Low-Temperature Plasma Processing of Materials: Past, Present, and Future

Evidently, all of our readers are well aware of the important role of plasma research as a modern discipline, but fewer are probably conscious of its historical roots, of its greater context, and of the impressive inventory of already-existing technological applications dispersed throughout an amazingly diverse industrial base. It is, therefore, the objective of this present Essay to bring closer to the readership these important characteristics of their chosen field, plasma science and technology, albeit in the form of a very brief overview. While this must necessarily be confined here to a few pages, more extensive documents with similar aims have appeared at various earlier dates. A partial list of these can be found as ref.,[1–4] and several of the illustrations in this Essay have been drawn from two of these (with permission).[3,4] We commence with an introduction to the plasma state, followed by some historical remarks and sketches of current technological applications and economics trends.

Plasma: Definition and Characteristics

When one provides energy to a solid, the relative motion among its constituent atoms or molecules increases which results, first, in a transition to the liquid state, then to a gas. If the energy supply increases even further, collision processes among the constituent particles become violent enough for these to break apart; this results in the formation of equal number densities of charge-bearing sub-particles, namely electrons and ions. This latter state, plasma, is therefore often called the ‘‘fourth state of matter’’. While temperatures and pressures encountered in the Earth’s atmosphere are mild enough to preclude the formation of plasmas, except under certain ‘‘unusual’’ conditions (lightning, and ‘‘Aurora borealis’’ or Northern Lights, for example), this is not the case elsewhere in our Universe. Quite the contrary, the vast majority of matter in the universe is in a plasma state, ranging, for example, from the hot, dense interior of stars like our Sun, to the much cooler solar corona and even cooler solar ‘‘wind’’, to the low-density ‘‘cold’’ plasma of intergalactic space. Figure 1, a log-log plot of temperature versus electron density, shows that these two fundamental plasma characteristics can vary over more than ten and about thirty orders of magnitude, respectively.

Plasmas can be deliberately created on the Earth’s surface, for example, in the laboratory or in an industrial environment, by applying direct or alternating high voltage to a gas. Depending upon whether the gas is at reduced pressure (partial vacuum) or at atmospheric pressure and above, one can thereby obtain either a low-temperature, non-equilibrium ‘‘glow discharge’’ type of plasma, or an equilibrium thermal plasma, respectively (see Figure 1), but conditions between these two extremes can also be created. The non-equilibrium plasma variety is of particular importance for the types of technological applications that interest the readers of this journal. The reason is that the gas molecules and ions, the ‘‘heavy’’ particles, can be kept ‘‘cold’’ (near ambient temperature, 300 K), while the electron gas can be made very ‘‘hot’’, well above 1×10^4 K. These highly energetic electrons are responsible for initiating chemical reactions, by breaking covalent chemical bonds of ground-state gas molecules in the course of collision-induced energy transfer. Through the judicious selection of gas or gas mixture, method of energy input, and reactor geometry, one can optimize the conditions for a very wide range of technological process applications, as will be shown below. Herein lies the great benefit and future promise of plasma technology, as well as the scientific interest in studying the very complex plasma phenomena, for example, with the help of plasma diagnostics and modeling investigations.

Brief History of Plasma Science

The earliest roots of plasma science extend as far back as the 18^{th} century, for example, to the discoveries of G. C. Lichtenberg (1752–1799), a mathematics professor at Göttingen University in Germany: he observed beautiful brush-like patterns on insulating surfaces following discharges from a pointed electrode. The first attempts to explain such phenomena, however, came from Michael Faraday (1791–1867), the discoverer of electromagnetism. His well-known exploding-wire experiments were clear precursors of the ‘‘fourth state’’, as was the glow observed by Sir William Crookes (1832–1919), another Englishman, when he applied voltage across electrodes in a partially evacuated glass tube. Crookes correctly postulated the existence of electrically charged particles, ions, in his tube. In 1857, Werner von Siemens, a German engineer, patented the first technological application of gas plasma, even though he was not aware of the underlying science at that time. Figure 2 shows Siemens’ ozonizer, made of glass, the forerunner to what is, even today, one of the largest industrial applications of plasma-chemical technology: the synthesis of ozone (O_3) from molecular oxygen (O_2). It was not until the Nobel-prize-winning discovery of the electron by Sir J. J. Thomson (1856–1940) at Cambridge

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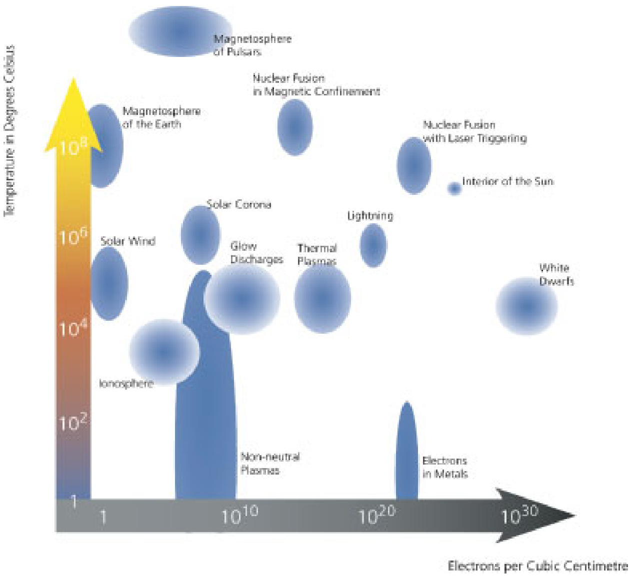


Figure 1. Plot of log T versus log n_e.[3]

University in 1897 that the true nature of atoms (composed of electrons and ions), and hence of plasmas, could be unraveled. Another Nobel laureate, the American industrial scientist Irving Langmuir (1881–1957), discovered "plasma oscillations" in ionised gases in 1923, and he is credited with first using the term "plasma" (from the Greek word plassein, to form or mold) in this context.[5] His portrait is shown in Figure 3, along with that of Johannes Stark, who was awarded the Nobel Prize for physics in 1919 for the effect named after him, the splitting of spectral lines

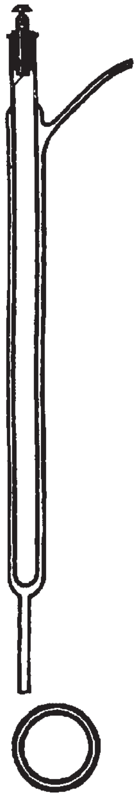


Figure 2. Siemens ozonizer tube.[3]

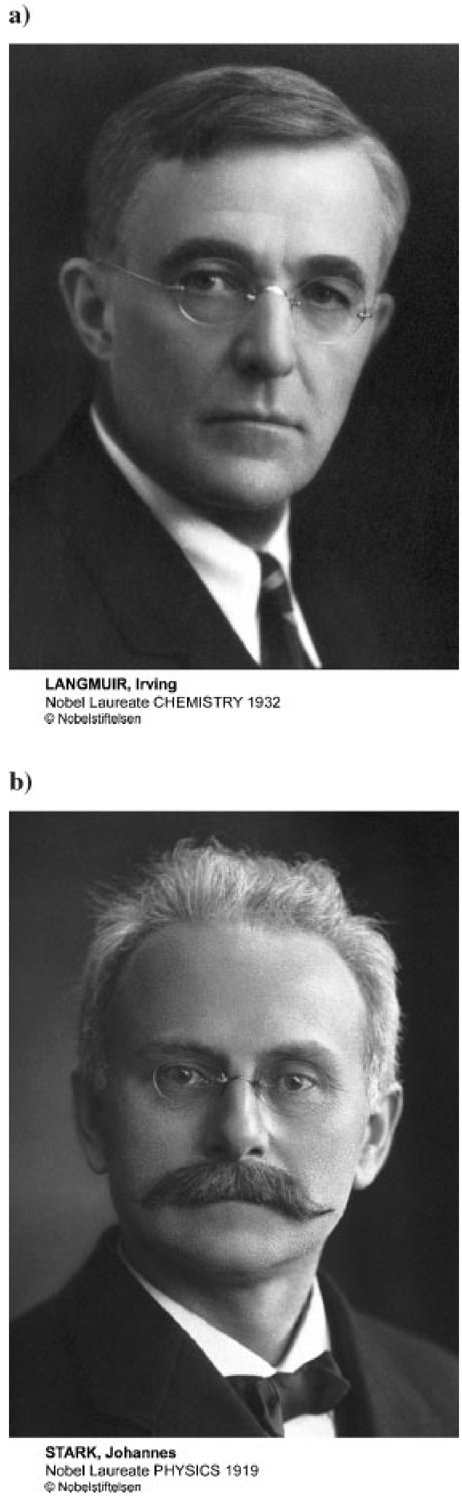
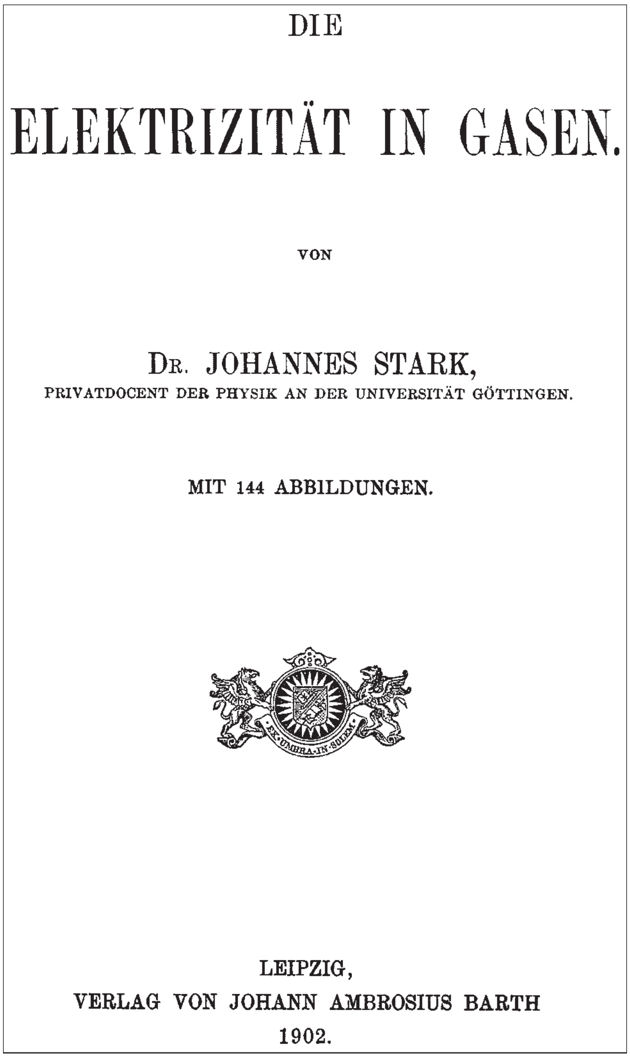


Figure 3. Photographs of I. Langmuir (a) and J. Stark (b). (© The Nobel Foundation).


DIE

ELEKTRIZITÄT IN GASEN.

VON

DR. JOHANNES STARK,

PRIVATDOCENT DER PHYSIK AN DER UNIVERSITÄT GÖTTINGEN.

MIT 144 ABBILDUNGEN.

LEIPZIG,
VERLAG VON JOHANN AMBROSIUS BARTH
1902.

Figure 4. Cover of ‘‘Electricity in Gases’’, by J. Stark (1902).

from a gas discharge under the effect of an intense electric field. Stark’s textbook ‘‘Electricity in Gases’’, published in 1902 (see Figure 4), can be considered the first full theoretical account of gas discharge physics. Although we have mostly mentioned the contributions to plasma science from German, English, and American researchers, individuals from many other nations have also made major contributions to the current understanding of plasma-related phenomena and to its use in modern technologies: France, Italy, Russia, Japan, and Korea, to name only a few.

Plasma Processes in Modern Technology

Plasma-chemical processes can be divided into two basic categories, homogeneous gas-phase reactions (for example, the earlier-mentioned synthesis of ozone from oxygen), and heterogeneous reactions involving the interaction of plasma with a solid (or sometimes liquid) surface. In the case of plasma-solid interactions, there exist three further sub-categories, namely one in which material is removed from the solid surface by plasma-induced etching or ablation; in a second sub-category, material is added to the surface in the form of a growing thin film deposit, a process known under the collective name of ‘‘plasma-enhanced chemical vapor deposition’’, or PECVD for short. Finally, in the third sub-category, material is neither added to nor removed from the solid in appreciable quantities, but the surface is chemically and/or physically modified during its exposure to particles and radiation from the plasma. The scientific and technological interest in plasma-solid processes of materials first arouse about 50 years ago, when deposition of thin films in a plasma process was found for the first time to present advantages, rather than to be a nuisance.[6] In one of the early monographs about plasma technology, dated 1979,[7] Bell and Shen stated that ‘‘. . .Since de Wilde[8] and Thenard[9] first reported the formation of solid products in a plasma of organic vapor more than a century ago, many workers in the field of plasma organic chemistry have observed the presence of high-molecular-weight materials as reaction by-products. These materials adhered tightly to the walls of reaction vessels, and were insoluble in most solvents. They were considered a nuisance until Goodman[6] demonstrated that a 1 μm thick plasma-polymerized styrene film deposited on a titanium foil made a satisfactory dielectric for a nuclear battery. Since that time, plasma-derived polymers have been suggested for numerous applications. . .’’.

Regarding the surface-modification of materials, the so-called corona treatment process in air at atmospheric pressure also goes back about 50 years, but then glow discharge processes sustained at low pressure (10 mtorr to 10 torr) came to the fore, and will probably continue to develop in the future. In recent years, though, impressive developments of atmospheric pressure plasma technologies, so-called dielectric barrier atmospheric pressure glow discharges (DBD or APGD for short) have also occurred, and these will increasingly compete with deposition, treatment, and etching processes at low pressure, mostly for economic reasons.

Among all of the processes mentioned above there exist far too many examples, even industrially important applications, to list in this brief overview. Therefore, we have selected a small number of technology sectors in which plasma processing plays a particularly important role, in order to illustrate how powerful a tool this ‘‘fourth state of matter’’ has become in the 21st century.

Microelectronics

There can be little doubt that the electronics industry has been the principal motor for the advancement of plasma processing, and this since the mid-1960s. The 1970s have seen a rapidly-expanding development of plasma technologies in microelectronics, for example dry etching processes for large scale integrated (LSI) circuits, along with plasma diagnostic methods; emission spectroscopy started to be applied extensively in attempts to understand etching and deposition mechanisms and kinetics, and these were coupled with the surface analysis techniques emerging in those years, namely X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES). It is worth mentioning here that the early 1980s were particularly important for the rationalization of etching processes, when researchers from IBM and AT&T seized the attention of participants at the Gordon Research Conferences with long, hotly-contested debates about the roles of atoms, radicals and positive ions. Since then, the design and production of the ubiquitous integrated circuit has faithfully followed ''Moore's Law'', the empirically observed two-fold size reduction of critical dimensions every 18 months. The current dimension, 90 nm, has only become possible through massive research and investment in plasma processes of all three types mentioned above (etching, PECVD, and surface modification or cleaning): currently, two-thirds of all process steps in the fabrication of semiconductor devices involve plasma, and this trend is steadily increasing, also in the connected industry sectors of information technology, automotive and consumer electronics. An example to illustrate why this is the case is shown in Figure 5, a scanning electron micrograph of vias with high aspect ratio, which have been etched into a silicon wafer by using anisotropic, plasma-assisted ''reactive-ion etching'' (RIE).[10] Clearly, it would be inconceivable to produce such fine nanopatterns if one were limited to the use of isotropic wet-chemical etch techniques of yesteryear! According to data from ref.[4] (Table 53, page 131), worldwide electronic equipment production was valued at 977 billion US dollars (B USD) in 2002, of which semiconductors comprised 140.7 B USD and semi-conductor equipment 19.8 B USD. A somewhat related industry sector is that of ''macroelectronics'', exemplified by photovoltaics. Over recent years the annual growth rate in this sector has been roughly 20%.[4] Here too, plasma processing is playing an ever-increasing role in the production and/or processing of solar cells, for example, in fabricating amorphous or microcrystalline thin layers of silicon by PECVD.

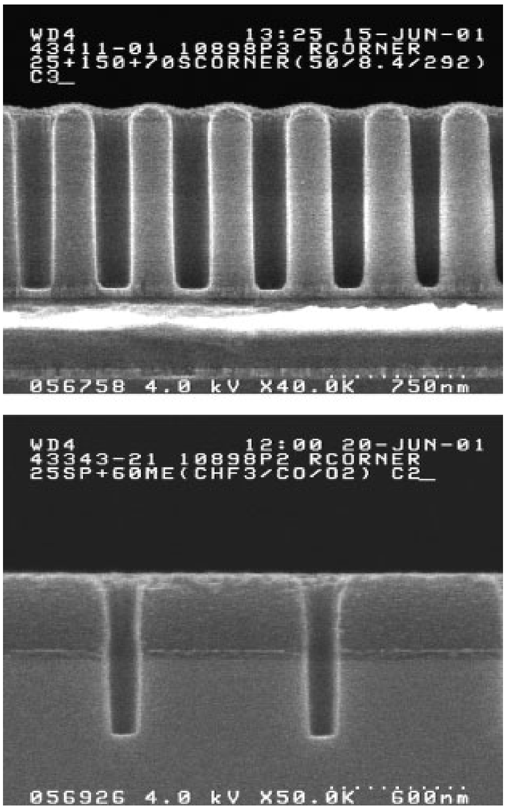


Figure 5. Scanning electron micrographs (SEM) of vias etched in silicon.[10]

Automotive

Another sector of modern technology that we encounter in everyday life, and that benefits greatly from plasma processing, is the manufacture of better, more efficient, and more environmentally benign automobiles. Figure 6 shows a schematic of a partial list of automotive components, present and near-future, whose performance is vastly improved through plasma processes. Manufacturing processes in this industry must be extraordinarily reproducible and stable, qualities inherent in plasma when all important parameters are known and controlled. Let us consider some of the examples depicted in Figure 6: Engine and transmission parts can be made lighter and more resistant to abrasion by surface coating or hardening processes. Plasma nitriding of steel is a good example of the latter, while diamond-like hard carbon coatings have enabled the design and manufacture of high-pressure, direct-injection nozzles for recent generations of diesel engines. Metal parts in the power train can, therefore, obviously benefit from plasma-based improvements, but so can plastic components on the outer body of the vehicle. For example, non-polluting water-based paints will adhere to the light-weight plastic bumpers only after their surfaces have been activated by a suitable plasma pre-treatment. Indeed, the surface functionalization of synthetic or natural polymers (for example, seat cover textiles, see Figure 6) constitutes another vast area of plasma implementation, separately addressed below. The same applies to the lighting industry: for example, high-pressure gas-discharge headlights now routinely outlive their vehicles and produce a very bright illumination similar to daylight. Finally, a likely future development is the inclusion, in every gasoline or diesel-fuelled vehicle, of a plasma reactor in the exhaust system, to reduce the emission of gaseous and particulate pollutants.

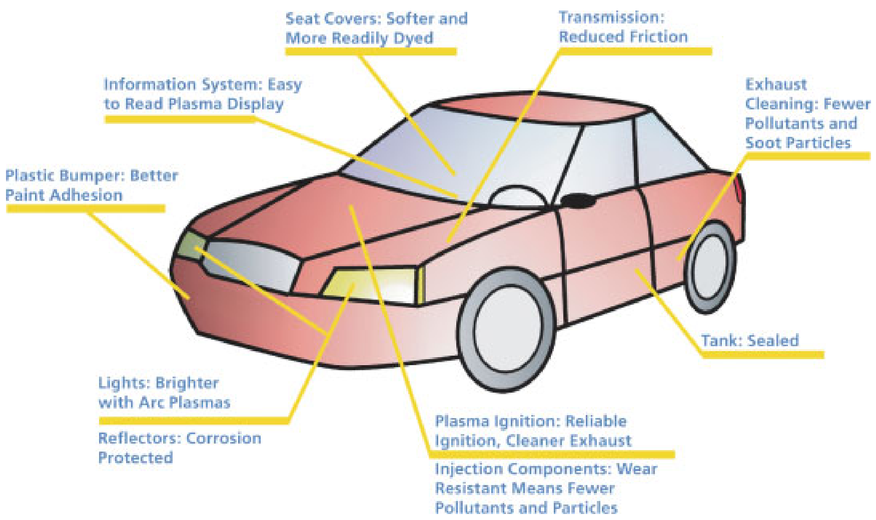


Figure 6. The use of plasmas in making better automobiles.[3]

Surface Modification of Polymers

As mentioned in the preceding section, polymers are characterised by an inherently low surface energy (or surface tension), the reason why liquids form bead-like drops instead of wetting the surface, and why coatings tend to adhere only poorly, if at all. However, when the surface is functionalized by exposure to a suitable plasma, its energy can be raised and the above-mentioned drawbacks can be resolved. These principles find application in all industries that make extensive use of plastics, be it in packaging, health care, textiles, etc. In the case of textiles, on the contrary, their large surface area facilitates ready entry of liquids through capillary forces (wicking), thus rendering them susceptible to soiling and staining. Figure 7 shows an atmospheric-pressure plasma system (a) in which technical textiles can be rendered water and oil repellent (b). In this case, the plasma-based coating process replaces an environmentally harmful wet-chemical treatment, as is also the case in plasma treatments of natural fibers such as wool. In cases like cellulose fibers (cotton) or polyethylene films, the surface wettability can be greatly enhanced by an oxygen plasma treatment, and this facilitates the adhesion of dye molecules or printing ink.

As a final example for this section, let us mention a PECVD process for polymers, namely the deposition of ultra-thin (typically 20 to 50 nm) gas- and vapor barriers. Such coatings, either ceramic (SiO_2) or amorphous carbon, can drastically reduce the permeation rate of gases (O_2 or CO_2, for example) or vapors (H_2O, aromas) through polymers used in packaging of foods, beverages (milk, juice, beer,. . .) or pharmaceuticals.

Biomedical Applications

Since the late 1960s,[11] non-equilibrium plasma techniques have been extensively investigated as a tool for improving the surface interactions between materials and biological systems, with the aim of rendering the treated surfaces biocompatible. Plasma processing in the health-care/biomaterials domain is currently experiencing spectacular growth. A wide range of promising processes and modified surfaces have so been produced on conventional and new materials and, occasionally, also commercialized. These include functionalized surfaces for the enhanced adhesion

a)

b)

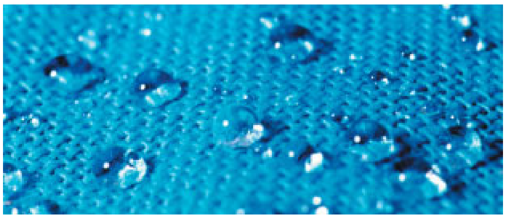


Figure 7. Plasma system for textile treatment (a); oil- and water-repellent textile surface (b). (Reprinted with permission by ITV, Denkendorf, Germany).

of living cells; non-fouling coatings designed to completely inhibit *in vitro* adhesion of biomolecules, cells, bacteria, etc.; primer layers for the immobilization of peptides, enzymes, antibodies, and other types of biomolecules; etching processes for the fabrication of bio-MEMS (micro-electro mechanical systems); and "smart" drug-release systems, to name only a few.

"Cell-adhesive" and "cell-repellant" domains of micrometric size can be created on suitable surfaces by means of PECVD or modification processes with the help of simple masking techniques. This approach, combined with the use of biodegradable substrate materials, is already being implemented into experimental tissue- and cell engineering protocols, to create a suitable scaffold for seeded cells to develop into a complete biological tissue. As an example, for the above-described principles, let us consider polystyrene, the polymer used in the manufacture of cell-culture Petri dishes. Plasma modification of polystyrene facilitates the adhesion and growth of living cells on the treated polymer; indeed, if regions of the pristine polymer surface are masked from the effects of the plasma, one can generate cell-adhesive "islands" on the otherwise non-adhering polymer, as illustrated in Figure 8.[12] Inversely, the highly reactive plasma environment can also rapidly destroy harmful living cells (bacteria, spores, or viruses), or proteins such as prions; this is leading to its increasing use for sterilisation, as a replacement of destructive or harmful procedures involving radiation, or toxic chemicals (e.g., ethylene oxide).

Evidently, the preceding brief survey has had to completely ignore a number of other important industries in which plasmas are finding ever-increasing use, for example, machine tools, aerospace, glass technology and optics, and environmental protection, to name but a few.

Plasma, Economics, and Future Prospects

Among the countries in which plasma science and technology are currently receiving the highest levels of private and public investment, it is probably appropriate to mention the USA, the European Union (especially Germany), Japan, and Korea. However, numerous other industrialised nations have also recognised the important contributions that plasma processes can make to their economic growth and well-being and they, too, are strongly supporting plasma-related scientific research and technological development, for example, China. Since reliable recent figures are available only for the case of Germany, we shall use these as an illustrative example for trends in the remainder of the industrialised world. Ref.[4] (section 3.5, pages 59 to 61) states that within the Federal Republic's total population of 82 million, 70 to 80 thousand workplaces can be directly associated with plasma technology. However, since plasma processes play key roles in the production of many other commodities, a more realistic number is currently closer to 500 thousand employees, or nearly 7% of jobs in the manufacturing sector. In monetary terms, this represents more than 50 billion Euros (64 B USD) per year for the German economy, with an estimated annual growth rate of 10%. Worldwide sales of plasma sources and systems is estimated to be 27 B Euros (35 B USD) in 2005.[3] In view of the enormous leverage that plasma technology can exert on many traditional sectors of the economy and on most of the newer ones, the German Federal Government commissioned the strategic study, ref.,[4] which appeared in print in September of 2004: Needless to say, recommendations voiced therein are all very strongly in favor of increased funding support for plasma technologies and research. Another very noteworthy aspect of this document are the results of surveys conducted among German and international experts; these are presented in chapter 5, for both the current and future status of plasma technologies. Regarding the latter, the 14 most important areas of future economic impact cited by the German (blue bars) and the international corps of experts (violet bars) are shown as a bar graph, Figure 9, along with their perceived relative importance (maximum 100%). Figure 10, on the other hand, shows the experts' views, this time regarding the 14 most important

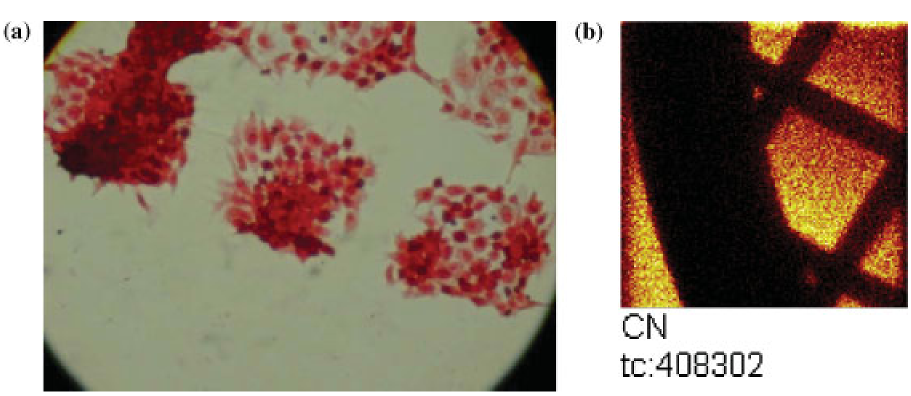


Figure 8. Microstructured growth of mammalian cells on a polymer surface that has been chemically micro-structured with the help of plasma (a). ToF-SIMS image of nitrogen-rich (bright) regions on the otherwise pristine surface (b) (squares are 100 μm × 100 μm).[12]

themes for future plasma-related research and development. Particularly striking aspects of these surveys are the importance assigned to the topics of atmospheric pressure plasmas, polymer treatments, and cleaning of surfaces, gases, and liquids.

To summarise, the success of plasma is derived, to a large extent, from several unique characteristics: (i) it is an enabling technology, capable of performing tasks which are inaccessible through other means; (ii) plasma processes can be readily controlled and performed with perfect reproducibility; this renders them highly amenable to automation, which is required for large-scale manufacturing operations; and (iii) equally important as (i) and (ii), environmentally benign plasma operations can increasingly and economically replace wet-chemical, polluting "traditional" processes.

Besides the ecologically favorable aspect mentioned in (iii), there are others, namely that plasma is a very efficient light source: higher light output of new plasma-based lamps accompanied by reduced energy consumption will bring important benefits to the world economy. Furthermore, plasma processes can be conducted at lower temperatures than their conventional counterparts; not only is this less damaging to materials being treated, but it again leads to a great reduction of the required energy budget.

To close this Essay, we repeat that plasma is still a young science and technology, one that has yet to reach its full potential. Some examples of additional new applications include exhaust purifiers for automotive vehicles, already mentioned, functional coatings for architectural glass, mercury-free lamps, plasma-treated packaging for food, beverage and pharmaceutical industries and, last but not least, nanomaterials. Of course, all new technological applications like these emerge from basic research in academic, industrial, or government laboratories; we, the Editors, hope that the present Essay has clearly demonstrated this

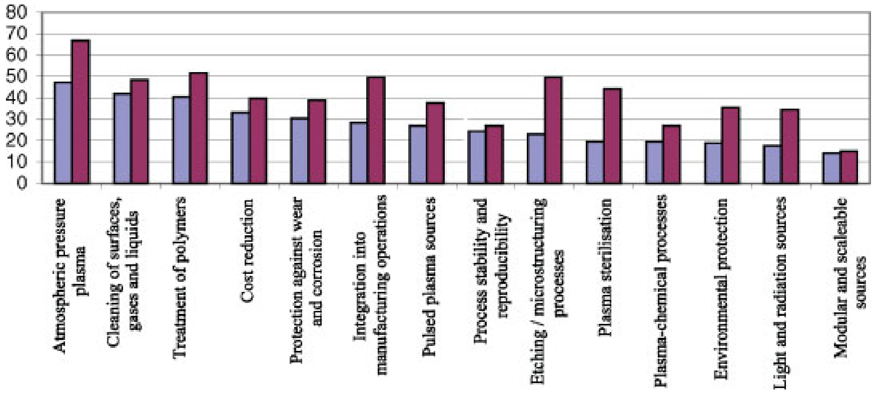


Figure 9. The 14 most important areas for future economic exploitation of plasma technology, as viewed by international experts (blue bars: German industrial scientists; violet bars: international corps of experts).[4]

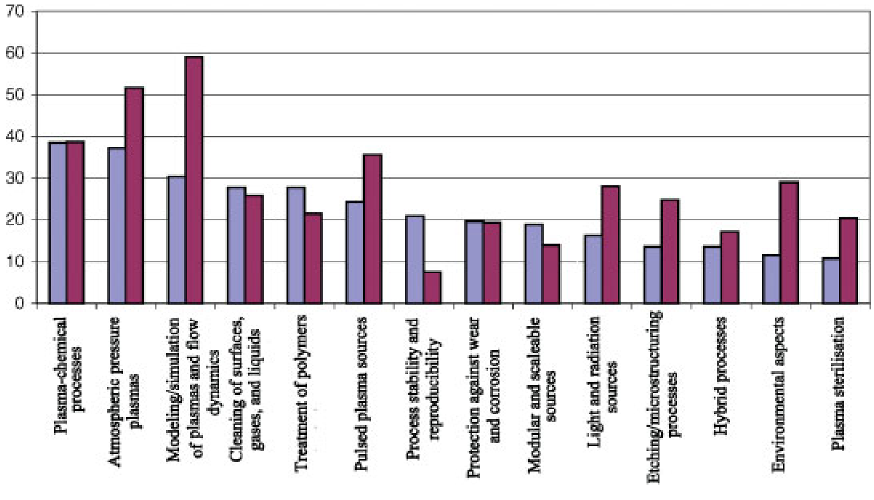


Figure 10. The 14 most important areas of future plasma research, as determined by international research scientists. (blue bars: German industrial scientists; violet bars: international corps of experts).[4]

link for the case of plasma, as well as the brilliant future of the ''fourth state of matter''.

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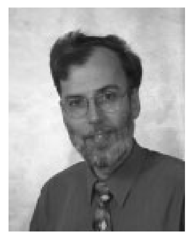
Pietro Favia is Associate Professor of Chemistry and Chemistry of Materials at the Department of Chemistry, University of Bari, Italy. He is author of about 100 scientific papers and patents, editor of 2 books and 1 international proceedings. He was plenary and invited speaker at many international conferences. He is an expert in low pressure plasma processes, plasma diagnostics and surface characterization techniques. His main fields of investigation are: surface modification of polymers, paper and textiles (activation for adhesion processes, PE-CVD of organic and nano-composite thin films); plasma processes for biomedical applications (cell-repulsive and cell-adhesive coatings; immobilization of biomolecules; bacterial-resistant layers; micro- and nano-structured surfaces cell adhesion/ spreading control); and process control of PE-CVD and plasma treatment processes. He is member of many organizing and scientific committees of international conferences on Plasma Chemistry; instructor at international schools on plasma modification processes and organizer of the IUPAC/IPCS course on Low Pressure Plasma Modifications of Materials (ISPC-16, Taormina 2003).



After studying at the Technical University of Clausthal-Zellerfeld and the University of Tuebingen, Christian Oehr finished his Ph.D.-Thesis "Plasma-induced deposition of thin films from metal-organic compounds" under the direction of Prof. Dr. H. Suhr, at the University of Tuebingen. After a Post-doctoral stay at the University of Tuebingen and being a scientist at the Fraunhofer-Institute of Interfacial Engineering and Biotechnology, he is now (since 1992) head of the Department of Interfacial Engineering at the Fraunhofer-Institute of Interfacial Engineering and Biotechnology (Stuttgart) and since 2002 head of the Department of Interfacial Engineering and Material Science at the Fraunhofer-Institute (Stuttgart). In the department emphasis is laid on surface modification mainly of polymers for application in different branches (medical devices, automotive components, textiles, foils and non-woven and on development of separation membranes) using plasma assisted techniques. Since 1997 he is member in several Committees related to plasma technology and polymers on the national as well as on the European level. He is member of the management committee of the German network "AK PLASMA", and therein chairman of the expert committee for plasma and polymer treatment.

Professor Michael R. Wertheimer obtained Engineering and Physics degrees at the universities of Toronto and Grenoble, respectively, the latter in 1967. He currently holds the NSERC Industrial Research Chair for Plasma Processing of Materials in the Engineering Physics Department of École Polytechnique in Montreal since 1996. He first joined École, one of Canada's largest engineering faculties, as a professor in 1973, after spending more than six years as a research scientist in industry. Dr Wertheimer is an IEEE Fellow and held a prestigious Killam Research Fellowship from 1990 to 1992. He is Co-Editor-in-Chief of the journal "Plasma Processes and Polymers" (Wiley-VCH); he has authored or co-authored more than 350 research articles, two dozen patents, and has edited or co-edited five books. Professor Wertheimer is an active member in numerous national and international scientific societies, and he has organized or co-organized many international conferences, most recently the 5th International Symposium on Ionizing Radiation and Polymers (IRaP 2002) in Sainte-Adèle, Quebec.

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