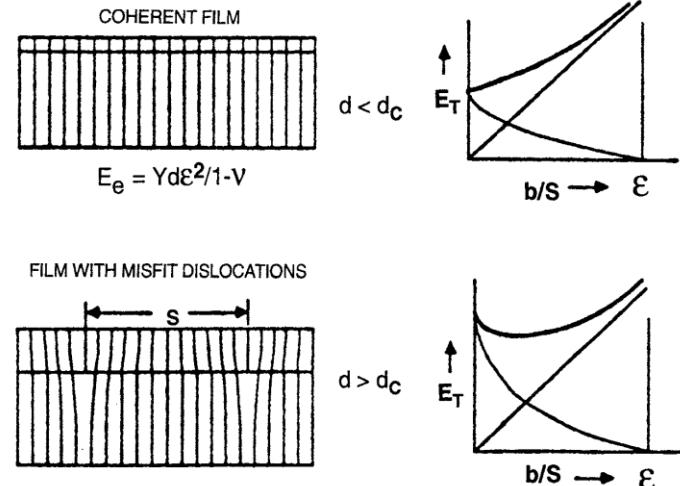
a) for 2 given film thickness cases see left scenarios. For $d < d_c$ total energy increases if dislocations are added.

For $d > d_c$ some dislocations are added until minimum of total energy

b) Experimental spacing is larger because of extra activation energy to nucleate dislocations and because nucleation and propagation and subsequent reactions of dislocations complicate the relaxation process

6) Compare elastic and plastic relaxation of strained epitaxial layers
 elastic \rightarrow surface topography as for Stranski-Krastanof case, plastic \rightarrow misfit dislocations

7) How do misfit dislocations form and how do they relax the film stress
 They form through nucleation from the surface or through propagation of existing threading dislocations



Q & A - epitaxy

- 5) Describe the overall approach of choosing a material with a required band-gap
First: select alloy with right bandgap (direct or indirect)
Second: select suitable (alloy) substrate with low misfit to grow onto
- 9) How does epitaxial overgrowth works?
Lithography based patterning of substrate to allow for local epitaxy and defect-free lateral overgrowth
- 10) Describe the LPE process in a few sentences
LPE = liquid phase epitaxy; precipitation of film from a supersaturated melt; typically series of crucibles for different temperatures
- 11) What are the basic components of an MBE system?
UHV vacuum chamber, effusion cells or electron beam guns with shutters, in-situ diagnostics such as mass spectrometer or electron diffraction setup, Knudsen cells is evaporation source with isothermal enclosure and small orifice

Summary - film structure

- Although greater directionality of atom transport occurs in sputtering and evaporation than in CVD processing, films from all three methods share common zone structures and morphological features.
- SZM rely on four basic processes: shadowing, surface diffusion, bulk diffusion, desorption, the latter three scale with the homologous T
- Zone 1: cone-like, voided boundaries due to limited adatom mobility at $T_s/T_m < 0.3$ and shadowing
- Zone 2: columnar, tight boundaries due to surface and grain-boundary diffusion at $0.3 < T_s/T_m < 0.50$
- Zone 3: Equiaxed due to bulk diffusion for $(T_s/T_m > 0.5)$.
- SZM pressure effect: reduction increases density, increase more open grain morphology
- SZM T effect: At elevated temperatures both surface and bulk diffusion allow atoms to access equilibrium lattice sites, fill voids, and enlarge grains.
- SZM ion bombardment: increase adatom motion same as T
- Grain morphology: Shadowing effects, substrate temperature, and energy of depositing atoms are the influential factors that affect grain morphology. Columns are observed on both crystalline and amorphous substrates, and in crystalline as well as amorphous films. Nested columns in thick films
- Tangent rule: columns oriented towards source, $\tan\alpha = 2\tan\beta$
- Film density: needs mass and thickness measured, increases with thickness, metals denser than dielectrics, up to 1% vacancies in films, 1nm sized voids in evaporated films
- Monte-Carlo & MD simulations revealed mechanisms of zone I growth
- Parabolic grain growth follows $R^2 - R_0^2 \simeq kt^{1/2}$, abnormal grain growth also common, grain growth stagnates often at 2-3x film thickness, interfacial energy minimization dominates at high T and (111) surface texture establishes, grain growth can be driven by processes that relieve more energy than grain growth needs such as precipitation or strain energy.

Summary - film structure

- Texture is orientation of grains and misorientation between grains, pole figures display texture, no texture in zone 1, texture evolves during growth due to optimization of surface and strain energies, and is influenced by substrate (epitaxy), ion bombardment and surface pattern.
- Deposition of sculptured film is possible exploiting the tangent rule via substrate rotations.
- Amorphous thin films are deposited typically in zone 1, characterized by RDF from XRD,
- amorphous SiN and SiO₂ include H

Q & A - film structure

- 1) Name the four most important mechanisms responsible for film microstructure
shadowing, surface diffusion, bulk diffusion, desorption.
- 2) What are the temperature ranges for zone I, zone II and zone III
some difference between evaporation and sputtering
in general: $Z1 < 0.3 T/T_m$; $Z2: 0.3 - 0.5 T/T_m$, $Z3 > 0.5 T/T_m$
- 3) What are the effects of process pressure, temperature in the structure of sputtered film?
Pressure: zone I depends on how much gas scattering the arriving materials undergoes (evaporation vs sputtering) -> high pressures more scattering and less shadowing, low pressures higher ion energies and more dense films makes $Z1$ smaller
Temperature: $Z1, Z2, Z3$ as shadowing, surface and bulk diffusion depend on T
- 4) How does the substrate bias influence structure of a sputtered film?
More bias makes zone 1 smaller as more dense
- 5) Give 3 arguments why SZM from evaporation differs from sputtering?
Evaporation: more directional flux, lower deposition pressures, no ion bombardment of substrate
- 6) If the flux of evaporating atoms is directed at an angle 45° to the normal to the substrate, assuming the tangent rule, determine the direction of growth of the columnar growth in the thin films.
Yes, in zone 1 & 2 we'll see the tangent rule "ruling" and columns will be inclined to the evaporation source
- 7) Differs film density from the density of the corresponding bulk materials?
Yes in particular in $Z1$ with voided space between the columns and nm sized voids in evaporated films,
Vacancy concentration up to 1% at RT,

Q & A - film structure

- 8) Discuss grain size in thin films based on deposition T and as a function of film thickness
With increasing T: columnar and voids (Z1), larger columns with tight boundaries (Z2), equiaxed (Z3)
- 9) Name 2 processes that can drive grain growth after deposition
mechanical stress, interface energy minimization, solute precipitation (and related heat)
- 10) Discuss texture in thin films based on surface energies and residual stress. Include the effect of film thickness.
In fcc materials (111) preferred for low surface energy, (100) textures for lowest strain energy
If film thickens strain energy increases and might trigger transition from (111) to (100)
- 11) Name typical materials of amorphous thin films
amorphous metals, SiN , SiO_2

Summary - stresses in thin films

Stress in thin films

- Film exerts bending moment on substrate plate which leads to curvature=1/R
- Stoney equation is independent of film properties:
- In textured films biaxial film modulus for <111> and <001> textures used, <110> more complicated
- In plane Young's modulus depends on grain size (10%less for <10nm>), texture (up to 2x), porosity (~ porevolume²)
- Stress of 1st, 2nd, 3rd order
- methods for residual stress
 - Mechanical methods: Substrate curvature via laser deflection, bending of FIB bi-metal beam
 - (Fib-)Hole drilling & edge relaxation,
 - XRD ($\sin 2 \Psi$ - method measures out of plane strain and converted to in-plane stress, epi-layers and reciprocal space map,
 - Raman spectroscopy stress dependence of opt phonon frequency,
 - EBSD cross.correlation method
 - Cantilver beam methods
 - Method comparison: spatial (lateral & depth), and spectral resolution
- Types of stresses (thermal, intrinsic, epitaxial)
$$\sigma = \left(\frac{E}{1 - \nu} \right)_f \quad \varepsilon = - \left(\frac{E}{1 - \nu} \right)_f (\alpha_f - \alpha_s) \Delta T$$
$$\sigma_1 = \sigma_2 = \left(c_{11} + c_{12} - \frac{2c_{12}^2}{c_{11}} \right) \varepsilon_1 = \left(c_{11} + c_{12} - \frac{2c_{12}^2}{c_{11}} \right) \left(\frac{a_s - a_f}{a_s} \right)$$
- Intrinsic: Capillary, Laplace pressure of islands, Zip stress during coalescence
- Stress evolution after coalescence, Impurities, vacancies, ion bombardment
- Evolution during growth: Capillary stress: Laplace-Young equation $p=2\gamma_s/r$; Zip stress like healing crack, following coalescence either compressive due to epitaxy, relaxed due to adatom mobility or compressive due to incorporation of excess atoms (at GB, or bigger Ar atoms)
- Evolution during or after: vacancy annihilation, densification, crystallization, grain growth
- The stress dilemma: intrinsic stress relaxes at high deposition T, thermal increases

Q & A - stresses in thin films

- 1) Name 3 industrial problems related to residual stresses

interfacial cracks and film delamination (after deposition or during use phase)

morphology evolution during film growth (elastic relaxation in epitaxy) or texture change with increasing film thickness

strain engineering of SiGe in computer chips for higher electron mobility

- 2) Write down the Stoney equation; why is the equation independent from the film material? properties? How would you measure stress based on this relationship?

$$\sigma_f = \left(\frac{E_s}{1 - \nu_s} \right) \frac{t_s^2}{6t_f} (\kappa - \kappa_o)$$

Materials properties of the film are not in the equation – just the stress that induces substrate bending. This means we can measure the film stress based on a substrate curvature measurement via a deflecting laser beam setup and we don't need to know the Young's modulus of the film

- 3) You are dealing with a textured film. Explain the term bi-axial modulus and give the equation for a <001> surface.

we are dealing with in-plane stresses. In either a monocrystalline film or a film with a fiber texture we need to take the crystal anisotropy into account to calculate the stress (deviation up to 2x compared to isotropic behavior)

$$B_{\{001\}} = c_{11} + c_{12} - \frac{2c_{12}^2}{c_{11}}$$

Q & A - stresses in thin films

4) Name 3 factors influencing the in-plane Young's modulus of a crystalline thin film on an amorphous substrate.

Texture (fibre growth texture, not epitaxy), porosity, grain size

5) Which are the 3 principal sources of residual stress in thin films? How do you calculate the stress?

Intrinsic, thermal, epitaxial

calculation for thermal

$$\sigma = \left(\frac{E}{1-\nu} \right)_f \varepsilon = - \left(\frac{E}{1-\nu} \right)_f (\alpha_f - \alpha_s) \Delta T$$

epitaxial

$$\sigma_1 = \sigma_2 = \left(c_{11} + c_{12} - \frac{2c_{12}^2}{c_{11}} \right) \varepsilon_1 = \left(c_{11} + c_{12} - \frac{2c_{12}^2}{c_{11}} \right) \left(\frac{a_s - a_f}{a_s} \right)$$

intrinsic is more complicated: Laplace stress, Zip stress or stresses during grain growth provide possible calculation schemes

6) Explain the measurement principle of residual stresses by X-ray's

the so-called 'sin²ψ' method relies on measurement of the out of plane strain by X-ray diffraction which gives the biaxial stress in the plane

$$\frac{d_{hkl} - d_{hkl}^o}{d_{hkl}^o} = \varepsilon_\psi = \frac{(1+\nu)}{E} \sigma \sin^2 \psi - \frac{2\nu}{E} \sigma$$

practically we measure the lattice spacing between planes under different angles to the film normal and determine the Y-axis intercept for the out of plane strain (phi=0) parallel to the surface

Q & A - stresses in thin films

7) Suggest 3 methods to measure residual stress of a 5 micrometer thick amorphous thin film on silicon wafers.
Wafer bending, hole drilling, cantilever beam - note that diffraction methods don't work

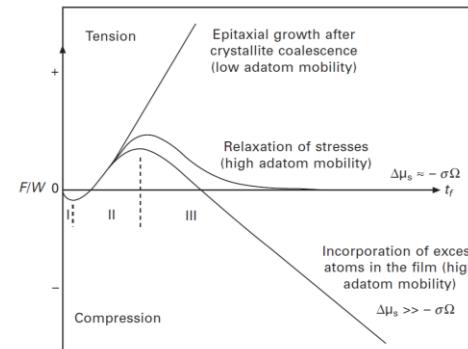
8) You want to measure residual stresses in an epitaxial SiGe Film on Silicon. Compare Raman, spectroscopy, EBSD and X-Ray methods in terms of spatial and spectral resolution
spatial lateral and depth: X-rays difficult to focus - mostly only collimated through tube: lateral 1mm and depth 50micrometer, Raman optical -> 1 micrometer lateral and depth diffraction limited, EBSD 100nm lateral and 50nm depth (limited by volume backscattered electrons come from),

9) What are the origins of residual stresses during film growth starting from nucleation of islands to thick films. Draw a typical force-thickness vs layer thickness curve from in-situ wafer curvature measurements and label different mechanisms.

I: Laplace

II: Zip

III: Epi, Relaxation or incorporation of excess atoms)



10) Through which processes can residual stresses be relaxed?
Texture changes (surface vs stress), grain growth, elastic (surface topography) or plastic (dislocation nucleation or propagation of threading dislocations) relaxation in epitaxy

summary - mech properties and hard coatings I

- Interface crit. energy release rate vs residual stress
- Atomistic view: chemical bonding?, Kirkendall effects, interface mixing due to ion bombardment, mechanical locking
- Adhesion mechanisms, improvement: glue layer (oxide role), ion beam processing (energy!), polymers (plasma) activation of surface
- Measurement techniques adhesion: tear-off test (not quantitative), Rockwell adhesion, scratch techniques
- Nanoindentation: hardness under maximum load of 3-sided Berkovich tip. Young's modulus from linear unloading curve
- Thin film indentation: thin ice effect, 1/10 , fracture toughness difficult due to unknown crack path

summary - mech properties and hard coatings II

- Definition hard coatings: hard 20-40GPa, superhard >40GPa, $\sim 10 \mu\text{m}$ thick, intrinsically + extrinsically hardness contributions
- Applications: cutting tools, moulds, machine parts, medical & decorative
- Classifications: metallic: transition metal -N/C/B; covalent: c-BN, SiC, Diamond; ionic: Al/Si/Zr/Cr - O
- high intrinsic hardness: high binding energy, short interatomic distance, high degree of covalent bonding, high number of bonds per unit volume, modelling opportunity for search by DFT
- Desired properties: High (hot) H, K_c , G_{adhesion} , G_c between phases, low σ_{res} , no reaction with substrate & environment, low friction coeff against material in application -> layered/gradient film to catch all properties & nanostructured for high extrinsic hardness
- Nitrides & Carbonitrides: "fcc TiN archetype", TiCN self-lubricating C layer, AlTiN and $\text{Al}_x\text{Cr}_{1-x}\text{N}$: oxidation resistant -> oxides of Al & Cr, AlTiSiN forms superhard coating with AlTiN nanocrystals in a-SiN matrix
- Carbides: "fcc TiC archetype" with more covalent bond compared to TiN, $\text{TiC}_x\text{N}_{1-x}$ better against C outdiffusion, TiCN nanocrystals in a-C:H matrix
- Borides: hexagonal TiB_2 with covalent B-B bonds, TiB_2 nanocrystals in excess B-rich matrix, used for cutting of Al as Nitrides don't work
- Oxides: "hex Al_2O_3 archetype" but many polytypes, dominating for cutting tools (oxid resistance & hot hardness)
- Nanolayers: nanolaminates incl. epitaxial superlattices; toughening of nanolayers via crack deflection, ductile interlayers and interface delamination; superlattices with additional toughening with coherency strains, dislocation arrays at interfaces and oscillating Youngs Modulus (compared to single crystals)

summary - mech properties and hard coatings III

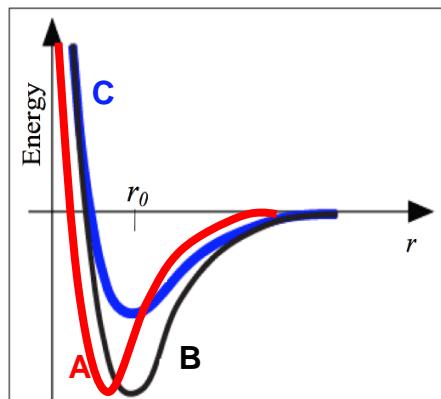
- Nanocomposites: strength due to grain refinement (Hall-Petch) and preventing GB sliding due to amorphous tissue phase at GB. Max hardness with 10nm grain size and 1-3nm tissue phase
- Arc plasma deposition: high I - low DC voltage, magnetically steered μm - sized spot with 10^{10} A/cm^2 leads to melting/evaporation/ejection of particles, ionization degree up to 100% leads to stoichiometric compounds in reactive arc deposition, ion energies up to 100eV leads to dense, well adhering films; samples (cutting tools etc.) on rotating planetary holder allows for nanolaminate deposition, all hard coatings possible but mostly used for forming and cutting tools as smaller grains compared to CVD as lower deposition T
- high-power impulse magnetron sputtering (HiPIMS): power densities on target like arc through 100 μs pulses with 10-100Hz with almost 100% ionization degree and high energy ions leading to dense and well adhering coatings, but without particles as in arc deposition
- Coating process line includes handling, decoating, cleaning, QS, pre/post annealing and actual deposition equipment

Q & A - mech properties and hard coatings I

- What are thin film deposition strategies to improve thin film adhesion?
glue layer (oxide role), ion beam processing (energy!), polymers (plasma) activation of surface
- You want to measure the Young's modulus of thin films. Explain the two rules of thumb related to the maximum indentation depth. Why is it important to stick to these rules?
Rules: Displacement $> 20 R_a$; Displacement $\leq 10\%$ of coating thickness, too deep stress expands into substrate and we measure substrate E and H, too shallow and we sit on asperities and not on flat surface
- Why is a Berkovich tip used instead of a Vickers tip in nanoindentation?
Easier to hit a pint with 3 faces,
- To calculate the contact area $A(h_c)$ from the contact depth h_c we do not assume a simple geometric relationship $A_c \sim h_c^2$. Explain why.
Tips are not perfectly sharp - \rightarrow need for correcting polynom!

Q & A - mech properties and hard coatings II

- What are the different ways to classify hard coatings and how are they related to each other?
Intrinsically according to the nature of their chemical bonds (covalent, ionic, metallic)
Extrinsically according to their microstructure (multilayers, nanolaminates, nanocomposites)
Hardness: hard ($20 \text{ GPa} < H < 40 \text{ GPa}$) and superhard ($H \geq 40 \text{ GPa}$)
- Interatomic bonding determines the intrinsic hardness of a coating. How can it explain the difference between TiN vs. TiB₂, and Diamond vs. Graphite?
TiB₂ is more covalent than TiN; Diamond sp₃ vs Graphite sp₂
- The figure below shows the interatomic potential of Material A, B and C. Rank them according to their expected intrinsic hardness and explain your choice. Which other factors, not visible in the interatomic potential are generally related to increased intrinsic hardness?



$A > B > C$

high intrinsic hardness: high binding energy, short interatomic distance, high degree of covalent bonding, high number of bonds per unit volume

Q & A - mech properties and hard coatings III

- Which considerations are crucial for material selection of a hard coating - substrate combination for a specific application?

Desired properties: High (hot) H , K_c , G_{adhesion} , G_c between phases, low σ_{res} , no reaction with substrate & environment, low friction coeff. against material in application \rightarrow layered/gradient film to catch all properties & nanostructured for high extrinsic hardness

- Discuss properties and microstructure of TiAlCSiN type coatings. Start with TiN and discuss the effect of adding other elements

"fcc TiN archetype",

TiCN self-lubricating C layer, TiC_xN_{1-x} better against C outdiffusion, TiCN nanocrystals in a-C:H
AlTiN oxidation resistant due to oxides of Al,
AlTiSiN forms superhard coating with AlTiN nanocrystals in a-SiN matrix

- What is the effect of adding C to TiN in terms of properties and microstructure?

TiCN self-lubricating C layer, TiC_xN_{1-x} better against C outdiffusion, TiCN nanocrystals in a-C:H

- Why is hexagonal TiB_2 used for machining of Al and not TiN? Why are hardness values of TiB_2 thin films above those of bulk material and which role does sputter deposition play in that hardening phenomena?

Borides: In Sputtering from TiB_2 targets B is less scattered and more Boron arrives at the substrate and Excess makes B-tissue phase at grain boundary \rightarrow higher hardness
TiN adheres more to Al and therefore during machining unwanted chip-formation behaviour

Q & A - mech properties and hard coatings IV

- Despite their relatively low intrinsic hardness, oxides are very frequently employed hard coatings. What are their main benefits? What are the main challenges during deposition of alumina?
Thermally stable, high hot hardness, chemical inert
We want to stabilize for $\alpha\text{-Al}_2\text{O}_3$ at lowest possible deposition T (substrate softening or cracking during cooling from 1000°C for stable $\alpha\text{-Al}_2\text{O}_3$ deposition) - Trick: add Cr_2O_3 .
- Explain most important hardening and toughening mechanisms of nanolayered coatings. What limits the minimum and maximum layer thickness and where is the hardness maximum located?
toughening of nanolayers via crack deflection, ductile interlayers and interface delamination; superlattices with additional toughening with coherency strains, dislocation arrays at interfaces and oscillating Youngs Modulus (compared to single crystals)
maximum hardness: 5-10nm sublayer thickness; smaller dislocation transmission and larger only Hall-Petch
- Cathodic arc deposition: What are the main advantages compared to conventional magnetron sputtering? What is meant by steered arc? State the challenges with arc evaporation deposition?
ionization degree up to 100% leads to stoichiometric compounds in reactive arc deposition, ion energies up to 100eV leads to dense, well adhering films; smaller grains compared to CVD as lower deposition T
Arc plasma deposition: high I - low DC voltage, magnetically steered mm - sized spot with 10^{10} A/cm^2 leads to melting & evaporation
Challenge ejection of particles, control of target usage (arc control steering)

Q & A - mech properties and hard coatings V

- How can magnetron sputtering achieve similar power densities on the target compared to arc deposition?

high-power impulse magnetron sputtering (HiPIMS): power densities on target like arc through $100\mu\text{s}$ pulses with 10-100Hz with almost 100% ionization degree and high energy ions leading to dense and well adhering coatings, but without particles as in arc deposition

- Name the different steps in the workflow of an industrial deposition setting

Coating process line includes handling, decoating, cleaning, QS, pre/post annealing and actual deposition equipment