Department of Mechanical Engineering

# Plasma technology

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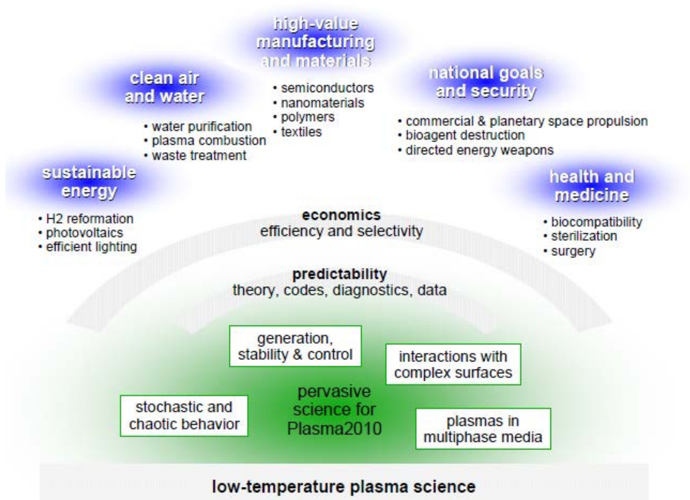
***Acknowledgements:***
- ***U. Kortshagen and S. Girshick (UMN)***
- ***B. Locke (Florida State University)***
- ***Input from lecture slides of A. Murphy, J. Hopwood, R. Brandenburg, A. Fridman and K. Wende***



## Man-made plasmas: use




*Plasma science: advancing the knowledge in the interest of national security, National research council (US, 2007)

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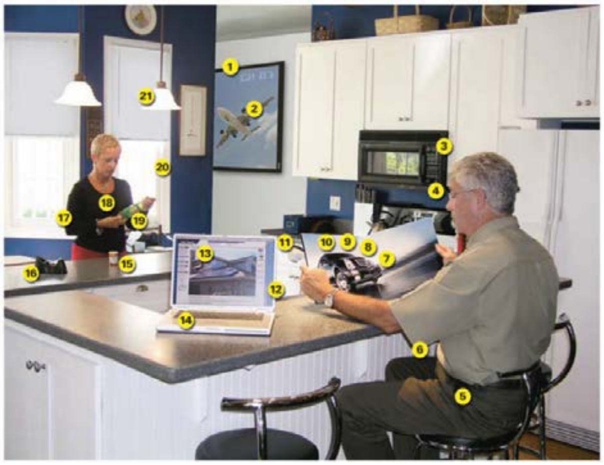
## Impact of plasma on every-day life



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 $H_2$ 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

*Plasma science: advancing the knowledge in the interest of national security, National research council (US, 2007)

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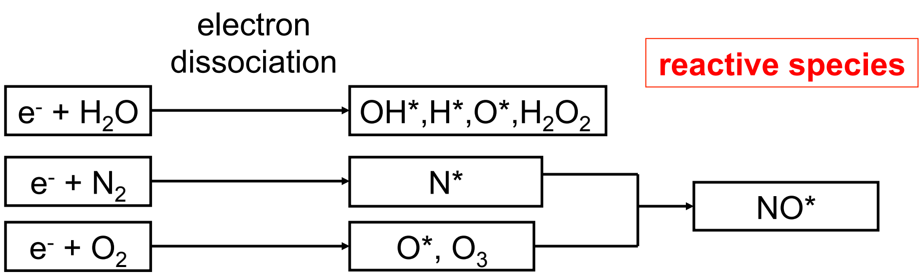
## Clean chemistry




**Non-thermal plasmas**
- **reactive chemistry @ 300K**
- **environmental friendly**

**Conventional chemistry**
- **high temperature**
- **nasty chemicals**

**Processes requiring low temperatures**

**Energy efficiency**

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## Simplified idea about plasmas in liquids

- **powerful (non-selective) oxidizing species**
- **UV**
- **shockwaves**

| |
|---|
| • $OH^*$ (2.80 V)<br>• $O^*$ (2.42 V)<br>• $H_2O_2$ (1.77 V) |

**Advanced Oxidation Processes**

→ **destruction of toxic organic compounds**

→ **decontamination / sterilisation / purification**

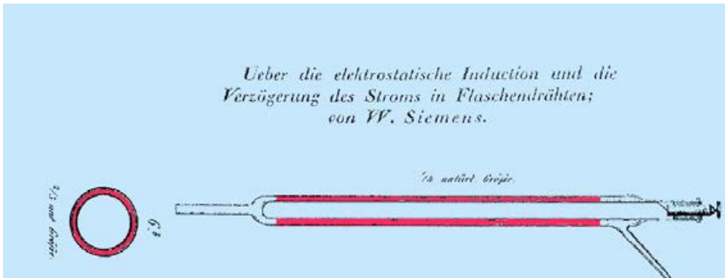


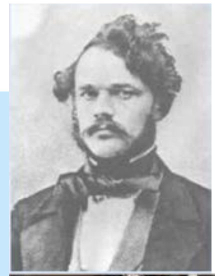
## Overview

- Chemical synthesis and conversion
- Material processing
- Environmental remediation
- Disinfection (non-medical)
- Bio-medical applications
- Light sources
- Sensing applications
- Energy, flow and propulsion applications
- Meta-materials
- Switching

# Historical example

Historical ozone tube of Werner von Siemens, 1857



$$O_2 + e \rightarrow 2O$$

$$O_2 + O + M \rightarrow O_3 + M$$

Poggendorff's Annalen der Physik und Chemie 102 (1857)



# $H_2$ and $H_2O_2$ production

**producing $H_2$ from water vapor is**

**$H_2O(g) \rightarrow H_2(g) + 0.5\ O_2(g)$ ΔH= 2.6 eV/molec (28.7 g/kWh)**

**produce $H_2O_2$ from water**

**$2H_2O \rightarrow H_2O_2 + H_2$ ΔH= 3.2 eV/molec (400 g/kWh)**

$$H_2O + e \rightarrow OH + H$$

$$OH + OH + M \rightarrow H_2O_2 + M$$

# $H_2O_2$ production

| | Input | Generation rate (g/h) | Energy efficiency (g/kWh) |
|---|---|---|---|
| Spark/pulsed corona | Liquid water | ~0.02-0.36 | 0.1-3.64 |
| Discharges in bubbles | Air/ Ar / $O_2$ in liquid $H_2O$ | 2.3 $10^{-3}$ - 26 | 0.4-8.4 |
| Gas phase corona / DBD | Air / Ar + water surface | 5.7 $10^{-5}$ – 0.12 | 0.04-5 |
| MW | Steam | 48 | 24 |
| DBD | Humid gas | 1.8 $10^{-3}$-1.6 $10^{-2}$ | 1.14-1.7 |
| Gliding arc | Water droplets (in Ar) | 0.02-0.14 | 0.57-80 |
| Electron beam | | | 8.9 |
| Vacuum UV | Vapor or liquid water | | 13-33 |
| electrolysis | | | 112.4-227.3 |

Bruggeman and Locke, Assessment of potential applications of plasma with water, Low temperature plasma technology methods and applications Eds Chu and Lu

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# $H_2$ production

| Plasma | Input | Concentration of $H_2$ (%) | Energy cost (g/kWh) |
|---|---|---|---|
| MW plasma | $H_2O$ vapor | 9 | 10 |
| AC gliding arc | Water spray in $N_2$ and Ar | 1.36 | 1.3 |
| Pulsed gliding arc | Water spray in Ar | 0.04 | 13 |
| Pulsed corona in liquid water | Liquid water | 0.4 | 0.25 |
| Packed bed | 2% $H_2O$ in Ar | 0.04 | 0.12 |
| Sliding discharge | $H_2O$ vapor | 60 | 1.2 |
| Microdischarge in porous ceramics | $H_2O$ vapor (preheated) | 0.9 | 15 |
| Arc submerged in liquid $H_2O$ | Graphite electrode | 55 | 0.83 |
| (thermal) steam arc jet | $H_2O$ | 0.4 | 0.13 |

Electrolysis: 20 g/kWh

Bruggeman and Locke, Assessment of potential applications of plasma with water, in Low temperature plasma technology methods and applications Eds Chu and Lu

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# $H_2O_2$ and $H_2$ production: conclusion

- necessities
  - water dissociation is efficient
  - not too much energy is wasted in heating water
  - rapid thermal quenching is necessary to favor the desired reaction products.

- Direct discharges in water are less efficient than gas phase discharge in contact with the liquid phase.

- Further work is needed to develop reactors of appropriate scale for applications.

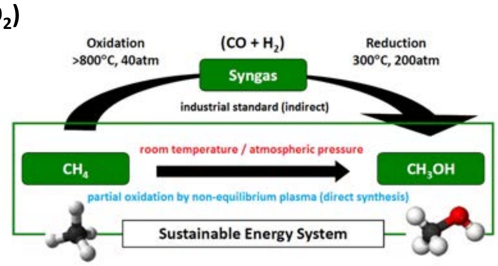


# Chemical synthesis: $CH_3OH$

- **`hydrogen economy ` – `solar fuels` (solar cells + storage)**

- **green house gas conversion ($CO_2$)**
  - **$CO_2 + 4H_2 \rightarrow CH_4 + H_2O$**
  - **dry reforming**

- **steam reforming**
  - **$CH_4 + H_2O \rightarrow CO + H_2$**




T. Nozaki et al

- **direct gas-to-liquid conversions (partial oxidation of $CH_4$ to methanol)**

**Standard processes often (large T and p, expensive catalyst)**
**→ use plasma as catalyst (T↓)**

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# Conversions: some general ideas

- several considerations for conversion processes
  - Energy efficiency
  - Conversion yield - % end product of total gas
  - selectivity

Thermal plasma – hot plasma → close to equilibrium chemical composition

Examples: $CO_2$ conversion, syngas production

Non-equilibrium plasma can favor products normally not produced under equilibrium
Examples: $O_3$, $CH_3OH$, $H_2O_2$

More information: Plasma Chemistry (A. Fridman)



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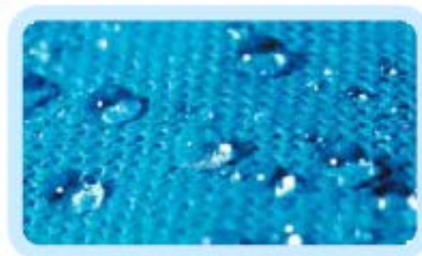
# Surface activation

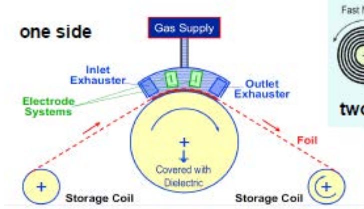
surface treatment of polymers, textiles,… to improve adhesion of dyes or before glueing

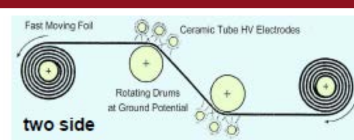


- heat sensitive materials
- hydrofobic → hydrophilic or
- hydrophilic → hydrophobic



# Corona treatment of materials




- web speed: 10 – 200 m/min
- residence time: a few seconds
- energy deposition: 0.1 – 1.0 J/cm$^2$



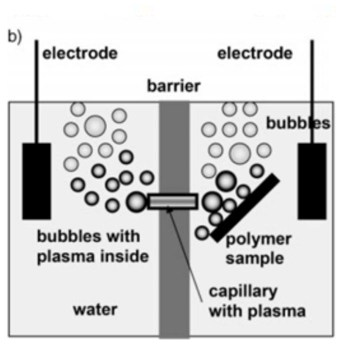
27

U. Kogelschatz, J. Salge in „Low Temperature Plasma Physics" Wiley-VCH Berlin (2001)

# Polymer treatment in liquids

**Feature Article**

Plasma Processes and Polymers




Underwater plasma, operating at atmospheric pressure, may be a new tool for polymer surface functionalization with high yield and selectivity. The yield in OH groups amounts up to about 24 OH/100 C-atoms with a selectivity of 25 to 45%. It seems to be important that water plays the role of an energy moderator repressing all processes with energy excess. Moreover, plasma-chemistry, electrochemistry and wet-chemistry can be combined simultaneously in one setup. The use of more chemistry-based processes in this system opens further possibilities. The operating expense is small.

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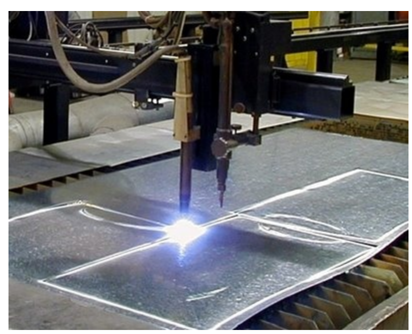
# Welding - cutting



Acknowledgement: A. Murphy

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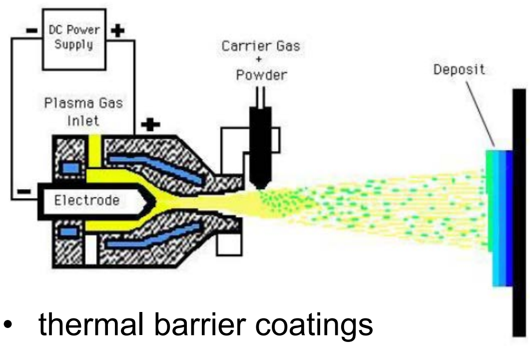
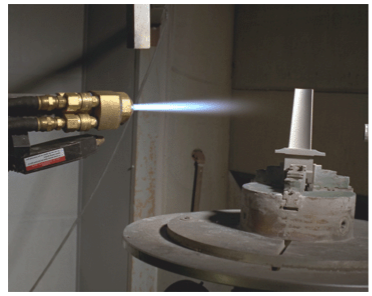
# Thermal plasma spraying



- thermal barrier coatings
- nanoparticles
- See work of Boulos, Fauchais and Heberlein

Acknowledgement: A. Murphy



# Low pressure plasma etching

inert gas

**F = very reactive radical**

$e^- + CF_4$ —electron dissociation→ $F^*$, $CF_2$, $CF_3$

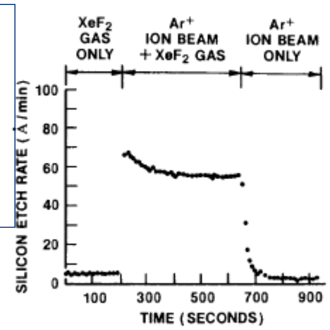
$Si(s) + 4F(g)$ —anisotropic etching→ $SiF_4(g)$

$e^- + CF_4$ —ionization→ $CF_3^+$

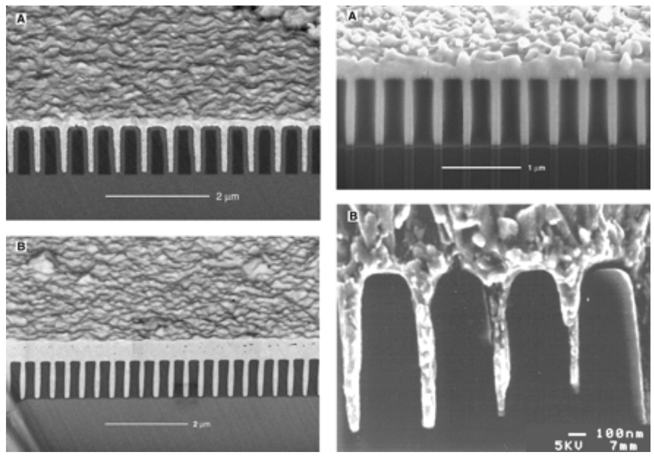
isotropic etching (ion bombardment / sputtering) Coburn and Winters (1979)

- **Also F, $CF_2$ for SiO**
- **O for photoresist**
- **Cl for aluminum**

**volatile etching products are formed**



# Anisotropy – ion bombardment




*Jason M. Blackburn, David P. Long, Albertina Cabañas, James J. Watkins*

*Science* 5 October 2001: Vol. 294. no. 5540, pp. 141 - 145

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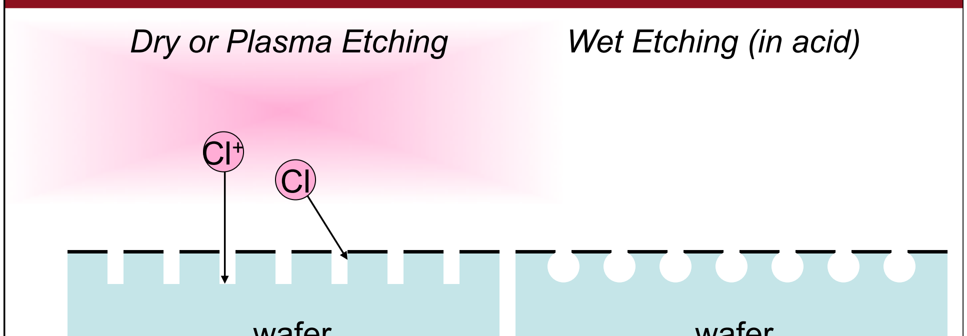
# Anisotropy – ion bombardment




Si(*s*) + 2Cl(*g*)+ ion energy → $SiCl_2$(*g*)

The directional ion energy drives the chemical reaction *only* at the bottom of the microscopic feature.

Acknowledgement: J. Hopwood

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# Etching

*Dry or Plasma Etching*

- *Control of ion energy (bias)*
- *Control of plasma density (e.g. dual frequency discharges)*

**The bombardment energy of $Ar^{+}$ (40 amu)**

$$E_{\text{bombardement}} = \frac{kT_e}{2} - e\Phi_w = (0.5 + 4.7)kT_e = 5.2kT_e$$

$$u(s) = \sqrt{\frac{2eV_0}{M}}$$



# Examples of liquid-plasma processes

→ microfluidics: surface modification of microchannel walls

(Evju et al. Appl. Phys. Lett. 2004)

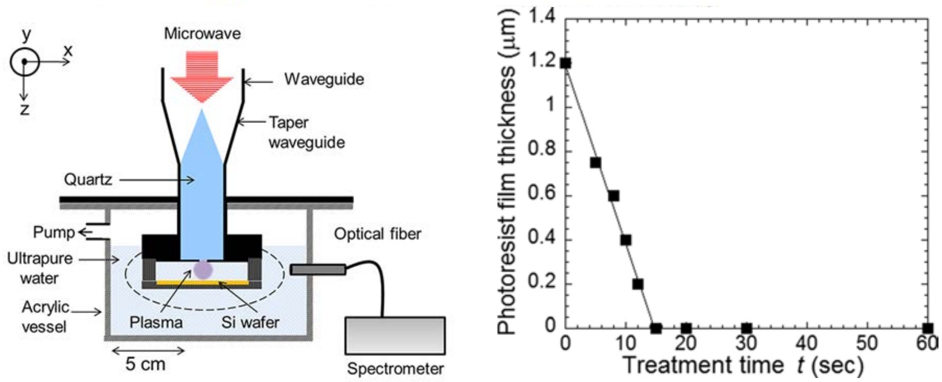
→ plasma-polishing of metallic surfaces in electrolyte solutions

(Beckmann-Institut für Technologieentwicklung)

# Photoresist removal

APPLIED PHYSICS LETTERS 103, 142101 (2013)

**A high-speed photoresist removal process using multibubble microwave plasma under a mixture of multiphase plasma environment**






# Plasma deposition: sputter deposition

In sputtering processes (Fig. 4), ions are extracted from a plasma, accelerated by an electric field, and impinge upon a target electrode composed of the material to be deposited. The bombarding ions dissipate their energy by sputtering processes in which the surface atoms are ejected primarily by momentum transfer in collision cascades. The ejected atoms are deposited upon wafers that are placed within line-of-sight of the target electrode, thus facilitating the vapor transport of material without appreciably heating either the target electrode or the wafer on which the film is deposited.

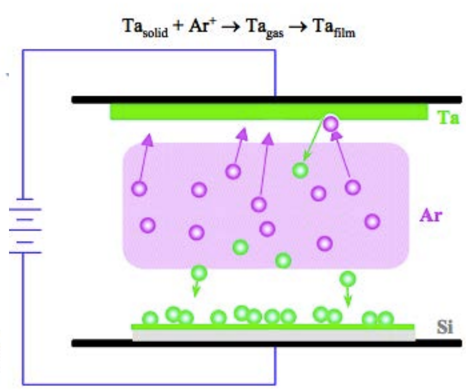



Fig. 4. Sputtering deposition process

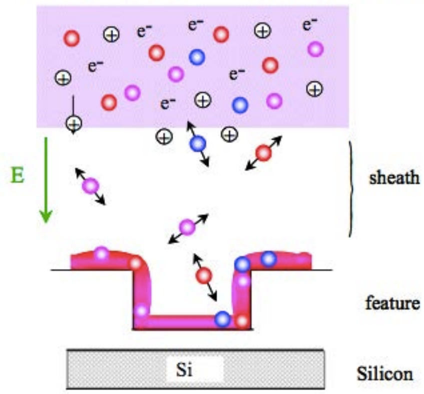
F. Chen, Principles of plasma processes

## Plasma enhanced chemical vapor deposition PECVD

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

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

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




Plasma enhanced chemical vapor deposition uses a discharge to reduce the temperature at which films can be deposited from gaseous reactants through the creation of free radicals and other excited species that react at lower temperatures within the gas-phase and on the surface (Fig. 5). The quality of the deposited film often can be improved by the use of the plasma ion flux to clean the surface before the deposition begins and by heating during processing. In addition, the ion flux can alter the film during deposition by cleaning, enhancing the mobility of adsorbed species, etc.

F. Chen, Principles of plasma processes

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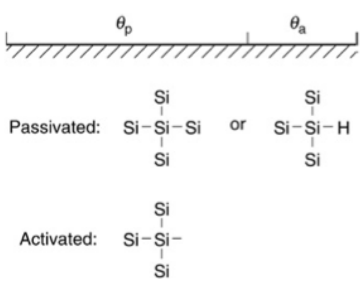
## PECVD: amorphous silicon for solar cells

**$SiH_4$**

**Important radicals: $SiH_3$, $SiH_2$**
**Ion: $SiH_3^+$**




$$SiH_3^+ + \theta_p \xrightarrow{K_i} \theta_a + Y_i H(g)$$

$$SiH_2 + \theta_a \xrightarrow{K_2} \theta_a$$

$$SiH_2 + \theta_p \xrightarrow{K_{2p}} \theta_p$$

$$SiH_3 + \theta_a \xrightarrow{K_3} \theta_p$$

$$SiH_4 + \theta_a \xrightarrow{K_4} \theta_p + SiH_3(g)$$

**Note that H flux is important!**

Lieberman, Principles of plasma discharges and material processing

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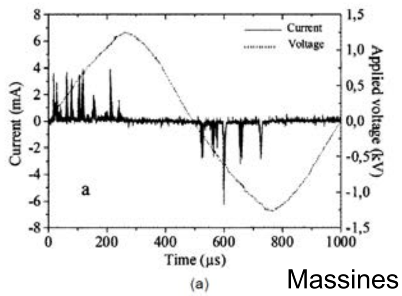
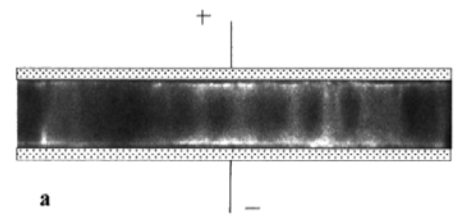
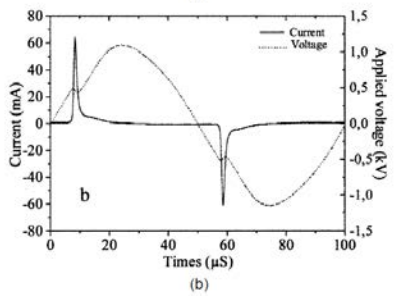
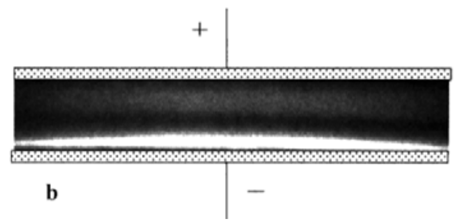
# Atmospheric pressure PECVD: challenges




Massines et al J. Phys. D: Appl. Phys. 31 3411, 1998

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# Atmospheric pressure PECVD - ALD

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Surface & Coatings Technology 200 (2005) 1855 – 1861

SURFACE & COATINGS TECHNOLOGY

www.elsevier.com/locate/surfcoat

Atmospheric pressure plasma deposition of thin films by Townsend dielectric barrier discharge

Françoise Massines *, Nicolas Gherardi, Antonella Fornelli, Steve Martin

*Laboratoire de Génie Electrique de Toulouse, CNRS, UPS, 118 route de Narbonne, 31062 Toulouse cedex 4, France*

Available online 15 September 2005

- **Role-to-role**
- **Diffuse discharge (but not a necessity- vd Sanden)**
  **– homogeneous coatings**
- **$SiH_4$ - Hexamethyldisiloxane (HMDSO)**

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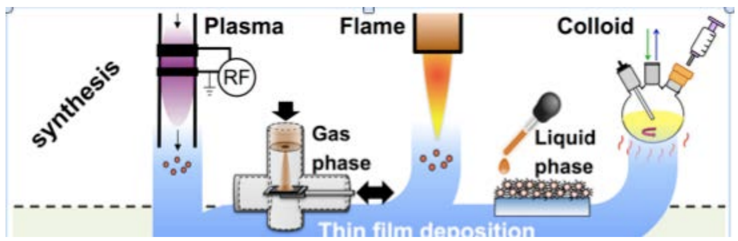
# Production of nano-materials




**Different processes:**
**plasma is competing with flame or colloidal chemical methods**

U. Kortshagen, UMN

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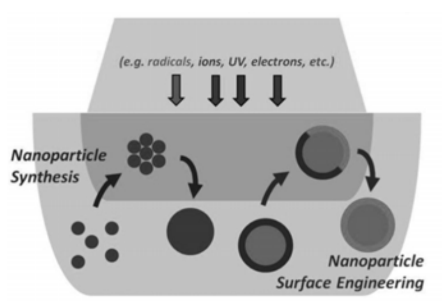
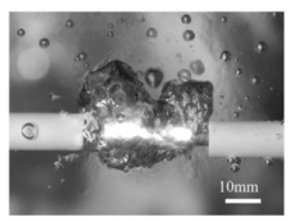
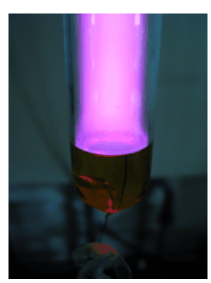
# Nanoparticles: plasmas and liquids



Mariotti et al PPP (2012) (9) 1074-1085
Kaneko et al PPP (2009) (6) 713-718
Takai (2008) Pure Appl. Chem. 80, 2003–2011
Meiss et al (2007) ChemPhysChem. 8 50-53
**Gubkin (1887) Ann. Phys. Chem. 32, 114**

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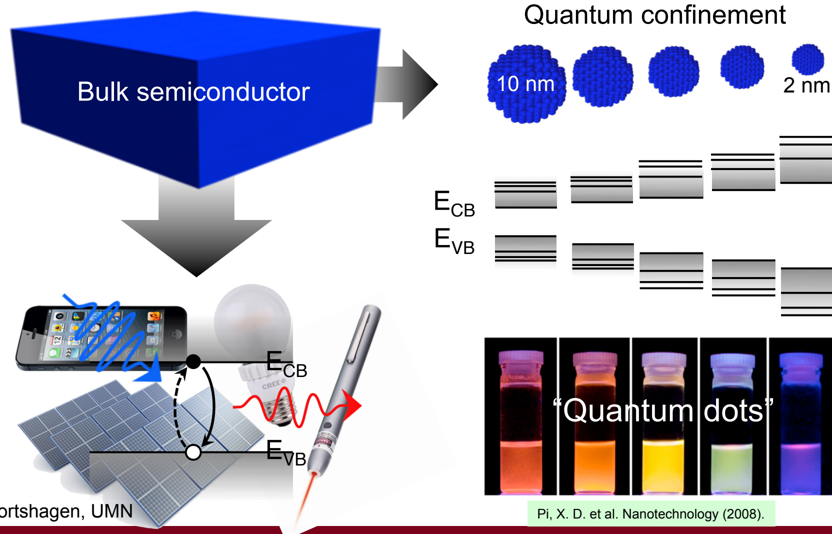
# Nano-crystals and particles




U. Kortshagen, UMN

Pi, X. D. et al. Nanotechnology (2008).

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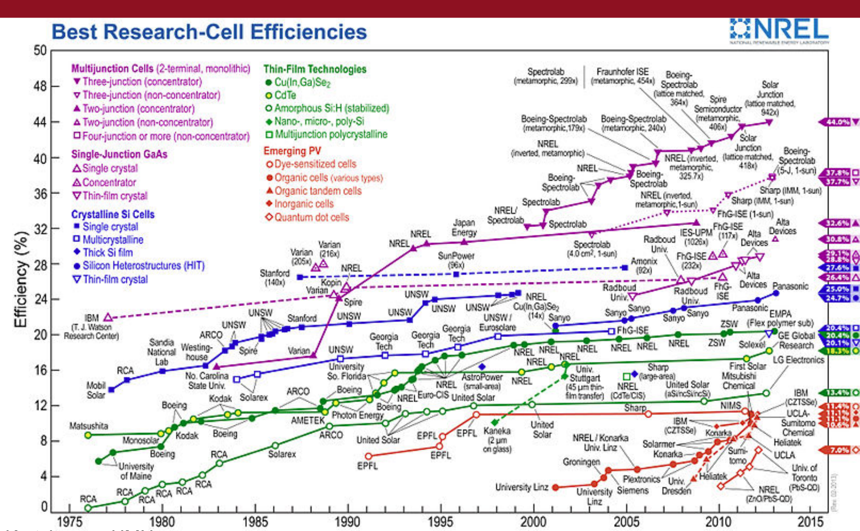
# Solar cells

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# (Possible) applications of nano-crystals

**DuPont Innovalight Si ink**

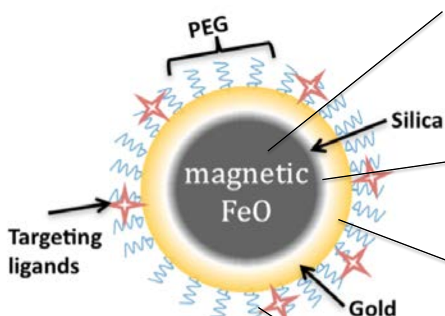

U. Kortshagen, UMN

Phys.org

http://news.cnet.com



# Example: nanoparticle for cancer theranostics




Superparamagnetic iron oxide enhances MRI contrast; magnetic-field-induced hyperthermia

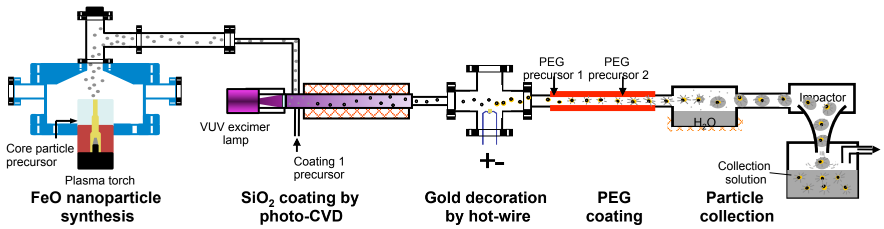
Silica shell suppresses coagulation, improves stability, modulates optical properties of gold layer

Gold layer — surface plasmon: surface-enhanced Raman scattering & fluorescence imaging; laser ablation

Organic molecules improve solubility & biocompatibility & provide active targeting

S. Girshick, UMN

## Nanoparticle manufacturing assembly line




Synthesis of $Fe_3O_4$ @ $SiO_2$ @ Au @ PEG nanoparticles

Key challenge: control of dimensions, morphology, chemical composition & properties of each layer

S. Girshick, UMN

**More than just plasma!**



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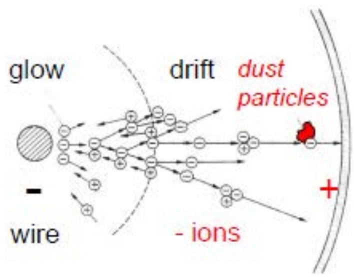
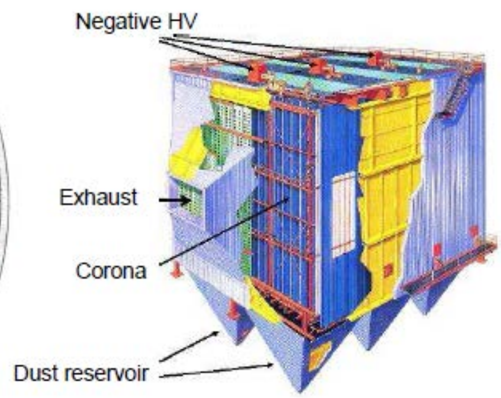
# Electrostatic precipitators

**Electro filter in power stations (dust filter)**

- standard technique !



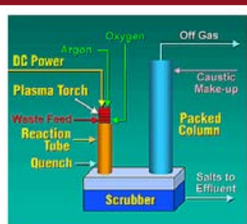

attachment: A+e → $A^-$

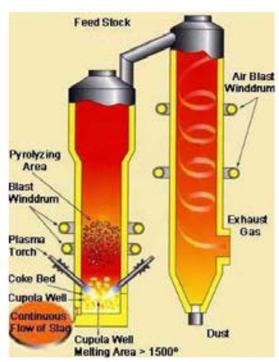



Acknowledgement: R. Brandenburg



# Thermal plasma waste treatment




- Plasma pyrolysis
- Plasma gasification (syngas)
- Vitrification

J. Heberlein and T. Murphy, Thermal plasma waste treatment, JPhysD 2008

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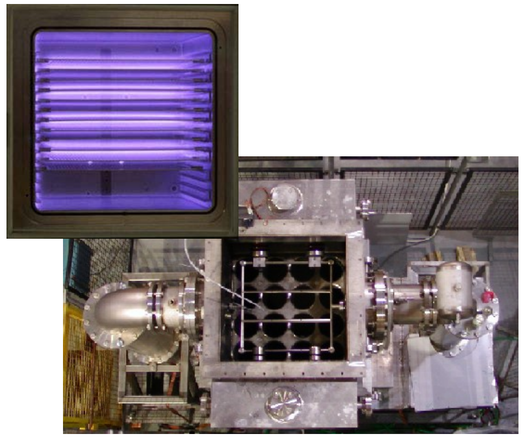
# Air remediation: VOC –$NO_x$ removal

$$RH + OH \rightarrow R^{\bullet} + H_2O$$

$$R^{\bullet} + O_2 \rightarrow RO_2^{\bullet}$$

$$RO_2^{\bullet} + RH \rightarrow RO_2H + R^{\bullet}$$

non-soluble — soluble



- high gas throughput
- low gas heating
- efficient water dissociation

→ nano-second pulsed corona, flowing water wall

Pemen, TU/e

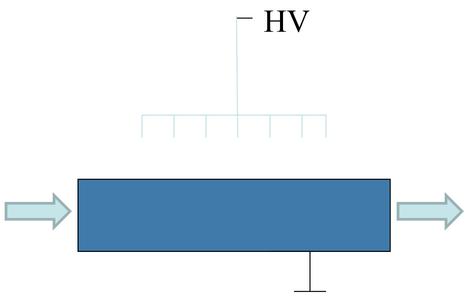
See also work of H. Akiyama and K. Yan

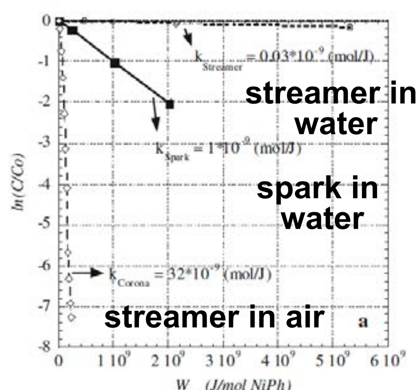


# Water treatment with plasmas

→ pulsed corona above water is most efficient!!

removal of phenol / dye

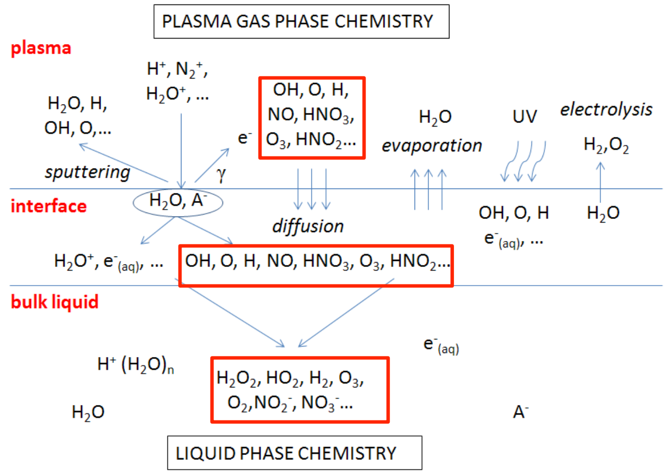



- **there exist successful applications for thermal arcs in water treatment**
- **direct discharges in liquid for desalination (group of Fridman)**

Grabowski, van Veldhuizen et al PCPP, **26**, 1 (2006)
Dang, Denat et al Eur. Phys. J. Appl. Phys. **47,** 22818 (2009)

# Transfer of reactivity… transport limited?




P. Bruggeman, Plasmas in and in contact with liquids: a retrospective and an outlook. In Plasma Roadmap, J. Phys. D (2012)

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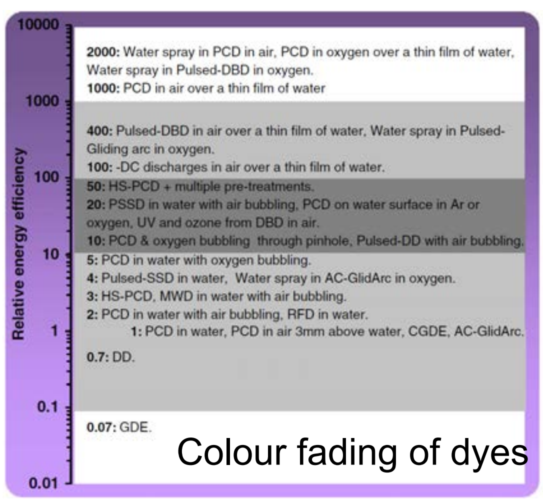
# Water treatment with plasmas




M.A. Malik, Plasma Chem Plasma Process, 2010

- **Pulsed corona in gas phase**
- **DBD**
  **Pulsed gliding arc**
- **Pulsed streamers in bubbles**
- **Pulsed streamers in water**
- **Diaphragm and glow discharge electrolysis**

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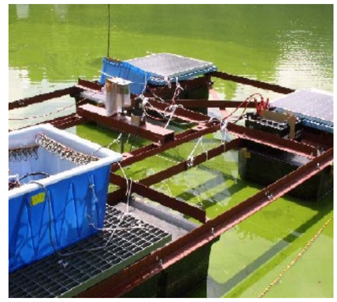
## Algae and wine

→ algae treatment of ponds and lakes

(group of prof. H. Akiyama, Kumamoto)



→ testing setup for plasma treatment of grapes in the wine producing process (it should provide a richer flavour to the wine)

(group of prof. Bluhm, Karlsruhe)

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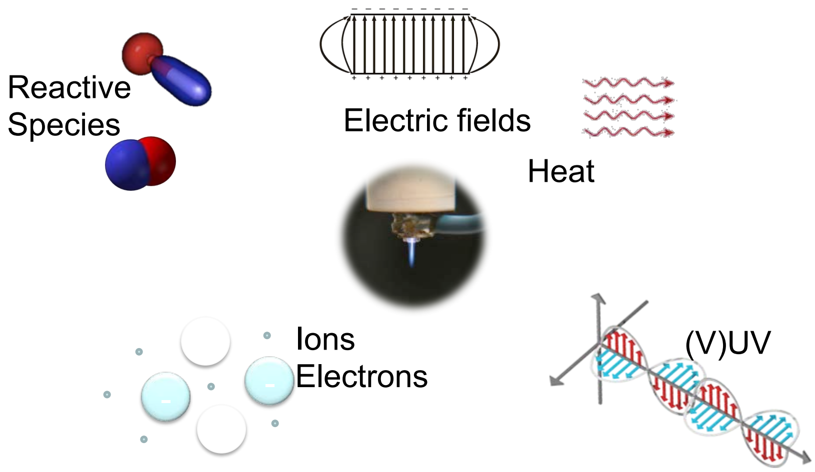
## The plasma cocktail…

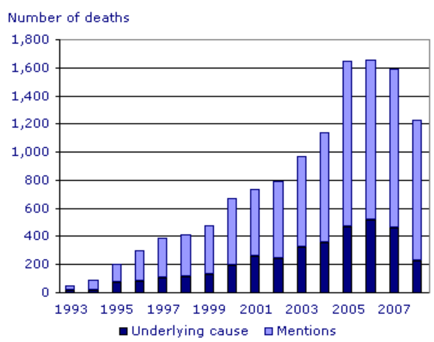





## Motivation…

**„Bacteria can become resistant to antibiotics“**

Alexander Fleming, 1945 when receiving the Nobel prize in Medicine.




***Number of deaths associated with MRSA in UK***

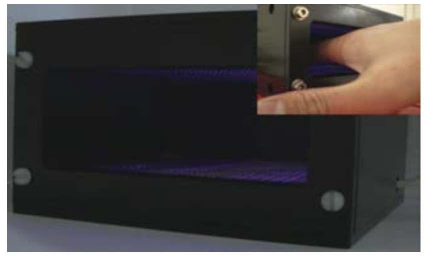
*(Office for National statistics, UK)*

*Grundmann et al. *Lancet 2006*; ***368: 874-85.***

Global Health Care Associations consider multi-resistant germs like MRSA as a global threat *

# Some applications…

Sterilization / disinfection (bacteria, fungi, virus)



- air
- surfaces (food packaging)
- surgical equipment
- hands
- operation rooms / hospital wards

**Hand disinfection:** `HandPlaSter'
(DBD, 18 $kV_{pp}$ at 12.5 kHz)
Max-Planck-Institute, Garching

work of Alexieff, Laroussi, Awakowicz, von Woedtke,…



# Disinfection: numbers (E. coli in $H_2O$)

| Plasma | D-value* (J/ml) | Liquid conductivity (mS/cm) | Initial bacterial density (CFU/ml) |
|---|---|---|---|
| Surface discharge | 0.3 | 0.1 | $10^6$ |
| Pulsed corona in water | 3 | 1.6 | |
| Pulsed arc in water | 18.7 | | $10^7$ |
| DBD in air (bubbling) | 0.29 | | |
| Pulsed corona in water | 33.3 | 0.365 | $10^4$-$10^5$ |
| Pulsed arc in water | 2.1 | Drinking water | $10^5$-$10^6$ |
| Pulsed corona in water | 45 | 0.1 | $10^6$-$10^7$ |
| Capillary discharge in water | 5.4 | 0.9 NaCl in $H_2O$ | $10^7$ |
| Corona in water | 18 | 0.2 | $10^5$ |
| PEF | <5 | 13 | $10^5$ |
| Streamers in air bubbles | 13 | | $10^5$-$10^6$ |
| Spark arc | 1 | | 4 $10^4$ |
| Pulsed corona in air | 0.1 | 0.9 | $10^7$-$10^8$ |
| 10 μs pulsed discharge in liquid | 158 | 0.9 NaCl in $H_2O$ | 2.5 $10^5$ |
| Surface streamers | 8.6 | Tap | $10^7$ |
| Spark discharges in water | 0.1-0.4 | 0.2 | $10^4$-$10^6$ |
| packed-bed air bubble discharge | 9 | 0.91-15.7 | $10^6$ |

Bruggeman and Locke, Assessment of potential applications of plasma with water, in Low temperature plasma technology methods and applications Eds Chu and Lu

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# Efficiency of bacteria inactivation

Necessities:
• the efficient production of radicals and UV
• efficient transport of the radicals

Both ROS and RNS inactivate bacteria!

Both spark discharges in liquids and DBD or pulsed corona discharges in the gas phase are most efficient for bacterial inactivation.



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## A key review

IOP PUBLISHING — JOURNAL OF PHYSICS D: APPLIED PHYSICS
J. Phys. D: Appl. Phys. 45 (2012) 263001 (42pp) — doi:10.1088/0022-3727/45/26/263001

**TOPICAL REVIEW**

# The emerging role of reactive oxygen and nitrogen species in redox biology and some implications for plasma applications to medicine and biology

**David B Graves**

Department of Chemical and Biomolecular Engineering, University of California, Berkeley, CA 94720, USA

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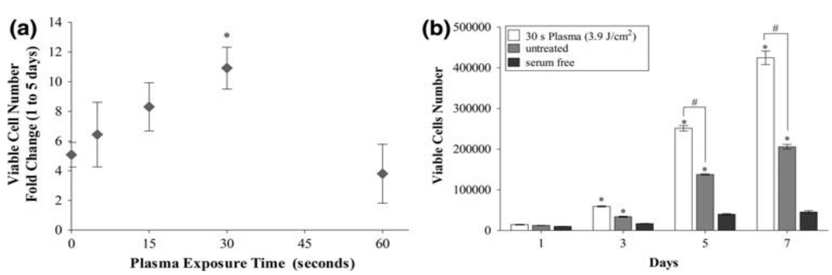
## More than disinfection!

**Endothelial Cell Proliferation is Enhanced by Low Dose Non-Thermal Plasma Through Fibroblast Growth Factor-2 Release**

SAMEER KALGHATGI,[1] GARY FRIEDMAN,[1] ALEXANDER FRIDMAN,[2] and ALISA MORSS CLYNE[2,3]

[1]Electrical and Computer Engineering, Drexel University, Philadelphia, PA 19104, USA; [2]Mechanical Engineering and Mechanics, Drexel University, 3141 Chestnut Street, Philadelphia, PA 19104, USA; and [3]School of Biomedical Engineering, Science, and Health Systems, Drexel University, Philadelphia, PA 19104, USA

*(Received 16 July 2009; accepted 2 December 2009; published online 15 December 2009)*

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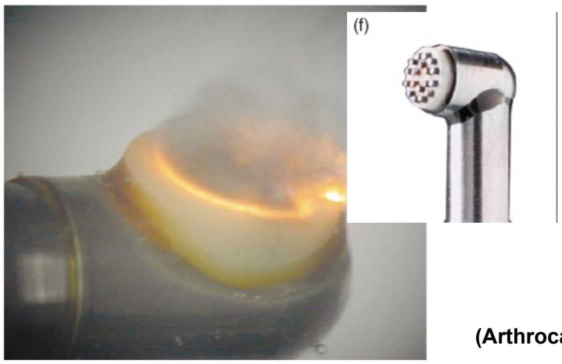
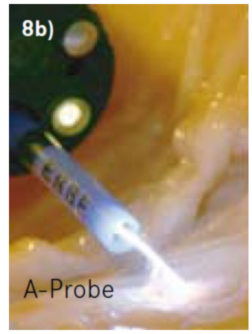
## Established medical applications (1)

- Blood coagulation (hemostasis)
- Tissue ablation




(Arthrocare Inc.)



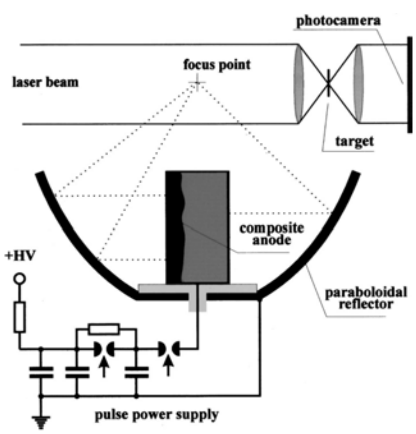

(Erbe USA Inc.)



## Established medical applications (2)

plasma generator of focused shockwave in medicine (lithotripsy)

(prof. Šunka, IPP Prague)



# Towards wound healing

Drexel University

Tu/e EPG


*(G. Fridman, et al, Plasma Processes and Polymers **5** (2008) 503-533).*

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# Wound healing: examples

-Study Munich (Isbary, Morfill)
-Study Greifswald (v Woedtke, Metelmann)
-Study Göttingen (Emmert, Viöl)
>> all with positive indications



J. Heinlin et al. 2010

Acknowlegdement: K Wende

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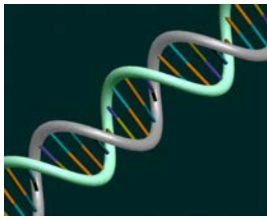
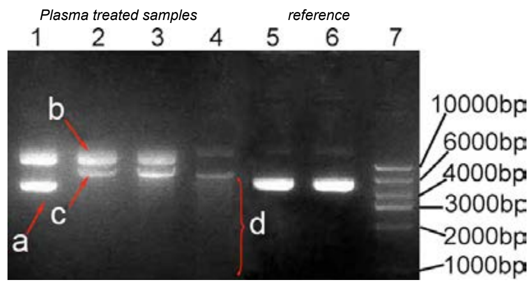
# Is it safe?



*If not right dose:*

- ***irreversible damage (cancer?)***
- ***cell death***




*Plasma induced DNA changes*

*(Lu et al App. Phys. Lett. 2009)*

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# Wound healing impact

## Wound healing

- 1% of the population in developed countries is suffering from chronic wounds
- wound healing corresponds in total to a (worldwide) market of US$1 bn*


*G. Lloyd et al, Gas Plasma: medical uses and developments in wound care, Plasma Processes and Polymers, 6 (2009)

Acknowledgement image: A. Fridman

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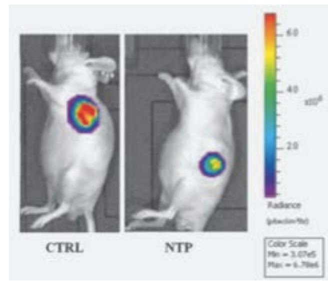
# Cancer treatment?

uicc global cancer control

IJC International Journal of Cancer

**ROS implication in a new antitumor strategy based on non-thermal plasma**

Marc Vandamme[1,2,3], Eric Robert[2], Stéphanie Lerondel[3], Vanessa Sarron[2], Delphine Ries[2], Sébastien Dozias[2], Julien Sobilo[3], David Gosset[4], Claudine Kieda[4], Brigitte Legrain[5], Jean-Michel Pouvesle[2] and Alain Le Pape[3,6]
[1] GERMITEC SAS, 30 rue Mozart, 92110 CLICHY, France
[2] GREMI UMR-6606 CNRS, Université d'Orléans, 14 rue d'Issoudun - BP 6744, 45067 ORLEANS cedex 2, France
[3] TAAM-CIPA, UPS44 CNRS, 3B rue de la Ferollerie, 45071 ORLEANS cedex 2, France
[4] Plateforme de Cytométrie et d'imagerie cellulaire, Centre de Biophysique Moléculaire, UPR4301 CNRS, rue Charles Sadron, 45071 ORLEANS cedex 2, France
[5] NOVAXIA, ZA Petit Four, 41220 Saint Laurent Nouan
[6] Inserm U618, Université Francois Rabelais, Tours, France




addition, *in vivo* experiments on U87MG bearing mice showed that NTP induced a reduction of bioluminescence and tumor volume as compared to nontreated mice. An induction of apoptosis was also observed together with an accumulation of cells in S phase of the cell cycle suggesting an arrest of tumor proliferation. In conclusion, we demonstrated here that the potential of NTP to generate ROS renders this strategy particularly promising in the context of tumor treatment.

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## Light sources

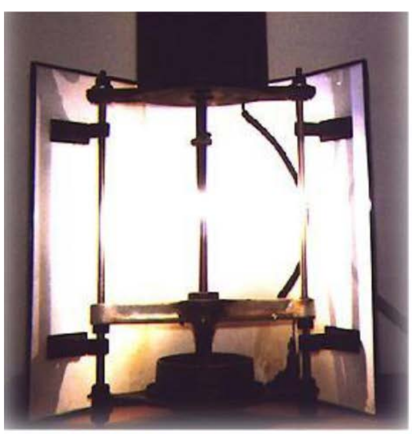
old fashion lighting?  LED??

Some applications depend still heavily on plasmas (HID lamps)

large buildings, street lighting, …



## Arc lamps



Carbon arc lamp

Xenon arc lamp

Acknowledgement: A. Murphy

# Excimer lamps

$$e + Xe \rightarrow e + Xe^* \quad \rightarrow \quad Xe^* \rightarrow Xe + \text{photon}$$

$$\tau \approx 10^{-4} s$$

$$Xe^* + 2Xe \rightarrow Xe_2^* \rightarrow Xe_2^* + Xe \rightarrow 2Xe + \text{photon}$$

$$\tau = \frac{1}{kn_{Xe}^2} \approx \frac{10^{-7}}{p^2(\text{bar})} s$$

| **$Ar_2^*$** | **$Kr_2^*$** | $F_2^*$ | **$Xe_2^*$** | ArCl* | ArF* | **KrCl*** | KrF* | XeI* | $Cl_2^*$ | XeBr* | $Br_2^*$ | **XeCl*** | $I_2^*$ | XeF* |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **126** | **146** | 157 | **172** | 175 | 193 | **222** | 248 | 253 | 259 | 282 | 289 | **308** | 342 | 354 |

high pressure microplasmas or DBDs

Kogelschatz (PCPP 2003)

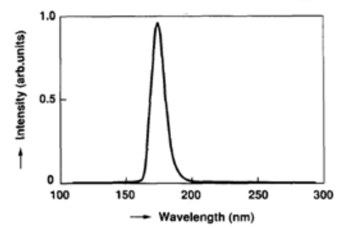
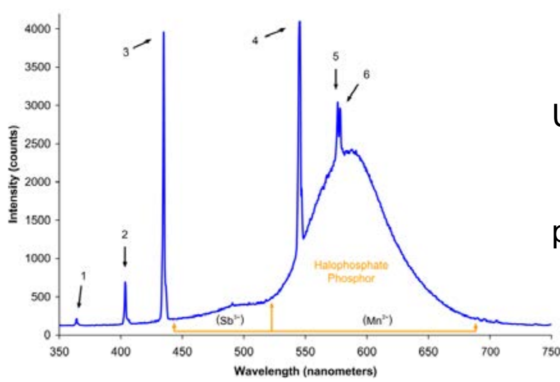



Fig. 23. Emission spectrum of a silent discharge operating in xenon (second continuum of $Xe_2^*$ excimer).



# Fluorescent lamp spectrum

$Hg + e^-_{(hot)} \rightarrow Hg^* + e^-_{(cold)} \rightarrow Hg + light + e^-$

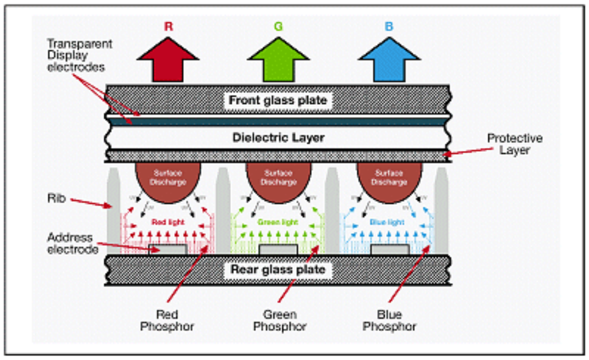


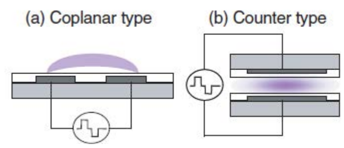

UV emission (254 nm)

phosphor

http://en.wikipedia.org

# Plasma display panel (PDP)



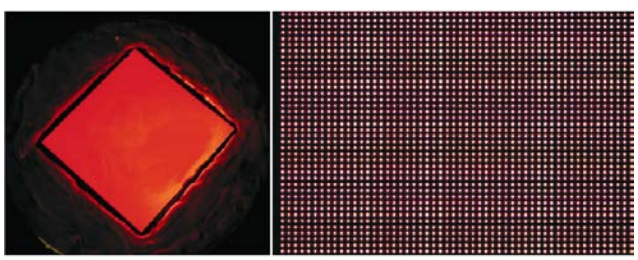



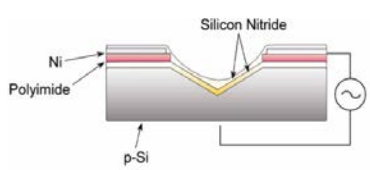

- each pixel: 3 DBD microplasma in e.g. Ne/Xe mixtures
- UV emission is converted by red, blue or green phosphor

Tachibana et al.



# Microplasma light sources






- flexible sheaths
- mercury-free
- high pressure (close to 1 bar)
- from VUV to near IR by selecting gas filling

Becker, Schoenbach, Eden, J. Phys. D: Appl. Phys. **39** (2006) R55–R70
Eden Park illumination

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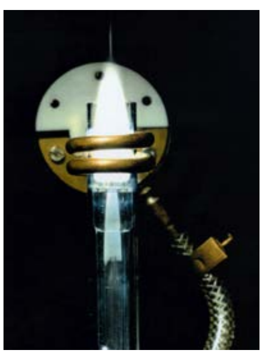
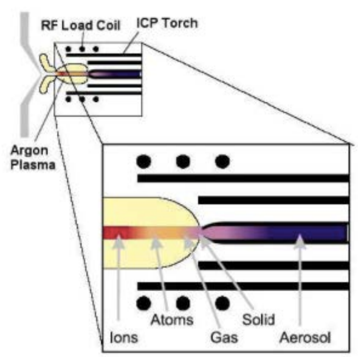
# Chemical analysis

ICP-MS and ICP-OES
Detection of elementary species



ICP –100 MHz, Ar
with liquid analyte
~1500 W

(EPG- TU/e)




Perkin Elmer Inc

chemical analysis (lab on chip sensors: OES, MS)
Review: V. Karanassios, Spectrochimica Acta Part B 59 (2004)

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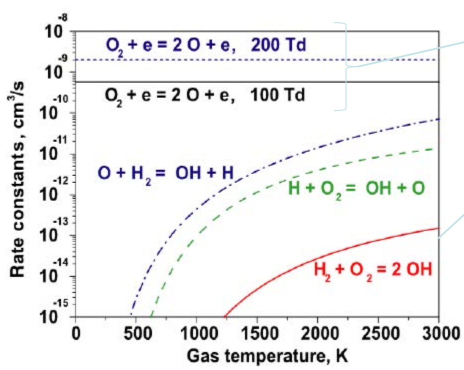
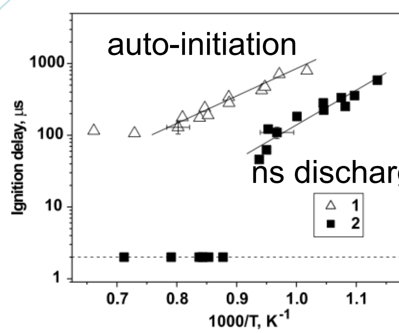
# Plasma assisted ignition




plasma-initiation reaction

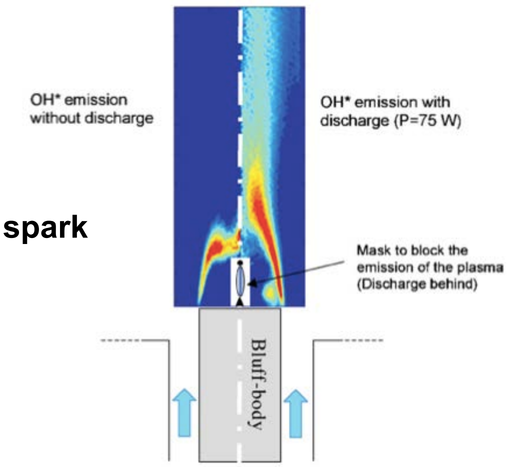
auto-initiation reaction




S.M. Starikovskaia, J. Phys. D: Appl. Phys. 39, 2006
Bozhenkov et al, Combust. Flame 133, 2003

# Plasma assisted combustion

**Flame stabilization by ns spark**




Laux et al, AIAA-2005



# Flow control

Coronas / DBDs can induce or influence flow patterns

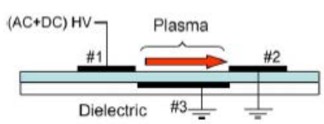



**Figure 37.** Schematic side view of the sliding discharge actuator.

E. Moreau, J. Phys D 2007 (review)

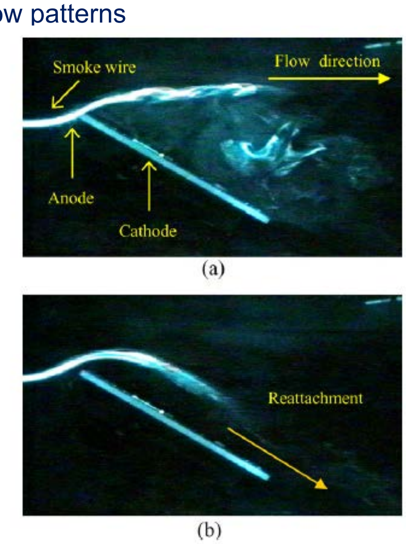



**Figure 41.** 2D visualization of the airflow at 0.4 m s$^{-1}$, (*a*) in the absence, and (*b*) in the presence of discharge.

# Propulsion

- neutral gas (combustion 3-5 kms[-1])

$$v_n = \sqrt{\frac{8kT_n}{\pi M_m}}$$

- electron propulsion (5-50 kms[-1])

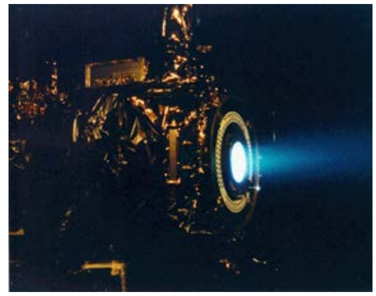
$$v_i = \sqrt{\frac{2qV}{M_i}},$$

- specific impulse $I_{sp} = v_{ex}/g$

Propellant fuel consumption

$$P_{loss} = A_{sheath} q n_{sheath} v_i \left( V_p + E_i + E_e + \frac{2kT_e}{e} \right)$$

$I_{sp}$ ↑, $v_i$ ↑, inert gas and $E_i$, M low → Xe



http://nmp.nasa.gov/ds1/images.html

| Gas | $E_i$ (V) |
|---|---|
| Xenon* (Xe) | 12.1 |
| Argon* (Ar) | 15.7 |
| Neon* (Ne) | 21.6 |
| Helium* (He) | 24.6 |

C. Charles, J. Phys D 2009 (review)



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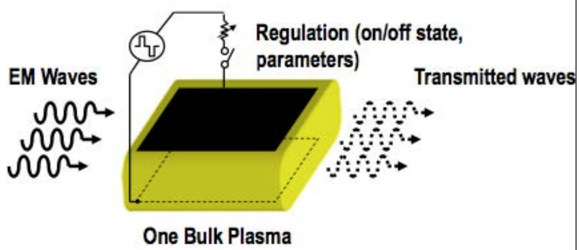
# Meta-materials: introduction

$$\varepsilon_p = 1 - \frac{\omega_{pe}^2}{\omega^2(1 + j\nu_m/\omega)}$$

Collisionless plasma:

$$\omega = \sqrt{\omega_p^2 + k^2c^2},$$

$\omega<\omega_{pe}$ absorber
$\omega>\omega_{pe}$ transmitter




Remember $10^{16}$ m$^{-3}$ → f~ 9 x10 $^8$s$^{-1}$ (f ~ $\sqrt{n_e}$)

dielectric media for controlling the transmittance of EM waves

Sakai and Tachibana, PSST 2012 (review)

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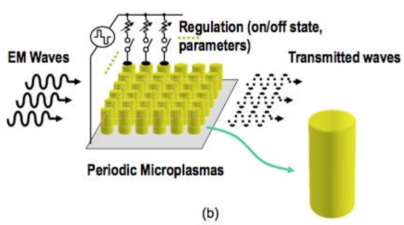
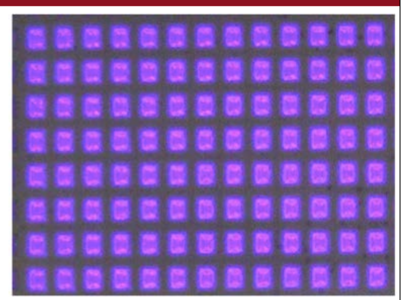
# Meta-materials



artificially structured dielectric media for controlling the transmittance of microwaves (photonic crystals)

→ Plasma array 1 mm – sub mm
→ frequency 1 GHz- THz
→ corresponds to $n_e$ ~ $10^{19}$-$10^{22}$ m$^{-3}$ (plasma frequency)

Sakai and Tachibana, PSST 2012 (review)

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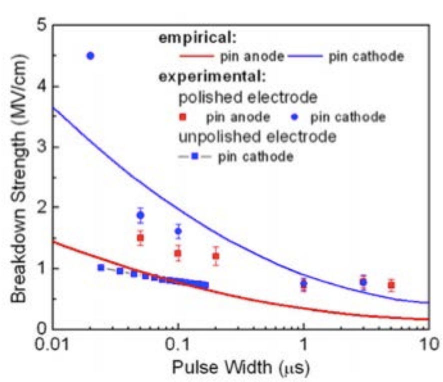
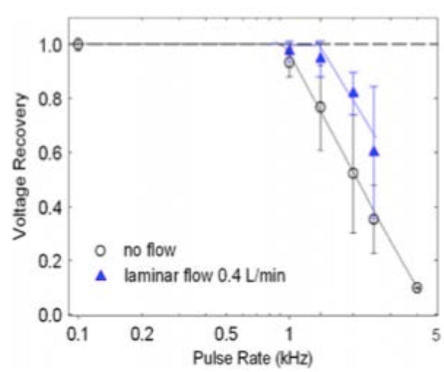
# Overview

- Chemical synthesis and conversion
- Material processing
- Environmental remediation
- Disinfection (non-medical)
- Bio-medical applications
- Light sources
- Sensing applications
- Energy, flow and propulsion applications
- Meta-materials
- Switching



# High voltage switching




Switches in dielectric liquids (water, oils)
Importance of breakdown strength and recovery after breakdown

Schoenbach et al PSST 17 (2008) 024010

# Overview

**Conclusions and some additional take-home messages**

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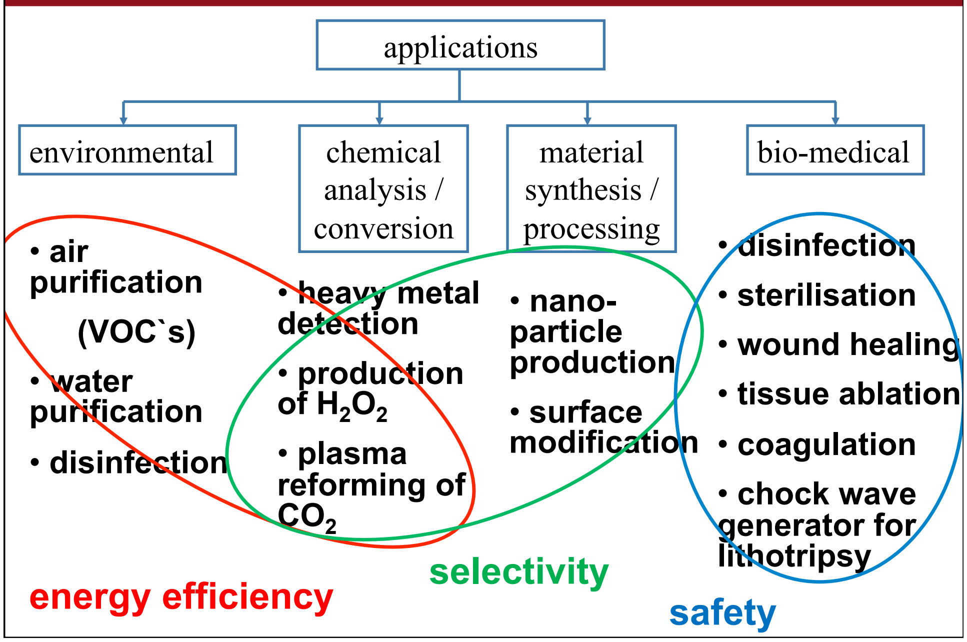
# Non-equilibrium plasma application challenges



## From Plasma Processes to applications

Plasma control – electrical excitation, gas composition

electron kinetics → Thomson scattering

gas phase chemistry → Laser diagnostics - model

- radical flux
- ion flux

→ Mass spectrometry (MS)

liquid phase chemistry → Ion chromatography, MS, chem. probes

application → In collaboration with specialist

## Good starting point to read…

IOP Publishing — Journal of Physics D: Applied Physics
J. Phys. D: Appl. Phys. 45 (2012) 253001 (37pp) — doi:10.1088/0022-3727/45/25/253001

REVIEW ARTICLE

### The 2012 Plasma Roadmap

Seiji Samukawa[1], Masaru Hori[2], Shahid Rauf[3], Kunihide Tachibana[4], Peter Bruggeman[5], Gerrit Kroesen[5], J Christopher Whitehead[6], Anthony B Murphy[10], Alexander F Gutsol[8], Svetlana Starikovskaia[9], Uwe Kortshagen[7], Jean-Pierre Boeuf[11], Timothy J Sommerer[12], Mark J Kushner[13], Uwe Czarnetzki[14] and Nigel Mason[15]

a brief summary of the status and challenges for the non-equilibrium plasma field for 15 specific research areas

## Conclusions

**Plasmas shape our world and will play an increasing role in health care, materials and environmental-energy applications.**

- **a lot of promising results on wound healing, safety is under investigation in clinical trials**
- **`cleaner' plasma-wet chemical processes**
- **nanoparticle production and complex materials**
- **disinfection**
- **chemical synthesis and conversion**
- **environmental remediation**
- **sensors**
- **energy applications**

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## Closing remarks:

- **Plasma is not the magic solution for every technological challenge!**
- **Plasma often plays a key role in a series of complex (non-plasma based) processes.**
- **Physical and chemical understanding of plasmas is a necessity!**
- **The key to success: control of the plasma process!**

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