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INTERACTIONS BETWEEN A CONDENSED TARGET AND A NON - EQUILIBRIUM PLASMA: ACID-BASE REACTIONS AT THE INTERFACE

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Abstract

A new approach of plasma processes of industrial use is presented, with emphasis on the chemical properties of the plasma gas. Reactions occurring at the gas/ target interface are for the first time interpreted in terms of acid-base reactions and pertinent examples are given of laboratory experiments and of industrial treatments (e. g., etching, plasma polymerization or surface modification processes). Proton exchanges between the plasma phase and an aqueous target gives evidence of Bronsted acid-base phenomena. Illustrations of Lewis acid-base characters are provided by the role of biradicals (e.g., halogenocarbenes, nitrene) which are the main reacting species in etching or in surface treatment processes.

Key words: Non-equilibrium Plasma ; Gas Phase Acid-Base Reactions; Plasma phase acid-base reactions; Plasma surface interactions; Plasma Processes ; Etching; Plasma Polymerization; Nitriding.

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Introduction

A number of the newest industrial techniques in the field of surface treatment, are connected to plasma processes. We plan first to recall briefly what is termed a chemical plasma and to examine from the chemist's point of view the particular properties of this (still) unusual medium which involves both ions and uncharged species such as radicals in their fundamental or excited state. Our approach will deliberately minimize energy transfers and cross sections which are familiar concepts to physicists. We will concentrate on the chemical aspect and consider the properties of a non-equilibrium plasma in terms of acid-base reactivity, which has not yet been done. This point of view needs first an outline of the acid-base classical concepts which will appear to chemists to be trivial; we will then illustrate them by selected examples taken in various fields of plasma treatments : the etching processes in microelectronics, which involve acid-base characters; the plasma polymerization processes in which radicals occur determinately; the surface modification of metals and catalysts.

At this juncture, it can be pointed out that reactions are much faster in the gas phase than in a condensed phase, also the value of the kinetic constant in a solvent depends strongly on its nature. For example, the reaction :

$$Cl^- + CH_3Br \longrightarrow CH_3Cl + Br^-$$

is more than 10^{10} times faster in the gas phase than in any classical solvent.

Solvent :	H_2O	CH_3OH	DMF	gas
k ($cm^3\ mol^{-1} l^{-1}$):	$8.2\ 10^{-27}$	$1.1\ 10^{-26}$	$6.7\ 10^{-22}$	$2\ 10^{-11}$

This is mainly due to solvation, which always occurs in a condensed phase but may not affect species in the gas phase.

Both duration of treatments and solvent occurrence are troublesome events in industrial processes ; this is the reason why the industrial world is looking for dry processes for the most modern technologies.

The plasma phase : definitions and general characters

A plasma results from the interactions between electrons and gaseous matter and includes neutral and ionic species both in fundamental or excited states. The neutral species are molecules (and occasionally clustered molecules) and radicals, while charged species involve electrons, anions and cations.

When the temperature of the electrons T_e balances that of the gaseous particles T_g, we have a "hot" plasma for which the thermal equilibrium is reached. Otherwise, and for most of the cases, the temperature of the electrons is much higher : this "cold" plasma is usually realized in low-pressure luminescent discharges or in corona discharges (for which p < 1 atm) [Fig. 1] and will be considered in this paper.

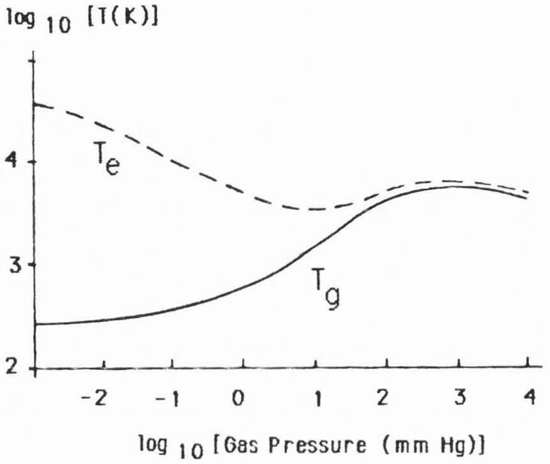


Fig. 1. - Gas Temperature (T_g) and Electron Temperature (T_e) in the plasma phase as a function of the pressure.

The energy balance shows that T_e and T_g are correlated :

$$(T_e - T_g)/ T_e = \pi m_g (\lambda_e * e E)^2 / 24 m_e (KT_e)^2 \qquad [1]$$

with m_g mass of heavy particles ; m_e mass of electrons; λ_e mean free path length of the electrons; E electric field strength; $\pi m_g/24.m_e$ mass ratio between heavy particles and electrons; $\lambda_e.eE$ amount of electron energy along one mean free path length; KT_e average thermal energy of the electrons.

In the considered plasmas, energy is carried on by the electrons and depends on various parameters such as gas pressure, gas composition and diameter of the reactor. Von Engel (1955a) suggests a semi-empirical relation to get within an order of magnitude of T_e :

$$\{eV_i / KT_e\}^{-1/2} * \exp (eV_i / KT_e) = 1.16\ 10^7 [CPr]^2 \qquad [2]$$

with: e, electron charge (coulomb); V_i, ionization potential (e.g., Ar = 13.12 volts ; Ne = 15.6 Volts); T_e, electron temperature (K); r, radius of the discharge reactor (cm) ; C , gas constant (e.g., He = 4.10^{-3}; $H_2 = 10^{-2}$; Ne = 6.10^{-3} ; Ar = $4\ 10^{-2}$); P = pressure (mm Hg); K, Boltzmann Constant.

Example for nitrogen :

P(torr):	20	5
C:	$4*10^{-2}$	$4*10^{-2}$
r:	5	1.25
CPr:	4	0.25
T_e(K):	18000	28000
E(eV) :	1.57	2.43

Energy is dissipated through collisions between electrons and particles : this governs the plasma composition as qualitatively sketched on Fig. 2. Besides, the energy distribution of the electrons obeys the Druyvesteyn law (von Engel 1955b):

$$f (\varepsilon) = C \varepsilon^{1/2} * \exp (- 0.55 (\varepsilon / \bar{\varepsilon})^2) \qquad [3]$$

with: ε energy of the electrons ; $\bar{\varepsilon}$ average energy; $f(\varepsilon)$ distribution function of the electrons.

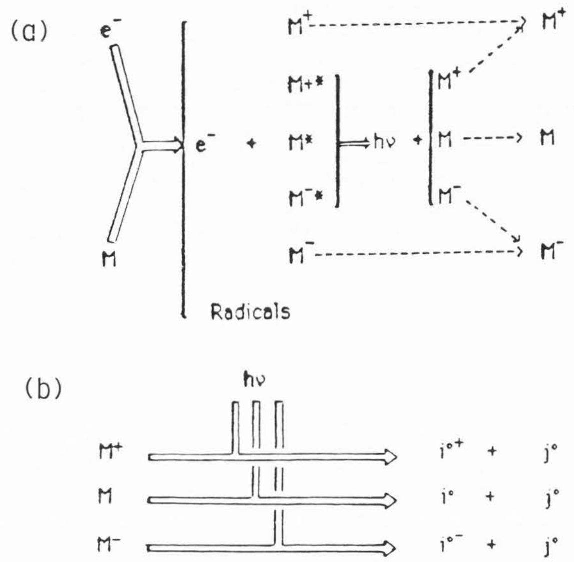


Fig. 2. -a-Sketch of energy dissipation between species in the plasma phase . Neutral species (molecules, radicals, photons) and charged species (ions and electrons) are formed. The heavy particles may be also found in an excited state.

-b-Interaction of the heavy particles (in excited or ground state) with photons give rise to charged or uncharged radicals (i°, j°) excited or not. By electron rearrangement the charged radicals generate ions in excited or ground state (not shown). As ultimate matter balance, a plasma involves mainly neutral species (molecules M, radicals i°) in excited or ground state, ions (M^+, M^-) in excited or ground state and electrons.

The intersection of f (ε) and the excitation cross section for a given molecule provides the population of an excited state [Figs. 3, 4 , 5]. We are now in position to determine the main excited (vibrational and electronic) states in the discharges which are responsible for the energy transfers and for changes of the chemical properties : new electronic states; increase of electronic density on antibonding orbital leading to weak chemical bonds and increase of reactivity; orbitals reactivity; triplet states, i.e., radical productions; vacancy orbitals and free pair of electrons (Lewis acid-base properties); ion formation;

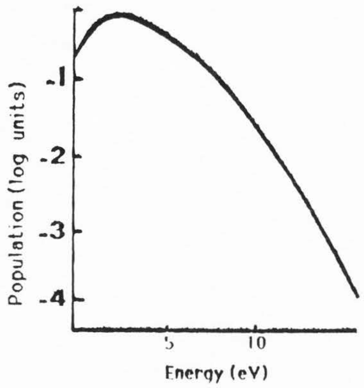


Fig. 3. -Energy distribution of the free electrons at T_e= 28,000 K (i.e. $\varepsilon \sim 2.43$ eV).

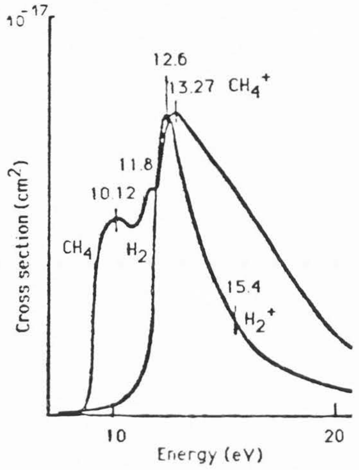


Fig. 4. -Excitation cross section (cm^2) as a function of the electron energy (eV).

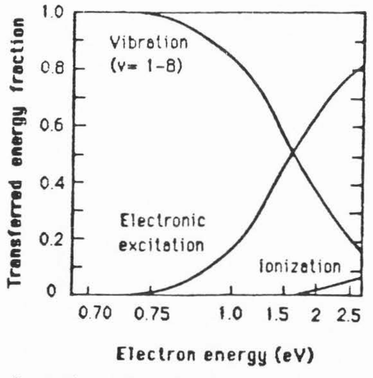


Fig. 5. -Energy transfer to the molecules by electronic collision in a N_2 discharge.

negative ions (reduction properties); positive ions (oxidation properties); modification of the molecular shape; modification of the symmetry, bond angle, hybridation, loss of atom and radical formation; vibrational excitation.

Radical Production

The sketch of energy dissipation [Fig. 2] shows that the collisions between electrons and gaseous species may result in the formation of radicals, which may also come from the interactions of photons with molecules or ions.

We report in Fig. 6 the electronic structure of the methyl radical chosen as an example. CH_3°, which results from a homolytic breaking of the CH_3 - H bonding if the discharge occurs in methane, can undergo combination reactions with other radicals H° or CH_3°. In suitable conditions CH_3° may also catch (or leave) an electron to give the corresponding anion radical $CH_3^{\circ -}$ (cation radical $CH_3^{\circ +}$) which has the same number of external electrons as the methyl anion (methyl cation respectively), but the electron distribution is different. After rearrangement $CH_3^{\circ -}$ gives rise to the methyl anion, all the quantic boxes of which are filled [Fig. 6]. CH_3^- may then share an electron pair with a convenient electron pair acceptor species. Similarly the methyl cation in the singlet excited state has a particular electron distribution characterized by an empty orbital, which can be filled by some electron pair given by an electron pair donor group.

A general survey of the shapes and properties of radicals occurring in plasma processes is given on Fig. 7 and in addition, the formation of biradicals has to be mentioned : as underlined by the example of the carbene :CH_2 [Fig. 6] (or the halogenocarbenes) these species may present one empty orbital in a singlet excited state.

One can point out that chemical reactions involving the plasma phase may occur in the plasma phase itself, e.g., $O_2(^1\Delta_g)$ for the synthesis of O_3 or NO. The chemical reactions may also take place in the plasma/ surface boundary layer and the relevant examples which are typical of plasma surface processes can be found in etching of silicon wafers or in plasma polymerization according to the main mechanism involved (respectively acid-base or radical mechanism).

Acid-base properties : general survey and definitions

Various aspects of the acid-base reactions

Acid-base phenomena are concerned with two typical processes according to the underlaying definitions. The proton exchange processes between the acid AH and the associated base A^- :

$$AH \ = \ A^- + H^+ \qquad [4]$$

are called Bronsted acidity (or basicity). The electron pair exchange between a donor species D (the base) and an acceptor molecule A (the acid) are called Lewis acidity (or basicity):

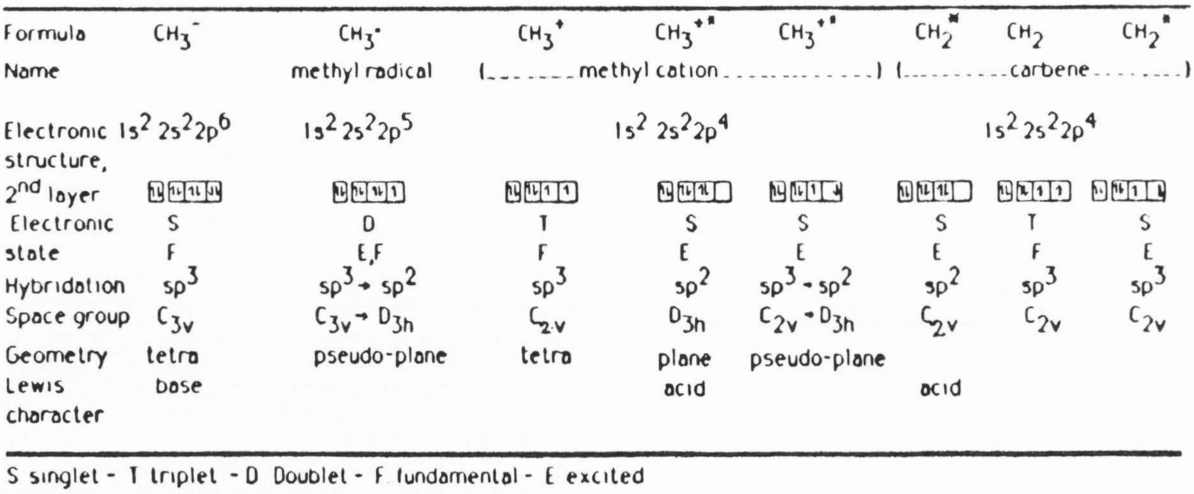
$$A + D \ = \ AD \qquad [5]$$

Molecules occurring in reactions of this kind present the following characters: acids are species with at least one empty orbital (e.g., BF_3), the positively charged end of a π bonding (e.g., $\partial +$>C=O), positively charged ions, which are able to catch electrons; bases are species with a lone electron pair, anions (e.g. F^-, OH^-), the negatively charged end of π bondings (e.g. >C=$O^{\partial -}$). The Lewis concepts for acidity or basicity thus defined display a more general character than Bronsted's definitions and include the proton exchange phenomena.

The question of the quantification

Any equilibrium is usually determined by the relevant equilibrium constant K (or by the associated standard free energy $\Delta G°$). For the proton exchange equilibria, H^+ occurs in every reaction and therefore plays a prominent part. The strengths of the bases are thus referred to their ability to combine with H^+.

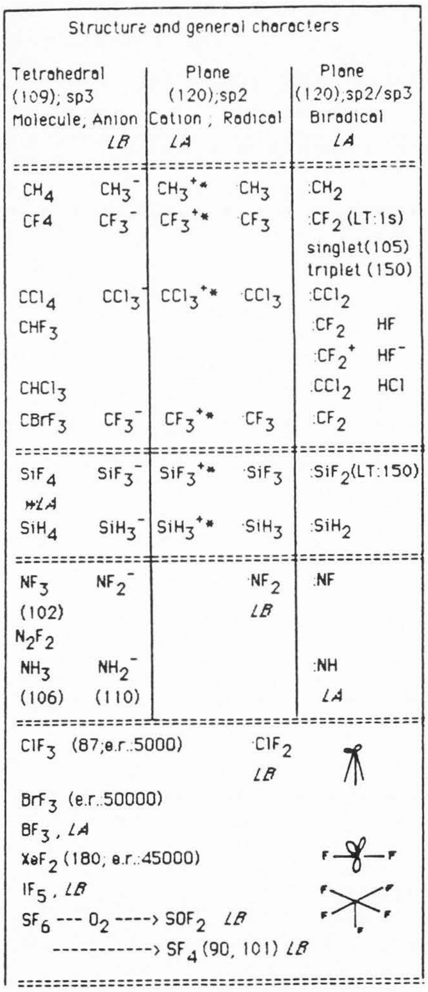
In the gas phase, the concerned species are often unsolvated or bare ; the acid-base character is then quantified by



Formula	CH_3^-	$CH_3^\cdot$	CH_3^+	CH_3^{+*}	CH_3^{+*}	CH_2^*	CH_2	CH_2^*
Name		methyl radical	(........ methyl cation		..............)	(.......... carbene		........)
Electronic structure, 2nd layer	$1s^2 2s^2 2p^6$	$1s^2 2s^2 2p^5$		$1s^2 2s^2 2p^4$			$1s^2 2s^2 2p^4$	
	[⇅][⇅][⇅][⇅]	[⇅][⇅][⇅][↑]	[⇅][⇅][↑][↑]	[⇅][⇅][⇅][ ]	[⇅][⇅][↑][↓]	[⇅][⇅][⇅][ ]	[⇅][⇅][↑][↑]	[⇅][⇅][↑][↓]
Electronic state	S F	D E,F	T F	S E	S E	S E	T F	S E
Hybridation	sp^3	$sp^3 \rightarrow sp^2$	sp^3	sp^2	$sp^3 \rightarrow sp^2$	sp^2	sp^3	sp^3
Space group	C_{3v}	$C_{3v} \rightarrow D_{3h}$	C_{2v}	D_{3h}	$C_{2v} \rightarrow D_{3h}$	C_{2v}	C_{2v}	C_{2v}
Geometry	tetra	pseudo-plane	tetra	plane	pseudo-plane			
Lewis character	base			acid		acid		

S singlet - T triplet - D Doublet - F fundamental - E excited

Fig. 6. -Geometry and electronic structure of Methyl ions and relevant radicals .



Structure and general characters				
Tetrahedral (109); sp3 Molecule;	Anion *LB*	Plane (120);sp2 Cation ; *LA*	Radical	Plane (120);sp2/sp3 Biradical *LA*
CH_4	CH_3^-	CH_3^{+*}	$\cdot CH_3$	$:CH_2$
CF4	CF_3^-	CF_3^{+*}	$\cdot CF_3$	$:CF_2$ (LT:1s) singlet(105) triplet (150)
CCl_4	CCl_3^-	CCl_3^{+*}	$\cdot CCl_3$	$:CCl_2$
CHF_3				$:CF_2$ HF
				$:CF_2^+$ HF^-
$CHCl_3$				$:CCl_2$ HCl
$CBrF_3$	CF_3^-	CF_3^{+*}	$\cdot CF_3$	$:CF_2$
SiF_4 *wLA*	SiF_3^-	SiF_3^{+*}	$\cdot SiF_3$	$:SiF_2$(LT:150)
SiH_4	SiH_3^-	SiH_3^{+*}	$\cdot SiH_3$	$:SiH_2$
NF_3 (102)	NF_2^-		$\cdot NF_2$ *LB*	:NF
N_2F_2				
NH_3 (106)	NH_2^- (110)			:NH *LA*
ClF_3 (87;e.r.:5000)			$\cdot ClF_2$ *LB*	
BrF_3 (e.r.:50000)				
BF_3, *LA*				
XeF_2 (180; e.r.:45000)				
IF_5, *LB*				
SF_6 --- O_2 ----> SOF_2 *LB*				
-----------> SF_4 (90, 101) *LB*				

Fig. 7. -Radicals: Shapes and Properties. In parenthesis: bond angle ; etching rate, e.r., expressed in Å.mn^{-1}; life time, LT, in seconds.In italics: strong or weak Lewis acid or base, *s/w LA/LB*.

either the gas basicity (GB) or the gas acidity (GA), which are defined in terms of standard free energies. For equations [6] and [7] in the gas phase :

$$AH = A^- + H^+ \qquad [6] \qquad\qquad BH^+ = B + H^+ \qquad [7]$$

we have

$$\Delta G°_6 = GA\,(AH) \qquad [8] \qquad\qquad \Delta G°_7 = GB\,(B) \qquad [9]$$

and we can consider

$$\Delta G°_6 \sim \Delta H°_6 \qquad [10] \qquad\qquad \Delta G°_7 \sim \Delta H°_7 \qquad [11]$$

as a first approximation since the entropy terms remain little with respect to the enthalpy term (Δ $S_i°$ may however be calculated (Hartman et al. 1979) on the basis of statistical thermodynamics).

The standard enthalpies can be calculated in terms of proton, hydrogen or electron affinities (resp., *PA, HA, EA*), binding energies *D*, ionization potentials *IP* by means of Haber cycles [Fig.8].Then :

$$\Delta H°_6 = PA\,(A^-) \qquad [12] \qquad\qquad \Delta H°_7 = PA\,(B) \qquad [13]$$

$$GA\,(AH) \sim D\,(AH) + IP\,(H) - EA\,(A) \qquad [14]$$

$$B\,(B) \sim HA\,(B^+) - IP\,(B) + IP\,(H) \qquad [15]$$

The proton affinities of the basic species B or A$^-$ provide a quantitative information on the basic character of the species.

Acidity scales

On the basis of a limited number of reference data, it is convenient to compare the acidity or basicity of various compounds. For this purpose we resort to the following equilibria [16], [17] :

$$A_1H + A^-_2 = A_2H + A^-_1 \qquad [16]$$

$$B_1H^+ + B_2 = B_2H^+ + B_1 \qquad [17]$$

The use of suitable Haber cycles leads to :

$$\Delta H°_{16} = [D\,(A_1H) - EA\,(A_1)] - [D\,(A_2H) - EA\,(A_2)] \qquad [18]$$

$$\Delta H°_{16} = PA\,(A^-_1) - PA\,(A^-_2) \qquad [19]$$

$$\Delta H°_{17} = PA\,(B_1) - PA\,(B_2) \qquad [20]$$

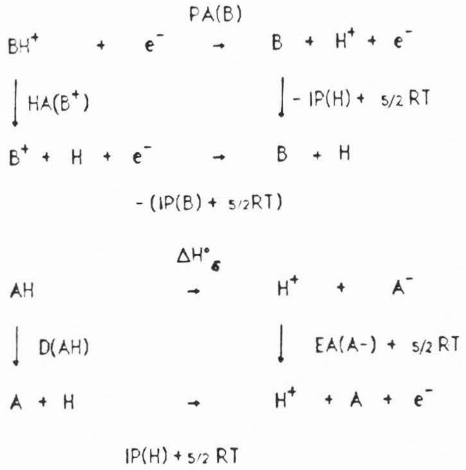


Fig. 8. -Haber cycle for gas acidity and basicity.

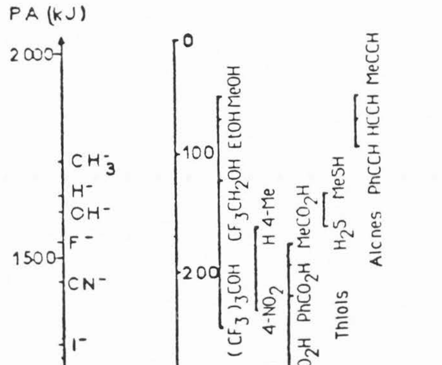


Fig. 9. -Proton Affinity Scale (from McIver 1981).

The calculated $\Delta H°_{16}$ or $\Delta H°_{17}$ values allow then to build numerous ladders by measuring the displacement of equilibria [16] and [17] which involve some reference species. A number of published data (Hartman et al. 1979; Aue and Bowers 1979; Bartmess and McIver1979; Berthelot and Gal 1984; McIver 1981; Arpino 1982) show that the PA values are generally included in a range of 1700 kJ mol^{-1} ; most of the organic acids can be found in a 300 kJ area the upper limit of which is H_2O (723 kJ mol^{-1}) and in a similar way, the organic bases are in a 300 kJ range centered around NH_3 (GA = 860 kJ mol^{-1}) [Fig. 9].

As already mentioned the solvation phenomena which occur in a solvent phase deeply modify the reactivity of the species. They prevent the direct use in the gas phase of any classical acidity function relevant to a solvent phase, like the pH scale in water, without the previous determination of solvation numbers and solvation standard free energies.

Applications

The published PA values relevant to a given family of compounds have been used to verify correlations with structural data (Yamdagni et al. 1974; McMahon and Kebarle 1977) (e.g. Hammett's σ or Taft's σ^* parameters). Besides the "natural" order for the acidities in the gas phase has been recovered for various families of compounds (Yamdagni and Kebarle 1971; Davidson and Kebarle 1976; Arshadi and Kebarle 1970; Payzant et al. 1971) (alcohols, amines RNH_2, R_1R_2NH, $R_1R_2R_3N$, or even substituted acetic acids) ; the different order of the pK_as is controlled by the stabilizing solvation effects on the charged species.

Bronsted acid - base phenomena in the plasma phase

Bronsted acidity

In the gas phase, the Bronsted acidity which is illustrated by the displacement of equilibria [6], [7] or [16], [17] has been examined by means of Ion Cyclotron Resonance, High Pressure Mass Spectrometry or various flow techniques (McIver 1981; Beauchamp 1971; Moylan and Brauman 1983).

In the plasma phase, no systematic investigation is available up to now, and this study was undertaken in our group, both to gather fundamental information and to explain a number of reactions occurring in the surface treatments (Amouroux et al. 1985a; Amouroux et al 1985b) by means of plasma and to foresee new possibilities. We selected first aqueous solutions (Brisset and Amouroux 1985) of coloured acid-base indicators as the condensed phase since this target leads to more easy interpretations on the basis of Bronsted's concepts and a point-to-plane dc. corona discharge as the plasma source.

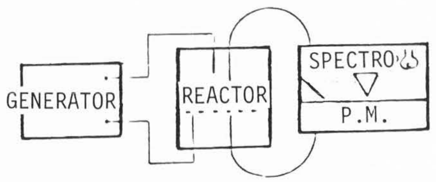
Experimental device

The general design of the 2-electrodes reactor is given in Fig. 10; particular details are displayed as follows: i) The gas inlet is made of a hollow needle, the active electrode; ii) The passive electrode is a stainless grid which acts as an ion collector; iii) The liquid target (cf. supra) laid on a microscope slide over or under the grid can be examined spectrophotometrically by means of two optical fibers connected respectively to a monochromator and a photomultiplier. The device allows us to follow the absorbance of the liquid slide at various wavelengths for various durations of the discharge [Fig 11].

Further developments of the reactor involve the use of a magnet and a modification of the axis of the active electrode.

Results with a cylinder-like symmetry device

When the active electrode set out was perpendicular to the grid, we obtained the following experimental results : whatever might be the nature of the gas (i.e. dry Ar, H_2O



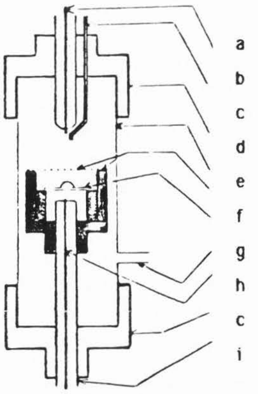


Fig. 10. -Diagrammatic view of the 2- electrodes reactor. [Typical working conditions: Plasma gas: Water saturated Argon; p = 1 atm.; flow rate = 0.3 liter/mn. Electric conditions: Distance between the two electrodes: 0.65 cm; Polarity: Rod + , grid - ; Voltage: 3 kV; Intensity: 200 µA. Target: Aqueous solution of Bromothymol Blue]. **a**: Optical fiber and guide (from the monochromator); **b**: hollow needle for gas inlet and active electrode (to R= 25 MΩ); **c**: plastic cap; **d**: glass reactor; **e**: stainless grid and metallic holder; **f**: microscope slide and liquid droplet; **g**: gas outlet; **h**: optical fiber and guide (to P.M.); **i**: Electrode (to generator).

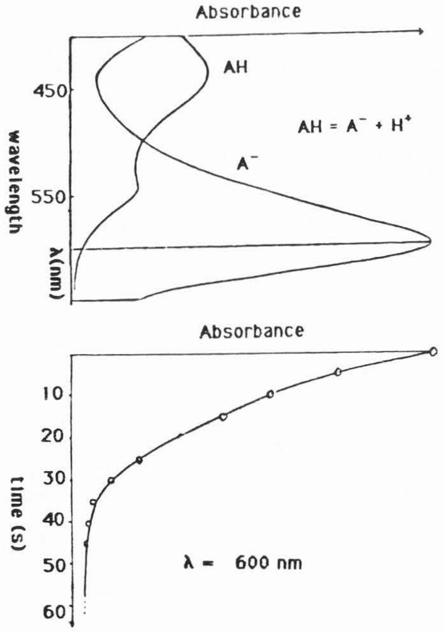


Fig.11.-Absorbance spectrum of an aqueous solution of Bromothymol blue and its evolution with the discharge duration; half life estd: 10 s.

saturated Ar, NH_3, CO_2); whatever be the position of the target with respect to the grid (target between or outside the electrodes); whatever be the polarity of the active electrode, the solution is always observed to become acidic as shown by numerous indicators.

The inter-electrode space can be divided into two areas ; the first one in the immediate surroundings of the point is the ionization region and the second a diffusion or drift region. In a negative rod configuration, for example, cations, anions, electrons and neutral species can be found in the ionization region while only neutral and negative species exist in the drift region. In the positive configuration only cationic and neutral species exist in the drift region.

Our results show obviously that the acidic effects in the solution are not governed by the electrode polarity and thus depend exclusively on the neutral species of the drift region. The number of protons created in the solution depends on the duration of the discharge and their formation may result from the interaction between the neutral species in the plasma phase and the water vapour at the plasma /solution interface. This model is strongly backed up by the use of NH_3 gas which leads to similar observations and by preliminary experiments performed with gel-dispersed indicators, which give evidence of the prominent influence of water at the interface.

In a more general way the influence of a liquid phase (in particular that of non aqueous aprotic solvents) is under investigation to get information on the mechanism of proton generation in the liquid phase.

Asymmetric discharge

In a cylinder-like symmetry device the electric wind which drifts the neutral species and the electric field which affects the ionic species are colinear.

In the case of a negative active electrode - both neutral and anionic species are confined in two co-axial cones and the neutral species have chemical prominent effects ; on lowering the symmetry - for instance by setting the active electrode non-perpendicular to the grid, the two cones have different axes and opposite chemical effects which can be then observed. Along the axis of the needle, acidic effects are observed while in the direction of the electric field (which remains perpendicular to the grid) the solution turns to be basic. Acidic and basic effects can then be characterized and separated. The separation is also improved by the use of a convenient magnetic field due to a magnet.

Lewis acid- base phenomena in the plasma phase

Evidence of Bronsted acidity processes at the plasma/solution interface has just been reported : its systematic study is under development in our laboratory.

Lewis acid-base reactions may also occur in the plasma phase if the concerned species act as electron pair donors (bases) or acceptors (acids), that is if the distribution of their molecular orbitals are convenient. These species are atoms or molecules either in the fundamental or in some particular excited state.

As (more or less classical) examples of acids, we can mention boron trihalogenides BX_3 which are of common use in the etching processes:

$$:SO_2 + BF_3 \longrightarrow :SO-O\,BF_3$$

Except for iodine I_2 which "accepts" the base I^-, the halogens X_2 show generally no acid character (Cl_2 forms a complex with PCl_3, but its formation involves a structure modification and is more likely considered as an oxidative addition). ICl_3 which is a good Cl⁻ acceptor behaves as an acid. SF_4 has been reported to accept F⁻ only from quaternary ammonium fluorides:

$$SF_4 + R_4NF \longrightarrow SF_5^- R_4N^+$$

(however, in the presence of $SbCl_5$, SCl_4 undergoes a chloride transfer to give (SCl_3) ($SbCl_6$)) . The interhalogen fluorides XF_n (n = 1, 3, 5 for X = Cl, Br ; n = 3, 5, 7, for X = I; e.g., ClF_3) act as Lewis acids toward the base F⁻ and give anionic species by fixing F⁻ (e.g., ClF_4^-) but in the presence of BF_3, SbF_5, AsF_5, which are better F⁻ acceptors, they form cationic species by loosing F⁻ (e.g., ClF_2^+).

$$ClF_3 + CsF \longrightarrow Cs^{+-}ClF_4$$
$$ClF_3 + AsF_5 \longrightarrow ClF_2^{+-}AsF_6$$

XeO_3 reacts with KF to give XeO_3 F⁻ K⁺ and has an acid behaviour in spite of its lone unshared electron pair; Xenon fluorides acts as fluoride ion donors (e.g., XeF_2 in the presence of strong acceptors such as SbF_5).

The trivalent compounds of N, P, S afford many examples of Lewis donors. In addition, phosphines, amines and sulfides undergo oxidation reactions to form stable compounds, the phosphine and amine oxides and the sulfoxides. The reaction involving NF_3 :

$$NF_3 + 1/2\,O_2 \longrightarrow F_3N\text{-}O$$

in which the oxygen atom may be considered as acting like an acid, has been observed under the electric discharge. Xenon fluorides are classified as F⁻ donors as well as ClF_3 (while Br F_3 is F⁻ acceptor according to the reaction :

$$ClF_3 + Br\,F_3 \longrightarrow (ClF_2)\,(Br\,F_4)).$$

Polarizability

The strong electric field created between the electrodes (i.e., 10^5 to 10^6 V cm^{-1}) interacts with the gaseous matter in the neighbourhood of the electrodes. It induces large changes of the electron densities of heavy molecules in the boundary layer and hence dipole formations. In the particular case of π bonding molecules, it affects the electron distribution and backs up the acidic or basic character of the bonding according to its direction. The relationship between Lewis acid-base behaviour and polarizability has already been examined (Hancock et al. 1983).

This is strongly supported by polymerization reactions performed in Acetonitrile solutions, such as the electrochemical coating of poly-acrylonitrile which is realized on the Fe or Ni electrode acting as the cathode (Lécayon et al. 1982). In the inner Helmholtz layer where the positively polarized end of the monomer (almost a carbene head) is close to the negatively charged metal a Lewis acid-base reaction may take place which is responsible for the chimisorption step: the binding of the monomer to the metal.

In the gas phase similar mechanisms may be considered and the modified species are then able to react as Lewis bases or acids with the solid electrodes according to their polarization.

Numerous applications in the field of surface polymerization, electrode modification, encapsulation or surface protection involve a polarization step in the general plasma organic polymerization processes . It has been pointed out that the properties of the polymers prepared electrochemically depended on the polarization of the working electrode. For an anodic coating, the polymer shows semi-conductor properties while on cathodic (or basic) polarization, one gets a piezoelectric polymer.

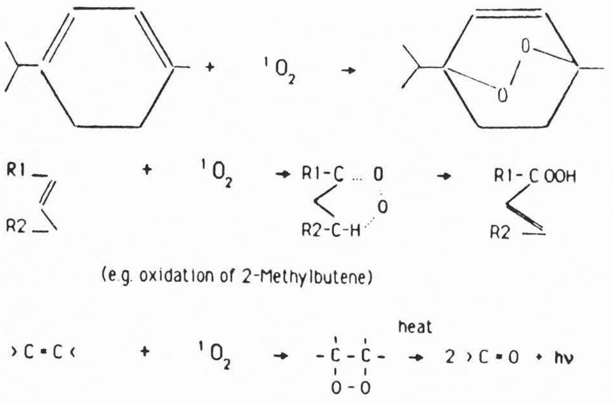


Fig.12.-Examples of reactions of O_2 (1Δg) with organic substances (from Ouelette et al. 1980).

Species in some excited states may also display Lewis acid-base characters. The most illustrative example is given by O_2 molecules in the singlet excited state, for which the reorganized electron configuration empties a quantic box. Then O_2 (1 Δg) behaves as a Lewis acid and accepts one electron pair from a donor group [Fig. 12]. A matching example is N_2 in the $A^3\Sigma u$, $B^3 \Pi g$, $C^3 \Pi u$ states, which will be illustrated later by the nitriding processes of transition metals. Polyradicals such as carbenes, chlorocarbenes, silenes or nitrenes, and ionic radicals may exhibit in the convenient excited state the same electron rearrangement and hence the same acid-base properties [Fig. 6]. They may undergo acid-base reactions in the plasma-surface boundary layer which are operated in the surface modification processes such as etching or grafting of microelectronic compounds [Fig. 13].

Applications to etching processes

The use of silicon, silicon derivatives, AsGa and other metals in micro electronic components has lead to a variety of elaborate etching processes which involve for most of them a plasma treatment [Fig. 14]. We must first point out that both etching and sputtering processes consist in passing a chemical from the solid to the gas phase by means of ionic or molecular beams (Snowdon and Heiland 1985), so that it is enhanced by the formation of volatile species. It is the reason why fluorinated species are generally involved in Si etching processes (since it allows volatile species such as SiF_4 to be formed) while halogen derivatives are preferred for metal etching. The working gas is usually selected for its ability to give F⁻ or CF_3^+ ions, which are generated from mixtures of fluorocarbons (CF_4, C_2F_6, C_2F_4,...), halogenocarbons (CCl_2, CCl_3 F,...) or halogen derivatives (Cl_2, Br_2, BCl_3, SF_6, NF_3,...) in various compositions.

The etching speed of a given solid material provides information on the reactivity of the gas (or the gas mixture) toward the solid under plasma conditions. It has been shown (Flamm 1981; Flamm and Donnelly 1981) that the etching speed was directly dependent on the number of F atoms present in the gas phase; however if the production of F atoms was the governing parameter, the etching speed of a given substrate should be greatest with pure fluorine as the active gas. Since

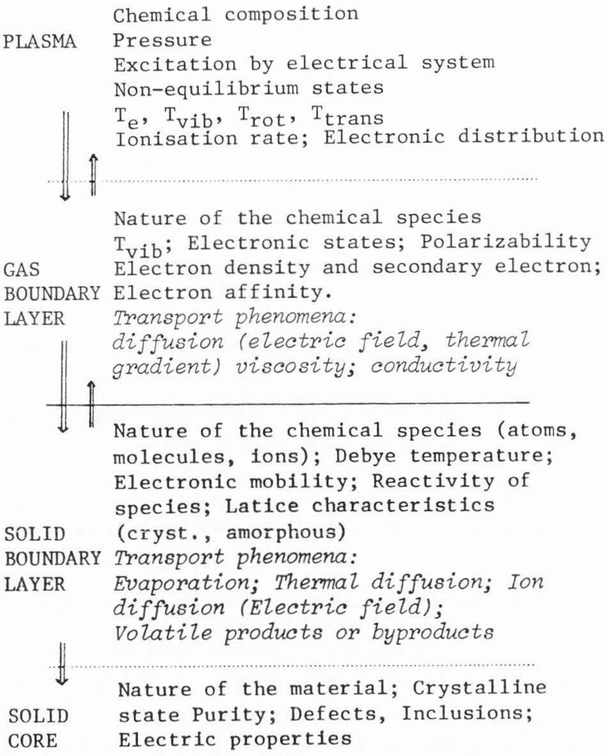


Fig. 13. -Plasma-surface Interactions.

experiments show that much higher speeds can be observed with other fluorine compounds, it is likely that some other mechanism occurs in the etching process, and we can therefore consider it in terms of acid-base properties.

The SiO_2 or Si_3N_4 etching is a much slower process than Si etching ; this may be related to the relative acidity of Si and SiO_2 (or SiN_3) toward the attacking agents which are most often basic compounds (like F^-). These mere considerations may explain the results gathered for plasmaless etching . In Si etching the matter now lies in the choice of the fluorine source and a number of experiments have been performed with highly reactive gases (e.g. XeF_2, ClF_3, NF_3,...).

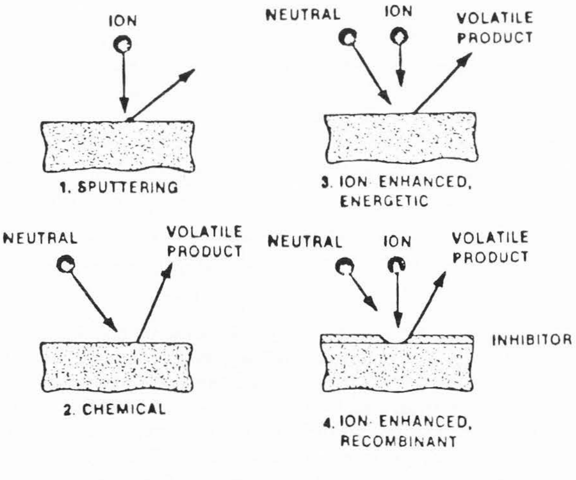
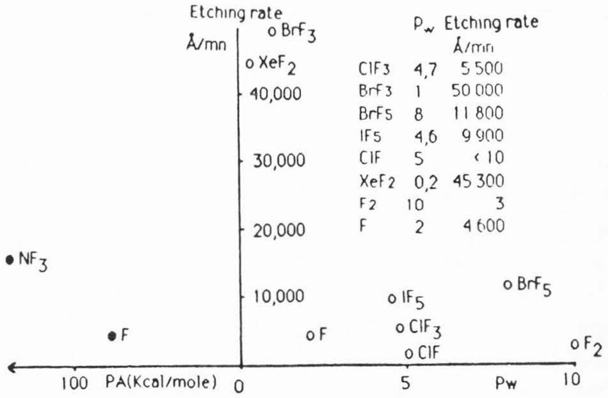


Fig. 14. -How does plasma etching take place? (from Herb 1985).



	P_w	Etching rate Å/mn
ClF3	4,7	5 500
BrF3	1	50 000
BrF5	8	11 800
IF5	4,6	9 900
ClF	5	< 10
XeF2	0,2	45 300
F2	10	3
F	2	4 600

Fig. 15.-Plasma etching rates of Si as a function of power or Proton Affinity.

In plasmaless processes [Fig. 15], no ion is concerned, and we have only chemical reactions between neutral species. The low etching speed observed with ClF confirms that it is a poor F^- donor (because Cl^+ links to a ClF molecule to form Cl_2F^+ which hinders its activity). ClF_3 is a weaker F^- donor than IF_5 or Br F_5, while the most reactive species are actually XeF_2 or Br F_3, which are known to be good F^- donors in the presence of strong F^- acceptors like Si.

However, it has been pointed out that the etching speed is largely enhanced by the presence of an ionic flow (e.g. Ar^+) or the excitation of the surface by a convenient laser beam. Authors also found that the desorption step of fluorinated species was the governing stage of the etching process.

In plasma etching processes, ions are associated to neutral species, a strong electric field and a photon flow; the conjugated action allows isotropic and anisotropic etching. The etching speed depends on the electric field and increases with the electric power ; this may be connected with the polarizability of the gaseous molecules, the reactivity of which is affected by $|\vec{E}|$. Anisotropic etching is governed by the influence of the electric field which affects both ionic and polarized species; for example NF_3, ClF_3 or XeF_2 allows one to reach etching speeds as high as 80,000 Å mn^{-1} under these conditions.

The electrode polarization is also a determining parameter as illustrated by the following sketch built on the order of the etching speeds.

Cathodic polarization ; Lewis acids : $CF_2^+ < CF^+ < CBrF_3 < BF_3$

Anodic polarization ; Lewis bases: $CF_3^- < ClF_3 < ClF_2^- < SF_4^-$

The speed depends also on the gas pressure and temperature, but the main parameter is the gas composition. For example the etching speed of Si by NF_3 in NF_3 + He mixtures is higher than 10,000 Å/mn for 80 % NF_3 (i.e. more than five times the relevant value for 10 % NF_3 i.e., 2,000 Å /mn). In a similar way the etching speed of AsGa by Cl_2 + Br_2 mixture increases with the percentage in Br_2 (20 - 80 µm mn^{-1}). In that case, two different chemicals, As and Ga, are concerned, and the etching speed is an average value depending on the etching speeds of each pure component . Besides, the desired electronic properties of the material need the same etching speed be realized for both species. Occasionally the etching speed may not be a mere increasing function of the gaseous mixture composition (Flamm 1981; Flamm 1985), as emphasized by the Si etching by CF_4 + O_2 mixtures. In this case, the speed presents a maximum for a particular mixture close to 40 % CF_4 . This feature may be related to the thermodynamic study of the gas mixture and sketched as follows; oxygen allows carbon oxides to be formed which result from the breaking of C-F bondings while fluorine attacks at Si to form volatile fluorinated species. In SiO_2 etching, no oxygen is needed in the working gas since the element is present in the solid phase; the formation of CO and fluoro compounds (e.g. SiF_2, SiF_4, $SiOF_2$) has been reported at the gas solid interface.

Polymerization process

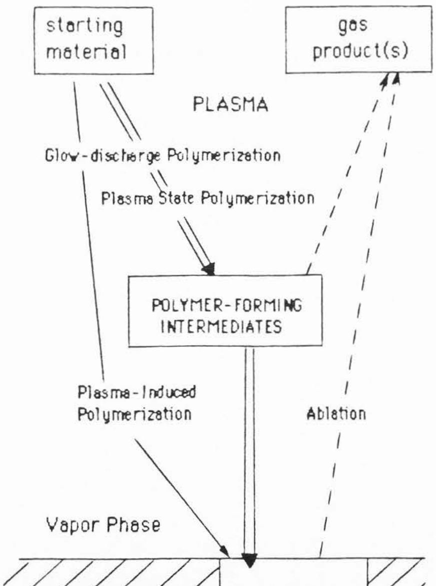
The plasma polymerization is controlled by different activation mechanisms such as ionic mechanisms, radical or photonic activation. However, in a plasma reactor the three phenomena generally occur and produce nonconventional polymers which are in most cases highly crosslinked and adhere to the solid surface. Nevertheless, we have to consider the degradation phenomena due to the plasma-polymer interactions.

On the other hand the polymerization phenomena depend on the nature of the substrate and we can consider the different interactions between radicals or ions with the substrate:

- Interaction between the substrate and the radicals : non-volatile species formation -----> grafting; volatile species formation -----> etching, ablation.
- No interaction between the substrate and the radicals and/or the ions; deposition phenomena.
- Interaction between the lattice of the substrate and the radicals; diffusion, doping.

Because the ionization of the gas or the vapor involves many highly energetic species on one hand, and the formation of the free radicals due to the fragmentation of organic compounds (monomers) in plasma on the other hand, it is difficult to distinguish clearly between atomic (plasma-state) or molecular (plasma-induced) polymerization (Yasuda and Hsu 1977).

The next scheme represents the plasma polymerization mechanisms proposed by Yasuda .



It is interesting to note that the electrical field strength in the boundary layer induces dipole-dipole formation and large modifications of the electronic density. The electrical field also influences the ionic polymerization as well as the orientation of the polymers formed.

Finally, general properties of gaseous mixtures can be easily transposed to plasma reactivity such as acid base properties.

Fluorocarbon polymerization on different targets

Fluorocarbon polymerization of monomers such as $C_2H_2F_2$ on different raw materials (silicon, glass, PET or pp) can be developed by corona discharge or glow discharge plasma (Amouroux et al. 1983a; Amouroux et al. 1985a; Amouroux et al. 1985b).

By using a tubular glow discharge reactor with an inductive RF plasma, the plasma deposition on a silicon target depends on the pressure and the power of the plasma. ESCA analysis of the polymer (i.e., film formed on silicon) shows the main chemical bonds present through a thickness of 100 Å of the layer [Fig. 16]. The presence of CF, CF_2, C_2F and SiF or F^- functions depend on the plasma conditions and are in agreement with the thermodynamic calculations [Fig. 17].

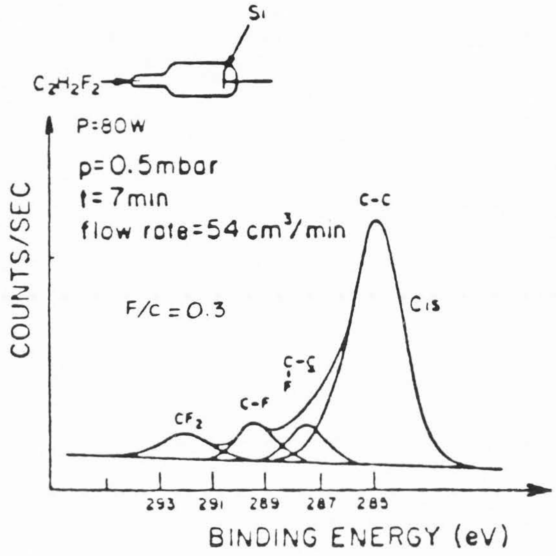


Fig. 16.-Decomposed carbon peak of ESCA analysis for the treated silicon in an atmosphere of $C_2H_2F_2$.

A decrease of the H/F and the C/F ratios of the gas mixture induces etching mechanisms of the target while an increase of these ratios allows a polymerization layer formation.

Taking the same monomer but employing another mode of electrical excitation (high voltage corona discharge) provides polymeric films grafted or deposited to the surface of a substrate such as PET film [Fig. 18].

Role of the oxygen contamination during a fluorocarbon plasma polymerization process

Oxygen molecules which are present in the plasma reactor interfere in the different steps of the graft polymerization. In the presence of O_2:

1 - during activation :

$$RH \xrightarrow[Ar + O_2]{\text{plasma}} \text{oxidation} + \text{weak concentration of free radicals.}$$

2 - after activation step :

$$RH \xrightarrow[Ar]{\text{plasma}} R^\circ \xrightarrow{O_2} R00^\circ \text{ peroxy radicals (not very reactive)}$$

3 - with the monomer :

$$O_2 + \text{monomer} \xrightarrow{\text{plasma}} \text{fluoroxide products, } CO_2, CO, ...$$

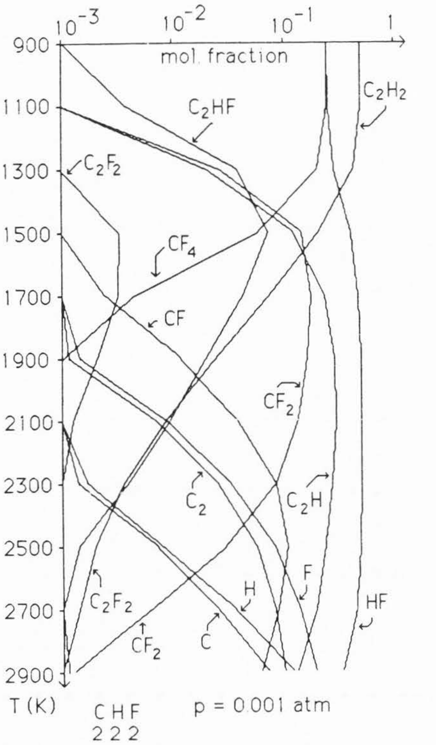


Fig. 17.-Complex chemical equilibrium diagram for the stoichiometry $C_2H_2F_2$.

The first two reactions decrease the efficiency of the graft polymerization by destroying the carbon free radicals and the last reaction decreases the formation of fluoropolymers in the plasma.

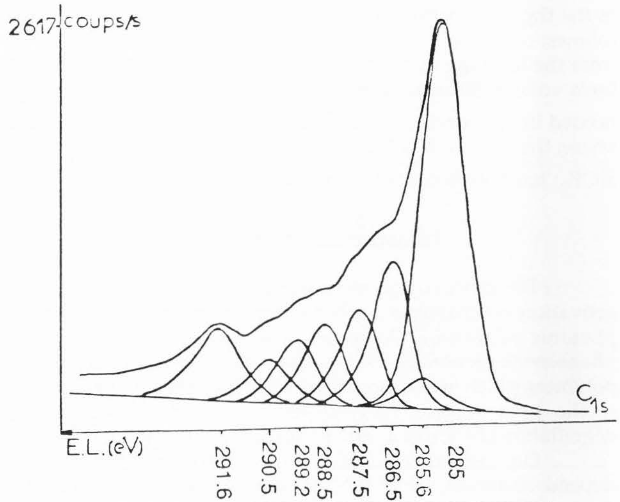
By using ESCA and ESR analysis [Figs.19-20] we have clearly demonstrated the competitive phenomena occurring during the deposition in the case of the copolymerization in a mixture of Ar + $C_2H_2F_2$ (15 % $C_2H_2F_2$ + 85 % Ar) onto the polypropylene (Rouzbehi, 1985; Rouzbehi et al.,1986).

The study of C_{1s} portion of a typical ESCA spectrum of the treated PP in the different gas compositions indicated that the structure of the polymeric film obtained depends directly on the oxygen residual in the plasma reactor.

In order to eliminate the short length oligomers and the nonfixed homopolymers the treated pp films are washed with water [Fig. 20 - II] and acetone, [Fig. 20 -III] respectively. We have pointed out that when oxygen is excluded from the reactor the high stability of the layer obtained is measured by only a slight decrease of F/C ratio when washed with acetone ; while the oxygen/argon/ $C_2H_2F_2$ mixture produces fluorocarbon oxide groups which are rapidly eliminated upon water or acetone washing.

Role of the target

By using glass or metallic targets plasma polymerization would depend on the reactivity of fluorocarbon radicals with the atoms of the lattice. For example, in the case of a glass substrate, large diffusion of the fluorine atoms in the lattice through a depth of 0.2 to 0.3 µm indicates the chemical affinity of the fluorine atoms for a calcosodic glass [Fig. 21]. Therefore a large part of the fluorine, resulting from the plasma polymerization of the fluorocarbon, diffuse in the lattice of the target.



B.E.	Reference
285	$CH_2 - CH_2$
285.6 + 0.1	$\underline{C}H_2 - CF_2$
286.5 + 0.1	$- CH_2 - CF_2$ n-, $\underline{C}$-O
287.4 + 0.2	C - ; C-F in β position
288.6 + 0.2	- CFH - CFH - ; $\underline{C} = O$
289.3 + 0.2	- CFH - CF ; - ; C - O - C
290.2 + 0.2	$- CF_2 - CH_2 -$
291.6	$- CF_2 -$ CFH -

Fig. 18.-Decomposed carbon peak of ESCA analysis for the treated PET film.

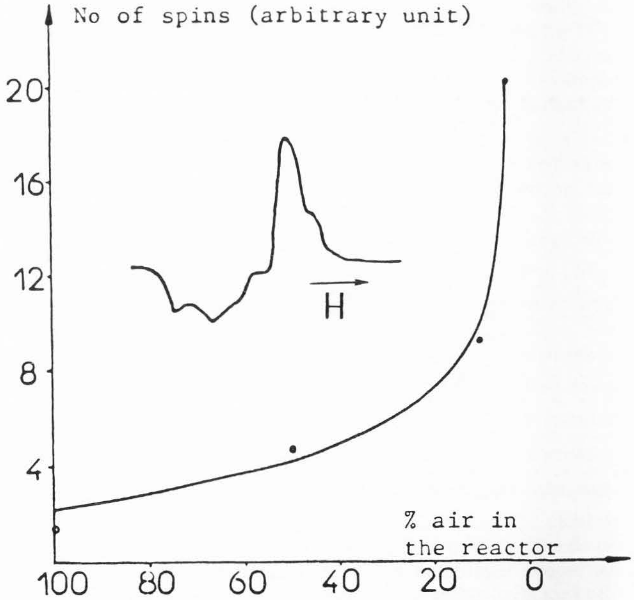


Fig. 19. -Variations of free radicals concentration in function of the residual air in the reactor; t= 2.8 s ; Ar flow-rate = 280 cm^3/mn ; P = 1 atm.

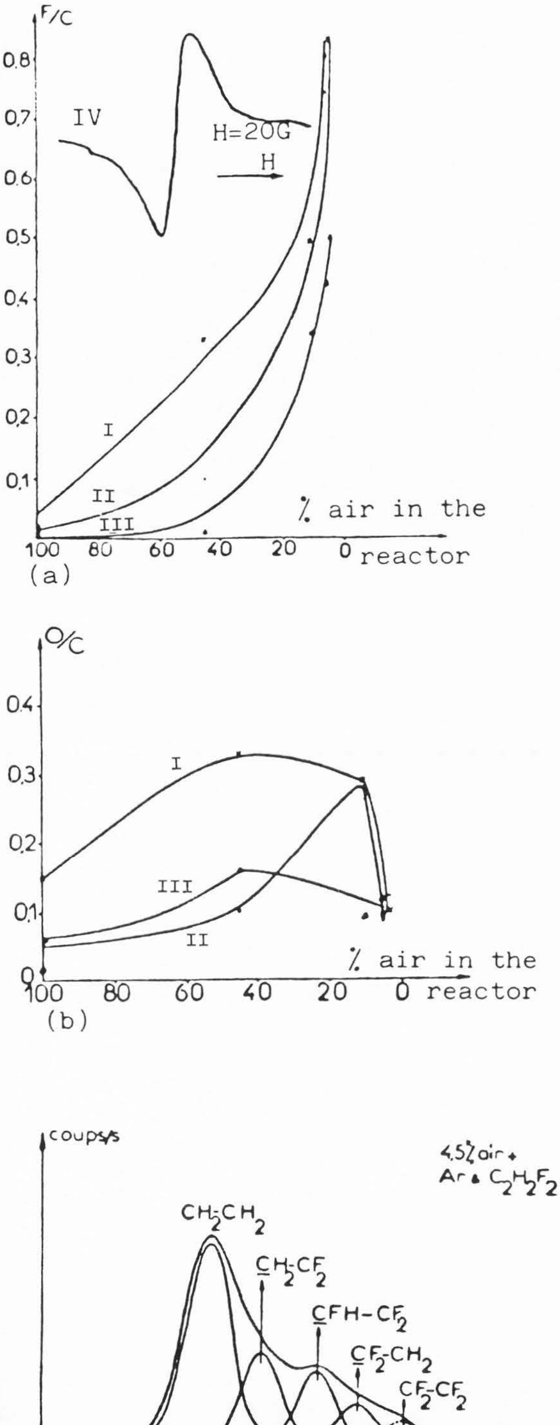


Fig. 20. -ESCA studies of the structure of polymeric film formed in function of the residual air in the reactor; I-after treatment, II-washed 1h in water, III-washed 1h in water and 1h in acetone, IV-ESR spectrum obtained on the PP treated in $Ar+C_2H_2F_2$ containing < 4.5/air (t=2 s; d= 1mm; $Ar+C_2H_2F_2$ flow rate = 150 cm^3/mn).

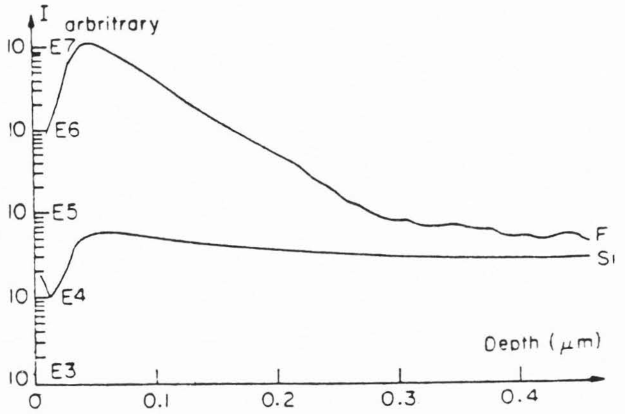


Fig. 21. -SIMS depth profiles of silicon and fluorine. Discharge conditions: T= 200°C, V = 8 kV, d=0.5 mm , CF_4 flow rate = 0.45 l/h.

Conclusion of our study by means of ESCA, ESR and Complex equilibria.

The results obtained in our study by means of ESCA, ESR, complex thermodynamic equilibria, are coherent and show the important role played by the free radicals on the polymerization process.

The concentration and the nature of the free radicals depend directly on the interaction of the parasite radicals such as O_2 ($^3p_2$) with the free radicals formed in the plasma. This reaction destroys the reactive species present in the gas phase by forming gas products which are not polymerizable (byproducts) as well as by destroying the carbon free radicals formed on the substrate (Fisher and Hellwage, 1962).

The ions and the electrons contribute as a whole to the development of the materials which are characterized by the space charges resulting from the discharge. Their stability in the time depends on the conductibility of the material and/or the inclusion of metallic atoms.

Role of NH radicals in nitriding process.

The comparative study of transition metals nitriding by various inductive (40 MHz, 1 kW), low pressure (5 mbars) plasmas : N_2, N_2 - H_2, NH_3 points out the role of NH radicals (Gicquel et al. 1983).

The presence of a lone pair in the external π_x bonding orbital of the first electronic excited state confers to the NH radical its basic properties. The proton affinities of the N_2, N_2H^+, NH_3, NH_2 and NH species, in their ground state, are given in table 1 ; the NH radical has therefore the highest basicity.

After 1.5 h of N_2, $N_2 + H_2$ or NH_3 plasmas action, the transition metal target reveals the formation, on its surface, of a

Table 1 : Proton affinities

Molecule	P A(kJ/mole)
N_2	522.5
N_2H^+	522.5
NH_3	911.2
NH_2	1672
NH	>1672

nitride layer (Gicquel et al. 1985a; Gicquel et al. 1985b). The ESCA and microhardness analysis of the metals make possible the determination of the nature and the thickness of the nitrided layer.

During the nitriding process, spectroscopic analysis of the plasma (Ricard, 1983) gives the emission intensity of the NH radical ($A^3\pi$ ---> $X^3\Sigma^-$) along the reactor and in the boundary layer at the plasma/target interface (D'Agostino et al. 1981).

Moreover, the vibrational temperature of N_2 ($C^3\pi_u$) gives a measurement of the excitation level of the reactive species (Amouroux et al. 1983 b; Polanyi and Wong 1969). Taking as an example the tungsten nitriding ; we observe the formation of a nitride WN after an ammonia plasma treatment while the formation of W_2N is produced after a N_2 - H_2 or a N_2 plasma treatment (Table 2).

Table 2. ESCA Analysis Results.

		Treated tungsten samples P = 5 mbar , Pl = 1 kW, D = 0.3 l/mn, time = 1 h 30			
		Gas NH_3	N_2-H_2 80%-20%	N_2-H_2 50%-50%	N_2
Binding energies (eV)	W_4 d5/2	244,3 247,3	247,8	247,3	246,7
	N_{1s}	396,7	396,2	396,5	396,6
	% W	-	-	-	10 %
	% WN	80 %	-	-	-
	% W_2N	20 %	100 %	100 %	90 %

		Standard samples		
		W	WN	W_2N
Binding energies (eV)	W_4 $d^{5/2}$	242,6	244,5	247,5
	N_{1s}	-	397	397
	% W	100 %	-	-
	% WN	-	100 %	-
	% W_2N	-	-	100 %

The thickness of the nitrided layer depends on the nature of the reactive gas, it varies as a function of the NH radicals density in the reactor [Fig. 22] : it is maximum for a NH_3 treatment and minimum for a N_2 treatment. We can notice that in the N_2 - H_2 plasmas, the thickness of the layer increases as the percentage of H_2 decreases [Fig. 23], simultaneously the NH emission intensity and the N_2 vibrational temperature rise [Fig. 24].

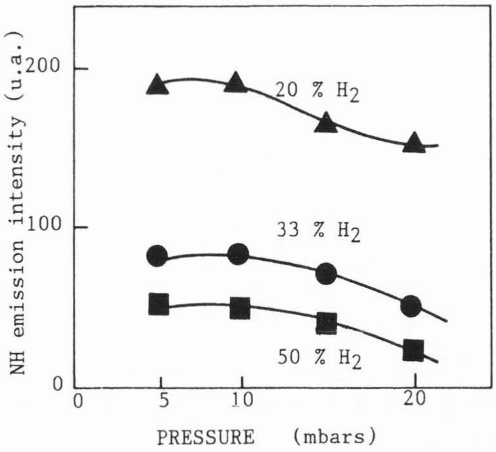


Fig. 22. -NH emission intensity as a function of H_2 content in a N_2-H_2 plasma (input power: 1kW; pressure: 5 mbar ; flow rate:0.3 l/mn)

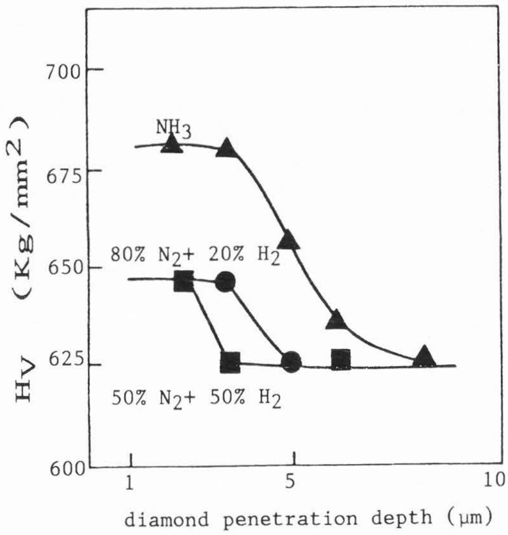


Fig. 23. -Vickers microhardness versus diamond penetration depth for different plasmas (NH_3; 80% N_2, 20% H_2; 50%, N_2, 50% H_2)(input power:1 kW; pressure: 5 mbar ; flow rate: 0.3 l/mn).

These results lead to the conclusion that a low hydrogen flow rate in the N_2 - H_2 mixtures controls the formation of the NH radicals. The nature of the nitride and the thickness of the layer depend on the flow of NH radical produced.

The second example deals with the nitriding of titanium by a NH_3 plasma under pressures varying from 2 to 40 mbars. The microhardness measurements indicate that the thickness of the nitrided layer increases as pressure decreases or as input power increases . NH_3 decomposition rate (G.C. analysis) increases from 20 % to 80 % as pressure decreases from 13 to 1 mbars [Fig. 25]; correlatively, the profiles of NH emission intensity measured

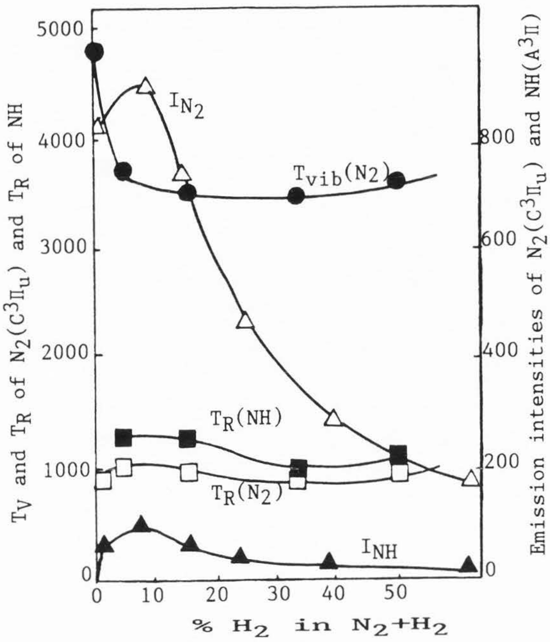


Fig. 24. -Vibrational temperature of N_2 ($C^3\pi_u$): $T_v(N_2)$; rotational temperatures of N_2 ($C^3\pi_u$) and of NH ($A^3\pi$) : I_{N2} and I_{NH}, variations as a function of H_2 content in the N_2-H_2 plasma in presence of tungsten. (input power: 1kW; pressure: 5 mbars; flow rate: 0.6 l/mn).

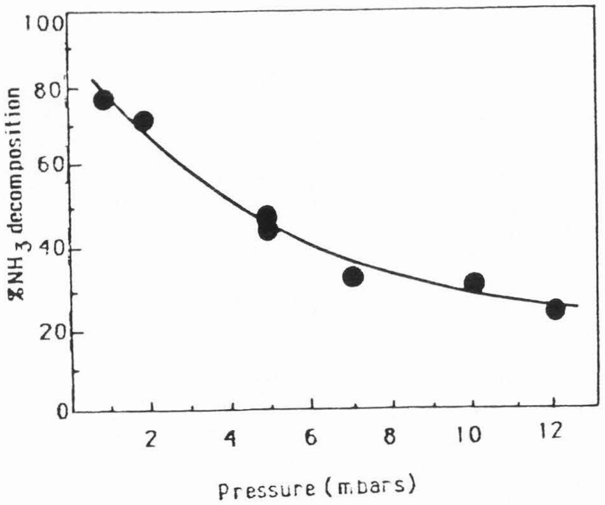


Fig. 25. -Variation of NH_3 decomposition rate, in the presence of titanium, as a function of pressure at constant residence time (20 ms) and constant input power (1.1 KW) (Ti-coil distance = 15.3 cm).

spectroscopically follow the same evolution with pressure [Fig. 26].

Finally, the vibrational temperature varies from 3000 K at 20 mbars to 3700 K at 2 mbars [Fig. 27]. The ESCA analysis reveals that the treated titanium target presents two Ti $2p_{3/2}$ photo electron peaks at 455 eV (TiN) and at 458 eV (Ti,O,N). The ratio of the relevant intensities increases with the thickness of the nitride layer (measured by microhardness) that means as the pressure decreases [Figs. 28, 29] (Table 3).

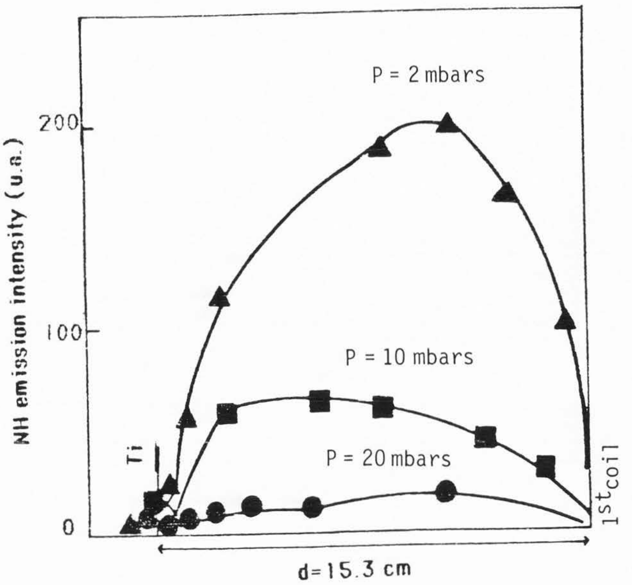


Fig. 26. -NH emission intensity along the reactor for different pressures. (input power: 1 kW; flow rate : 0.3 l/mn).

Therefore, there is a correlation between the evolution of the gaseous phase (reaction rate, NH emission intensity) and the evolution of the titanium surface (nature and thickness of the nitride).

As a conclusion, the nitriding process of transition metals, with an acid character due to the d orbitals, is determined by proton affinity of the species in the plasma phase, by the NH flow and by the vibrational excitation of the reactive species in the boundary layer (Purvis et al. 1979).

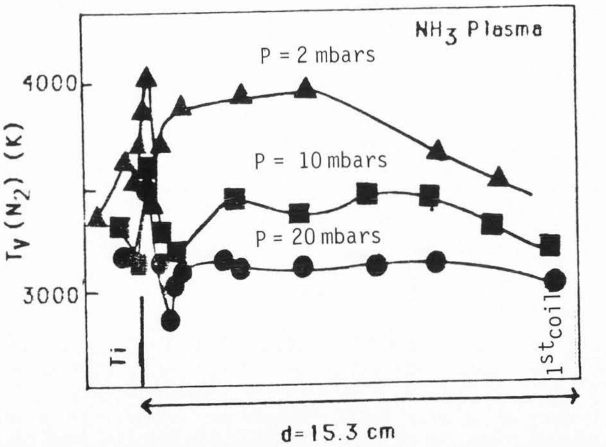


Fig. 27. -Vibrational temperature variation along the reactor and in the boundary layer for various pressures. (input power: 1kW; flow rate: 0·3 l/mn).

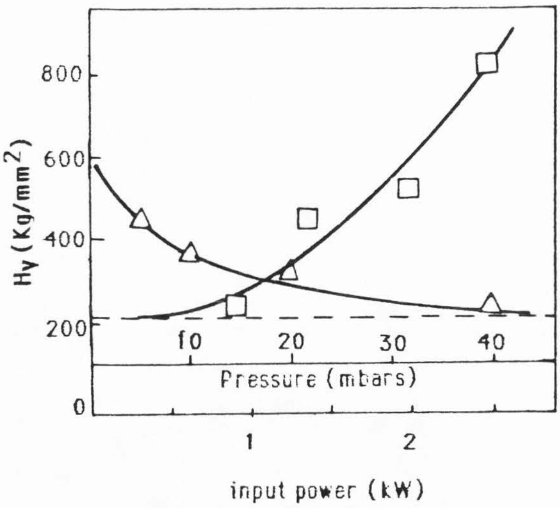


Fig. 28 -Treated titanium superficial Vickers microhardness for 25 g load as a function of pressure and input power.(flow rate: 0.3 l/mn).

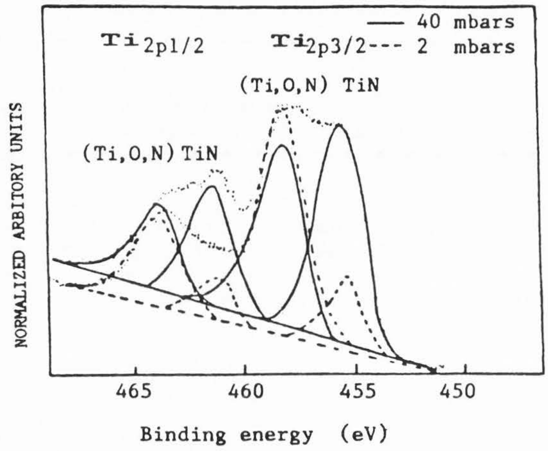


Fig. 29. -Deconvolution of the Ti_{2P} spectrum for P = 40 mbar and P = 2 mbar NH_3 treatments.(input power: 1kW; flow rate: 0.3 l/mn).

Conclusions

In this work we attempted to focus the attention on the acid-base phenomena in the plasma phase and we selected three typical examples in addition to demonstrative experiments: etching of microelectronic components, polymerization and nitriding processes. The basic concepts are derived from those developed in the gas phase. We have also to consider the influence of the charged species (ions and electrons), that of the electric field close to the electrodes which acts on the polarization of the species, and the presence of radicals and molecules in various excited states (especially the singlet or triplet states). All these species may undergo reactions and explain in part the observed kinetic mechanisms.

Table 3. Microhardness Measurements

Experimental conditions	Input power: 1040 W-Time: 1h30 Flow rate: 0.35 l/min. - d = 15.3 cm			
Pressure (mbars)	5	10	40	
Thickness (μm)	7	6	3.5	
Conditions	Pressure: 5 mbars- Time: 1h30 Flow rate: 0.35 l/min.- d = 15.3 cm			
Input Power (W)	750	1040	1600	2000
Thickness (μm)	4	7	13	16
Conditions	Input power: 1040 W-Time: 1h30 Pressure: 5 mbars - Flow rate : 0.35 l/min.			
Distance (cm)	17	15.3	7.5	
Thickness (μm)	3	7	13	

Data on the proton affinities of the species in the plasma phase might lead to definition of an overall characteristic of the reactive system. However it appears to be more realistic to consider a "shadow" of the acid-base properties of the plasma phase obtained from a flow procedure similar to that which has been initiated in our laboratory. It is likely that this method might be adapted to low-pressure plasmas, provided the relevant measurements be realized on solids; at this juncture etching may be considered as an example for the application of this method.

In conclusion, we wish to underline that the acid-base properties of a plasma phase seem to be one of the chemical parameters that we have to control to foresee and quantify the evolution of a plasma system with the type of the considered reaction, the excitation process and the gas composition. It is therefore a point of major interest in the development of the plasma applications.

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References

Amouroux J, Gicquel A, Cavvadias S, Morvan D, Arefi F (1985a). Progress in the Applications of Plasma Surface Modification and Correlation with the Chemical Properties of the Plasma Phase. Pure Appl. Chem., 57, 1207-1222.

Amouroux J , Gicquel A, Arefi F, Cavvadias S, Brisset JL (1985b). Surface Treatment and Plasma Polymerization. In: Advanced Course on low pressure plasma: technology and applications . P. Masse & W.H. Merck (Eds.). Eindhoven. Vol. 1, 8/1 - 8/23.

Amouroux J , Goldman M, Arefi F, Rouzbehi F (1983a). Procédé de Dispositif de Réalisation d'un Revêtement Polymérisé sur un Substrat. FR. P. (1983) n°83125, US. P. (1984) n° 634741, JP. P. n° 1585, E.P. n° 844015925.

Amouroux J, Bergougnan MP, Gicquel A, Arefi F (1983b). Les mécanismes chimiques de l'interaction plasma hors équilibre-surface. Ann. Chimie Fr. 8 , 319-333.

Arpino PJ (1982). L'ionisation chimique: une façon de modéliser les réactions de chimie organique dans un spectromètre de masse. L'actualité chimique,19-28.

Arrhenius S (1887). Uber die Dissoziation der in Wasser gelosten Stoffe. Z. physik. Chem. 1, 631.

Arshadi M , Kebarle P (1970). Hydration of OH^- and O_2^- in the Gas Phase. Comparative Solvation of OH^- by Water and the Hydrogen Halides. Effects of Acidity. J. Phys. Chem. 74, 1483-1485.

Aue DH, Bowers MT (1979). Stabilities of positive ions from equilibrium gas phase measurements. In : Gas Phase Ion Chemistry, M.T. Bowers (Ed.)Vol.2, Academic, London, 2-51.

Bartmess J, McIver RT (1979). The gas phase acidity scale . In: Gas Phase Ion Chemistry, M.T. Bowers (Ed.) Vol.2, Academic, London, 88-121.

Beauchamp JL (1971) . Ion Cyclotron Resonance Spectroscopy . Ann. Rev. Phys. Chem., 22, 527-561.

Berthelot M, Gal JF (février 1984). La résonance cyclotronique des ions et son application à l'étude des transferts de protons en phase gazeuse. L'actualité chimique, 19-23.

Boisiau C, Lécayon G (1986). An organic Reference Specimen: Polyacrylonitrile Film Deposited on Oxidizable Metals by Electro-polymerization. Scanning Electron Microsc. 1986; I: 109-116.

Brisset JL, Amouroux J (1985) . Evidence of the Acid-Base Properties of a H.P. Water Plasma. Proc. 7 th Int. Sympos. Plasma Chem. , C.J. Timmermans (Ed.), Eindhoven, 497 - 501.

D'Agostino R, Cramarossa F, De Benedictis S, Ferraro G (1981).Kinetic and Spectroscopic Analysis of NH_3 decomposition under RF plasma at moderate pressures. Phase Chem. and Plasma Proc. 1, 19-35.

Davidson WR, Kebarle P (1976). Ionic Solvation by Aprotic Solvents. Gas Phase Solvation of the Alkali Ions by Acetonitrile. J. Amer. Chem. Soc.,98, 6125-6132.

von Engel A (1955a). Ionized Gases . Clarendon, Oxford. p. 242.

von Engel A (1955b). Ionized Gases . Clarendon, Oxford. p. 292.

Fisher H, Hellwage KH (1962). Elektronenspinresonanz -Untersuchungen an Bestrahltem Polypropylen. J. of Poly. Sci. , 56. 33-45.

Flamm DL (1981). Mechanisms of Radical Production in CF_3Cl, CF_3Br, and Related Plasma Etching Gases: The Role of Added Oxidants. Plasma Chem. Plasma Proc. 1, 37- 52.

Flamm DL, Donnelly VM (1981). The Design of Plasma Etchants. Plasma Chem. Plasma Proc. 1, 317-363.

Flamm DL (1985) . Plasma Chemistry Physics . In : Advanced Course on Low Pressure Plasma: Technology and Applications. P. Masse, W.H. Merck (Eds.).Vol. 1. Eindhoven 3/1-3/30.

Gicquel A, Bergougnan MP, Amouroux J, Rapakoulias D (1983). Heterogeneous catalytic reactions in a non equilibrium plasma. Analysis of the plasma - solid boundary layer. Proc. 6 th Int. Sympos. Plasma Chem. , M. Boulos (Ed.) B, 351-356.

Gicquel A, Laidani N, Morin M, Amouroux J (1985a). Nitriding of Titanium by an NH_3 low pressure Plasma. Spectroscopic Analysis and characterization of the solid surface. Proc. 7th Int. Sympos. Plasma Chem., C.J. Timmermans (Ed.) 2, 418-423.

Gicquel A, Laidani N, Morin M, Amouroux J (1985b). Titanium nitriding by an inductive NH_3 low pressure plasma. Actes du 5ème Coll. Int. Pulvérisation Cathodique; Le Vide, Les Couches Minces, 226 supp., 107-112.

Hancock RD, Nakani BS, Marsicano F (1983) . Relationship between Lewis Acid-Base Behavior in the Gas Phase and in Aqueous Solution. 1. Role of Inductive, Polarizability, and Steric Effects in Amine Ligands . Inorg. Chem., 22, 2531-2535.

Hartman KN, Lias S, Ausloos P, Rosenstock AM, Schroger SS, Schmidt C, Martensen D, Milne GA. (1979). Compendium of gas phase basicity and proton affinity measurements, U.S. N.B.S, Washington, D.C.

Herb GK (1985). Applications of Plasma Etching and Deposition to microelectronic device. In: Advanced Course on Low Pressure Plasmas: Technology and Applications. P. Masse, WH. Merck (Eds.). Eindhoven . Vol. 1, Chap. 7.

Lécayon G, Bouizem Y, Legressus C, Raynaud C, Boiziau C, Juret C (1982). Grafting and growing mechanisms of polymerized organic films onto metallic surfaces. Chem.Phys. Lett., 91, 506-510.

McIver RT (1981). Les réactions chimiques en l'absence de solvatation. Pour la Science,39,103.

McMahon TB, Kebarle P (1977). Intrinsic acidities of substituted Phenols and Benzoic acids determined by Gas Phase Proton Transfer Equilibria. J. Amer. Chem. Soc. 99, 2222-2230.

Moylan CR , Brauman JI (1983) .Gas phase acid-base chemistry. Ann. Rev. Phys. Chem.,34,187.

Ouelette RP, Barbier MM, Chereminisoff PN (1980). In: Electrotechnology Vol. 5. Low-Temperature Plasma Technology Applications. Ann Arbor Science, Ann Arbor, MI, USA, 67-80.

Payzant JD, Yamdagni R, Kebarle P (1971). Hydration of CN^-, NO_2^-, NO_3^- and OH^- in the Gas Phase - Can. J. Chem. ,48, 3308-3313.

Polanyi JC, Wong WH (1969). Location of Energy barrier. II. Correlation with Barrier height. J. Chem. Phys. 51, (4), 1451-1469.

Purvis III GD, Redmon MS , Wolken G (1979). Vibrational Excitation from Heterogeneous Catalysis. J. Phys. Chem. 83, 1027-1033.

Ricard A (1983). Spectroscopie des plasmas pour le traitement de surface. Ann. Chimie Fr. 8 , 303-312.

Rouzbehi F (1985). Polymérisation sous Plasma Froid (Type Décharge Couronne); Applications aux Traitements de Surface des Matériaux Textiles et des Films Polymériques. Thèse de Docteur - Ingénieur, Paris .

Rouzbehi F, Amouroux J, Goldman M. (1986). Fluorination of Polymeric Films by a Nonequilibrium Plasma at an Atmospheric Pressure. Materials Research Society Meeting (MRS), Palo Alto, CA, USA , April 15-19. Symp. Proc. Electronic Packing Material Science II , Vol 72, pp. 235-240.

Snowdon KJ, Heiland W (1985). Basic Mechanisms of Energetic Molecule Ejection from Surface. Pure Appl. Chem.,57,1245-1252.

Usanovich MI (1939). J. Gen. Chem. USSR, 9, 182.

Yamdagni R, McMahon TB, Kebarle P (1974). Substituent Effects on the Intrinsic Acidities of Benzoic Acids Determined by Gas Phase Proton Transfer Equilibria Measurements . J. Amer. Chem. Soc. 96,4035-4037.

Yamdagni R, Kebarle P (1971) . Hydrogen-Bonding Energies to Negative Ions from Gas-Phase Measurements of Ionic Equilibria. J. Amer. Chem. Soc.,93,7139-7143.

Yasuda H, Hsu TS (1977). Some Aspects of Plasma Polymerization of Fluorine-Containing Organic Compounds. J. of Poly. Sci. Polymer. Phys. Ed. 15, 2411-2425.

Discussion with Reviewer

C.Boiziau : How do you explain that the etching speed is enhanced by ion bombardment or laser irradiation? What is the main parameter: the energy of the incident particle (ion or photon) or the beam intensity ?

Authors : Reactions occurring at a solid surface (e.g. etching) usually involve 5 steps-i) the diffusion of the reacting species in the gas boundary layer, ii) the adsorption of the resulting species at the surface, on activated sites, iii) the chemical reaction between the adsorbed species and the substrate molecules, iv) the desorption of the reaction products from the surface, and v) the diffusion of the products through the boundary layer. Ions and photons act on the chemical reaction steps (i. e. steps ii) to iv)):

- the beam intensity is the major parameter for increasing the number of excited sites, and hence affects step ii.
- by contrast, ions and /or photons bring the species to an activated energy level and allow the reaction to take place (step iii). They also bring the products to an activated desorption process (step iv). Both steps depend on the energy carried by the particle .
- it is widely accepted that desorption occurs as a limiting step for surface reactions, and hence the overall kinetic mechanism is controlled by the desorption step. Therefore the main parameter is the energy of the incident particle (ion or photon).

C. Boiziau : It was demonstrated that the electrode polarization plays an important role in the electropolymerization processes (Boiziau and Lécayon 1986). For example the anodic polarization leads the metal surface to behave as a strong Lewis acid, which permits a large probability for acid-base reactions between metal and polarized molecules. You observe the same phenomena in the plasma etching and in the plasma polymerization processes, but you don't point out an eventual effect of anodic polarization in the nitriding process of transition metals- Why ?

Authors : An etching reaction may be performed by gaseous ions of both signs which react with the substrate and act then as acids or bases. The plasma gases selected for polymerization and for etching processes are usually aliphatic halogen compounds (e.g., CF_4, NF_3, CH_2F_2, CCl_2F_2,...) which are used as single gases or as gaseous mixtures. Due to their electrophilic character these chemicals give rise more easily to anionic (e.g., CF_3^-, F^-, ...) than to cationic species: that means that the prominent etching reaction involves the base (the anions in the gas phase) and the substrate acting as a Lewis acid. In addition, an anodic polarization also favors the formation of anionic species which enhance the effect and is thus of classical use in etching and polymerization processes.

Nitriding processes may occur according to two different ways.

On one hand the reaction path is characterized by a dissociative adsorption mechanism and concerns the neutral species: N_2^*, NH, NH_2, NH_3 react at the target according to classical mechanisms (adsorption/reaction /diffusion). The substrate polarization favors the grafting of polar species (i.e. NH, NH_2, NH_3). Then, the reaction can be considered as an example of acid-base reaction between species in the gas phase and the substrate.

On the other hand, ionic species are concerned and lead to cathodic bombardment or sputtering processes according to the kinetic energy of the acting ions.

The low energy (10-20 eV) reacting species such as N_2^+, NH^+, NH_2^+ are implanted in the negatively charged metal according to a cathodic bombardment process.

The high energy ions which are usually cations of 50-100 eV are accelerated through the cathodic sheath . The sputtering of the target then gives rise to metal clusters in the gas phase. The reaction between the nitrogen plasma and the clusters generates new nitride species which are usually redeposited on the target or on another polarized substrate .

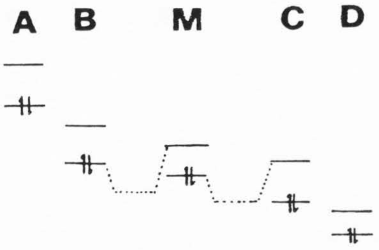
V. Young : It has been indicated that ${}^1\Delta_g$ state of O_2 behaves as a Lewis acid, and yet it is evident from Fig 12 that both ends of oxygen become involved in bond formation. It seems to me that $O_2({}^1\Delta_g)$ should be regarded as an amproteric substance, because it has both an empty quantic box and a quantic box containing a lone pair which probably don't differ much in energy. Why is O_2 $({}^1\Delta_g)$ considered to be a Lewis acid ?

Authors : This question is right in the axis of our approach, and in addition gives evidence of our limited knowledge of the chemical properties of species in an excited state.

A number of compounds called "ampholytes" show both acid and basic behaviours with respect to the Bronsted criteria. Examples in water are HCO_3^- (the acid associated to CO_3^{2-} and the base conjugated to H_2CO_3), the zwitterion forms of amino acids or even some oxides. This character may be of large occurrence in spite of the difficulty to find the conjugated form in the proper solvent. For example the protonation of amines (or anilines) is easy in "classical" solvents but the deprotonation which generates the amide ion RNH^- requires the use of highly basic media.

A similar approach could be formally applied to Lewis acid-base criteria although it would be rather unusual. We have to remember that oxidation and reduction can be considered as degenerated situations with respect to Lewis donor-acceptor criteria. In the following distribution of LUMOs and HOMOs of compounds A, B, C, D compared to M, A is oxidized, M reduced ; B acts as the base and M as the acid; C is the acid and M the base; D is reduced and M oxidized. The question then is to select illustrations of these situations where M is the dioxygen, to complete the following examples relevant to O atoms. In numerous molecules the O atoms are donor centers, but in a limited number of situations O can be considered as a Lewis acid. Textbook examples are related to oxide formation:

$$R_3N/X_3P\ /R_2S\ /R_2SO\ \underline{\text{O atom transfer}}_{>}R_3NO/X_3PO\ /R_2SO/\ R_2SO_2.$$



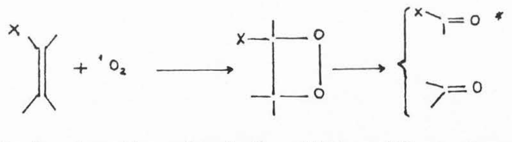
O_2 is easily reduced into the oxide ion O_2^- which is of wide occurrence, so that the A/M system is illustrated by paramount examples. The oxidation of dioxygen occurs in the formation of O_2F_2 from O_2 and F_2 in a glow discharge (D/M system). Examples of C/M systems are provided by oxygen adsorption onto metals which act as Lewis acids.

Before we review the most typical reactions involving dioxygen as a ligand we have to come back briefly to the mechanism itself. We will limit it to the electrophilic reactions and keep in mind that this label refers to reactions provoked by electron poor species (e.g. H^+, Lewis acids with their empty quantic box) which first attack at electron rich molecules (e.g., olefins, Lewis bases). The mechanism follows then two ways which result in an addition or a substitution.

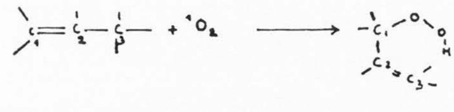
Dioxygen gives adducts with molecules called "oxygen carriers" which are usually transition metal complexes. The fixation of O_2 takes place at the metal center. Recent studies suggest an angular superoxo structure M-O-O and arguments are given in favour of "oxidative addition" for several compounds. Examples are also reported of peroxo structures characterized by bondings between the metal center and both ends of the dioxygen molecule. A matching example is the famous Vasca's complex, Ir^{I} Cl (CO) $(Ph_3P)_2$ which has been thoroughly studied; its structure has been examined in terms of occurrence of small molecules in an activated state. This point of view has been discussed by Vasca himself but it is backed up by some classical mechanisms which characterize $O_2(^1\Delta_g)$ occurrence.

The most important chemical reactions which are specific to singlet oxygen concern alcenes, dienes or aromatic compounds, and also some heterocycles. In addition particular reactions take place with amines, phenols or sulfides. Most of the relevant examples illustrate the electrophilic character of $O_2(^1\Delta_g)$; the details of the mechanisms are however still under consideration:

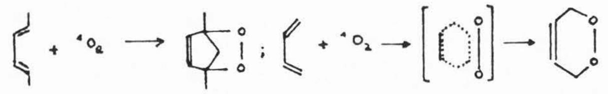
i) The cycloaddition of singlet oxygen at an activated double bond leads to the formation of 1,2 dioxethanes. These compounds of generally poor stability give rise to a couple of carbonyls (one of them is in an excited state):



ii) The "ene" reaction refers to the addition of O_2 on alcenes with a labile hydrogen in the 3 position. It leads to the following hydroperoxides



iii) The 1,4 cycloaddition (Diels-Adler type) gives endoperoxides



These reactions may be compared to those previously quoted of the oxygen carriers or those of singlet oxygen quenchers which are usually polyethylenic molecules.

iv) We also mentioned various reactions of $O_2(^1\Delta_g)$, for example with amines, phenols and sulfides, but except for the last case the relevant mechanisms are different and do not involve the electrophilic character of singlet oxygen. Even for the reaction with sulfides

$$R_2S + {}^1O_2 \rightarrow [RSO_2] - R_2S \rightarrow 2R_2SO$$

the mechanism and the structure of the intermediate are still under discussion.

V. Young : Notice that Eq. 7 is identical in every way to Eq.6 except that the acid is charged instead of neutral. Then it seems that $\Delta G°_7$ should be equal to the gas acidity of BH^+, GA(BH^+), and that - $\Delta G°_7$ should be equal to GB(B). If it is not so, why not?

Authors: A few decades ago, a classical use in solution chemistry was to consider the acidity and basicity constants which appeared as direct consequences of Arrhenius's (1887) or Usanovich's (1939) definitions for acidity and basicity.

When an acid or a base is dissolved in water, an hydrolysis reaction takes place:

$$\text{Acid} + H_2O = \text{Base} + H_3O^+ \qquad (1)$$

$$\text{Base} + H_2O = \text{Acid} + OH^- \qquad (2)$$

Both equilibria (1) and (2) are equivalent to each other since we have:

$$2H_2O = H_3O^+ + OH^- \qquad K_w$$

The strength of the acid/base system is defined by any constant K_a or K_b:

$$K_a = (\text{Base})*(H_3O^+)/(\text{Acid}); \qquad K_b = (\text{Acid})*(OH^-)/(\text{Base})$$

with $K_a * K_b = K_w$. Let us consider the example of an aqueous solution of ammonia:

$$NH_3 + H_2O$$
$$NH_4OH = NH_4^+ + OH^-; \quad K_b = (NH_4^+)(OH^-)/(NH_4OH)$$
$$NH_4^+ + H_2O = NH_3 + H_3O^+; \quad K_a = (NH_3)(H_3O^+)/(NH_4^+)$$

We verify that $K_a{*}K_b = K_w$. In order to simplify, only one constant is now used, and we keep the acidity constant K_a.

When people became interested in gas acidity or gas basicity, the same historic way was likely followed and it was found clearer to keep the symmetry between H^+ and OH^-. In fact only one parameter is needed provided the acid/ base system considered be unambiguously defined. The proton affinity PA appears now to be the most popular parameter to characterize an acid/base system. The strongly basic species are associated to high PA values; since GB varies in the same way as PA, the strong bases are related to high GB values. For example, the 1-Me-2,6-t-butylpiperidine (PA= 1001 kJ/mol; GB = 968 kJ/mol) is among the strongest bases known in the gas phase.

The protonated form associated to a strong base is a very weak acid, as easily guessed from classical considerations. We demonstrate in the paper that the strength of an acid can be estimated by means of the GA parameter: the high GA values are relevant to very weak acids and the low GA values to the rather strong acids.

A given acid/base system involving the acid and the conjugated base can be characterized by a unique parameter, the GA of the acid or the GB of the base (or as well the PA of the base). These parameters are equivalent since the use of GA(acid) or GB(base) is unambiguous. Besides, they take the same numerical value, and we have for the example of the ammonia system

$$\mathrm{GA}(\mathrm{NH_4}^+) = \mathrm{GB}(\mathrm{NH_3}).$$

The piperidine derivative previously mentioned is a stronger base than ammonia, and its associated acid is a weaker acid than $\mathrm{NH_4}^+$. Then we have:

$$\mathrm{GB(Pi)} > \mathrm{GB}(\mathrm{NH_3}) \qquad \mathrm{PA(Pi)} > \mathrm{PA}(\mathrm{NH_3})$$

$$\mathrm{GA}(\mathrm{PiH}^+) > \mathrm{GA}(\mathrm{NH_4}^+)$$

with also $\mathrm{GA}(\mathrm{PiH}^+) = \mathrm{GB(Pi)}$.

In other words, the lower GA values correspond to the stronger acids while the higher GB values are related to the stronger bases. The direction of the GA variations with the strength of the acids is rather disturbing to our mental schemes; one may find here the reason why GB, or PA, is presently preferred to GA as the characteristic parameter of a given acid/base system.