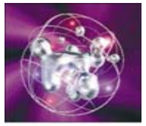




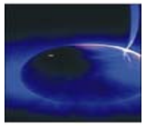


Technology Moving Forward - Plasma for the Food Industry

James W Bradley

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University of Liverpool

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Overview

Plasmas – in the food industry

Talk covers

- Brief introduction on plasmas
- Surface treatment and barrier coatings for packaging
- Bio-active coatings
- Application of plasmas for food preservation
- Detection of bacteria
- Future prospects and summary

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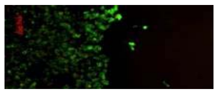
Technological Plasma Group
Dept. of Electrical Engineering and Electronics, University of Liverpool

Prof. J W Bradley — **Low and high-pressure materials processing plasmas**
Dr. X Tu — **Plasma catalysis and material reforming**
Dr. J Walsh — **Atmospheric pressure plasmas**



Physical Vapour Deposition of functional thin films/coatings (magnetron sputtering)


Low-pressure plasma surface modification and polymerisation




Atmospheric-pressure plasmas and micro-plasma meso-scale functional film deposition and treatment, decontamination and sterilization

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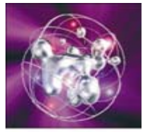
The group has a senior experimental officer, a lab technician and 3 post docs and 10 PhD students

Last 5 years has topped £5M

We have 2 laboratories, one with five research-scale industrial systems and a laser and complex plasma laboratory - £0.6M

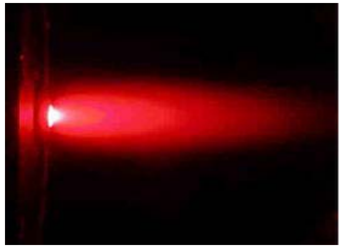






What is a plasma?

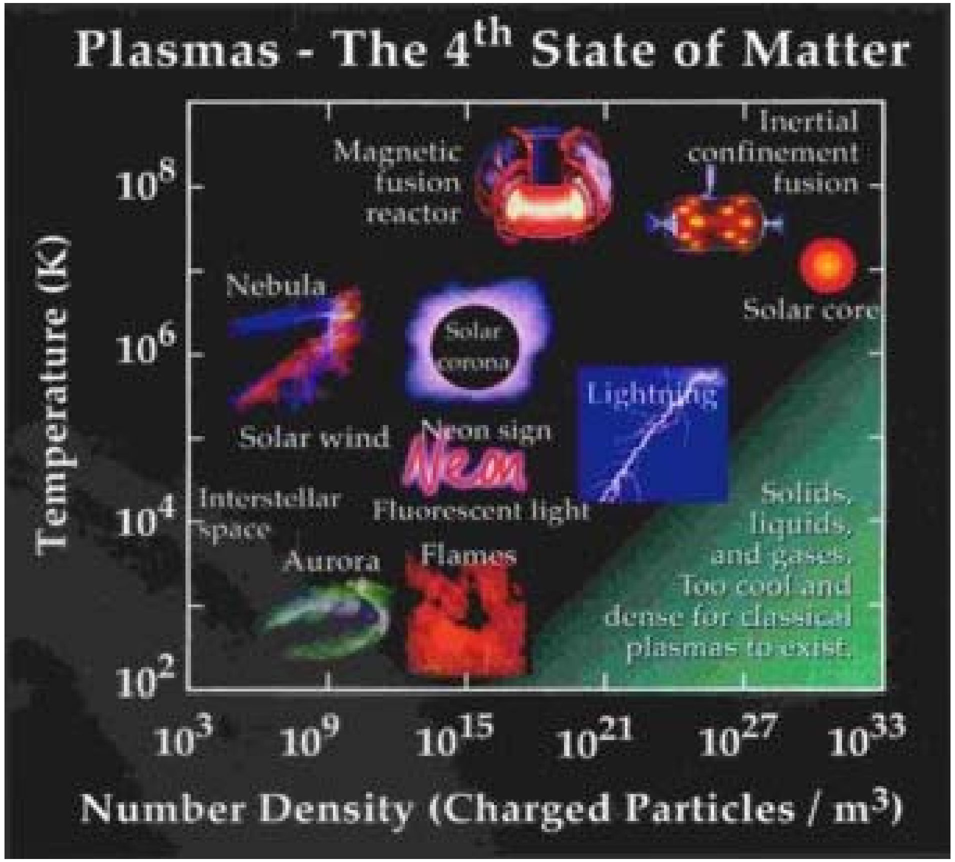
- Plasma is an ionized gas consisting of free electrons, ions, reactive atoms, neutral molecules and photons

H_2O (s)	H_2O (l)	H_2O (g)	H, H_2, H^+, e^-, H_2^- O, O_2, O_3, O^-, O_2^-
			
Solid	Liquid	Gas	Plasma

→ Add energy

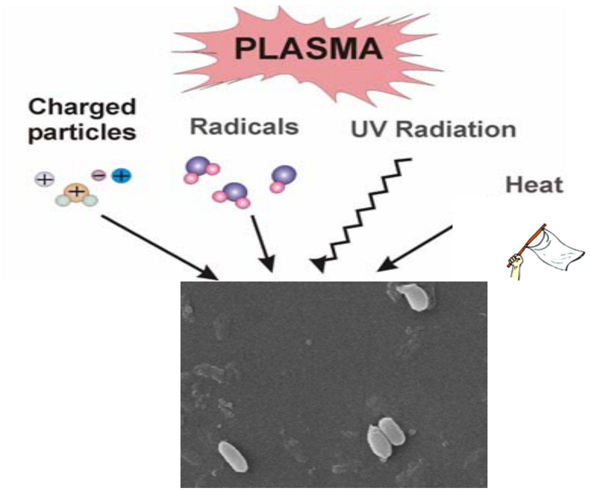
- The plasma state can be reached by supplying sufficient energy (heat or electric power) to a gas or mixture of gases
- Plasmas can be operated both at low and atmospheric pressure

Dr. Ariël de Graaf, ariel.degraaf@tno.nl

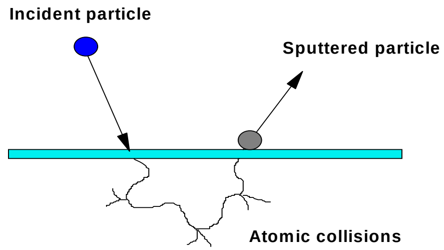


Plasma: A mixture (soup) of positive and negative charges as well as neutral particles and photons

Plasma exist over a massive range in temperatures and densities

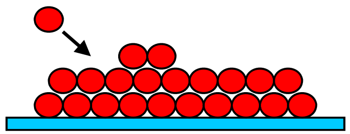


Plasma constituents
are not in thermal equilibrium
$kT_e >> kT_i \cong kT_{gas} \cong kT_{surface}$

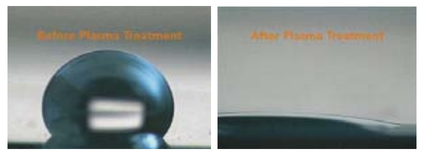


1) Remove material

2) Add material



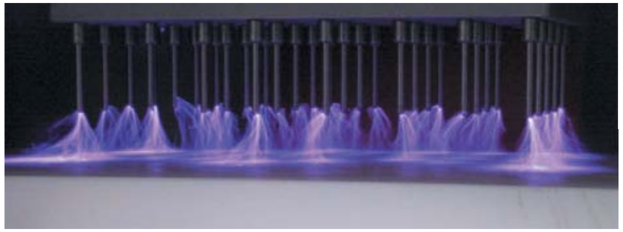
3) Change chemical or physical nature of the surface



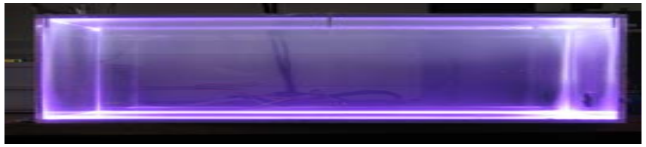
01—Plasma TV
02—Plasma-coated jet turbine blades
03—Plasma-manufactured LEDs in panel
04—Diamondlike plasma CVD eyeglass coating
05—Plasma ion-implanted artificial hip
06—Plasma laser-cut cloth
07—Plasma HID headlamps
08—Plasma-produced H_2 in fuel cell
09—Plasma-aided combustion
10—Plasma muffler
11—Plasma 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

Courtesy of Prof Mark Kushner - Iowa

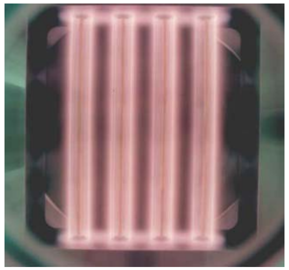
Many different possible types of plasma discharges
Atmospheric pressure and vacuum based low pressure

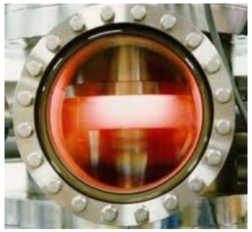


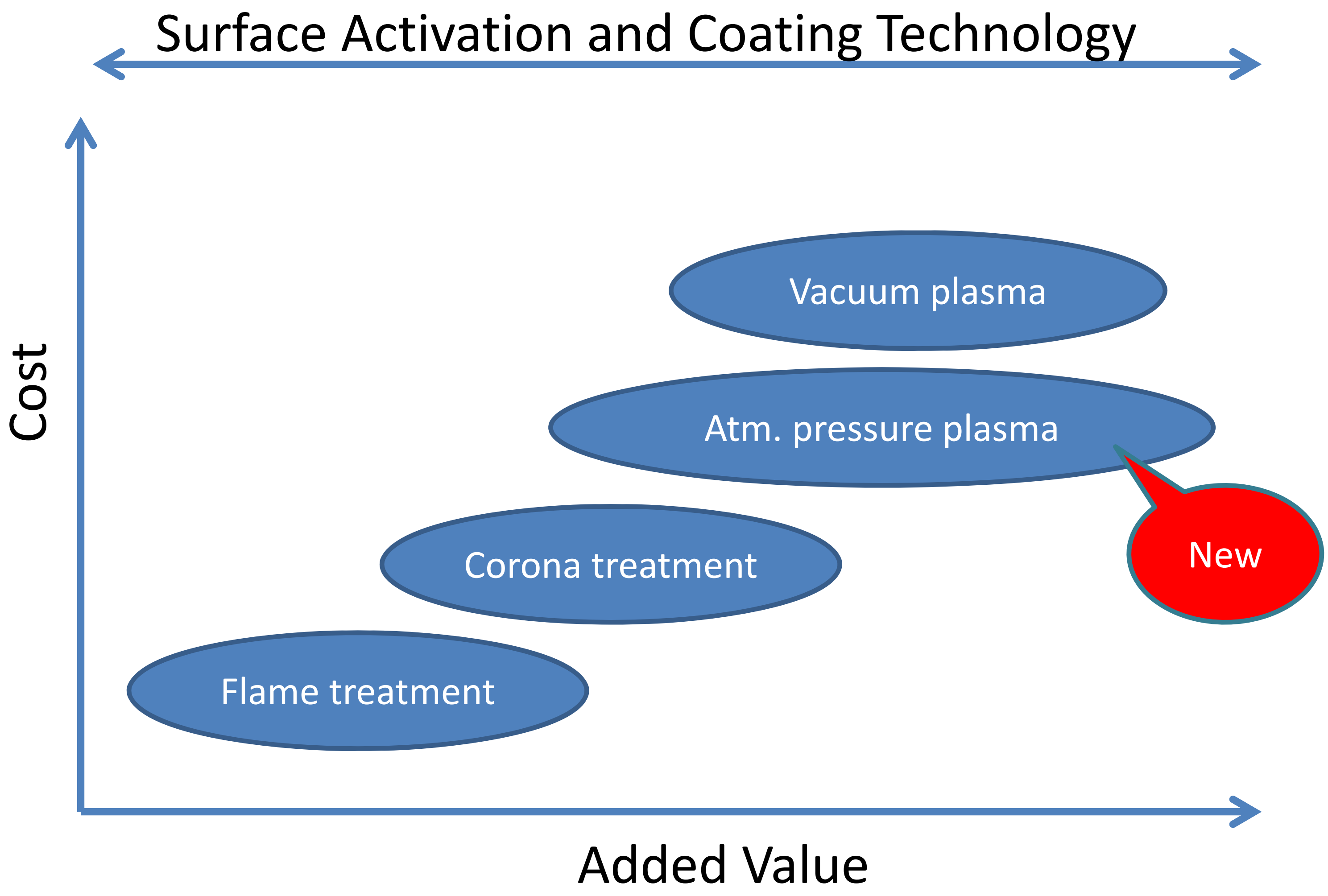
1. Corona discharges
2. Glow discharges
3. Dielectric Barrier Discharges
4. Arc Discharge



4. Microwave
5. RF plates
6. Magnetron






Surface Activation and Coating Technology
Cost
Vacuum plasma
Atm. pressure plasma
New
Corona treatment
Flame treatment
Added Value

Applications of Plasma Technology in Food Packaging

Common properties required for (polymer) food packaging

- Easy printability
- Anti-mist properties
- (Gas) permeation barrier
- Chemical safety
- Microbiological safety
- …

Easy printability, Anti-mist properties: Surface activation and functionalisation by plasma

(Gas) permeation barrier, Chemical safety: Plasma deposition of barrier coatings

Microbiological safety: Plasma sterilisation

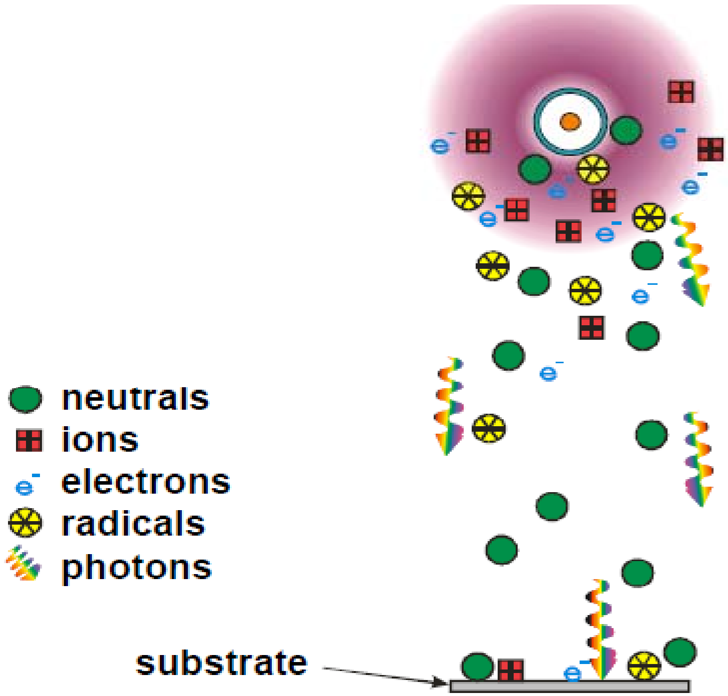
Materials such LDPE , PET, PP ……….

Typically, polymer packaging for food ought to exhibit good printability, gas permeation, chemical inertness, anti-microbial action and anti-mist formation.

Surface-Treatment Technologies

Technique	Process(es)	Types	Technology Status	Comments
Abrasion	Mechanical	Dry or wet blasting, hand or machine sanding	Obsolete	Labor-intensive,dirty, applicable only forlow production volumes, must deal with residuals.
Solvent cleaning	Physical and Chemical	Wiping, immersion, spraying or vapor degreasing	Obsolete	Safety, disposal and environmental concerns (i.e, emissions)
Water-based cleaning	Physical	Multistep power wash	Contemporary	Low environmental systems impact, high volume capacity, and relatively low cost.
Chemical etching with acids or bases	Chemical	Immersion, brushing, rinsing, spraying	Obsolete	Safety issues due to the use of corrosive, toxic materials and hazardous-waste disposal problems.
Chemical primers	Chical	Solution application of poly ethyleneamine, polyurethanes, acrylates, chlorinated polymers, nitrocellulose, or shellac	Mature	Requires specific equipment, and different primers are necessary for specific end-use requirements.
Flame treatment	Thermal and chemical	Available for flat films or three-dimensional configurations	Mature	Fire hazard, limited to some extent to thermally insensitivematerials.
Corona discharge	Electrical and chemical	Available for both conductive and dielectric substrates	Contemporary	Applicable primarily to films and webs
Gas plasma	Electrical and Chemical	Available for film or three dimensional applications can use ac, dc, or microwave frequency	Contemporary	Convenient and cost effective; non toxic materials or disposal issues; can be effective in numerous different configurations
UV and uv/ozone	Electrical and Chemical	For distinct parts in batch systems.	Developmental, Contemporary	Generally only in batch format and requires longer residence times
Evaporated acrylate coatings	Physical and Chemical	Currently for webs and films only	Developmental, Contemporary	Still being developed for commercial-scale applications
Fluorination	Chemical	Short exposure to elemental fluorine can be batch or continuous	Developmental, Contemporary	Specialized equipment required for delivery and monitoring fluorine.
Electrostatic discharge control	Electrical	Can be in the form of charge dissipation or charge neutralization	Contemporary	Equipment can be simple through complex and expensive, depending on the application

Plasma surface treatment for food packaging



Through plasma technology, the packaging industry is becoming capable of three unique abilities:

(1) To remove all unwanted ‘organic contaminants’

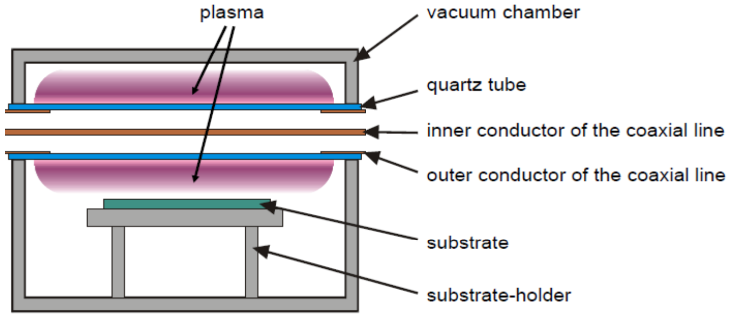
(2) Surface treatment, or activation of a material for increased wettability

(3) The deposition of substrates onto a material, adding desired new qualities

- **For achieving hydrophilic surface – O_2, N_2, H_2O, CO_2, SO_2 etc.**
- **For achieving hydrophobic surface – halogen (CF_4) plasma**

Plasma surface treatment for food packaging

Linear vacuum plasma source
e.g. Duo-Plasmaline® Microwave plasma



Excitation frequency: 2.45 GHz
typical microwave power: 1 to 4 kW
length of plasma source: 20 cm up to 3 m
working pressure: 10 Pa up to 100 Pa

Planar plasma source: **Planartron® Electron Cyclotron Resonance (ECR) plasma**

Plasmodul® array consisting of 4 Duo-Plasmalines®

J. Schneider et al Universitaet Stuttgart, Institut fuer Plasmaforschung, Stuttgart, Germany, H. Muegge et al Muegge Electronic GmbH Reichelsheim, Germany

Universität Stuttgart
Institut für Plasmaforschung
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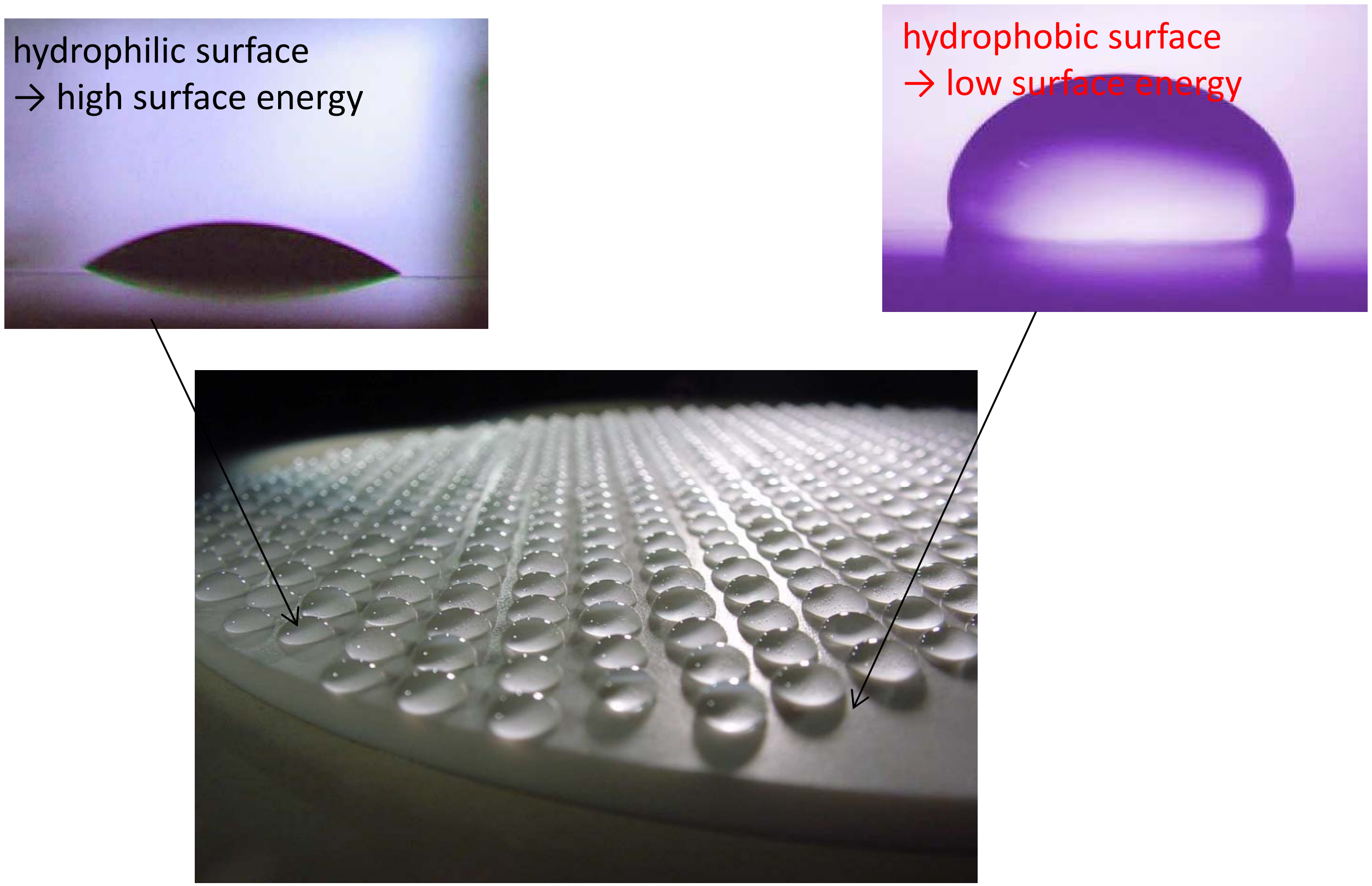

Adjustability of the surface energy
by plasma treatment

Surface activation of Teflon®

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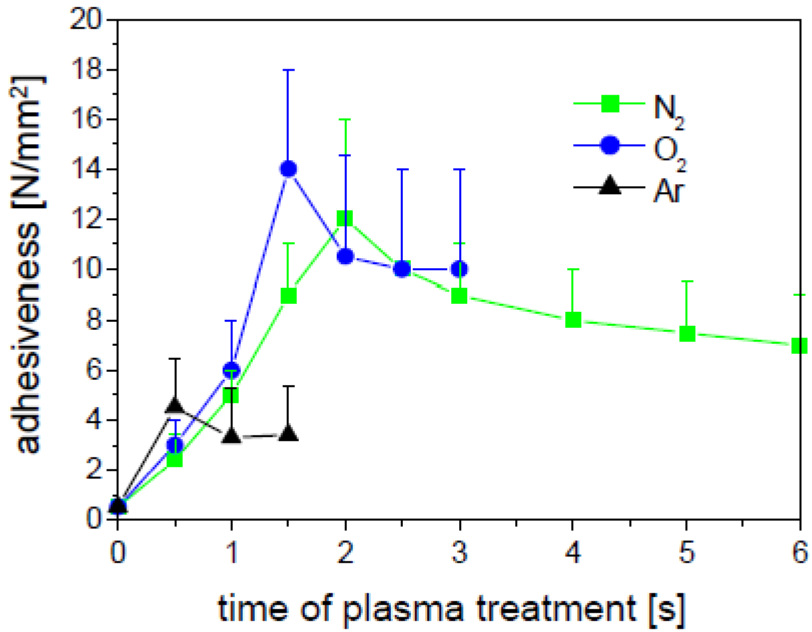
Surface activation of Teflon® by different working gases



Plasma treatment on surfaces where adhesion improvement is required, properties of untreated surfaces remain unchanged

Surface activation for adhesion improvement

Surface energy increased from 35 mN/m to 65-70 mN/m

Use of water-based paint and ink possible

⇒ **positive environmental impact**

Atmospheric plasma treatment for packaging

Bobst –UK

Plasma pre-treatment of the cap ensures firm adhesion for wet-glue tamper-evident seals

CPI – France

Problems with corona treatment, low-pressure plasma processes and flame treatment

- Activation but the effects deteriorate rapidly on storage
- Corona treatment can lead to undesirable double-sided pre-treatment which may result in the film jamming on the roll
- Flame treatment considerably impairs a film's sealability

Atmospheric-pressure plasma eliminates these and allows high through-put roll to roll webs to be treated

Deposition of barrier coatings for packaging

Advantages of homopolymeric materials compared to multi-layer polymer packaging materials:

- less material required → less weight
- lower-cost
- improved recyclability

Disadvantages

- minor barrier properties

Required properties

- (gas) permeation barrier
- chemical safety
- chemical functionality

⇒ **Surface coating/deposition**

Barrier coating: flexibility transparency
good adhesion to the surface of the polymer

Requirements to be met by the SiO_x barrier

Direct plasma enhanced chemical vapour deposition (PECVD) of SiO_2-like films

Organosilicon compounds

- hexamethyldisiloxane (HMDSO)
- tetramethylsilane (TMS)
- Tetraethoxysilane (TEOS)

used in mixtures with O_2

PET foils, PP substrates, etc…

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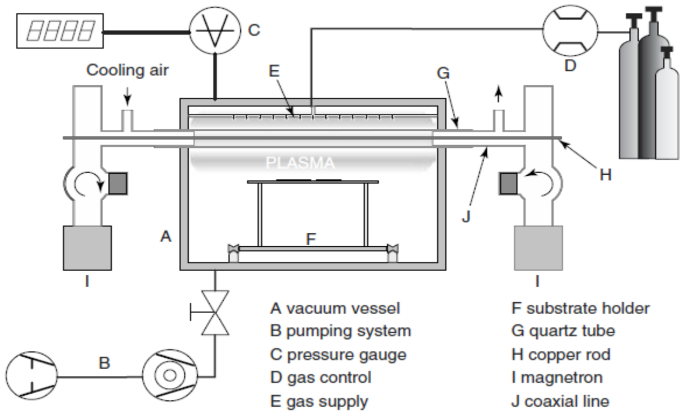
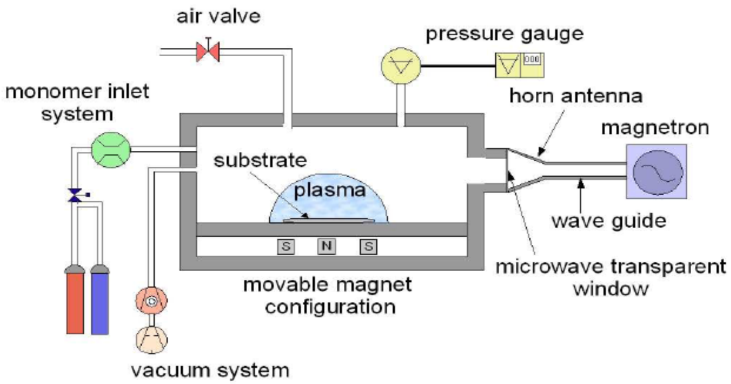
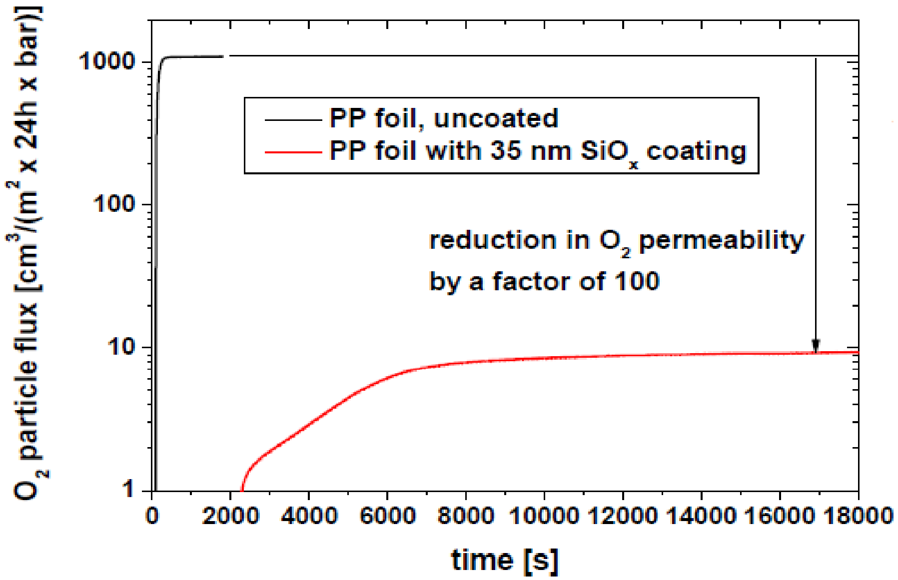


Duo-Plasmaline

$$Si_2O(CH_3)_6 + 16O \rightarrow 2SiO_2 + 3CO_2 + 3CO + 4H_2O + 5H_2$$



Oxygen permeability - PP



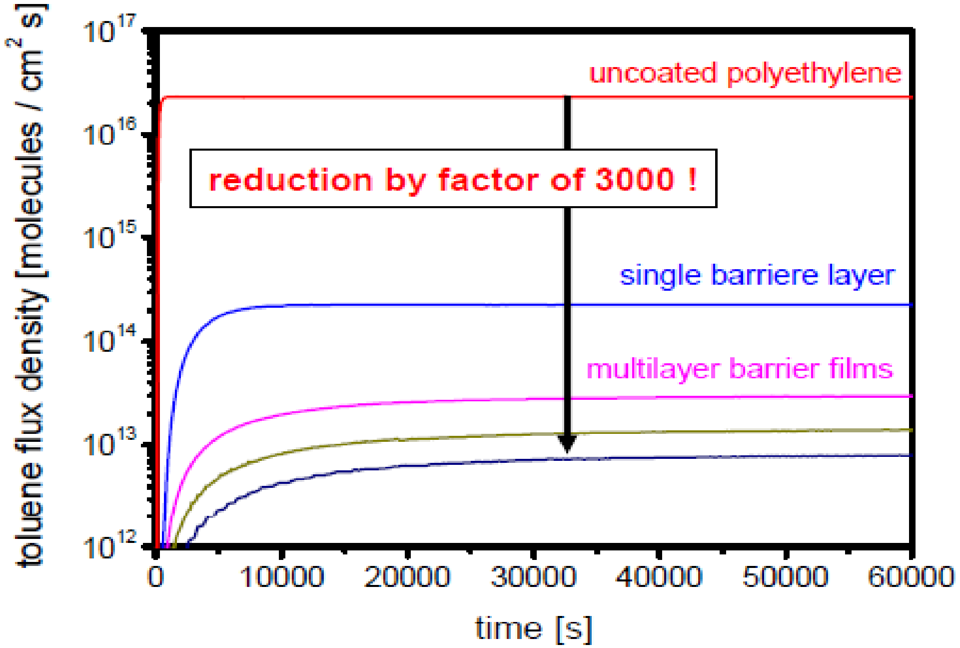
The O_2 particle flux through the uncoated and coated PET and PP foil samples, using a Zr O_2 detector

Single barrier layer 35 nm in thickness reduces oxygen permeability of polypropylene by already a factor of 100.

Schneider, J et al (2007) Development of plasma polymerised SiOx barriers on polymer films for food packaging applications. *Plasma Process. Polym.*, **4** S155

Best performing SiOx barrier layers obtained for O2:HMDSO mixture ratios between 20:1 and 25:1 by use of the ECR plasma source.

Barrier to organic solvents - PE



To be prevented:

• rediffusion of (organic) solvents (e.g. residues of cleaning agents)

• diffusion of plasticisers

from the polymer packaging into the beverage or foodstuff (particularly important for recycled polymer material)

Barrier films on polyethylene (PE) multilayer barrier films

CH/CF-layers deposited on PE as barrier against organic solvents

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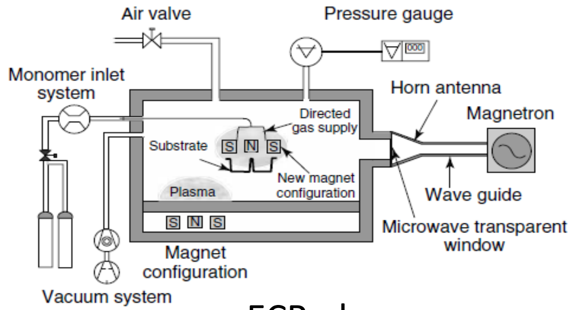
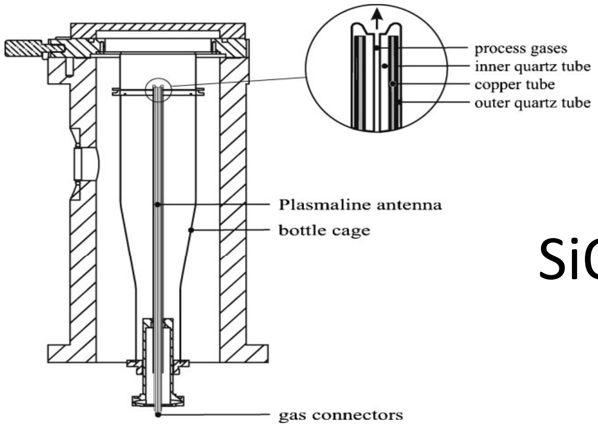
ECR plasma deposition of SiO_x barrier films on polymer trays designed for food packaging

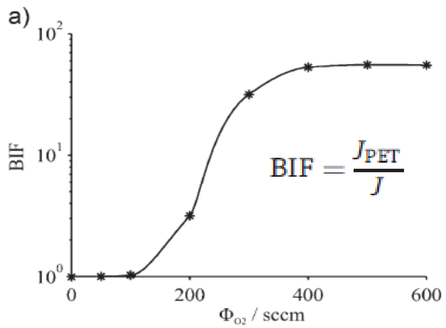
PP food tray sample - deposition of SiOx barrier films. The O2: HMDSN gas mixture in the range of 29 : 1 up to 50 : 1

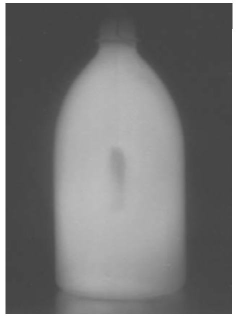


ECR plasma source

23 mm thick PET foils are coated



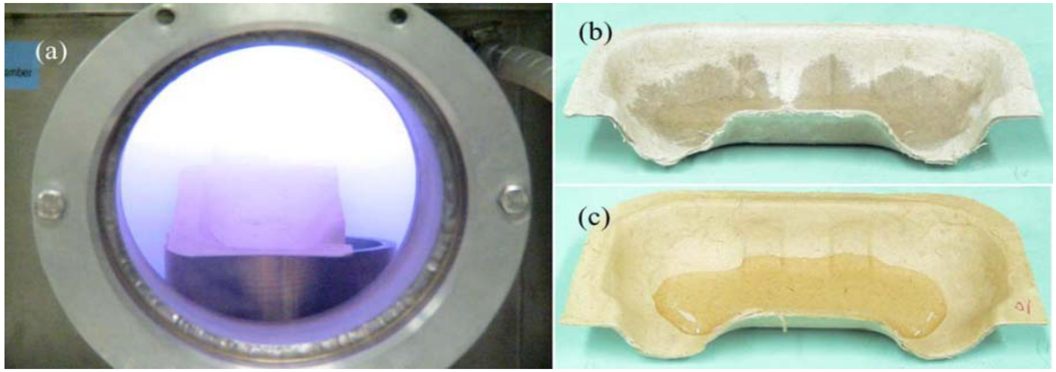




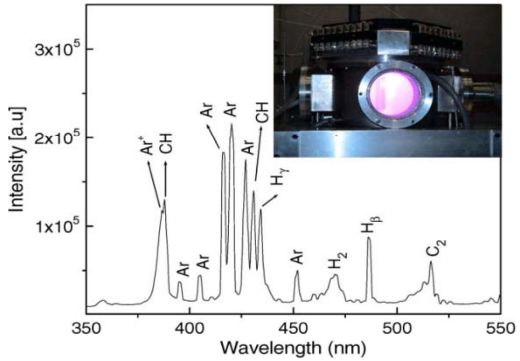
SiO_x barrier films on PET Bottles

M Deilmann et al, Plasma Process. Polym. 2009, 6, S695–S699

Hydrocarbon plasma for treatment of biodegradable food containers



Argon + methane discharge



Plasma species recorded during the (inset) treatment of the food package.

middle-frequency (2 MHz) inductively coupled plasma (ICP) source

500-W input RF power at 1.5-Pa total pressure of Ar/CH_4

Environment-friendly concepts, food and paper packaging products developed by GRENIDEA Company

Y Ren et al , IEEE Trans. Plasma Sci. 36, 4, 2008

Plasma deposition of SiO_2-like films at atmospheric pressure

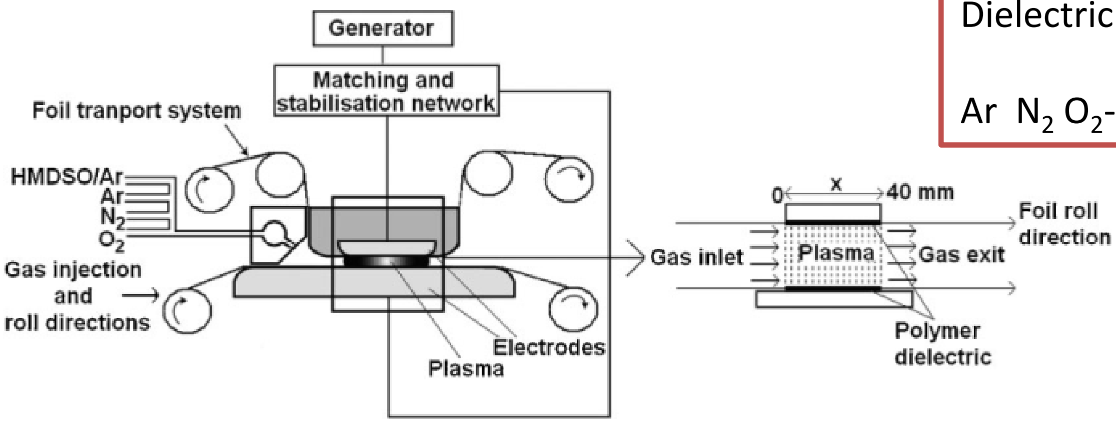
In comparison with vacuum processes, atmospheric pressure plasma has the advantage that the pre treatment can be integrated into existing film manufacturing processes and plants

Large width as evenly as possible at high throughput - roll to roll

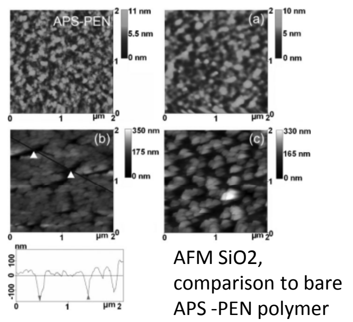
"Cold" plasma most appropriate for plasma treatment of thermally sensitive polymers

Dielectric barrier discharge (DBD)

Ar N_2 O_2-HMDSO mixtures



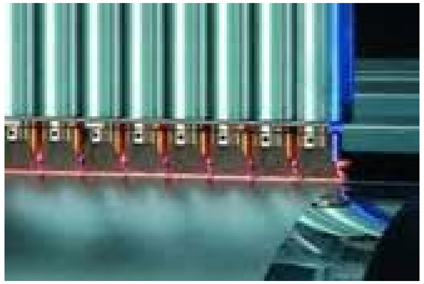
PA Premkumar et al Plasma Processes and Polymers Volume 6, Issue 10 (2009), 2009, 6, 693

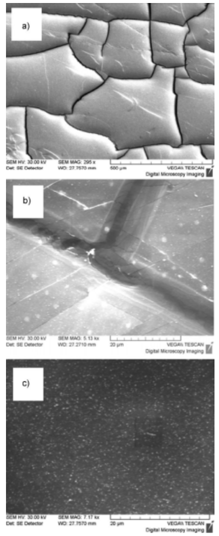


AFM SiO2, comparison to bare APS -PEN polymer

Plasma deposition of SiO_2-like films by atmospheric pressure plasma jet

SEM micrographs for a coated PP sample





jet system provided by Plasmatreat GmbH

HMDSO precursor on a thermally sensitive PP films - Gas barrier properties improved by factor of 2

SiO_xCyH_z coatings

" APPJ-coated PP could become a cheaper alternative to polyethylene therephthalate (PET) for the food packaging industries, especially for the oxygen barrier properties"

Development of silica barrier coatings; inorganic barrier layers like SiNx and SiOx

P Scopece, et al, Plasma Processes and Polymers 6, Issue 1 16 (2009)

Plasma technology for bio-active coatings and surfaces

Food safety and food quality for fresh food will be improved by

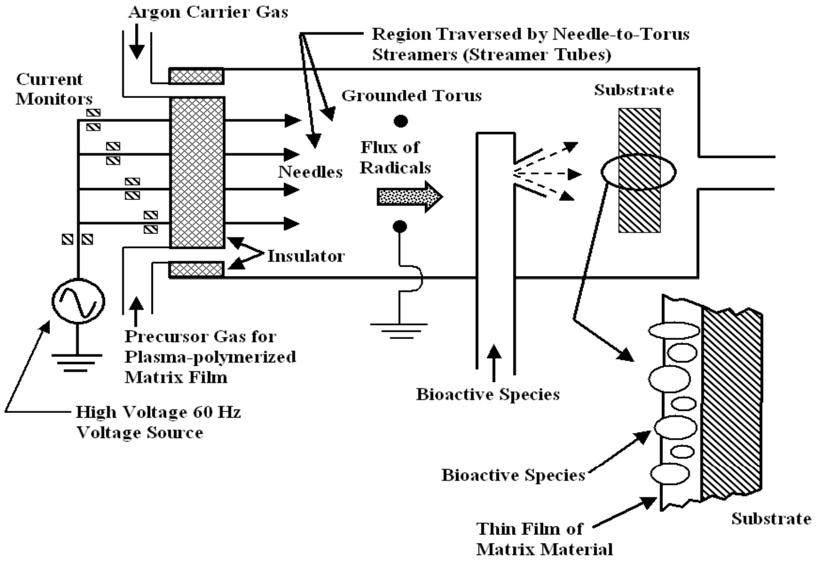
- Improved nutrient content
- Improved sensory qualities for the consumer
- Introduction of antimicrobials
- Improved gut health via probiotics
- Extension of produce shelf life
- Improved dietary choices
- Economic return

Antimicrobial activity on packaging by:

•addition of sachets or pads containing antimicrobial volatiles,
•incorporation of antimicrobials into the matrix of the packaging material,
•coating or adsorbing antimicrobials onto the packaging surface,
•using inherently antimicrobial substances as packaging for raw materials
•immobilization of antimicrobial substances onto the packaging surface

Bioactive thin-film packaging is a novel technology

Bioactive thin-film packaging can use a wide variety of immobilized molecules, antimicrobials, probiotics, proteins, vitamins, yeasts and bacteria to improve many features of fresh fruits and vegetables.



Bioactive packaging for extension of lifetime of meat. Plasma treatment improves the adhesion of antioxidant and antibacterial coatings

A Vesel Institute, Plasma lab Ljubljana, Slovenia

The acetylene-based radicals flow downstream.

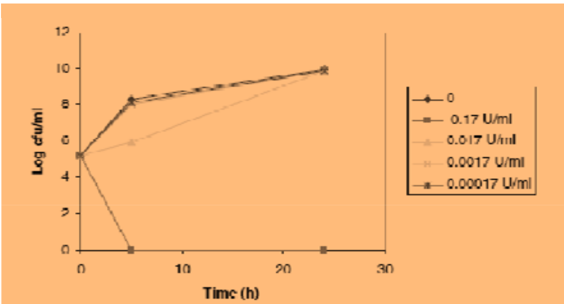
Substrates include glass, highly ordered pyrolytic graphite (HOPG), mica and eventually **fresh fruits and vegetables**.
Initial work - antimicrobial molecule benzoic acid

P Pedrow et al School of EECS, Washington State University, Pullman, Washington

Antimicrobial Coatings by Atmospheric pressure Dielectric Barrier discharge

Activity of Glucose Oxidase-immobilized Plasma-activated Polypropylene Films

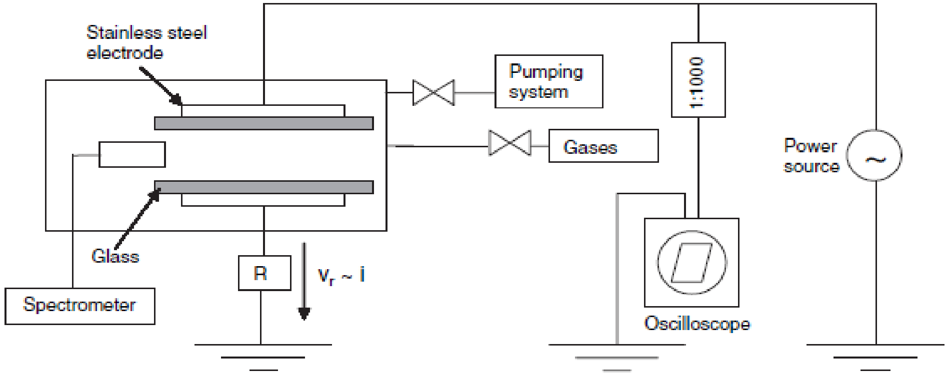
Antimicrobial enzyme, GOX immobilized onto amino- and carboxyl-plasma-activated biorientated polypropylene films (BOPP)



Inhibited the growth of* Escherichia coli *and substantially inhibited the growth of Bacillus subtilis

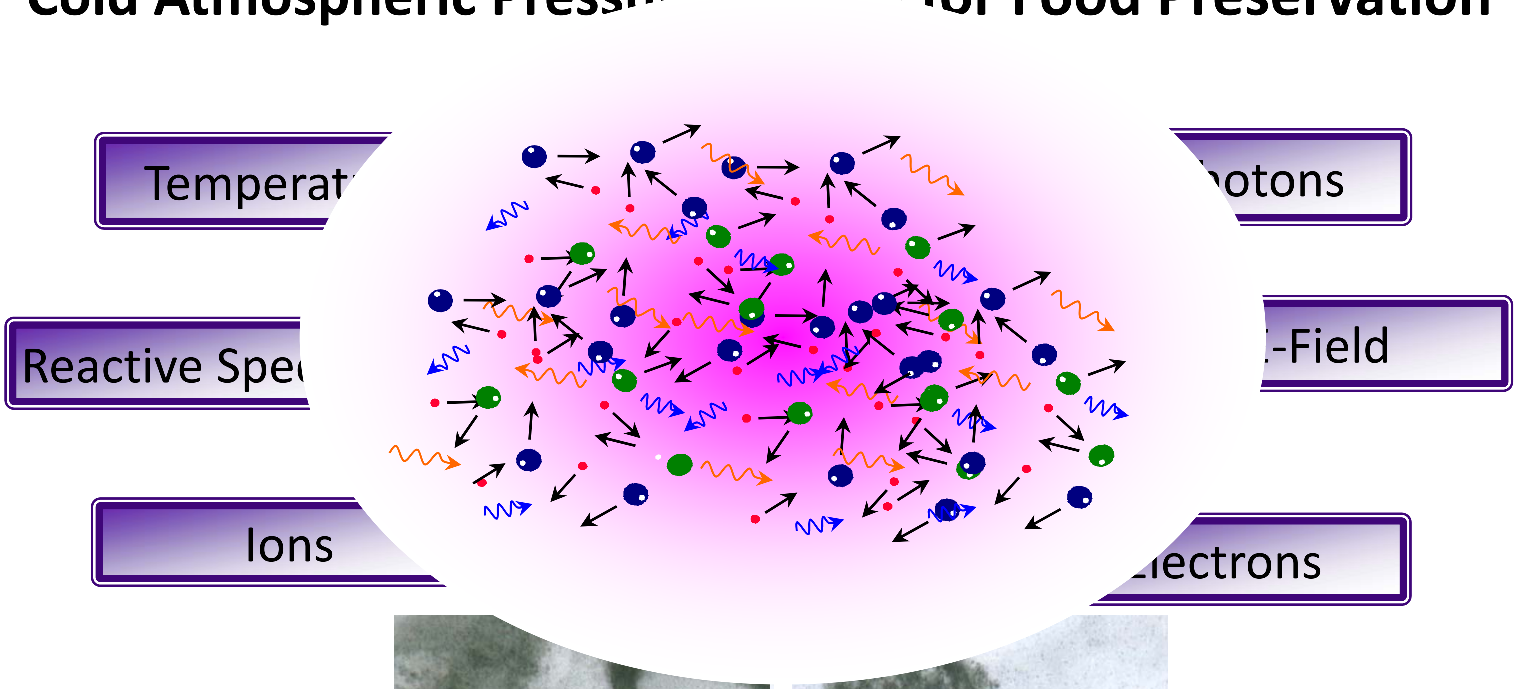
Atmospheric pressure DBD

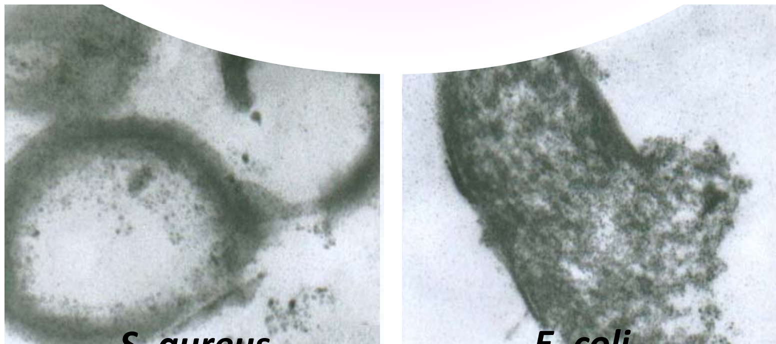
Generate suitable anchor groups for active substances: *N_2-plasma + NH_3 and N_2-plasma + CO_2 treatments BOPP films*



J Vartiainen et al Packing Technology and Science (*2005*) ***18 243***

Cold Atmospheric Pressure Plasma for Food Preservation

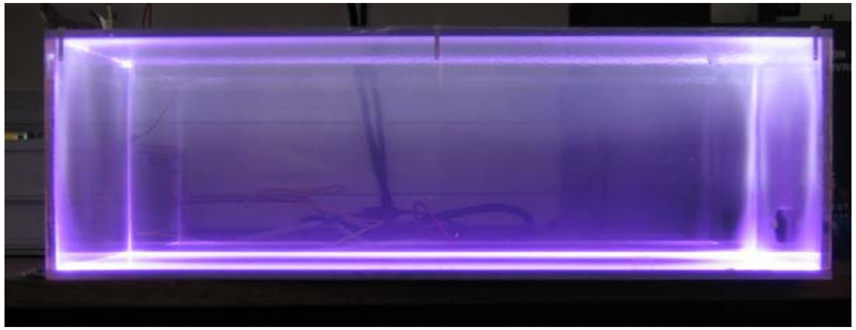


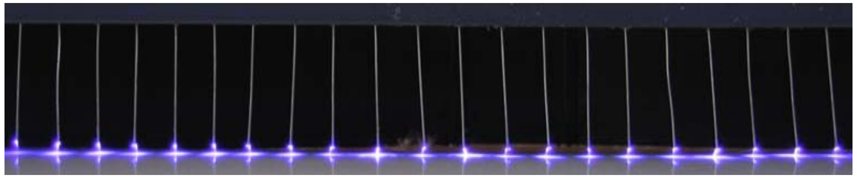


S. aureus *E. coli*

J Walsh
Liverpool

Challenge: How to generate large area plasma?

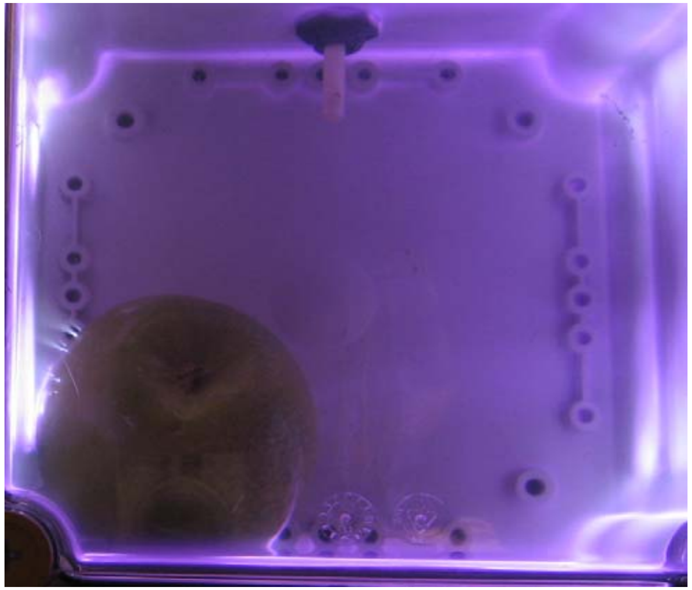


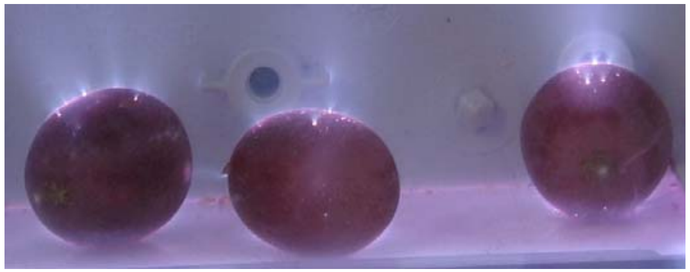


- **Stable & cold plasmas are difficult to generate on a large scale.**
- **Move away from expensive gases (especially helium!).**

Large volume plasmas

- Plasmas like irregular shaped and conductive objects (e.g. a lightening conductor!).
- Food surface is not regular and often conductive.
- Needs an understanding of underpinning physics and an appreciation of engineering challenges.



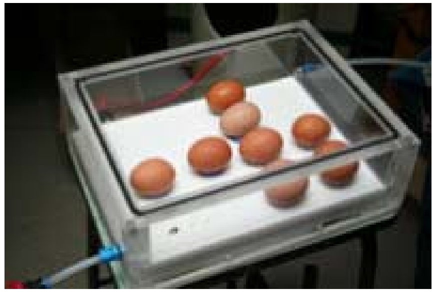


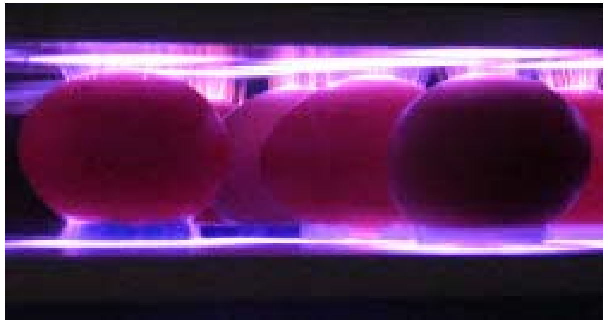
Bacteria-free eggs with plasma technology

European research project on egg sterilisation. Development of new technology in which plasma is used as a method for killing Salmonella on egg shells.

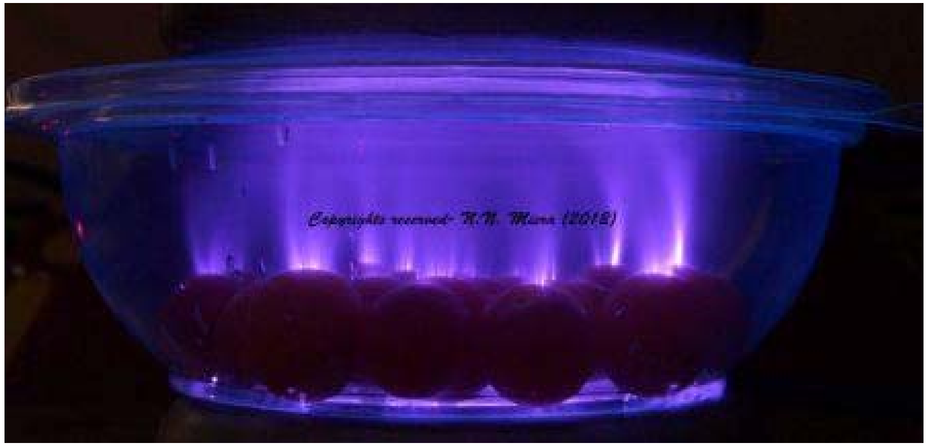
Askild Holck, senior research scientist at Nofima:

“By using plasma treatment, we have succeeded in removing 99.5 per cent of all bacteria on the egg shell but because this is a gentle method, the egg yolk and white are unaffected."





Treatment of tomatoes inside a helium cold" plasma (with traces of air as contaminant)



NN Misra et al , Non-thermal Plasma Inactivation of Food-Borne Pathogens Food Engineering Reviews (2011), 3, Issue 3-4, 159

Plasma for food preservation: How?

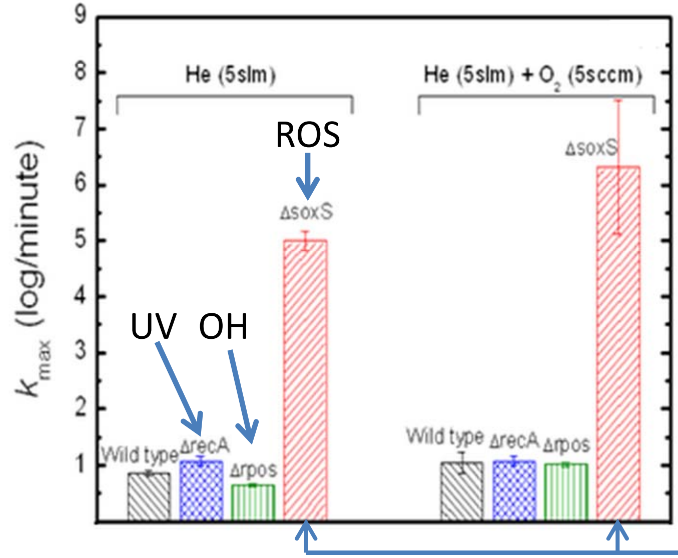
APPLIED PHYSICS LETTERS 90, 073902 (2007)

Probing bactericidal mechanisms induced by cold atmospheric plasmas with *Escherichia coli* mutants

Stefano Perni and Gilbert Shama
Department of Chemical Engineering, Loughborough University, Leicestershire LE11 3TU, United Kingdom

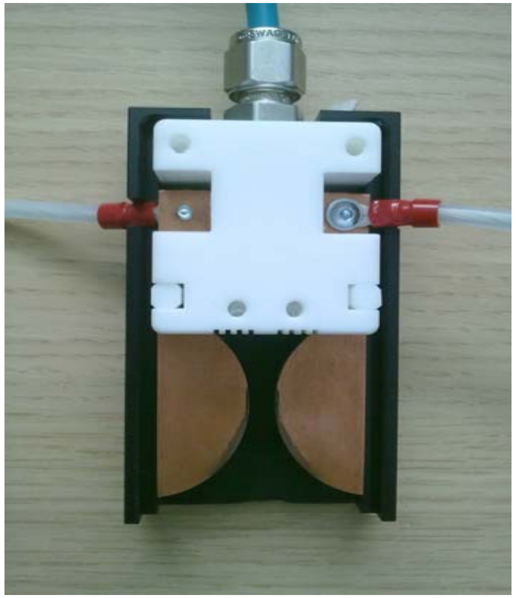
J. L. Hobman, P. A. Lund, C. J. Kershaw, G. A. Hidalgo-Arroyo, and C. W. Penn
School of Biosciences, University of Birmingham, Edgbaston, Birmingham B15 2TT, United Kingdom

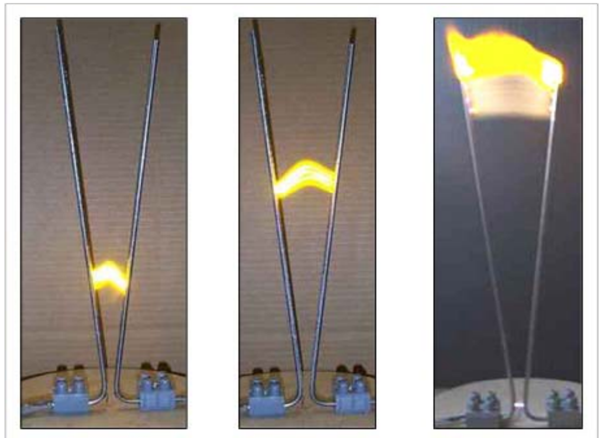
X. T. Deng, J. L. Walsh, and M. G. Kong[a)]
Department of Electronic and Electrical Engineering, Loughborough University, Leicestershire LE11 3TU, United Kingdom



E. Coli. K-12 Δ*soxS* mutants that are susceptible to Reactive Oxygen Species show significantly higher log reductions than Δ*recA* and Δ*rpoS* mutants.

Detoxification of seeds by plasma treatment





Pre-treatment of barley seeds for germination enhancement

Seed protection against fungi but what about nutrition properties of the seeds?

P. Špatenka[1,]J Department of Applied Physics Technology, University of South Bohemia, Ceske Budejovice, Czech Republic
[2] Surface Treat Inc., Turnov, Czech Republic

Uncooked poultry and other meat products

Campylobacter and *salmonella*, the two bacteria most responsible for foodborne illnesses, are found on as much as 70% of chicken meat tested.

Brian Dirks Drexel University Research Magazine

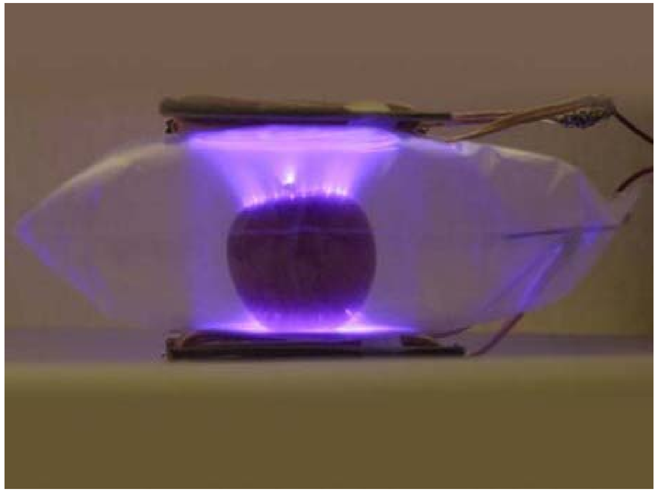
January 2012 issue of the *Journal of Food Protection*, plasma can be an effective method for killing pathogens (harmful bacteria) on uncooked poultry.

The treatment either entirely or nearly eliminated *salmonella enterica* and *campylobacter jejuni* bacteria in low levels from skinless chicken breast and chicken skin. It significantly reduced the level of bacteria when contamination levels were high.

In-pack decontamination of food products

The **SAFE-BAG** project aims at developing a novel continuous in-pack decontamination system for fresh produce, that is in line with market trends and consumer demands to move away from the use of methods such as chlorine washing.

SAFE-BAG is 3 year R&D project funded by the Seventh Framework Programme of the EC under the “Research for SME Associations” sub-programme.



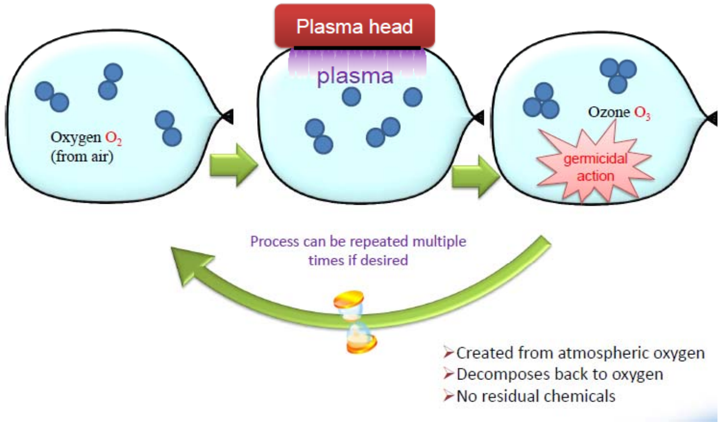
In-pack decontamination of food products undertaken by Purdue University and project partner Dublin Institute of Technology

In packaging plasma treatment

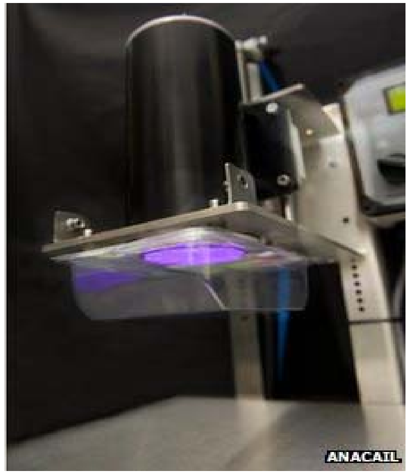
Ozone generation in a sealed package

ozone naturally returns to its original state after just a couple of hours - enough time for mould, fungi or bacteria on the packaging's contents to be destroyed.

does not adversely affect the taste of the food and extends shelf-life by at least one extra day.



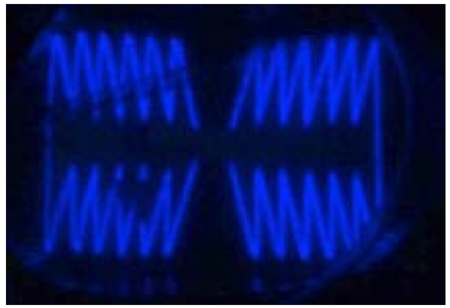
Anacail



Glasgow University Project

Commercial plasma sterilization systems

- Plasma-label for food conservation (“PlasEt” by JE PlasmaConsult)
- Plasma created inside packaging via antenna on label
- Few minutes plasma generation
- Ozone generation
- Label can be equipped with sensors

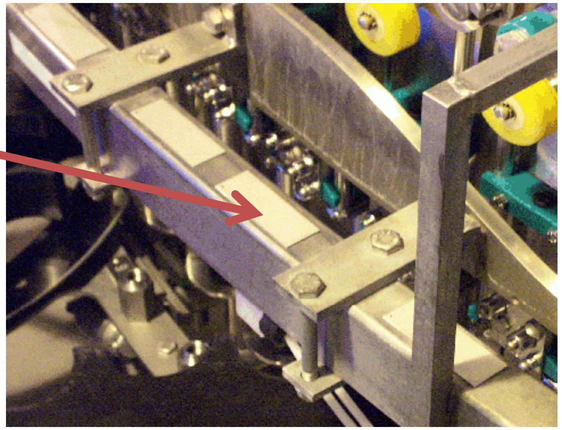


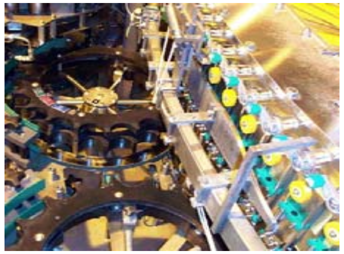
tomatoes

Photo-catalytic self-cleaning TiO_2 coatings
Beer bottle filling lines

P Kelly MMU In collaboration with Panimolaboratorio - Bryggerilaboratorium Ab (PBL), a company devoted to research and development in malting and brewing on behalf of Finnish industry

Coupons are our coated samples. Positioned where affected by contamination and cause spoilage. In practice the whole of the stainless panels could be coated - small samples are easy to test.





Microbiology Process Study at Hartwall Brewery, Lahti

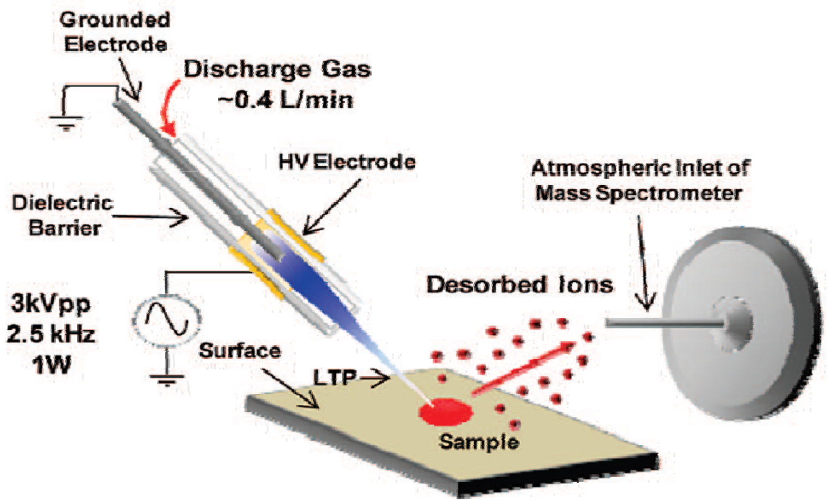
- Mari Raulio & Outi Priha
  VTT Technical Research Centre of Finland

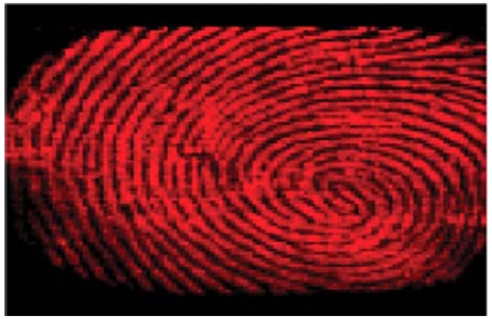
Also at Liverpool: Plasma for rapid detection of pathogens

✓Plasma Assisted Desorption Ionization (PADI) is a technique to determine the chemical composition of a surface in its native environment directly with minimal sample preparation.

✓EPSRC EP/I028722/1 : Micro-PADI sources for applications in 2-D chemical imaging. In collaboration with National Physics Laboratory and School of Pharmacy, University of Nottingham.

UNIVERSITY OF LIVERPOOL





Harper *et al.* Anal. Chem. 80, 9097–9104, 2008

Alberici *et al.* Anal, Bioanal, Chem, 398, 265–294, 2010.

Summary:

- Plasma processing can be a valuable tool for food industry
- Advanced packaging and labeling
- Sterilization and food preservation
- Detection of food born bacteria and pathogens

Future Prospects:

- Promising results so far – but what does plasma do to nutrition?
- Need to determine optimum operating conditions for a given application
- Safety of treated products