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PLASMA CHEMISTRY AND ITS APPLICATIONS

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Translation of "Purazuma kagaku to sono riyō," Kagaku kōgyō
[Chemical industry], April, 1980, pp. 337-341

(NASA-TM-75841) PLASMA CHEMISTRY AND ITS
APPLICATIONS (National Aeronautics and Space
Administration) 15 p HC A02/MF A01 CSCL 20I

N81-27925

Unclas

G3/75 26810



NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
WASHINGTON, D.C. 20546 JULY 1980

STANDARD TITLE PAGE

1. Report No. NASA TM-75841		2. Government Accession No.		3. Recipient's Catalog No.	
4. Title and Subtitle PLASMA CHEMISTRY AND ITS APPLICATIONS				5. Report Date July 1980	
7. Author(s) Keiichiro Hozumi				6. Performing Organization Code	
8. Performing Organization Name and Address Leo Kanner Associates Redwood City, California 94063				9. Performing Organization Report No.	
12. Sponsoring Agency Name and Address National Aeronautics and Space Administration, Washington, D.C. 20546				10. Work Unit No.	
15. Supplementary Notes Translation of "Purazuma kagaku to sono riyō," <u>Kagaku kōgyō</u> [Chemical industry], April, 1980, pp. 337-341.				11. Contract or Grant No. NASW-3199	
16. Abstract The relationship between discharge phenomena and plasma chemistry, as well as the equipment and mechanisms of plasma chemical reactions are described. Various regions in which plasma chemistry has been, or might be applied are surveyed, such as manufacturing of semiconductor integrated circuits, synthetic fibers, high-polymer materials for medical uses, optical lenses and membrane filters ("reverse-penetration films").				13. Type of Report and Period Covered Translation	
17. Key Words (Selected by Author(s))				14. Sponsoring Agency Code	
18. Distribution Statement Unclassified-Unlimited				19. Security Classif. (of this report) Unclassified	
20. Security Classif. (of this page) Unclassified		21. No. of Pages		22. Price	

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PLASMA CHEMISTRY AND ITS APPLICATIONS

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1. Discharge Phenomena and Plasma Chemistry

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When a gas molecule is exposed to the action of an electric field, the small amount of free electrons which are present in the gas are accelerated and acquire kinetic energy. However, if the electric field is extremely intense, or if the gas has a low pressure and the electrons have sufficient space for being accelerated, the molecules which have undergone electron collisions become dissociated and are transformed into electrically conductive gases, i.e. plasmas, and discharge phenomena are seen [1, 2]. The former is known in lightning and spark discharge, while the latter is very familiar to us in daily life in the form of neon signs or fluorescent lamps, which utilize the light emitted by low-pressure gases sealed inside glass tubes.

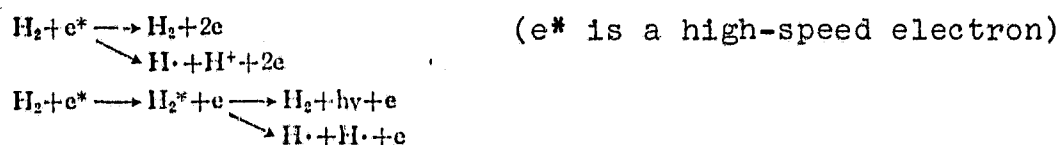
Not only do ionized gases have luminescence phenomena, but large numbers of ions and radical species are contained inside their systems. It has gradually become increasingly clear that these chemical species in a highly excited state are helpful in the creation of useful substances which cannot be obtained easily by means of the ordinary chemical reactions [3-8].

Gas discharge at atmospheric pressure has been utilized for a long time among chemists, for instance in the manufacturing of ozone and in the fixation of nitrogen in the air. However, low-pressure gas discharge has been of interest mainly for electrical engineers, for example in connection with lighting or current controls. Consequently, such discharge has been remote from the range of interest of chemists, and only slightly more than a decade has gone by since a movement was started, under the name of plasma chemistry, to make positive use of the various active

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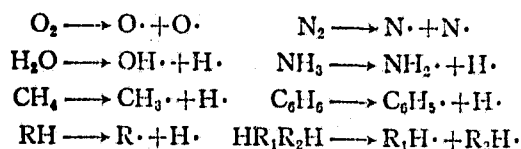
chemical species contained in ionized gases. Another important part of the repertory of plasma chemistry is gas discharge at atmospheric pressure, but its most characteristic area of utilization has been opening up rapidly in the field of low-pressure gas discharge.

At pressures in the vicinity of 1 mm Hg, the intermolecular distances of gases are far greater than at atmospheric pressures. The free electrons will be accelerated at a high speed by relatively weak electric fields and will dissociate the gas molecules. The processes of dissociation may be illustrated by taking hydrogen as an example. There is ion dissociation as in the following:



There is also radical dissociation, which proceeds at a lower energy than the above. The plasma state is supported by ion dissociation. However, the ions produced here disappear rapidly as a result of recombination with the stalled electrons. On the other hand, the radicals produced as a by-product (in the case of hydrogen, the radicals are atomic hydrogen), being neutral species, have a remarkably long lifetime in low-pressure spaces, where there are few chances of their collision with other radicals. Thus they are accumulated with a high concentration in the gaseous phase. Atomic hydrogen is the same as nascent hydrogen. Whereas the latter is produced and disappears in an instant when exposed to the action of a reagent, a characteristic of atomic hydrogen in low-pressure gas discharge is the fact that it can be obtained continuously and stably.

The same applies equally to oxygen, nitrogen and other compounds.



Various inorganic and organic gases can be radicalized [3].

It is believed that the radicals produced in this way follow the normal rules for chemical reactions in their behavior. However, the fact that the kinetic energy of accelerated electrons is utilized in radical production is a big difference from other chemical reactions, /338 for example thermochemical or photochemical reactions, and this difference is reflected also in the methodologies and the properties of the products.

2. Plasma Chemical Reactions

A description of the equipment for performing plasma chemical reactions will be left for a separate article. Morphologically, the equipment can be classified into two main types shown in Fig. 1: the circulating type, as shown in (a), and the diffusion type, as in (b).

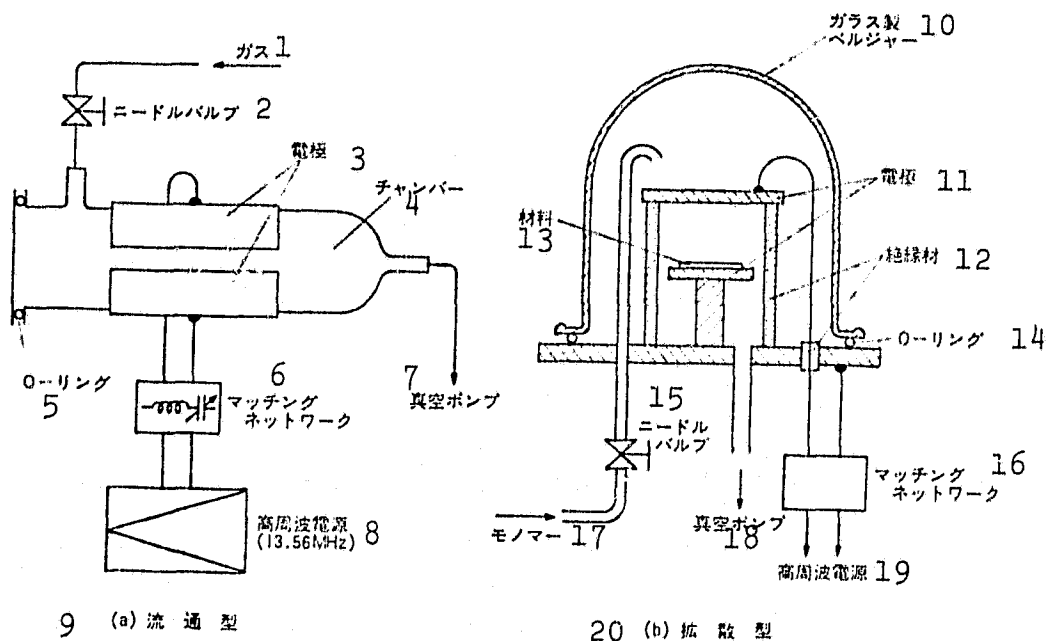


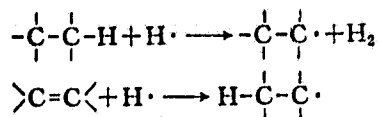
Fig. 1. Equipment for plasma chemical reaction
[Key on next page]

Key to Fig. 1:

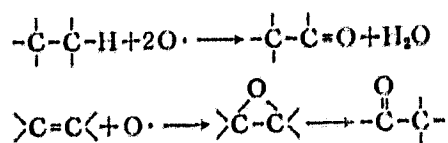
- | | |
|--|---------------------------------|
| 1. Gas | 11. Electrodes |
| 2. Needle valve | 12. Insulating materials |
| 3. Electrodes | 13. Material |
| 4. Chamber | 14. O-ring |
| 5. O-ring | 15. Needle valve |
| 6. Matching network | 16. Matching network |
| 7. Vacuum pump | 17. Monomer |
| 8. High-frequency power source (13.56 MHz) | 18. Vacuum pump |
| 9. (a) Circulating type | 19. High-frequency power source |
| 10. Glass bell jar | 20. (b) Diffusion type |

The former is suitable for cases where the plasma gas is circulated onto the surface of a material placed inside a cylindrical chamber, and the gas produced by the reaction is expelled rapidly in order to carry out the reaction quickly. The latter is suitable in cases where the material is placed on a stand inside a bell jar, and the purpose is to use gas diffusion to deposit gently the products obtained from the plasma gas. However, in actual fact it is possible to obtain a great deal of variety in the composition of the equipment, for instance by adopting a power source with a high or low frequency, by varying the shapes and sizes of the materials, and by changing the methods by which the gas is supplied.

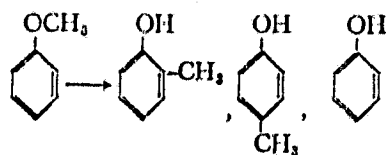
The radicals in the plasma obtained inside the equipment will have active chemical effects, even in the gaseous phase, and even on the surfaces of solid materials. Atomic hydrogen can be obtained easily, not only from hydrogen plasma, but also by dissociation of the alkyl group. However, it does not display a very great reducing action against organic substances, and abstraction of hydrogen or radicalization of the π electrons mainly occur [3].



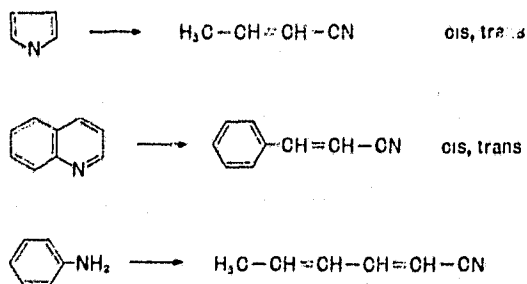
When atomic oxygen acts with organic substances, the hydrogen is first abstracted from the alkyl group, and carbonylation next occurs. However, as the oxidation proceeds, there is finally a splitting into CO_2 and H_2O . For alkenes, carbonylation proceeds through an epoxy stage [7, 8].



Trans-cis isomerization, which occurs when a relatively weak electron energy is absorbed, is observed in stilbene and the like, but in this case too, when the plasma conditions are intensified, there is an increase in the production of phenanthrene caused by radicalization of the aromatic ring [9]. The ortho-para transition reactions of allyl ethers such as anisole also tell us that there is pronounced production of methyl or phenyl radicals in the plasma space [7].

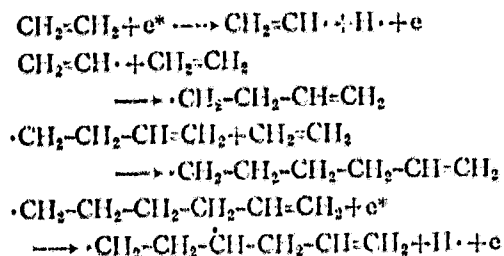


If the plasma conditions are intensified even further, ring opening /339 of the aromatic ring will become active, chain type hydrocarbons will be produced from the benzene ring, and unsaturated compounds having nitrile as their terminal will be produced from the nitrogen separate ring [7].



Examples which best express the nature of plasma chemical reactions may be seen in plasma polymerization reactions in which a simple monomer is radicalized in the plasma space and high-molecular compounds are formed without a catalyst. We may suppose the following polymerization

reaction for ethylene.



As the polymerization proceeds, the alkyl group expands. However, even during this it is constantly exposed to electron bombardment. As a result, the radical site appears at a random position in the alkyl group, as shown in the final formula, and ramifications and cross-links are produced from this site. Therefore, plasma-polymerized polyethylene has a chemical structure which is quite different from that of ordinary straight-chain polyethylene. It is characterized by being insoluble in organic solvents, having a high resistance to heat (up to temperatures of 300°C) and a high density ($d = 1.12$), and being amorphous.

Polymers with different properties can be obtained from various monomer raw materials. Table 1 shows the structural elements of polymers obtained from chain or ring monomers [7, 10]. One can infer the nature of the characteristic radical reactions which occur when they are subjected to electron bombardment in the plasma space. For example, unsaturated alkyls are obtained from saturated alkyl monomers, saturated and unsaturated alkyls are obtained from aromatic monomers, and methyl substituents are obtained from naphthalin.

TABLE 1.
STRUCTURAL ELEMENTS IN PLASMA-POLYMERIZED HYDROCARBONS

1モノマー	2 化学構造の要素	
3 ペンタン	アルカン, アルケン, メチル末端, ペンタン分子1個ごとに枝分れ	9
4 エチレン	アルカン, アルケン, メチル末端, アルカンの橋かけ	10
5 ブタジエン	アルカン, アルケン, メチル末端, アルカンおよびアルケンの橋かけ	11
6 ベンゼン	アルカン, アルケン, アルキン, アレン, メチル末端, ベンチル側鎖	12
7 スチレン	ベンゼンと同様, ベンジル基	13
8 ナフタレン	アルカン, アルケン, アルキン, アレン, メチル末端	14



- Key: 1. Monomer
2. Elements of chemical structure
3. Pentane
4. Ethylene
5. Butadiene
6. Benzene
7. Styrene
8. Naphthalene
9. Ramified one-by-one into alkane, alkene, methyl terminal, and pentane molecules
10. Cross-linking of alkane, alkene, methyl terminal and alkane
11. Alkane, alkene, methyl terminal, and cross-linking of alkane and alkene
12. Alkane, alkene, alkyne, allene, methyl terminal, pentyl side-chain
13. Same as benzene, benzyl group
14. Alkane, alkene, alkyne, allene, methyl terminal

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3. Utilization of Plasma Chemistry

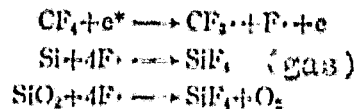
Already in 1962, when the name "plasma chemistry" did not yet exist, Gleit et al. were carrying out noteworthy experiments [11]. When oxygen excited by low-pressure glow discharge is put into contact with an organic substance, it undergoes oxidation and decomposes into CO₂ and H₂O without giving off heat. A substance which is the same as nascent oxygen can be obtained simply and continuously in this way in the gaseous phase. This fact attracted the interest of analytical chemists, and the technique soon won widespread acceptance as a new technique for pre-treating organic specimens, well known in connection with the low-

temperature incineration method. It is still today highly valued as a clean treating method in which there is no need to worry about volatilization of the components to be measured by high temperatures or about the production of corrosive gases, as is the case in the crucible incineration method or in Kjeldahl's method of wet decomposition. It also has a good rate of recovery of the components [7, 8].

Another advantage of the low-temperature incineration method is that the chemical composition and three-dimensional distribution of the inorganic substances in the samples are well preserved. This is because the combustion proceeds gradually on the sample surface only at the places where there is contact with atomic oxygen, and the sample as a whole is not heated. Organic metal compounds and simple metal substances usually become low-order oxides when exposed to atomic oxygen, but metal oxides and other stable inorganic compounds are transformed into ash and remain almost unchanged. This is the only method by which it is possible to remove in a non-destructive manner organic substances which would interfere with the analysis of the state of inorganic substances or crystals in high-polymer materials, coal, vegetable matter, or organ specimens [7, 8]. The plasma incineration method can also be used in a manner in which organic contaminations can be removed from the surfaces of utensils or materials. In particular, oily stains can be removed from glass utensils more perfectly than by means of chromic acid and sulfuric acid, and /340 the problem of disposing of the acidic solution is also eliminated. The same effect can no doubt be applied also in germ-free treatment.

As for industrial utilization of plasma chemistry, epoch-making successes have been achieved in the manufacturing of semiconductor integrated circuits [7, 8]. The process of manufacturing integrated circuits, as is described in another report, involves a complicated combination of circuit formation by means of photoresists (isoprene type photo-sensitive resins which are polymerized and cured by exposing the circuit patterns to ultraviolet light) and etching of the silicon printed circuit board. In the wet process, in which chemicals are used, it is necessary to use large amounts of chemicals such as hydrofluoric acid, strong phosphoric acid, and special organic solvents which are

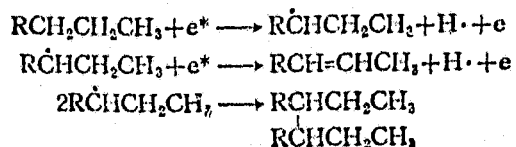
hazardous and troublesome to dispose of. During the early period, oxygen plasma was used to remove the photoresists, but soon there was developed an etching technique using atomic fluorine produced by Freon plasma.



The introduction of this dry process brought about immeasurably great results in improving the yields in production of integrated circuits, in improving their durability, and in lowering their production costs. In LSI and super-LSI, circuit patterns with a width of about 1 μm are required. Such fine fabrication cannot be realized by means of the wet etching method.

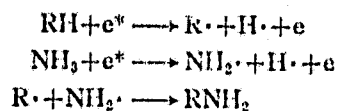
When atomic oxygen is brought into contact with a hydrophobic high-polymer material for a very short time, carbonyl groups are chiefly produced on the surface, and it can be made hydrophilic [7, 8]. The water absorption properties of synthetic fibers will on the whole be improved by this, and better textures and improved dyeing properties will be attained [12]. The polarity on the surface of the materials is connected partly with the bonding strength, and the adhesive properties of plates, pipes and films are increased by a similar treatment.

In the adhesive properties, it is not enough for merely the surface layers to be activated; it is necessary at the same time for the activated surfaces to be given a good chemical bond with the interior. Plasmas of inert gases such as argon or helium are used for this purpose. The reaction mechanism has not yet been elucidated, but it is believed to be attributable to the formation of unsaturated bonds on the surface and to increases of the degree of cross-linking. The following reaction is conjectured [7, 8].

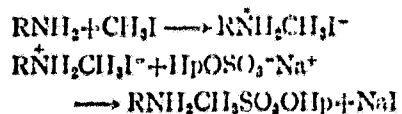


This treating technique is known as "cross-linking by activated species of inert gases" (CASING). It is effective even in materials such as Teflon which have especially poor adhesive properties. However, in addition to the above-mentioned reaction mechanism, in connection with this treatment it should be added that when the materials are taken out of the reaction device and put into contact with the air, the radicals remaining on the surface of the materials undergo air oxidation, and also that the ultraviolet light emitted from the plasmas of the inert gases contributes to the radicalization of the interior of the materials. It has been reported [7, 8] that CASING is applicable also to natural high-polymer materials and is also helpful in improving the shrink-proofing and dyeing properties of wool and the like.

A region in which plasma chemistry may be successfully applied in the future is that of imparting compatibility with living tissues to high-polymer materials for medical use. When the surfaces of polyethylene or silicone rubber materials to be embedded in organisms were subjected to plasma oxidation and polar groups were formed, and collagens of low-grade protein were implanted in them, their adhesion to the tissues was remarkably improved [13]. Polyvinyl chloride has physical properties which are highly suitable for use as blood pipes for transfusions or dialysis, but it also has the drawback that coagulation of the blood tends to occur easily on the inner surfaces. Grafting of heparin has been attempted in order to prevent blood coagulation. Heparin is a sulfonate with a sugar-like structure which is present also in small amounts in the blood. However, it adheres to the walls of the blood vessels and prevents coagulation of the blood because of its strong hydrophilic properties. In grafting, the high-polymer materials are first exposed to the action of NH_3 plasma. Then alkyl radicals are formed on the surface of the materials, and amino radicals are formed in the gaseous phase. Therefore, it is possible to introduce an amino group.



The amino group is exposed to the action of methyl iodide and is converted into ammonium. Then it is subjected to ion exchange with heparin sodium, and the graft is completed with this [8].



Polyvinyl chloride also contains large amounts of phthalates as softeners, and attempts have been made to prevent their elution. It is said that elution of the phthalates has been reduced to approximately 1/100 by coating the surface of the materials with a thin plasma-polymerized film of about 1,000 Å. Pyridine, triethyl silane or tetrafluoroethylene were used as the monomers [14].

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Plasma-polymerized films using fluorine type monomers have superior optical properties and are highly hydrophobic. In the visible range they are completely transparent, and when a thin film of about 500 Å is coated onto a lens surface, the reflectivity is reduced and the light permeability is improved by about 5%. Similar films have also been formed on window materials of ionic crystals necessary for infrared measuring instruments such as NaCl or CsI, and the window materials produced as a result have had almost no infrared absorption but have had excellent moisture-proofing effects [15]. On the contrary, there have been examples of the application of hydrophilic coatings on hydrophobic materials. That is, hard contact lenses were exposed to the action of a mixed plasma of acetylene, nitrogen and water to form a nitrogen-containing polymer film approximately 200 Å thick. This was done in order to improve the wettability of the lenses and also to improve the comfort when the lenses were worn [16].

Since plasma-polymerized films are formed on the surfaces of solid materials directly from a low-pressure gaseous phase which has good diffusion properties, one may mention the following noteworthy features. That is, they have a uniform film thickness, and there are no pinholes. For this reason, attempts have been made to apply plasma-polymerized films to high-pressure filter mediums such as reverse-penetration films.

Polymer films were formed from various monomers as the substrates for membrane filters, and their reverse penetration properties were compared. Thus far it has been learned that pyridine homologs as well as nitrogen type monomers such as allylamine are superior in their water permeability and desalting ratio [7, 8]. Technological development of reverse-penetration films is now under way, the purpose being to develop separation techniques which require no thermal energy for desalination of sea water, treatment of waste water, or concentration of extracts. Studies are also being made of plasma-polymerized films as one of their raw materials.

It is expected that the utilization of plasma chemistry will be expanded more and more as new raw materials and new needs are developed. In the field of inorganic thin films, progress is being made in the manufacture of amorphous silicon used in solar batteries from silane plasma. There are also possibilities that silicon nitride (Si_3N_4) obtained from a mixed plasma of silane and ammonia can be used in the semiconductor industry, and furthermore that its unique physical properties can be used for surface treatment of various materials. In the field of organic thin films, it will be necessary in the future to exert efforts to create functions suiting the purposes from monomers with different characteristics.

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