Introduction to Plasma Discharges for Material Processing

Andrea Macchi

www.df.unipi.it/∼macchi

polyLAB, INFM-CNR, University of Pisa, Italy

References

[1] J. Reece Roth, *Industrial Plasma Engineering*, Voll.1–2 (Institute of Physics Publishing, 2004)

[2] M. A. Lieberman and A. J. Lichtenberg, *Principles of Plasma Discharges and Materials Processing*, Second Edition (John Wiley and Sons, 2005)

[3] K. Ostrikov, “*Colloquium: Reactive plasmas as a versatile nanofabrication tool*”, Rev. Mod. Phys **77**, 489 (2005)

[4] C.-M. Chan, T.-M- Ko, H. Hiraoka, “*Polymer surface modification by plasmas and photons*”, Surf. Science Rep. **24**, 1 (1996)

[5] A. Macchi, *Appunti su scariche di plasma per applicazioni tecnologiche*, and references therein (2005–, in progress!)

Example 0: nature

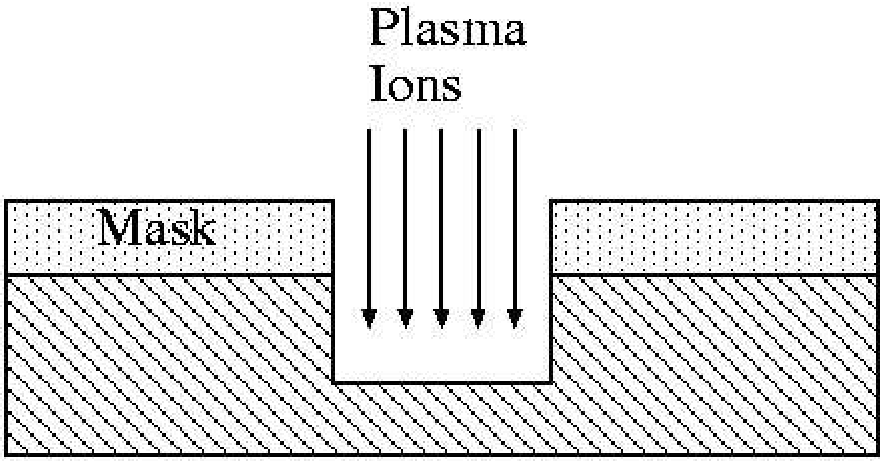
Principle of plasma chemistry: discharge creates chemically reactive species (either ions or neutrals)

Ligthning creates ozone, fixed nitrogen and light [a]

---

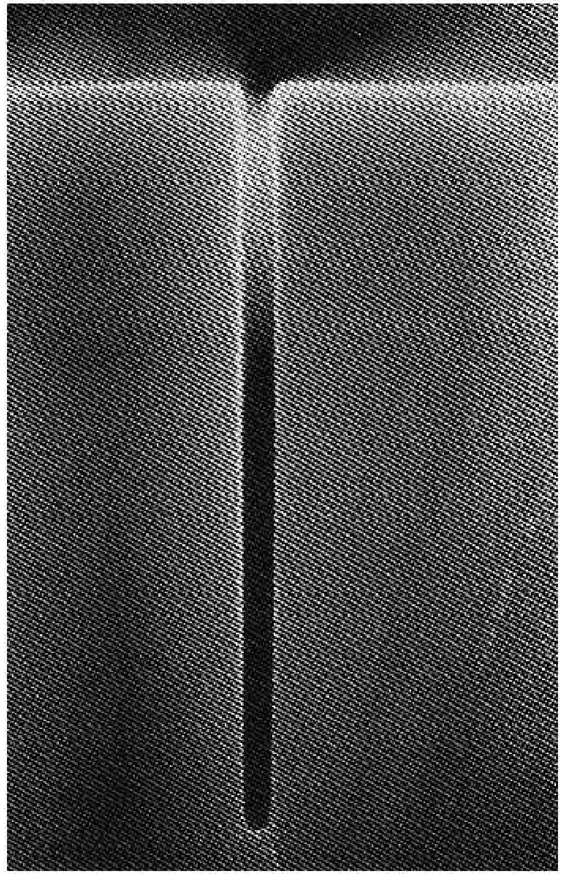
[a] see e.g. M. A. Uman, *The lightning discharge* (Dover, 2001)

Example 1: *etching* on Silicon



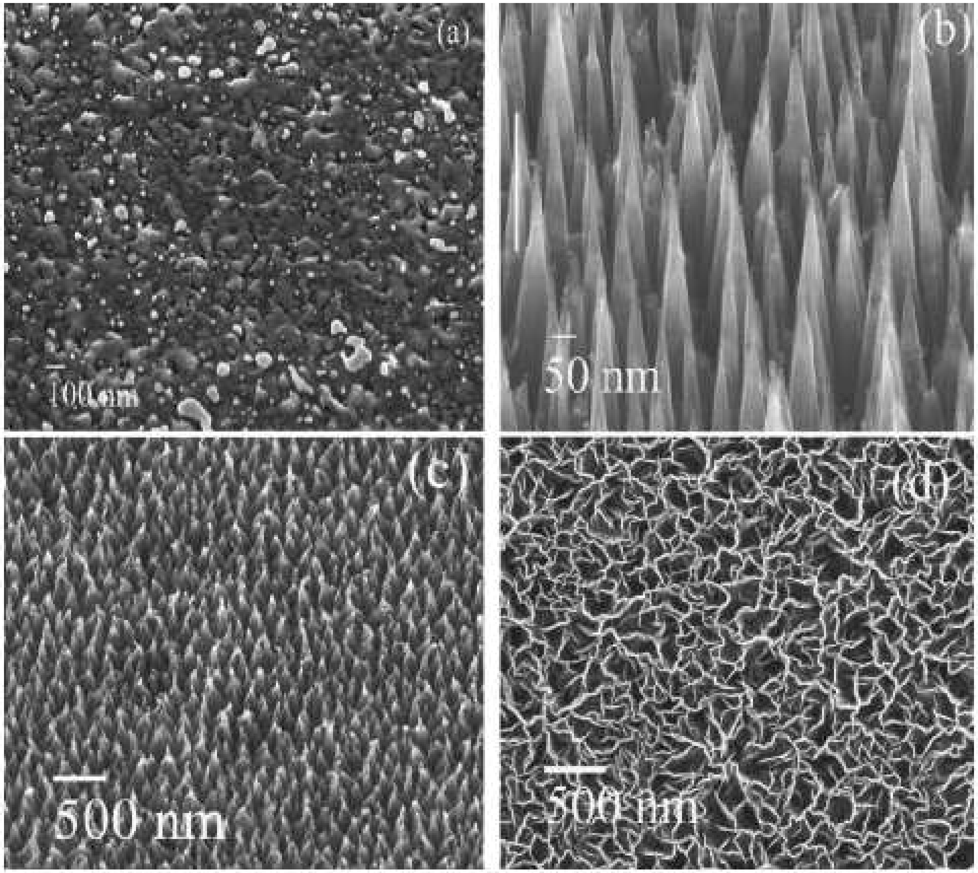
Scheme of directional plasma etching on the surface of Si, for the production of microchips

(see [1], p.2)



Result example in monochrystalline Si (dimensions: $0.2 \times 4\ \mu$m)

Example 2: Carbon nanostructures



Scanning electron micrograph [3] of
a) Silicon surface *before* hydrocarbon plasma processing
b) nanotips c) nanopyramids d) nanowalls

A list of possible applications

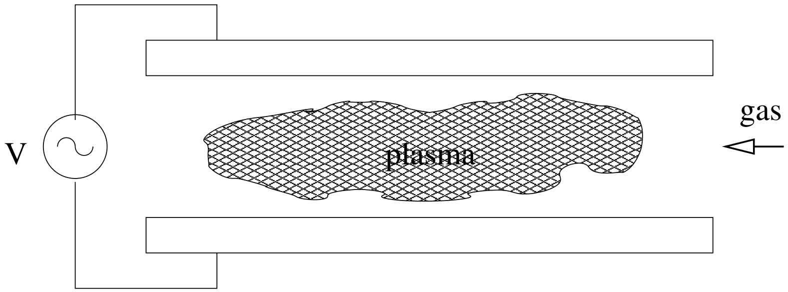
- Microelectronics etching, deposition, oxidation, implantation, passivation
- Liquid crystal display and solar cell depositions
- Aerospace and automotive ceramic and metal coatings, films, paints
- Metallurgical melting, refining, welding, cutting, hardening
- Ceramics synthesis, ultrapure powders, nanopowders
- Food packaging permeability barriers
- Textile adhesion treatments
- Medical materials bio-compatibility treatments, sterilization, cleaning
- Architectural and automotive glass coatings

- …

Why plasmas?

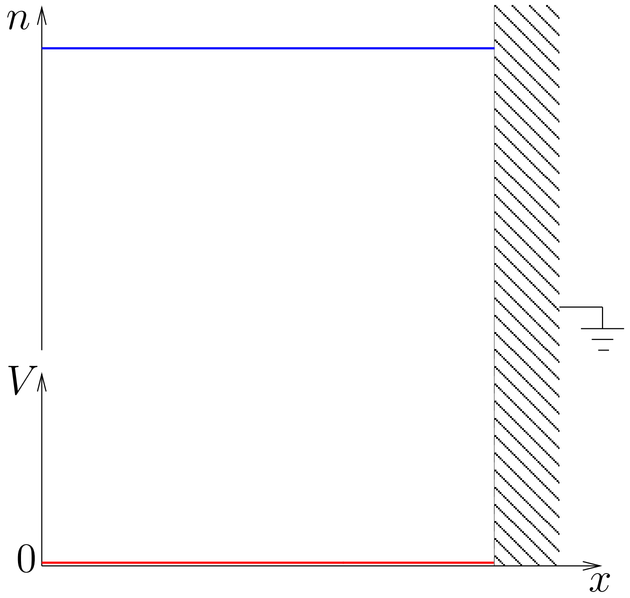
- In a discharge, energetic particles (electrons or ions) drive *chemical reactions with high activation energy* which may be problematic to obtain in other ways
- An important issue is often the *absence of thermal equilibrium*: active species particles may have high energy but the overall energy density is low (example: avoid heating surfaces to high temperatures)
- plasma chemistry is activated and controlled by electric fields; plasma processes are much more clean than wet (chemical) ones!

Characterization of discharge plasmas

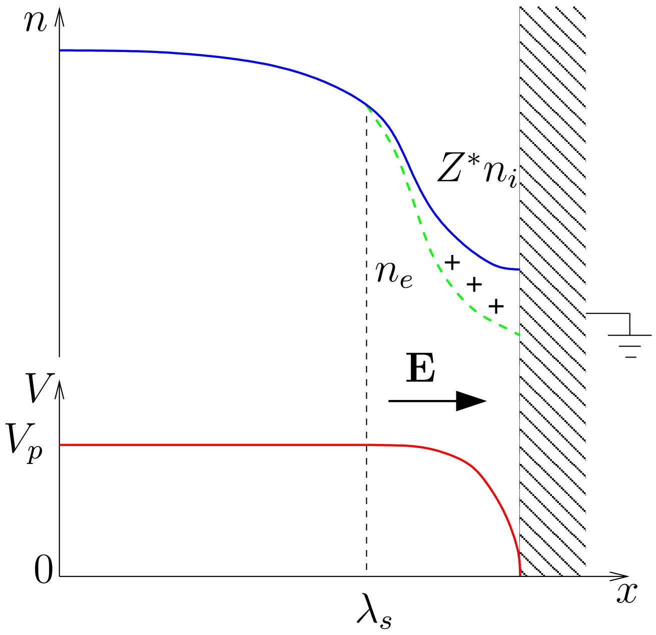


- Background gas pressure $P \approx 10^{-4} \div 1$ atm
- Free electron density $n_e \approx 10^8 \div 10^{14}$ cm^{-3} $(Z^* \ll 1)$
- Electron Temperature $T_e \approx 1 \div 10$ eV
- Device size $L \approx 10 \div 10^2$ cm
- AC frequency: $\omega \approx 10$ Mhz $\div\, 10$ Ghz (rf to μWs)
- Surface interaction with walls (electrodes, processing material)

Elementary discharge model



A neutral plasma with $n_e = Z^* n_i$ is created between grounded walls at $t = 0$



Electrons drift to the walls, creating a negative *sheath* where ions are accelerated

Ions bombard the walls with energy $\mathcal{E}_i = V_p$ (plasma potential)

Sheath modeling

- Sheath modeling (even in DC and thermal equilibrium conditions) is an old, classical, and still discussed problem of plasma physics [a]
- For plasma *etching* and *nanofabrication*, the desired regime is that of *non-collisional*, *high voltage* ($eV_s \gg T_e$), DC sheaths, to have well-oriented ion fluxes on the surface
- Depending on the application, modeling of AC sheaths, collisional sheaths, . . . , is desirable

---

[a] [see e.g. Riemann et al, Plasma Phys. Control. Fusion **47**, 1949 (2005)]

Child-Bohm's sheath modeling

Assumptions: $eV_s \gg T_e$, $n_e \ll n_i$

λ_s: sheath thickness $V(x)$: electric potential
J_0: ion current V_0: bias potential of the wall

$$\lambda_s = \left(\frac{4\sqrt{2}\epsilon_0}{9en} \right)^{1/2} T_e^{-1/4} V_0^{3/4} \qquad V(x) = -V_0 \left(\frac{x}{\lambda_s} \right)^{4/3}$$

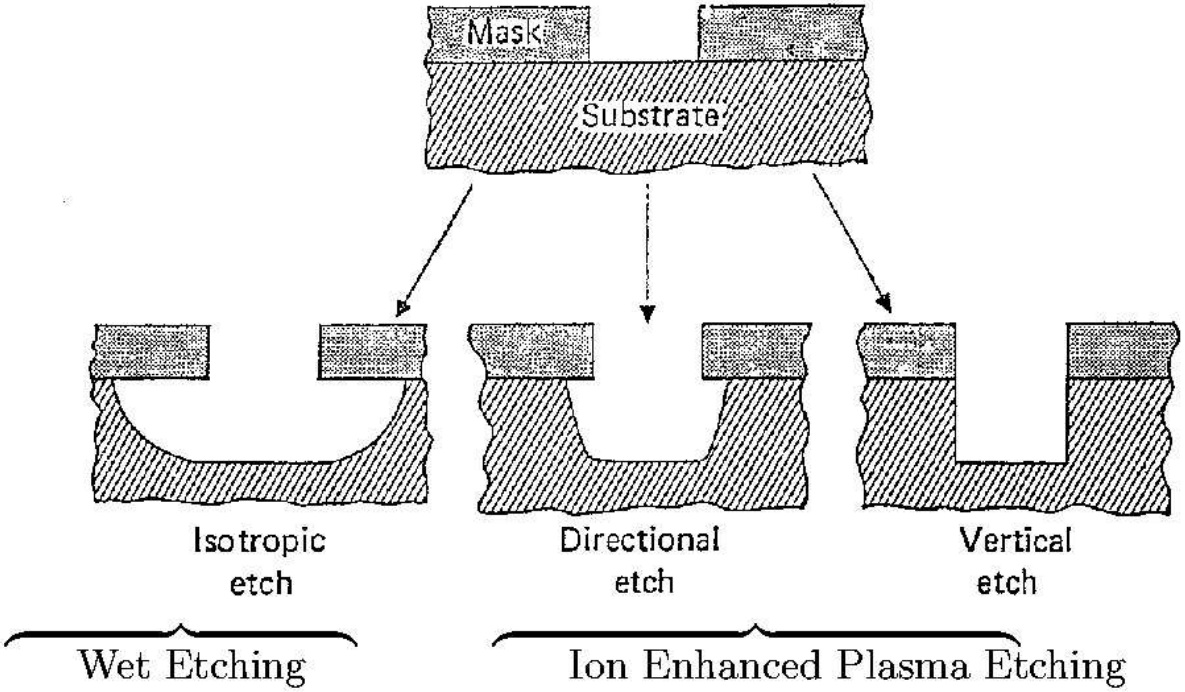
$$J_0 = Zen_0 v_b = Zen_0 \sqrt{\frac{ZT_e}{M_i}}$$

See e.g. [1], vol.I, par.9.4.5

Plasma anisotropy is the key to etching

Discharge creates ions → sheath accelerates ions → ions catalyze surface reaction creating volatile specie

Example: $2\mathrm{XeF}_2 + \mathrm{Si} \overset{Ar^+}{\longrightarrow} 2\mathrm{Xe} + \mathrm{SiF}_4 \uparrow$



Plasma treatment of surfaces

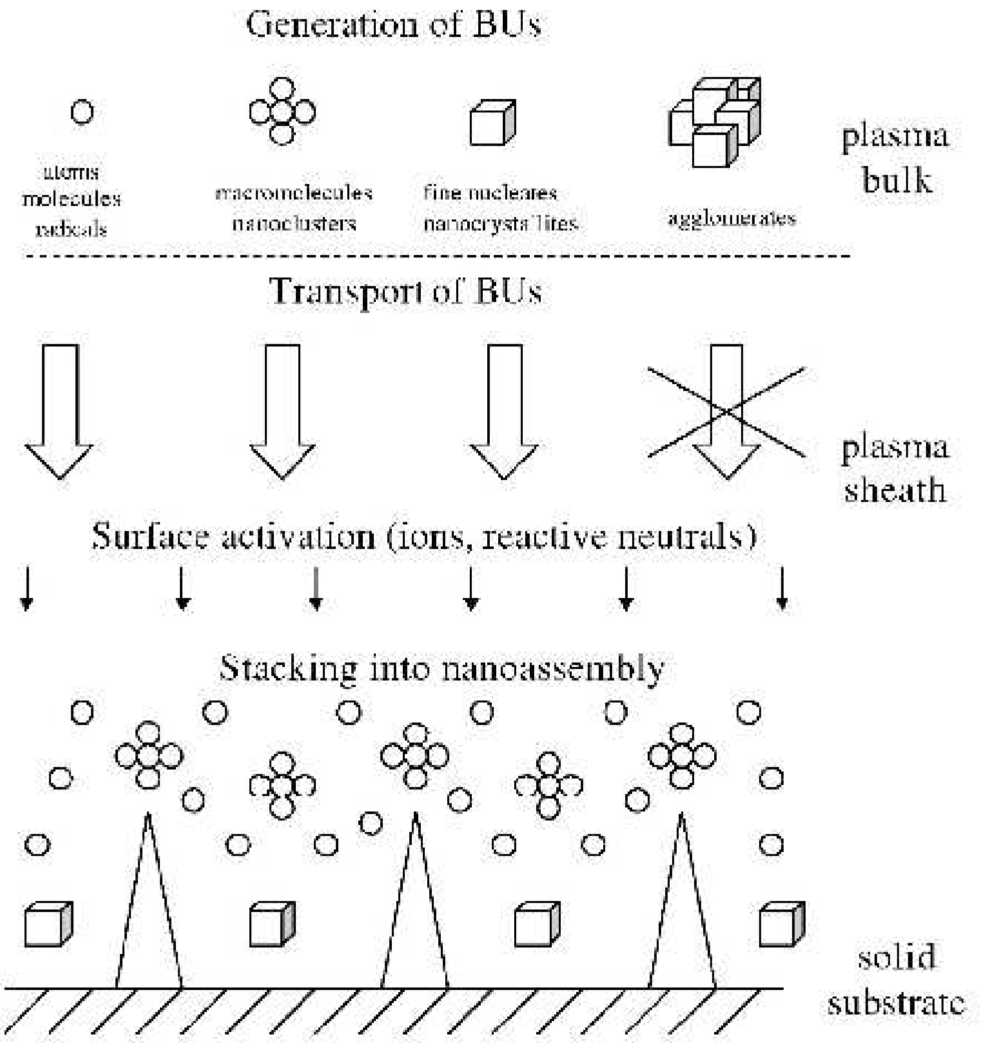
The surface energy may be modified by plasma processing in various ways (depending on exposure time and other parameters)

- plasma *cleaning* (attive/passive): removal of surface contaminants
- attachment of polar groups (C=O, OH, COOH) yielding hydrogen bonding
- rotation of bulk polar group by the electric fields at the surface
- surface etching

Plasma deposition

- Plasma Chemical Vapor Deposition (PCVD) is used to produce *thin film* with special properties.
- In a discharge, the feedstock gas id dissociated into molecular fragments and eventually monomers which recombine of the surface of the substrate (*plasma polymerization*).
- The physical details are now well understood, but several “recipes” (chemical composition, plasma parameters, reactor geometry . . .) for thin film fabrication have been found.

Plasma-based nanofabrication



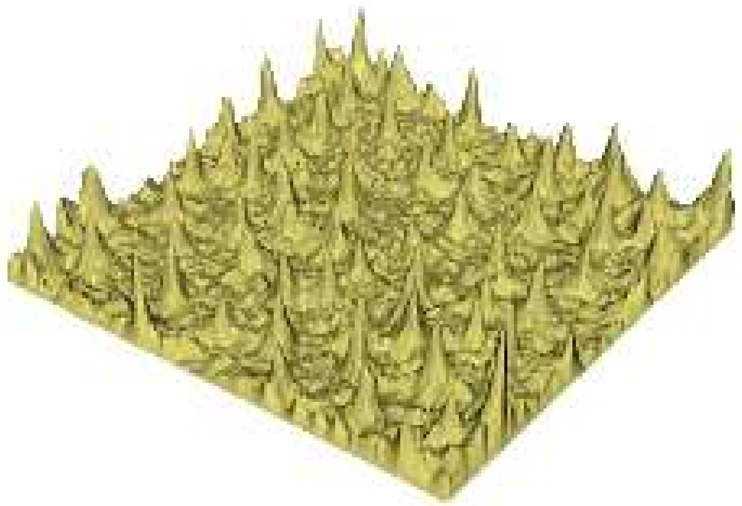
Building Units (BUs) are
- generated in plasma discharge bulk
- accelerated (when charged) in plasma sheath
- transported to the surface
- sometimes able to drive surface activation (no external heating necessary)

The role of sheath fields

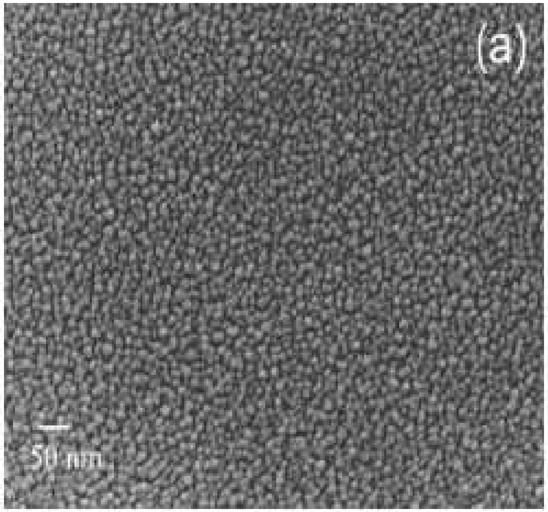
The electric field $\mathbf{E}$ in a collisionless, high-voltage sheath controls

- the flux of ions to the surface
- the landing energy (just that required for activation)
- the orientation (normal to the surface)

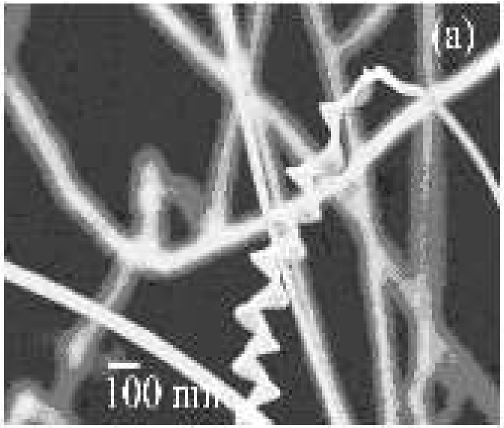
“Lucky” effect: lines of $\mathbf{E}$ converge towards sharp ends
$\rightarrow$ nano-focusing of BUs
to desired sites
(example: current distribution from simulations of
carbon nanotips fabrication) [3]

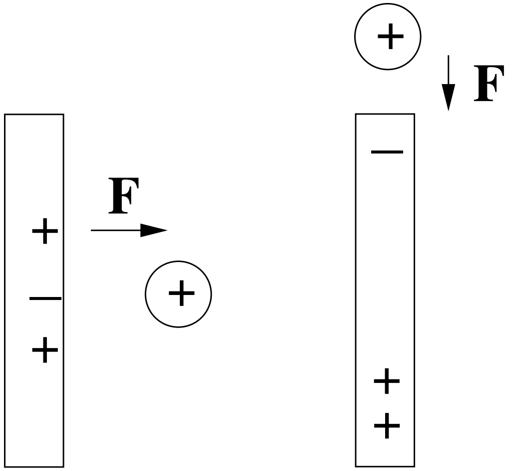


Other nanofabrication examples



Quantum dots produced by plasma RF sputtering [3]





Silicon nanowires grown by charged nanocluster BUs in a plasma: electrical induction favors one-dimensional growth [3]

Atmospheric plasma discharges

Plasma processing at 1 atm is desirable for industrial applications because

- vacuum operation not needed: reduce costs
- continuous (instead of batch) processing possible: increase productivity
- higher flux of particles possible: reduce processing time

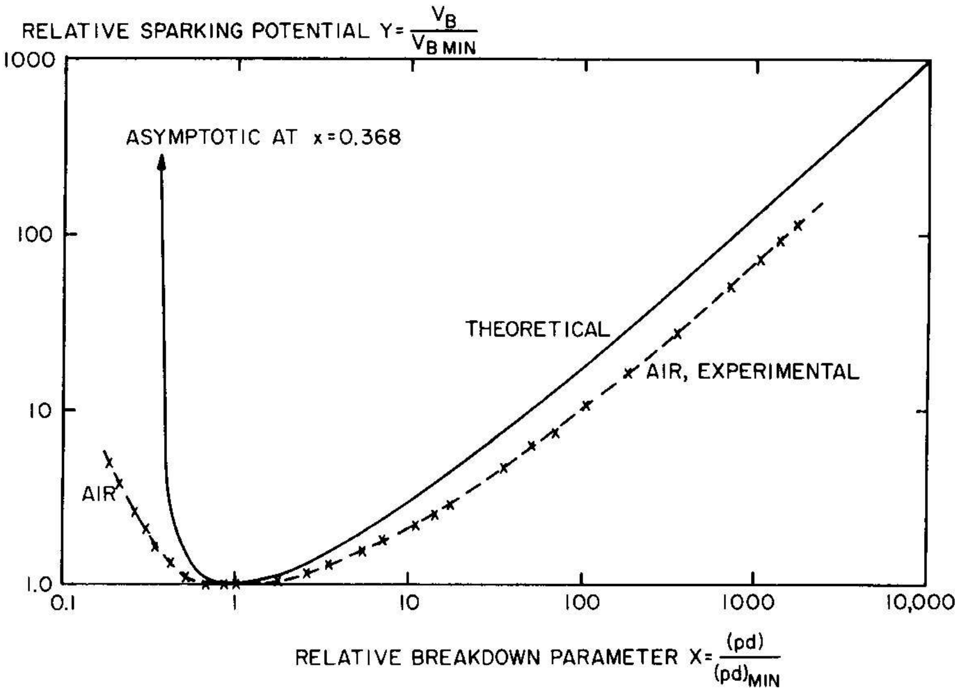
Drawbacks:

- plasma control is more complex
- higher breakdown voltage is required

Paschen law of breakdown

$$V_b = \frac{Cpd}{\ln[Apd/\ln(1+1/\gamma)]} = f(pd)$$

V_b: voltage, p: pressure, d: electrode spacing,
γ: *secondary emission coefficent from cathode*



Optimal condition for ionizing collisions

$$eE\ell_c = I_z\,; \qquad E = V_b/d\,,$$

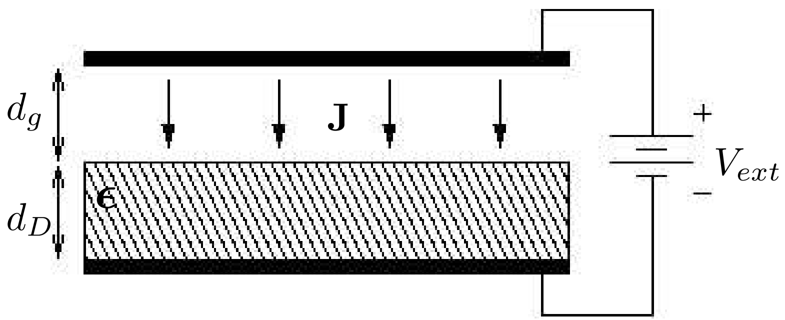
$$\ell_c \propto n^{-1} \propto p^{-1}$$

Secondary emission provides positive feedback

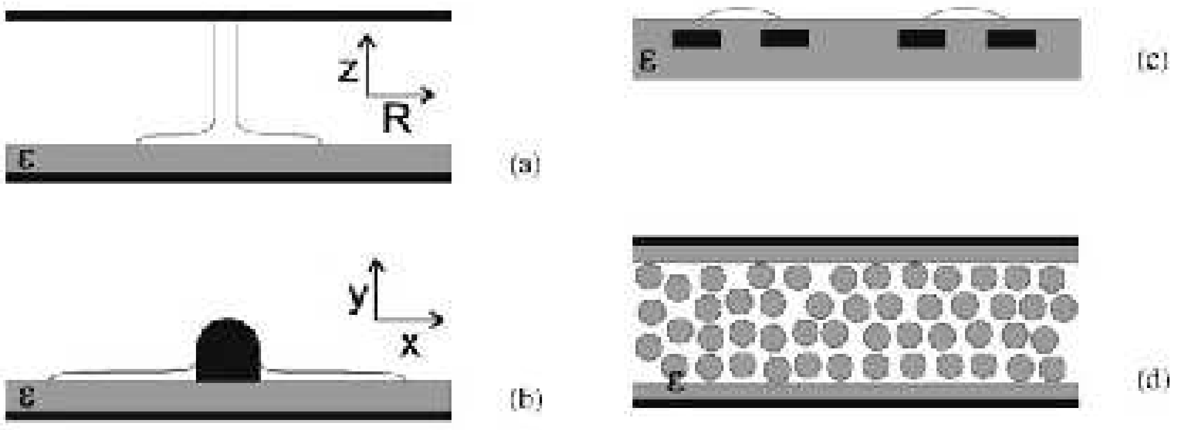
Dielectric barrier discharge (DBD)

A dielectric layer (*barrier*) is posed over (both) electrode(s) to:

- provide a non-dissipative current limiter (ballast)
- distribute charges over the surface



Several DBD schemes exist:



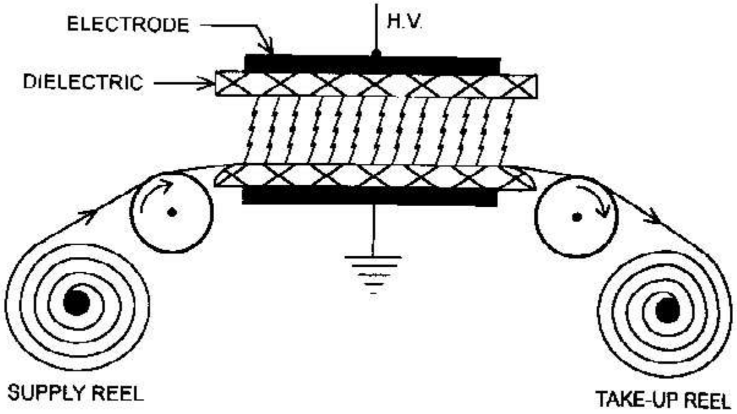
a) simple planar cell

b-c) coplanar electrodes cell

d) “packed bed” reactor

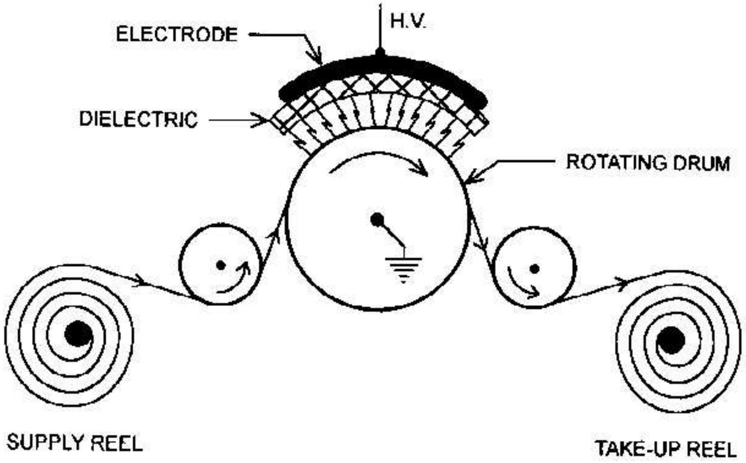
DBD reactors for bulk processing

Parallel plate reactor
for non-adherent webs
processing



a) PLANAR EXPOSURE CONFIGURATION

Cylindrical annulus reactor
with rotating cylinder
for adherent web processing



b) ROTATING CYLINDER DBD CONFIGURATION

DBD phenomenology

The discharge is filamentary and short-lived:

- microdischarge initiated by avalanche ionization
- electrons on avalanche head reach the barrier depositing surface charge
- electric field is quenched; discharge stops

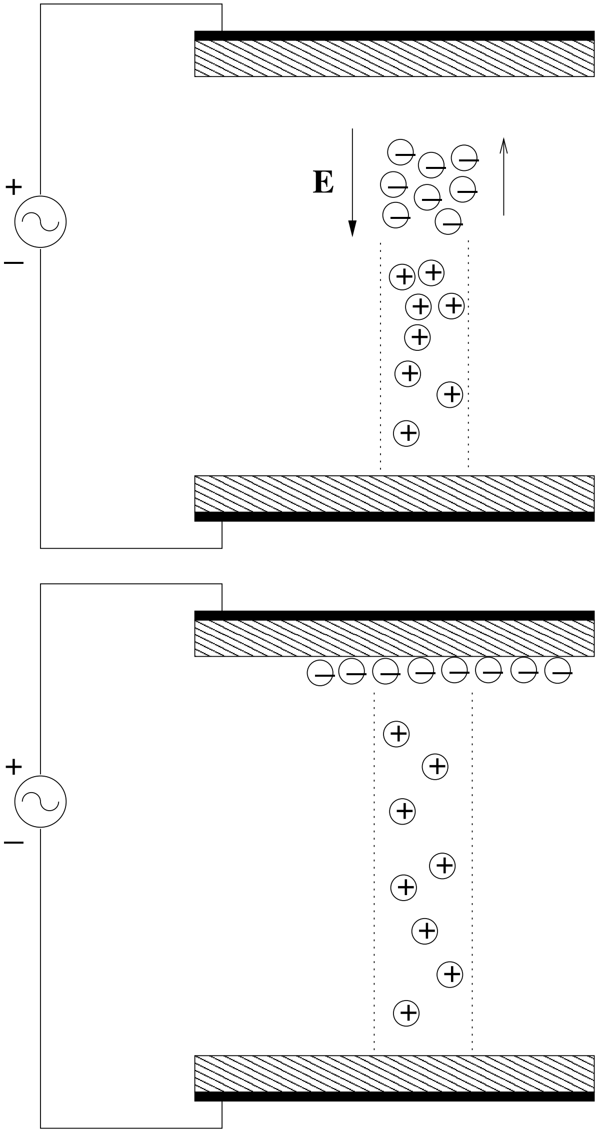
Typical microdischarge parameters @ $p = 1$ atm:

$\tau \approx 10 \div 100$ ns $\qquad n_e \approx 10^{14} \div 10^{15}$ cm^{-3}

$T_e \approx 1 \div 10$ eV $\qquad r_s \approx 100\ \mu$m

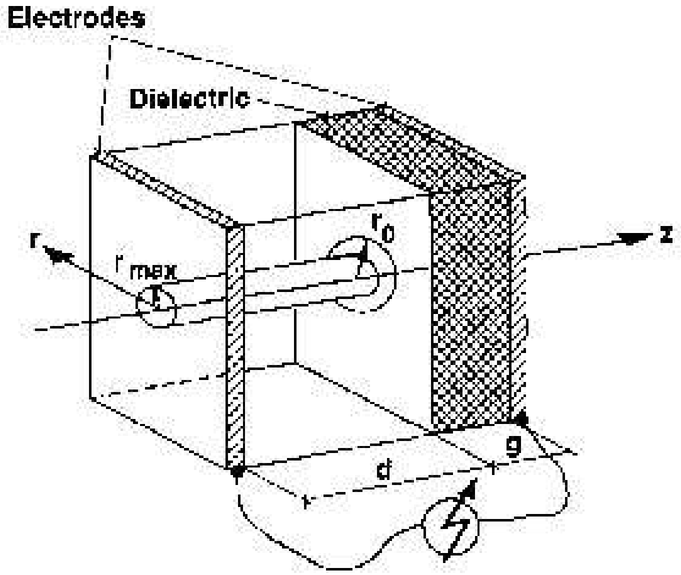
$Q \approx 1$ pC $\qquad U \approx 1\ \mu$J

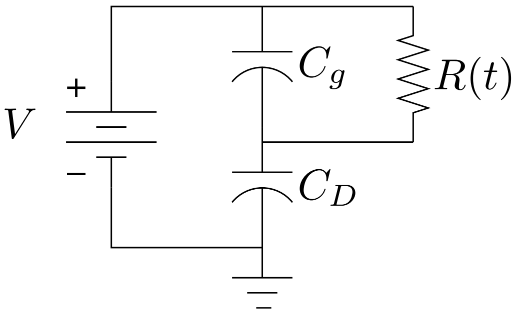
$E \approx 10^4$ V cm^{-1}



Simple model of DBD

Consider single filament and an equivalent circuit:





$$S_c = \pi r_s^2 \quad , \quad S_d = \pi r_0^2 \qquad C_d = \epsilon S_d/d_d \quad , \quad C_g = \epsilon S_d/d_g$$

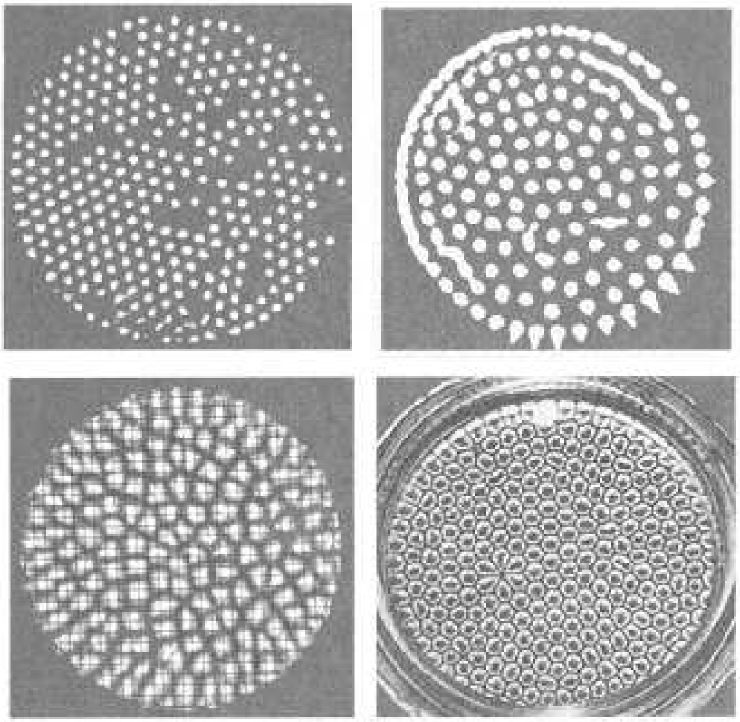
Deposited charge Q and absorbed energy U_{ass} do *not* depend on $R(t) = \rho(t) d_g/S_c$:

$$Q \simeq \epsilon E_b (d_g/d_d) S_{dep} \, , \qquad U_{ass} = \frac{1}{2} \frac{C_d^2}{C_g + C_d} V_{min}^2 \, , \qquad V_{min} \simeq E_b d_g$$

Duration $\tau \simeq \bar{\rho} \epsilon (d_g/d_d)(S_d/S_c) \simeq E_b (\epsilon/e n_e v_d)(S_d/S_c)$

Collective effects in DBD

- Space-charge fields drive ionization waves: *streamers*
- Competition of microdischarges for available dielectric surface yields spatial (anti)correlation
- Interaction between microdischarges leads to 2D pattern formation: similarity with Bènard convection cells



Atmospheric diffuse ("glow") discharges

- Issue: transition from filamentary to uniform discharge
- Simple criterion: avalanche electron "heads" must overlap before streamer phase

Spherical head model:

$r_h \approx \sqrt{z_a \ell_d}$ (diffusion), $N_a \approx e^{\alpha z_a}$,

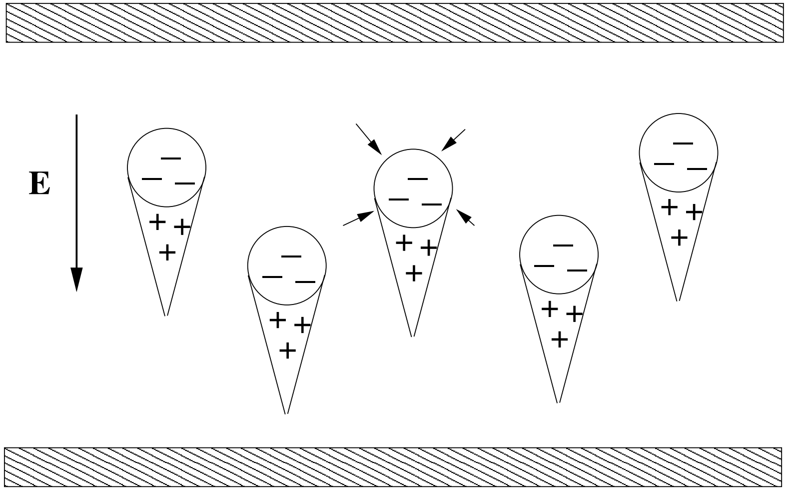
$E_a \approx \frac{1}{4\pi\epsilon_0} \frac{N_a e}{r_h^2} \doteq E_b$ for streamers

$\rightarrow$ yields "critical distance" z_{cr}

Heads must overlap:

$n_{e0} > r_{cr}^{-3} = (\ell_d z_{cr})^{-3/2}$

n_{e0}: "preionization" density



An example: OAUGDP™

The “One Atmosphere Uniform Glow Discharge Plasma” scheme has been patented and registered by Roth [1].

Concept: there is a frequency range (RF) in which ions are *trapped* between electrodes (planar, symmetric, capacitive DBD configuration) and electrons are not.

$$\bar{x}_{osc,i} \leq d/2 \quad \bar{x}_{osc,e} \geq d/2$$

$$\frac{2e\bar{V}}{m_i \nu_{ci} d^2} \leq \omega \leq \frac{2e\bar{V}}{m_e \nu_{ce} d^2}$$

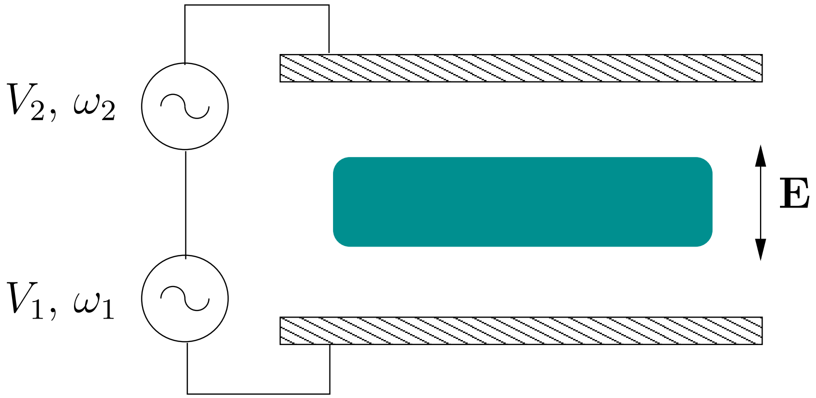
Outside the frequency range: filamentation instabilities

Underlying physics (and chemistry?) needs to be studied

Applications: etching, surface treatment, sterilization, . . .

Dual frequency discharges

Purpose: enhanced control of ion flux for etching (Lieberman)



Plasma density and ion energy are controlled indipendently

$$n_e \propto P_{abs} \propto \omega^2 V\ , \qquad \mathcal{E}_i \propto V = V_h + V_l$$

$\omega_h^2 V_h \gg \omega_l^2 V_l \rightarrow \boxed{V_h \text{ controls } n_e}$ $\qquad V_l \gg V_h \rightarrow \boxed{V_l \text{ controls } \mathcal{E}_i}$

Detailed scheme involves the physics of *double AC sheath* structure, *stochastic* and *anomalous skin effect* heating, electromagnetic *surface wave* coupling of RF power to the plasma, . . .

Conclusions

- Plasma discharges work very well :-) . . .

  although we do not fully understand why :-(
- Recipes for specific applications can be found
- Current research has lot of issues: empirical application and optimization, enhanced control of plasma parameters, numerical modeling, understanding of basic physics

  Let's start the discussion!