

Gaseous and vacuum deposition methods: physical vapor deposition, magnetron sputtering, chemical vapor deposition (by Tavo Romann)

These techniques are expensive; however some are being actively exploited, especially for semiconductor technologies, but also in fuel cells and solar cells.

Physical vapor deposition (PVD)

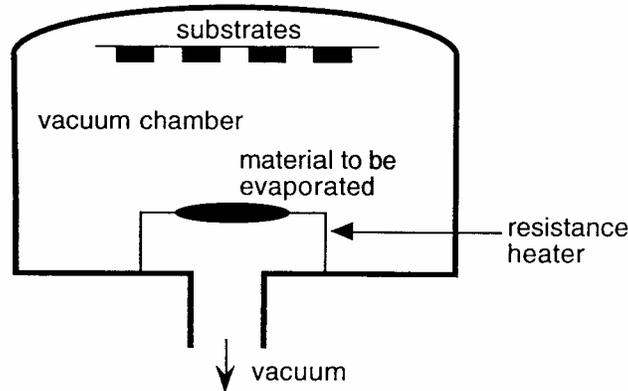


Fig. 1. Vacuum evaporation equipment for thin film deposition. Atoms evaporate from the source as it is heated and deposit on the substrates.

Evaporation-condensation consists simply of evaporating a target material and condensing the vapor onto a substrate with the compound stoichiometry maintained (Fig. 1). For example, some material in vacuum environment is heated in a tungsten boat, until it evaporates. The evaporated molecules or metal atoms condense on a suitable substrate and a film of material develops (Fig. 2).

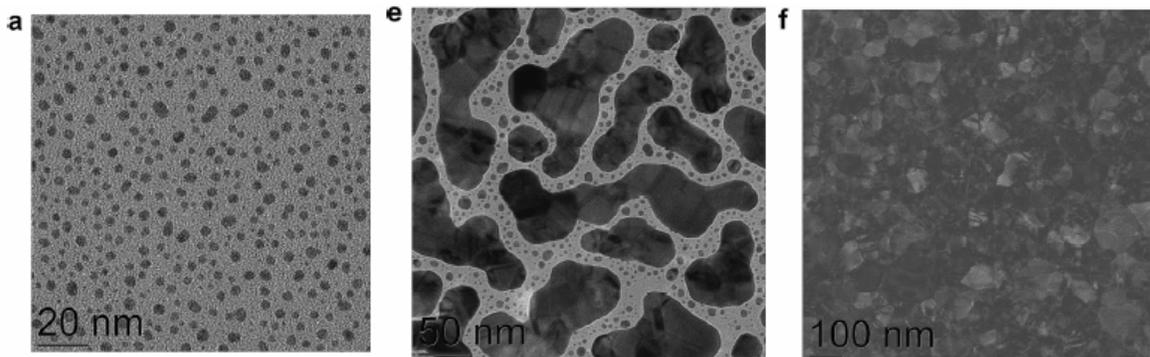


Fig 2. TEM images of thin film Au electrodes. Nominal film thickness 0.25 (a); 5 (e); and 20 (f) nm.

A better control for film thickness, purity and other properties is achieved if only the outermost layers of the target atoms are ablated (evaporated) using *pulsed laser deposition*

(PLD), electric arc, sputtering or other methods. In addition the illumination of deposited material layer with laser pulses can be applied as well to increase the density of material layer deposited if we need compact layers.

Laser pulses as an energy source for evaporation of material as well as for generation of highly reactive intermediate compounds can be generated as well (preparation of diamond like carbon (DLC) films from organic oils as a carbon source). This method is known as laser ablation method (LAM). Raman spectra measured demonstrate that in mainly amorphous carbon phase the diamond-like regular crystals exist (Fig. 3). The same results can be seen from the AFM data given in Fig. 4.

Fig. 3. Schematic representation of DLC films synthesis. 1 – vacuum pump, 2 – valve, 3 – liquid N₂ reservoir, 4 – liquid N₂, 5 – substrate (window), 6 – o-ring seal, 7 – vacuum oil, 8 – reaction chamber, 9 – vacuum gauge, 10 – controller, 11 – H₂O₂ reservoir, 12 – H₂O₂, 13 – lens, 14 – mirror, 15 – semitransparent mirror, 16 – regulator of laser beam intensity, 17 – excimer laser (248 nm), 18 – pyroelectric laser pulse energy meter, 19 – step-motor driver, 20 – analogue-digital converter, 21 – PC.

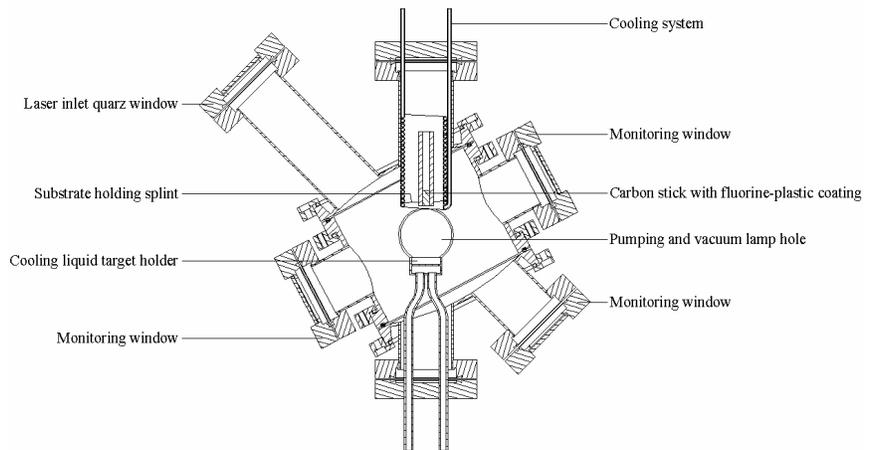
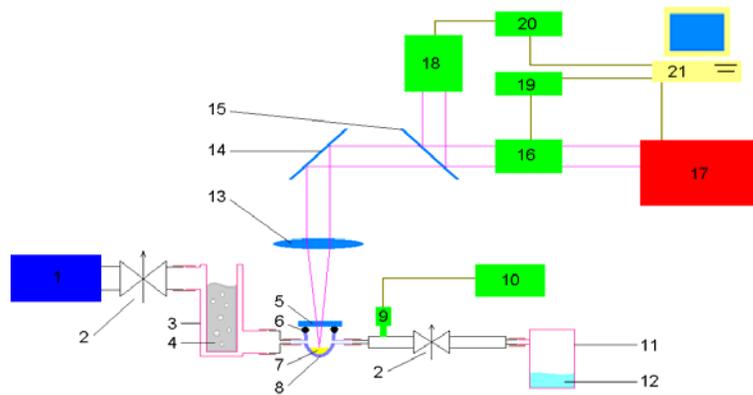


Fig. 4. Scheme of the PLD chamber in the synthesis setup.

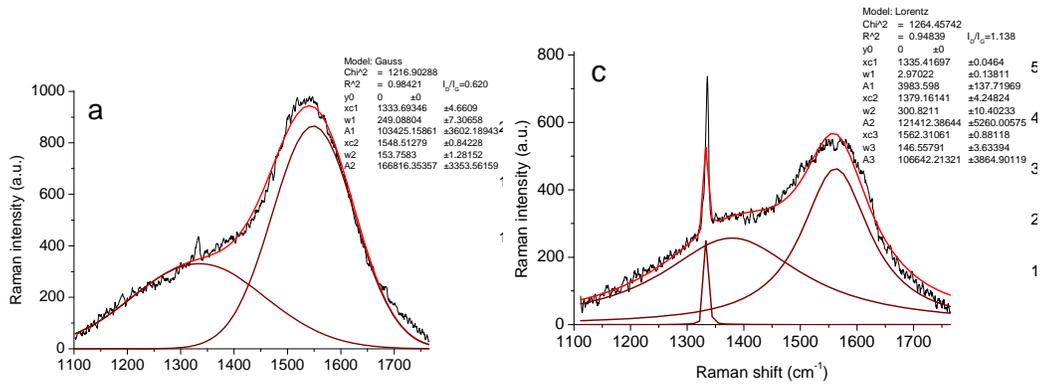


Fig. 5. Raman spectra of the amorphous carbon (a-C) film regions, deposited at room temperature, $\sim 10^{-3}$ mbar pressure, by the 3 laser impulses (frequency 5 Hz and 100 mJ energy per impulse). Between the depositions, substrate has been irradiated by the laser impulses (20 mJ energy per impulse) and total 1000 cycles has been used. “a” to “c” are listed by the applied irradiated laser beam local intensity increasing (different film regions on substrate).

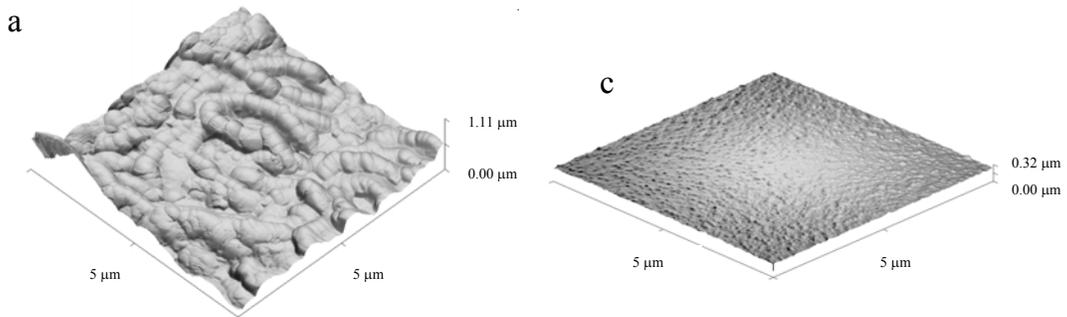


Fig. 6. AFM 2D images (noncontact regime) for DLC film areas $5 \times 5 \mu\text{m}$ “a” for the similar areas like it was used for the Raman spectroscopy analysis given in figure 5c (i.e. for more diamond crystals containing areas of carbon films) and $5 \times 5 \mu\text{m}$ “c” for the similar areas like it was studied in figure 5a (amorphous deposits).

Sputtering (video <http://www.chemicum.com/?v=Sputtering.fly>)

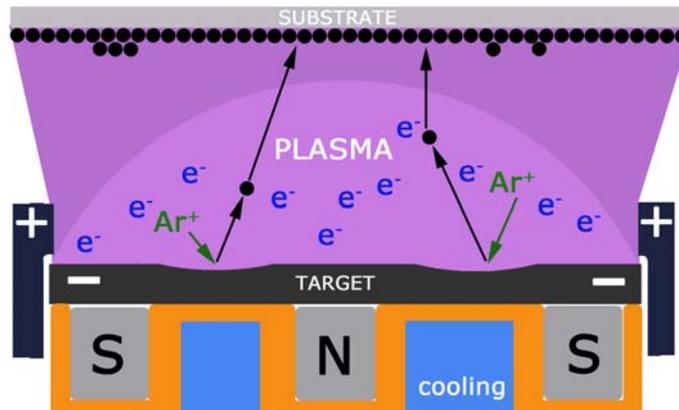


Fig. 1. Principle of magnetron sputtering.

Normal sputtering is a well established technology characterized by low deposition rates ($0.1-1 \mu\text{m h}^{-1}$), but large areas can be coated homogeneously. Sputtering is basically the removal of atomised material from a solid by energetic bombardment of its surface layers by ions or neutral particles (Fig. 1). A negative voltage of typically -300V or more is applied to the target. When an Ar^+ ion collides with atoms at the surface of a solid an energy transfer occurs. A surface atom becomes sputtered if the energy transferred to it normal to the surface is larger than about 3 times the surface binding energy. In *magnetron sputtering* a permanent magnet is positioned behind the target. It traps electrons in plasma close to the target and hence the collision probabilities and deposition rates. DC source is used for conductive materials and radio frequency (RF) source is used for dielectric materials. However, oxides and ceramics can only be deposited at relatively low deposition rates ($0.01- 0.2 \mu\text{m h}^{-1}$).

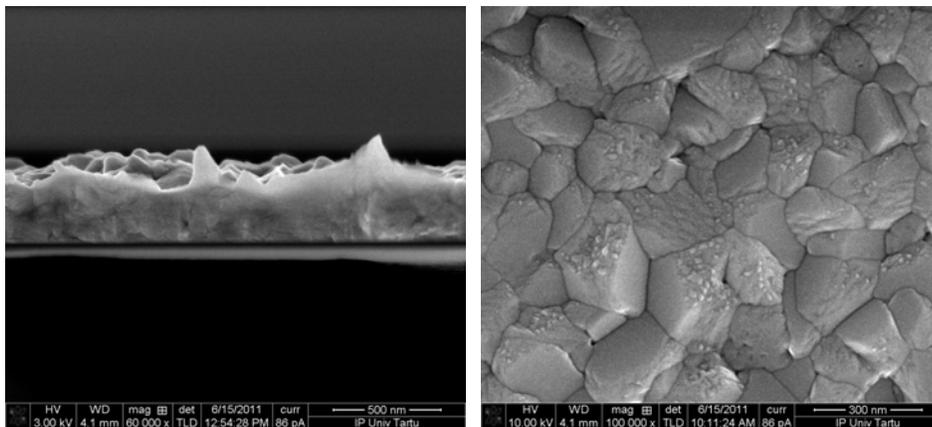


Fig. 2. SEM images of 600 nm thick Al film on glass (cross and top view). Sputtering conditions: 3 mTorr Ar, 300 W DC.

There are some possibilities how to make films more compact or in reverse, more porous. Surface biasing (it is creating smaller plasma field on sample as well) during sputtering or pulsed DC may produce smoother surfaces. Additional high temperature processing with the main aim of densification of materials can be applied.

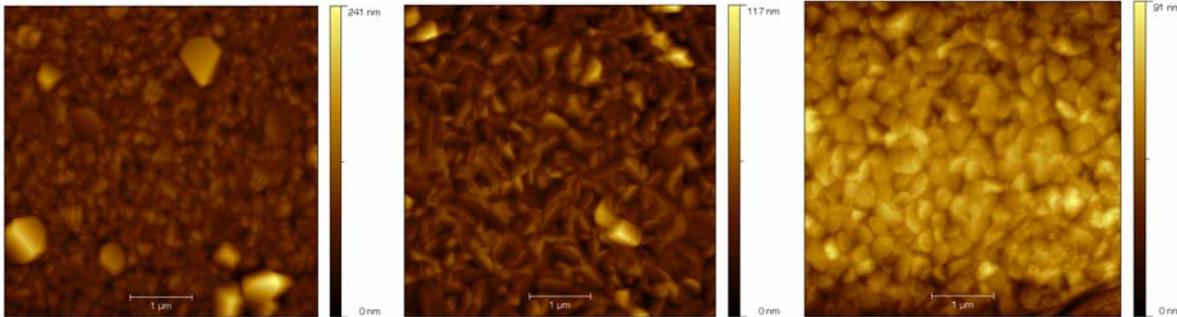


Fig. 3. AFM images of $\sim 1 \mu\text{m}$ thick Al film surfaces. Magnetron sputtering conditions: 3 mTorr Ar and 300 W DC (a). Pulsed DC avoids large particles (b) and 50 W sample biasing (c) creates flatter grains. Notice the change in roughness scale.

Grazing angle sputtering: If sample is not rotated and is placed at large angle relative to the sputtering target surface, micrometer sized pillars grow due to shielding effect.

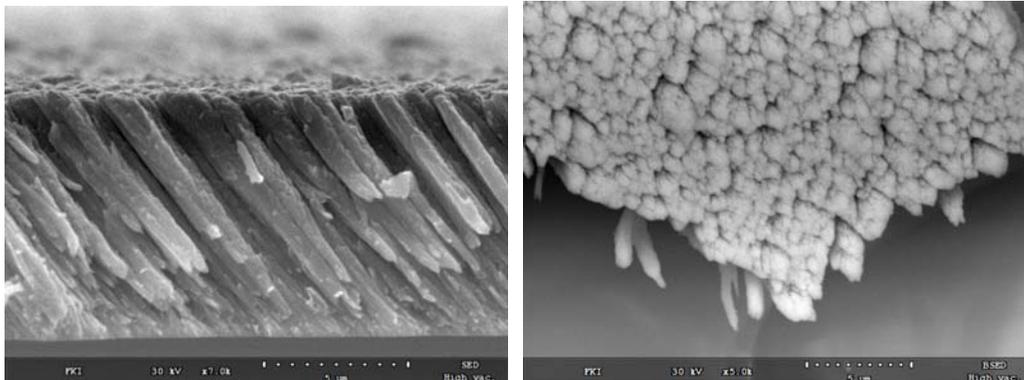


Fig. 4. $7 \mu\text{m}$ thick Ni film achieved by magnetron sputtering at 75 degrees of incident angle.

High temperature sputtering with a catalyst: High temperature increases particle diffusion and usually more dense film is produced. However, often it also creates various structures and the presence of a catalyst may completely change the film structure. For example, sputtering of carbon at high temperatures: in the presence of nickel catalyst, carbon nanotubes are produced. Gold is a catalyst for silicon microstructure formation at high temperatures.

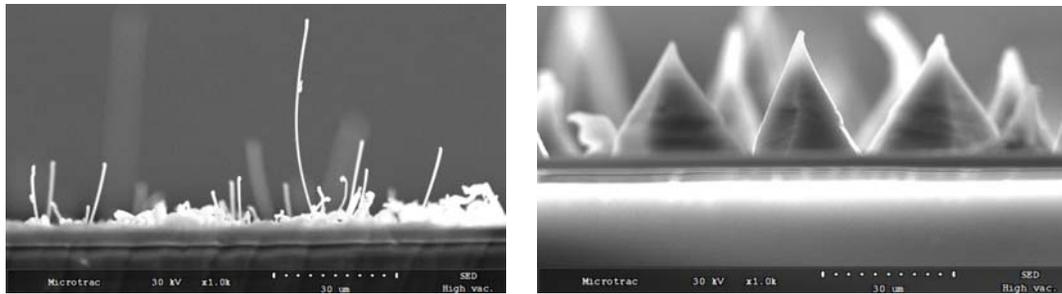


Fig. 5. 1 μm of Si sputtered on 200 nm Au|glass surface at 500 $^{\circ}\text{C}$, 3 mTorr Ar pressure. Instead of compact film, silicon nanowires or pyramids are produced.

EXAMPLES: Sputtering is used extensively in the semiconductor industry to deposit thin films of various materials in integrated circuit processing. Sputtering is also used as the process to deposit the metal (e.g. aluminium) layer during the fabrication of CDs and DVDs or to metalize plastics such as potato chip bags.

A few micrometers thick Al, Ni, Ti, or Cu metal layer can be deposited onto an electrode surface in order to increase the conductivity. For example, Al is deposited onto a porous carbon supercapacitor electrode to have a good electrical contact between C and aluminium foil current collector (Fig. 6a).

Inorganic ion-conductive electrolyte layers are often deposited on electrodes by magnetron sputtering method. For example Li-ion conductive layers for Li-ion battery or oxygen conductive layers for fuel cells. In Fig. 6b, there is a 1 μm thick magnetron sputtered gadolinium doped ceria (GDC) film, which can be used as an oxygen conductive membrane for a high temperature solid oxide fuel cell.

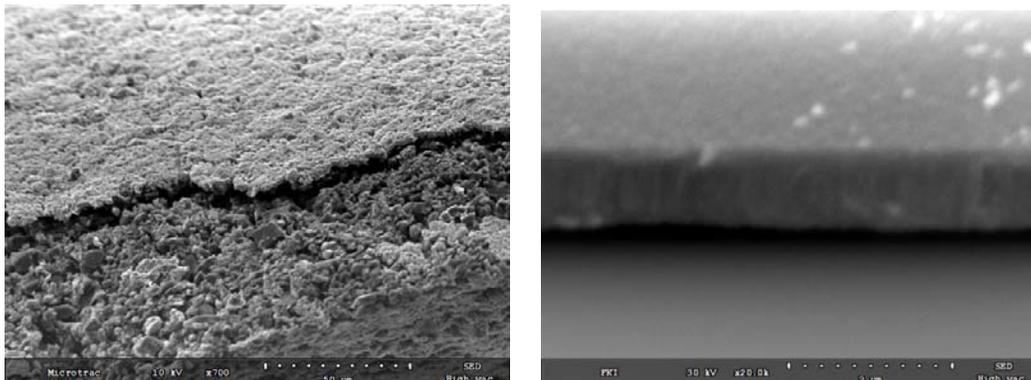


Fig. 6. a) 2 μm thick Al layer magnetron sputtered on porous carbon electrode. b) 1 μm thick sputtered GDC layer (deposition rate 0.04 $\mu\text{m h}^{-1}$).

In *reactive* direct current magnetron sputtering the metal target atoms react with intentionally introduced reactive gas, for example oxygen, and the oxide layer is deposited. Various oxide and halide compositions and structures can be grown by varying the target, introduced gases (N_2 , O_2 , Cl_2) and sputter conditions. Reactive sputtering of Ti in the presence of oxygen is faster and cheaper than direct sputtering from TiO_2 target with an RF source.

For example, TiO_2 can be prepared from Ti as:

$Ti \rightarrow TiO_2$ (a constant dc current of 550 mA and a power of 240 W were applied).

Sputtering system was evacuated to $p < 10^{-7}$ mbar. Ar gas (99.999%) was introduced into the sputtering chamber. To remove surface contaminations on the target pre-sputtering was done for ~10 min in pure argon. Then oxygen gas (99.98%) was introduced into the chamber with the O_2/Ar ratio at 0.07, while the working pressure was 0.007 Torr. Substrates were positioned ~13 cm from the target, rotated during deposition and kept at $T = 330$ °C. The deposition rate for TiO_2 was $0.25 \mu m h^{-1}$.

EXAMPLES: TiN films - a large industry has been developed around tool bit coating using sputtered nitrides, such as titanium nitride, creating the familiar gold colored hard coat.

Al_2O_3 dielectric layers – in capacitors and electronics. However, in new processor's transistors HfO_2 is used instead.

Chemical vapor deposition (CVD)

In CVD process the reactant vapors (e.g. metal chlorides, oxides, organometallic compounds, etc.) are transported to the substrate surface where they adsorb and a chemical reaction at the surface takes place (crystal growth of metal layers, metal oxide, metal carbide or metal halide layers, etc.). Deposition rates are typically $1\text{-}10 \mu\text{m h}^{-1}$. For example, polycrystalline silicon is deposited from silane, using the following reaction: $\text{SiH}_4 \rightarrow \text{Si} + 2\text{H}_2$. Temperatures between 600 and $650 \text{ }^\circ\text{C}$ yield silicon growth rate about $1 \mu\text{m h}^{-1}$. Polysilicon may be grown directly with doping, if gases such as phosphine, arsine or diborane are added to the CVD chamber.

The CVD process is also used to produce synthetic diamonds. The substrate preparation includes choosing an appropriate material and its crystallographic orientation; cleaning it, often with a diamond powder to abrade a non-diamond substrate; and optimizing the substrate temperature (about $800 \text{ }^\circ\text{C}$) during the growth. The gases always include a carbon source, typically methane, and hydrogen with a typical ratio of 1:99. Hydrogen is essential because it selectively etches off non-diamond carbon. The gases are ionized into chemically active radicals in the growth chamber using microwave power, a hot filament, or other means.

Atomic layer deposition (ALD) is a more precise variation of CVD. The ALD reaction breaks the CVD reaction into two half-reactions, keeping the precursor materials separate during the reaction. Due to the characteristics of self-limiting and surface reactions, ALD film growth makes atomic scale deposition control possible.

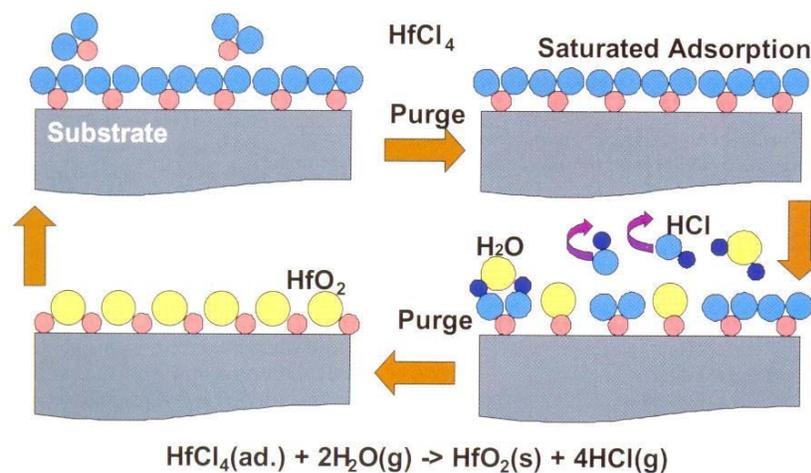


Fig. 1. Schematic of ALD process where alternating HfCl_4 and H_2O exposure is used to deposit HfO_2 on silicon.