Control and diagnostics of reactive plasma by photochemical and photoionization techniques

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ABSTRACT

Photo-irradiation of molecules generates excited species
with quantum-state and species specificities. By using photo-
chemical techniques involving photodissociation, photoionization,
and internal excitation, plasma may become controllable since
species, spatial, and temporal changes can be externally con-
trolled.

Reactive plasma is a conducting gas, that is, a gas which
contains a small portion of charged particles (electrons and
ions). The other proportion involves reactive species (atoms and
molecules) excited electronically, vibrationally, and rotational-
ly. Thus, reactive plasma is so complicated that it has been
considered uncontrollable because inelastic collisions between
atoms (molecules) and electrons generate excited species without
quantum-state and species specificities. The uncontrollability
is caused not only by the wide distribution in energies but also
by the development of sheath region near the electrode surfaces.

Plasma may become controllable if (a) species, spatial, and
temporal changes are externally controlled, (b) new techniques
are applied to generation of plasma, and (c) plasma parameters
are obtained both for homogeneous reactions in the gas phase and
for inhomogeneous ones in the sheath region.

Optical excitation generates excited species with optical
selection rules. Firstly, the energy difference between two
states must equal a photon energy. Secondly, there must be an
interaction of the electric vector associated with the radiation
and the electron of the species undergoing the transition. The
probability of transition is summarized by selection rules for
atomic system, $\Delta L = \pm 1$, $\Delta J = 0$, ± 1, and $\Delta S = 0$. The transition
moment integral depends on the symmetry of the orbitals of the
initial and final states as well as the spin factor. As an
example, Table I shows the behavior of the transition probability
between pairs of electronic states of homonuclear diatomic mole-
cules.[1] The transition probability for electronic dipole
transitions induced by photons is non-vanishing only where a P
appears: that for collisions with electrons is non-vanishing
where either a P or an E appears. Obviously, photo-excitation is
selective while electron-collision is not so selective.
Especially the laser provides the ability to prepare a specific
state of an atom or a molecule according to a precise prescrip-
tion. Laser excitation can align an ensemble of absorbing atoms
or molecules. Polarized laser light will excite molecules whose
transition dipole moments lie parallel to the axis of plane
polarization. Thus optical pumping creates an anisotropic
distribution of molecular orientations. An example is the reac-
tion between photoselected I_2 and an atomic beam of In.[2] The
formation of InI^* was enhanced by preferential population of I_2^*
molecules aligned with respect to the In atomic beam.

Acceleration of bimolecular reactions have been reported by
internal excitation of reactants. The transient energy content
resides in different degrees of freedom:translational, rota-
tional, and vibrational. Tanaka et al.[3] have reported state-
selected ion-molecule reactions in:

$$H_2^+ (v) + Ar \longrightarrow ArH^+ + H, \qquad [I]$$
$$\longrightarrow Ar^+ + H_2. \qquad [II]$$
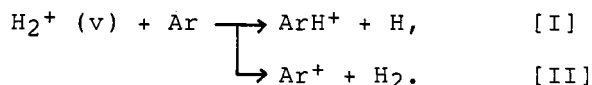
Product ions were taken at five excitation wavelengths corre-
sponding to the $v = 0-4$ thresholds of H_2^+. A typical example
obtained is shown in Fig. 1 at the collision energy of 1.2 eV.
The reaction [II] is enhanced by the vibrational energy deposited
in H_2^+.

Internal excitation of molecules can also accerelate
heterogeneous reactions. An example is the CO_2 laser assisted
CVD of silane.[4] The observed dependence of deposition rate on
laser wavelengths indicates that vibrational excitation of SiH_4
increases inhomogeneously the ambient temperature in the gas
phase. Direct heating of the substrate causes homogeneous
increase of the gas temperature. Thus photochemical excitation
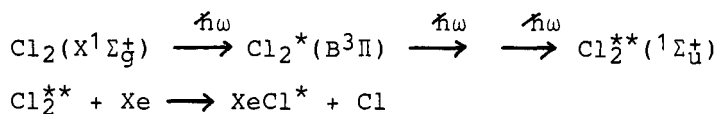is the spatial and quantum-state selective.

Molecule specific reactions are possible by multiphoton
absorption. The $O(^1D)$ atoms are formed by a sequential three-
photon absorption of NO_2[5]

$$NO_2 \xrightarrow{\hbar\omega} NO_2(^2B_2) \xrightarrow{\hbar\omega} \xrightarrow{\hbar\omega} NO + O(^1D)$$
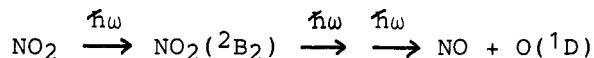
The vibrationally and rotationally excited O_2 molecules are
generated through a chemical reaction following the multiphoton
absorption of NO_2:

$$O + NO_2 \rightarrow NO + O_2 \ (v'' \leq 24, \ T_r = 1000 \ K)$$
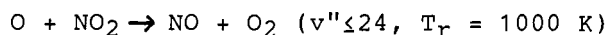
Especially by multiphoton absorption, highly excited states
are selectively generated. The rare gas-halogen complex is
generated in the electrical discharge of mixture of these gases.
Photochemically, XeCl emission appears following multiphoton
excitation of Cl_2 in presence of the Xe gas.[6]

$$Cl_2(X^1\Sigma_g^+) \xrightarrow{\hbar\omega} Cl_2^*(B^3\Pi) \xrightarrow{\hbar\omega} \xrightarrow{\hbar\omega} Cl_2^{**}(^1\Sigma_u^+)$$

$$Cl_2^{**} + Xe \longrightarrow XeCl^* + Cl$$

The rate constant is also obtained for the collisional formation
of the complex.

As an example of bond specific reactions, photodissociation
of alkyl benzenes have been studied by the 193 nm laser photo-
lysis.[7] The major process is the formation of hot alkyl
benzenes, followed by decomposition yielding benzyl radicals:

$$\phi CH_2R + \hbar\omega \longrightarrow \phi CH_2R^* \longrightarrow \phi CH_2 + R.$$
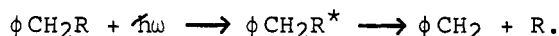
The UV laser irradiation of phenylsilane yields $C_6H_5 + SiH_2 + H$.
The photodissociation processes are much simpler than the plasma
processes since plasma decomposes benzene derivatives into much
smaller fragments.

Since the elementary processes occurring in a reactive
plasma are essentially those between atoms, radicals, and mole-
cules, the number density and kinetic lifetimes of the species as

Table I. Behavior of the transition probability between pairs of electronic states of homonuclear diatomic molecules. Ref. (1).

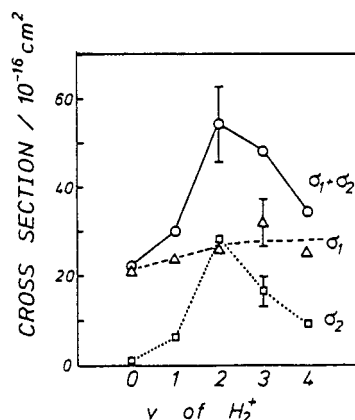|	Σ_g^+	Σ_g^-	Σ_u^+	Σ_u^-	Π_g	Π_u	Δ_g	Δ_u
Σ_g^+	E		P			P	E	
Σ_g^-		E		P		P	E	
Σ_u^+			E		P			E
Σ_u^-				E	P			E
Π_g					E	P		P
Π_u						E	P	
Δ_g							E	P
Δ_u								E

Fig. 1 State selected cross sections for reactions [I] and [II] as a function of vibrational quantum number v of H_2^+. Ref. (3).

well as the spatial distribution are externally controllable by photochemical-plasma-hydbrid techniques. Hayasaka et al.[8] have reported one of examples of the hybrid techniques, that is, during the dry etching procedure of an Si wafer by microwave discharge of Cl_2, methyl methacrylate is introduced to the reaction chamber. A KrF laser beam is incident normal to the wafer. Eventually, the etching proceeds only on the normally photo-irradiated surface, while the deposition film remains on the side-wall without photo-irradiation to protect the undercutting.

Understanding of reactive plasma behavior requires knowledge of elementary processes involving chemical reactions, transfer of internal energies and electronic excitation. Optical measurements are particularly useful for obtaining such informations on elementary processes without intrusiveness.

Among of all, laser induced fluorescence is one of most useful techniques. Using this technique, SiH radicals are detected in the rf glow discharge of SiH_4 gas during CVD of amorphous silicon.[9] The spatial distribution of SiH is not uniform and has a maximum near the rf electrode or at the middle of the ion sheath and the glow space. This distribution reflects that of the dissociation of SiH_4 by electron impact. Using the CARS method, the concentration had a minimum at the position near the rf electrode.[10] The rotational temperature of the SiH radicals is the room temperature or the translational temperature. The rf glow discharge belongs to a low temperature plasma where the electron temperature is very high while that of the molecules is low. The temperature measured by LIF is reasonable for the rf glow discharge.

REFERENCES

(1) G.H. Dunn, Phys. Rev. Lett., 8, 62 (1962).
(2) R.N. Zare, Laser induced processes in molecules (K.L. Kompa and S.D. Smith ed.) Springer-Verlag (Berlin, 1978).
(3) K. Tanaka et al., J. Chem. Phys., 75, 4941 (1981).
(4) M. Kawasaki et al., Nippon Kagakukaishi, 1484 (1984).
(5) K. Shibuya et al., J. Chem. Phys., 85, (9) (1986).
(6) T. Ishiwata et al., Chem. Phys. Lett., 112, 356 (1984).
(7) Y. Kajii et al., J. Chem. Phys., in press.
(8) N. Hayasaka et al., XIIth Internat. Conf. Photochem., (Tokyo, Aug. 4-9, 1985) 2B12.
(9) Y. Matsumi et al., J. Vac. Sci. Technol., in press.
(10) N. Hata et al., Proc. Internat. Ion Engineer. Congress - ISIAT '83 IPAT'83 (T. Takagi ed., Kyoto, 1983) p. 1457.