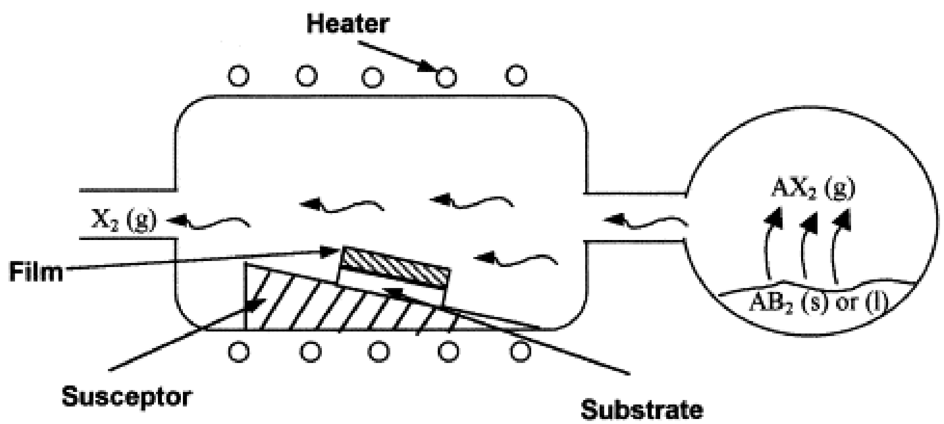
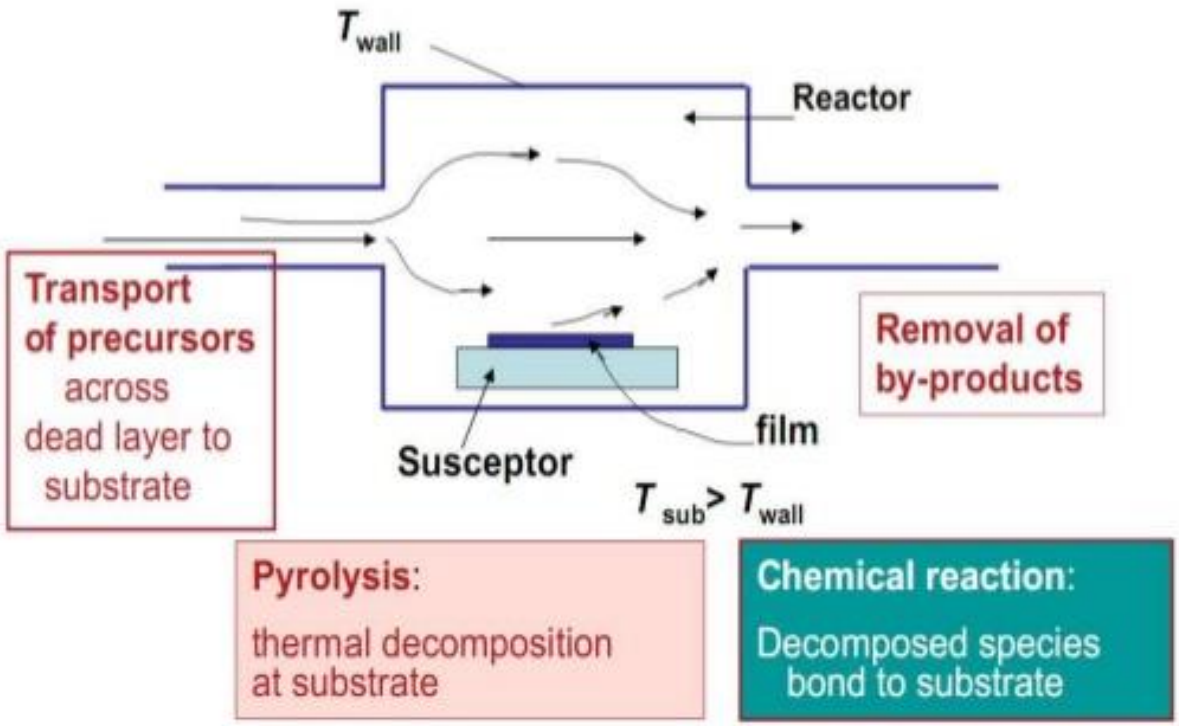
Chemical Vapour Deposition (CVD)*

*** CVD is coating of a preheated substrate with desired metal in metallic or compound form by using a vaporizable compound of the metal which forwards to vacuum chamber with a carrier reactive gas.**



Prof. Dr. Kerem Altuğ GÜLER

STEPS INVOLVED IN A CVD PROCESS (SCHEMATIC)



- CVD is an old multifunctional technique is used for either carbon, silicon, carbides, nitrides, oxides and intermetallic coatings to suitable substrates or powder and fiber production.

- In present, this technology is especially used for production of semi-conductors and electronic components.

Process parameters of conventional CVD process

- Temperature: 800 – 2000°C
- Pressure: 10^{-6} to 1 atmosphere (atm)
- Precursors:
  - Reactive gasses: Metal halides*, carbonyls**
  - Reducing gasses: H_2
  - Inert gasses: Ar, N_2
  - Other gasses: CH_4, CO_2, NH_3 and other hydrocarbon gasses.

Halide* (salt): It is a binary compound of a halogen (AgF, AgCl)

Carbonyl** group: Carbon atom double bonded to oxygen atom (C=O).

In CVD, there are several reactions occur during deposition. Examples of these reactions:

1- Thermal decomposition:

$$Ni(CO)_{4(g)} \rightarrow \underset{\text{coating}}{Ni_{(s)}} + 4CO_{(g)}$$

$$W(CO)_{6(g)} \rightarrow \underset{\text{coating}}{W_{(s)}} + 6CO_{(g)}$$

- Carbonyls decompose under 200 °C. For better adherence substrate is heated up to 800-1000 °C.
- The most important disadvantage of carbonyls is being highly toxic.
- Decomposition of halides (WF_6) and hydrides (B_2H_6) occurs over 500 °C. So process temperature must be high.

2- Reduction:

$$\underset{}{WF_{6(g)}} + 3H_{2(g)} \rightarrow \underset{\text{coating}}{W_{(s)}} + 6HF_{(g)}$$

Working temperatures:

- Ti $\rightarrow$ 1100 °C
- Mo and W $\rightarrow$ 600 – 700 °C

3- Oxidation:

$$Si_{(s)} + O_{2(g)} \xrightarrow[\text{dry oxidation}]{} SiO_{2(s)} \text{ (Deposition temp: 900-1100°C)}$$

- SiO_2 also can be deposited with oxidation of silane gas in lower temperatures (450°C).

$$\underset{\text{silane}}{SiH_{4(g)}} + O_{2(g)} \rightarrow SiO_{2(s)} + 2H_{2(g)}$$

4- Hydrolysis

$$2AlCl_3 + 3H_2O \rightarrow Al_2O_3 + 6HCl$$

5- Co-reduction (birlikte indirgenme)

$$TiCl_{4(g)} + 2BCl_{3(g)} + 5H_{2(g)} \rightarrow TiB_{2(s)} + 10HCl_{(g)}$$

$$Al_2Cl_6 + 3CO_2 + H_2 \rightarrow Al_2O_3 + 3CO + 6HCl$$

Advantages of CVD technique

- Capability of production and decomposition of ultra dense and pure materials.
- Complex shaped parts can be coated uniformly.
- Conformal* and multifunctional coatings can be obtained.
- Deposition rate can be easily adjust.

  - Low deposition rates are preferred for epitaxial** thin film growths of microelectronic applications.

  - High deposition rates are preferred for deposition of thick protective coatings.

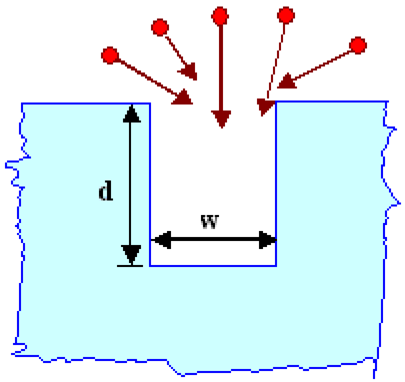
*Conformal: Polymeric thin films for protection of PCB.

**Epitaxy: The process of growing a crystal of a particular orientation on top of another crystal, where the orientation is determined by the underlying crystal.

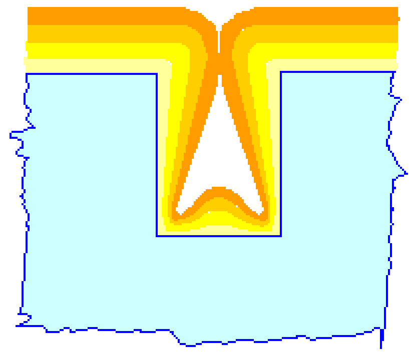
- Depositions can be carried out at low substrate temperatures. Dense coatings which covers whole surface or field selective coatings can be obtained. This is only possible with CVD.
- High melting point materials can be coated at lower temperatures. E.g. Refractory materials like SiC can be deposited at 1000 °C.
- Various kinds of chemical precursors can be used.
- Capability of controlling crystal structure, surface morphology and orientation of CVD products by controlling process parameters.

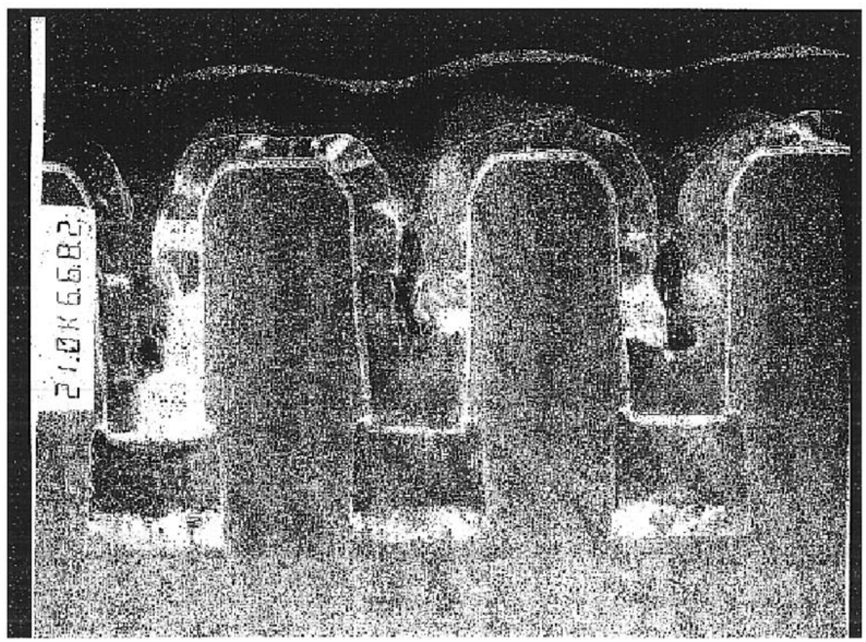
Disadvantages of CVD technique

- The most significant disadvantages of conventional CVD technique is necessity of substrate heating up to 800 – 1000 °C. E.g. High speed steels can not be coated with conventional CVD.
- Input and output gasses may be in toxic, corrosive, flammable and/or explosive properties. Thus it can be dangerous and unsafe.
- It is not suitable for material mixtures.
- Excessive reactive gasses can create keyhole*.



Idealized Contact Hole





*Keyhole formation

Applications of CVD technique

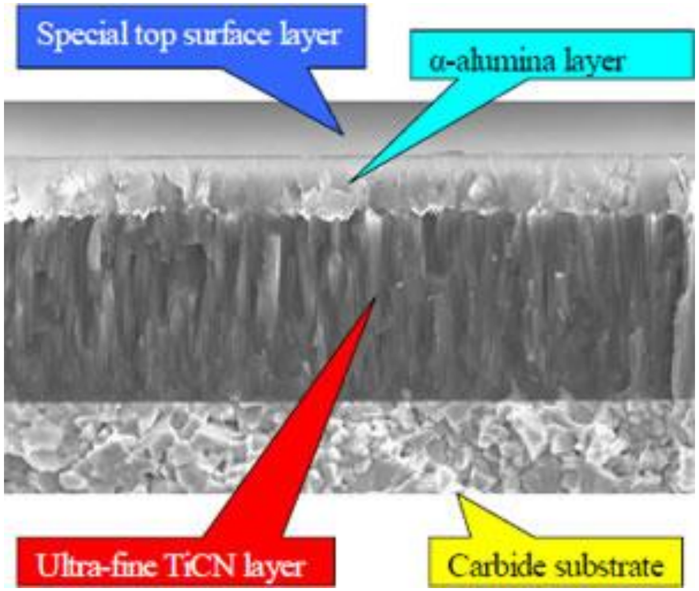
- Semi-conductors and some electronic compounds.
- Tools, bearing materials and coating of other wear resist parts.
- Optic, optoelectronic and corrosion resist products.
- Monolithic parts, ultra fine powders and high strength fibers can be produced.
- Multilayer coatings can be obtained with CVD.

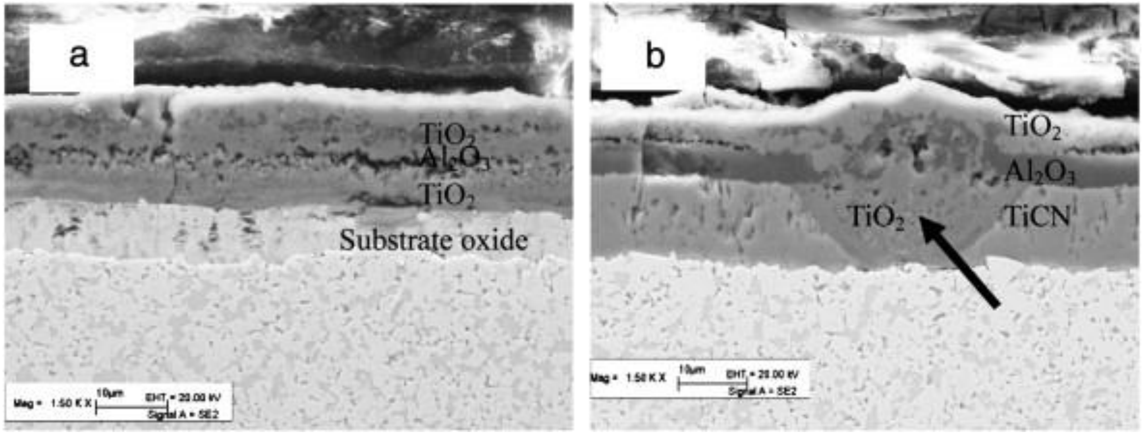
__________TiN (Provides slipperiness and has gold yellow colour. Layer thickness 2-3 μm)

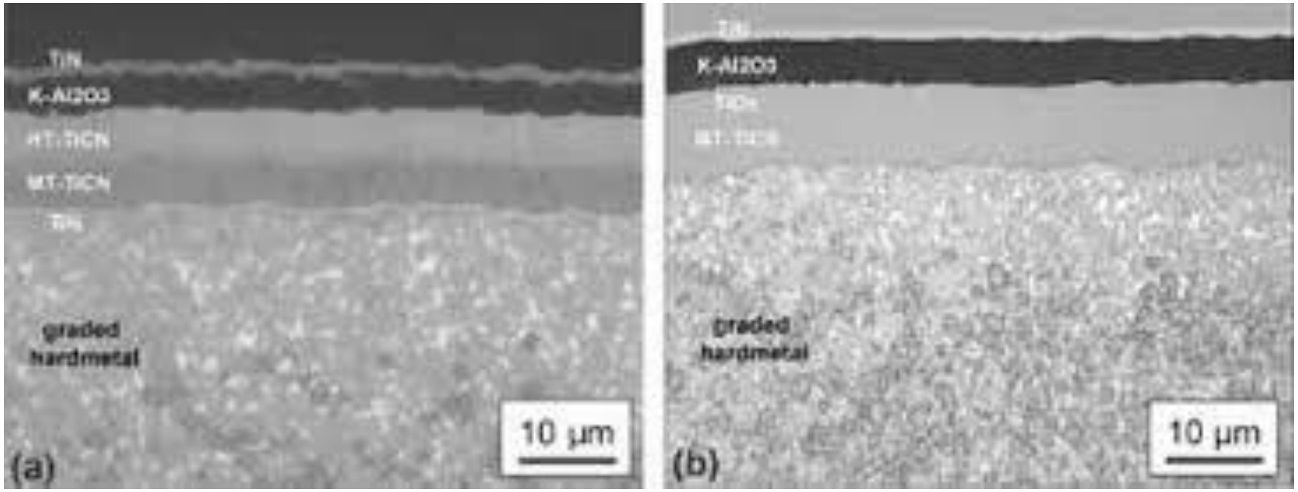
__________Al_2O_3 (Thermal barrier layer)

__________TiC (Adhesive layer)

__________Substrate







Multilayer CVD coating examples.

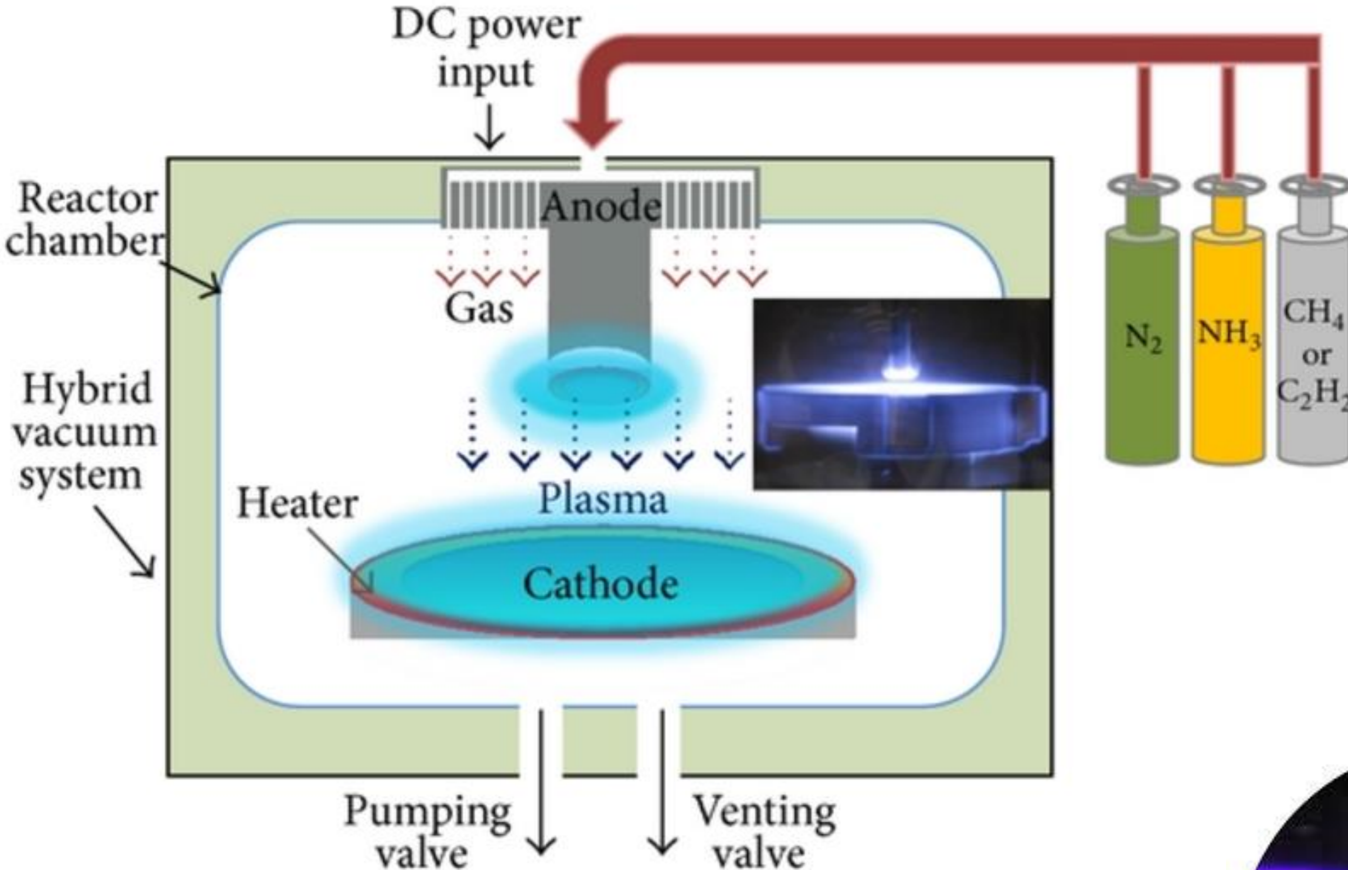
Types of CVD

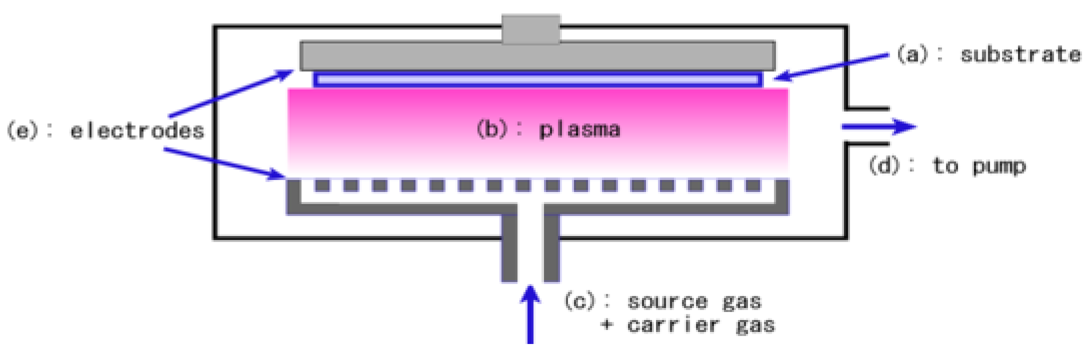
- Atmosphere pressured CVD (APCVD).
- Low pressured CVD (LPCVD).
- Plasma enhanced CVD (PECVD).
- Photon assisted CVD (PACVD)
- Metalorganic CVD (MOCVD).
- Epitaxial atomic layer growth (CBE) (Chemical beam epitaxy)

Plasma enhanced CVD (PECVD)

- Plasma is used to achieve reactions which are impossible at low temperature.

- In this technique activation energy for decomposition of reactive particles and interactions of these particles with other particles to form deposition are provided with high kinetic energy electrons in the plasma.


DC power input
Reactor chamber
Anode
Gas
Hybrid vacuum system
Heater
Plasma
Cathode
Pumping valve
Venting valve
N_2
NH_3
CH_4 or C_2H_2


(a): substrate
(e): electrodes
(b): plasma
(d): to pump
(c): source gas + carrier gas

Major advantages of PECVD

- Low deposition temperatures (20-150 °C / 200-350°C).
- Deposition of unstable phases.
- Better control of purity and stoichiometry.
- Much better film adhesion and bonding strength.
- Suitable for deposition of insulating layers and temperature sensitive multilayer films.

Disadvantages of PECVD

- Coatings occurred with low density and high imperfection content when compared to high temperature coatings.
- There is difficulty for deposition of pure metals.

Applications of PECVD

- Si wafers of integrated circuits.
- DLC* and DCC** coatings for cutting tools.
- Fiber optic coatings
- Magnetic tape head coatings.

*DLC: Diamond like carbon with shining black colour.

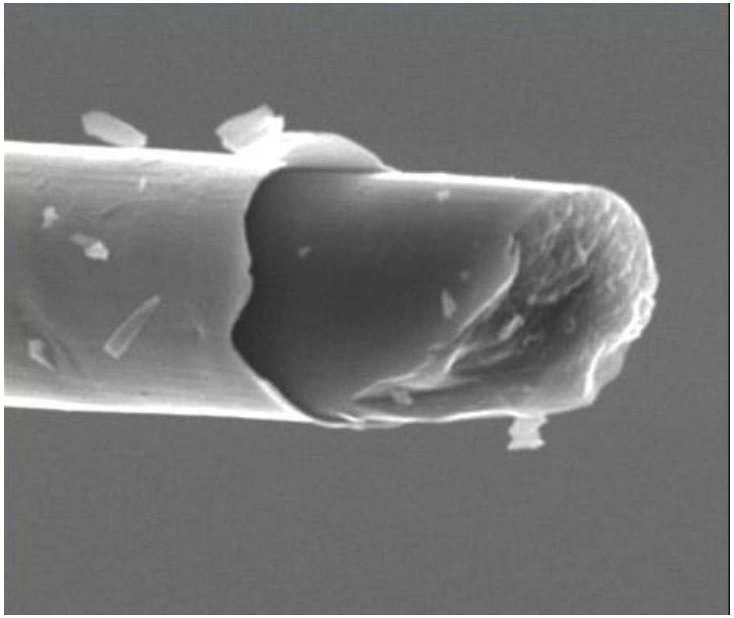
**DCC: Diamond coated carbon.


TiN

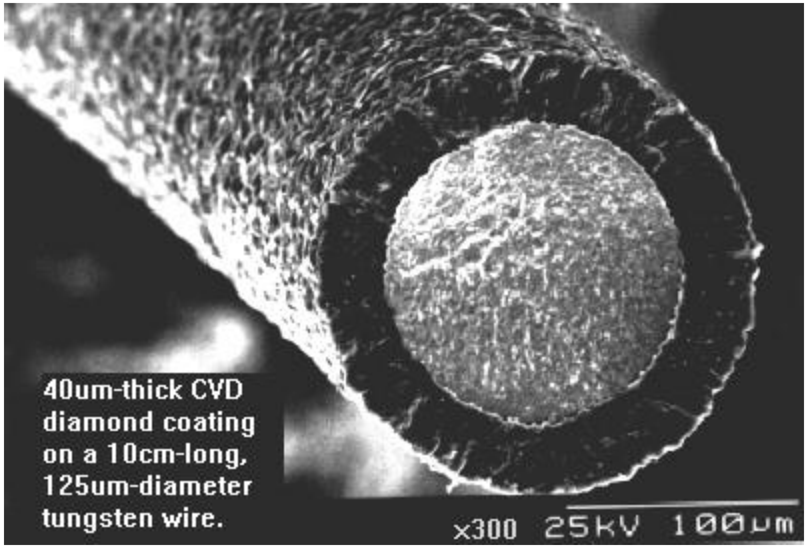

DLC

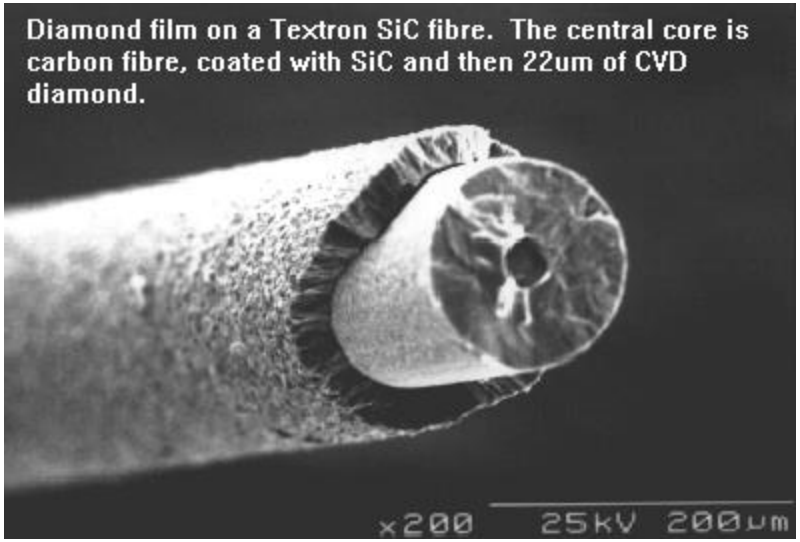

TiCN


DCC



CVD nickel coated carbon fiber.





Video links

- https://www.youtube.com/watch?v=hkYb35e5JGo
- https://www.youtube.com/watch?v=j80jsWFm8Lc
- https://www.youtube.com/watch?v=1MFz0QToX6Q
- https://www.youtube.com/watch?v=HEATKNByyg0
- https://www.youtube.com/watch?v=xV32RrTu0ik
- https://www.youtube.com/watch?v=_i-3SPiWEHo
- https://www.youtube.com/watch?v=UGFkgLZ6EVI