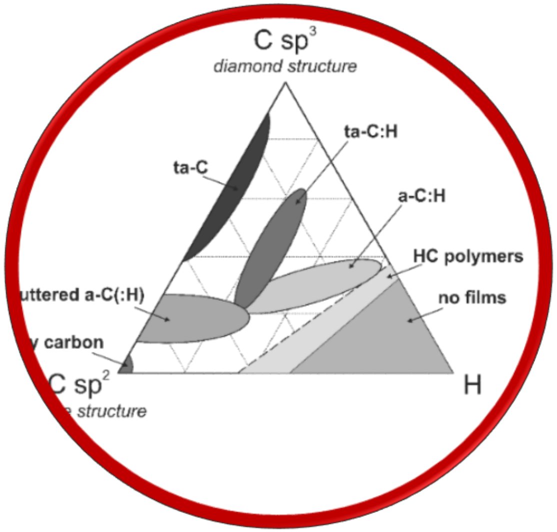
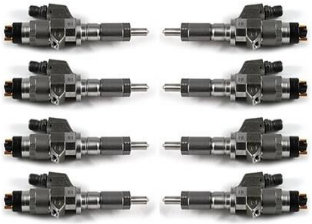
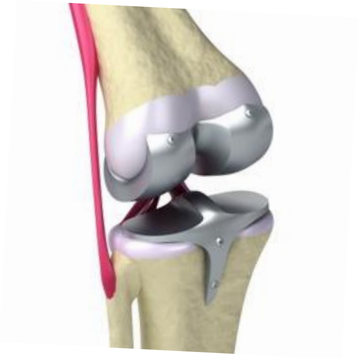
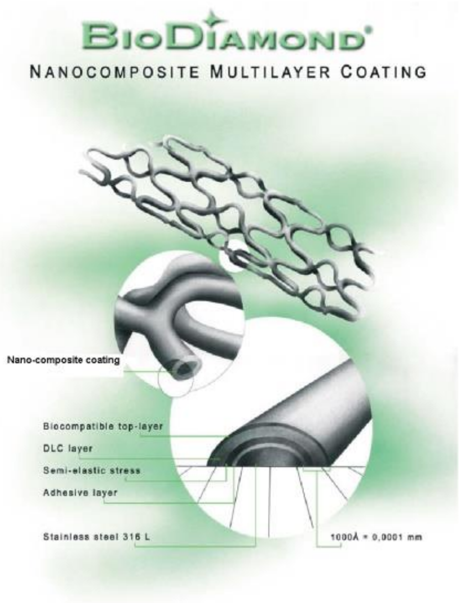
Diamond and amorphous Carbon

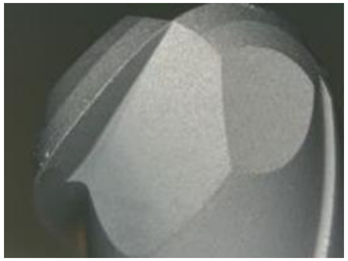


Applications of carbon materials







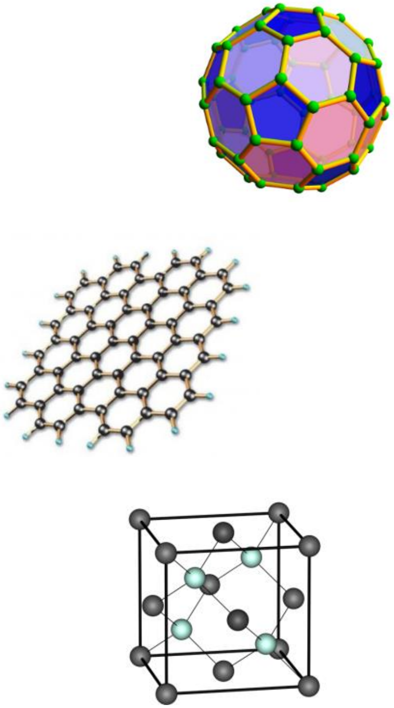


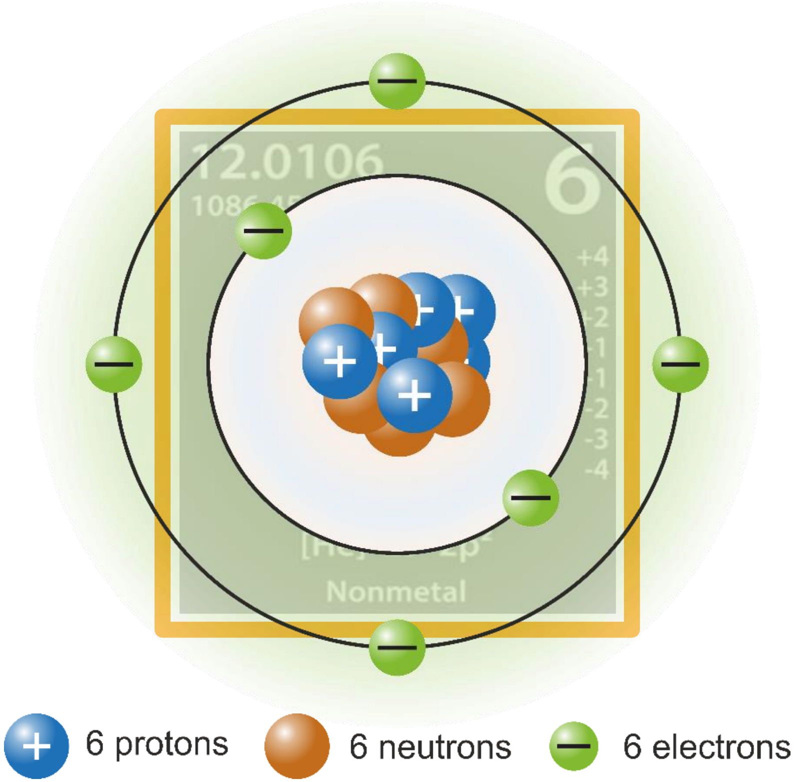
Courtesy from Caroline Hain, BFH, Biel

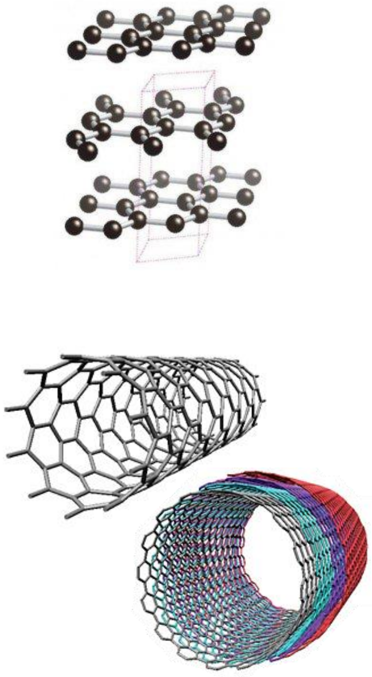
content

- Carbon allotropes
- Graphite vs diamond vs a-C: phase stability
- **CVD Diamond**
    - growth mechanism
    - Nucleation of CVD diamond
    - Influence of Temperature and Methane concentration
    - Deposition methods: Hot filament vs Microwave CVD
    - C-H-O diagram
    - Deposition methods: growth rate vs gas temperature
    - Nucleation rate enhancement: bias enhanced and mechanical seeding
    - "epitaxy" or highly oriented diamond
    - Nanocrystalline films
    - Microstructure summary
    - Applications of diamond films
- **Amorphous carbon**
    - Terminology a-C, ta-C, a-C:H ….
    - Hydrogen content
    - Deposition conditions CVD
    - PECVD of a-C:H
    - Growth mechanism
    - Growth of a-c:H:X with X=N,F,Si, Me
    - Selected properties of carbon materials
    - Deposition methods PVD
    - Applications

Carbon and carbon allotropes







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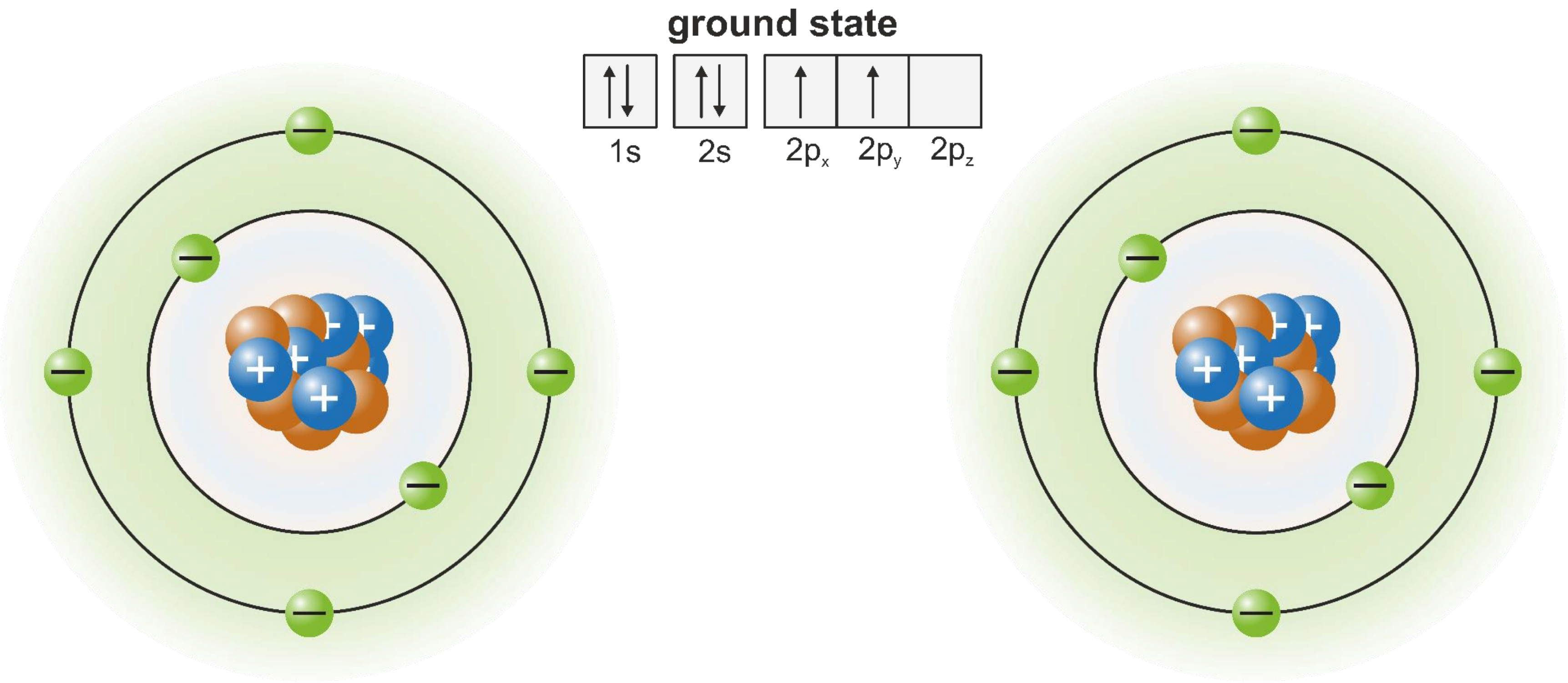
Carbon and carbon allotropes



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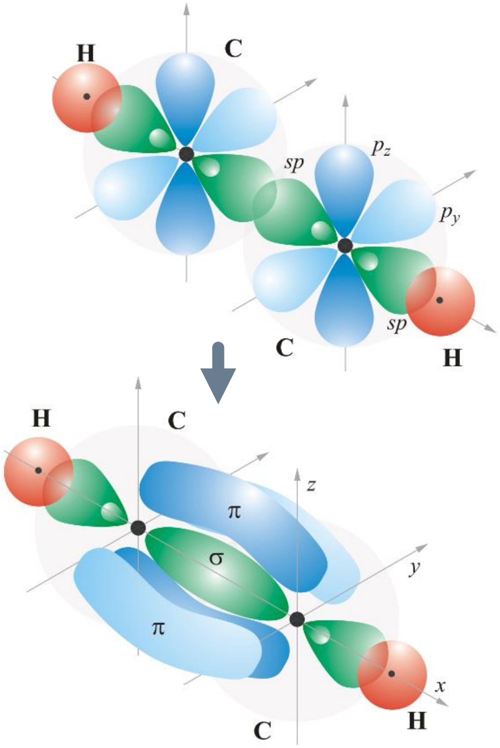
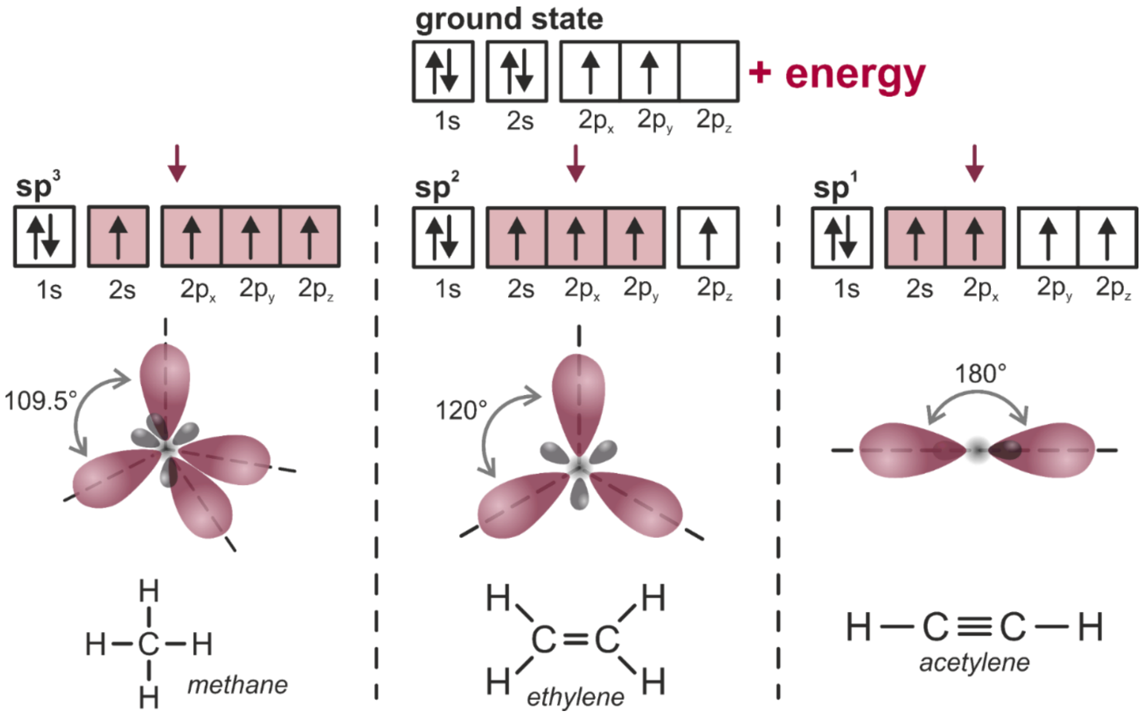
hybridisation and bonding





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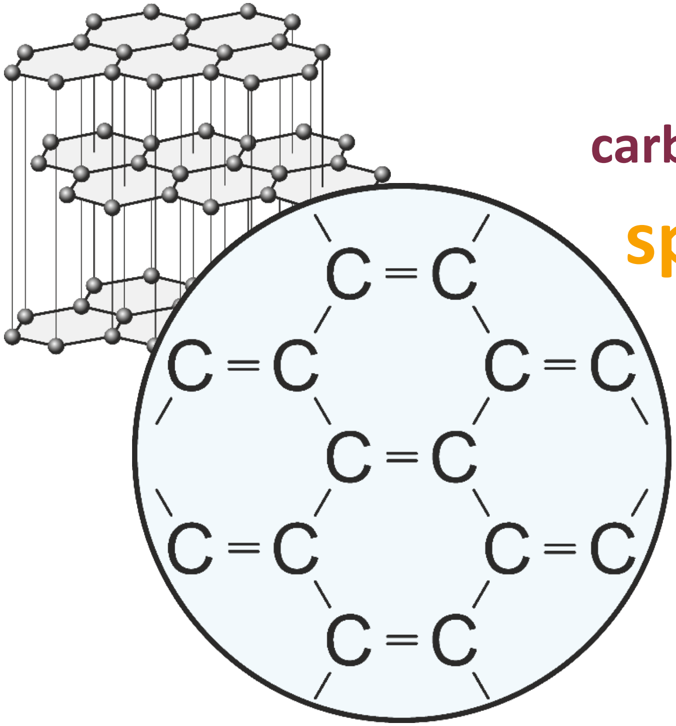
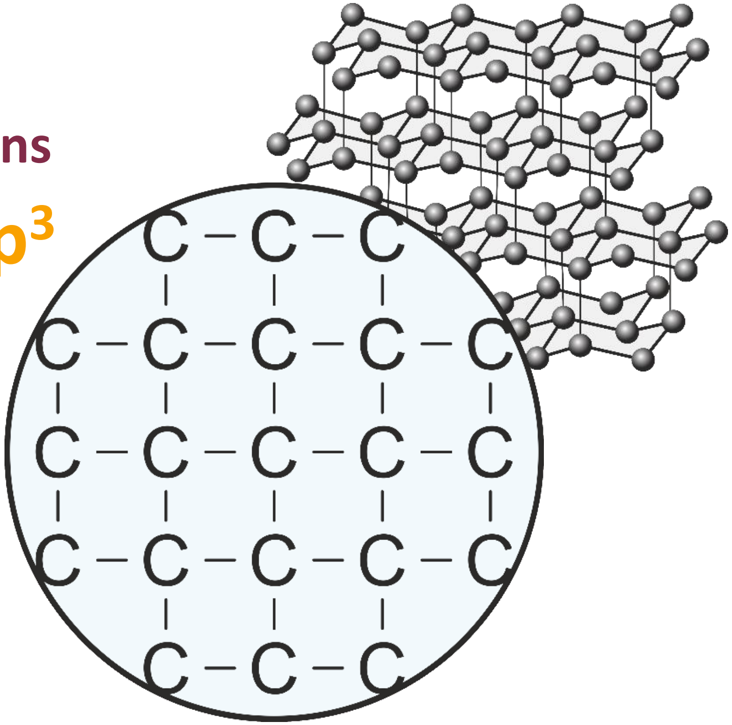
Graphite vs diamond

carbon hybridisations



sp^2

sp^3



Courtesy from Caroline Hain, BFH, Biel

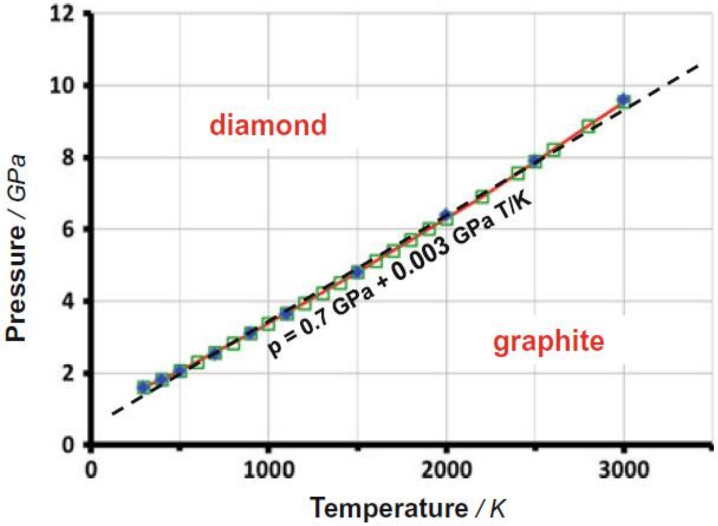
Graphite vs diamond

Under standard conditions (T = 25 °C, p = 1 atm = 1.013 10^5 Pa), the **free enthalpy of diamond exceeds that of graphite** by 2.48 kJ/mole or 0.026 eV/atom.

But due to **kinetic barriers**, the diamond-graphite transition is impeded and diamond crystals are preserved up to 1700 °C in vacuum.

The graphite transformation of diamond is favored by **graphitic impurities** and by the contact with **hot carbon dissolving metals** (e.g. in machining of ferrous materials with diamond tools).

Due to its higher density the diamond modification is favored at higher pressures.



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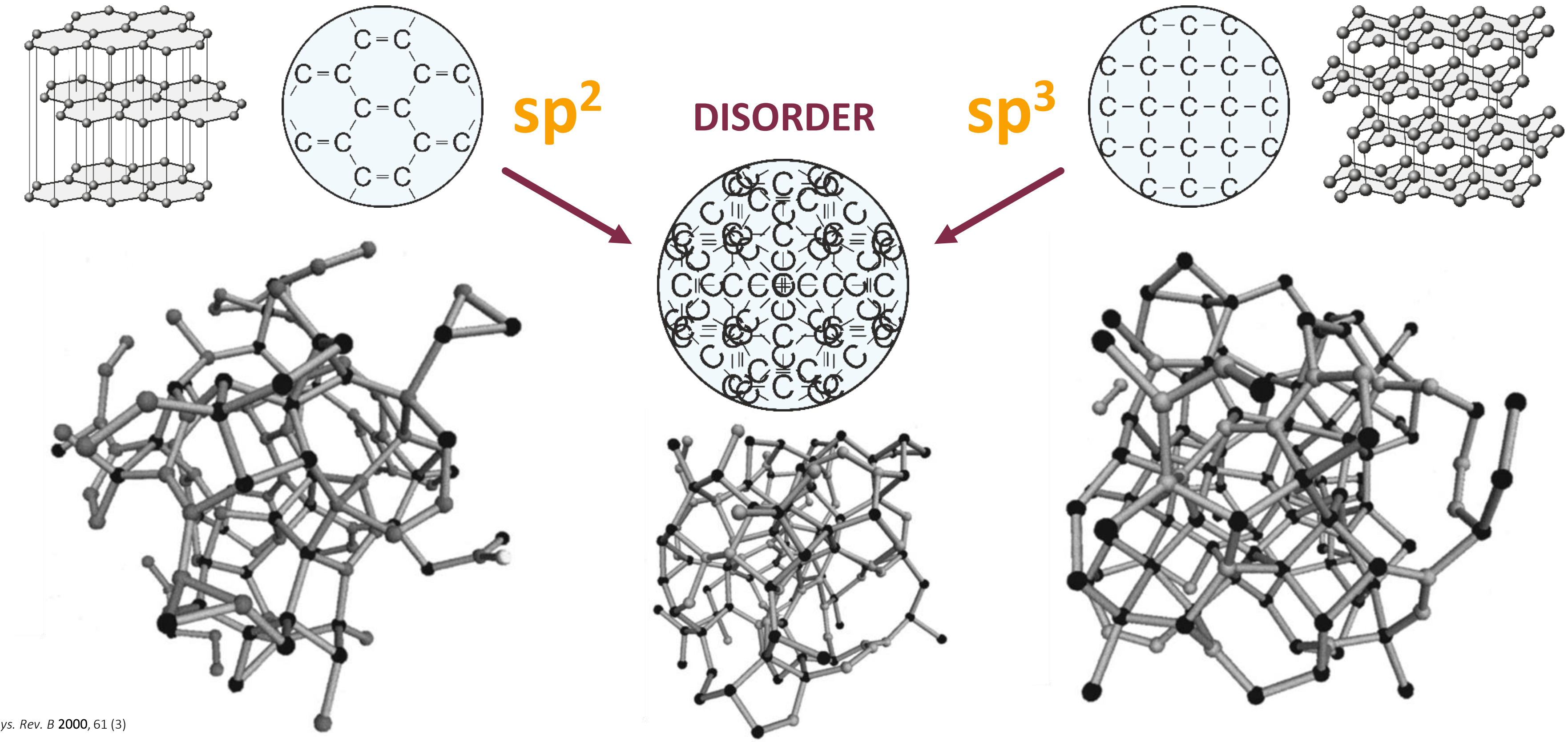
Diamond-like carbon



sp^2

DISORDER

sp^3

Phys. Rev. B 2000, 61 (3)

Courtesy from Caroline Hain, BFH, Biel

CVD of diamond

The now mostly used standard process is based on **activated CVD in an atmosphere of hydrogen** with only around 1% hydrocarbon, mostly methane CH_4.

By **thermal dissociation at high gas temperatures above 2000 °C** or by **electron collisions in dense plasmas**, **atomic hydrogen** is generated, the key factor in diamond deposition.

Originally its decisive role has been explained by the **preferential etching of sp^2 bonded carbon** in comparison to sp^3 bonded material. Indeed the hydrogen induced gasification of non-diamond phases is important for the favored selection of the diamond growth and thus for the film quality.

But thorough investigations of the **surface chemical processes** have also revealed, that **hydrogen** or **related reactive species as fluorine or oxygen/OH** are unavoidable constituents of the diamond formation process itself.

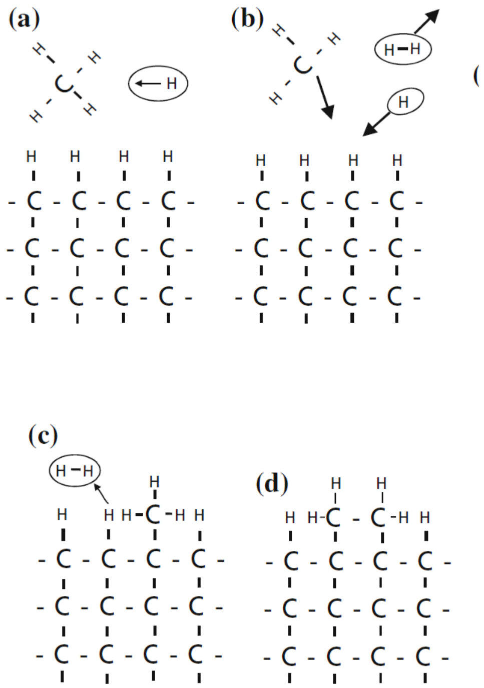


Fig. 2.1 Scheme of the diamond deposition by activated CVD, using atomic hydrogen and CH_3 radicals (**a**), generation of CH_3 radicals by atomic hydrogen (**b**), creation of free sites by hydrogen abstraction and their occupation by CH_3 radicals (**c**), extension of the diamond lattice by connection of neighbored CH_3 groups (**d**)

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CVD of diamond

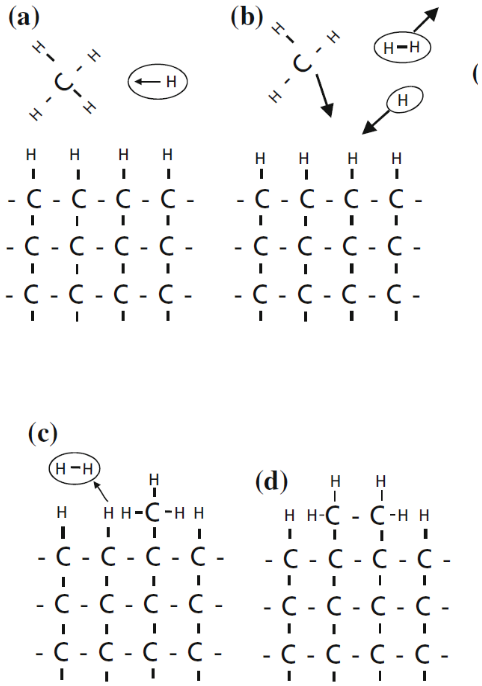
Atomic hydrogen plays an important role in **several decisive growth steps**:

- the **generation of radicals** (especially methyl groups CH_3) from the used hydrocarbons,

- the temporary saturation of free surface bonds by hydrogen atoms, thus stabilizing the sp^3 hybridization at the surface,

- the abstraction of terminating hydrogen (by Hs + Hgas ! H_2) to create active sites for the adsorption of the diamond precursor radicals (mostly CH_3),

- the hydrogen abstraction from attached radicals transferring their tetrahedral C–H bonds into C–C diamond bonds between neighbored groups.



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Nucleation phase in CVD of diamond

whether or not sufficient nucleation occurs here depends on the carbon being **soluble in the support material** or easily forming **carbides** with the substrate.

if neither of these characteristics is very pronounced, a system **supersaturated with regard to carbon** is fast to evolve on the substrate 's surface.

This leads to the deposition of first tiny carbon nuclei (usually CH_x). They are **frequently sp^2 - hybridized**, which, without further influences, would give rise to a precipitation of graphitic material

At the same time, however, atomic hydrogen, generated in situ from the molecular **hydrogen present in the mixture of reactant gases, settles** on the surface.

The hydrogen radicals are very reactive and quickly enter into conversions with the sp^2 - clusters on the substrate.

The latter are hydrogenated with new C – H - bonds being formed on their surface

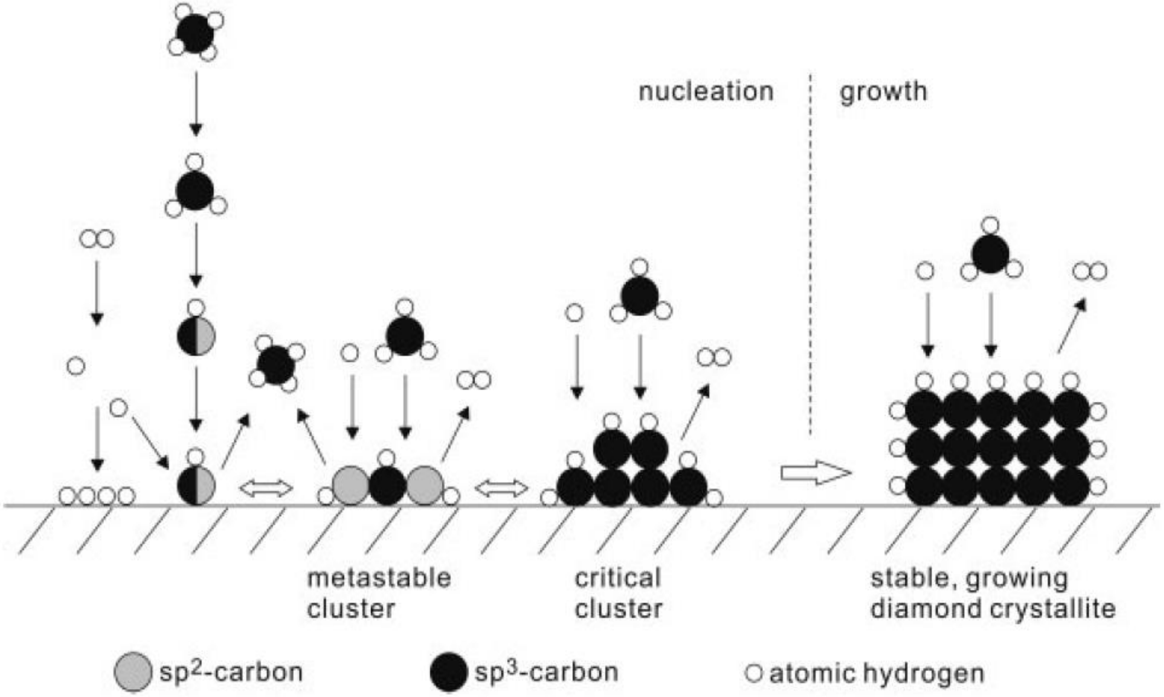


Figure 6.18 The mechanism of diamond deposition from the gas phase on a substrate.

Krüger 2010

Nucleation phase if CVD of diamond

eventually **sp^2 - carbon atoms are transformed back into sp^3** - carbon, and the resulting species C_yH_x are more stable than the respective sp^2-clusters.

The **bound hydrogen passivates the cluster surface** that consequently cannot graphitize just like that.

The clusters then grow laterally and vertically by the **addition of further CH_x - fragments** that each of them replace a hydrogen atom on the surface.

It can grow laterally as well as vertically until **a closed film** on the substrate surface is obtained.

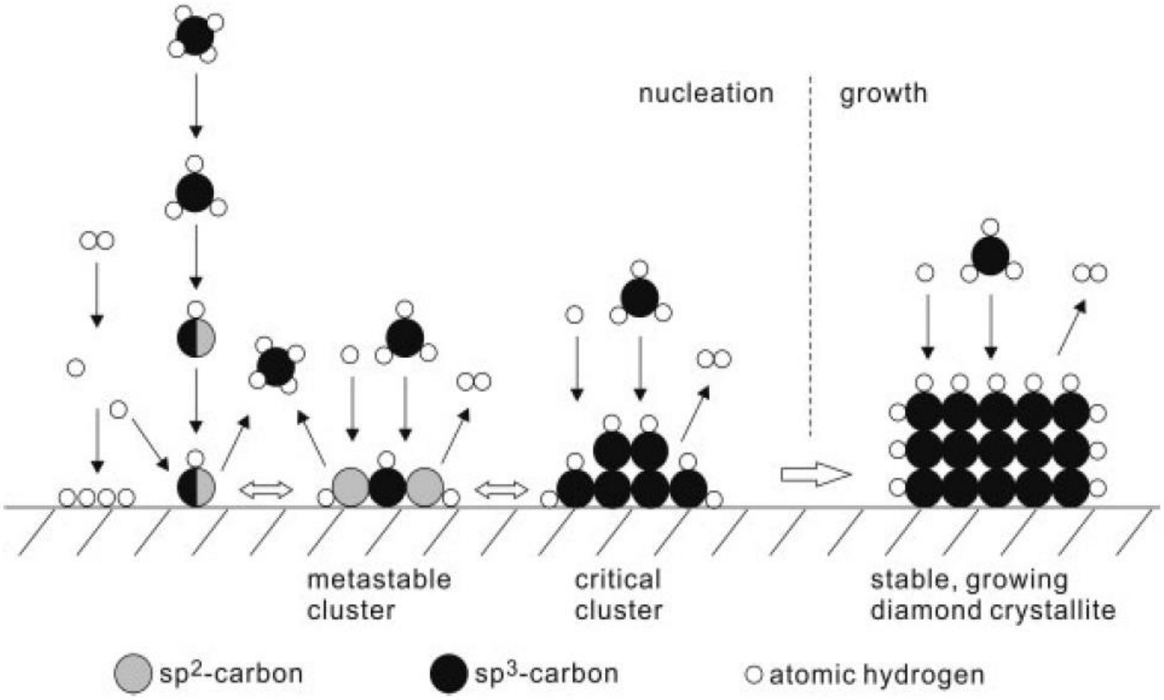


Figure 6.18 The mechanism of diamond deposition from the gas phase on a substrate.

Krüger 2010

Nucleation phase if CVD of diamond

After having been adsorbed to the surface of the substrate, the **activated CH_x - fragments can move by surface diffusion** until finally being attached to the already existing clusters.

Throughout this process the surface is **protected from graphitization** by the adsorbed hydrogen atoms.

If some graphitic material should emerge nevertheless, it is selectively attacked by the hydrogen radicals and **converted into hydrocarbons that return into the gas phase**.

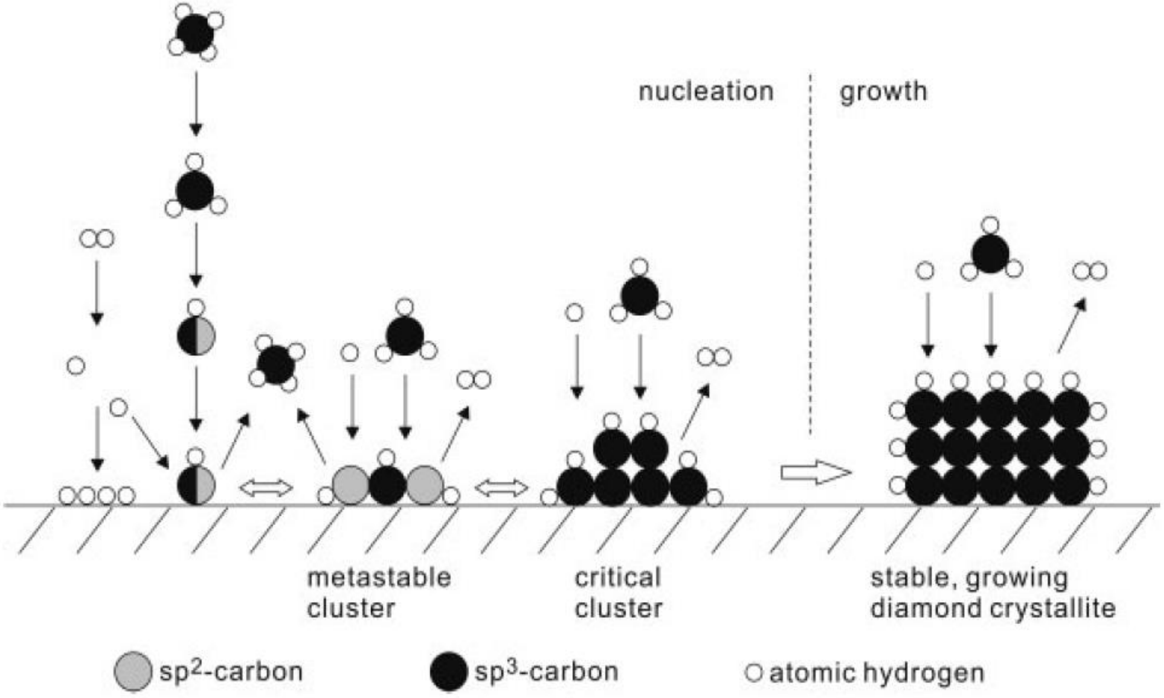


Figure 6.18 The mechanism of diamond deposition from the gas phase on a substrate.

Krüger 2010

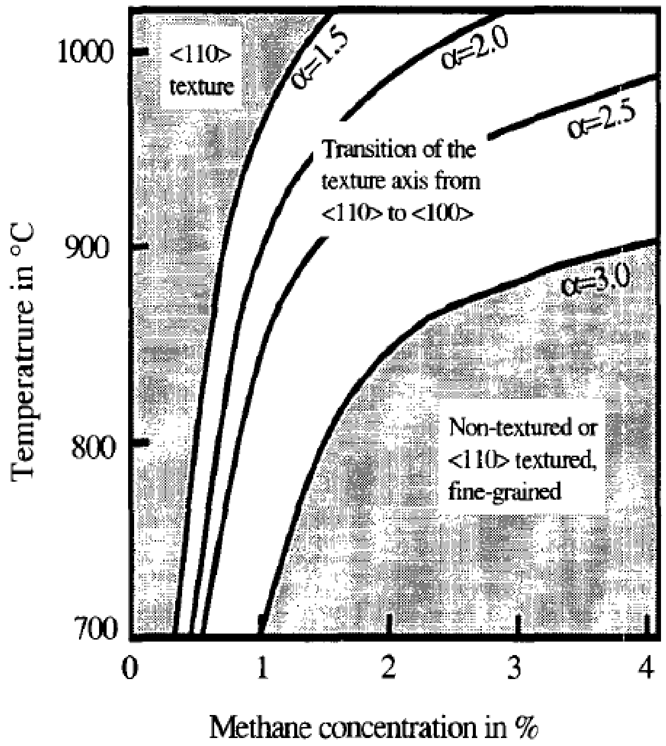
Growth temperature

The diamond growth demands a sufficient high surface temperature, mostly **between 700 and 1000 °C.**

In the **high temperature range** the rate increases with the substrate temperature according to an activation energy of 0.2 eV. It corresponds to the hydrogen abstraction from diamond surfaces by reactions with impinging hydrogen atoms.

At **lower temperatures** the surface activation is too small, the deposition rate drops down and a rising amount of sp^2 bonded (often amorphous) carbon and of hydrogen is included.

(b)



Michler 2000

Carbon/hydrogen ratio

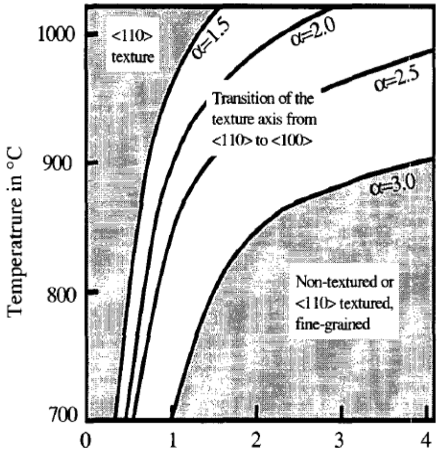
The specific kind of hydrocarbons is of less importance: Under the **high temperature conditions** intense chemical reactions occur, the resulting concentrations correspond to the local chemical equilibrium. The decisive factors are the **local temperature** and the **carbon-hydrogen ratio**.

For ratios between 0.1 and 1% the growth rate increases roughly proportional to the CH_4 concentrations.

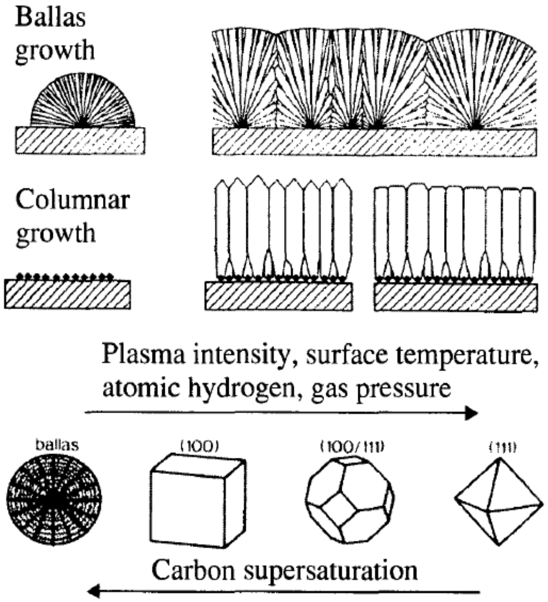
For **low carbon concentrations** in the gas phase, the film **quality rises** due to less non-diamond phases, which are efficiently etched by the abundant hydrogen. In the limiting case, carbon etching exceeds the deposition.

At **higher hydrocarbon** contents above some percent the top surface is **increasingly covered by methyl groups and non-diamond phases at the expense of active sites for the diamond growth**. The growth rate saturates. **Nanoscaled mixtures of nanodiamonds** and **disordered sp² bonded carbon** and finally only graphitic structures are produced.

(b)



(a)



Michler 2000

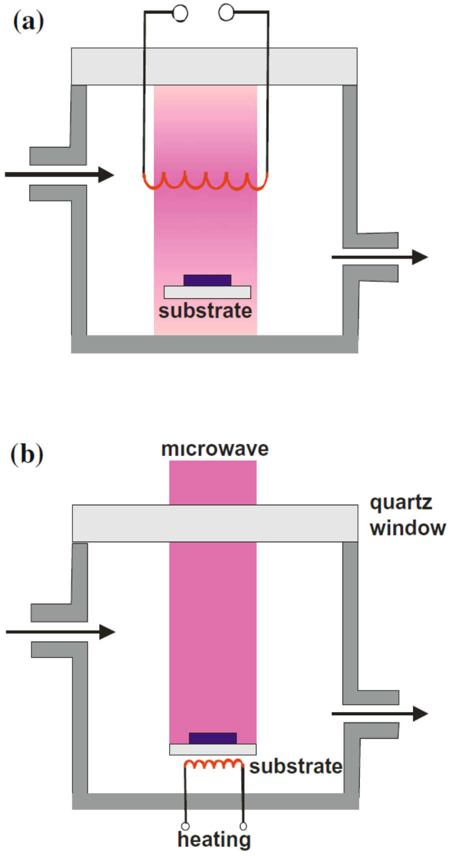
Deposition methods

Hot filament CVD and **microwave plasma CVD** are the most important deposition methods for industrial applications.

Usually both technologies work under comparable conditions with 0.5–5% CH_4 in hydrogen atmospheres of some kPa and with substrate temperatures between 700 and 1000 °C.

The **hot filament technique (HFCVD)** uses local excitation of the CVD atmosphere by thin wires heated by passing currents to temperatures between **1900 and 2200°C**. Atomic hydrogen is generated by **thermal dissociation** at the hot surface. The process can be scaled up by using multifilament wire arrays.

Microwave plasma enhanced CVD (MPCVD), using frequencies in the Gigahertz range, and in contrast to the prevailing surface interaction in dc and RF discharges, microwave plasmas allow **a very intense activation of the gas volume**. From there the excited species diffuse to the surrounding walls, including the substrate. Diamond coatings of extreme purity and high perfection can be prepared in this way.



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Deposition methods

Oxygen may **replace hydrogen** in the carbon compounds in a narrow range around the C-O line. Oxygen allows diamond depositions **at lower temperatures**. Due to the **oxygen etch, especially of the non-diamond phases**, the growth rate decreases and the film quality increases by the oxygen addition.

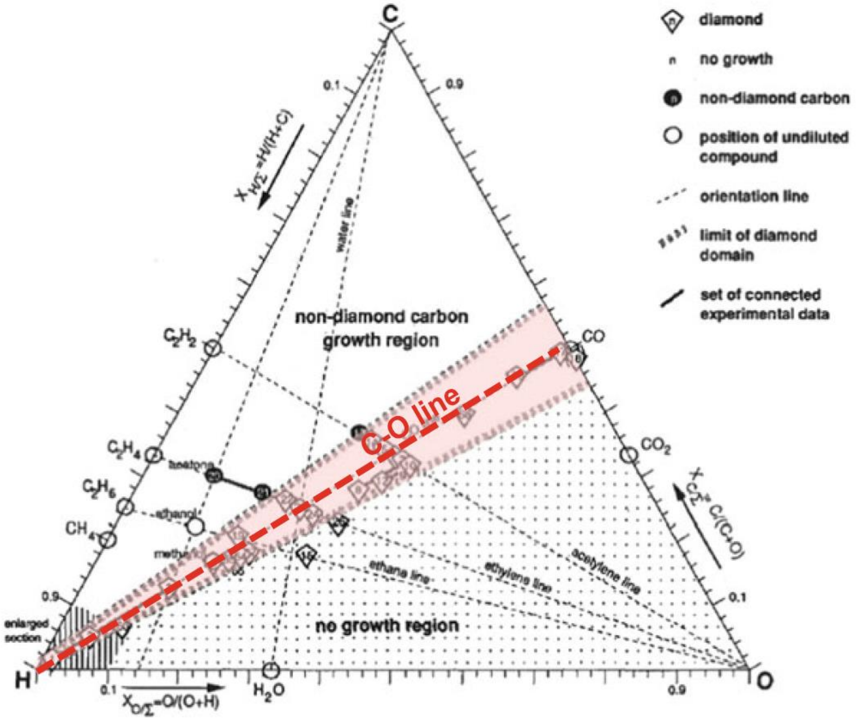

Fig. 2.4 C–H–O diagram for the deposition of diamond. Diamond films can only be prepared by a gas composition in a narrow range around the red C–O line [68]

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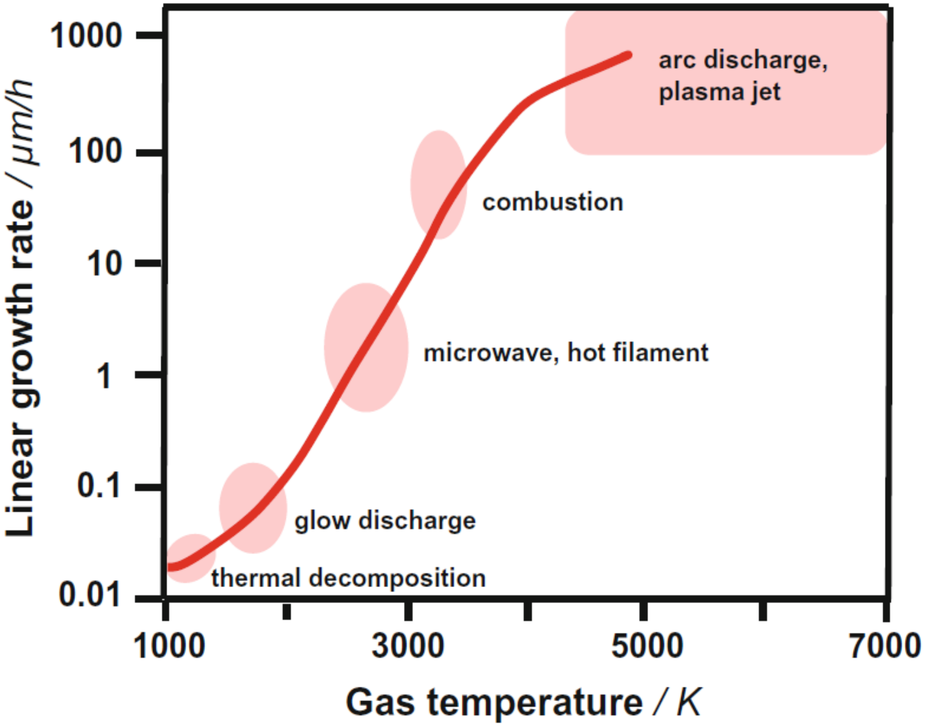
Deposition methods

Usually the deposition rates are in the range of some micrometers per hour. Small amounts of nitrogen in the gas atmosphere (<1%) increase the growth rate by a factor 2 and more to values between 10 and 100 µm/h (depending on the reactor type) and improve the crystallinity under high rate conditions.

Higher gas temperatures increase the growth rate and the film quality.

The enhancement of the growth rate by a higher carbon supply is limited by the increasing amount of non-diamond phases.



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nucleation

The growth of the diamond film emanates from tiny diamond clusters.

The standard nucleation method consists in the **mechanical surface conditioning with microsized diamond grains**. Scratching or polishing with fine-grained diamond grit or **ultrasonic exposure in a diamond powder** containing suspension produce splintered diamond debris and surface defects as active sites.

Embedded nanoscaled diamond crystals and atomic steps represent the potential nuclei for local homoepitaxial growth. The nucleation density increases for smaller diamond powders used for the mechanical pretreatment.

The nucleation density is further **enhanced by additional nanometer carbon layers**, deposited before or after the diamond seeding. The layers can be the result of an **intended predeposition or unintentionally deposited by fingerprints or vacuum oil**. By surface diffusion the ultrathin carbon overlays supply material for the growth of the diamond nuclei.

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Nucleation – bias enhanced nucleation

Generally a bombardment of the surface with energetic ions supports the self-nucleation during the predeposition stage with enhanced methane concentration.

In the bias-enhanced nucleation (BEN) the positive ions are accelerated by a negative bias of −50 … −300 V of the substrate against the plasma or the filament.

High densities of oriented nuclei up to 10^{11}cm^{-2} have been prepared without any external diamond seeding.

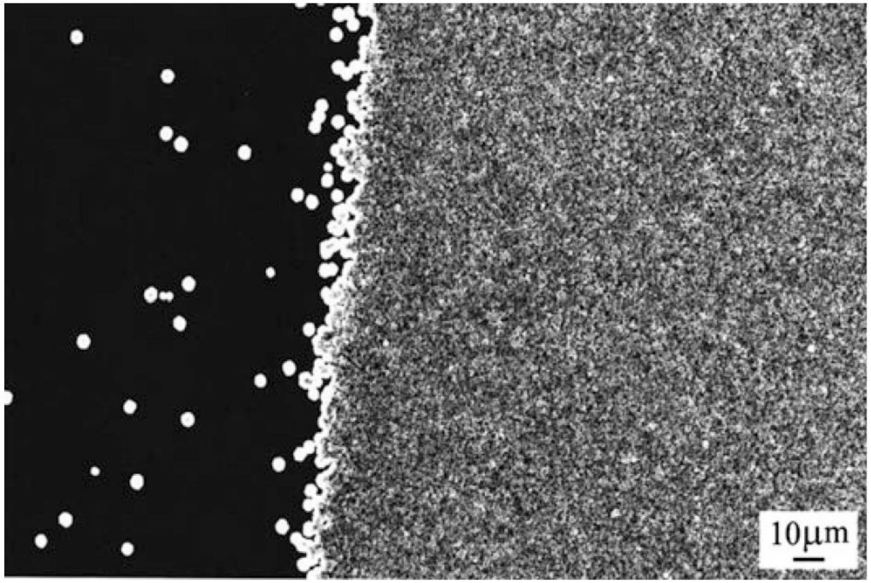

Fig. 2.9 Surface of a silicon sample after 20 h hot filament diamond deposition, demonstrating the efficiency of the bias enhanced nucleation: left without any pretreatment, right: after bombardment with 150 eV ions of a CH_4, H_2, Ar mixture (1:14:4) [143]

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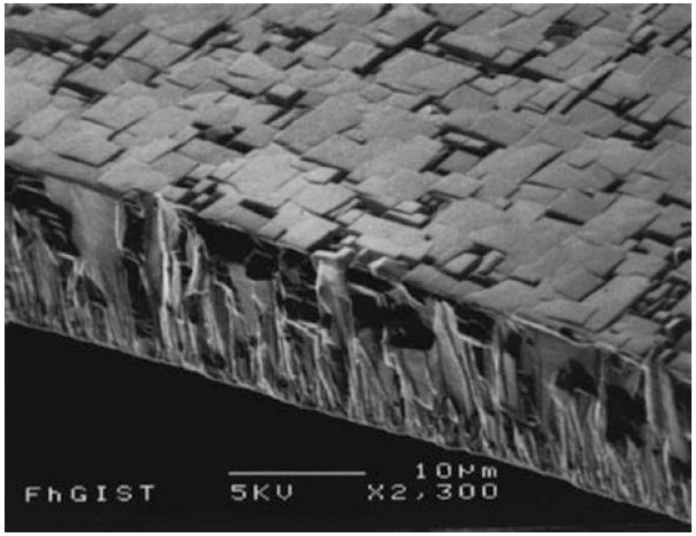
Highly oriented diamond

The formation of the (100) surface morphology is influenced by the directional selectivity of the primary continuous film and thus by the nucleation density and the orientation distribution of the nuclei.

Hence, very smooth films can be prepared by heteroepitaxial growth on suitable single crystalline substrates

On (100) silicon or ß-SiC the bias enhanced nucleation generates oriented nuclei, where the (100) planes and the [100] directions of both lattices are preferentially parallel.



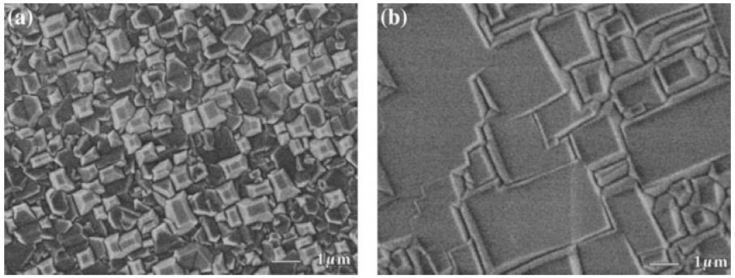


Fig. 2.15 Surface morphology of highly oriented diamond films [176] **a** after the initial microwave deposition (film thickness 1 µm after 13 h) **b** after the subsequent combustion flame deposition (film thickness 15 µm after 3 h)

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Nanocrystalline films

Under standard conditions, the diamond films develop a columnar structure with textured crystallites growing from the nuclei at the substrate surface and coarsening conically with increasing film thickness.

At higher CH_4 contents or lower temperatures, renucleation set in, initially on (111) facets, at even higher CH_4 concentrations also on (100) facets.

The repeated nucleation interrupts the columnar growth and results in smaller grains and increasing amounts of non-diamond phases in the boundaries and very smooth surfaces

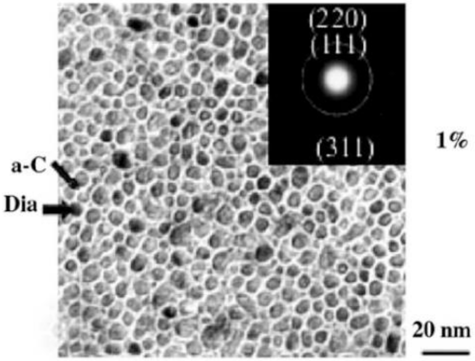
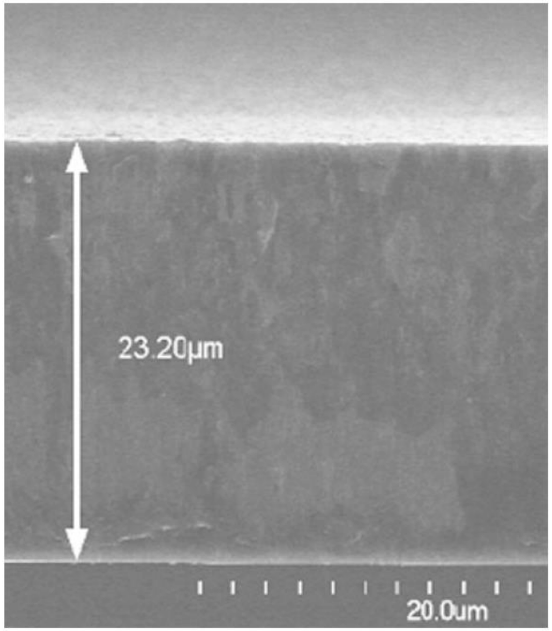


Fig. 3.5 Nanocrystalline diamond films, prepared by bias enhanced growth in a hot filament system with 1% CH_4 in hydrogen [86]. Inset: electron diffraction pattern



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Microstructure summary

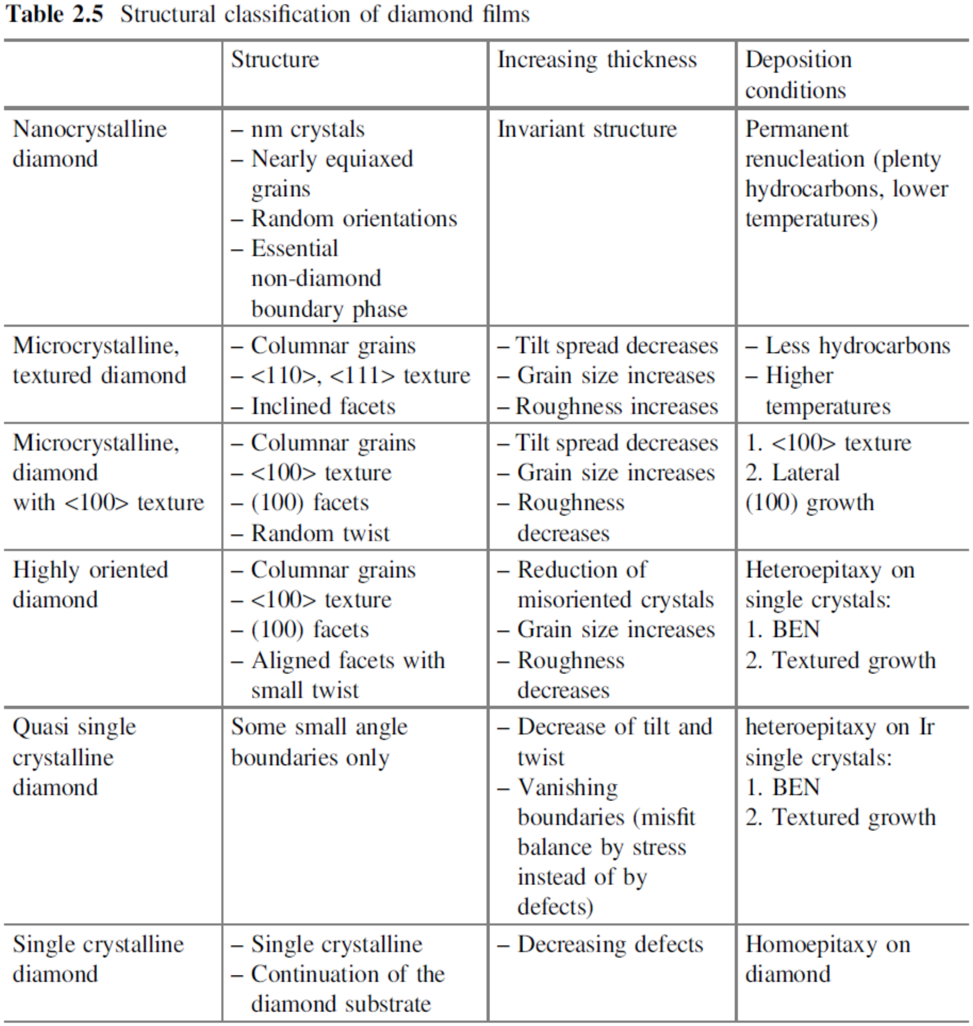

Table 2.5 Structural classification of diamond films

	Structure	Increasing thickness	Deposition conditions
Nanocrystalline diamond	– nm crystals – Nearly equiaxed grains – Random orientations – Essential non-diamond boundary phase	Invariant structure	Permanent renucleation (plenty hydrocarbons, lower temperatures)
Microcrystalline, textured diamond	– Columnar grains – <110>, <111> texture – Inclined facets	– Tilt spread decreases – Grain size increases – Roughness increases	– Less hydrocarbons – Higher temperatures
Microcrystalline, diamond with <100> texture	– Columnar grains – <100> texture – (100) facets – Random twist	– Tilt spread decreases – Grain size increases – Roughness decreases	1. <100> texture 2. Lateral (100) growth
Highly oriented diamond	– Columnar grains – <100> texture – (100) facets – Aligned facets with small twist	– Reduction of misoriented crystals – Grain size increases – Roughness decreases	Heteroepitaxy on single crystals: 1. BEN 2. Textured growth
Quasi single crystalline diamond	Some small angle boundaries only	– Decrease of tilt and twist – Vanishing boundaries (misfit balance by stress instead of by defects)	heteroepitaxy on Ir single crystals: 1. BEN 2. Textured growth
Single crystalline diamond	– Single crystalline – Continuation of the diamond substrate	– Decreasing defects	Homoepitaxy on diamond

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Applications of diamond thin films

tools for machining due to extreme hardness

loudspeaker membranes, SAW and MEMS devices due to high stiffness.

Electrodes for wastewater treatment due to chemical inertness and oxidation potential

Heat spreaders due to high thermal conductivity

Electronic applications due to wide band gap etc.

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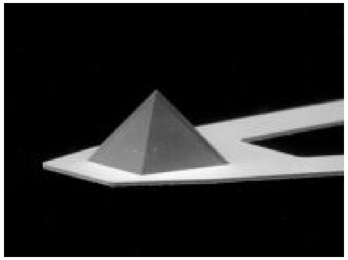
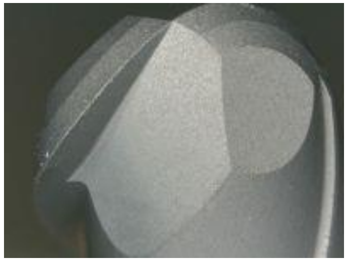
Industrial excursion: Neocoat SA , La Chaux-de-Fonds

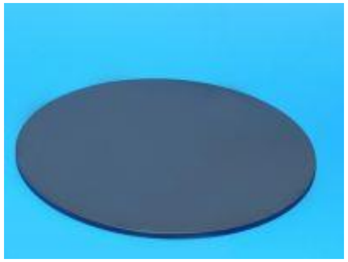
Double-walled water cooling, 100KW



microengineering



drills



electrodes

https://www.neocoat.ch/

amorphous carbon

Amorphous carbon films can be prepared by **CVD** or **PVD**

For **high hydrogen contents**, there is a continuous transition to **plasma polymers**. In this way carbon based films are able to realize an extreme broad variety, **from superhard** and ceramic-like behavior to metal-like conductors and **to polymers**.

The often used term "diamond-like carbon (DLC)" for the amorphous carbon films masks the large differences between the different modifications and suggests a similarity to diamond, which does not always exist.

VDI 2840 or in the international standard ISO 2053:2017 (Carbon based films - Classification and designations), states:

- hydrogen-free amorphous carbon films (<3 atom-% hydrogen)
    - **a-C** for dominating sp^2 bonds,
    - **ta-C** (tetrahedrally bonded amorphous carbon) for dominating sp^3 bonds

- hydrogen-free amorphous carbon films alloyed with metals (Me) or nonmetals (X):
    - **a-C:Me** and a-C:X, respectively,
- hydrogenated amorphous carbon films (>3 atom-% hydrogen):
    - **a-C:H** for marginal sp^3 C–C bonds,
    - ta-C:H for dominating sp^3 C–C bonds
- hydrogenated amorphous carbon films alloyed with metals (Me) or nonmetals (X):
    - **a-C:H:Me** and a-C:H:X, respectively.

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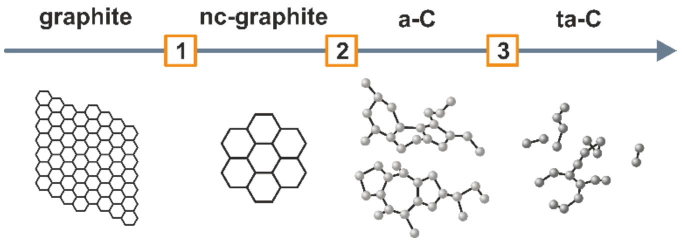
Amorphous carbon - Hydrogen content

NON-HYDROGENATED:

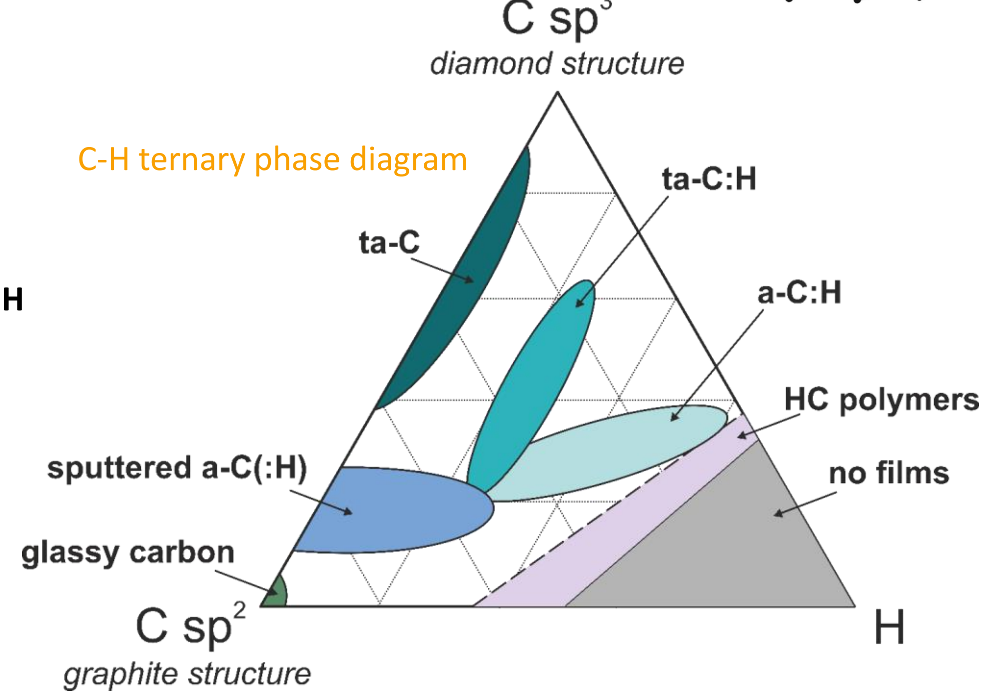
- amorphous carbon **a-C**
- tetrahedral amorphous carbon **ta-C**

HYDROGENATED:

- hydrogenated amorphous carbon **a-C:H**
- hydrogenated tetrahedral amorphous carbon **ta-C:H**



C-H ternary phase diagram



Courtesy from Caroline Hain, BFH, Biel

Amorphous carbon - Hydrogen content

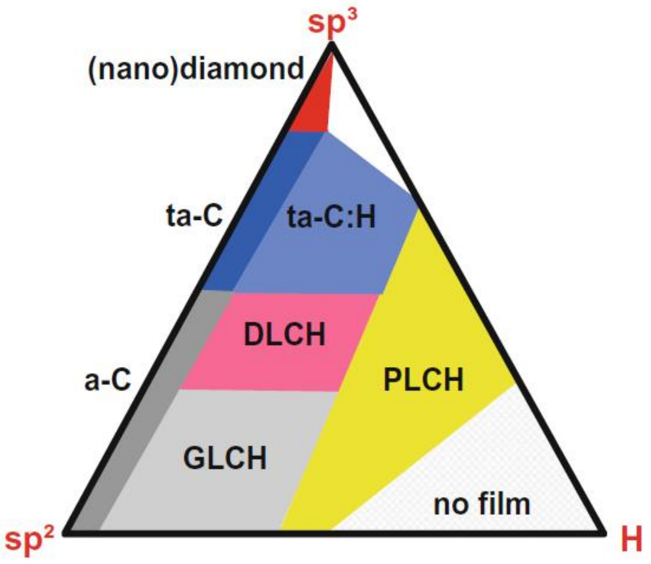
According to the various states (sp^1, sp^2, sp^3) with C–C and with C–H bonds, a-C:H films realize a very broad structural spectrum:

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

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).



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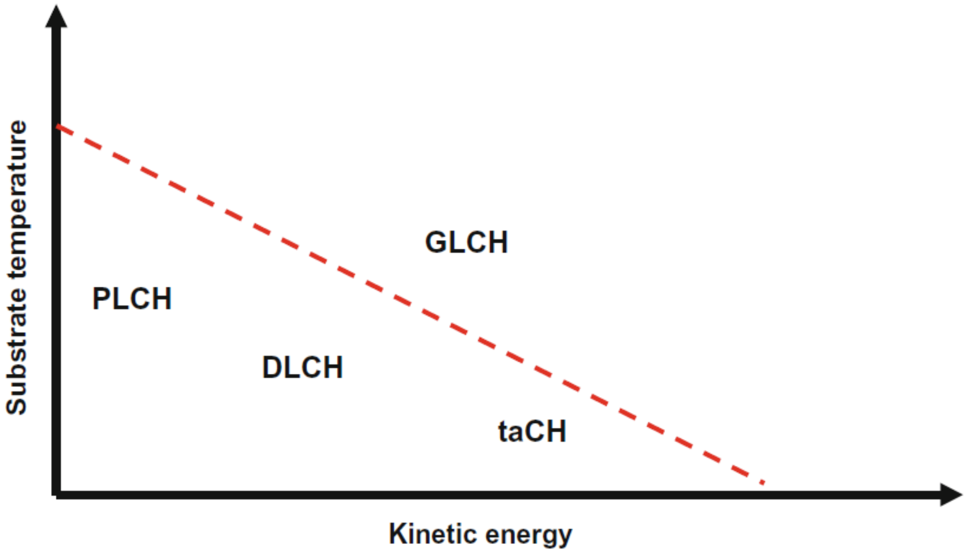
Deposition conditions CVD of a-c:H

With increasing ion bombardment and at low temperatures the structure changes from PLCH over DLCH to GLCH.

In the case of **low or missing ion impact**, **soft polymer-like films** with a high hydrogen content above 40% are deposited (PLCH) Most carbon atoms bond at least one hydrogen atom and they form a rather loose structure.

At **higher deposition temperatures** above 300 °C, most of the hydrogen evolves immediately. Without the hydrogen stabilization of the sp3 bonds and due to the enhanced thermal mobility the structure relaxes to **graphitic arrangements (GLCH)**.

The preparation of **hard a-C:H films (DLCH)** means the formation of a strong carbon-carbon network. Such three-dimensionally connected carbon structures demand a **rather intense ion bombardment at not too high temperatures**.



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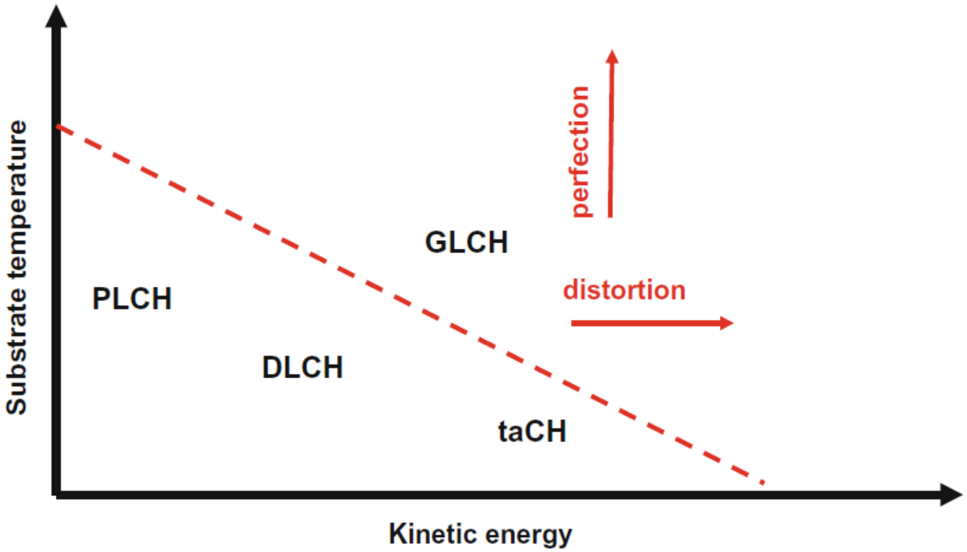
CVD of a-c:H

The deposition of hydrogenated amorphous carbon films may be considered as an **extension of the conditions beyond the preparation of nanocrystalline diamond** structures.

Due to the **abolition of crystalline perfection**, lower substrate temperatures, higher carbon concentrations in the gas atmosphere and an intensified ion bombardment of the growing film

The densification by high-temperature growth is replaced by the ballistic effect of energetic ions. In order to limit the collisional losses of ion energy, the pressure must be rather low, around 0.01mbar in comparison to pressures above 10mbar for the diamond CVD.



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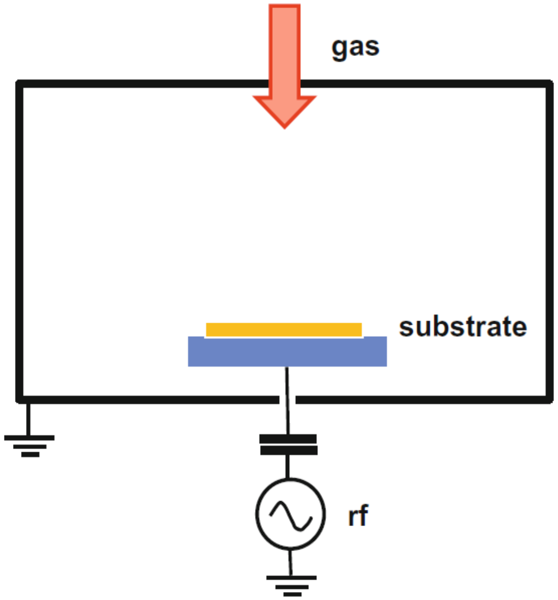
PE-CVD of a-c:H

In the **standard a-C:H process** a capacitively coupled rf glow discharge at the industrial frequency of 13.56 MHz is used with the chamber wall as ground electrode and the substrate holder as the powered electrode.

The **ions cannot follow the fast field variations**. Due to the lower area of the substrate electrode an asymmetric potential with an averaged negative self-bias - Ubias against ground is build up there, which ensures the zero mean current.



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growth of a-c:H

Within the plasma region of the discharge, precursor molecules are excited and ionized.

Concomitantly the plasma composition is modified by fragmentation of larger molecules to reactive radicals and by coalescence of smaller radicals.

Hydrogen is dissociated and partially ionized. The film formation results from the complex interaction of these various particle fluxes.

Table 5.3 Particle fluxes at the surface and their role in the growth of a-C:H films

Molecules	– No direct influence on the growth process (negligible sticking) – Reduction of ion energy by collisions
Radicals	– Adsorption at surface (sticking at free places, generated by ion impact) – Incorporation into the film (using neighbored bonds broken by ions) – Desorption from the surface (thermally or by atomic hydrogen)
Hydrocarbon ions	– Shallow subplantation into the film – Removal of hydrogen from the surface (generation of dangling bonds) – Release of bound hydrogen from the near surface zone – Rearrangement of the film structure by atomic collisions
Atomic hydrogen	– Removal of hydrogen from film surface and from adsorbed radicals – Saturation of dangling bonds – Reaction with adsorbed radicals to volatile molecules (at higher temperatures also with bonded carbon, leading to film erosion)
Hydrogen ions	– Release of bound hydrogen from the surface and from the surface zone

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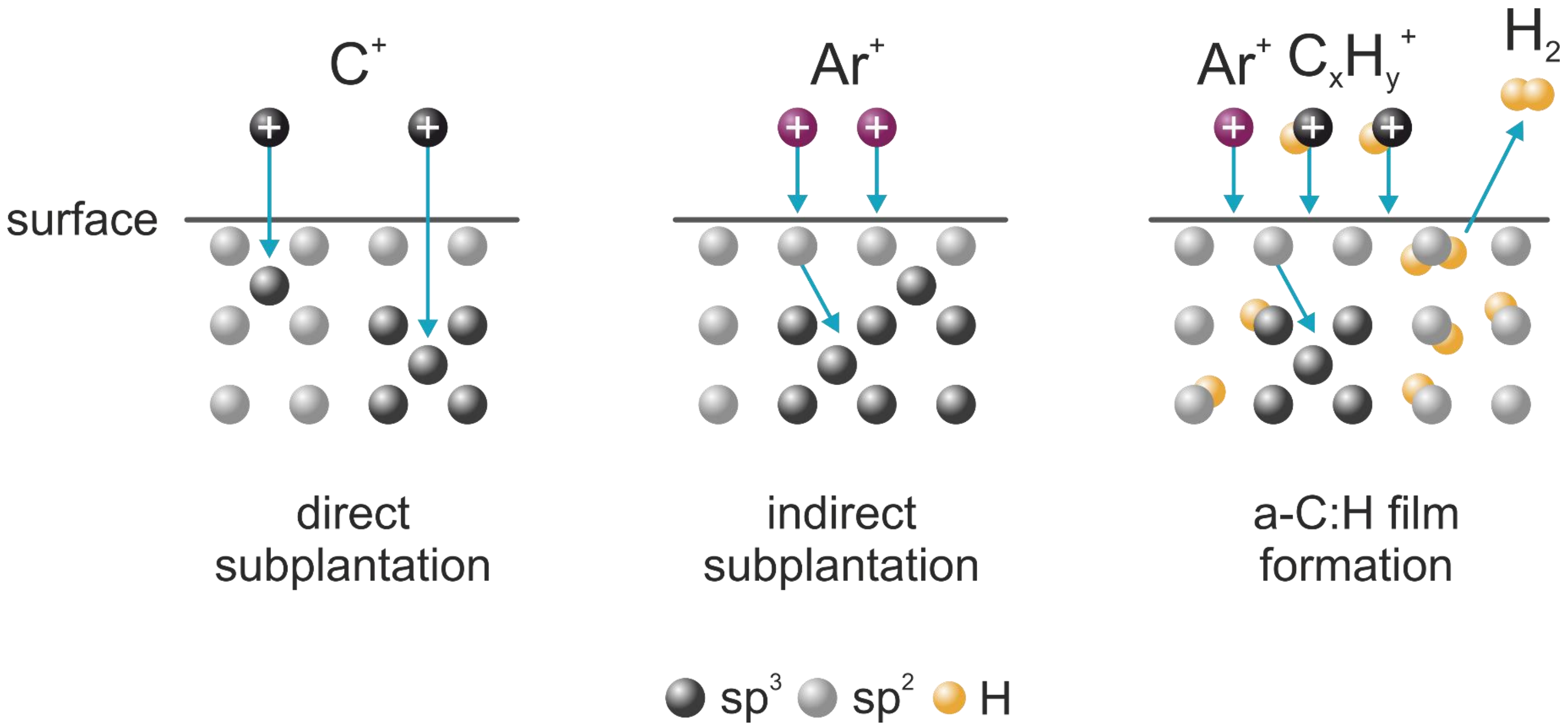
Possibe growth mechanism a-C



The growth of the a-C:H films occurs preferentially by sticking of hydrocarbon radicals on free surface sites with dangling bonds. These free sites are generated by ion impact.

Additionally the ions push weakly bonded carbon atoms into tight bonds. Thus the film growth results from the cooperation of the fluxes of radicals and of ions.

The growth rate is determined by the minority carrier, the ions.

Courtesy from Caroline Hain, BFH, Biel

growth of a-c:H:X

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 nonmetal incorporation results in a marked reduction of the intrinsic stress and the hardness is lowered.

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**. The conventional rf plasma source is supplemented or replaced by an unbalanced magnetron.

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 (nanocomposite).

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Selected properties of carbon materials

		diamond	**ta-C**	**a-C:H**	**graphite**
crystallographic system		diamond cubic	amorphous	amorphous	hexagonal
mass density, g/cm^3		3.51	2.5 - 3.3	1.5 - 2.4	2.26
sp^3 contents, %		100	50-90	20-60	0
hydrogen contents, at.%		0	≈1	10-50	0
hardness, GPa		100	50-80	10-45	<5
friction coefficients	humid air	0.1	0.05 - 0.25	0.02-0.3	0.1 - 0.2
	dry air	0.1	0.6	0.02-0.2	> 0.6
band gap, eV		5.5	1 - 2.5	1 - 4	0.04
electrical resistivity, Ω·cm		10^{18}	10^{6} - 10^{10}	10^{4} - 10^{12}	10^{-6} - 10^{-2}
thermal stability in air, °C		800	400 - 600	300 - 350	> 500

Surface & Coatings Technology **2014**, 242 (214–225)

Courtesy from Caroline Hain, BFH, Biel

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 CH_4) 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)

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Summary amorphous carbon based materials

- According to the various states (sp1, sp2, sp3) 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 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 (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

Exercises

- State the application of diamond coating in mechanical manufacturing
- Explain the growth mechanism of diamond. State the CVD reactions for growth of diamond coating
- Why is H2 used in CVD of diamond? Which other element can replace it under which conditions?
- How does the grain size depend on Temperature and hydrocarbon concentration
- Which deposition techniques for diamond films you know?
- State the advantage of HFCVD process over other process of diamond CVD.
- Explain the nucleation of diamond. How is nucleation enhanced in practice?
- Why does cemented carbide substrate require special surface treatment before the CVD process?
- Name at least 3 applications of diamond films

- Explain the differences between PLCH, DLCH and GLCH and ta-C:H. Under which deposition conditions they form?
- What is the standard process for a-C:H deposition
- Compare briefly the growth mechanisms of diamond to PECVD of a-c:H in a few lines.
- What additional alloying elements are used for a-C:H and what is their effect on coating properties?
- Rank diamond-Ta-C,a-c:H and graphite in terms of hardness, sp3 content, band gap and electrical resistivity
- Name 3 applications for amorhous carbon based materials