Plasma Applications

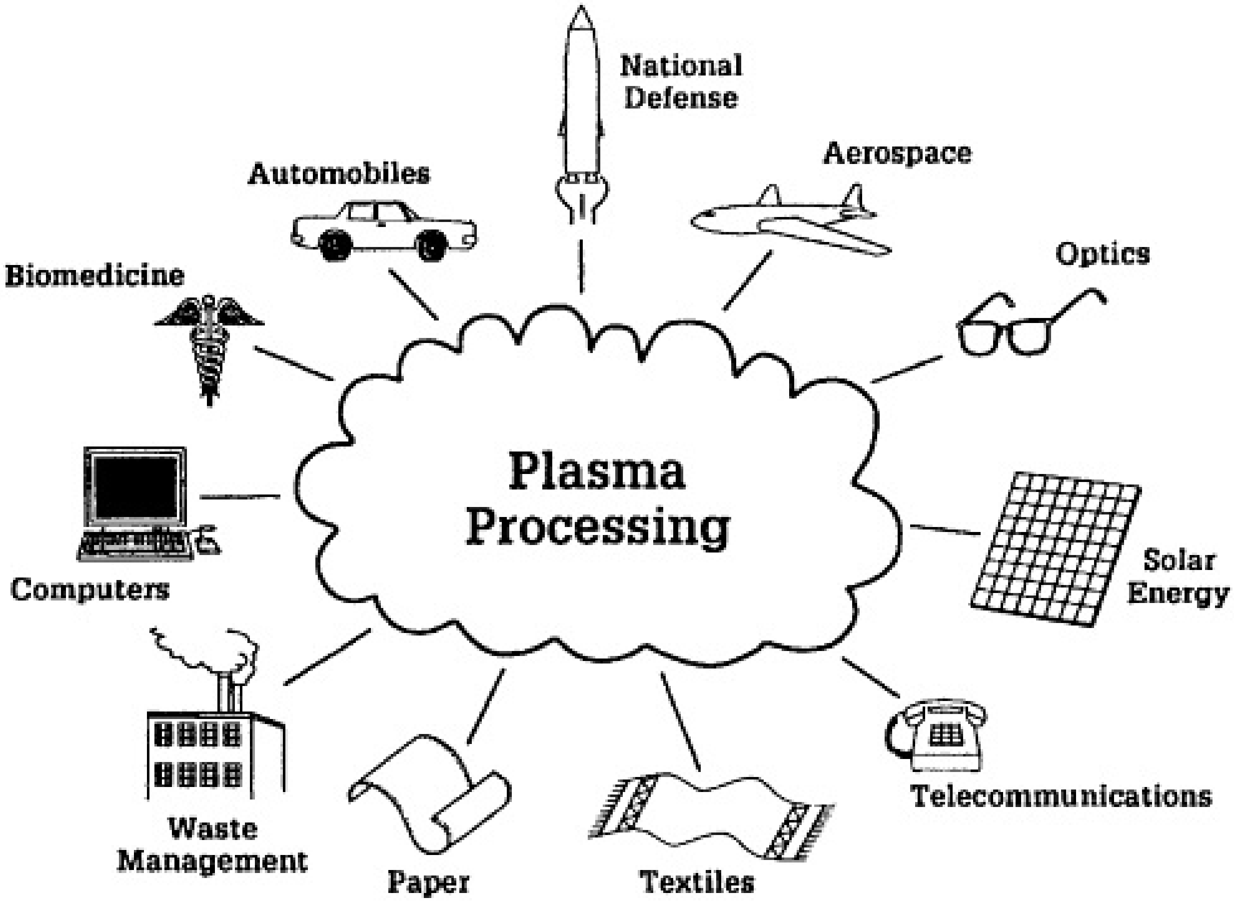
Fall, 2022

Kyoung-Jae Chung

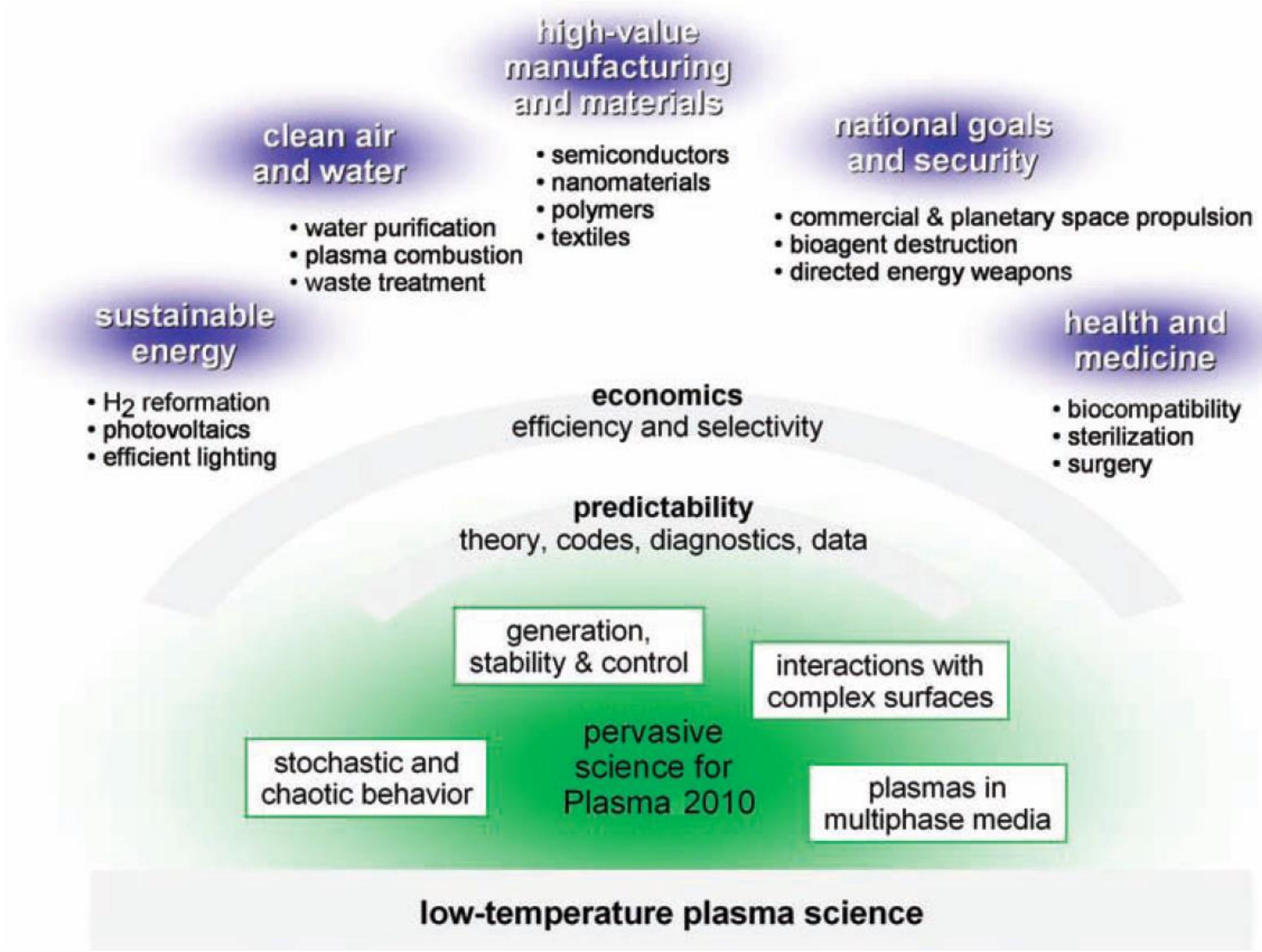
Department of Nuclear Engineering

Seoul National University

Various applications of plasma technology



Low-temperature plasma



high-value manufacturing and materials
- semiconductors
- nanomaterials
- polymers
- textiles

clean air and water
- water purification
- plasma combustion
- waste treatment

national goals and security
- commercial & planetary space propulsion
- bioagent destruction
- directed energy weapons

sustainable energy
- H_2 reformation
- photovoltaics
- efficient lighting

health and medicine
- biocompatibility
- sterilization
- surgery

economics
efficiency and selectivity

predictability
theory, codes, diagnostics, data

generation, stability & control

interactions with complex surfaces

stochastic and chaotic behavior

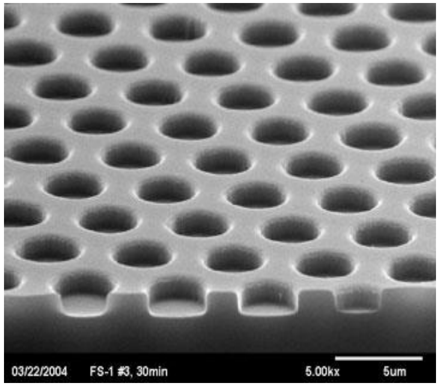
pervasive science for Plasma 2010

plasmas in multiphase media

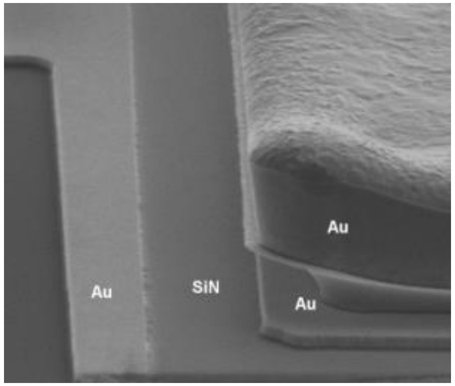
low-temperature plasma science

Plasma Science: Advancing Knowledge in the National Interest (2007)

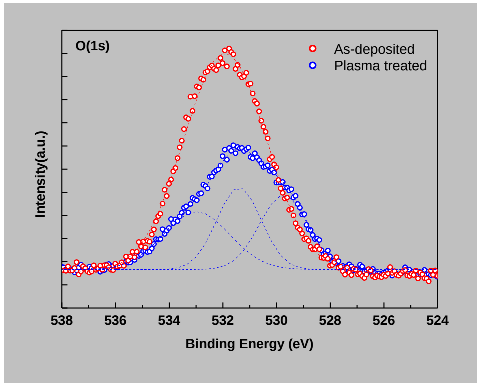
Plasma processing technology in industry



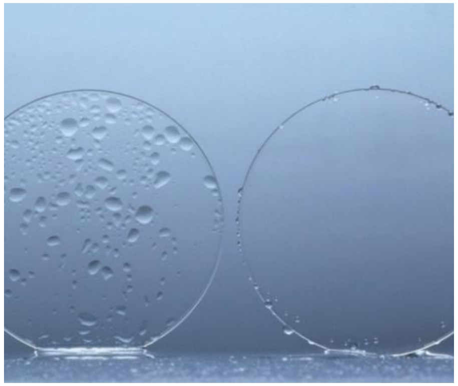
깎기 (etching)



붙이기 (deposition)



바꾸기 (modification)

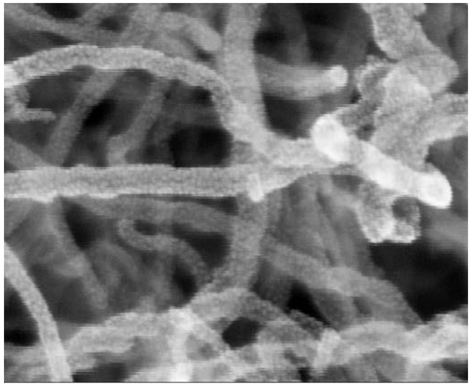


닦기 (cleaning)

빛내기 (lightening)

녹이기 (melting)

분해하기 (decomposition)



만들기 (synthesis)

Plasma processing technology is vitally important to several of the largest manufacturing industries in the world

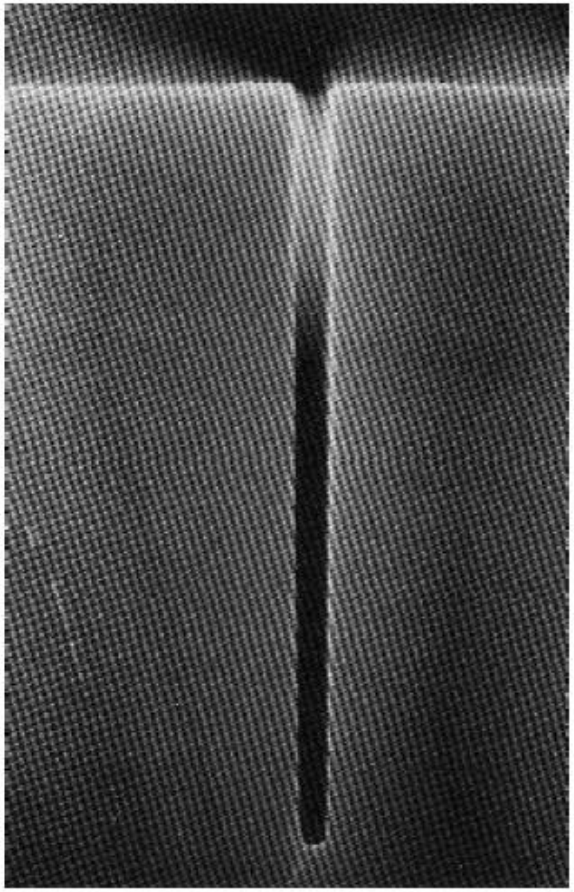
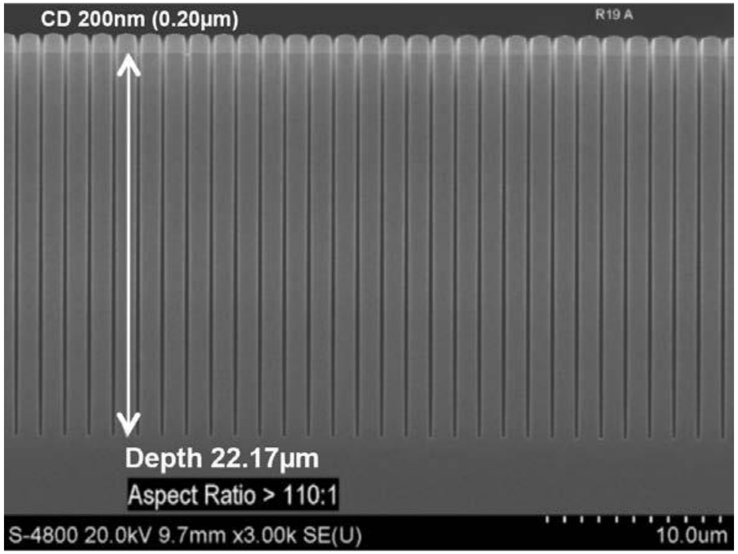


FIGURE 1.1. Trench etch (0.2 μm wide by 4 μm deep) in single-crystal silicon, showing the extraordinary capabilities of plasma processing; such trenches are used for device isolation and charge storage capacitors in integrated circuits.

All-in-One Etch
(Oxide / DRIE / PR Clean)



Plasma processing in integrated circuit fabrication

- Argon or oxygen discharges are used to sputter-deposit aluminum, tungsten, or high-temperature superconducting films.
- Oxygen discharges can be used to grow SiO_2 films on silicon.
- SiH_2Cl_2/NH_3 and $Si(OC_2H_5)_4/O_2$ discharges are used for the plasma-enhanced chemical vapor deposition (PECVD) of Si_3N_4 and SiO_2 films, respectively.
- BF_3 discharges can be used to implant dopant (B) atoms into silicon.
- $CF_4/Cl_2/O_2$ discharges are used to selectively remove silicon films.
- Oxygen discharges are used to remove photoresist or polymer films.

- These types of steps (deposit or grow, dope or modify, etch or remove) are repeated again and again in the manufacture of a modern IC.
- For microfabrication of an IC, one-third of the tens to hundreds of fabrication steps are typically plasma based.

Typical IC fabrication process

a. Film deposition
b. Photoresist deposition
c. Optical exposure
d. Photo development
e. Etching
f. PR removal

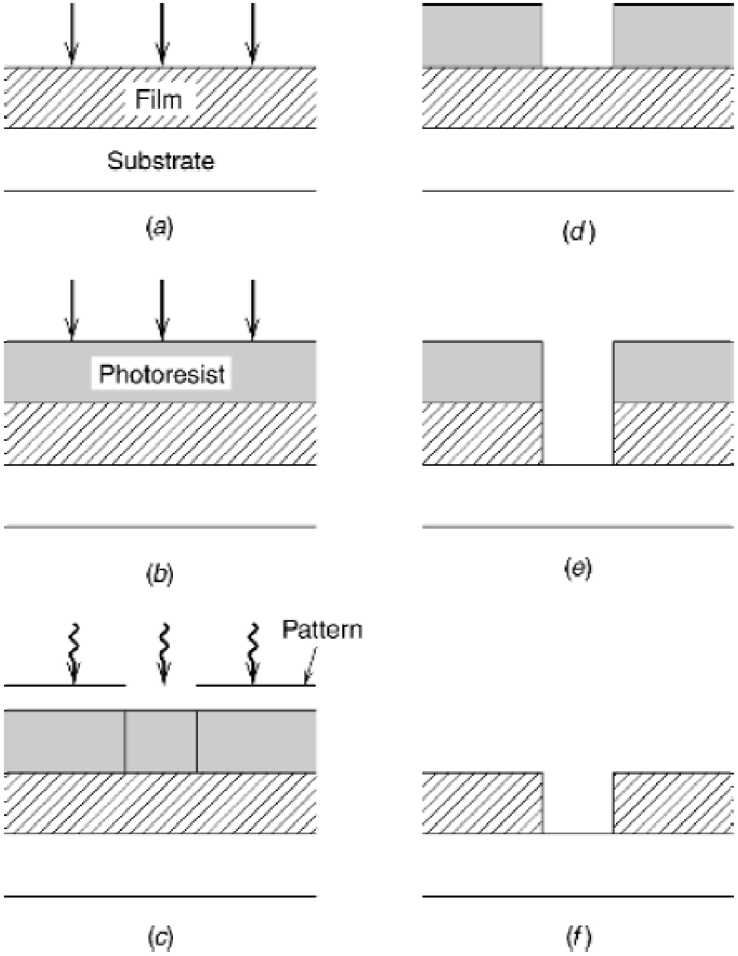


FIGURE 1.2. Deposition and pattern transfer in manufacturing an integrated circuit: (*a*) metal deposition; (*b*) photoresist deposition; (*c*) optical exposure through a pattern; (*d*) photoresist development; (*e*) anisotropic plasma etch; (*f*) remaining photoresist removal.

Silicon etching using a plasma discharge

- Start with an inert molecular gas, such as CF_4.
- Excite the discharge to sustain a plasma by electron–neutral dissociative ionization,

$$e + CF_4 \rightarrow 2e + CF_3^+ + F$$

and to create reactive species by electron–neutral dissociation,

$$\begin{aligned} e + CF_4 &\rightarrow e + CF_3 + F \\ &\rightarrow e + CF_2 + 2F \end{aligned}$$

- The etchant F atoms react with the silicon substrate, yielding the volatile etch product SiF_4:

$$Si(s) + 4F(g) \rightarrow SiF_4(g)$$

- Finally, the product is pumped away.
- It is important that CF_4 does not react with silicon, and that the etch product SiF_4 is volatile, so that it can be removed.

Plasma etching in integrated circuit manufacture

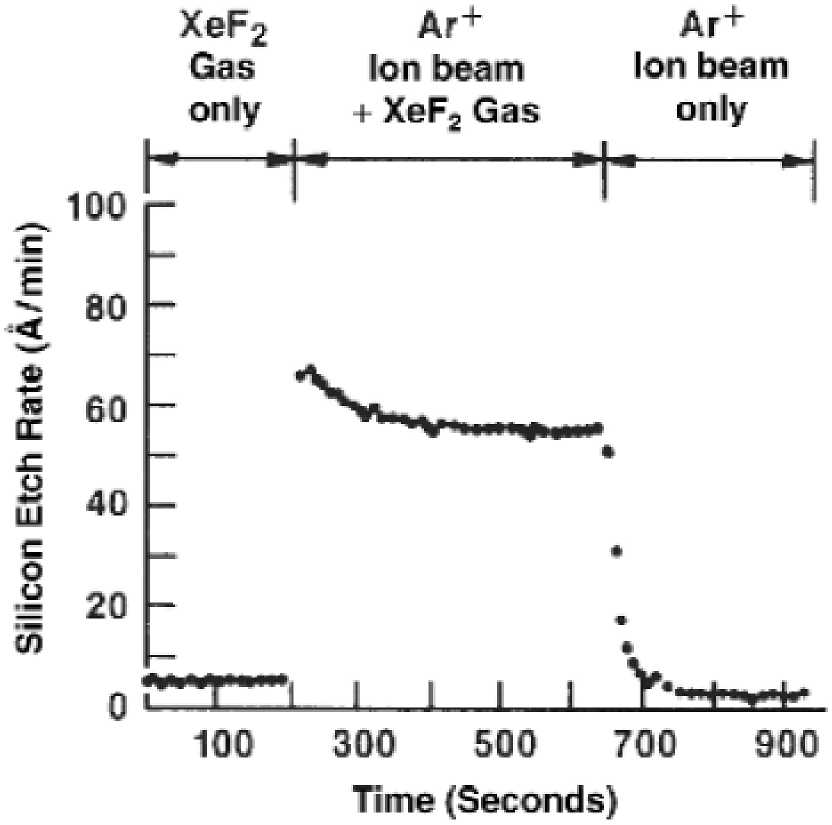


FIGURE 1.4. Experimental demonstration of ion-enhanced plasma etching. (Coburn and Winters, 1979.)

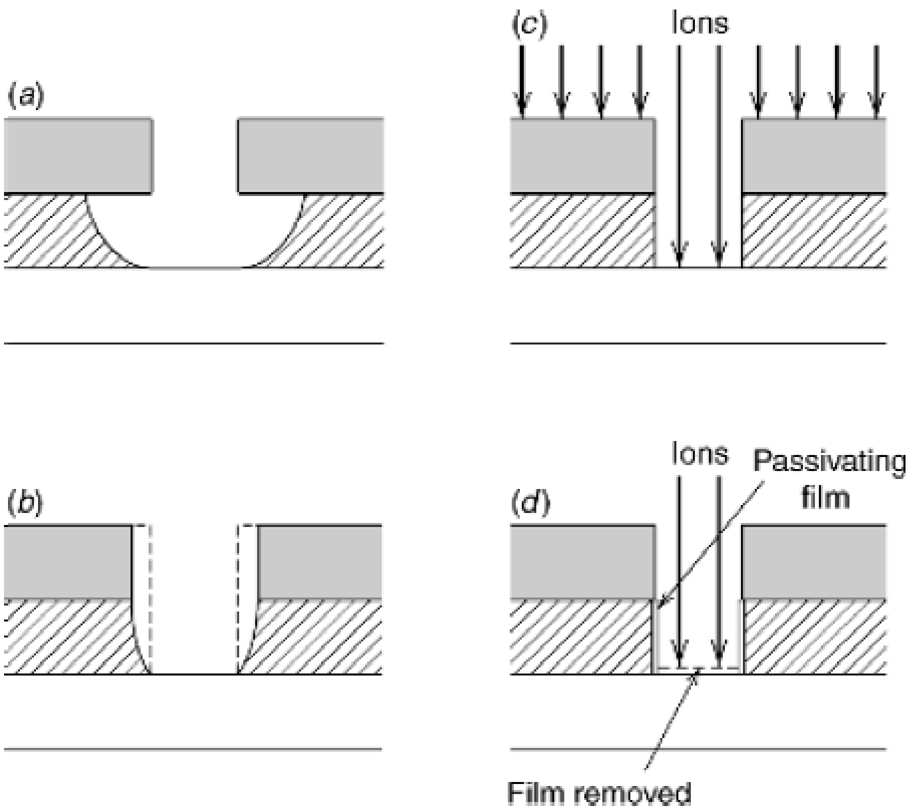


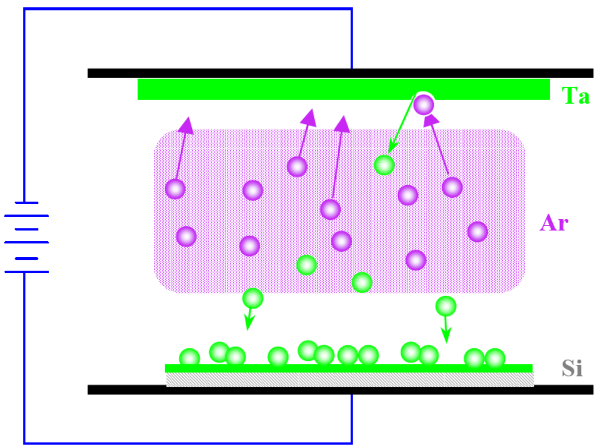
FIGURE 1.3. Plasma etching in integrated circuit manufacture: (*a*) example of isotropic etch; (*b*) sidewall etching of the resist mask leads to a loss of anisotropy in film etch; (*c*) illustrating the role of bombarding ions in anisotropic etch; (*d*) illustrating the role of sidewall passivating films in anisotropic etch.

- 화학적 반응: 플라즈마 내의 전자들은 중성입자와 충돌하여 화학 반응에 필요한 radical을 생성
- 물리적 반응: 기판 표면에 들어오는 이온들은 쉬스 전기장에 의해 가속 (이방성)

Plasma processing for semiconductor fabrication

Sputtering Deposition

$\mathrm{Ta_{solid}} + \mathrm{Ar}^+ \rightarrow \mathrm{Ta_{gas}} \rightarrow \mathrm{Ta_{film}}$

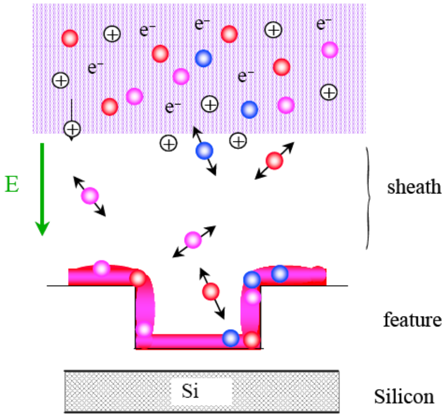


PECVD (Plasma Enhanced Chemical Vapor Deposition)

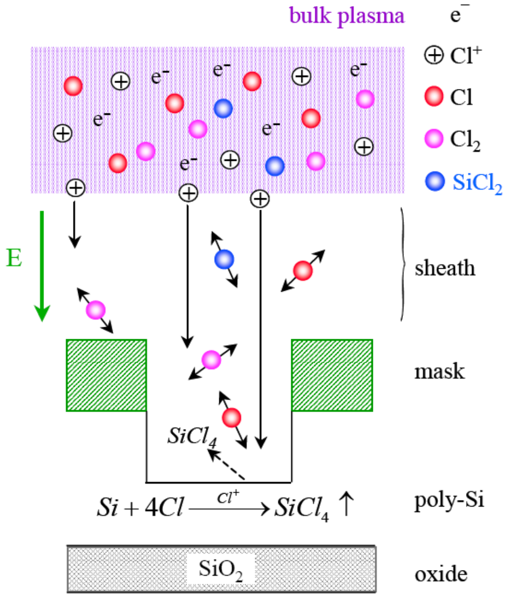
$Si(OC_2H_5)_4 + e^- \rightarrow Si(OC_2H_5)_3(OH) + C_2H_4 + e^-$

$O_2 + e^- \rightarrow 2O + e^-$

$O + Si(OC_2H_5)_3(OH) \rightarrow Si(OC_2H_5)_2(OH)_2 + C_2H_4O$



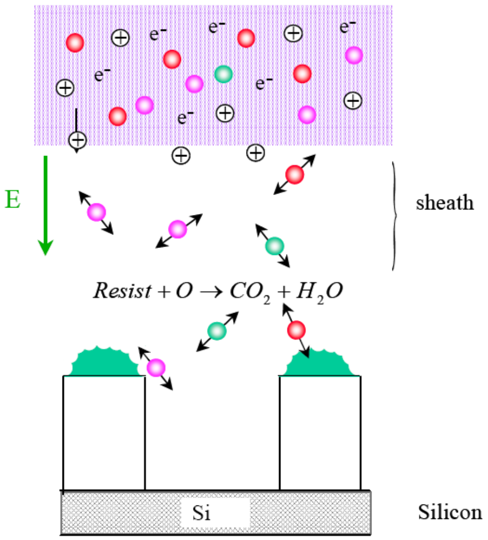
Reactive Ion Etching (RIE)



$Si + 4Cl \xrightarrow{Cl^+} SiCl_4 \uparrow$

Ashing

$O_2 + e^- \rightarrow 2O + e^-$



$Resist + O \rightarrow CO_2 + H_2O$

Characteristics of weakly-ionized plasmas

- A plasma is a collection of free charged particles moving in random directions that is, on the average, electrically neutral.

$$x_{iz} = \frac{n_i}{n_g + n_i}$$

- Weakly-ionized plasmas have the following features:

  (1) they are driven electrically;

  (2) charged particle collisions with neutral gas molecules are important;

  (3) there are boundaries at which surface losses are important;

  (4) ionization of neutrals sustains the plasma in the steady state;

  (5) the electrons are not in thermal equilibrium with the ions.

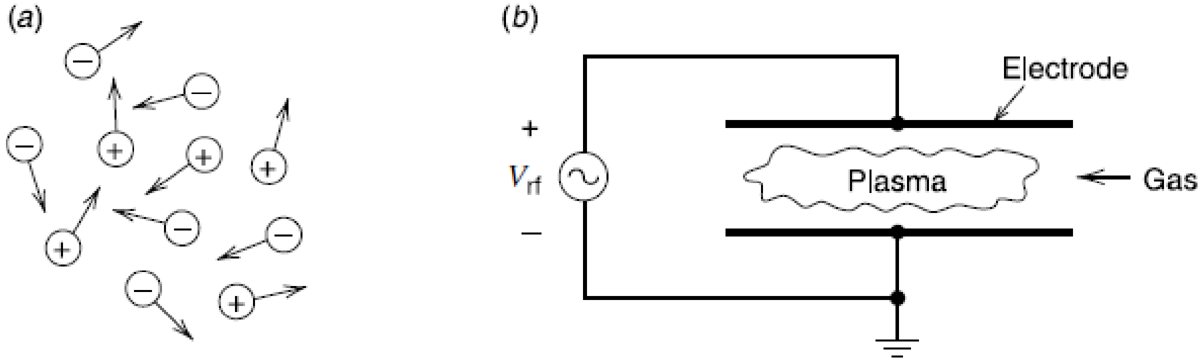
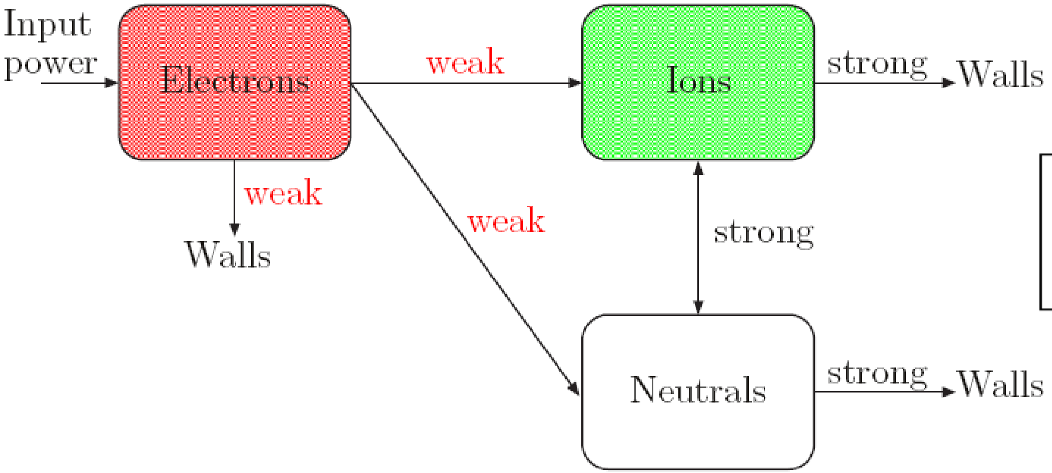


FIGURE 1.6. Schematic view of (*a*) a plasma and (*b*) a discharge.

Non-equilibrium is important in semiconductor fabrication

- For low-pressure discharges, the plasma is not in thermal equilibrium and the electrical power is coupled most efficiently to electrons. Energy is transferred inefficiently from electrons to ions and neutrals due to mass difference.

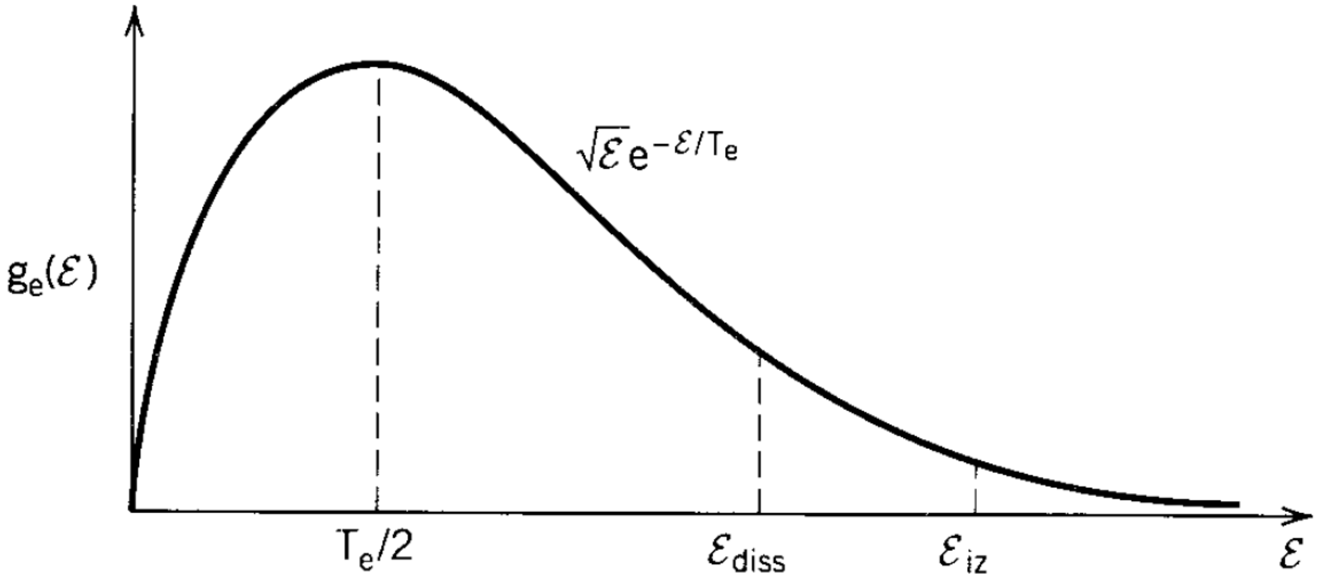


$T_e \gg T_i$ in plasma bulk

Bombarding $\mathcal{E}_i \gg \mathcal{E}_e$ at wafer surface

- Plasma processing: high temperature processing at low temperatures
  - Wafer can be near room temperature
  - Electrons produce free radicals : Chemistry
  - Electrons produce electron-ion pairs : Ion bombardment

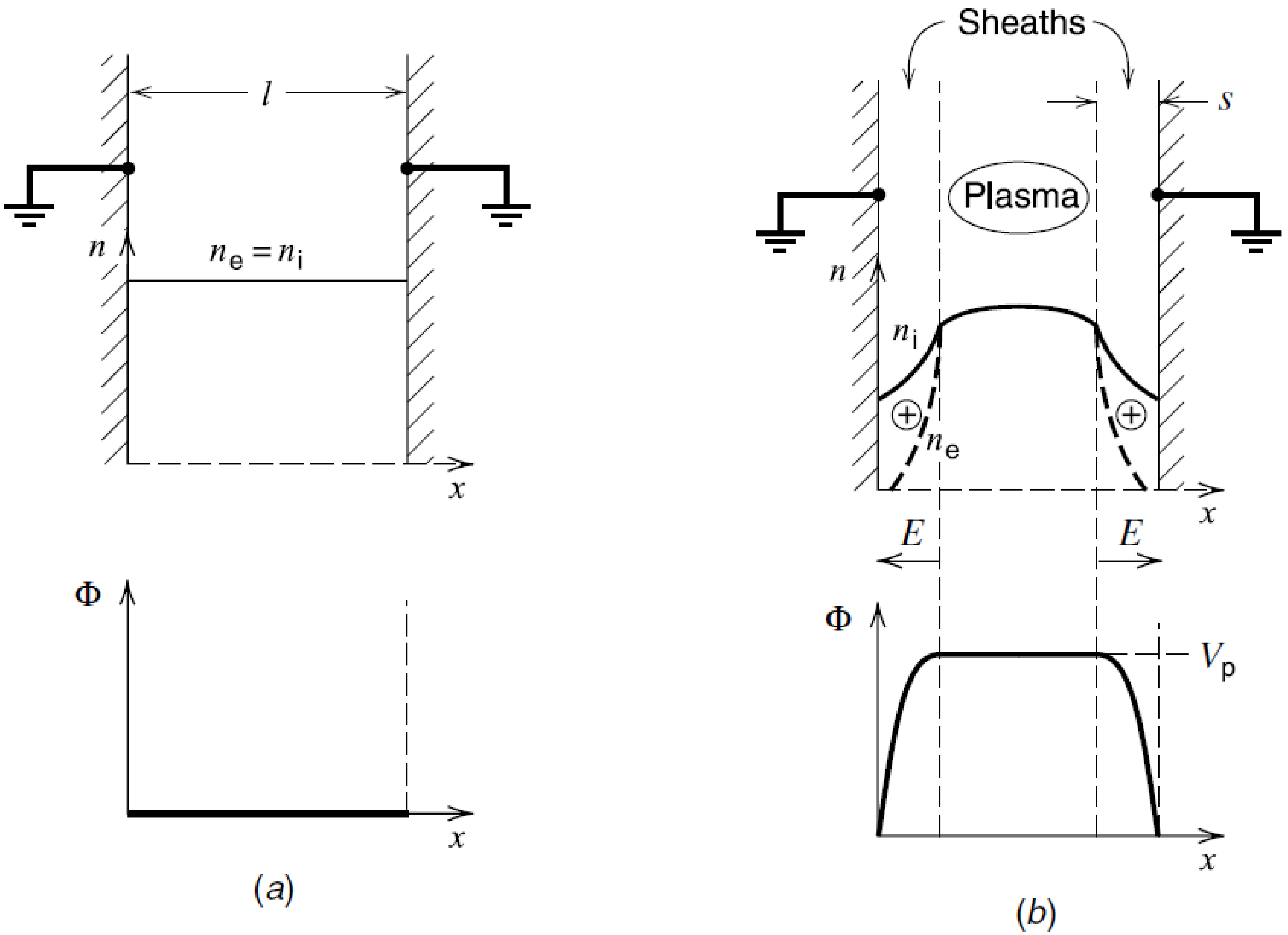
Electron energy distribution function (EEDF)



- Energetic electrons undergo collision with neutrals to generate excited neutrals, atoms, free radicals, ions, and additional electrons

- E < 2 eV	: elastic	→ heating
	: attachment	→ electron loss, electronegative plasma
- E = 2 – 6 eV	: excitation	→ light emission
- E = 6 – 15 eV	: dissociation	→ radicals, chemistry
- E > 15 eV	: ionization	→ positive ion, plasma

Formation of plasma sheaths

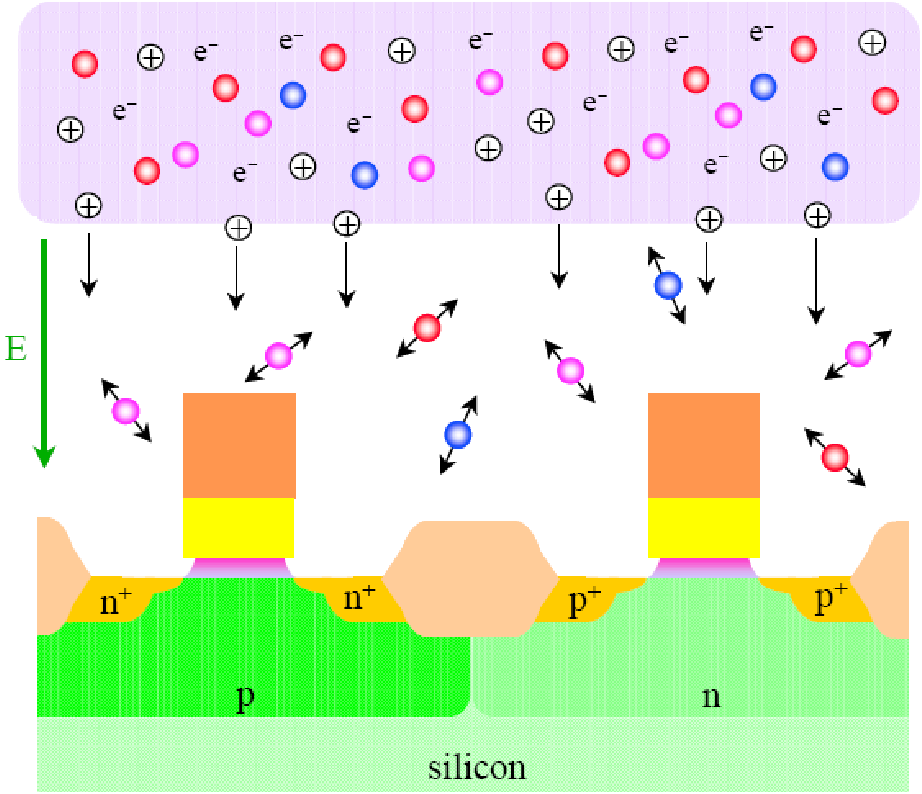


(a)

(b)

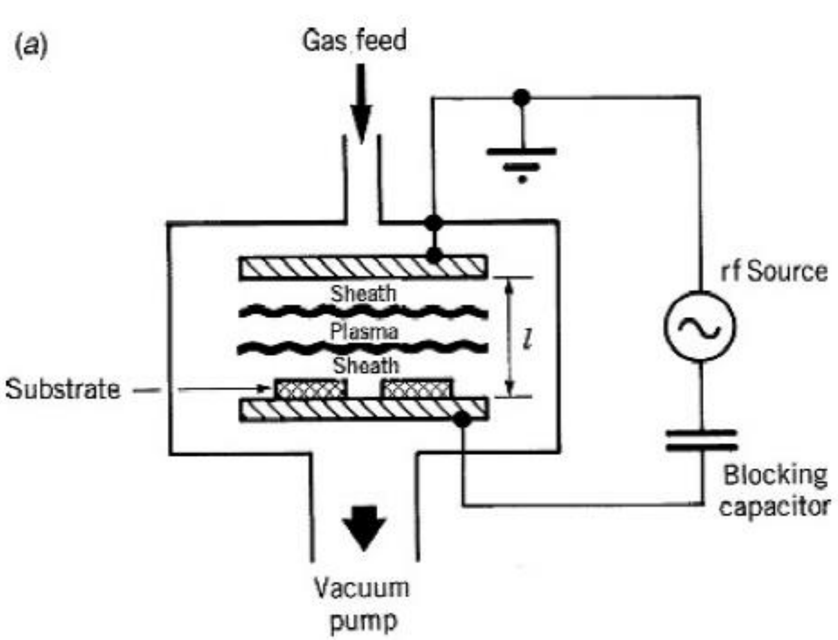
FIGURE 1.10. The formation of plasma sheaths: (*a*) initial ion and electron densities and potential; (*b*) densities, electric field, and potential after formation of the sheath.

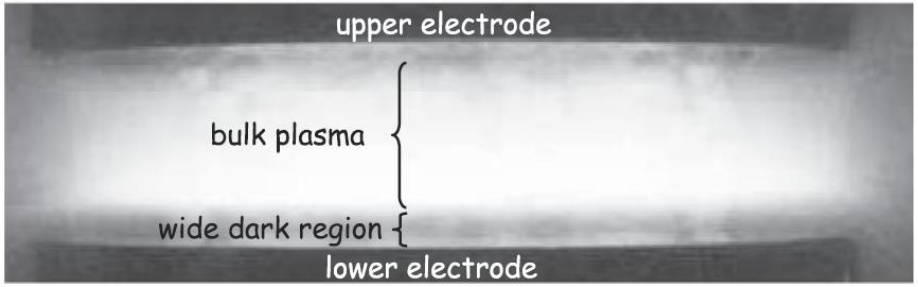
Importance of sheath

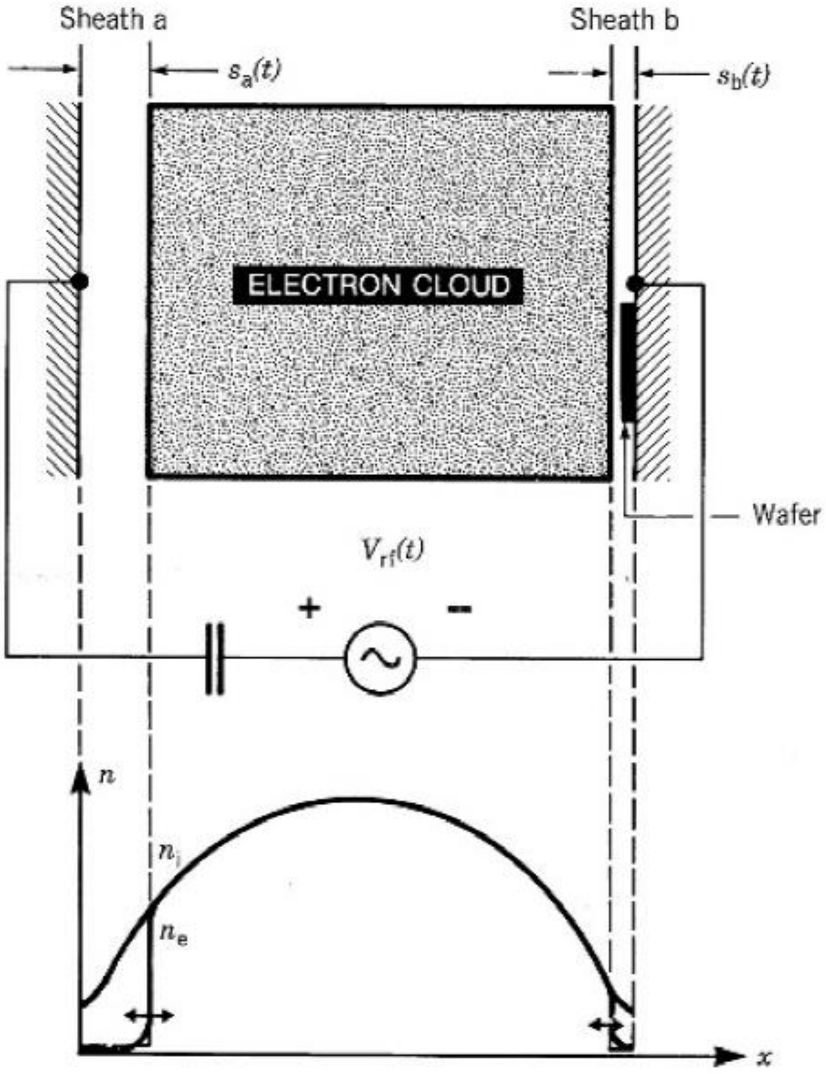


- Radicals, neutrals, fractional ions and electrons are generated in plasma.
- Energetic particles are produced at the electrode sheaths.
- To control the ion energy, flux and directionality, the understanding of plasma and sheath is required.

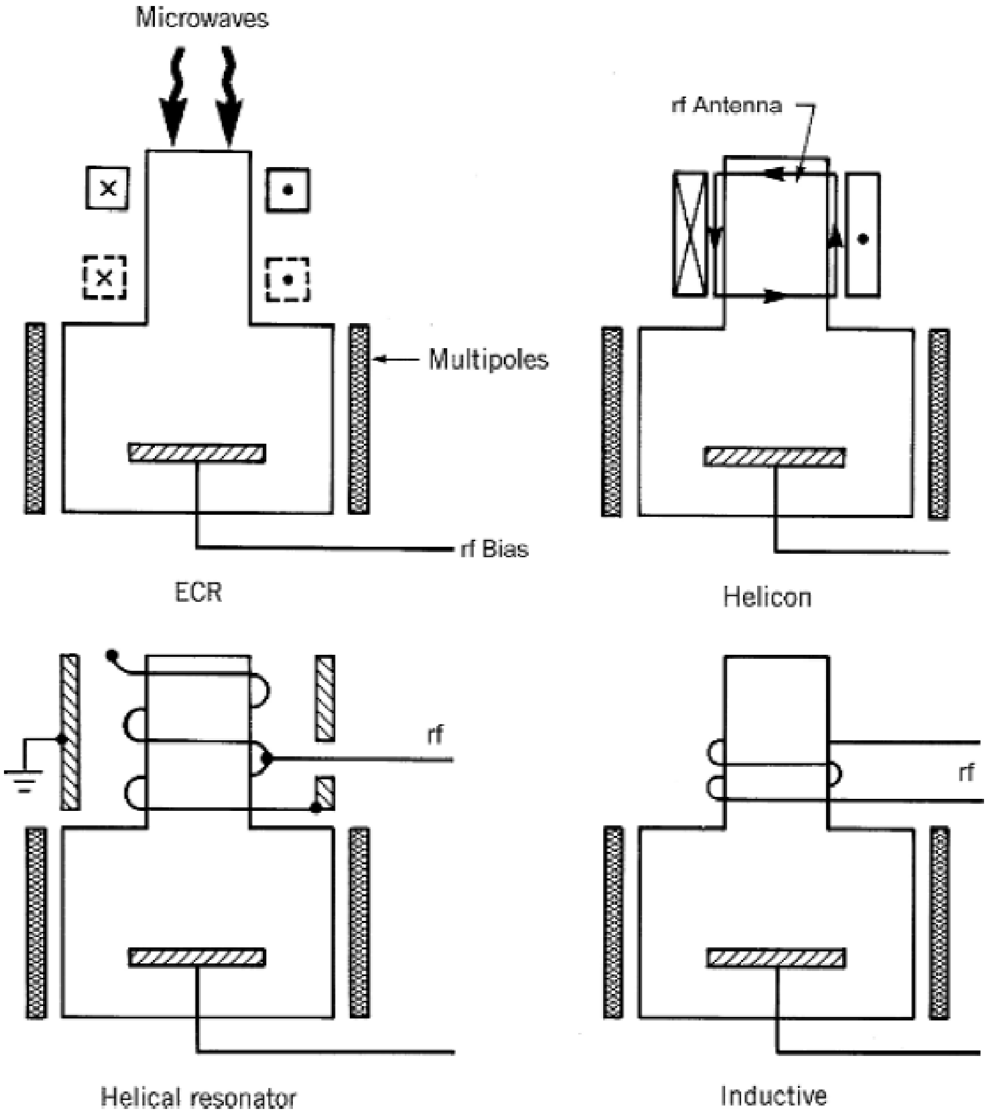
Capacitive rf discharge



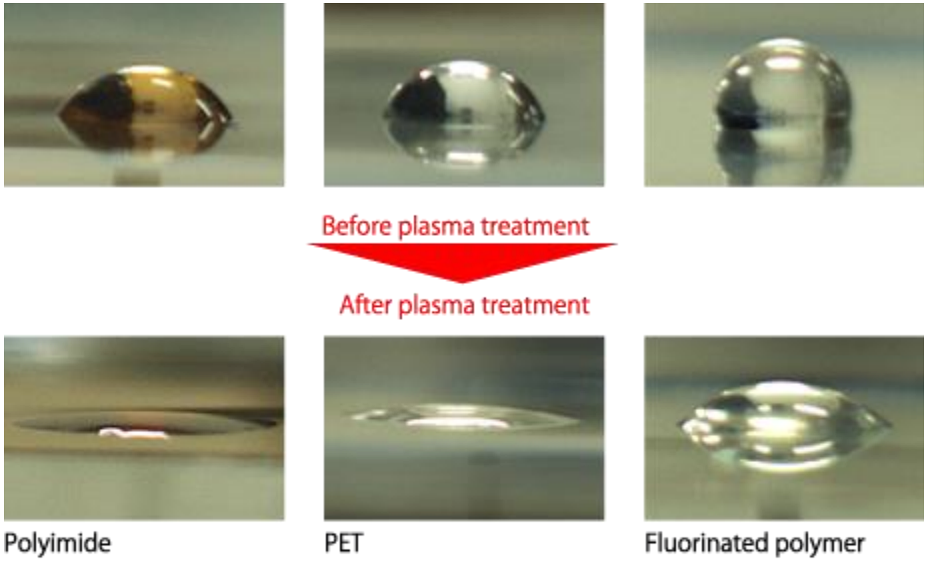




High density plasma sources



Surface treatment with atmospheric plasmas

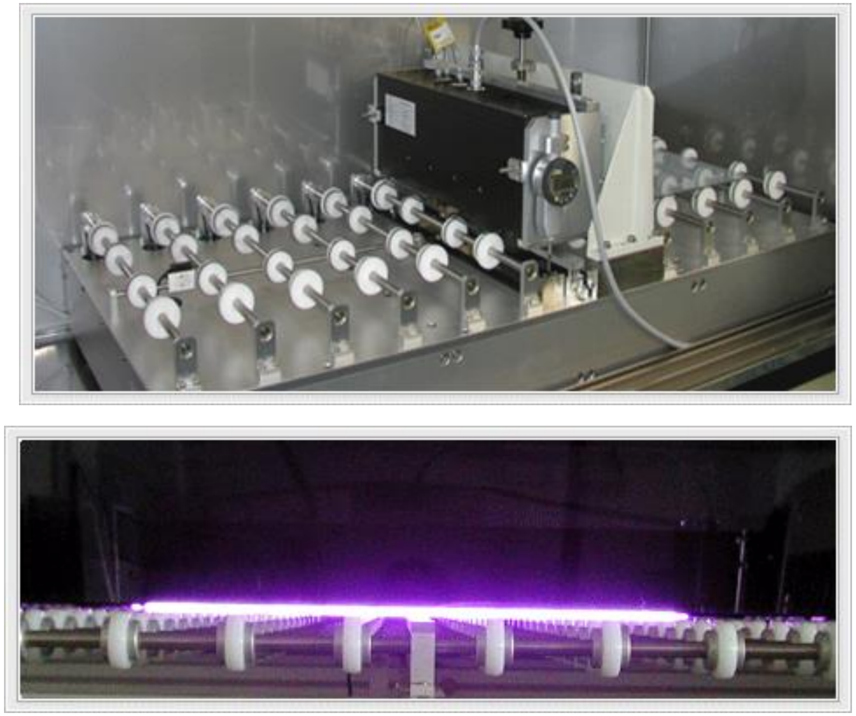

Before plasma treatment

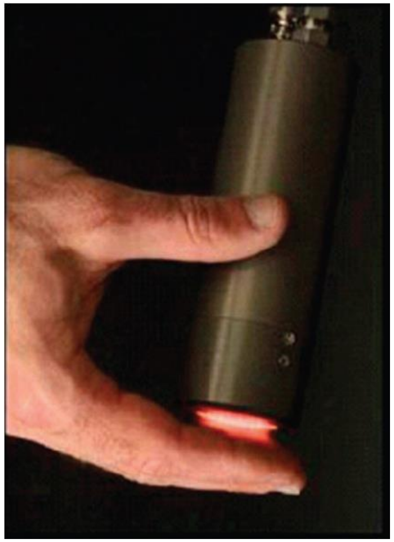
After plasma treatment

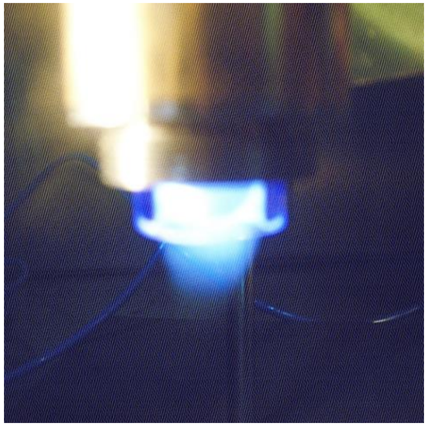
Polyimide

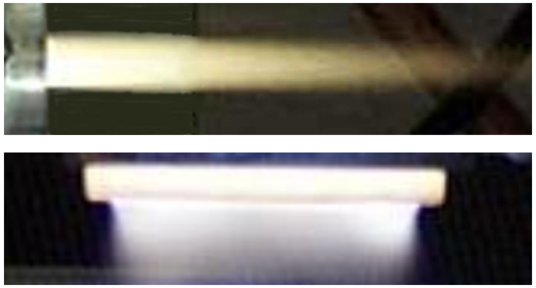
PET

Fluorinated polymer

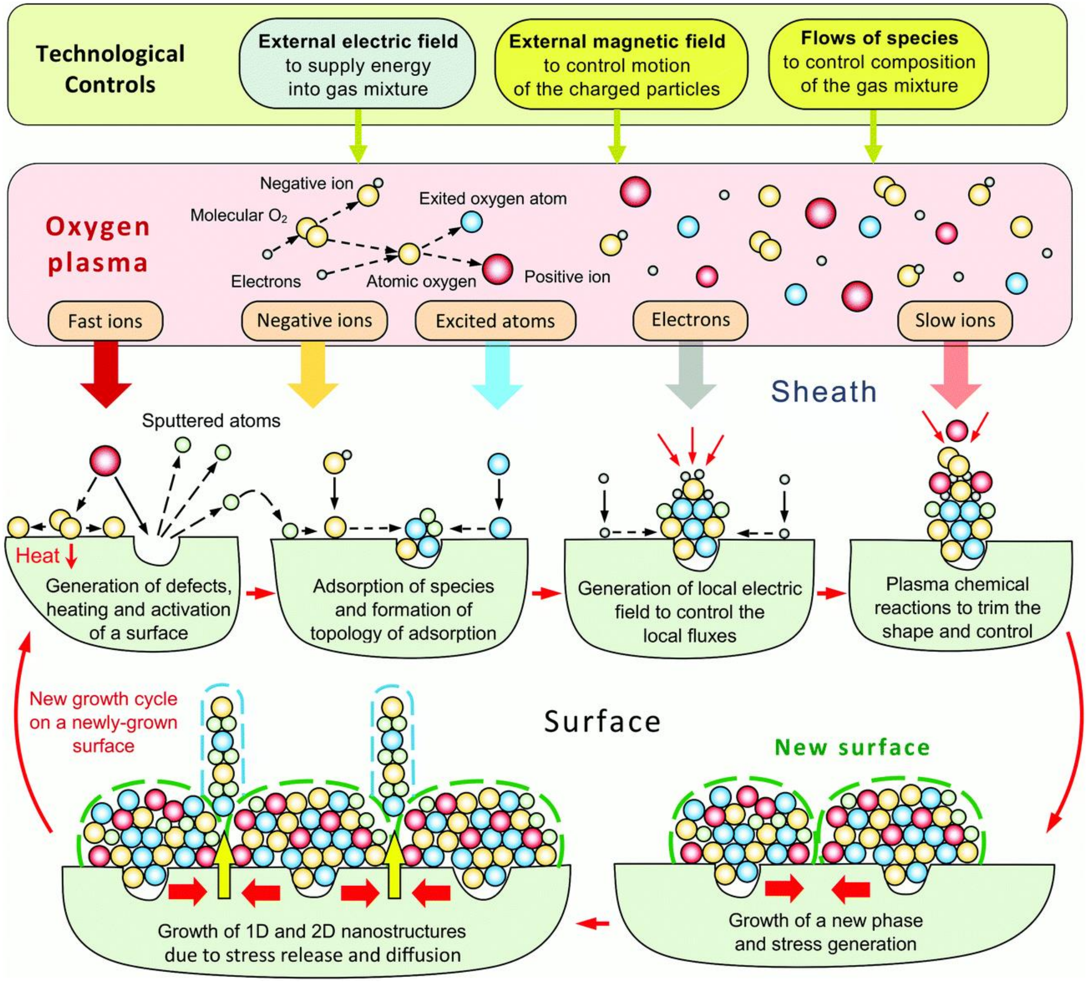

LCD glass cleaning







Nano-fabrication



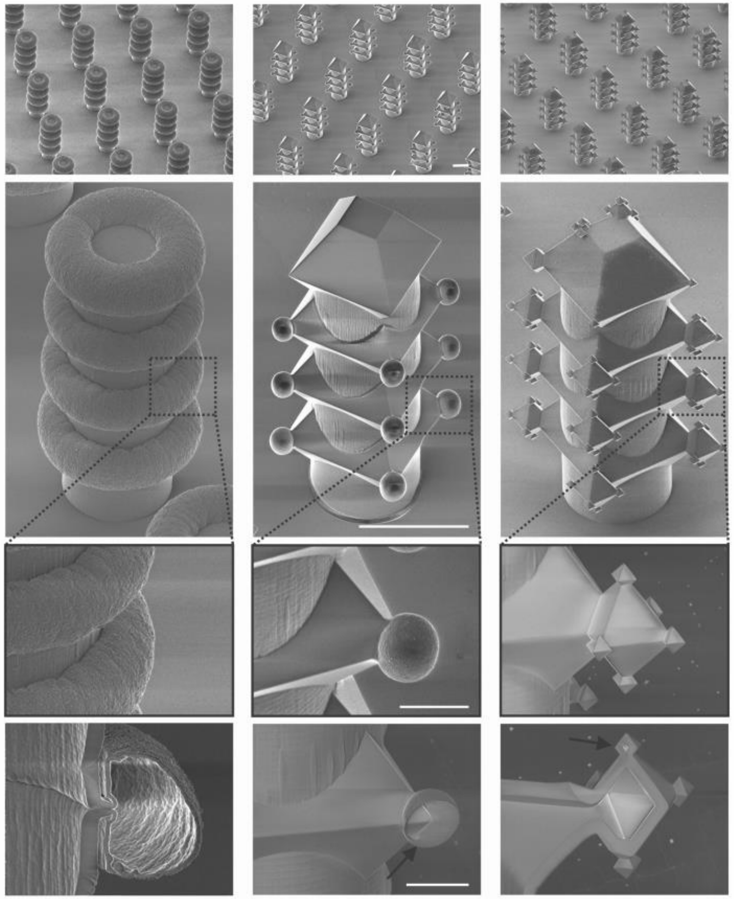
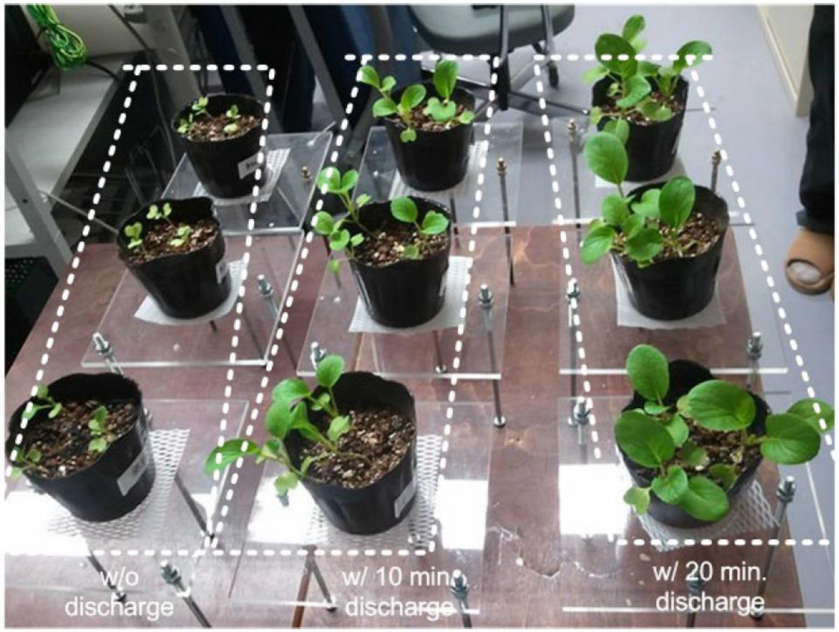


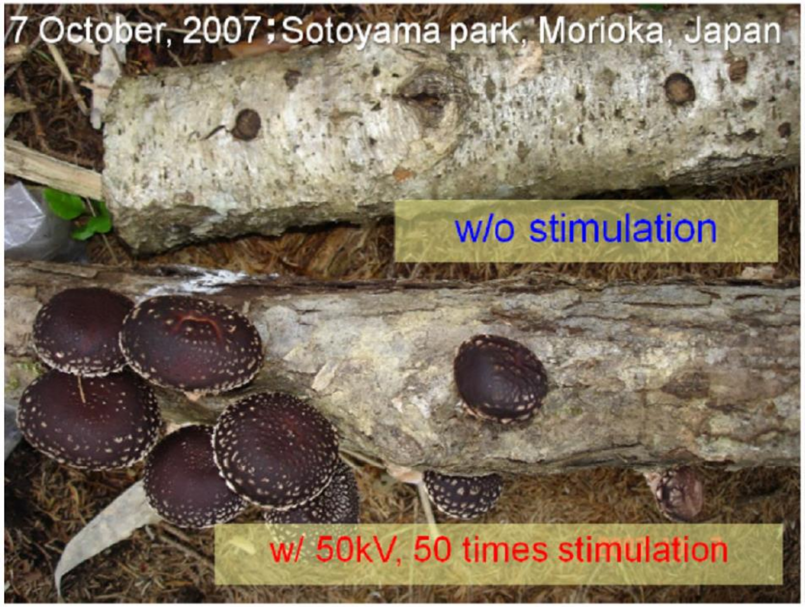
Fig. 7 Cross-sectional HR-SEM images of various 3D structures fabricated by using different combinations of isotropic etching with anisotropic etching. Scale bars represent 20 μm (first and second rows) and 5 μm (third and fourth rows)

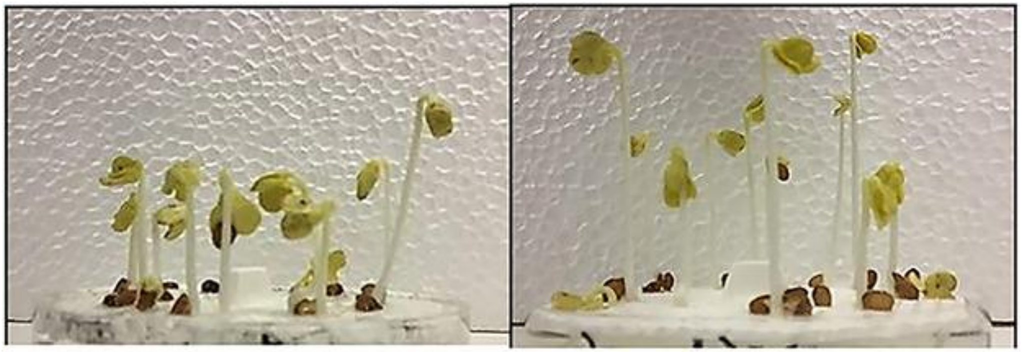
***Nanoscale* 10**, 17494-17511 (2018)

Microsystems & Nanoengineering **6**, 25 (2020)

Plasma agriculture

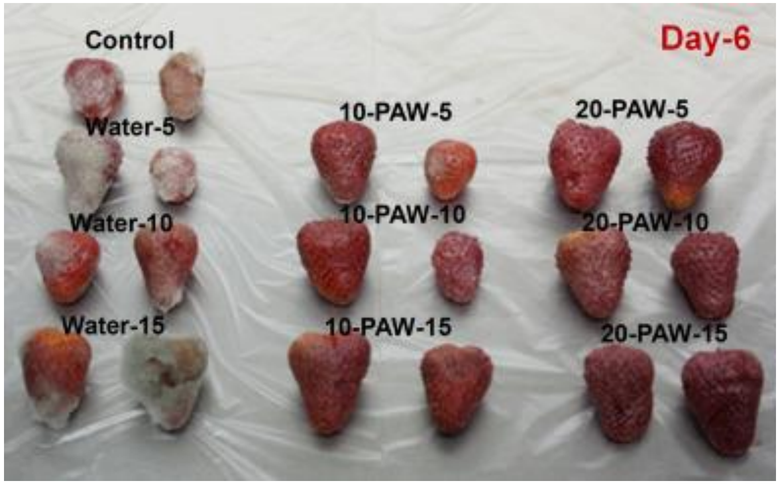






(a) Cultivated in non-treated water

(b) Cultivated in plasma-treated water



Biomedical applications

- **Biocompatibility**
- **Sterilization**
- **Surgery**

FIGURE 2.8 Plasma surgical instruments are in clinical use for cutting and cauterizing. The instrument shown here can sculpt tissue by producing reactive gaseous species under a liquid saline solution; the orange light is emitted by sodium atoms from the solution. Scientific advances on the interaction of plasma species with living tissue may lead to much more selective and beneficial use of plasmas in medicine, analogous to the fine control that is now exercised in semiconductor processing plasmas. Courtesy of K.R. Stalder, and ArthroCare Inc. SOURCE: K.R. Stalder and J. Woloszko, “Some physics and chemistry of electrosurgical plasma discharges,” *Contributions to Plasma Physics* 46 (1-2): 64-71 (2007). Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission.

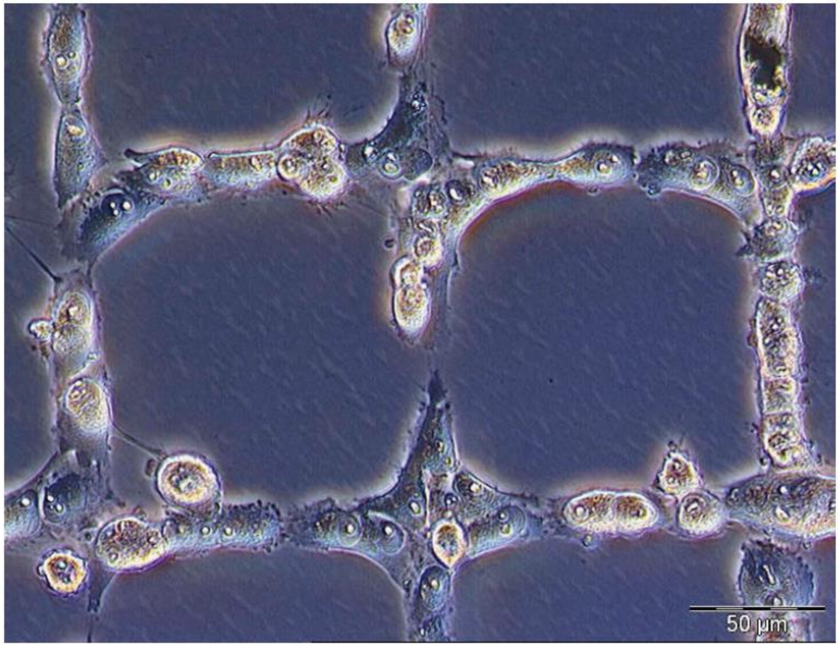
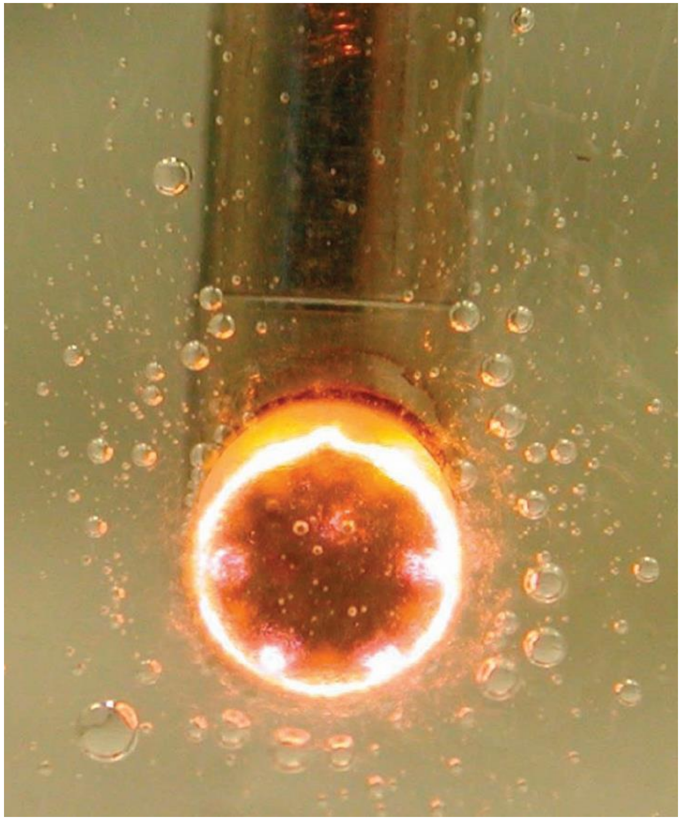


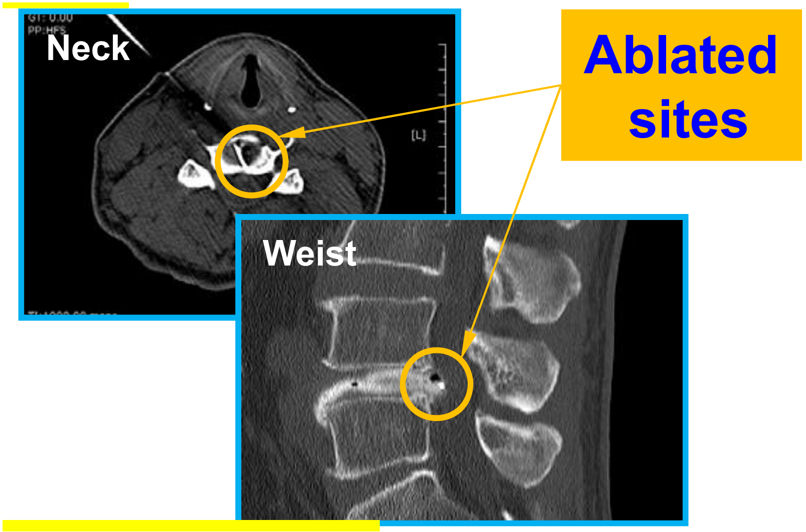
FIGURE 1.4 Plasmas and biology. Using low-temperature, reactive plasmas, the surface of polymers may be functionalized and patterned to allow the cells to adhere. In this example, amine functional groups were patterned on a polymer, resulting in a predetermined network of adhering cells. Courtesy of INP Greifswald, Germany.



Plasma surgery

(From Plasma Surgical Inc.)

Plasma ablation of
Herniated Nucleus Pulpous

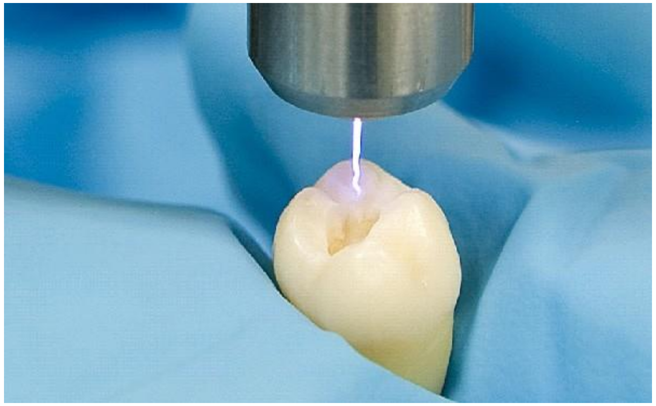


Ablated sites

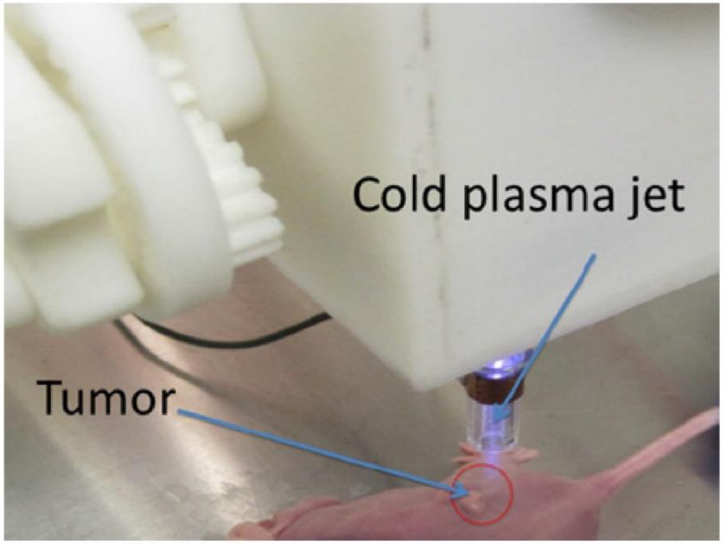
- Sterilization of living tissue
- Bacteria inactivation
- Hemostasis

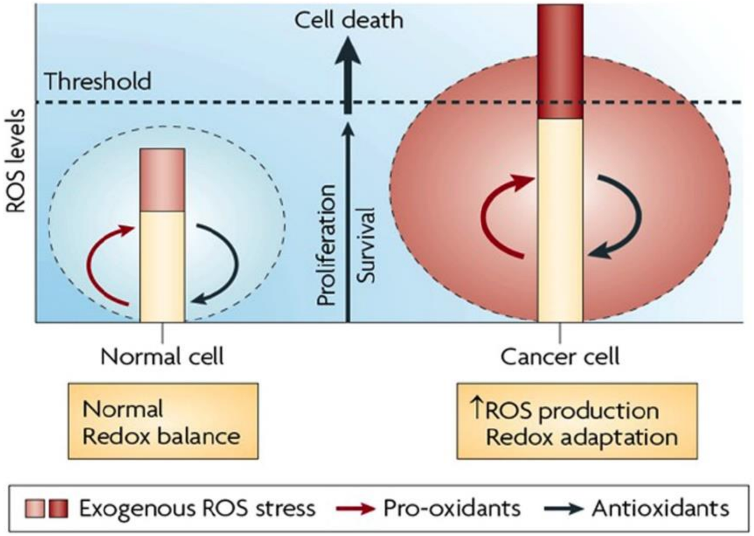
Plasma dentistry

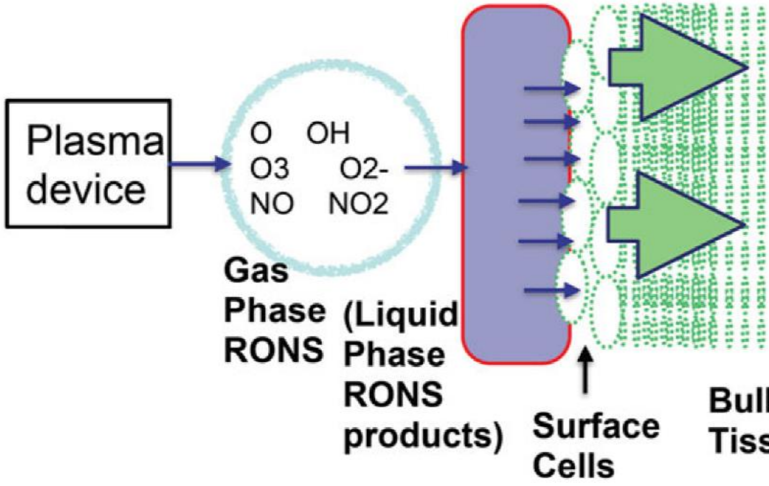
- Deactivation of Biofilms
  - Root canal disinfection
  - E. faecalis in the root canal
  - Ex-vivo biofilms on root canals of extracted teeth
  - E. coli, L. casei, S. mutans and C. albicans on agar and dentine plates
- Tooth Bleaching (surface treatment)
  - Hydrogen Peroxide + CAP enhanced the tooth bleaching
  - CAP + saline
  - Carbamide Peroxide + CAP
  - Plasma plume + 36% H_2O_2 gel on extracted teeth
- Instrument Sterilization
  - Removal of biofilms on microstructures titanium
  - Dental instruments
  - Ti discs inoculated with biofilms
- Composite Restoration
  - CAP treatment increases dentin/adhesive interfacial bonding
  - CAP treatment improves the tensile-shear bond strength between post and composite



Plasmas for cancer treatment





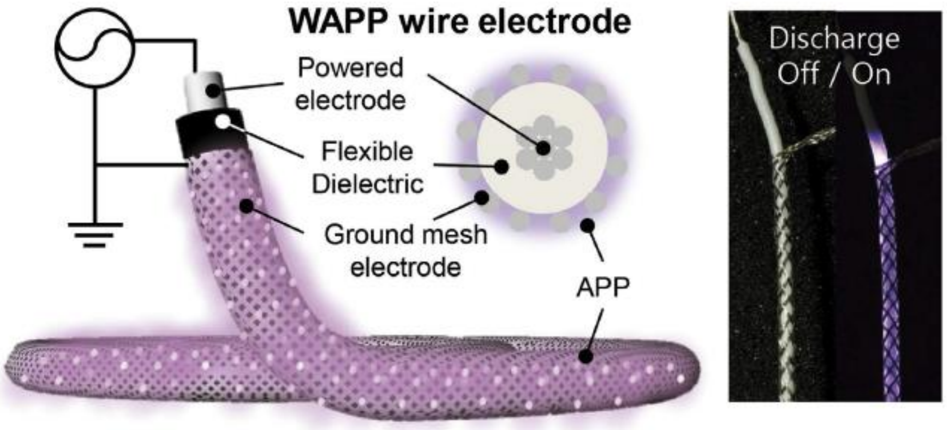


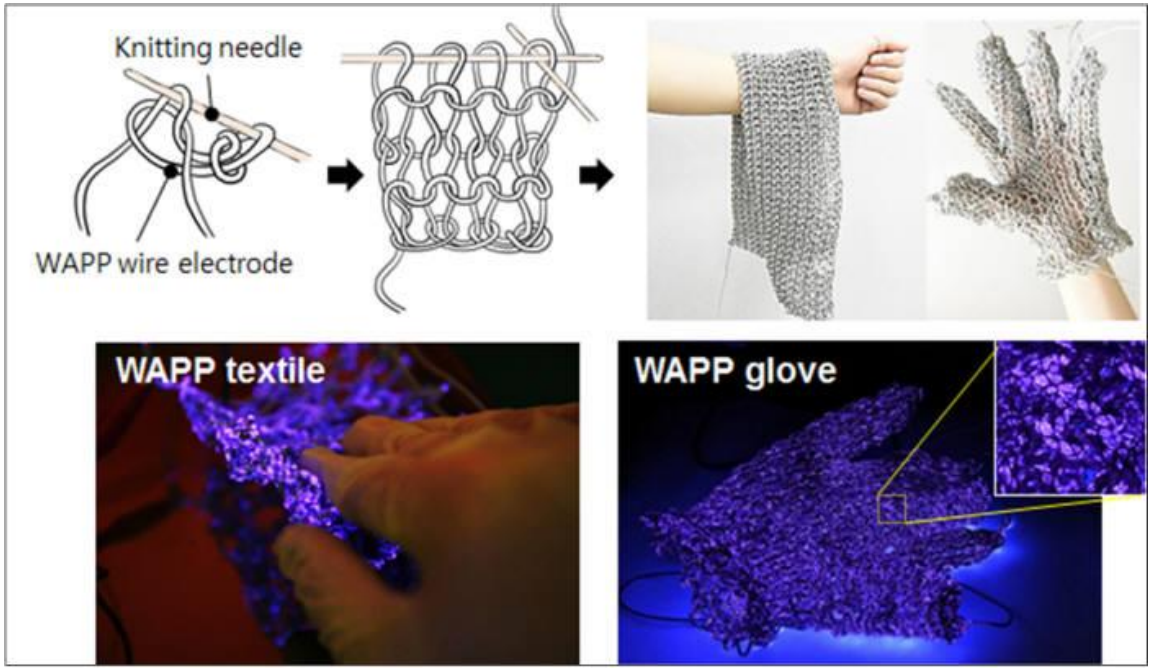
Cell-cell communication: 'bystander effect' leading to tumor apoptosis?

Immune cell involvement?

Plasma-induced increased blood flow/O2?

Wearable atmospheric pressure plasma fabric

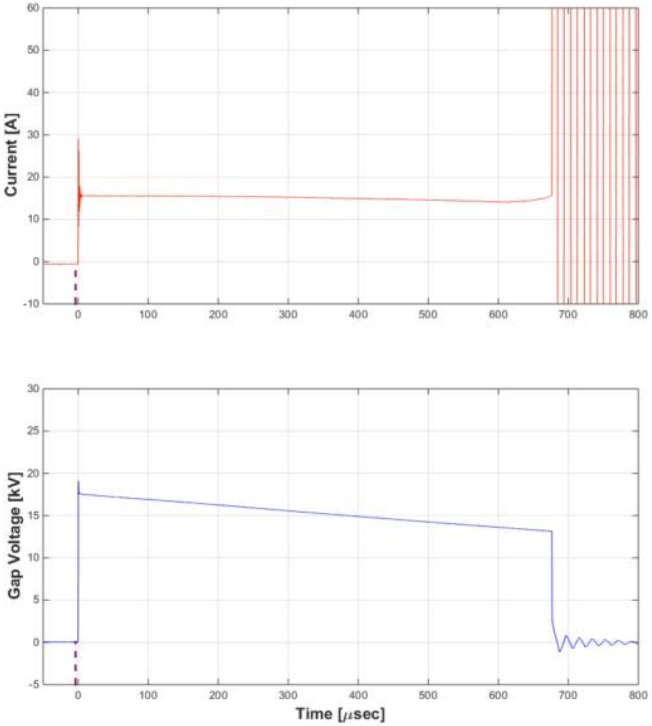


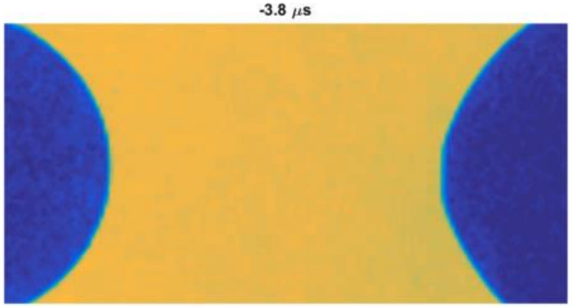


Plasma propulsion

Underwater spark discharge

$V_0 = 16\ kV$





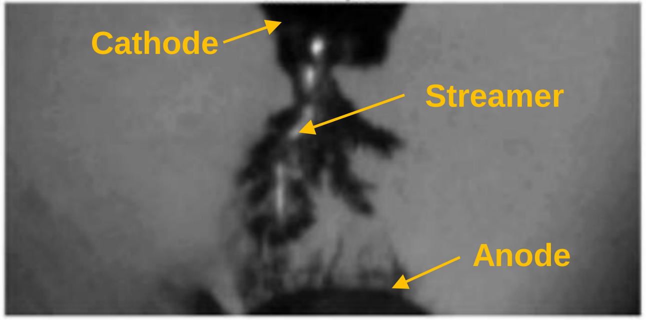
cathode

anode

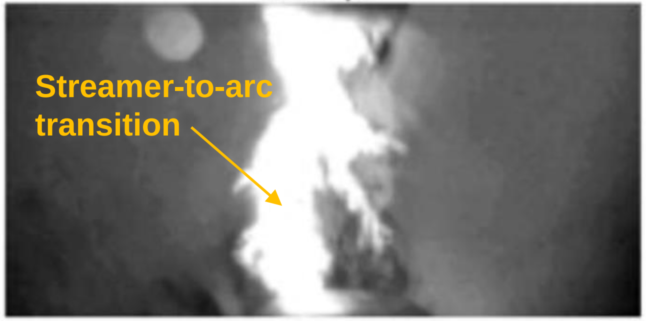
- 긴 pre-breakdown time 동안 버블 발생 → 버블 내 스트리머 발생 및 전파
- 매우 짧은 시간 동안 스트리머-아크 천이 → 고온,고압 플라즈마 생성 → 충격파 발생

Underwater shockwave generation

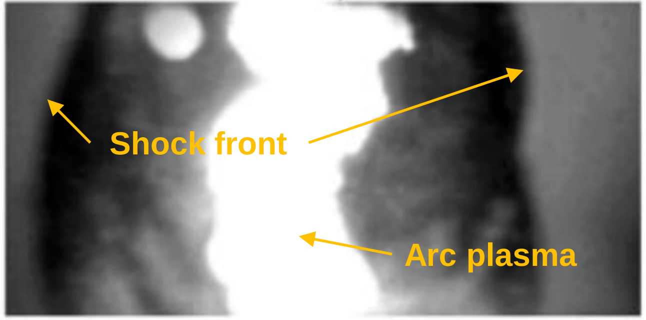
28.78 μs



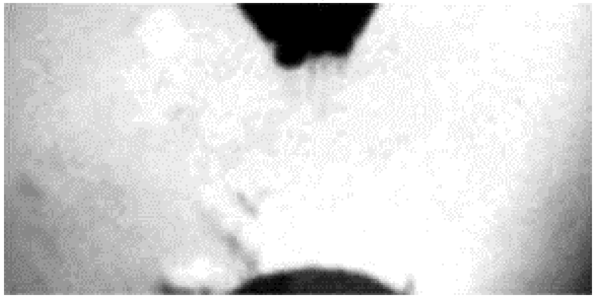
31.34 μs

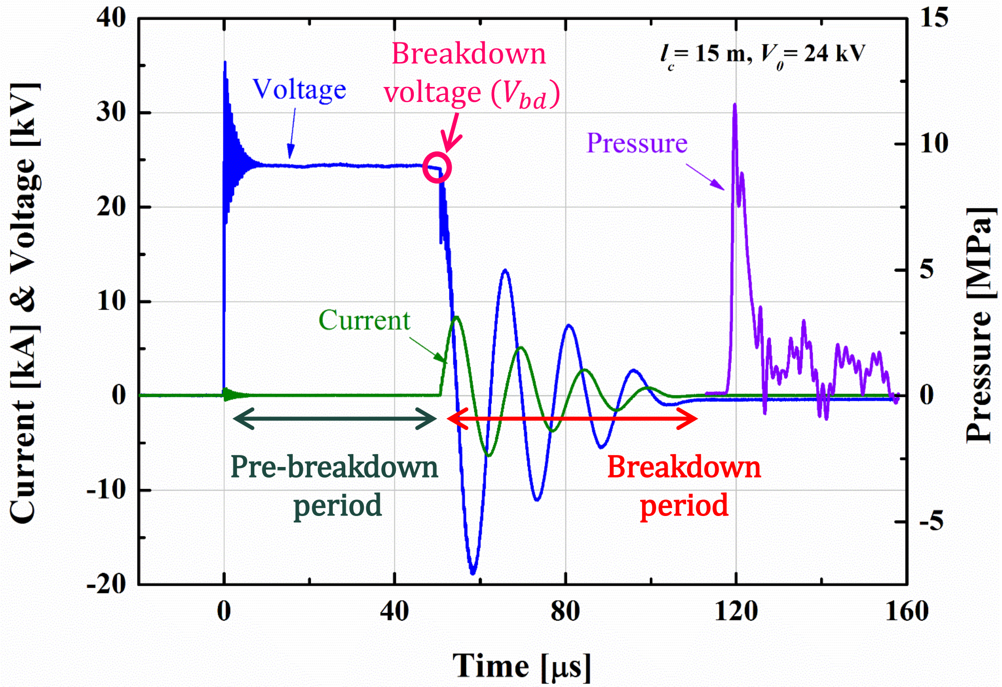


33.9 μs



-1.485 μs

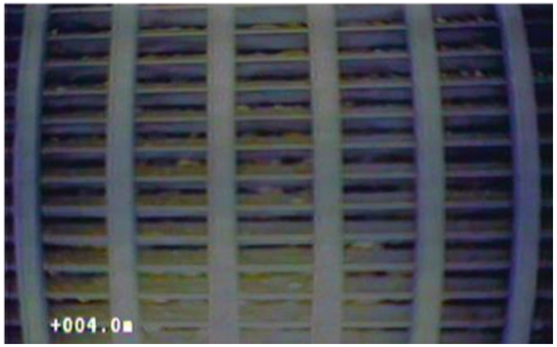


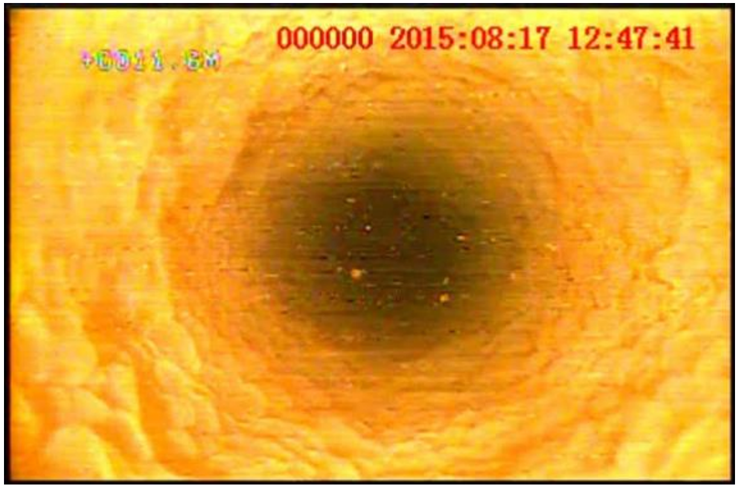


Water well cleaning

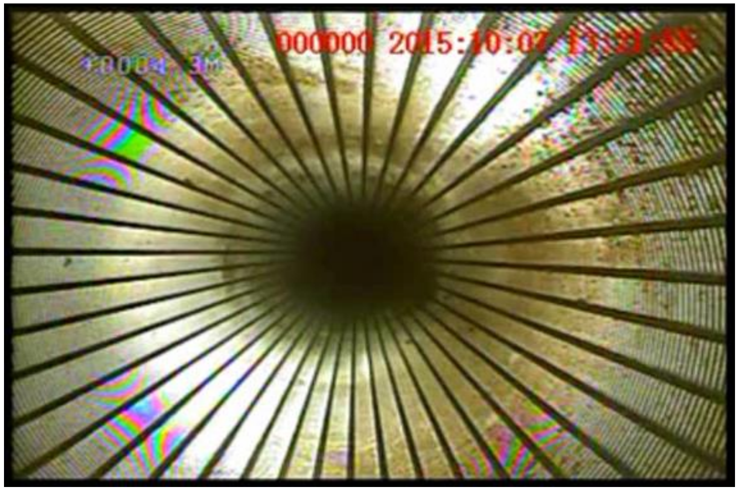
(a) Before treatment

(b) After treatment





기술 상용화(지하수 관정 세정 기술)

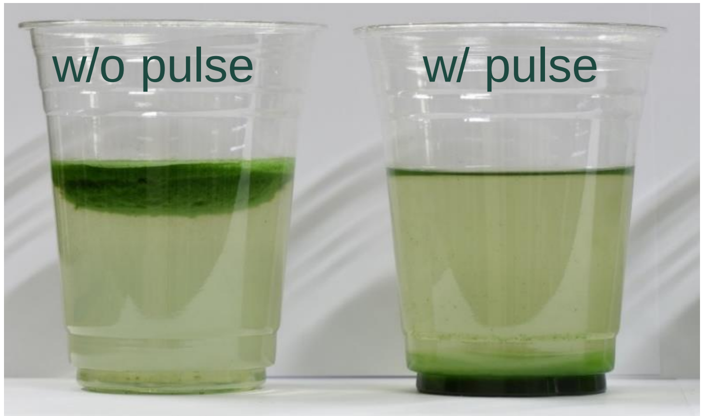


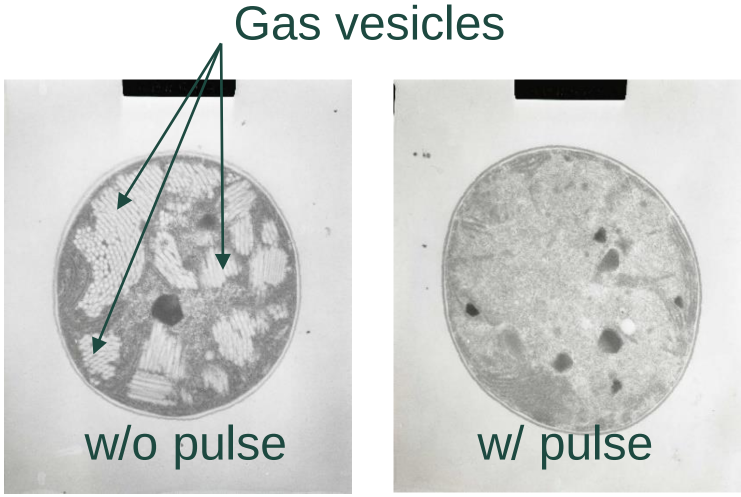
정경재 외, 대한지질공학회지 23, 29 (2013)
K. J. Chung et al., Contrib. Plasma Phys. 53, 330 (2013)
K. J. Chung et al., Curr. Appl. Phys. 15, 977 (2015)
S. G. Lee et al., J. Korean Phys. Soc. 66, 1845 (2015)
K. Lee et al., J. Appl. Phys. 121, 243302 (2017)
K. Lee et al., Appl. Phys. Lett. 112, 134101 (2018)

SUN & SEA
Always think GREEN
(주) 썬앤씨

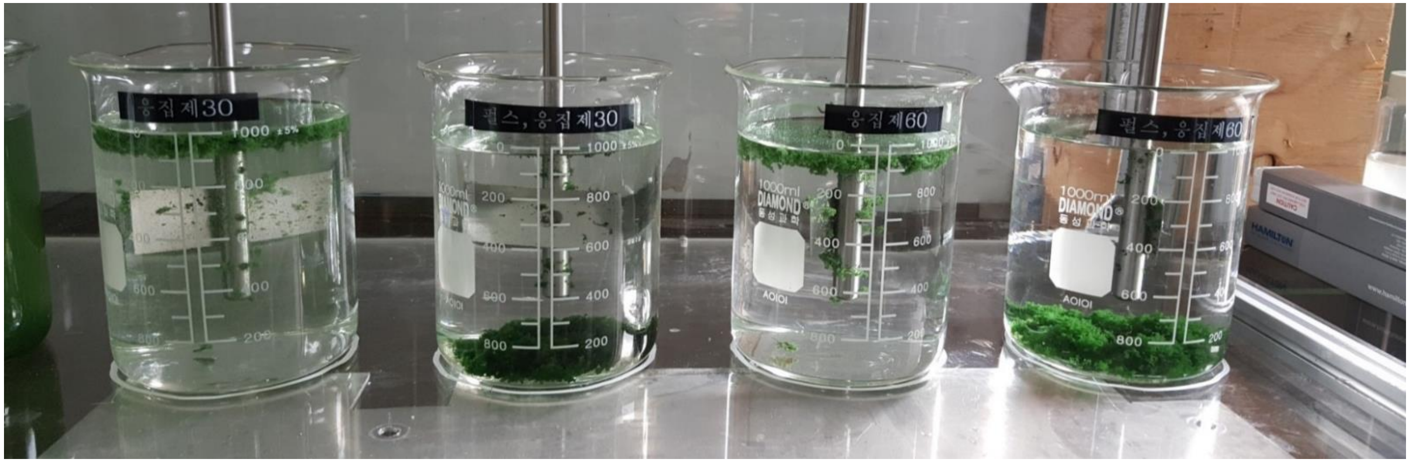
Water-bloom removal

- 녹조 제거 기술





→ Shock wave destroys gas vesicles to sink the water-bloom down to the bottom



NOx reduction

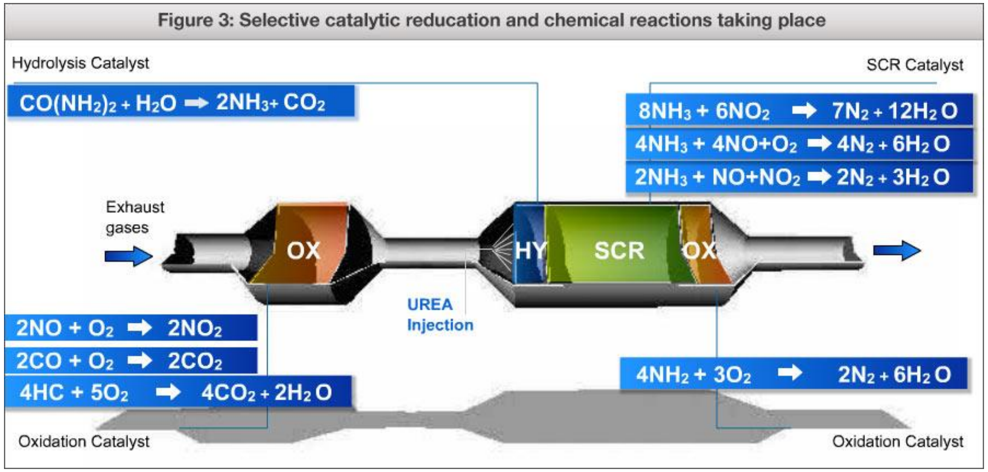


Figure 3: Selective catalytic reducation and chemical reactions taking place

Hydrolysis Catalyst

$CO(NH_2)_2 + H_2O \rightarrow 2NH_3 + CO_2$

SCR Catalyst

$8NH_3 + 6NO_2 \rightarrow 7N_2 + 12H_2O$

$4NH_3 + 4NO + O_2 \rightarrow 4N_2 + 6H_2O$

$2NH_3 + NO + NO_2 \rightarrow 2N_2 + 3H_2O$

Oxidation Catalyst

$2NO + O_2 \rightarrow 2NO_2$

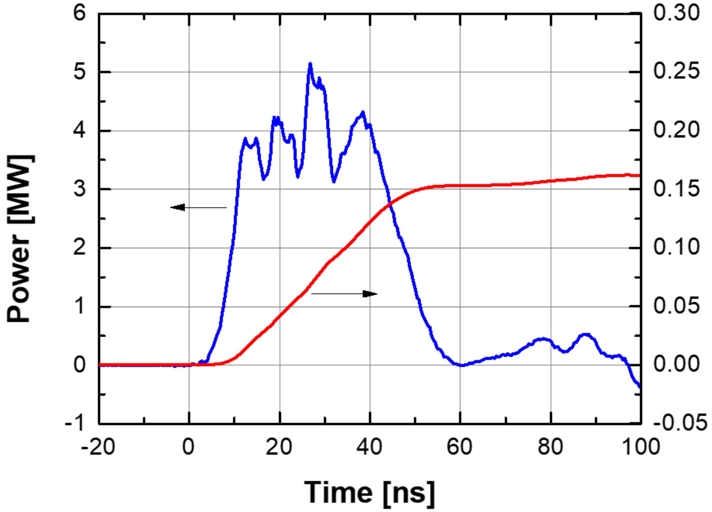
$2CO + O_2 \rightarrow 2CO_2$

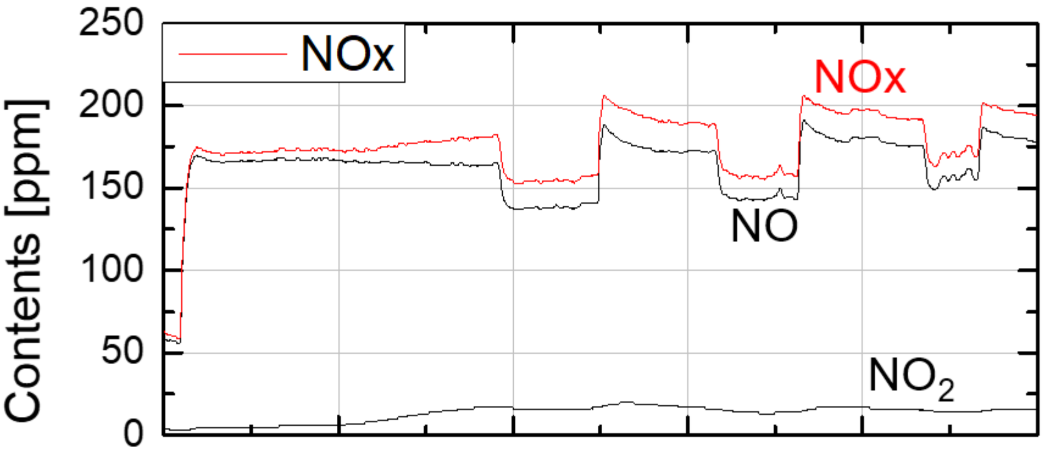
$4HC + 5O_2 \rightarrow 4CO_2 + 2H_2O$

Oxidation Catalyst

$4NH_2 + 3O_2 \rightarrow 2N_2 + 6H_2O$

40 kV, 4 MW, 0.15 J/pulse, 100 Hz
→ 20% reduction of NOx with 15 W

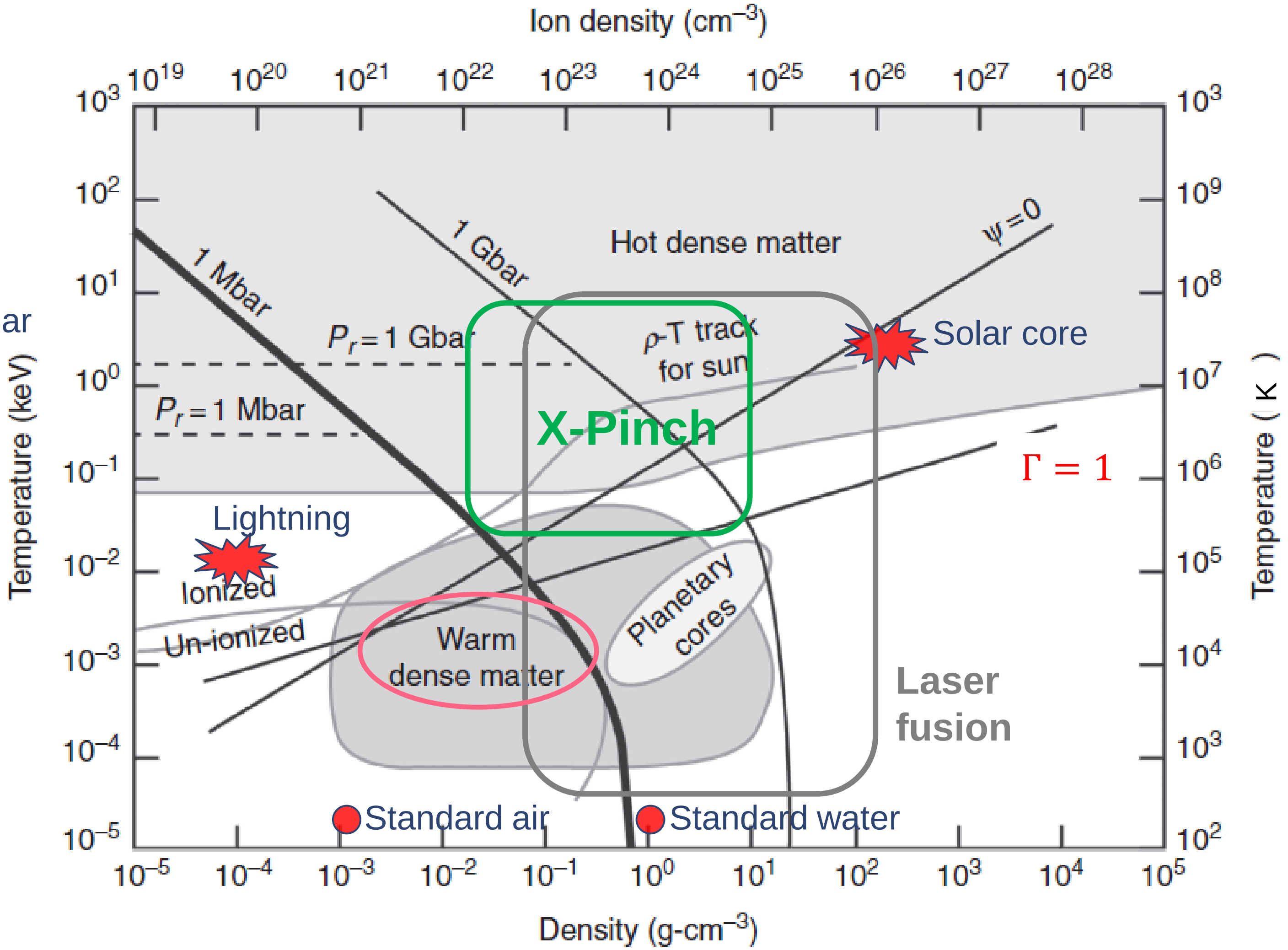




High-energy-density (HED) plasma (p > Mbar) research

Magnetic fusion ~ 5 bar
(10^{14} cm^{-3}, 10 keV)

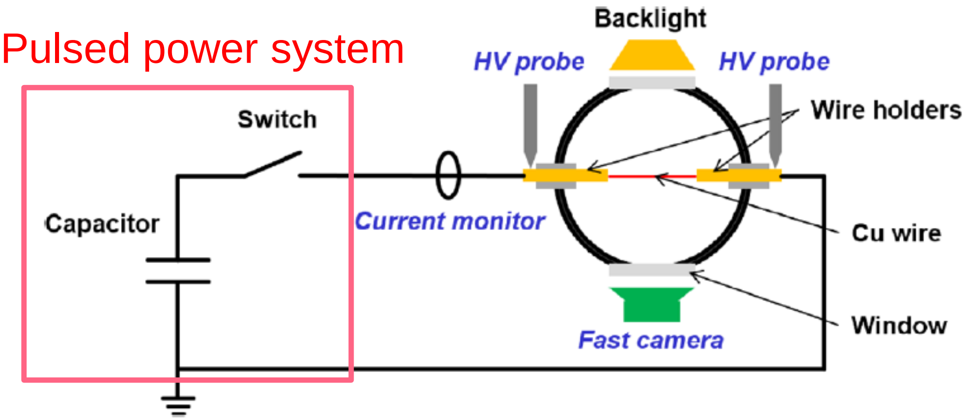
Processing plasma
(10^{10} cm^{-3}, 4 eV)

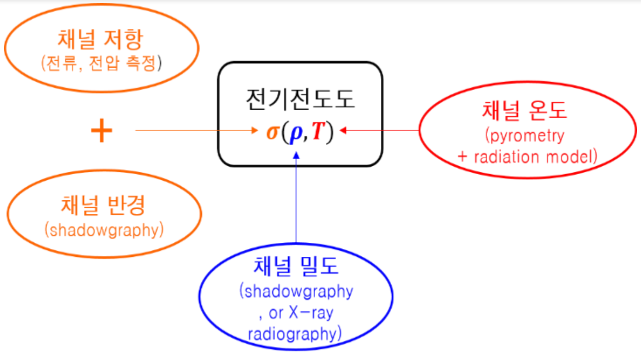


- Pulsed power enables us to study high energy density physics in a laboratory, because it can provide huge power (~GW) for a very short time (~ns)

Warm dense matter research via underwater wire explosion

Pulsed power system





채널 저항
(전류, 전압 측정)

+

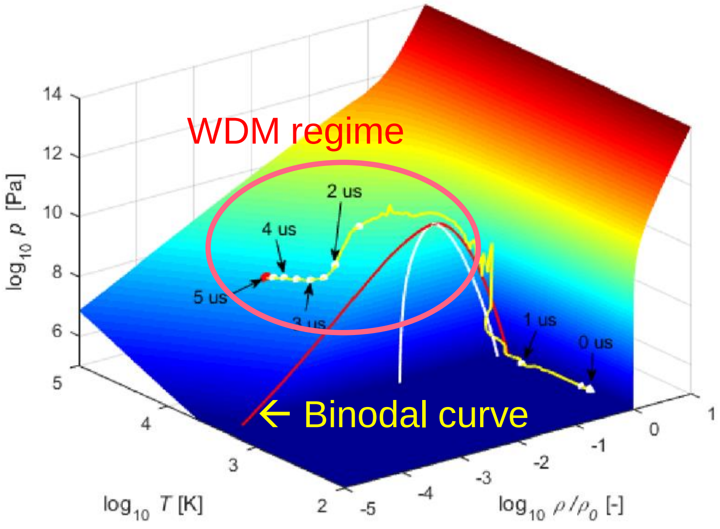
채널 반경
(shadowgraphy)

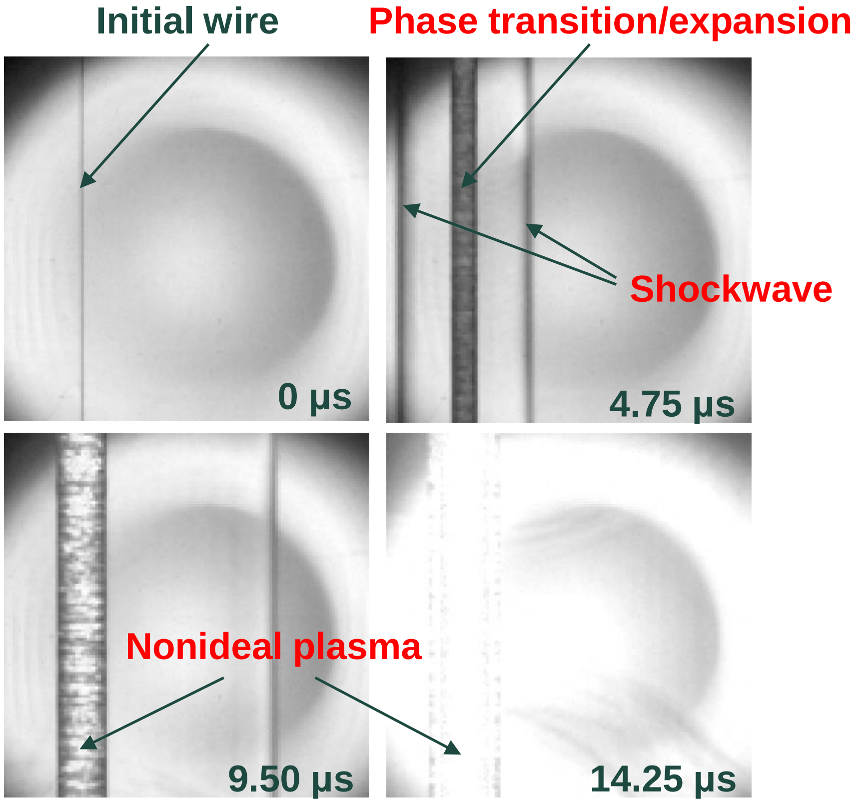
전기전도도
$\sigma(\rho, T)$

채널 온도
(pyrometry
+ radiation model)

채널 밀도
(shadowgraphy
, or X–ray
radiography)

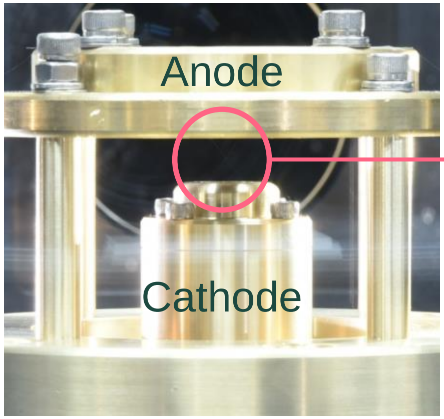
3D EOS of Cu



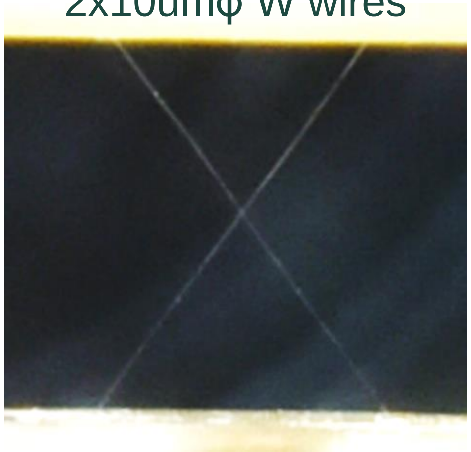


K. J. Chung et al., J. Appl. Phys. 120, 203301 (2016)
S. Park et al., Appl. Phys. Lett. 119, 174102 (2021)

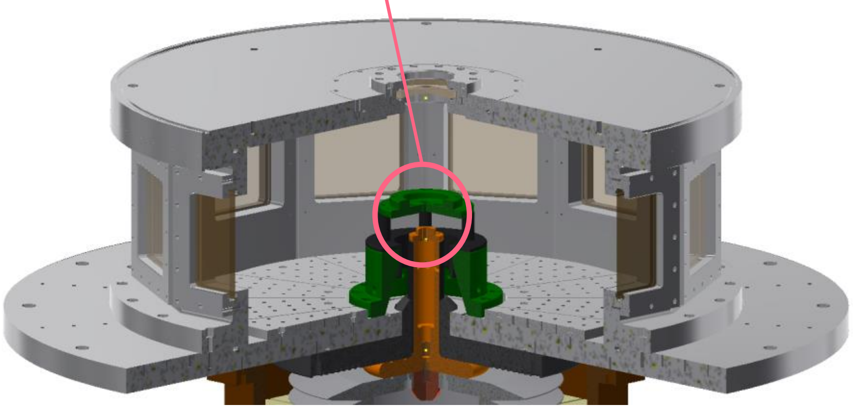
Hot dense matter research using X-pinch in vacuum

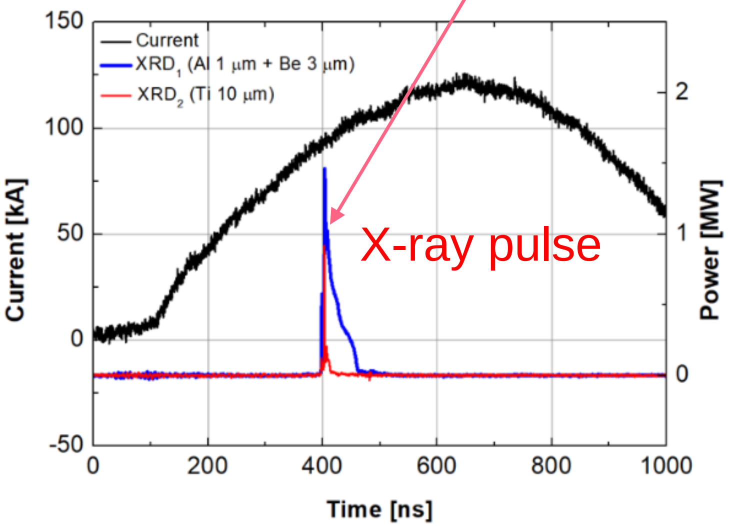


2x10umφ W wires



Hot spot



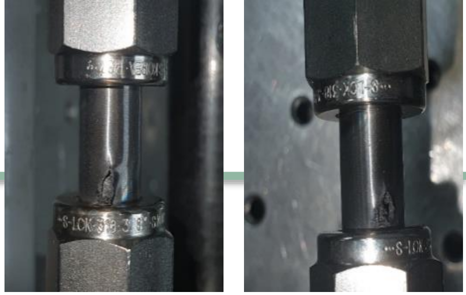


X-ray pulse

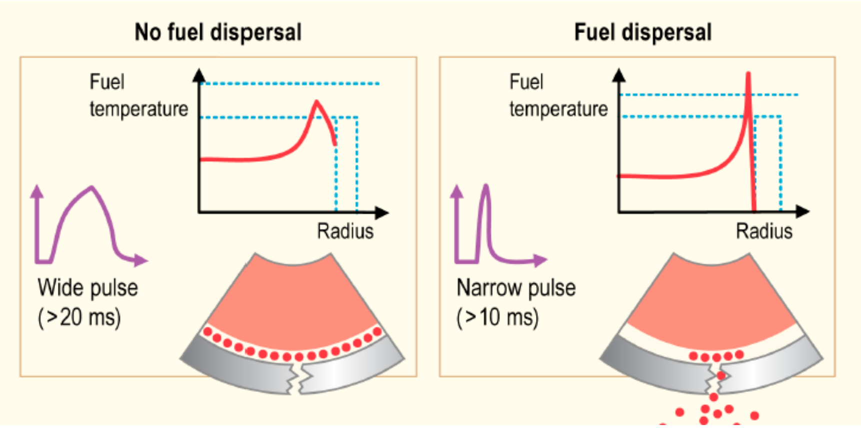
High current from pulsed power system

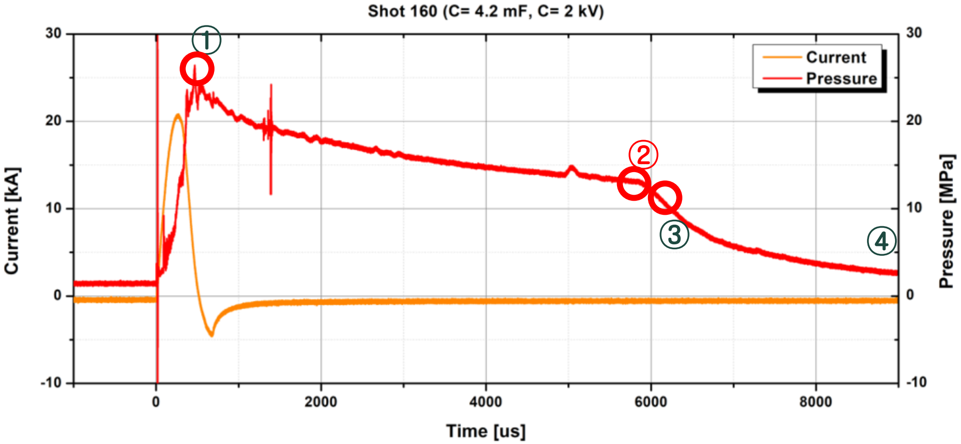
J. Ryu et al., RSI 92, 053533 (2021)

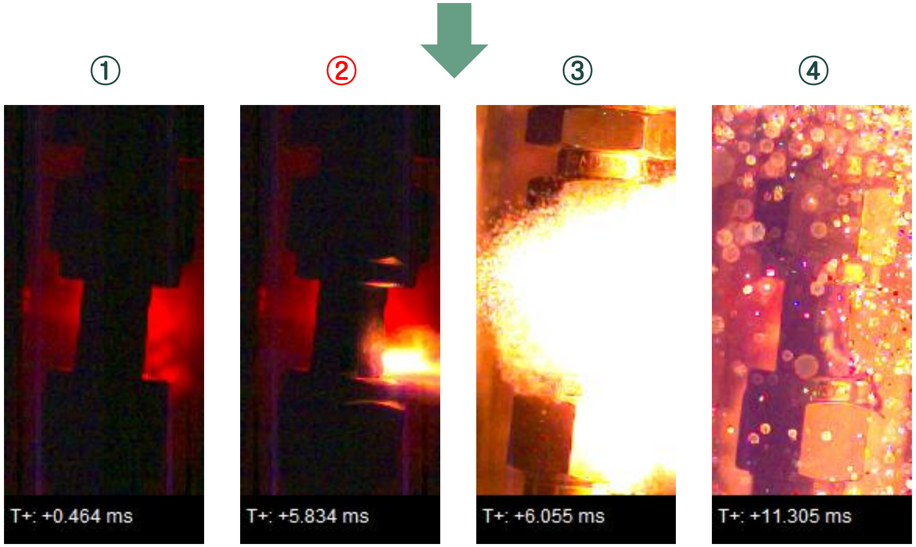
RIA (Reactivity-Initiated Accident) simulator



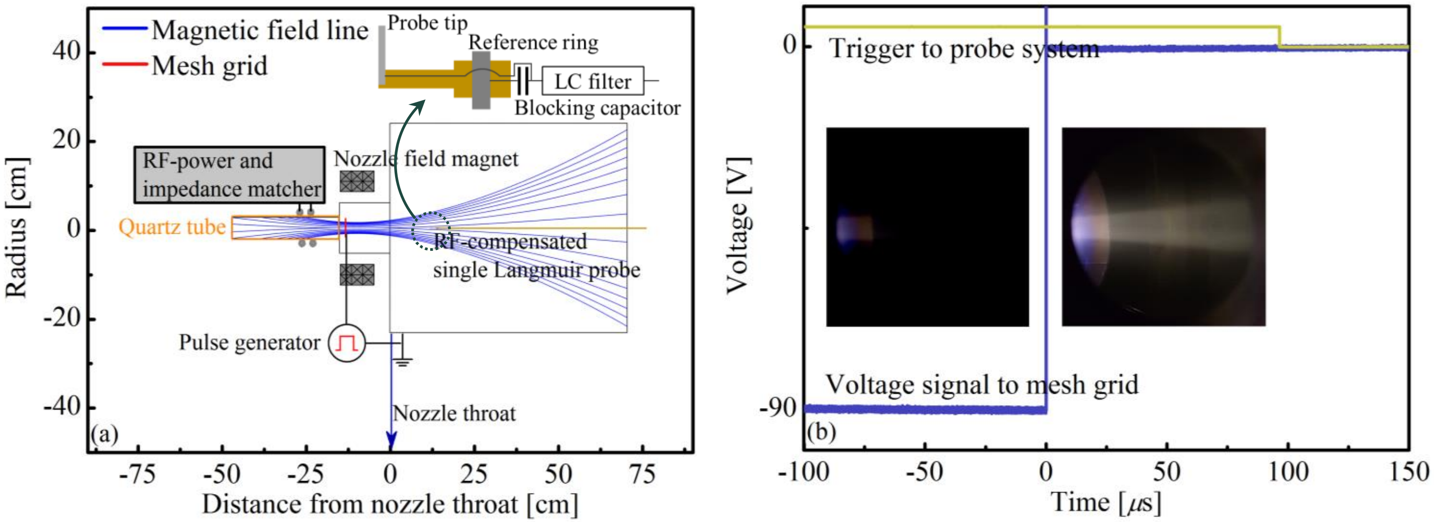
KoFONS 한국원자력안전재단 KOREA FOUNDATION OF NUCLEAR SAFETY

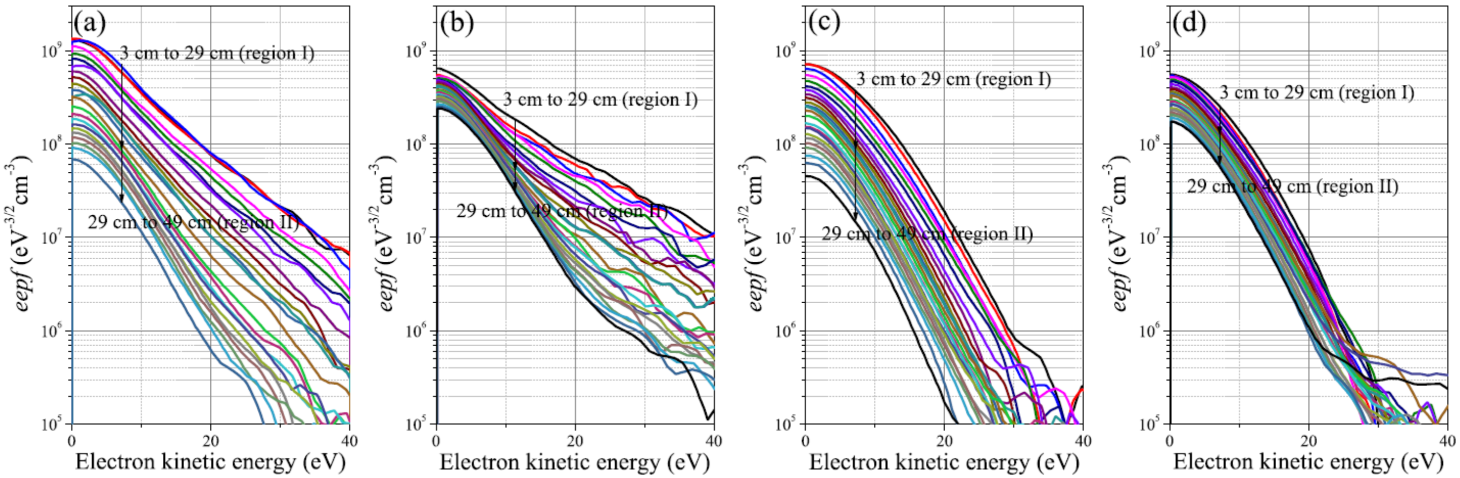






Electron thermodynamics in magnetic nozzle



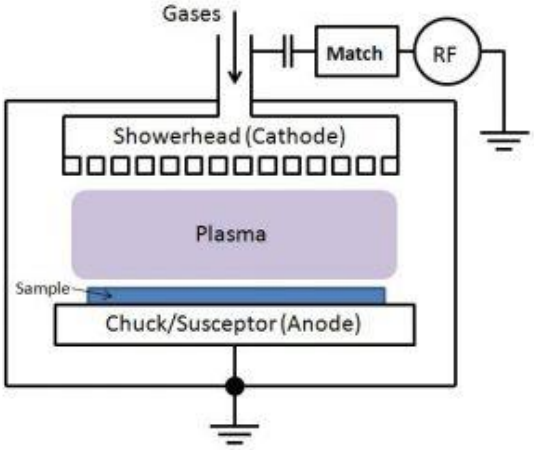


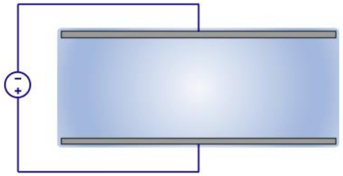
J. Y. Kim et al., New J. Phys. 20, 063033 (2018)

J. Y. Kim et al., PSST 28, 07LT01 (2019)

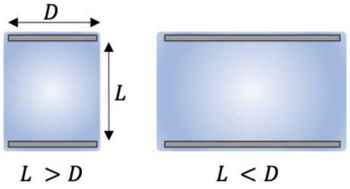
J. Y. Kim et al., Phys. Rev. E 104, 045202 (2021)

Arcing in DC or RF applications





DC discharge



주파수 효과

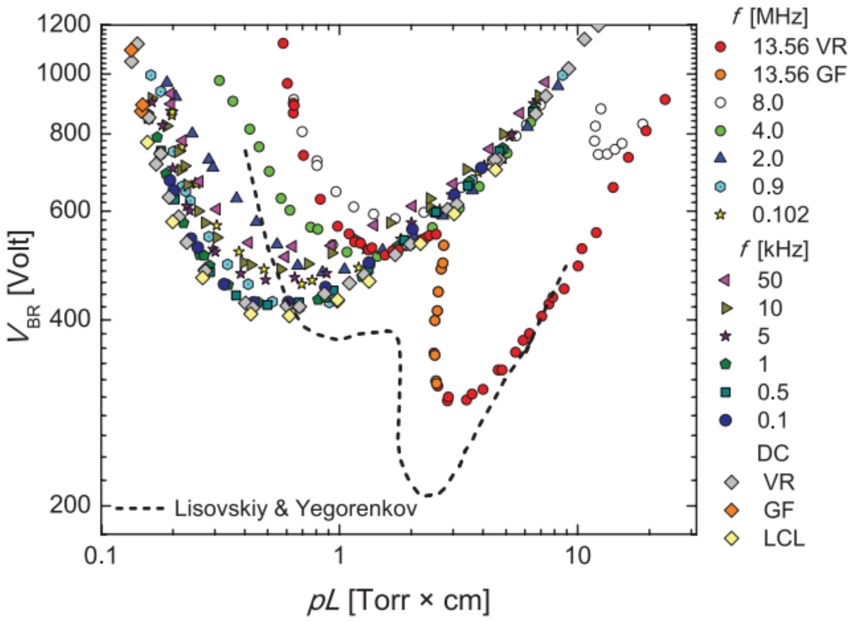
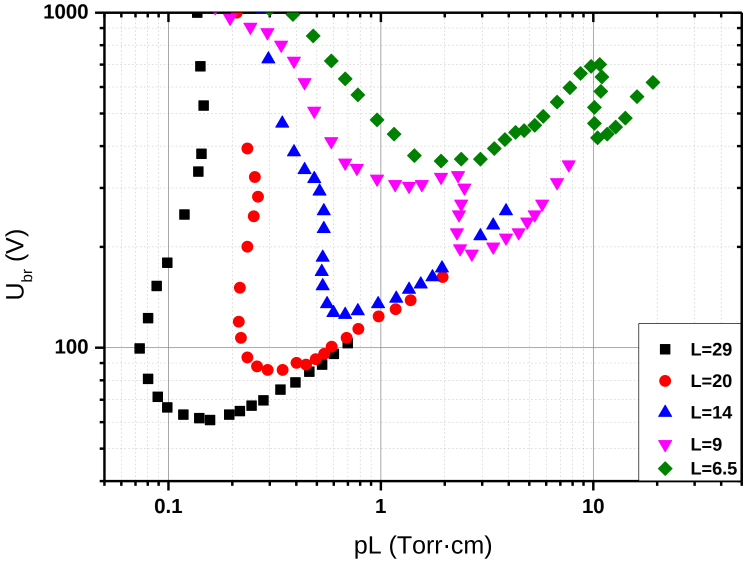


Figure 3. Breakdown voltages obtained in the experiments at different frequencies, including the limiting, dc, case (voltage ramp 'VR', gas filling 'GF' and low current limit 'LCL'). The dashed line shows the results of Lisovskiy and Yegorenkov presented in figure 2 of [5].

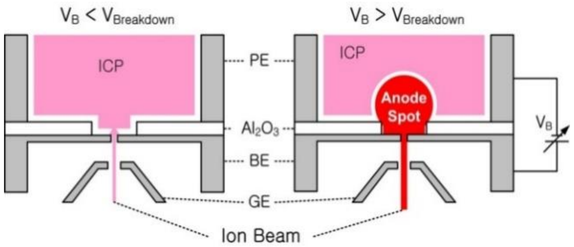
종횡비 효과

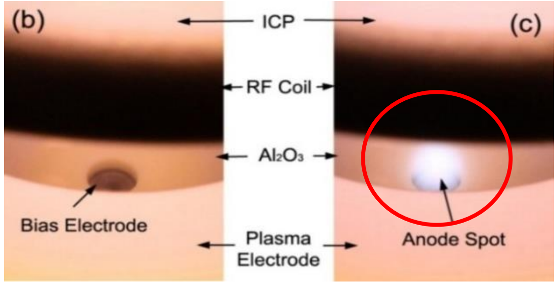


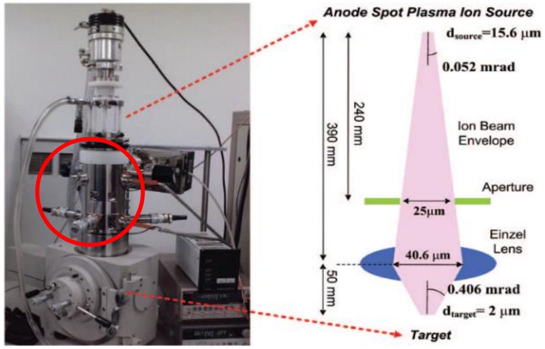
V. Losovskiy et al., J. Phys. D: Appl. Phys. 31, 3349 (1998)
I. Korolov et al., J. Phys. D: Appl. Phys. 47, 475202 (2014)

RF ion sources

RF ion source for FIB



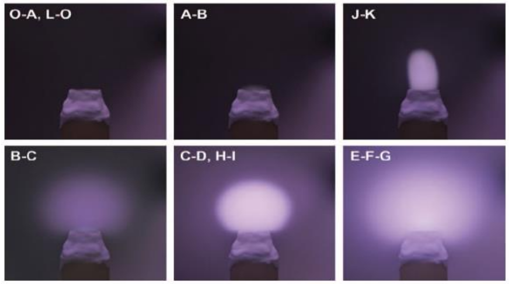




Y. S. Park et al., RSI 82, 123303 (2011)
Y. Lee et al., Curr. Appl. Phys. 15, 1599 (2015)

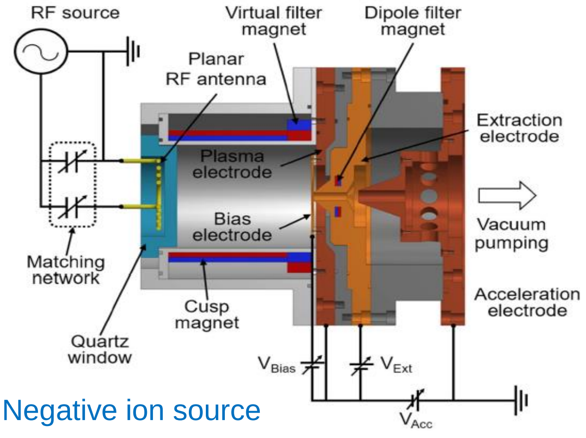
RF ion source for Nano-MEIS

	Multi-Cusp RF PIS	PIS with Anode Spot
Aperture Dia.	2 mm	0.5 mm
Power	1~1.4 kW (RF)	200 W (RF) + 40 W (DC)
Current	1,000 μA	1,000 μA
Curr. Density	32 mA/cm²	510 mA/cm²
Curr. Dens / Power	0.032 mA/cm²W	21 mA/cm²W



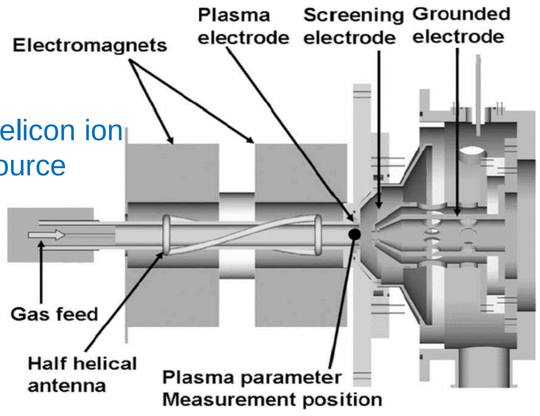
Y. S. Park et al., RSI 83, 02B313 (2012)
Y. S. Park et al., RSI 85, 02A508 (2014)

RF ion source for accelerator



Negative ion source

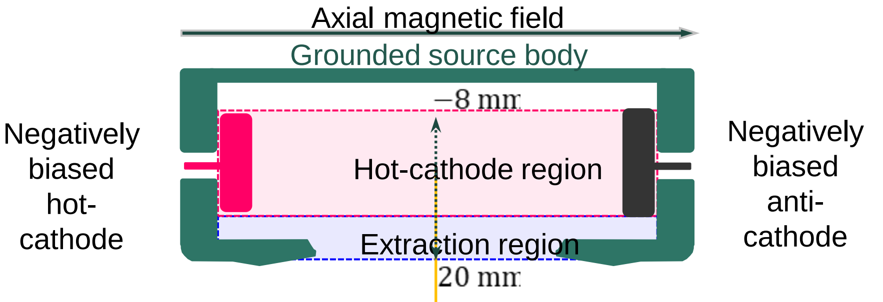
Helicon ion source



H. D. Jung et al., IEEE TPS 35, 1476 (2007)
K. J. Chung et al., RSI 85, 02B119 (2014)
K. J. Chung et al., New J. Phys. 18, 105006 (2016)

DC ion sources

Hot cathode PIG ion source for ion implanter



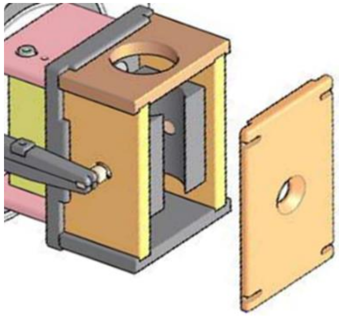
Axial magnetic field

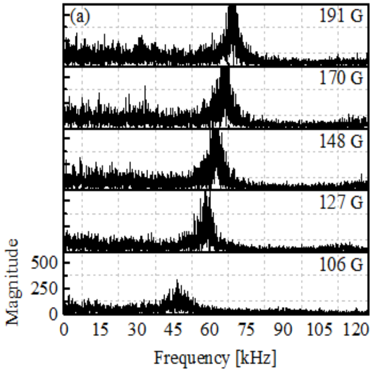
Grounded source body

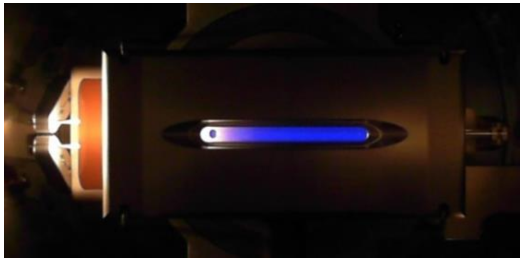
Negatively biased hot-cathode

Negatively biased anti-cathode

Radially movable Langmuir and Mach probe



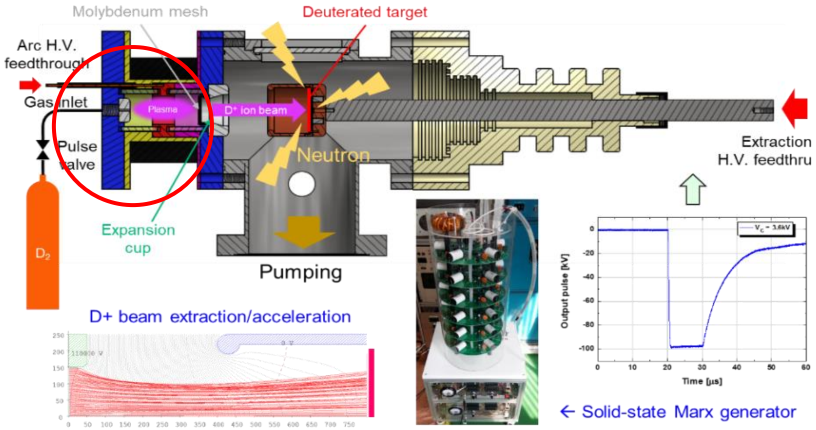




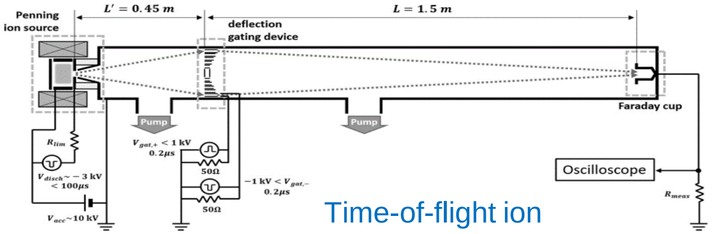
APPLIED MATERIALS®

J. Y. Kim et al., PSST 30, 025011 (2021)
J. Y. Kim et al., AIP Advances 11, 085113 (2021)

Cold cathode PIG ion source for accelerator

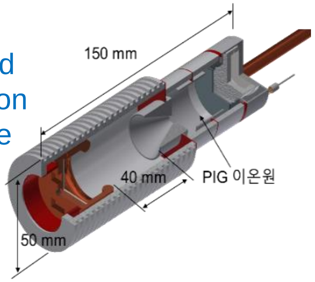


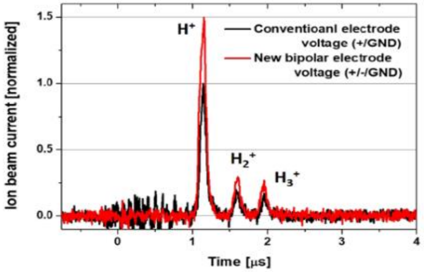
← Solid-state Marx generator



Time-of-flight ion mass spectrometer

Sealed tube ion source





K. Choi et al., RSI 90, 033305 (2019)