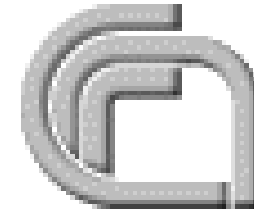




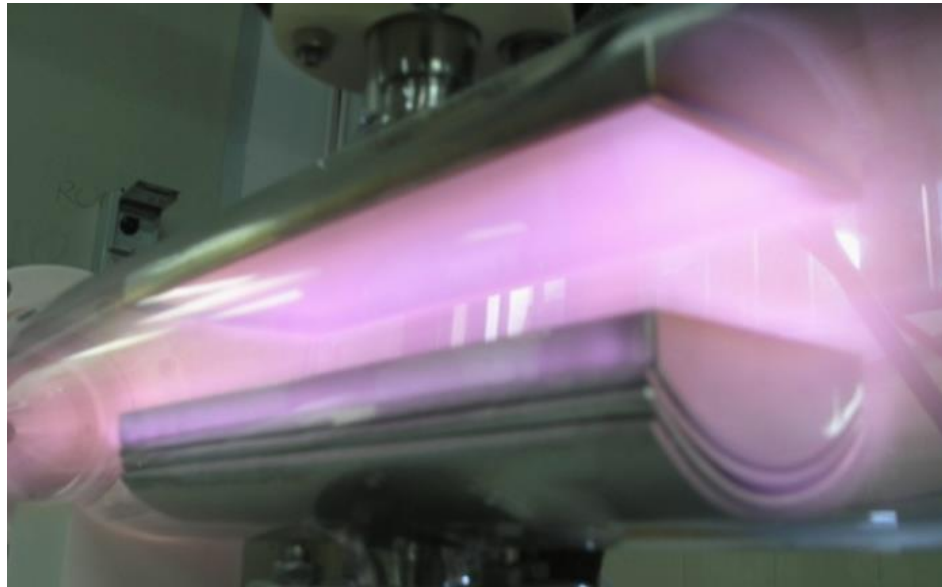
*Department of Chemistry  
University of Bari "Aldo Moro"  
ITALY*

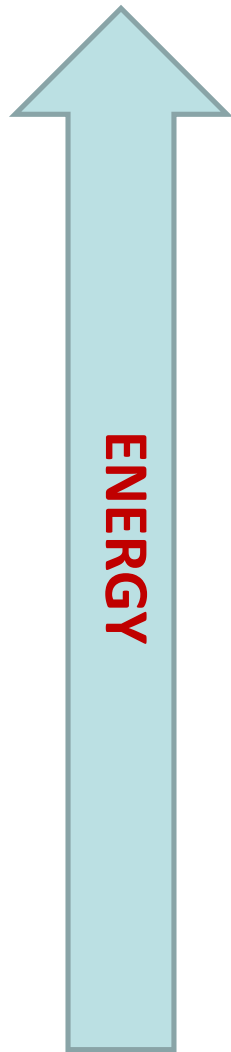
# chimica inorganica industriale PROCESSI INDUSTRIALI VIA PLASMA



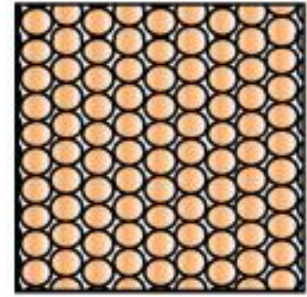
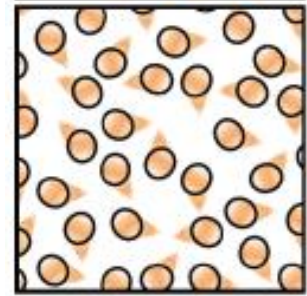
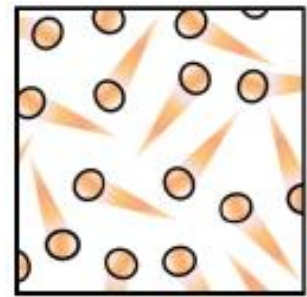
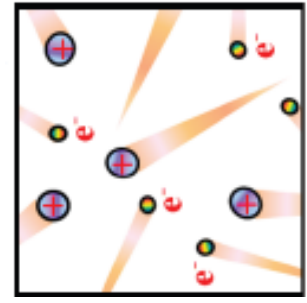
*Institute of Nanotechnology  
CNR NANOTEC Bari  
ITALY*

**PIETRO FAVIA**  
080 5443430  
[pietro.favia@uniba.it](mailto:pietro.favia@uniba.it)





partially ionized gas  
electrically neutral

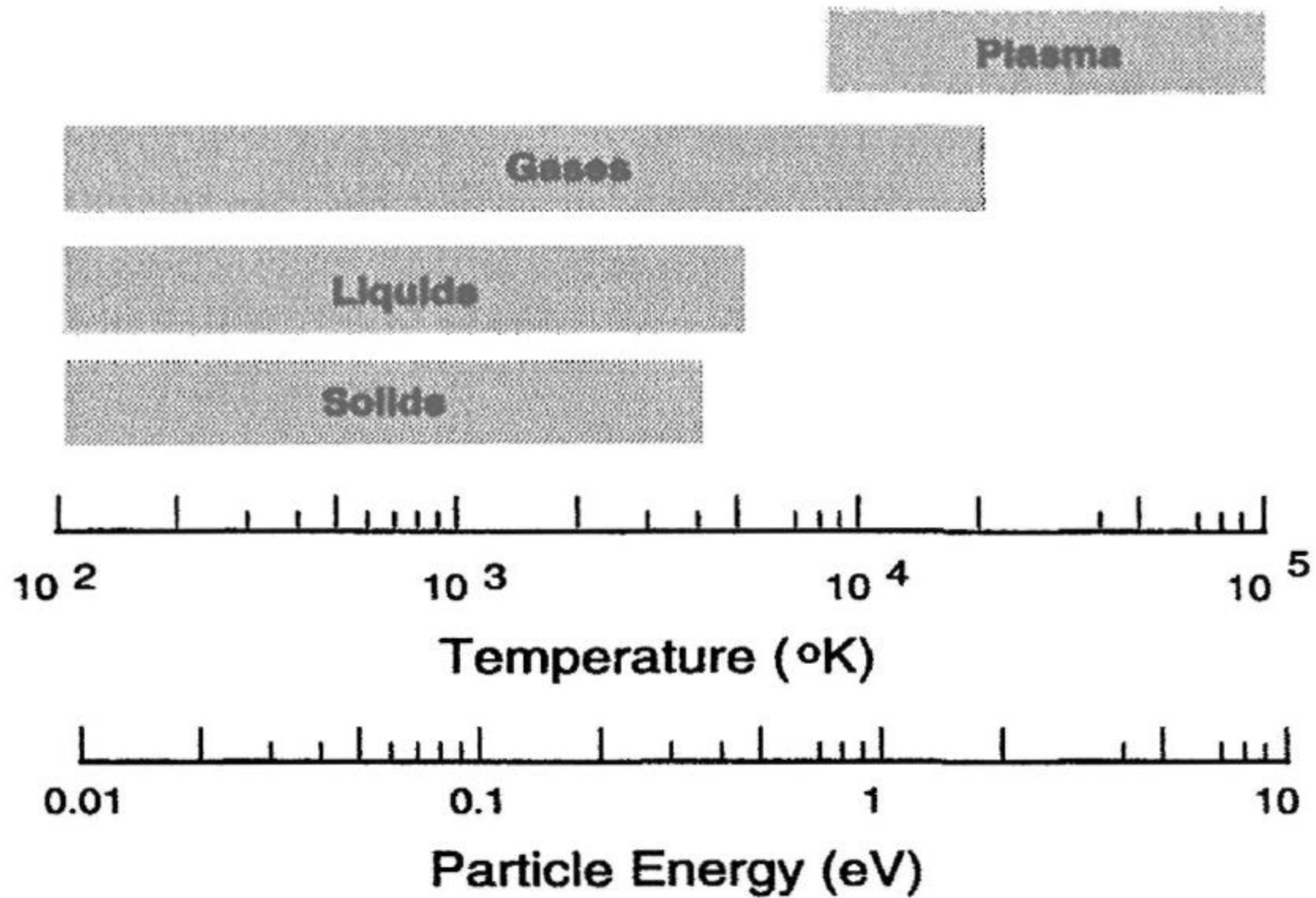


**SURFACES**  
interphase zones  
between different phases

**COLLOIDS**  
dispersions of matter  
among phases  
large surface/volume ratio

**THERMAL PLASMAS**  
(thermodynamic equilibrium)  
Atm Pressure

**COLD PLASMAS**  
(non equilibrium)  
Low/Atm Pressure



**Fig. 1-1** State of matter versus temperature.

1928

## I. LANGMUIR INTRODUCES THE WORD “PLASMA”

I. Langmuir, *Oscillations in Ionized Gases*  
Proc. Nat. Acad. Sci. 14, 627, Aug 1928

“Except near the electrodes, where there are sheaths containing very few electrons, the ionized gas contains ions and electrons in about equal numbers, so that the resultant space charge is very small. We shall use the name plasma to describe this region containing balanced charges of ions and electrons.”

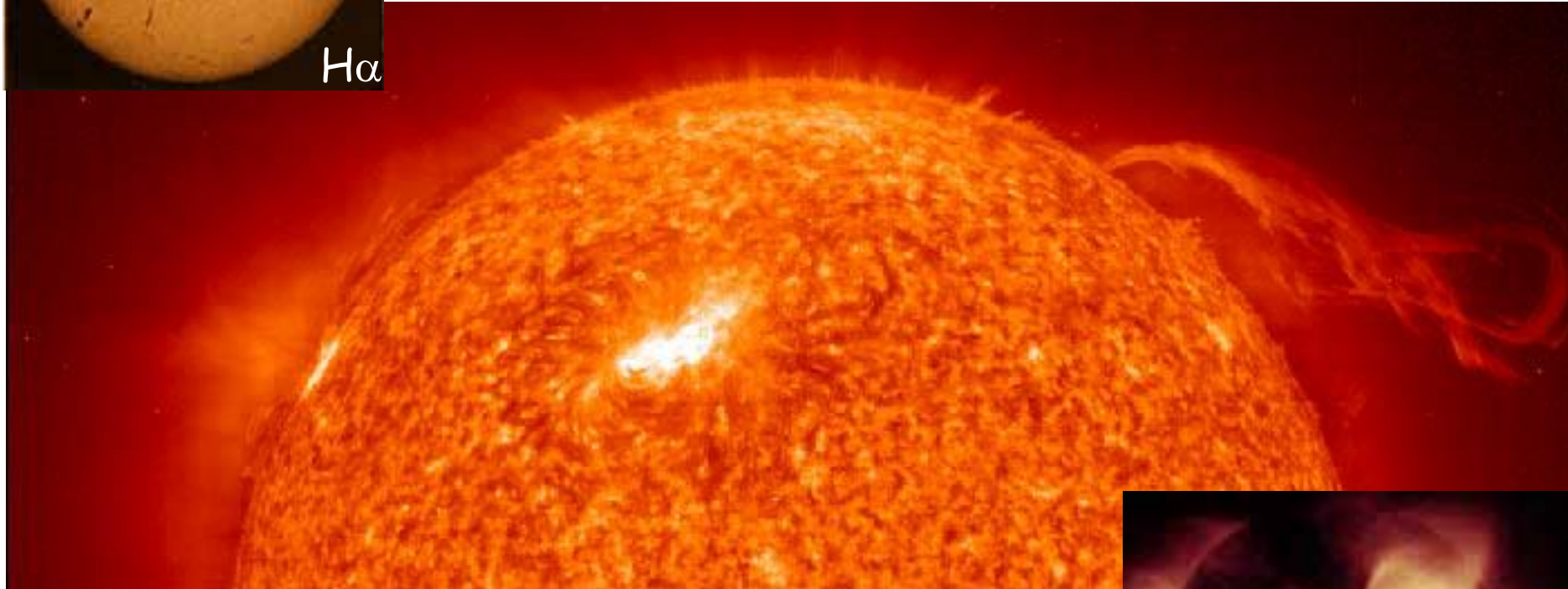
Irving Langmuir  
(1881-1957)



**Nobel Laureate in Chemistry 1932**

*... for his discoveries and investigations  
in surface chemistry ...*

# THERMONUCLEAR PLASMA



# PLASMA CALDO



# PLASMA FREDDO



# PLASMA CALDO







**PLASMA  
FREDDO**

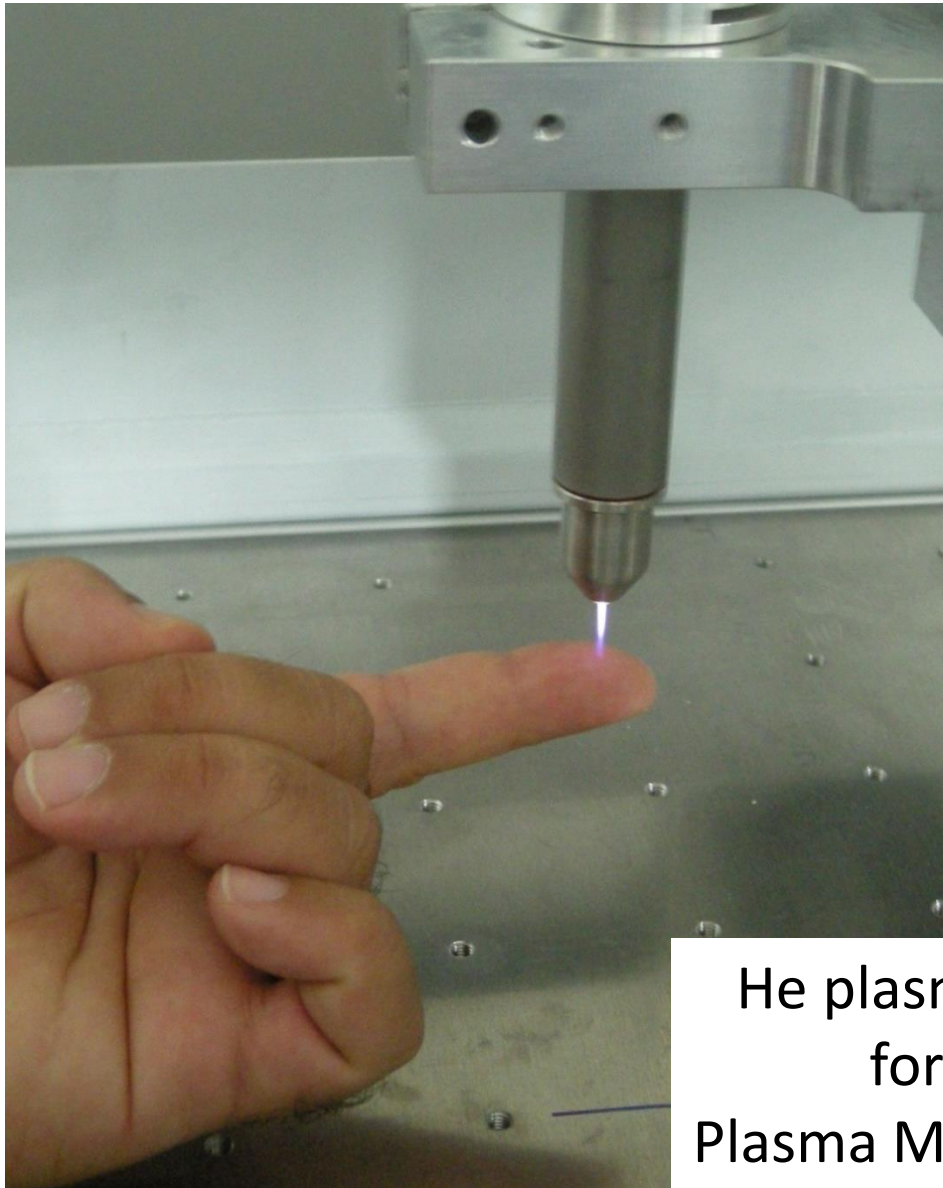


# PLASMA CALDO



# PLASMA FREDDO





He plasma jet  
for  
Plasma Medicine

**PLASMA  
DEPOSITION/TREATMENTS  
atmospheric pressure**

**REALLY  
COLD !**

**THE 4th STATE  
OF THE MATTER:**  
*birth of a concept*

**V sec B.C.** Empedocles defines EARTH, AIR, WATER, FIRE as the 4 elements

**XVII century** First observations of lightnings

**XIX century** German scientists find that electric discharges in hydrocarbon gases originate oily droplets

**1857** Siemens develops the first Ozone generator, mainly used for water purification

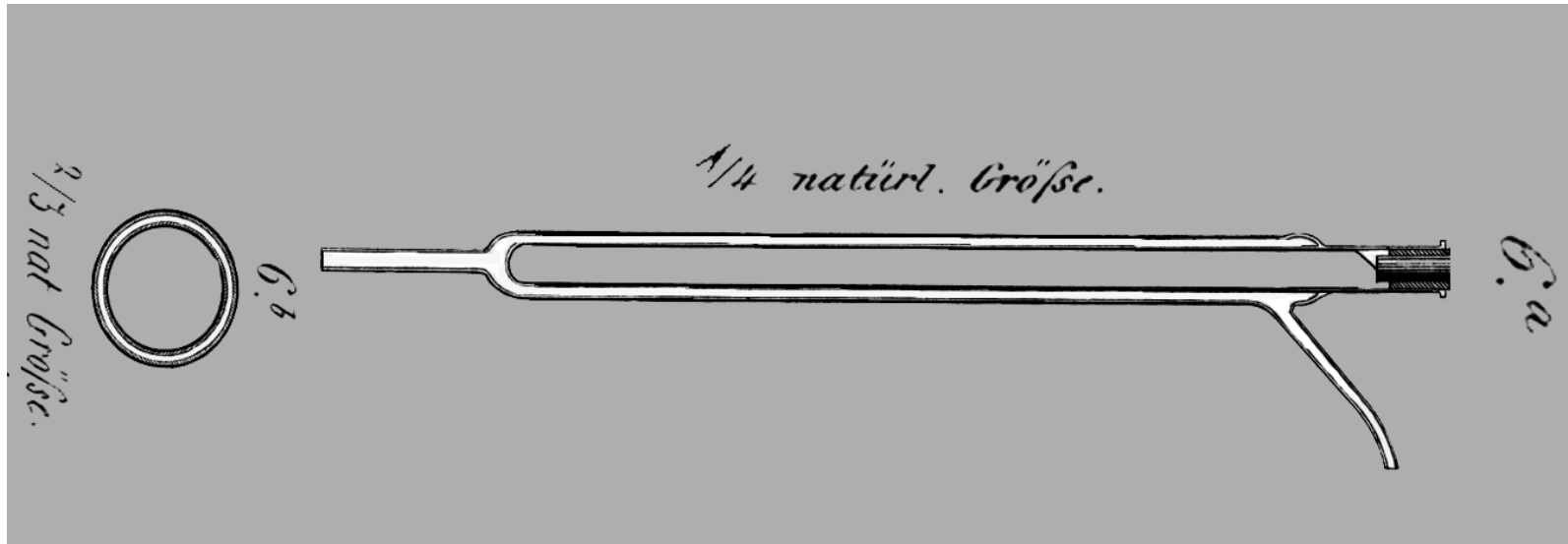
**1879** W. Crookes defines the state of a ionized gas as “... a world where matter may exist in a **4th state** ...”.

**1910** G. Claude exhibits **neon lights** in public at the Paris Motor Show

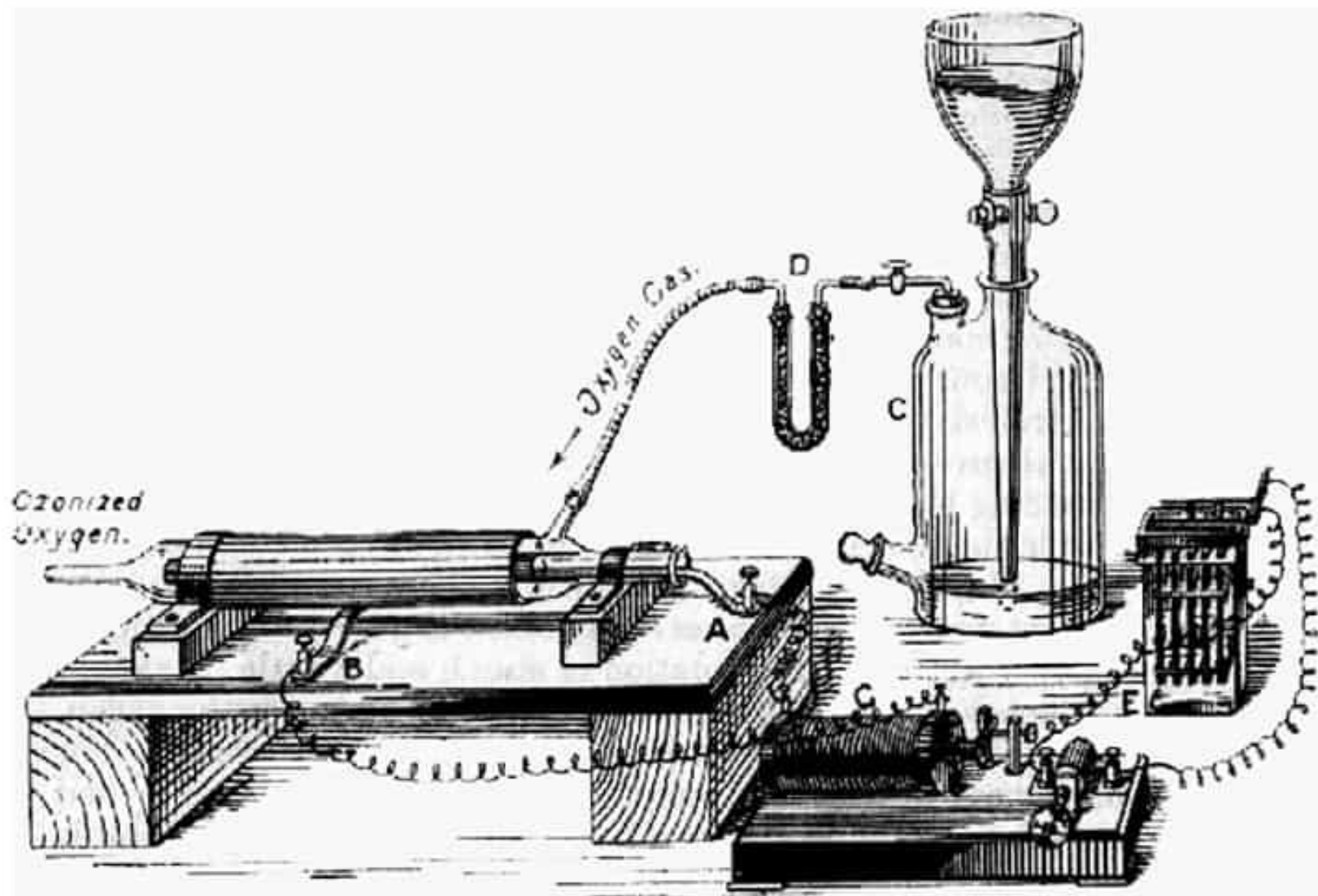
**1928** I. Langmuir uses the word **plasma** to define a **neutral ionized gas** made of electrons, ions atoms and molecules as the “**4th state of the matter**”.

**late XIX, first half XX sec** DC/AC low pressure gas discharges and flames are used to investigate the structure of atoms and molecules by means of Emission Spectroscopy

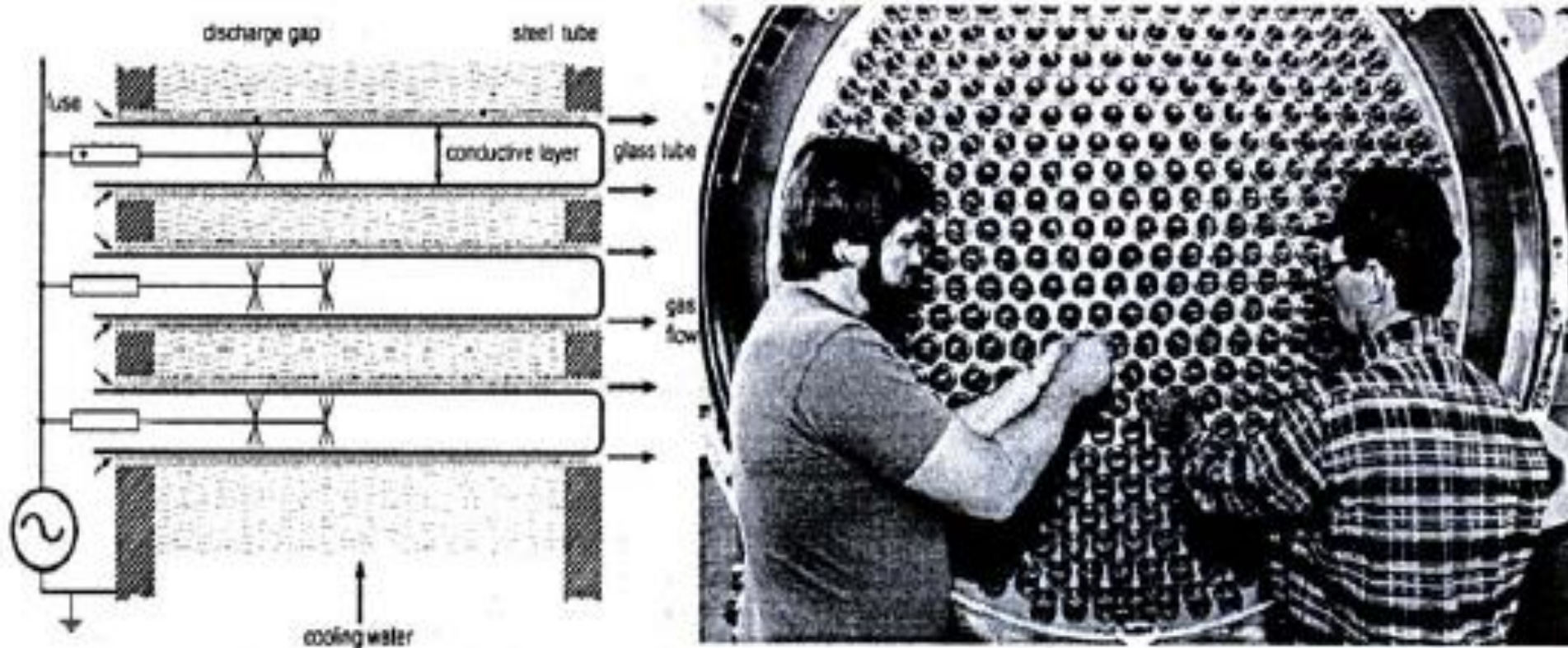
## Historical Ozone Tube of W. Siemens 1857



Poggendorff's Annalen der Physik und Chemie  
102 (1857), 66-122



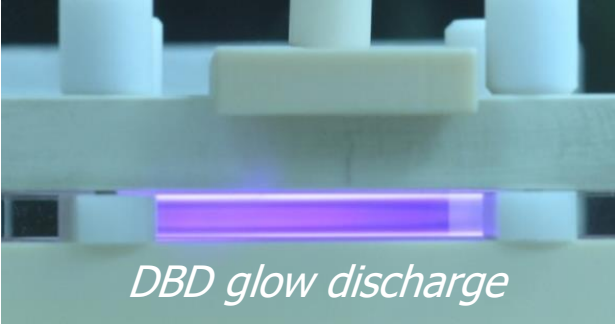
# applicazioni delle Dielectric Barrier Discharge: O<sub>3</sub>



i generatori sono in grado di produrre centinaia di Kg/h di ozono per trattamento delle acque e sbiancamento della polpa di legno

generatore di O<sub>3</sub>  
Los Angeles  
Aqueduct Filtration Plant





*DBD glow discharge*



*plasma ball*



*plasma jet*

# COLD PLASMAS



*HID car lights*



*aurora borealis*



*RF glow discharge*



*neon lights*



*plasma TV*



**THE 4th STATE  
OF THE MATTER:**  
*developments and maturity*

50'-60's

- Plasma chemistry for producing chemicals
- First depositions of thin films
- Miller experiment

70's

- First plasma etching processes
- Equilibrium/non equilibrium debate
- Deposition of  $\alpha$ -Si:H

80's

- Solar cells ( $\alpha$ -Si:H) produced
- Microelectronics at large
- Other applications start

90's

- Extreme miniaturization in microelectronics
- Polymers, textiles, packaging, biomaterials, paper, composites, MEMS,... sterilization ...

2000

- Micro- , nano- surface plasma-engineering in different fields
- Large area easy processing
- Old processes in new fields; plasmas very common also in low-tech fields

2010 →

- Plasma Medicine ( Agriculture, Food, ...)

# PLASMAS AND THE ORIGIN OF LIFE

"A Production of Amino Acids Under Possible Primitive Earth Conditions

Stanley L. Miller

G. H. Jones Chemical Laboratory  
University of Chicago, Chicago, Illinois"  
Science, Vol. 117 p.528 (1953)

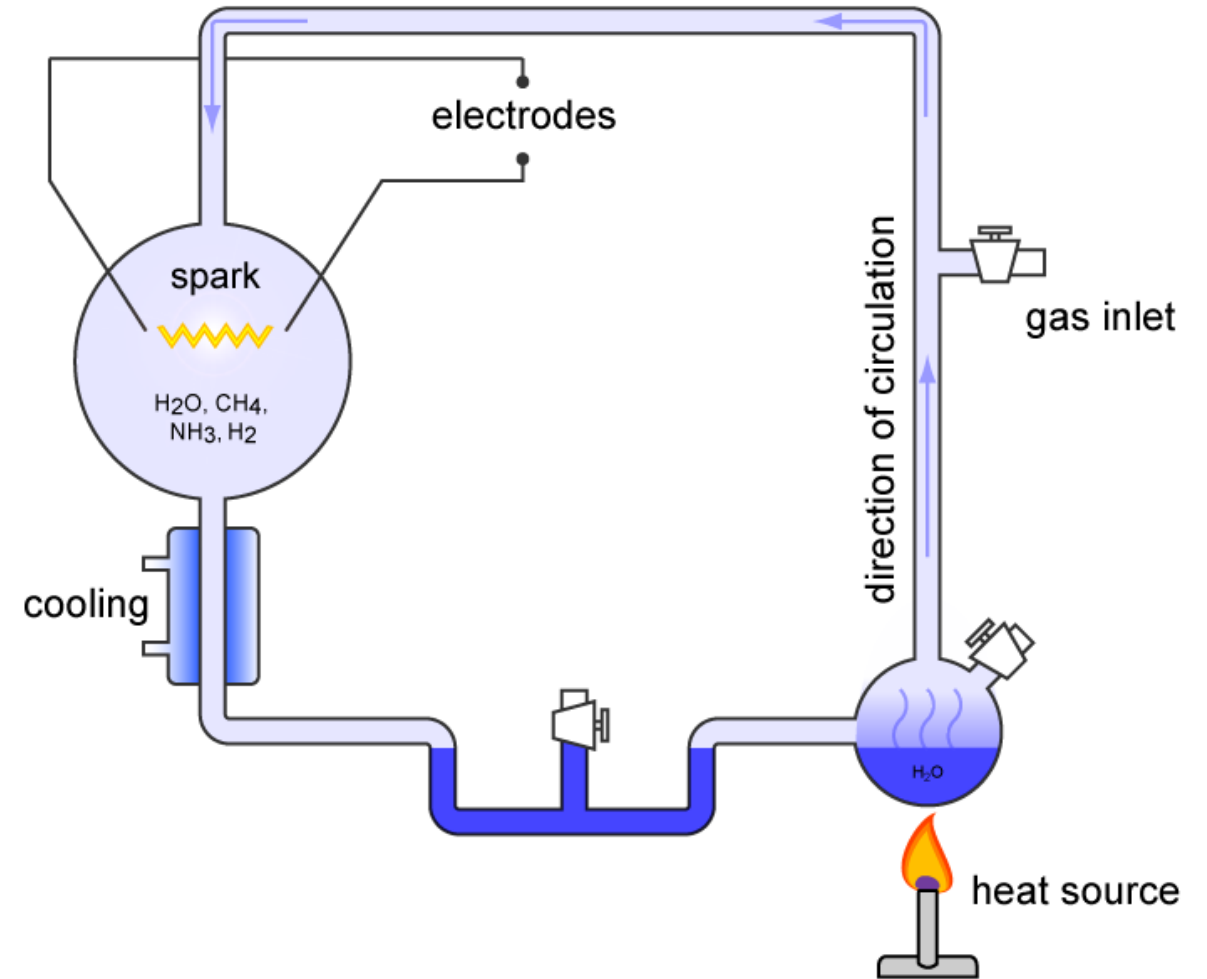
"Production of org Compounds under Primitive Earth Conditions"

Stanley L. Miller

G. H. Jones Chemical  
Laboratory

University of Chicago, Chicago,  
Illinois"

J. Am Chem Soc. Vol. 77,9 p.2351ff  
(1955)



**plasma (spark) processing**

**of the pristine atmosphere on EARTH**

**a mixture of  $H_2O$ ,  $CH_4$ ,  $NH_3$  and  $H_2$**

# amino acids were produced in the discharge !

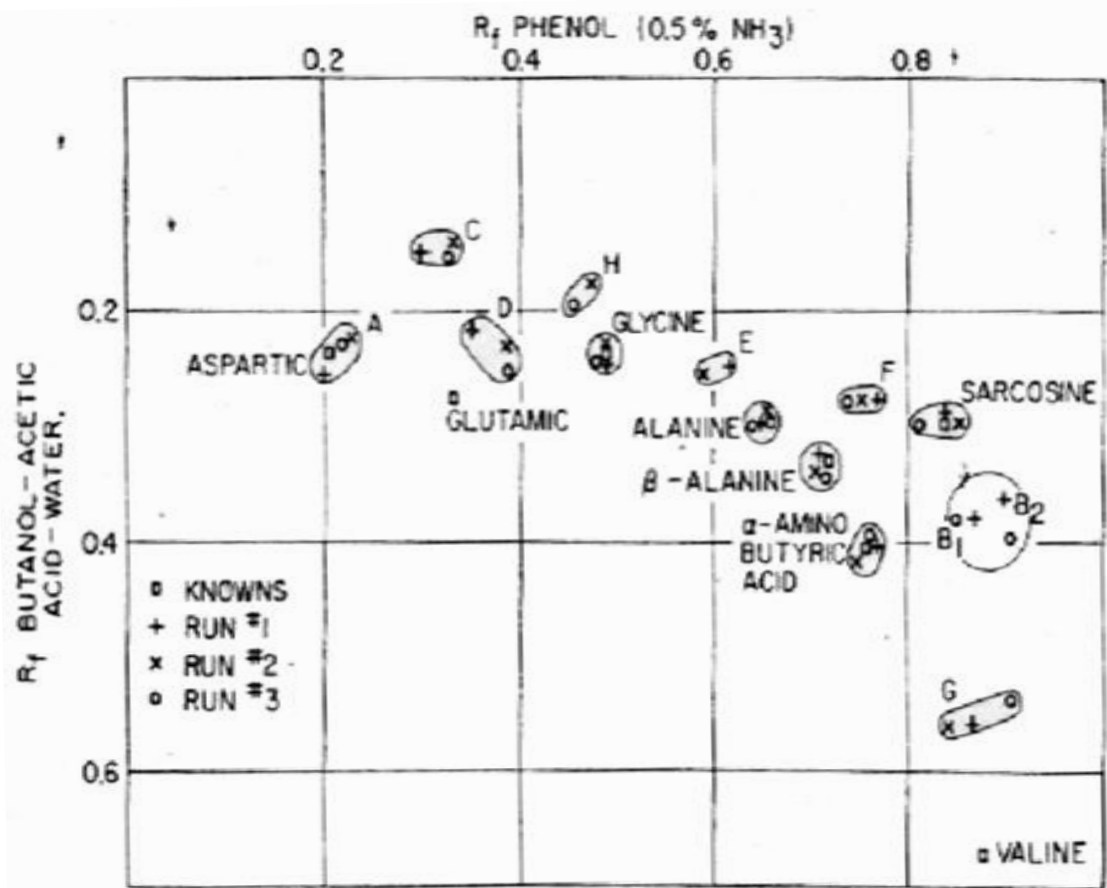
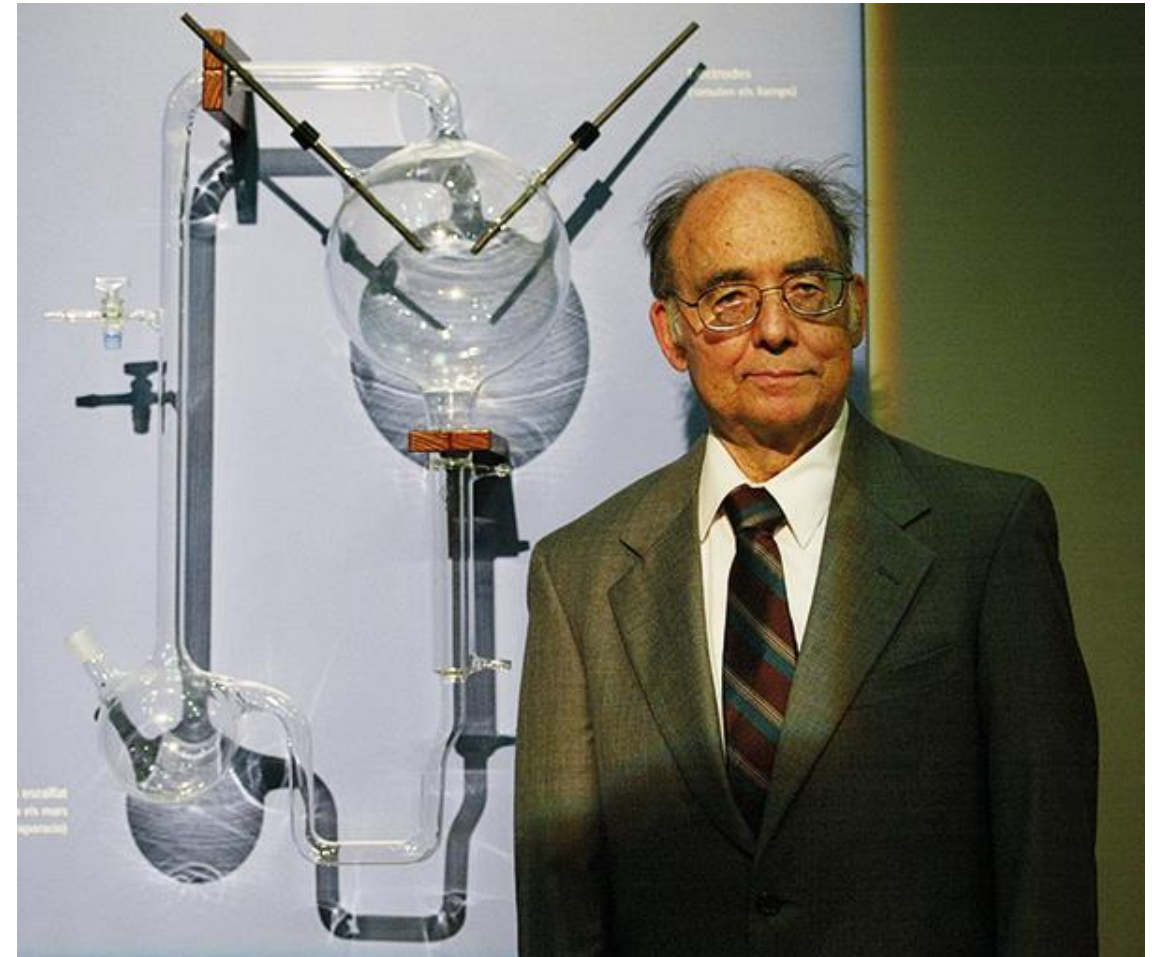
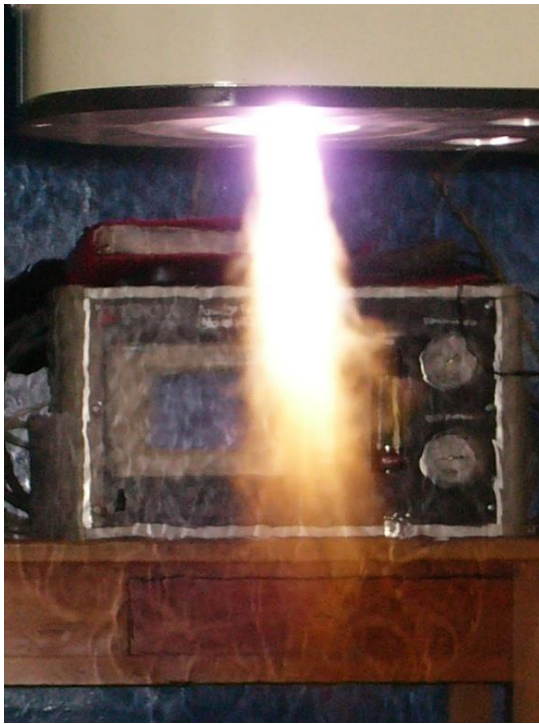
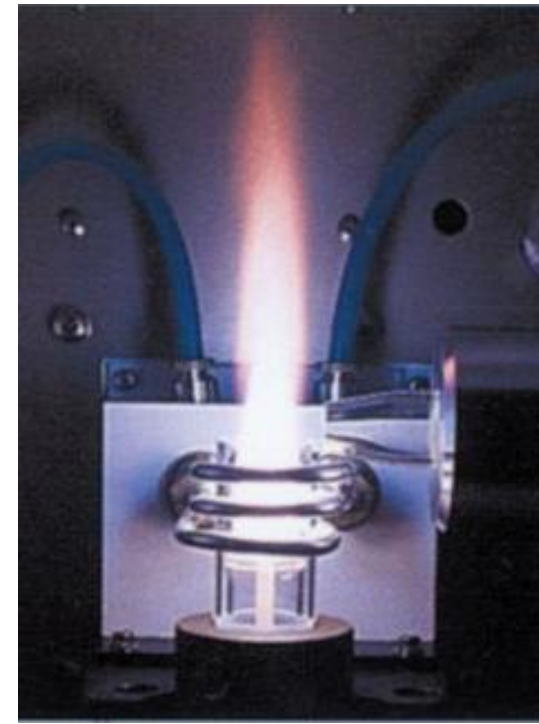


Fig. 8.—Paper chromatography of the amino acids.





## THERMAL PLASMAS



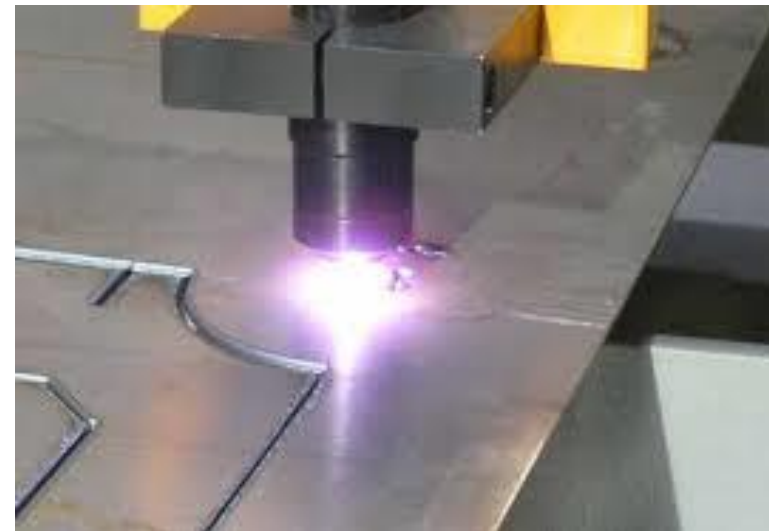
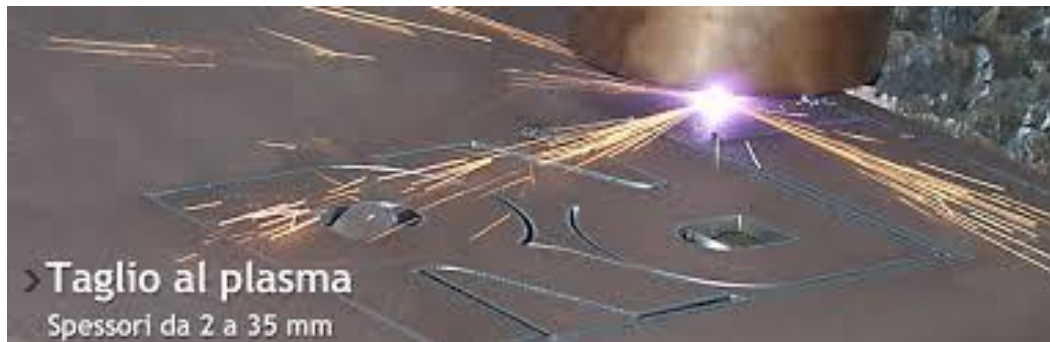
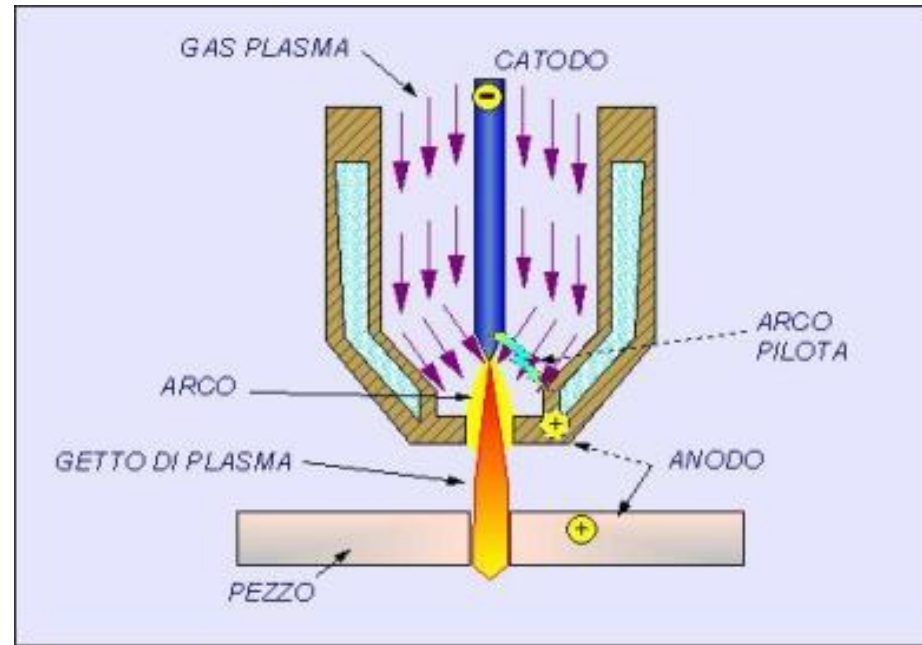
welding, cutting, metallurgy,  
plasma spray deposition,  
ICP spectroscopy,  
waste abatement

# TAGLIO A PLASMA

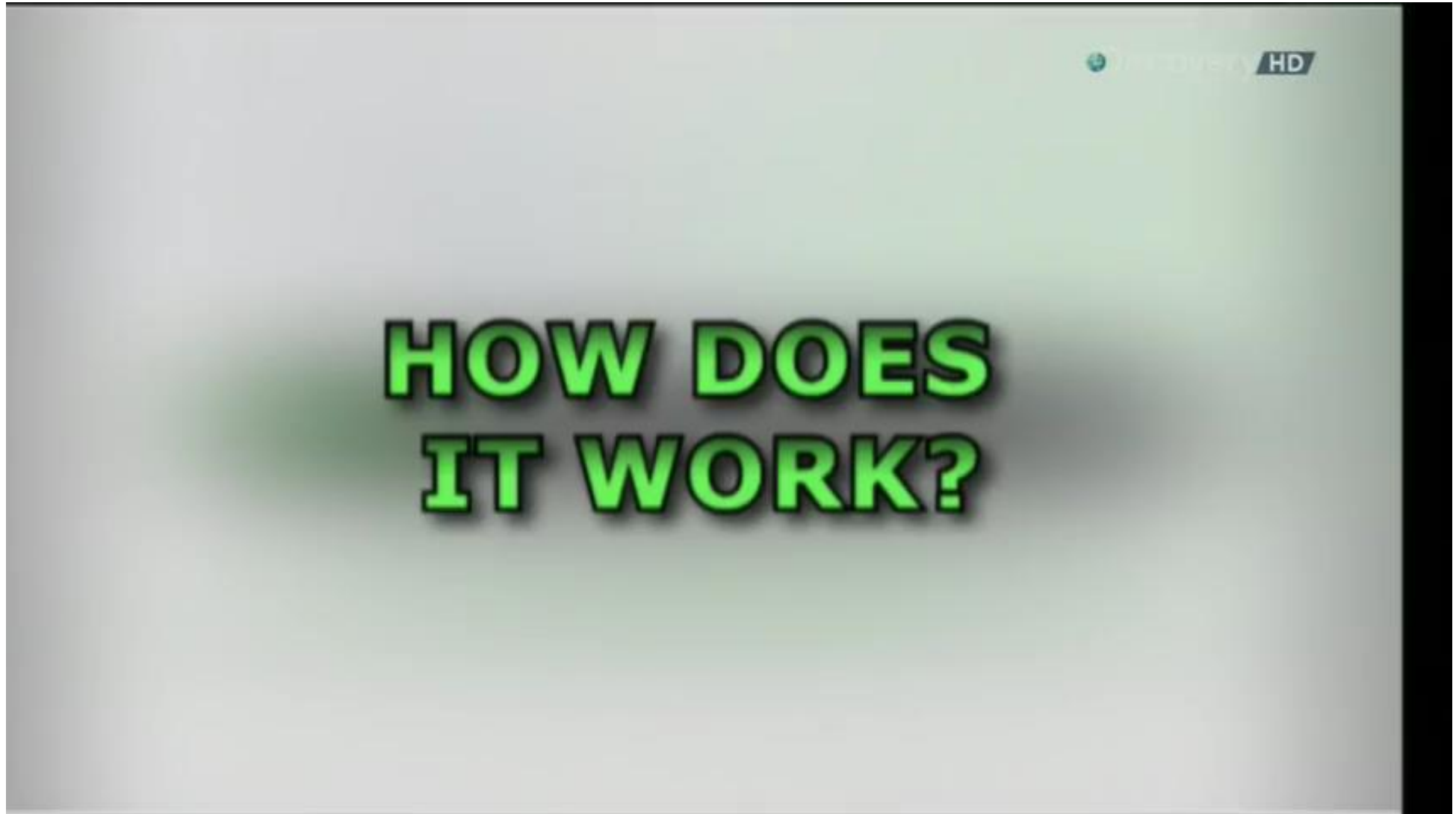
metalli

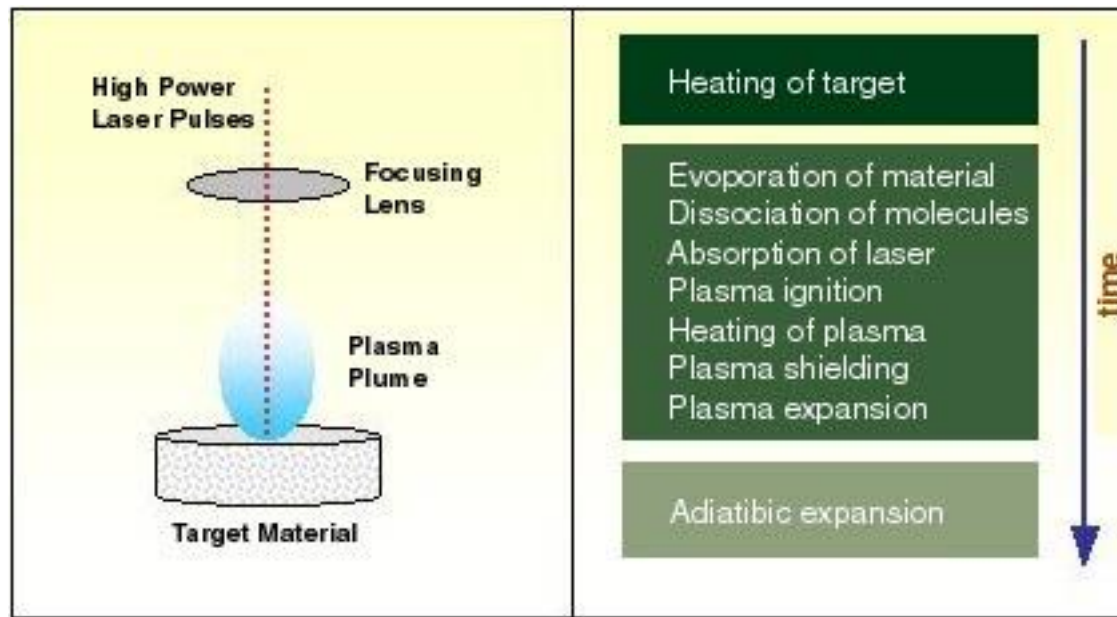
aria compressa

T  $10^4$  K



taglio al plasma  
video

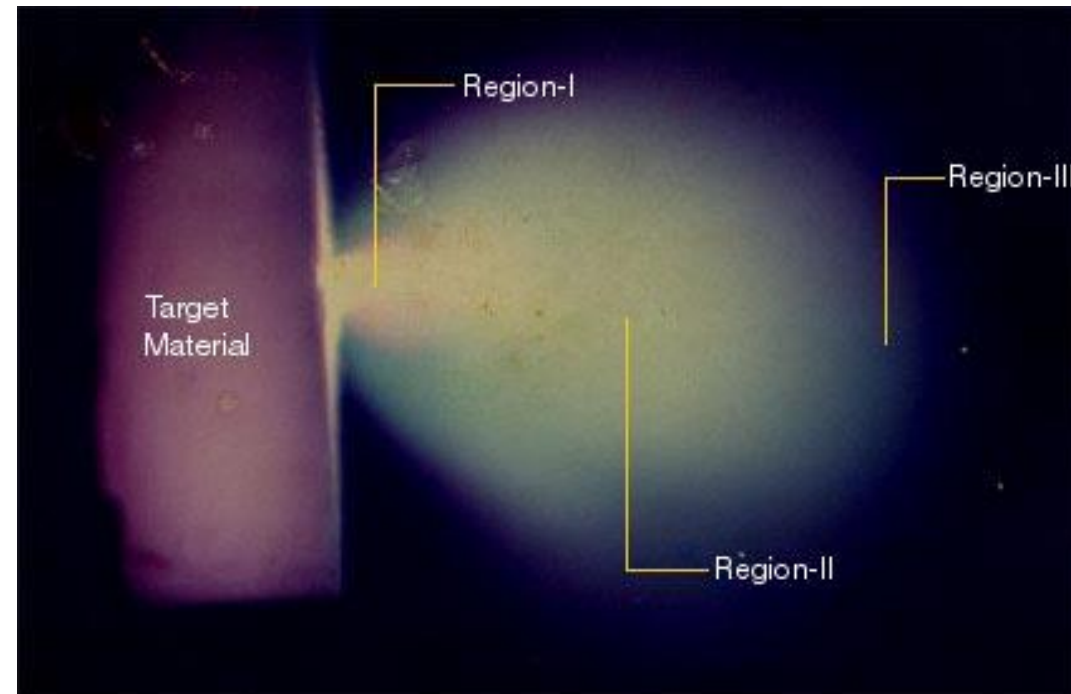




Evolution of laser induced plasma from a target material

# LASER INDUCED PLASMA

a plasma can also be obtained when high-density energy is supplied to a liquid or a solid by a laser or by an electric field strong enough



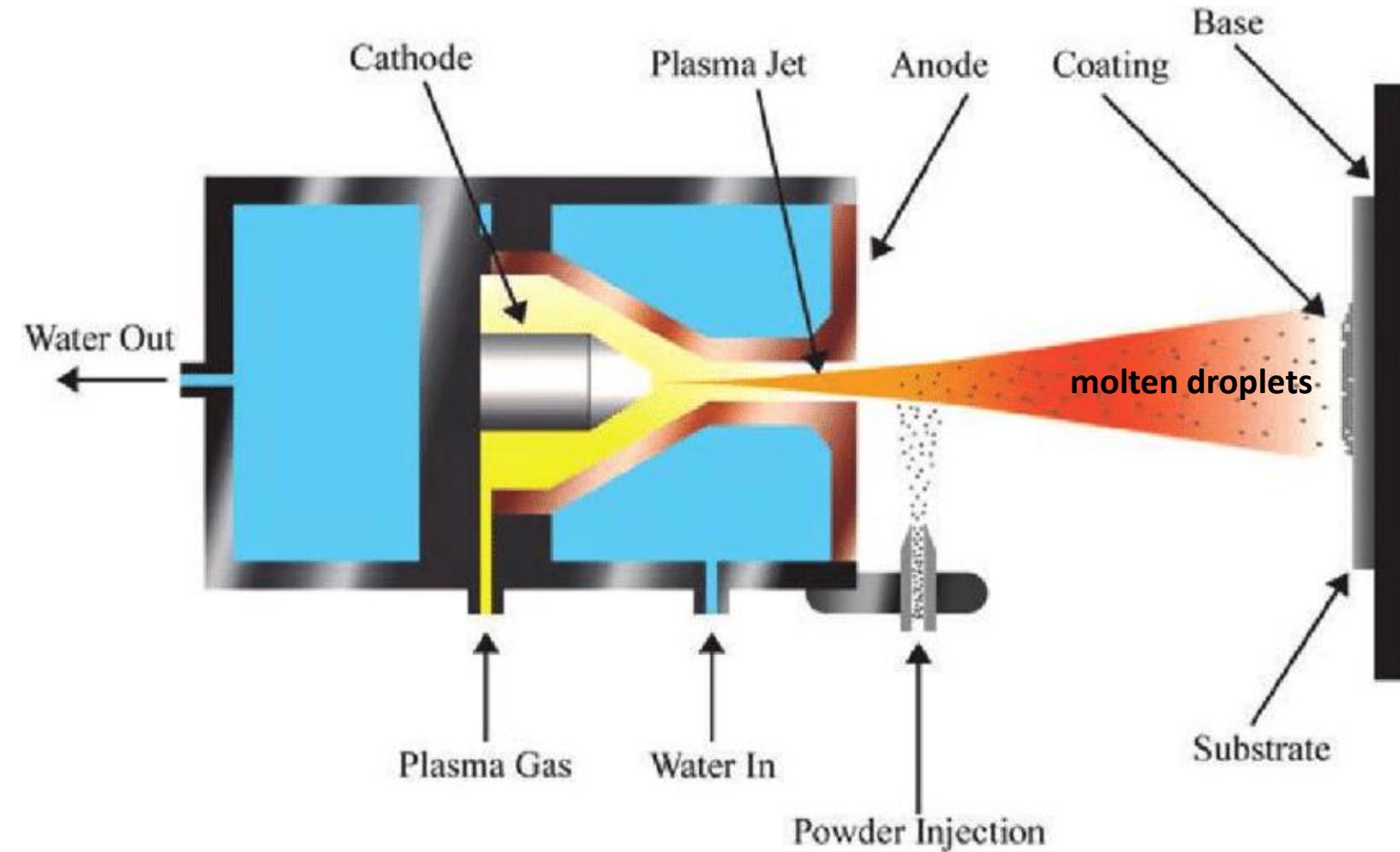
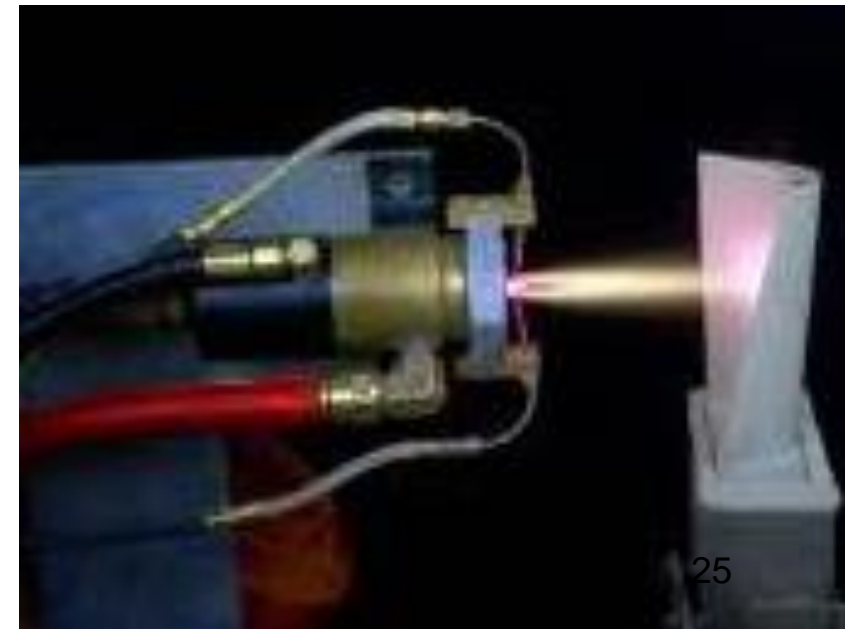
Laser produced plasma plume from a metal target

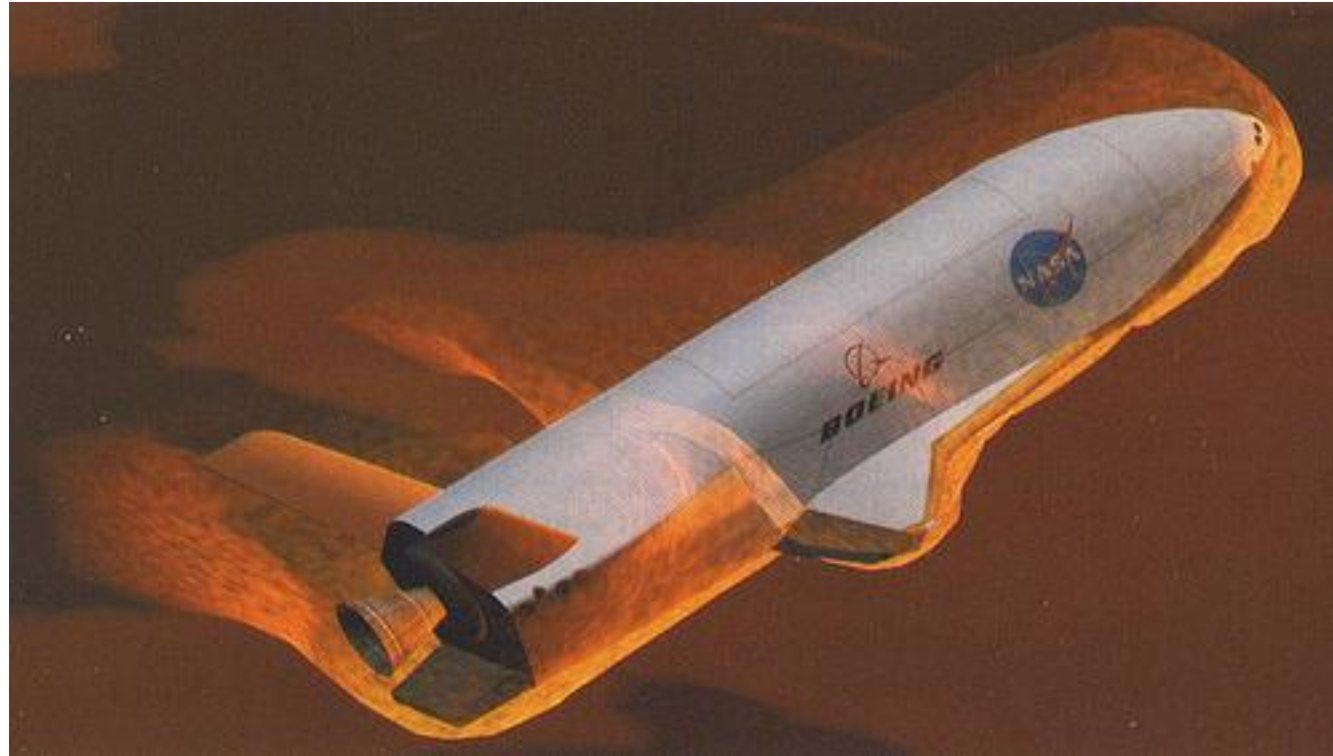


# PLASMA SPRAY

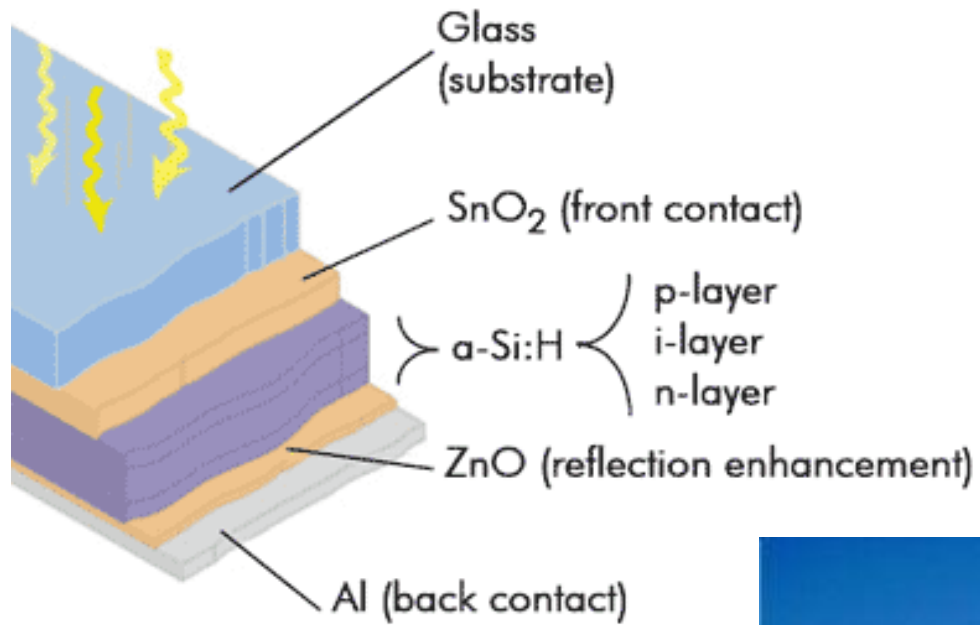
thermal plasmas for materials

hydroxyapatite coatings for orthopedic and dental implants





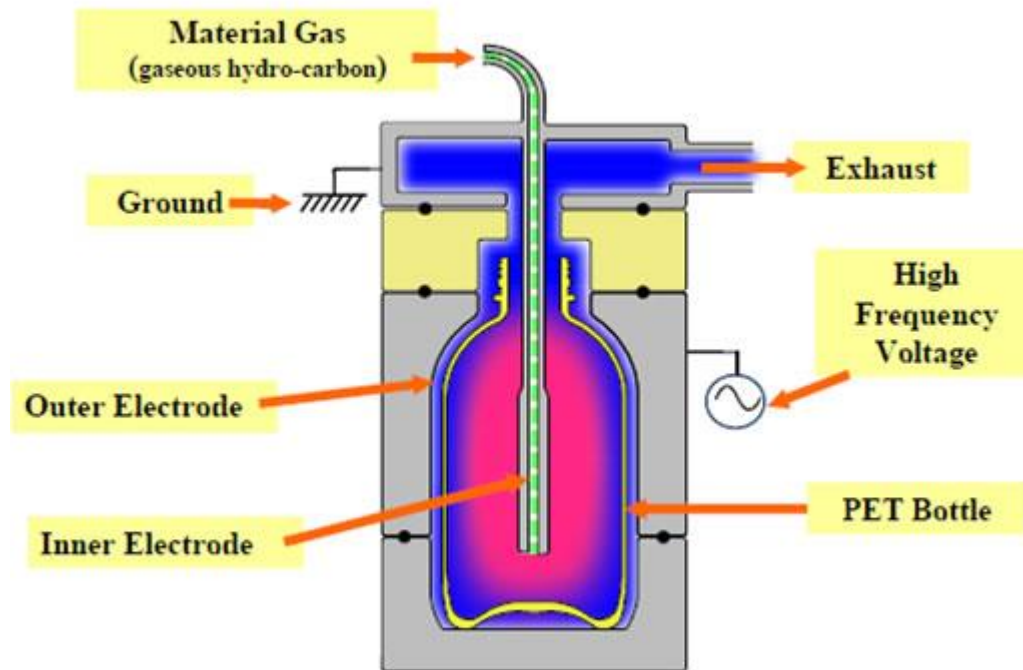
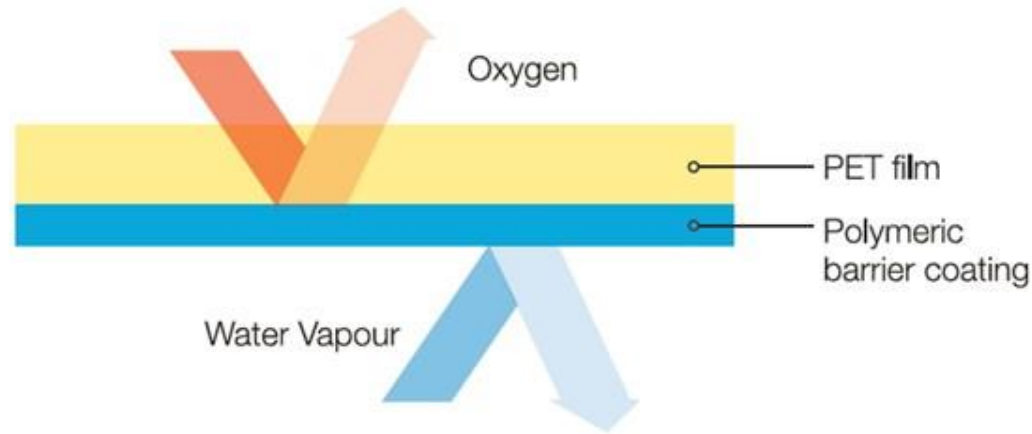
**re-entry plasma sheath**



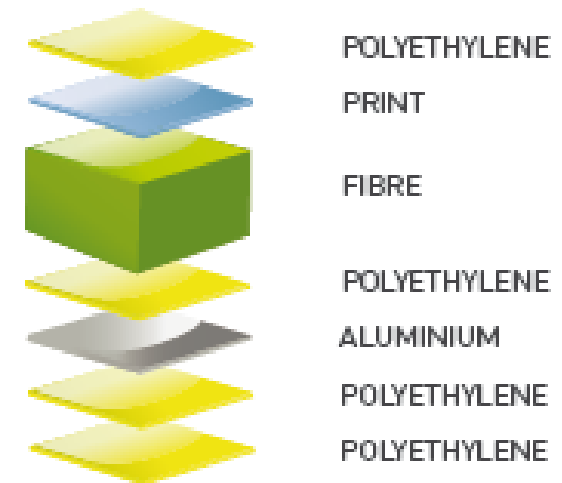
**PLASMA DEPOSITED  
ACTIVE LAYERS  
IN SOLAR CELLS**

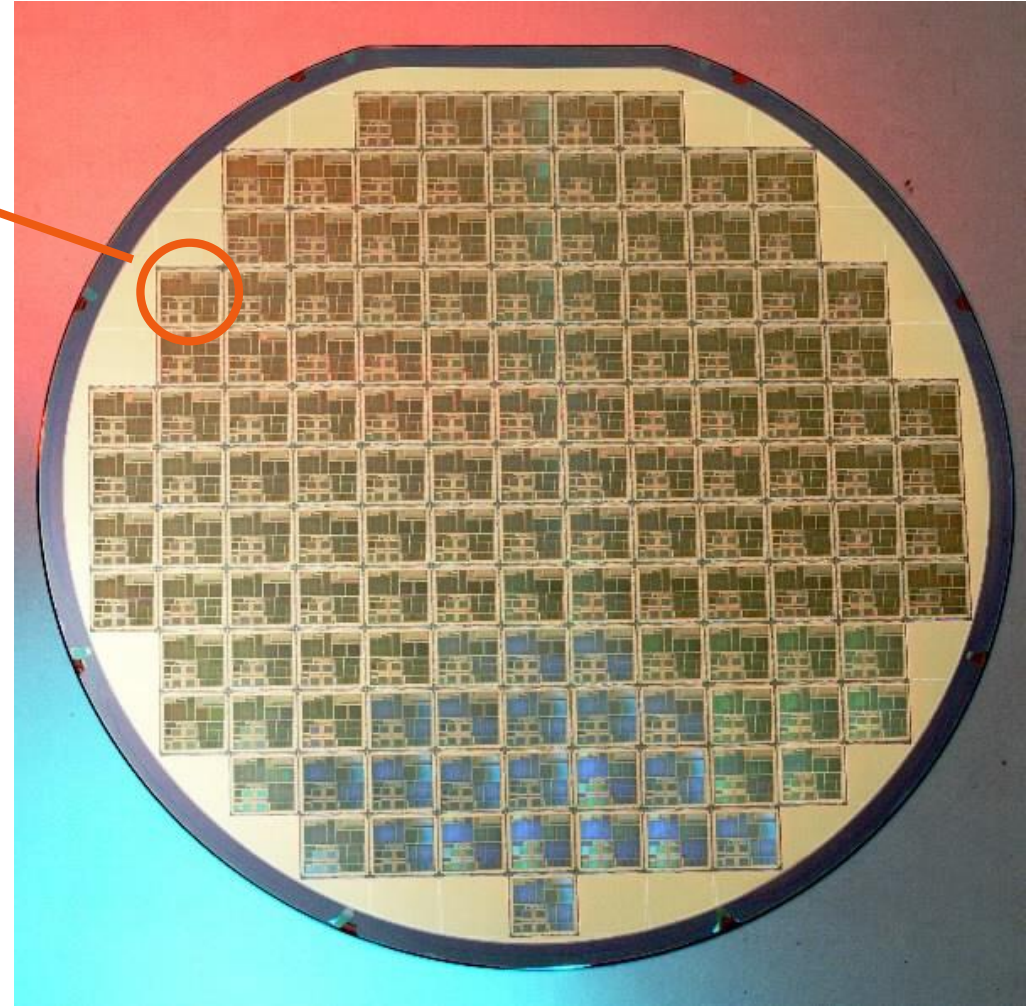
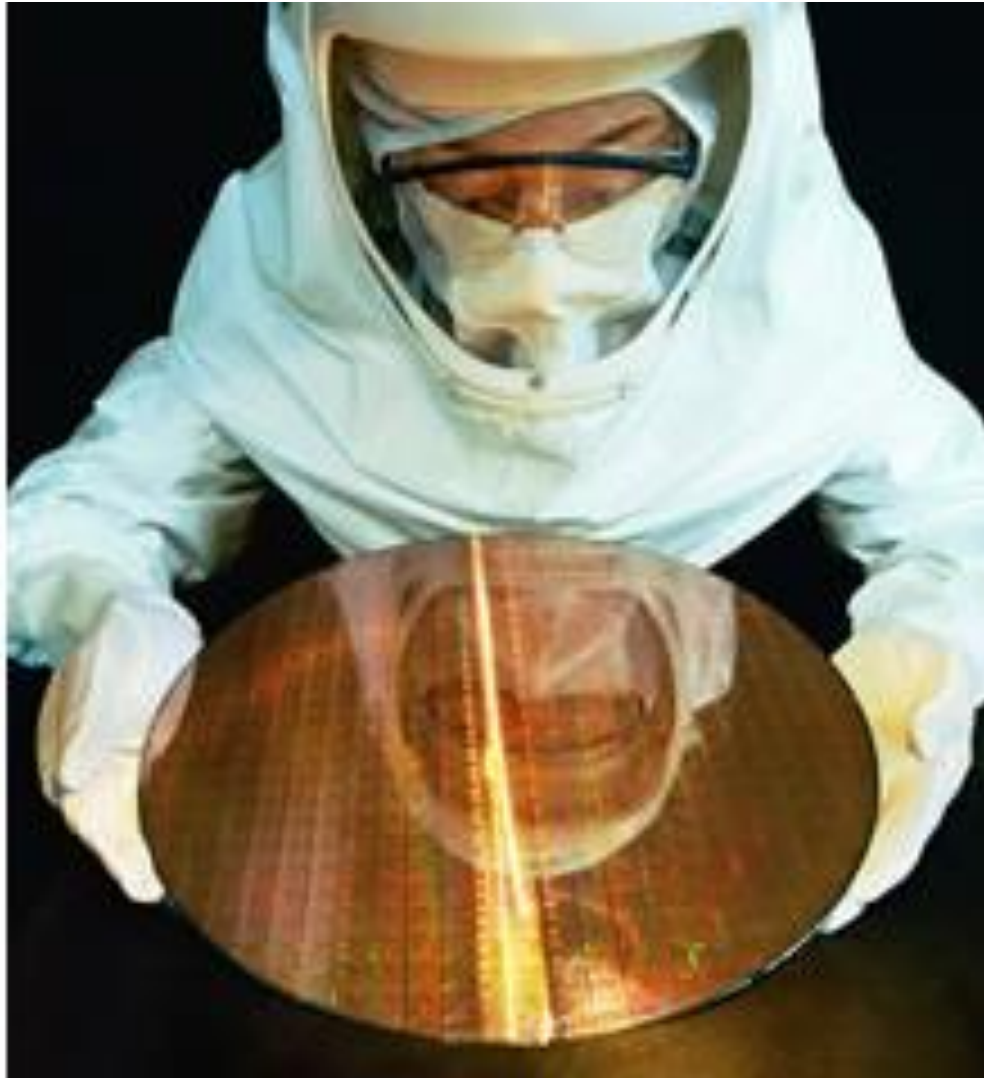
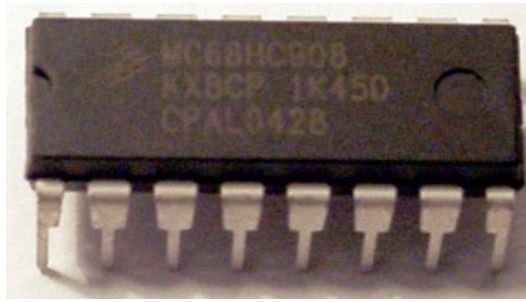


# gas barrier coatings



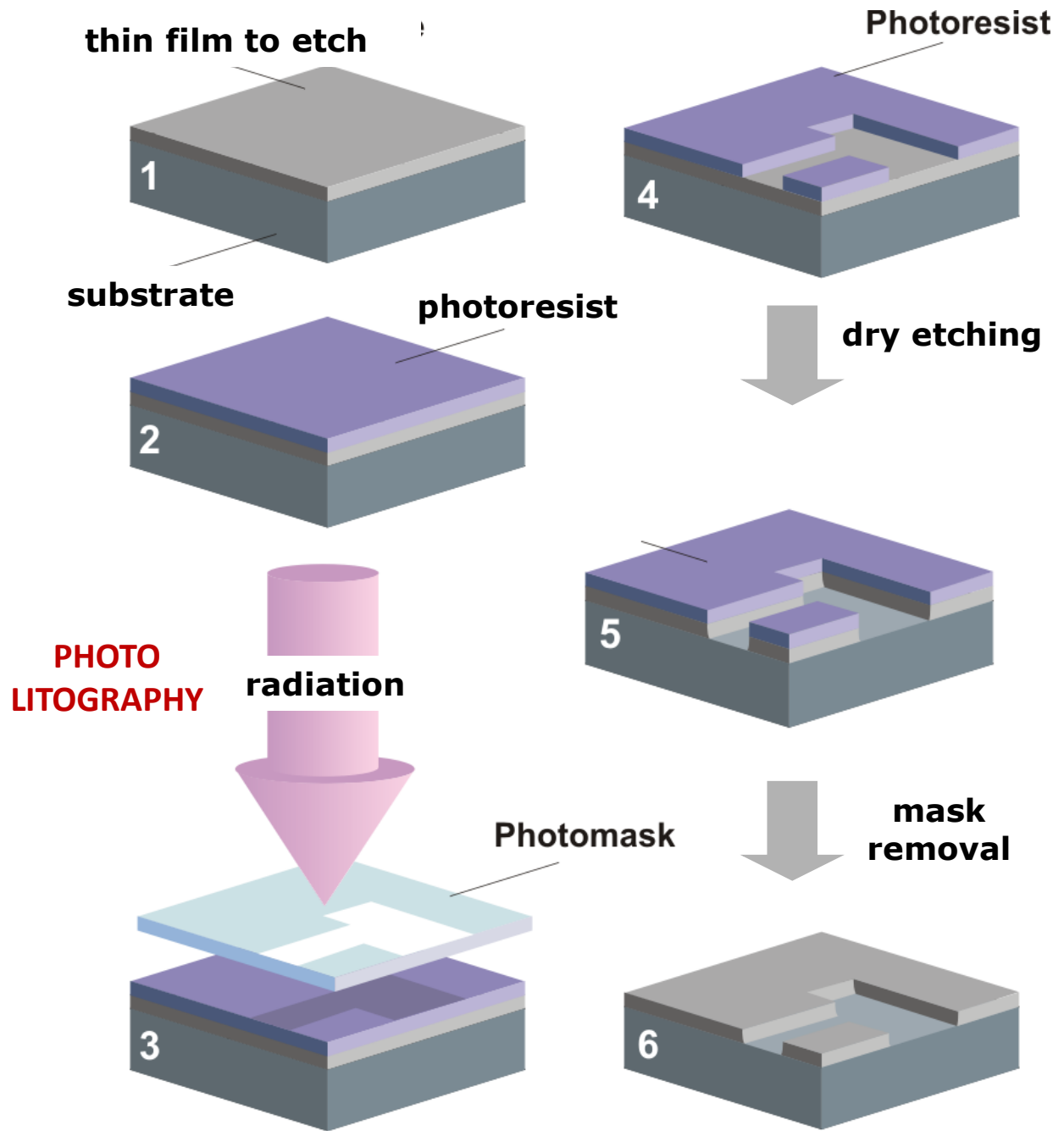
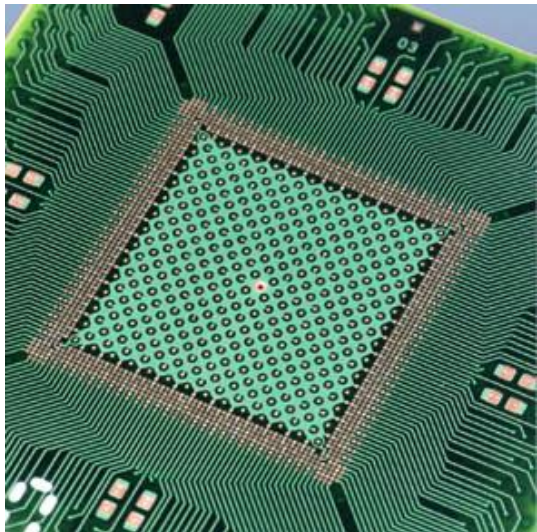
## THE LAYERS OF A BEVERAGE CARTON



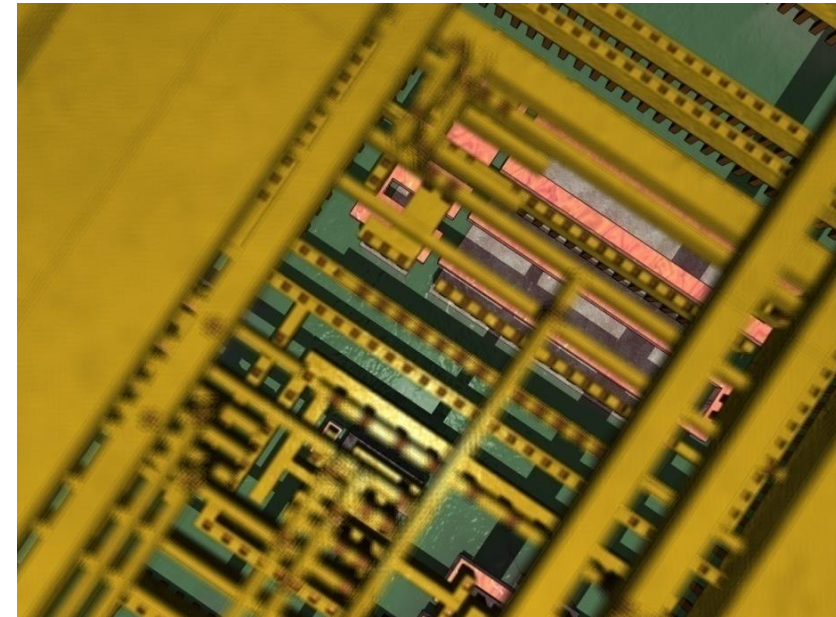
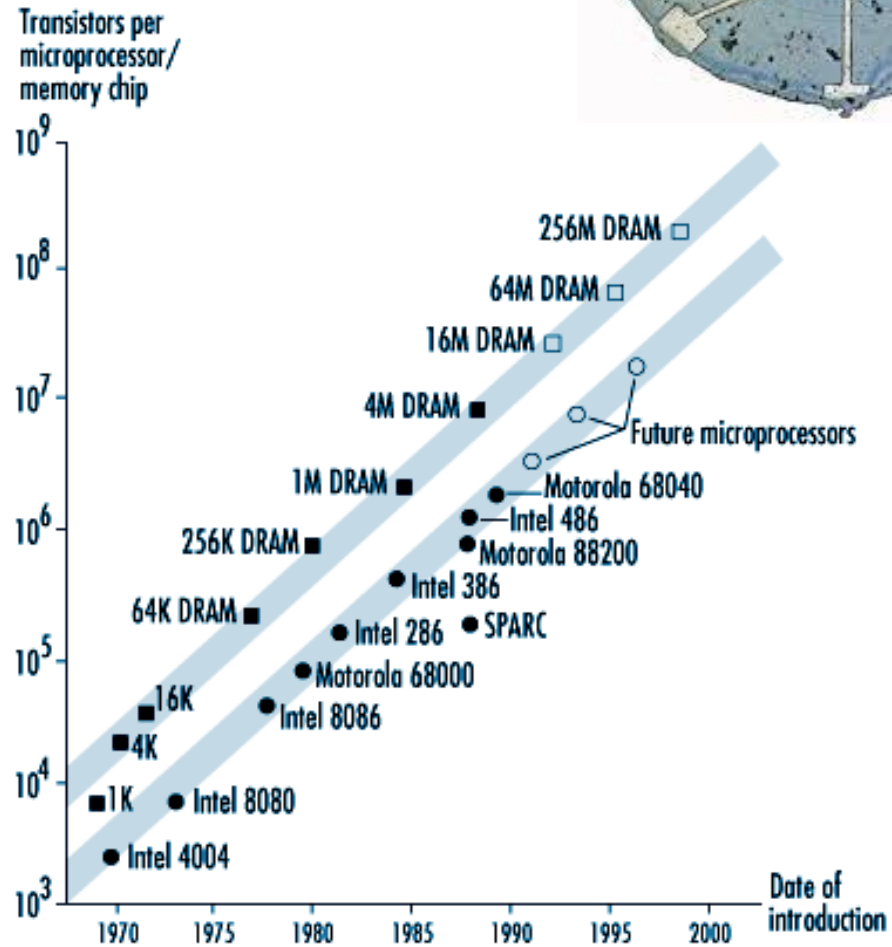
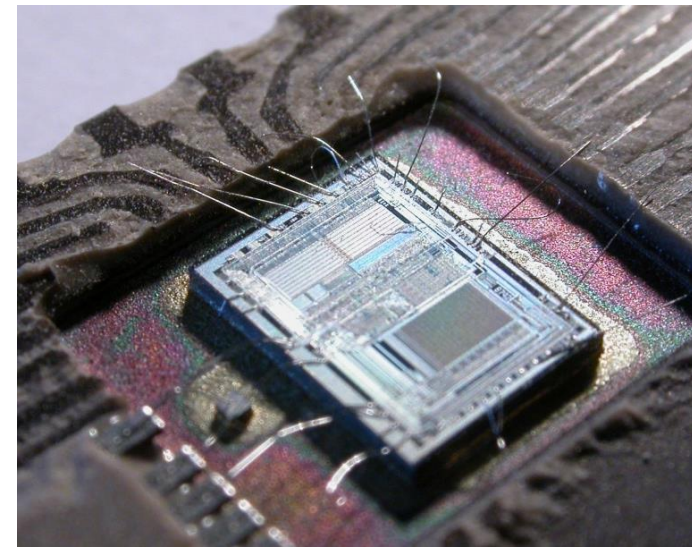
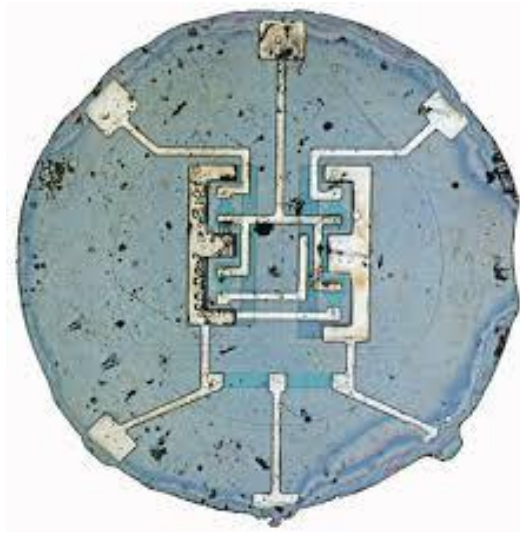


**CIRCUITI INTEGRATI  
IN MICRO ELETTRONICA**

**PLASMA  
(DRY) ETCHING**



# Integrated Circuits



**"Moore's law"** observes that, for computer hardware, the number of transistors in an integrated circuit doubles approximately every 2 years. The law is named after **Gordon E. Moore**, co-founder of **Intel Corporation**, who first described the trend in 1965 and stated it in 1975. His prediction has proven to be accurate, the law is used in SC industry to guide long-term planning and to set R&D targets.

The capabilities of many digital electronic devices are linked to Moore's law: quality-adjusted microprocessor prices, memory capacity, sensors and number/size of pixels in digital cameras. All of these improve at roughly exponential rate. This improvement has dramatically enhanced the effect of digital electronics in global economy. Moore's law describes a driving force of technological and social change, productivity, and economic growth in the late 20<sup>th</sup> / early 21<sup>st</sup> centuries.

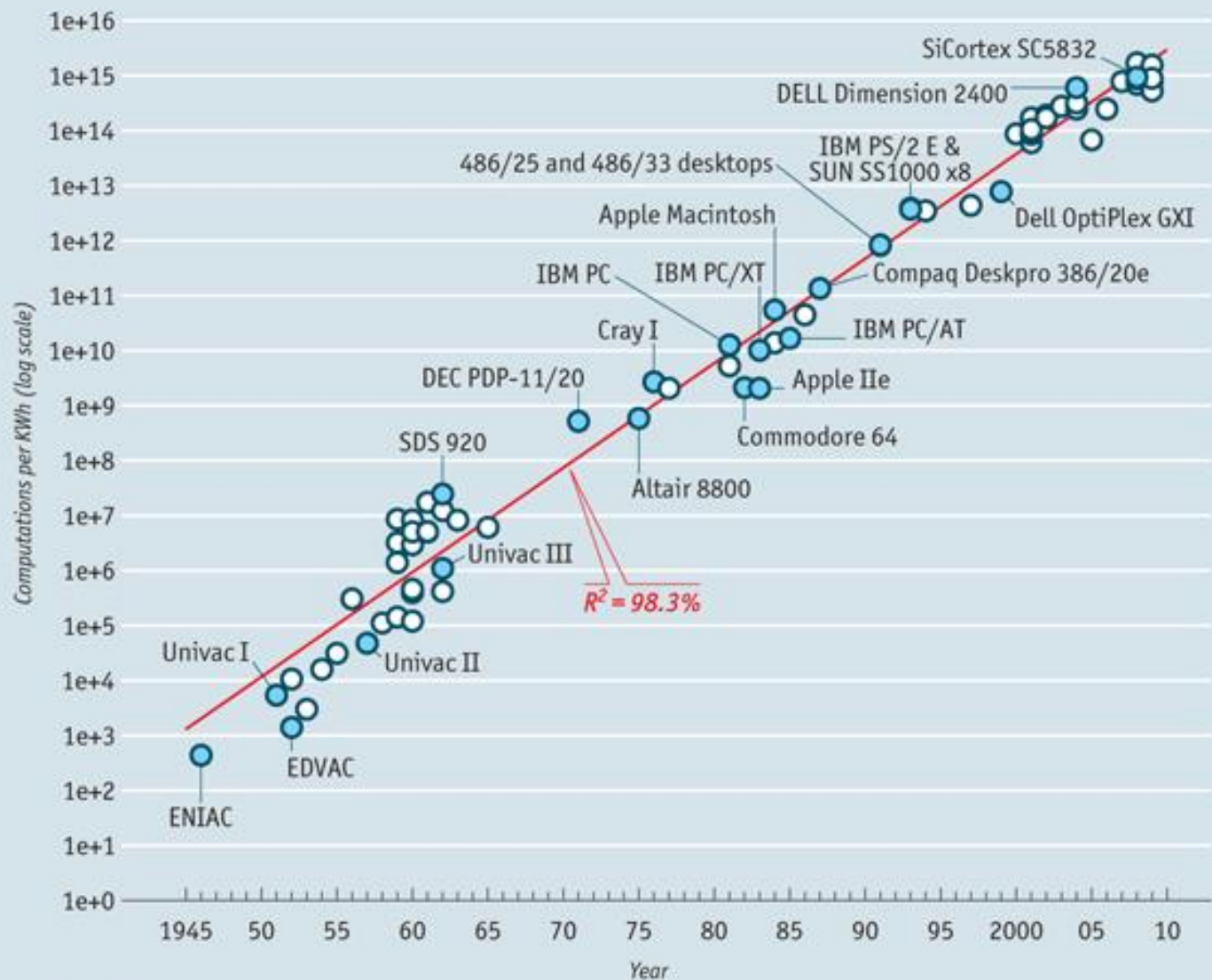
The period is often quoted as 18 months because of Intel executive **D. House**, who predicted that chip performance would double every 18 months (a combination of the effect of more transistors). Although this trend has continued for about 60 years, "Moore's law" has to be considered an observation, not a physical law, expected to continue until at least 2015/20. The 2010 update to the **International Technology Roadmap for Semiconductors** predicted that growth will slow in 2013, when transistor counts and densities will start to double "only" every 3 years.





## Computing efficiency

Computations per kilowatt-hour



Source: Jonathan Koomey

# 1993 vs 2013





*aurora borealis*

PVD sputtering

LPGD  
*Low Pressure Glow Discharges*

DBD  
*Dielectric Barrier Discharges*

APGD  
*Atmospheric Pressure Glow Discharges*

plasma TV  
*Plasma Display Panel*

corona discharges

ionosphere

solar wind

sparks

flames

plasma torches

ICP

plasma spray

# APPLICATIONS OF COLD PLASMAS

**OZONE PRODUCTION** *(since XIX century)*

**LIGHTS**

**MODIFICATION OF SURFACE PROPERTIES**

*etching, deposition of thin films, grafting*

**TV DISPLAYS**

**STERILIZATION**

**SYNTHESIS OF NANOMATERIALS**

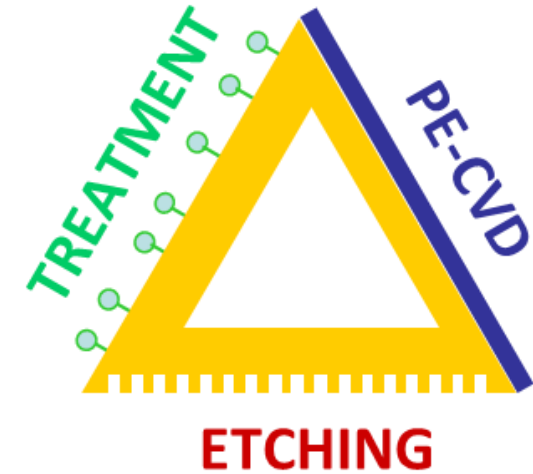
*Carbon nanotubes (CNTs), semiconductor (SC) nanocrystals*

**PLASMA MEDICINE (food, agriculture, ...)**

# PLASMA SCIENCE AND TECHNOLOGY

first applications

LIGHT SOURCES	CATALYSIS
OZONE PRODUCTION	MEDICINE
MICROELECTRONICS	POLYMERS
SEMICONDUCTORS	PAPER
SOLAR CELLS	WETTABILITY
AUTOMOBILE	ADHESION
FOOD PACKAGING	METALLIZATION
TEXTILE	PRINTING, DYEING
BIOMATERIALS	CORROSION PROTECTION
MICROFLUIDICS	CULTURAL HERITAGE
MEMS	COMPOSITES
CLEANING	SENSORS
STERILIZATION	OPTICS
BIOLOGY	BUILDINGS
ENVIRONMENT	AGRICULTURE



- IN MATERIAL SCIENCE TECHNOLOGY  
NON EQUILIBRIUM «COLD» PLASMAS ALLOW**
- **SURFACE ALTERATIONS OF PROPERTIES**
  - **AT ROOM TEMPERATURE**
  - **WITH NO BULK MODIFICATION**

# Plasma Science Technology

## Materials Science

## Surface Engineering

**Plasma Science: Advancing Knowledge in the National Interest**  
Plasma 2010 Committee, Plasma Science Committee,  
National Research Council (2007), The National Academies Press



- 01—Plasma TV
- 02—Plasma-coated jet turbine blades
- 03—Plasma-manufactured LEDs in panel
- 04—Diamondlike plasma CVD eyeglass coating
- 05—Plasma ion-implanted artificial hip
- 06—Plasma laser-cut cloth
- 07—Plasma HID headlamps
- 08—Plasma-produced H<sub>2</sub> in fuel cell

- 09—Plasma-aided combustion
- 10—Plasma muffler
- 11—Plasma ozone water purification
- 12—Plasma-deposited LCD screen
- 13—Plasma-deposited silicon for solar cells
- 14—Plasma-processed microelectronics
- 15—Plasma-sterilization in pharmaceutical production

- 16—Plasma-treated polymers
- 17—Plasma-treated textiles
- 18—Plasma-treated heart stent
- 19—Plasma-deposited diffusion barriers for containers
- 20—Plasma-sputtered window glazing
- 21—Compact fluorescent plasma lamp

## Topical Review

# The 2017 Plasma Roadmap: Low temperature plasma science and technology

I Adamovich<sup>1</sup>, S D Baalrud<sup>2</sup>, A Bogaerts<sup>3</sup>, P J Bruggeman<sup>4</sup>,  
M Cappelli<sup>5</sup>, V Colombo<sup>6</sup>, U Czarnetzki<sup>7</sup>, U Ebert<sup>8,9</sup>, J G Eden<sup>10</sup>,  
P Favia<sup>11</sup>, D B Graves<sup>12</sup>, S Hamaguchi<sup>13</sup>, G Hieftje<sup>14</sup>, M Hori<sup>15</sup>,  
I D Kaganovich<sup>16</sup>, U Kortshagen<sup>4</sup>, M J Kushner<sup>17</sup>, N J Mason<sup>18</sup>,  
S Mazouffre<sup>19</sup>, S Mededovic Thagard<sup>20</sup>, H-R Metelmann<sup>21</sup>, A Mizuno<sup>22</sup>,  
E Moreau<sup>23</sup>, A B Murphy<sup>24</sup>, B A Niemira<sup>25</sup>, G S Oehrlein<sup>26</sup>,  
Z Lj Petrovic<sup>27</sup>, L C Pitchford<sup>28</sup>, Y-K Pu<sup>29</sup>, S Rauf<sup>30</sup>, O Sakai<sup>31</sup>,  
S Samukawa<sup>32</sup>, S Starikovskaia<sup>33</sup>, J Tennyson<sup>34</sup>, K Terashima<sup>35</sup>,  
M M Turner<sup>36</sup>, M C M van de Sanden<sup>9,37</sup> and A Vardelle<sup>38</sup>



## The future for plasma science and technology

Klaus-Dieter Weltmann<sup>1</sup> | Juergen F. Kolb<sup>1</sup>  | Marcin Holub<sup>2</sup> |  
Dirk Uhrlandt<sup>1</sup> | Milan Šimek<sup>3</sup>  | Kostya (Ken) Ostrikov<sup>4,5</sup> |  
Satoshi Hamaguchi<sup>6</sup> | Uroš Cvelbar<sup>7</sup> | Mirko Černák<sup>8</sup> | Bruce Locke<sup>9</sup> |  
Alexander Fridman<sup>10</sup> | Pietro Favia<sup>11,12</sup> | Kurt Becker<sup>13</sup>

The application of gas discharge plasmas has assumed an important place in many manufacturing processes. Plasma methods contribute significantly to the economic prosperity of industrialized societies. However, plasma is mainly an enabling method and therefore its role remains often hidden. Hence the success of plasma technologies is described for different examples and commercial areas. From these examples and emerging applications, the potential of plasma technologies is discussed. Economic trends are anticipated together with research needs. The community of plasma scientists strongly believes that more exciting advances will continue to foster innovations and discoveries in the first decades of the 21st century, if research and education will be properly funded and sustained by public bodies and industrial investors.



**LOW PRESSURE**

**ATMOSPHERIC PRESSURE**

**COLD PLASMAS**

**THERMAL PLASMAS**

## **PLASMA**

- partially ionized gas
- equal number of positive and negative charged particles
- uniform charge density
- thermodynamic equilibrium or non-equilibrium

## **GLOW DISCHARGE**

- partially ionized gas
- not uniform charge density
- in some zones (walls, surfaces) the neutrality is not respected
- always in non-thermodynamic equilibrium