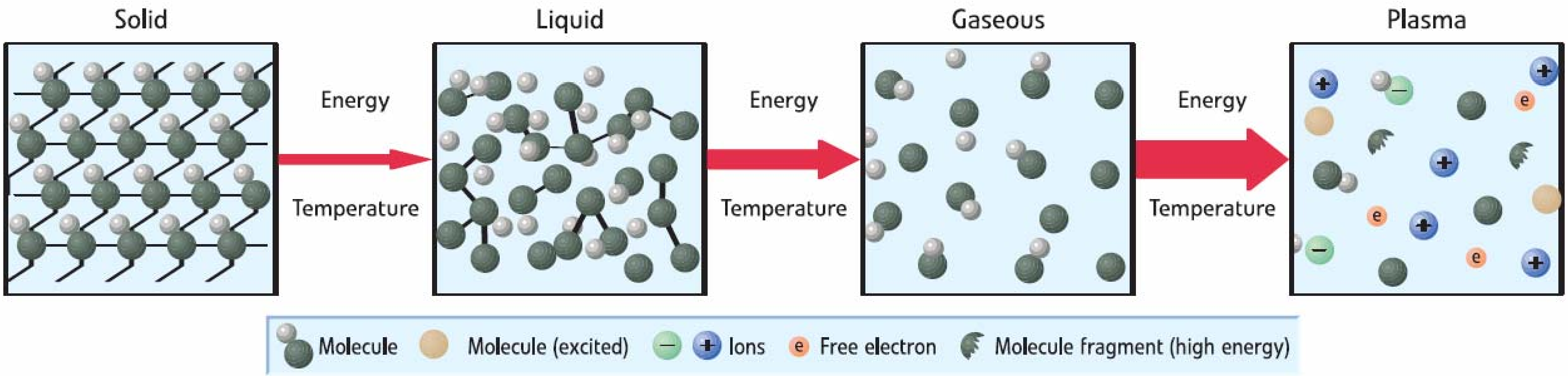
대기압 플라즈마 기술 및 응용

(Atmospheric Plasma Technology & Applications)

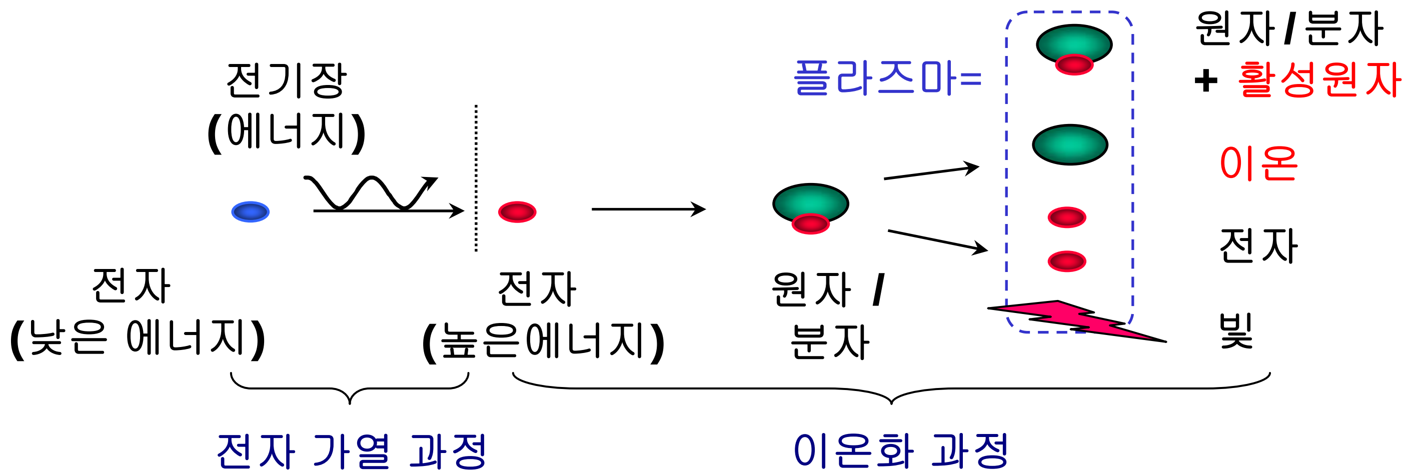
강원대학교

이원규

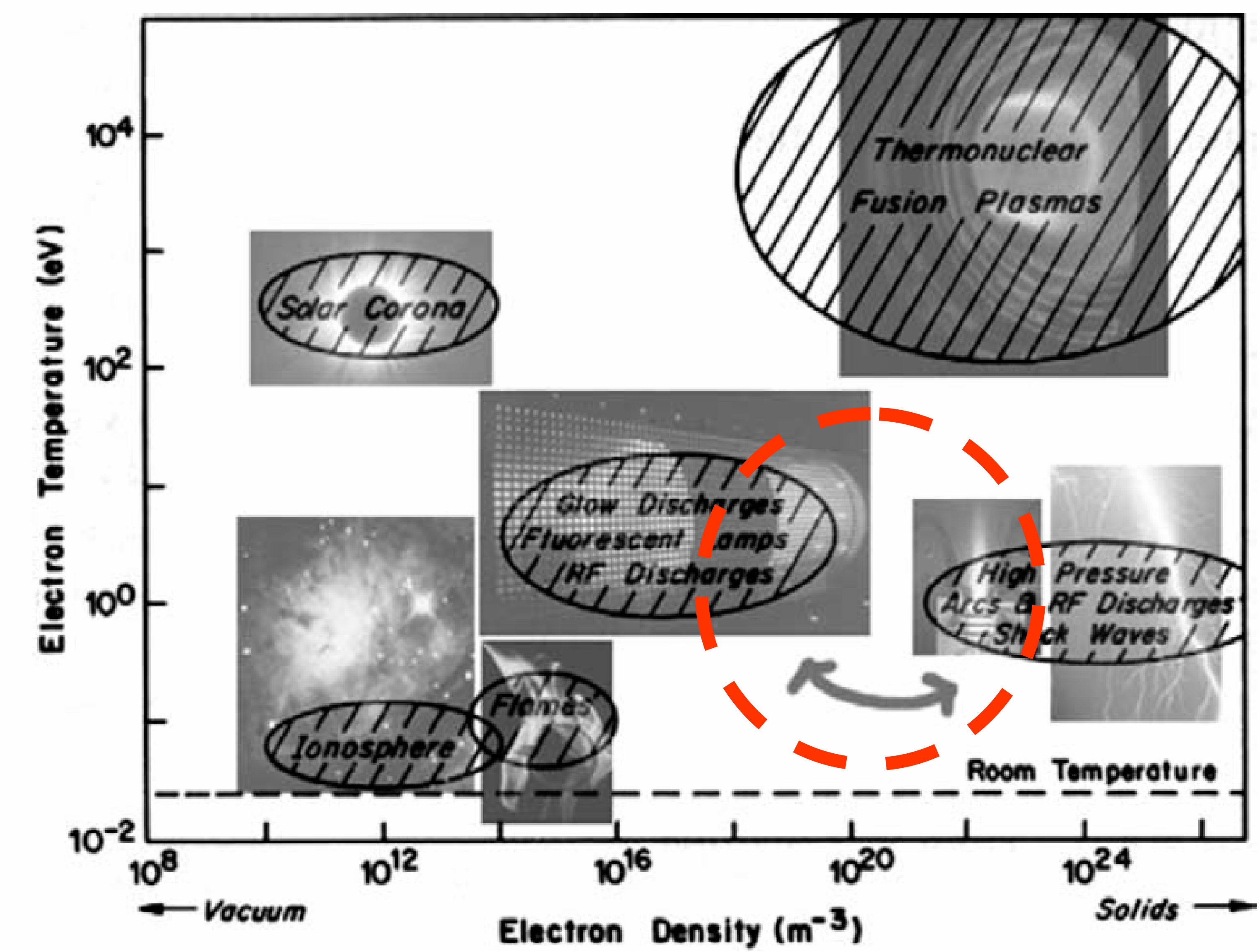
Plasma?



- 전기장에 의한 전자의 가속 및 충돌에 의해 원자 및 분자의 이온화



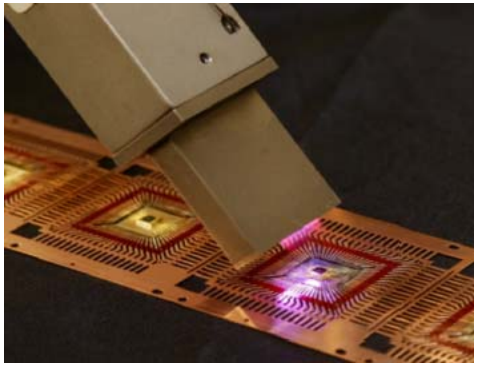
전자온도와 밀도에 따른 플라즈마의 분류

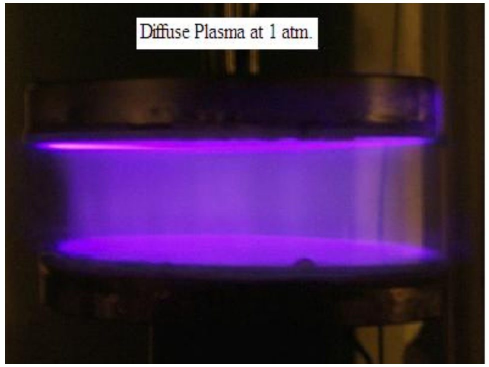


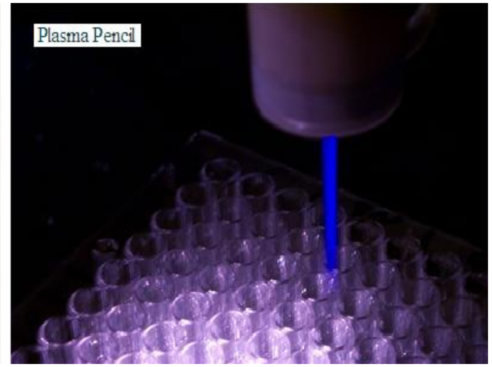
LTE 와 non-LTE Plasma의 비교

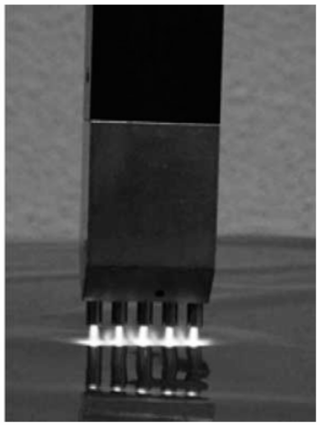
	LTE plasmas	Non-LTE plasmas
Current name	Thermal plasmas	Cold plasmas
Properties	$T_e = T_h$ High electron density: $10^{21} - 10^{26}\ m^{-3}$ Inelastic collisions between electrons and heavy particles create the plasma reactive species whereas elastic collisions heat the heavy particles (the electrons energy is thus consumed)	$T_e \gg T_h$ Lower electron density: $< 10^{19}\ m^{-3}$ Inelastic collisions between electrons and heavy particles induce the plasma chemistry. Heavy particles are slightly heated by a few elastic collisions (that is why the electrons energy remains very high)
Examples	Arc plasma (core) $T_e = T_h \approx 10{,}000$ K	Glow discharges $T_e \approx 10{,}000 - 100{,}000$ K $T_h \approx 300 - 1000$ K

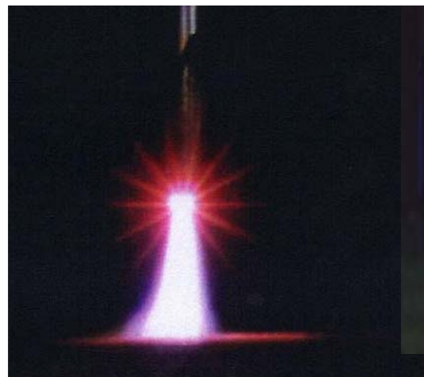
다양한 대기압 플라즈마 발생 장치들

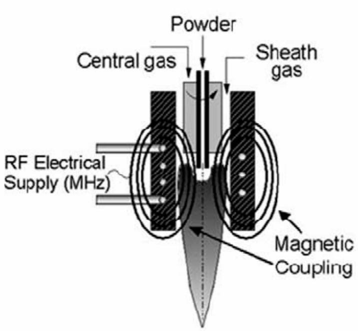










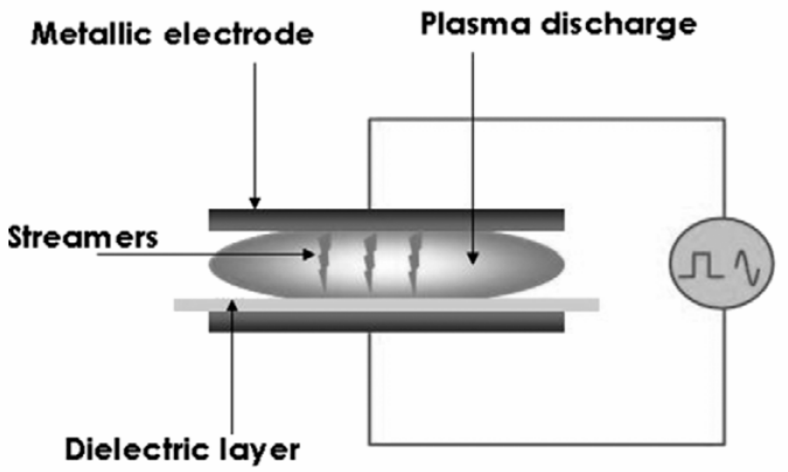


"Hot"과 "Cold" 대기압 플라즈마

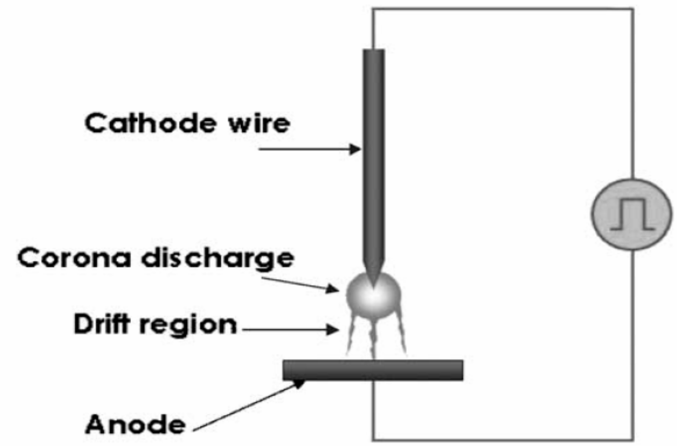
Atmospheric, "hot" (thermal) plasma for remelting	Atmospheric, "cold" (non thermal) Plasma for surface modification (close to room temperature)
Gas temperature: 1000℃ to 20000℃ Energy density: >10^6J/m^3 Usually isothermal, thermally induced emission of electrons	Gas temperature: <70℃ Energy density: usually <10^2J/m^3 Not isothermal Specific increase in the electron temperature through short-term gas discharge phases
After ignition: Continuous gas discharge, high current density	After ignition: Short-term, usually pulse-shaped gas discharge
Goal: Melting as much material as possible in a short time, high density	Goal: Surface modification without melting • Micro-cleaning: Removal of undefined adsorbates • Wetting: Changing the surface morphology (changing the chemical composition of the top atom layers) • Cross-linking: Stabilization of the material properties on a surface
Source: Arc torch, ICP	Source: DBD, Low T Plasma jet, Corona

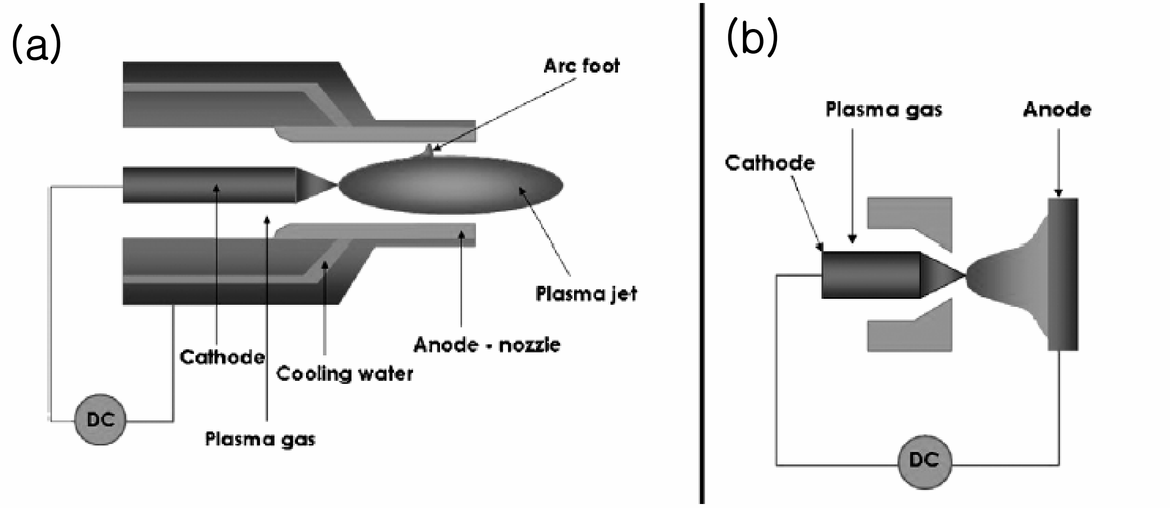
대기압 플라즈마 소스

Dielectric Barrier Discharge (DBD) Type



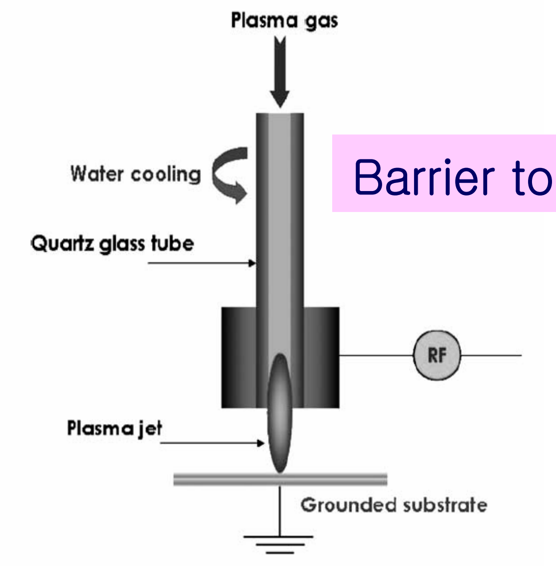
Corona Discharge Type



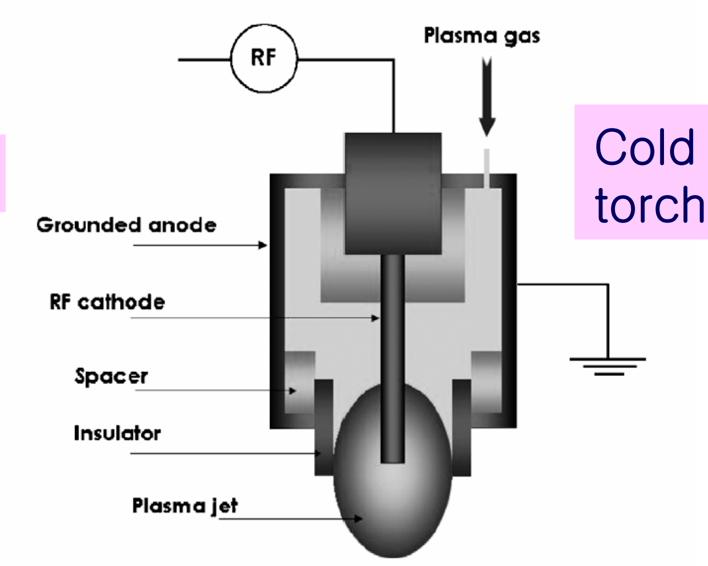


Arc Plasma Torches
(a) current-carrying
(b) Transferred

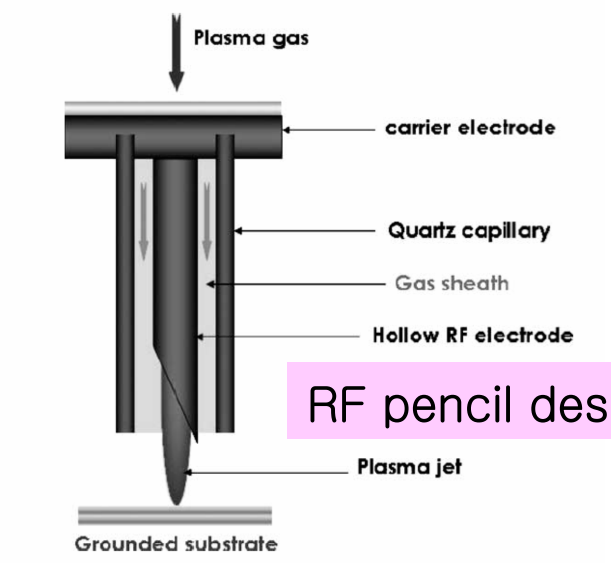
다양한 형태의 대기압 **Plasma Jet**형 장치설계



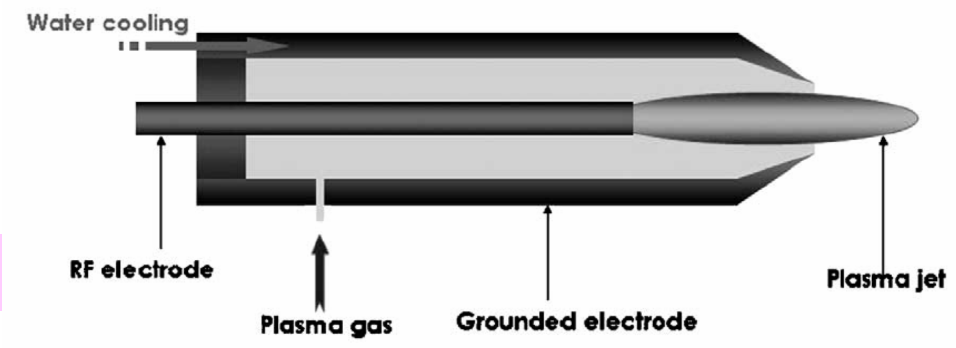
Barrier torch design



Cold plasma torch design



RF pencil design



APPJ design

산업적으로 응용되는 대기압 플라즈마의 특성

에너지 구조형태

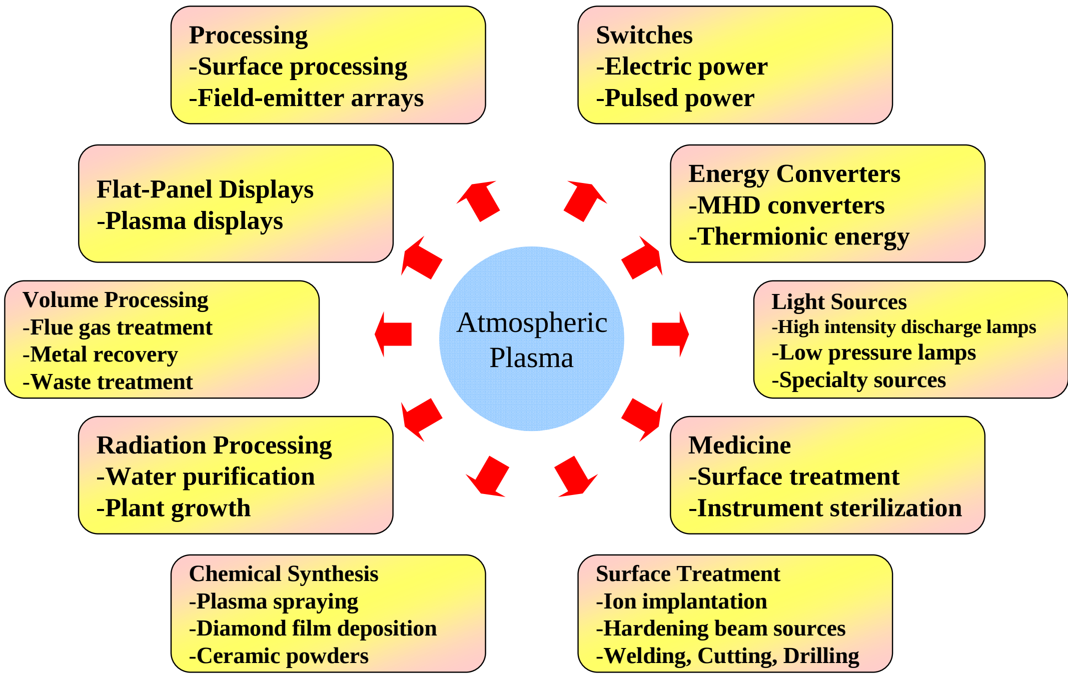
Excitation	Source	Plasma properties	Operating conditions
Industrialized sources			
DC/Low frequency	Arc torch	$T_e = T_h \approx 8000-14,000$ K[s] $n_e = 10^{21}-10^{26}$ m^{-3}	Gas: Ar /He Gas flow: 10–150 slm Power: 10–100 kW
	Plasmatreat®	$T_h < 700$ K	Gas: air Gas flow: 117 slm
Pulsed DC/Low frequency	Corona	$T_e = 40,000-60,000$ K $T_h < 400$ K $n_e = 10^{15}-10^{19}$ m^{-3}	Gas: air
	DBD	$T_e = 10,000-100,000$ K[m] $T_h < 700$ K $n_e \approx 10^{18}-10^{21}$ m^{-3}	Some 100 W Plasma gas: 5–40 slm
Radio frequency	ICP	$T_e = T_h = 6000-11,000$ K[s] $n_e = 10^{21}-10^{26}$ m^{-3}	Gas: Ar/He Gas flow: 10–200 slm Power: 50–700 kW
Pulsed radio frequency	IST	$T_h < 400$ K	Gas: surrounding air No gas flow Power: 20 kW
Microwave	Cyrannus	$T_h < 700$K	Gas: Ar/O_2 Power: 6 kW

다양한 형태의 대기압 플라즈마 소스들이 연구되고 있음

저압과 대기압 플라즈마의 비교 및 응용분야

일반적으로 평형(열)플라즈마와 비평형(저온)플라즈마로 구분하며
산업적응용에는 저온플라즈마가 대다수 적용됨

	저온 저압 플라즈마	저온 대기압 플라즈마
공정온도	상온~70℃	상온~70℃
공정압력	수백 mTorr 이하	760mTorr(대기압) 부근
진공장치	필요	필요없음
표면처리 능력	우수	우수
플라즈마 발생용이성	비교적 용이	플라즈마 발생기의 정밀 설계필요
환경보호	우수	우수
장치가격	높음	낮음



대기압 플라즈마의 표면처리 응용

- 표면활성 에너지가 낮은 재료의 접착력 향상
- 친환경적 공정
- 표면손상의 최소화
- 상대적 저 원가 가능

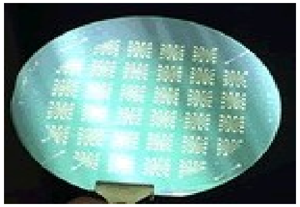
표면 개질 기술 활용

- 고분자의 표면 접착력 향상
  - **- PTFE, PP, PVDF, PI**
- 첨단 정보 통신 분야 소재
  - **- PTFE/Flexible PCB, PTFE MLB**
- 복합소재 분야
  - - 고분자/고분자, 고분자/금속
- 의료/환경 분야
  - - 인공장기, 배양접시, 환경 정화장치

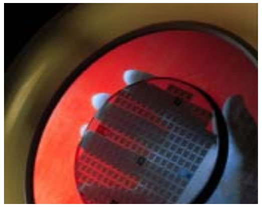
LCD

인쇄기판**(PCB)**

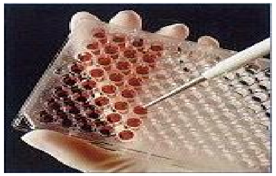
유기**EL**



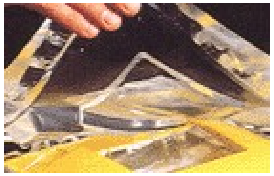
반도체



의료 소재



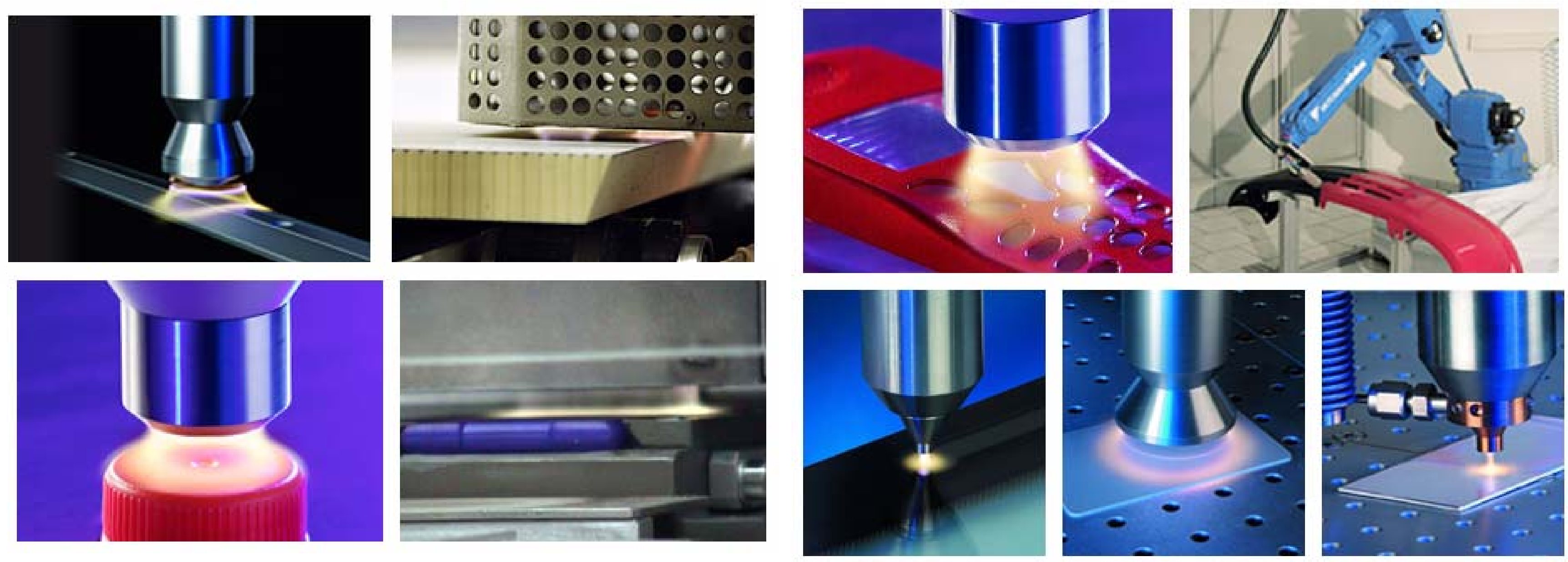
고분자 소재

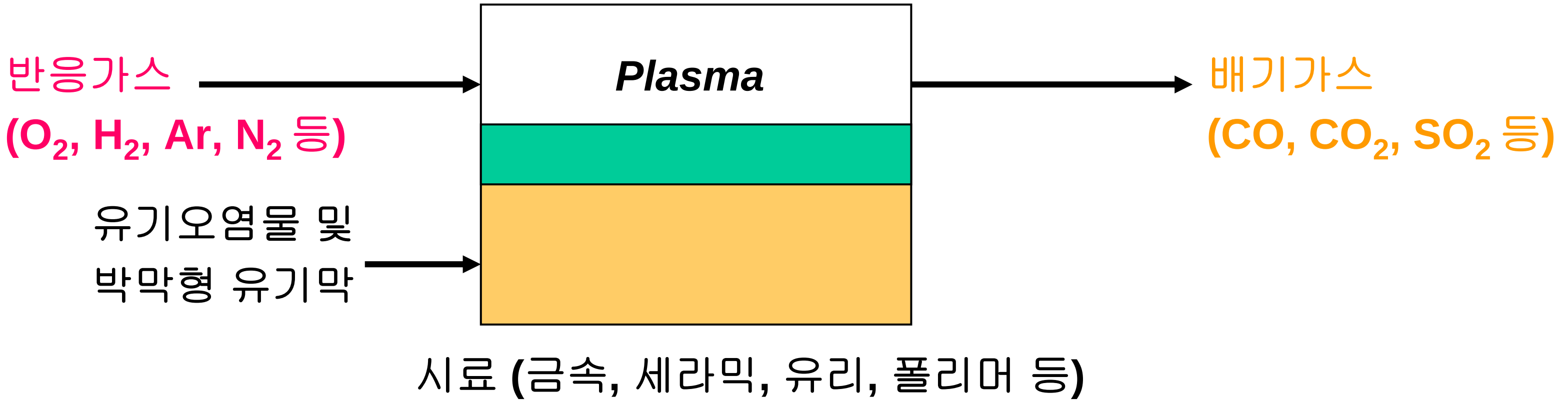


섬유

고무

다양한 표면에서의 대기압 플라즈마 처리

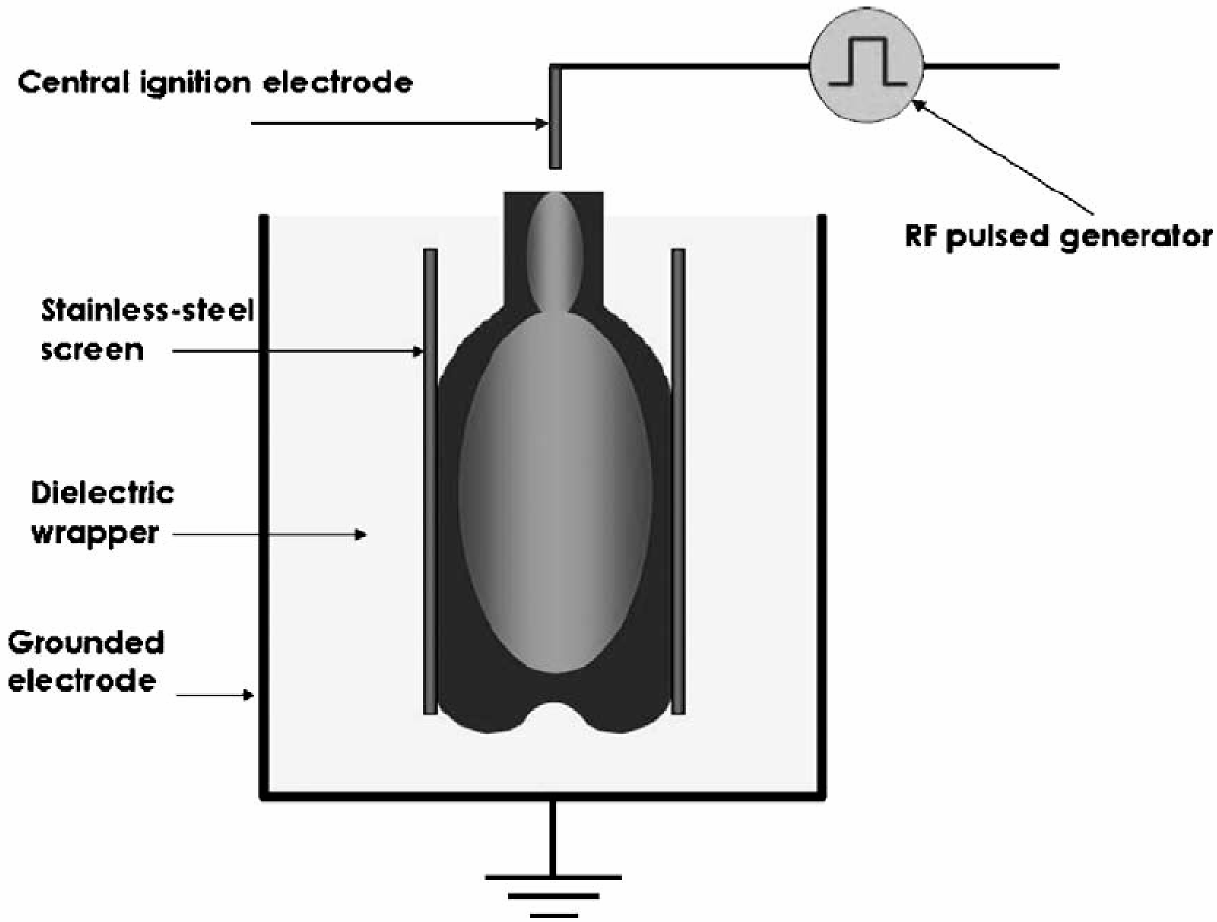




대기압 플라즈마의 표면세정 응용

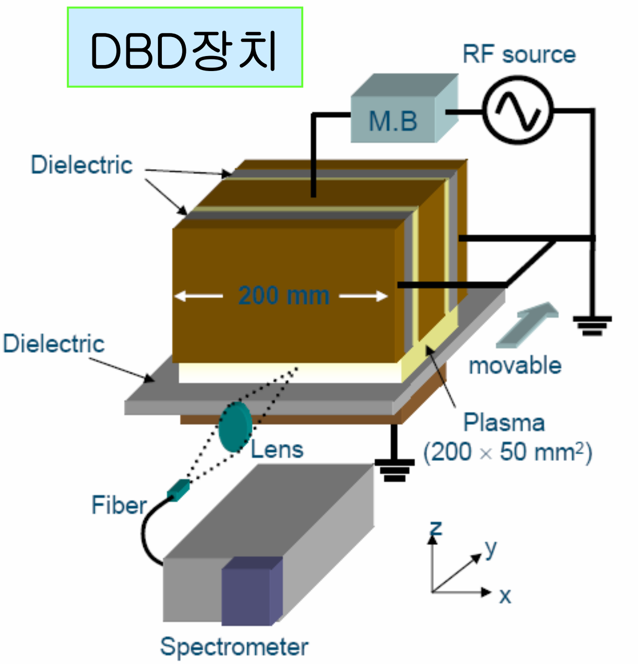
Excitation	Source	Contaminant (substrate)	Plasma	Treatment duration	Observations
Low frequency	DBD	Ag2S (Ag)	Ar	180 s	Ag_2S layer is removed
		Oil (Al, Si)	Air, O_2	A few sec	Lubricant is totally removed if the plasma gas flow rate is low (1–5 slm). With a high flow rate, polymerization of the oil occurs Plasma cleaning is more efficient in air than in O_2: importance of the metastable N_2 species
		Fe_2O_3 (Fe)	Ar/N_2	60 s	Surface is cleaned Complete cleaning mechanism is not yet established: it is different from a simple etching mechanism by nitrogen active species)
Pulsed low frequency	Glow DBD	Oil (Fe)	O_2	10 min	Oil is removed DBD is as efficient for oil removal as ultrasonic cleaning in acetone
Radio frequency	Plasma pencil	Corrosion (archeological metal artifacts)	Ar	30 s	Reduction of the corrosion products on antique metallic artifacts The object is immersed in a chemically reactive liquid in order to combine the efficiency of the plasma treatment and the selectivity of the chemical processes
	APPJ	Biological, chemical agents (glass)	He/O_2	30 s	Neutralization of chemical and biological agents (e.g. mustards, anthrax) APPJ operates at low temperature and does not generate harmful or toxic products: thus it is suitable for rapid decontamination of material and safe for personnel
Pulsed radio frequency	IST system	Micro-organism (PET bottle)	Air	15 ms	Sterilization and deodorization inside PET bottles No damage (mechanical, thermal) on the surface Industrial process: 36,000 bottles per hour
Semi-metallic microwave torch	MPT	Fe_2O_3 (Fe)	He, Ne, Ar	120 s	Surface is cleaned: FeOOH groups are completely removed. Importance effect of metastable species for breaking bounds Negligible influence of the temperature and the UV photons on cleaning
	Sugiyama and al torch	Iron oxide (Fe)	Ar/H_2	15 s	Oxide layer is removed but the surface is slightly damaged

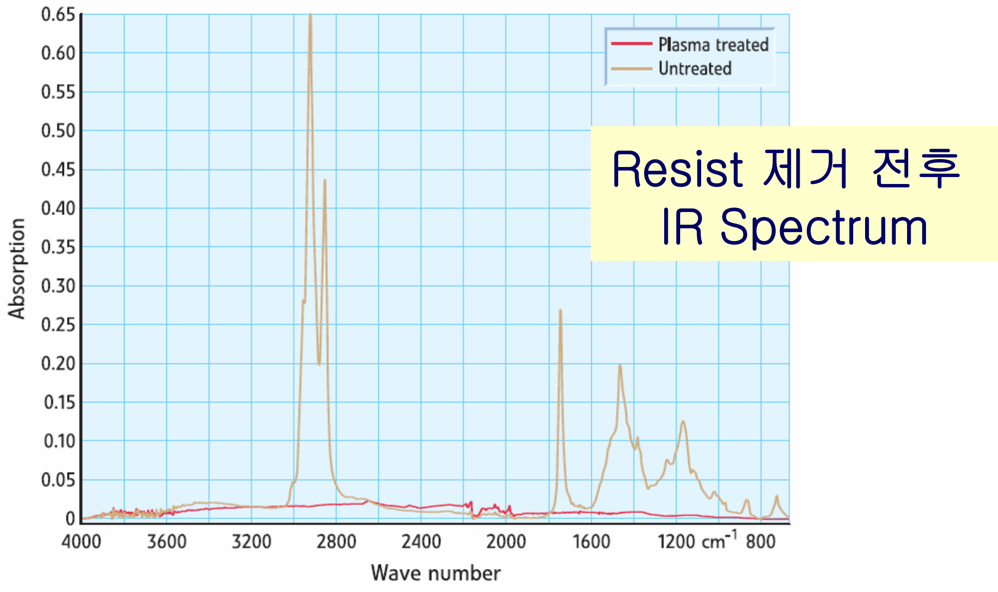
Sterilization & Deodorization inside PET Bottles

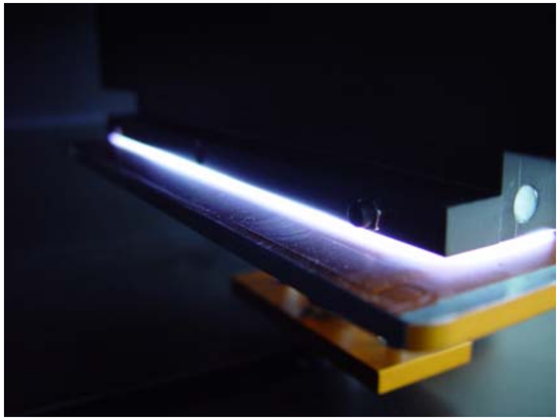


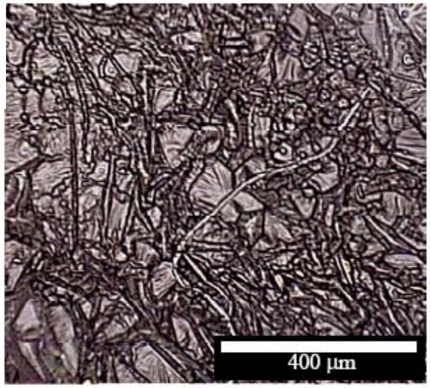
- The IST society has developed an RF pulsed discharge to decontaminate the interior of plastic bottles
- The process is the DBD adaption to the complex surfaces treatment

대기압 플라즈마의 유기물 제거(반도체공정 적용 예)

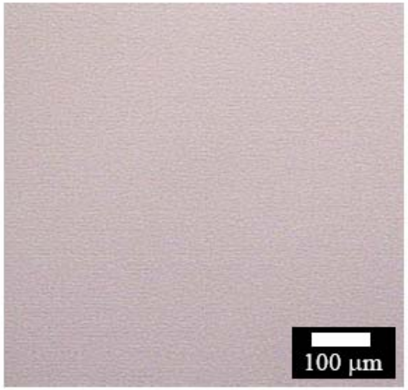








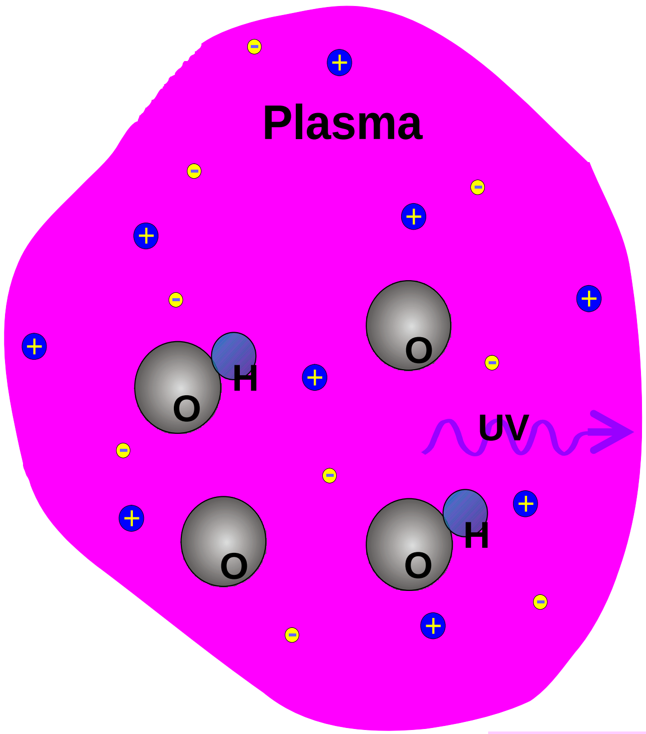
APP



Popped resist film after P dose of $1x10^{16}$ cm^{-3} at 30 keV, and heating to 150 °C.

The same sample after stripping the ion implanted resist with Surfx's plasma process.

대기압 플라즈마를 이용한 의료용 멸균(1)



Atmospheric plasma can have:

- **Energetic charged particles**
- **UV radiation emission**
- **Heat**
- ***Radicals O, OH***

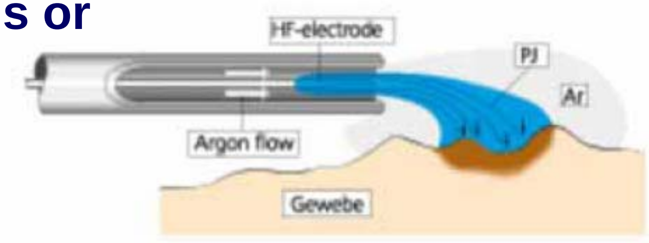
Ozone density in atmospheric plasma discharges

Excitation	Source	Ozone density (cm^{-3})
DC	Arc plasma torch	$<10^{10}$
Pulsed DC	Corona	10^{18}
Low frequency	DBD	10^{18}
RF	APPJ	10^{16}

대기압 플라즈마를 이용한 의료용 멸균(2)

(1) Plasma needle:

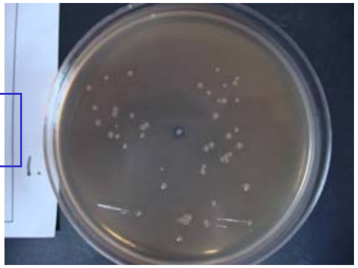
- **a low-power atmospheric plasma jet**
- **proposed for using in sterilizing teeth and treating burns or wounds on skin**

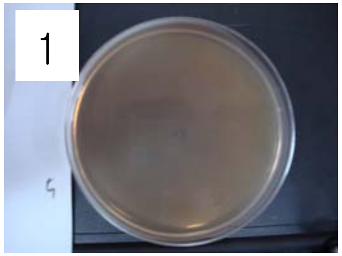


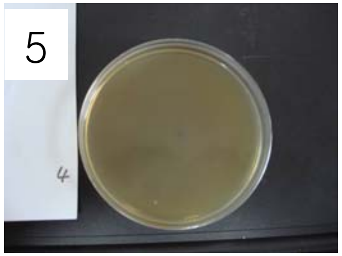
(2) DBD :

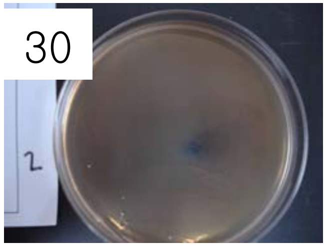
- **sterilization of E-coli**
- **Ar plasma**
- **can kill E-Coli under the short exposure**

Control









대기압 플라즈마 처리 조건
Ar 유량 : 5LPM
처리시간 : 1, 5, 30분
플라즈마 발생원과의 거리 : 3cm

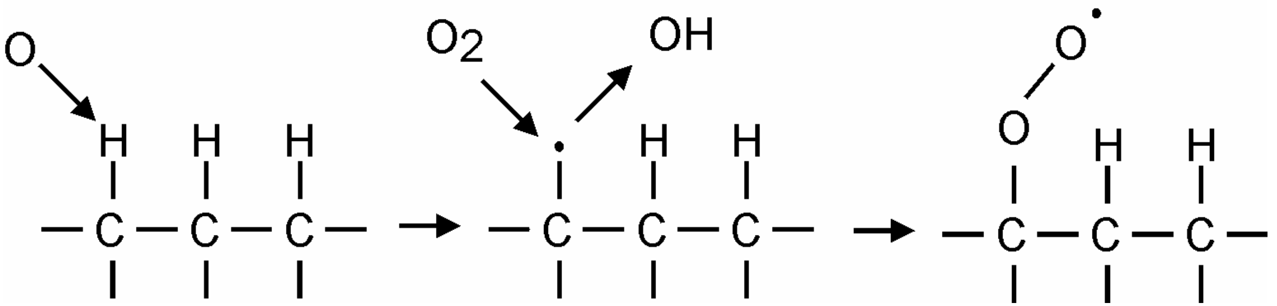
대기압 플라즈마의 표면 활성화 응용

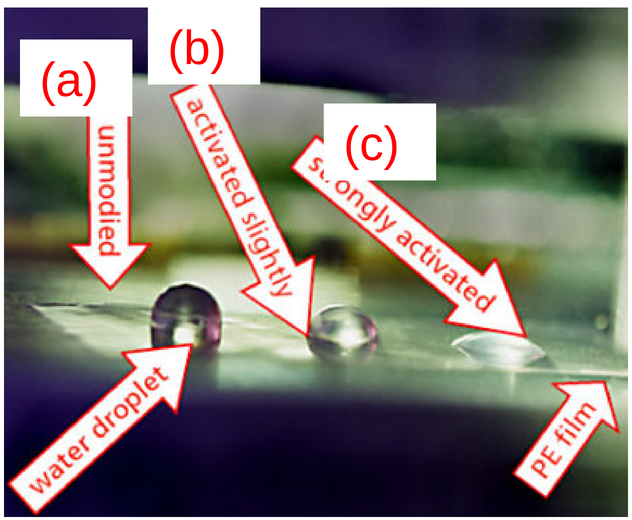
Excitation	Source	Plasma	Substrate	Observations
Pulsed DC	Corona	Air	PP (E: 26 mJ m^{-2})	Increase in PP surface energy: 43 mJ m^{-2} Surface energy value remains stable during 100 days
Low frequency	DBD	He	PP (E: 26 mJ m^{-2})	Activation efficiency depends on the discharge mode Filamentary discharge increases the PP surface energy value to 45 mJ m^{-2} Values as high as 62 mJ m^{-2} are obtained with a glow discharge Improvement of wettability is due to O implantation and N atoms density at the PP surface O comes from impurities in the plasma gas (N_2, H_2O) that are excited, ionized by highly energetic He metastable species
	Aldyne™	Gas mixture based on N_2	PP (E: 26 mJ m^{-2})	Increase in PP surface energy: 60 mJ m^{-2} Surface energy value remains stable during 100 days
	AcXys	Air	PP (θ: 95°)	Decrease in water contact angle: 25° Contact angle value remains stable over 3 weeks
	Plasmatreat	Air	PP (E: 26 mJ m^{-2})	Increase in PP surface energy: 56 mJ m^{-2} Improvement of wettability due to the increase of oxygen concentration and the changes of the topology substrate surface induced by the thermal component of the plasma
Radio frequency	HELIOS	Air/Ne	PE (E: 33 mJ m^{-2})	Increase in PE surface energy: 57 mJ m^{-2} Dehydrogenation + C=C bonds formation (FTIR) Uniformity of the activation over 20 cm^2
Semi-metallic microwave torch	Sugiyama and al. torch	Ar/O_2	PP (θ: 100°)	Decrease in water contact angle: 80° CO, O–CO–O bounds formation (XPS)
		Ar/CF_4		Increase in water contact angle: 125° CF, CF_2, C-CF_n, CF-CF_n bounds formation (XPS)

고분자 표면의 기능성화

- **Functionalization occurs by the chemical interaction of plasma produced species - ions, radicals and photons with the surface.**

$$e + O_2 \rightarrow O + O + e$$

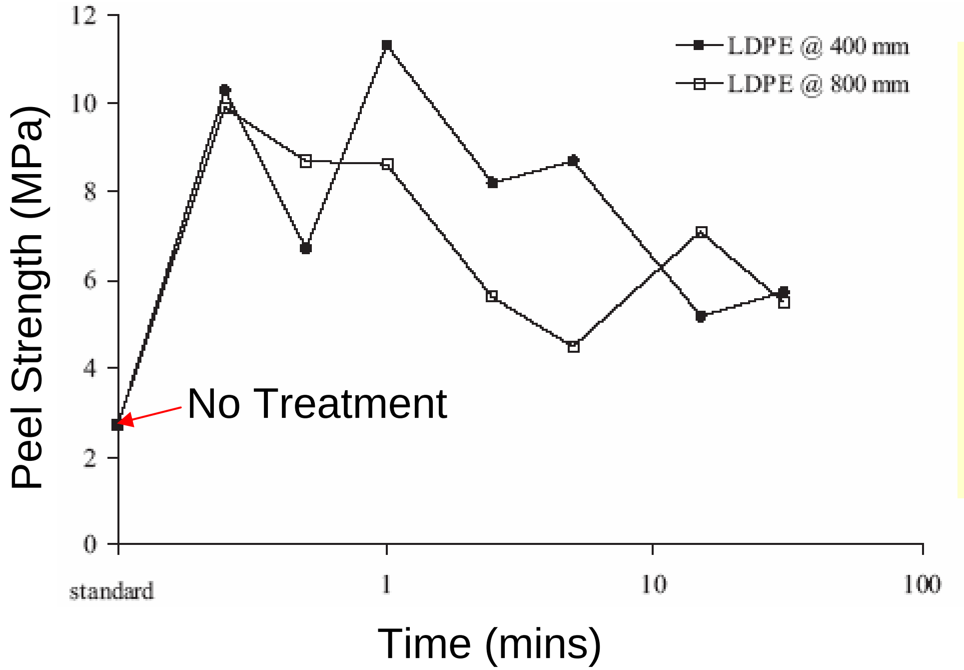




- **Chemical groups are incorporated onto the surface which change surface properties.**
- **Process usually only treats the top mono-layers not affecting the bulk.**

Wettability on PE film with 3 zones of treatment: a)untreated b)slightly treated c) strongly treated.

접척력 향상을 위한 대기압 플라즈마 처리 결과



- **Adhesion strength of PE improves by a factor of 2-3 within a few seconds of treatment in a plasma.**
- **Adhesion shows some atmospheric degradation indicating long term reactivity.**

- **Peel strength of Polyethylene (PE) downstream of an atmospheric pressure air non-equilibrium discharge.**

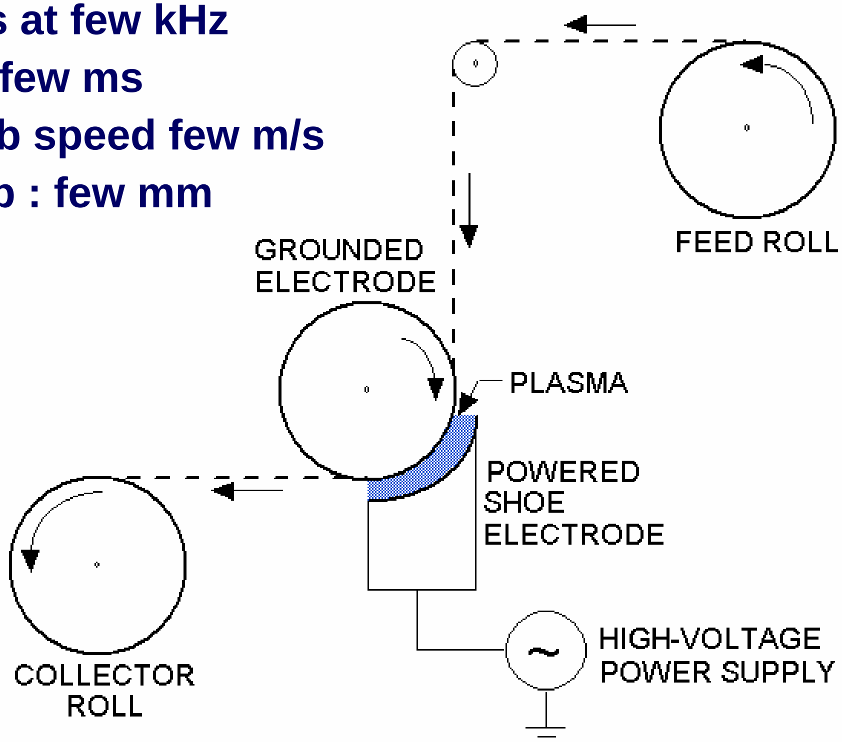
M.J. Shenton et al, J. Phys D. 34, 2754 (2001)

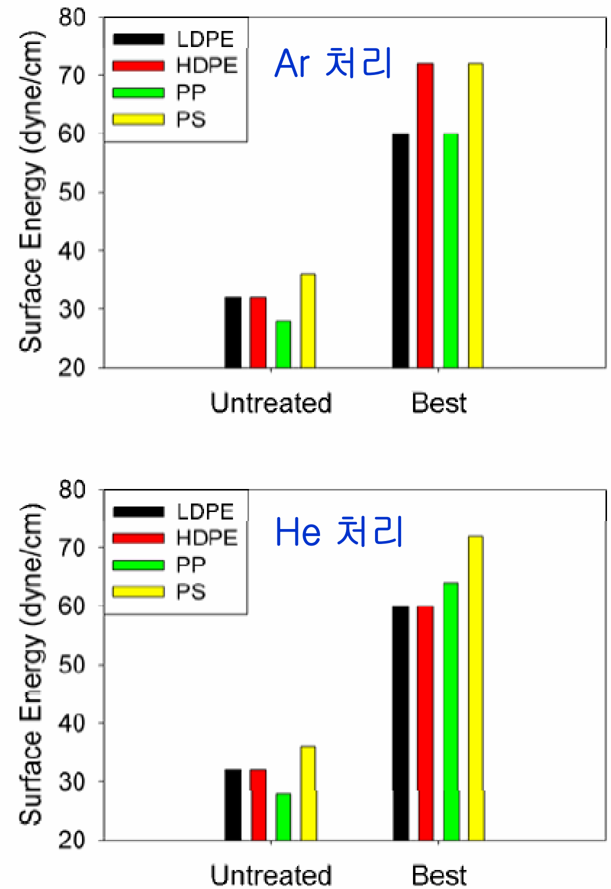
고분자 표면개질을 위한 공업적 처리

- **Pulsed atmospheric filamentary discharges (coronas) are routinely used to web treat commodity polymers like polypropylene (PP) and polyethylene (PE).**

TYPICAL CONDITIONS

- **kVs at few kHz**
- **τ ~ few ms**
- **Web speed few m/s**
- **Gap : few mm**



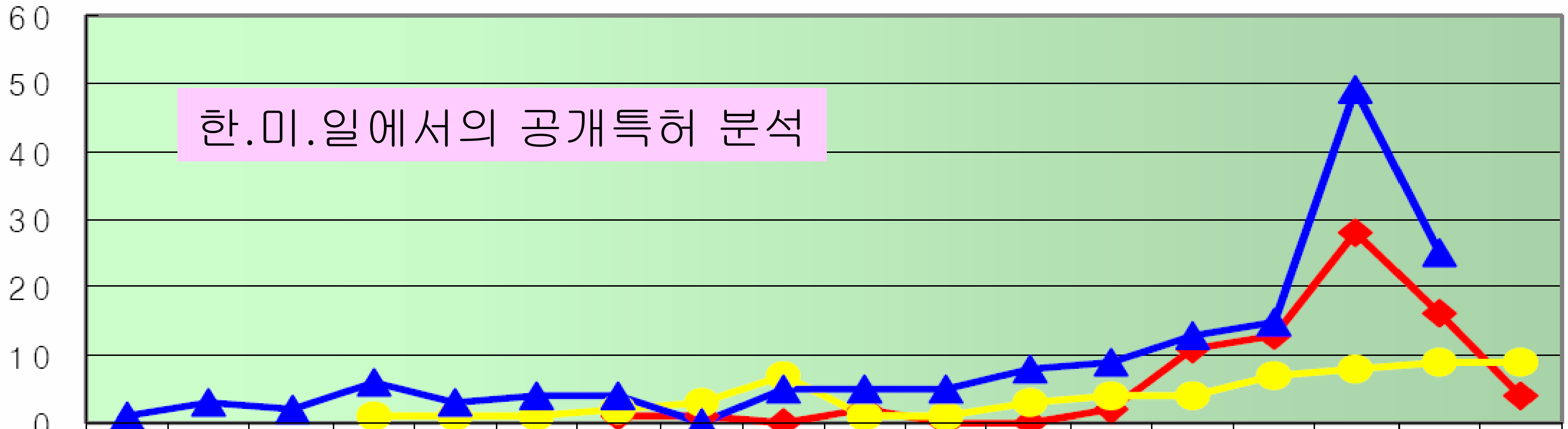


대기압 플라즈마 처리 후
고분자들의 표면특성변화

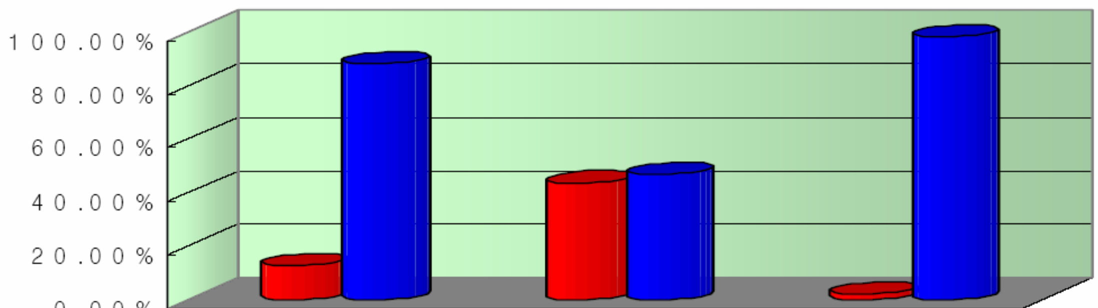
산업적 응용을 위한 대기압 플라즈마 장치 분석

Excitation	Source	Applications	Advantages	Limits
DC	Arc plasma torch	Coatings (APS) Machining Toxic waste treatment Powder treatment Lamps	Can be adapted to a robot Complex surfaces treatment High deposition rate, thick coatings, wide range of deposited materials	Noise, powder emission, radiations Cathode erosion Various parameters make the process control difficult
RF	ICP torch	Spectroscopic analysis Coatings (TPCVD) Toxic waste treatment Powder treatment	Can work with very high power No electrode Complex surfaces treatment	Noise, powder emission, radiations Not easy maneuverable: the substrate has to move
Pulsed DC	Corona	Ozone production Surface activation	Complex surfaces treatment Easy handling	Inhomogeneous treatment Surface can be damaged
Low frequency	DBD	Ozone production Surface activation, cleaning	Treatment of large plane surfaces Easy to handle	Problems of stability (deposition on the electrode) Gap size limits the thickness of the treated piece
	Plasma treat®	Surface cleaning, activation	Multi-nozzle system Complex surfaces treatment Can be adapted to a robot	High flow rate Not enough energy to remove oil
	AcXys	Surface activation, cleaning	Treatment of large surfaces, complex pieces Can be adapted to a robot	High flow rate Not enough energy to remove oil
Pulsed radio frequency	IST	Sterilization, deodorization	Fast treatment of complex surfaces 36,000 bottles per hour Reduced cost comparing to other sterilization methods	–
Microwave	Cyrannus®	Cleaning and activation of polymer surfaces	Stable and homogeneous discharge Complex surfaces treatment	The quartz tube diameter limits the size of the treated surface The closed design avoids direct integration to production lines

대기압 플라즈마 기술관련 특허동향



	1986	1988	1989	1990	1991	1992	1993	1994	1995	1996	1997	1998	1999	2000	2001	2002	2003	2004
한국							1	1	0	2	0	0	2	11	13	28	16	4
미국				1	1	1	2	3	7	1	1	3	4	4	7	8	9	9
일본	1	3	2	6	3	4	4	0	5	5	5	8	9	13	15	49	25	



	한 국	미 국	일 본
외 국	12.60%	43.50%	2%
내 국	87.80%	46.50%	98%

나라별 출원인의 국적 분류