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GASEOUS FUNCTIONAL MATERIALS FOR ADVANCED TECHNOLOGIES BASED ON KNOWLEDGE ON ELECTRON-ATOM/MOLECULE INTERACTIONS

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Abstract. Basic research on low energy electron-atom/molecule interactions has provided fundamental knowledge which allowed an understanding of the behavior of gaseous matter in externally applied electric fields. This understanding, in turn, enabled the tailoring of gaseous materials for use in many advanced technologies. The transition from basic research to application, facilitated by this knowledge, is illustrated for the case of gas-discharge lasers, particle detectors, gaseous dielectrics for use by the electric power industry, pulsed power switching, and plasmas for use in the semiconductor industry.

1. LOW ENERGY ELECTRON-ATOM/ MOLECULE INTERACTIONS

To illustrate how basic knowledge on electron-atom/molecule interactions enables the right choice and tailoring of gaseous materials for a number of today's advanced technologies, we first elaborate on the nature and multiplicity of ways via which slow electrons interact with matter, and, for our purpose, with atoms and molecules. By low-energy (or slow) electrons we mean those with kinetic energies, ε, lower than about 100 eV [1-3]. They are generated by a multitude of mechanisms in all states of matter [1-4]. Once generated in the medium – say, in a gas made up of molecules – the low-energy electrons interact with the gas molecules in a number of ways. Some of the most significant of these interactions are those in which electrons lose energy via *elastic and inelastic collisions* with the gas molecules symbolized by the reactions

$$e(\varepsilon)+AX \rightarrow AX+e(\varepsilon) \quad \text{elasic electron scattering (1a)}$$

$$\rightarrow AX^{*}+e(\varepsilon') \quad \text{inelastic electron scattering (1b)}$$

$$\rightarrow A+X+e(\varepsilon') \quad \text{molecular dissosiation. (1c)}$$

In the above reactions *AX* represents an unexcited molecule, *AX** an excited molecule, $e(\varepsilon)$ an electron with kinetic energy ε before the collision, $e(\varepsilon')$ an electron with kinetic energy $\varepsilon' < \varepsilon$ after the collision,

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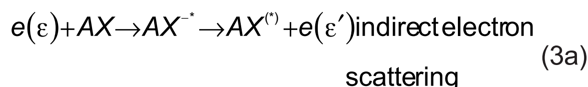
and A and X represent atomic or molecular fragments with or without excess internal energy.

Another group of significant electron-molecule reactions are the *ionizing collisions* in which additional free electrons are generated in the gas when the colliding electron has sufficient kinetic energy to ionize the gas molecule. These reactions can be represented as

$$e(\varepsilon) + AX \rightarrow AX^{+} + 2e \quad \text{ionization} \quad (2a)$$

$$\rightarrow A + X^{+} + 2e \quad \text{dissociative ionization.} \quad (2b)$$

There is a third type of reactions which are characteristic of electrons with energies below ~ 15 eV, namely, indirect (capturing) collisions. These are collisions in which the slow electron enters an empty orbital of the molecule and occupies it for a while, becoming temporarily captured by the molecule. The negative ion formed this way is temporary because it has excess energy and is thus unstable toward electron ejection. Its lifetime (the time the captured electron stays on the molecule) can be as short as a few femtoseconds and as long as or longer than milliseconds [1,2,5]. However, when the transient anion AX^{-*} is autodestructed by electron ejection, the neutral molecule may retain part or all of the electron's initial energy, becoming itself excited. Alternatively, the temporary negative ion AX^{-*} can be destructed (decay) by autodissociation forming permanent fragment negative ions X^{-} and free radicals. This dissociative electron attachment process takes place when it is energetically possible and when the fragments X (and/or A) have a positive electron affinity (that is, when they can "permanently" bind the extra electron). In addition, the transient anions AX^{-*} of many molecules with positive electron affinities can rid themselves of the excess energy (symbolized by the asterisk *), mostly by collision with other molecules, and form stable parent AX^{-} ions. Pictorially, these processes can be written as follows:



$$e(\varepsilon) + AX \rightarrow AX^{-*} \rightarrow AX^{(*)} + e(\varepsilon') \quad \text{indirect electron scattering} \quad (3a)$$

$$\rightarrow A + X^{-} \quad \text{dissociative electron attachment} \quad (3b)$$

$$\rightarrow AX^{-} + energy \quad \text{parent negative ion formation.} \quad (3c)$$

Such indirect collisions occur only when the slow electron has energies in restricted energy ranges, in the neighborhood of the energies of the empty orbitals which the electron occupies when captured. These energy regions define the positions of the so-called negative ion states (or resonances) of molecules. Negative ion states occur abundantly in nature. Their numbers and energy positions depend on the electronic structure of molecules [1,2].

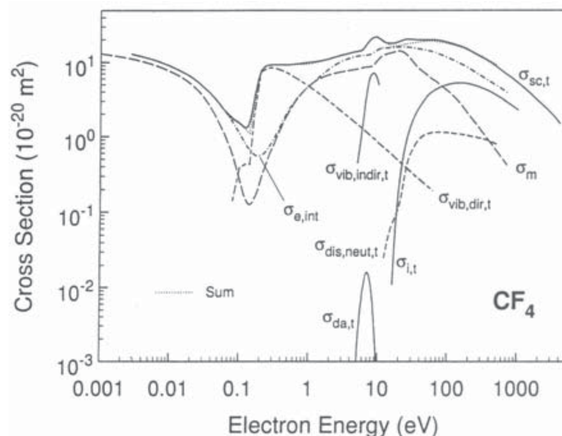


Fig. 1. Electron interaction cross sections for CF_4 [3].

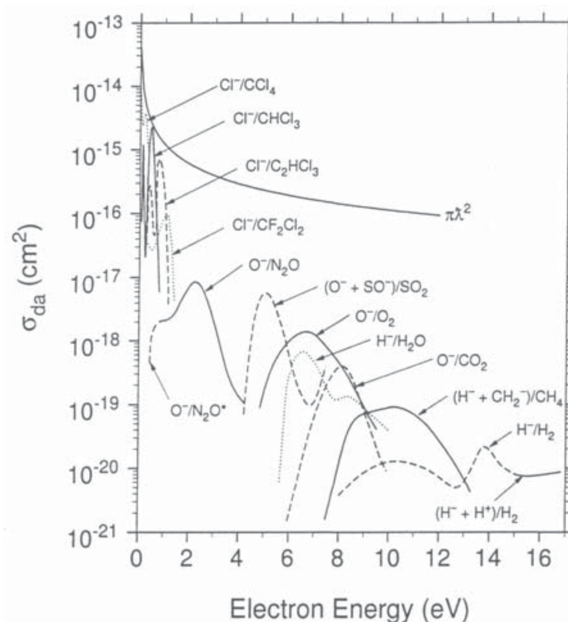


Fig. 2. Dissociative electron attachment cross sections as a function of electron energy for a number of molecules. The line designated by $\pi\lambda^2$ represents the upper limit of the electron capture cross section [2].

Table 1. Electron interactions control the energies and number densities of charged particles in electrically stressed matter and plasmas.

Process	Description
Electron-Energy-Controlling Processes#	
Direct Processes	
$e(\varepsilon) + AX \rightarrow AX + e(\varepsilon)$	Elastic electron scattering (direct)
$\Rightarrow AX^{*} + e(\varepsilon')$	Inelastic electron scattering (direct)
$\Rightarrow A + X^{(*)} + e(\varepsilon')$	Dissociation into neutrals
$\Rightarrow A + X^{*} + e(\varepsilon')$	Dissociative excitation
$\Rightarrow AX^{+*} + 2e$	Molecular ionization
$\Rightarrow A^{(*)} + X^{+(*)} + 2e$	Dissociative ionization
$\Rightarrow A^{+} + X^{-} + e(\varepsilon')$	Ion-pair formation
Indirect Processes	
$e(\varepsilon) + AX \rightarrow AX^{-*} \rightarrow AX + e(\varepsilon)$	Indirect elastic electron scattering
$\Rightarrow AX^{*} + e(\varepsilon')$	Indirect inelastic electron scattering##
Electron-Number Density-Controlling Processes#	
Electron Generating (Direct)	
$e(\varepsilon) + AX \rightarrow AX^{*} \rightarrow AX^{+*} + 2e$	Molecular ionization
$\Rightarrow A^{(*)} + X^{+*} + 2e$	Dissociative ionization
Electron Depleting (Indirect)	
$e(\varepsilon) + AX \rightarrow AX^{-*} \Rightarrow A + X^{-}$	Dissociative electron attachment
$\rightarrow AX^{-}$ + energy	Parent negative ion formation

The double arrow indicates a multichannel process.

This is the most efficient process for **vibrational excitation** of molecules.

Knowledge of the ways slow electrons interact with molecules, principally via the reactions (1) to (3) just mentioned, allows control in electrically-stressed matter (matter under an applied electric field) of (i) the kinetic energies and transport properties of the free electrons present, and (ii) the free electron production and loss, that is, the number of free electrons in the gas and their conversion to negative ions and vice versa [2,3]. Table1 lists the major electron-energy-controlling and electron-number-density controlling processes. While the electron-energy controlling processes cover a broad electron energy range (Fig. 1), the electron attaching processes occur at the extreme low energy range and have their highest cross sections at thermal and near thermal energies (Fig. 2). Besides these primary electron-molecule interaction processes, in practical systems there are other significant (secondary) processes and also other particles (*e.g.*, photons, ions) besides electrons whose interactions with the gas molecules are important.

The fundamental knowledge on the electron-molecule interaction processes just described underpins the development of many advanced technologies such as those of gas-discharge lasers, particle detectors, gaseous dielectrics for electric power transmission and distribution, pulse power, and plasmas for use in the semiconductor industry.

2. EXAMPLES OF APPLICATIONS

2.1. Gas discharge lasers

The importance of electron-molecule interactions in the production and optimization of lasing radiation in gas lasers is illustrated by the development of an efficient CO_2 laser. Lasing action in pure CO_2 gas was discovered [6] in 1964. The CO_2 laser is a vibrational-excitation laser. Its radiation originates from transitions between the vibrational levels of the electronic ground state of the CO_2 molecule. The relevant energy-level diagram of the CO_2 molecule is shown [2,7] on the left-hand-side of Fig. 3a. The lasing transitions are those between the $00^{0}1$ and the $10^{0}0$ (10.4 μ) and the $02^{0}0$ (9.4 μ) vibrational levels [2,7]. The lasing state may be populated by direct electron excitation of CO_2, and this can be done by controlling the density, *N,* of the CO_2 gas and the applied electric field, *E*, in such a way that

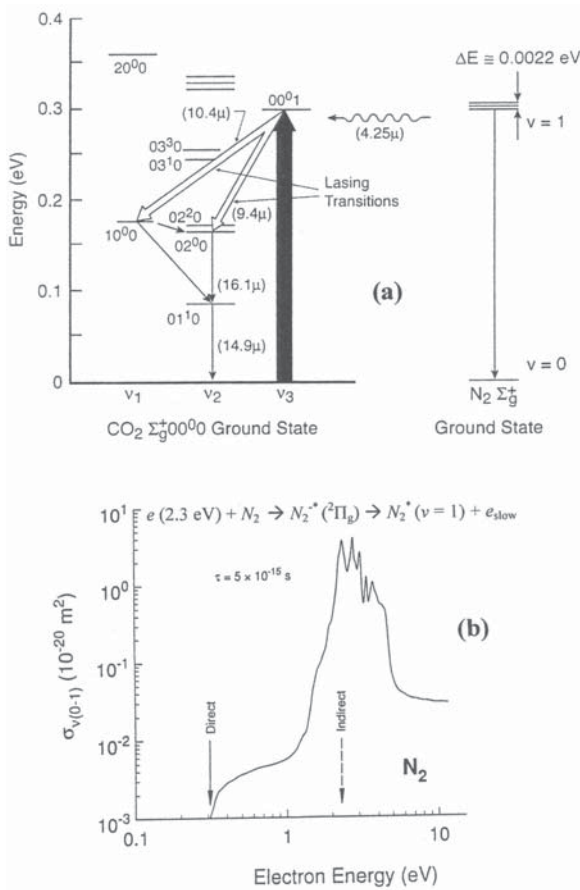
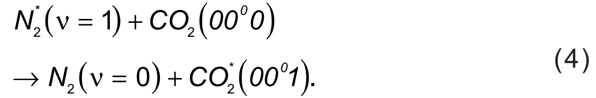


Fig. 3. (a) Simplified energy level diagram for the CO_2 and N_2 molecules illustrating the lasing transitions in the CO_2 laser [2, 7].(b) Cross section $\sigma_{\nu(0,1)}$ (ε), for the ν = 0-1 vibrational excitation of N_2 via the decay of the N_2^{-*}shape resonance at 2.3 eV [3,8].

most of the electrons that are present in the electrically stressed gas have energies where the excitation cross section for the lasing state is maximum. However, this process is inefficient because the cross sections for electron-impact excitation of the CO_2 molecule to the non-lasing and lower states are also significant in comparison to the *00⁰1* state cross section.

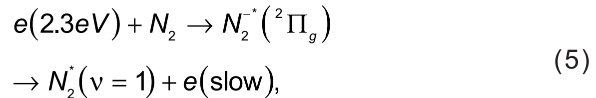
How, then, can the efficiency of the CO_2 laser be improved? One way is, of course, by pumping the lasing state more efficiently. Is there a way to do this? To answer this question let us first look at the right-hand-side in Fig. 3a. It is seen that the first vibrational level, v = 1, of the ground state N_2 molecule is isoenergetic with the lasing level *00⁰1* of the CO_2 molecule. If, then, a CO_2/N_2 mixture were to be used as the lasing medium instead of pure CO_2, and if it were possible to find a way to produce efficiently vibrationally excited N_2 molecules in the v = 1 level, N_2^* (v = 1), it would be possible to pump efficiently the lasing state *00⁰1* via the process



$$N_2^*(\nu = 1) + CO_2(00^00) \rightarrow N_2(\nu = 0) + CO_2^*(00^01). \quad (4)$$

That is, it would be possible to generate excited CO_2^* (*00⁰1*) molecules via energy transfer from N_2^* (v = 1). The efficiency of this process is high because the excitation energy of the v = 1 level of N_2 is almost equal to that of the lasing state, *00⁰1*, of CO_2. How, then, can we efficiently produce vibrationally excited N_2^* (v = 1) in a lasing CO_2/N_2 mixture? Reaction (3a) holds the answer since it has been shown to be an effective way to excite vibrations of molecules.

Indeed, quantitative measurements of the cross section for vibrational excitation of the N_2 molecule into the v = 1 state by electrons indirectly scattered via the lowest negative ion state of N_2 at 2.3 eV, that is, via the reaction



$$e(2.3eV) + N_2 \rightarrow N_2^{-*}(^2\Pi_g) \rightarrow N_2^*(\nu = 1) + e(\text{slow}), \quad (5)$$

have shown (Fig. 3b, Refs. [3,8]) that the cross section for process (5) is very large, and thus reaction (5) is an efficient means of producing vibrationally excited nitrogen molecules in the v = 1 vibrational level, N_2^*(v = 1).

In a lasing CO_2/N_2 mixture the production of the desirable N_2^*(v = 1) species is optimized by arranging the value of the ratio *E/N* so that most of the electrons present in the electrically stressed gas mixture have kinetic energies around 2.3 eV. This can be done easily, and the indirectly produced vibrationally excited N_2^*(v = 1) molecules act as an excitation source for the *00⁰1* lasing state of CO_2. In this way the efficiency of the CO_2^* laser is significantly increased. The CO_2 laser is, really, a CO_2/N_2 laser!

2.2. Particle detectors

Many devices used in radiation detection and dosimetry - as, for instance, the Geiger and proportional counters - rely on the total ionization produced in the gas by the ionizing particles. The characteristics of the counting gas that most affect the performance of these devices relate to what happens

to the electrons produced by the ionizing particle, their diffusion, their attachment to gas molecules or to impurities, their multiplication, and the time required for their collection. Furthermore, in those applications where gas-filled detectors are employed for particle detection and positioning, or for particle discrimination in mixed radiations, collection of the electrons produced in the slowing down of the particle in as short a time as possible is required and a fast counting gas (one with large electron drift velocity, *w*) is necessary. In practice, not only a high drift velocity is desirable, but also the drift velocity should remain high and relatively constant over a range of applied electric fields *E/N*.

Basic knowledge on electron-atom/molecule interactions allowed development of functional materials for such applications. The speed of the counting gas – a measure of which is *w* – depends on the electron scattering properties of the gas and the value of *E/N*, both of which determine the distribution of the kinetic energies of the electrons in the counting gas. To illustrate how functional materials, namely fast gases, can be developed for advanced detectors, let us oversimplify the physics involved and simply say that the electron drift velocity in a detector gas at a particular fixed value of *E/N* can be approximated by [2,9]

$$w \sim 1 / \langle\sigma\rangle\langle\varepsilon\rangle^{1/2}, \quad (6)$$

where $\langle\sigma\rangle$ is an average of the overall electron scattering cross section and $\langle\varepsilon\rangle^{1/2}$ is the square root of the mean electron energy at that *E/N* value. A gas with a large *w* (that is, a fast gas) can thus be one for which the product $\langle\sigma\rangle \langle\varepsilon\rangle^{1/2}$ is small [2,9].

Basic research has shown that the cross sections of the rare gases are very small in the energy range of ~ 0.1 to 1 eV (see, for instance, the cross section for Ar in Fig. 4, Ref. [10]). However, this gas is not a good detector medium because the *E/N* values which correspond to this energy range are quite low (which is impractical). It is known, however, that addition of a polyatomic gas to the rare gas substantially reduces the mean energy of the electrons $\langle\varepsilon\rangle$ compared to that of the pure rare gas [1,2]. If, therefore, a molecular gas which has a small electron scattering cross section in the region of the Ar cross section minimum and a large inelastic electron scattering cross section to the right of the Ar minimum ($\varepsilon > 0.5$ eV) is added to Ar, the combined effect of a lowering in $\langle\varepsilon\rangle$ into a region of small overall electron scattering cross section would effect a high *w* at *E/N* values convenient for applications [2,9]. That is, a molecular gas could be added

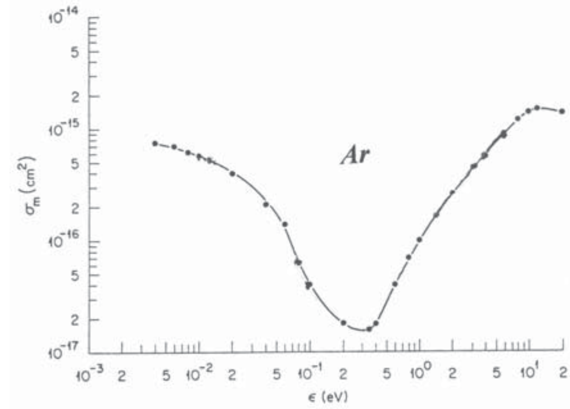


Fig. 4. Electron scattering cross section (for momentum transfer) for Ar [2,10].

to a rare gas to scatter the electrons into an energy range in which the mixture is "transparent" for electrons with kinetic energies in that range.

Let us, then, look at Fig. 1 where the various electron scattering cross sections for the CF_4 molecule are shown. We see that this gas is ideal to mix with Ar to develop a fast functional detector material as has just been described, because the elastic electron scattering cross section for CF_4 has a minimum near where the *Ar* atom cross section does, and also it has a very large inelastic electron scattering cross section due to direct ($\sigma_{vib,dir,t}$ in Fig. 1) and indirect ($\sigma_{vib,indir,t}$ in Fig. 1) vibrational excitation of CF_4 to the right of the Ar minimum. In addition, the CF_4 molecule does not attach electrons at low electron energies (< 4.5 eV [3]) and electrons would thus not be lost by attachment in these mixtures at the *E/N* values normally employed in practice.

In Fig. 5 fast gases comprised of Ar and CF_4 are shown. These are seen to be not only much faster than the commonly used P-10 (= 90%Ar + 10%CH_4) mixture, but they also maintain their high and relatively constant *w* over wide *E/N* ranges appropriate for many applications (e.g., the 80%Ar + 20%CF_4 mixture). They are the fastest counting gases known today and improve the performance of gas-filled detectors widely used in many basic and applied areas.

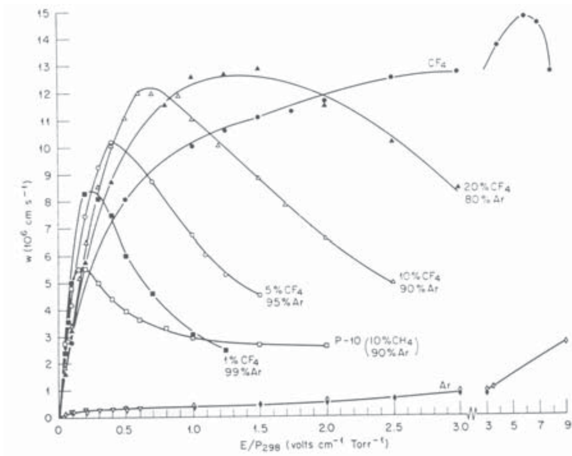


Fig. 5. Electron drift velocity *w* as a function of E/P_{298} for Ar, CF_4, P-10, and for Ar/CF_4 mixtures [2,9].

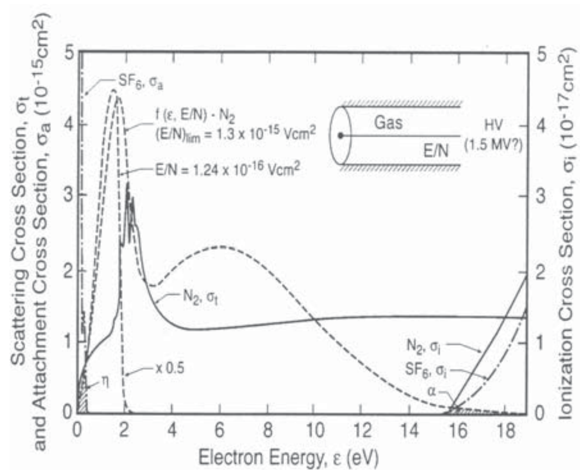


Fig. 6. Total ionization cross section $\sigma_i(\varepsilon)$ for N_2 (___) and SF_6 (- . -) close to the ionization threshold. Total electron scattering cross section $\sigma_t(\varepsilon)$ as a function of electron energy for N_2 (___) , and total electron attachment cross section $\sigma_a(\varepsilon)$ for SF_6 (- . -). Electron energy distribution functions $f(\varepsilon,E/N)$ in pure N_2 for two values of *E/N*: at $1.24 \cdot 10^{-16}$ V cm^2 (this value of *E/N* is about ten times lower than the *E/N* value at which breakdown occurs under a uniform electric field) and at the limiting value of *E/N*, $[(E/N)_{lim} = 1.3 \cdot 10^{-15}$ V cm^2] at which breakdown occurs under a uniform electric field. The shaded areas designated by η and α are, respectively, a measure of the electron attachment and electron-impact ionization coefficients for SF_6 [11].

2.3. Gaseous dielectrics for transmission and distribution of electric energy

Through reactions (3b) and (3c) are provided effective means to remove electrons from a given medium by transforming them from free and highly mobile particles to slow moving bulky negative ions. Fig. 2 shows a sample of the findings of basic science regarding reactions (3b) and (3c). A most distinct feature of these findings is the discovery that the closer to zero energy a molecular negative ion state is, the larger is the ability of molecules to remove electrons from the medium by attachment. In fact, Fig. 2 indicates that as the position of the negative ion states of molecules approaches thermal energy, the probability of electron capture becomes almost equal to one.

Knowledge on reactions (3) along with knowledge on reactions (1) and (2) has underpinned the development of gaseous insulation for the transmission, distribution - and conservation - of electric energy. Until recently, the most common insulation medium for high-voltage transmission of electricity was (and still is) air, which has many disadvantages including substantial energy losses. Many of the disadvantages of air insulation can be overcome by using alternative gaseous dielectrics such as sulphur hexafluoride (SF_6) to insulate electric power transmission lines and also other equipment, especially substations and circuit breakers. Because these 'functioning' gaseous materials have superior high-voltage insulating properties than air and because they can be used at pressures higher (500 kPa or so) than one atmosphere, they allow for more compact equipment and for use of closed underground cables that are aesthetically more acceptable and can operate at higher voltages with substantial energy savings.

This technology is now used worldwide and is founded on functional materials developed on the basis of knowledge on electron-atom/molecule interactions. To illustrate how this has been accomplished let us turn to Fig. 6 which links the basic physical processes that underline the development of high-voltage (voltages up to ~ 1,000,000 Volts) gaseous insulation. In the inset of the figure is sche-

matically depicted an enclosed gas-insulated transmission line. In practice, the conductor (or conductors) is held in place in the center of the pipe by solid insulators and the pipe is at ground potential. When there is no voltage on the conductor the gas is, naturally, a perfect insulator. When the gas is electrically stressed, the free electrons present in the gas (originated from natural radiation) gain energy from the applied electric field. At a certain level of the applied voltage, an appreciable number of these free electrons have sufficient kinetic energy to ionize the gas molecules (reactions 2) and multiply rapidly in an avalanche-like fashion so that the gas breaks down (i.e., it makes the transition from an insulator to a conductor). The minimum critical voltage at which this happens (that is, the value of the applied voltage at which the electrical conductivity of the gas increases by many orders of magnitude) is known as the breakdown voltage and the phenomenon as electrical breakdown.

While a multiplicity of physical processes involving electrons, photons and ions play a role in determining the breakdown strength and other electrical properties of the gas, basic research has shown that the slow electron is the key particle and its interactions with the gas molecules are the critical processes, especially those processes which produce (reactions 2), deplete (reactions 3b and 3c), or slow down (reactions 1 and 3a) free electrons [11]. Basic knowledge on these processes and measurement of their corresponding cross sections allowed prediction of the dielectric properties of gases and choice of appropriate functional gaseous materials for use by the electric power industry in the transmission and distribution of electric energy. To see how this has been accomplished let us return again to Fig. 6. In a gas – at a number density N – under an applied electric field E, the free electrons present in it attain an equilibrium energy distribution $f(\varepsilon,E/N)$, which is a function of the gas and the ratio E/N. When the value of E/N is low, the electron energy distribution $f(\varepsilon,E/N)$ lies at low energies and the number of electrons capable of ionizing the gas is negligible (i.e., the gas is an insulator). As the voltage is increased, $f(\varepsilon,E/N)$ shifts to higher and higher energies. For sufficiently high E/N, a small fraction of the electrons have sufficient kinetic energy to ionize the gas molecules and the gas makes the transition from an insulator to a conductor (i.e., it breaks down). The shaded area designated by the Greek letter α in Fig. 6 is a measure of the so-called ionization coefficient of the gas. For a non-electron attaching gas such as N_2, knowledge of α/N as a function of E/N provides a way to determine the breakdown field (when $\alpha/N \rightarrow 0$). For an electronegative gas such as SF_6, which attaches free electrons very efficiently, the situation is rather different. In this case, the free electrons are captured by the SF_6 molecules forming stable SF_6^- negative ions and are thus removed (prevented from initiating breakdown). As can be seen from Fig. 6, the cross section for electron attachment to SF_6 is large at very low energies and thus only electrons with energies at the extreme low-energy range can be removed efficiently from the dielectric by attachment. The shaded area designated by the Greek letter η in Fig. 6 is a measure of the so-called electron attachment coefficient η/N of the gas. Knowledge of α/N and η/N as a function of E/N allows prediction of the value of E/N at which the gas insulation breaks down and hence for a given gas pressure and system dimensions determination of the maximum value of the applied voltage. For uniform electric fields, this is the value, $(E/N)_{lim}$, at which $\alpha/N - \eta/N \rightarrow 0$.

The dielectric strength of a gaseous insulator can be optimized by using basic knowledge on the ionization coefficient $\alpha/N(E/N)$ which must be small, the electron attachment coefficient $\eta/N(E/N)$ which must be large, and the electron energy distribution function $f(\varepsilon,E/N)$ which must be shifted to lower energies to minimize electron production and to maximize electron removal by attachment. Many basic studies have shown that high breakdown strengths require gaseous media with large electron attachment cross sections ([2,11]). It is thus apparent that the insulating properties of gases can be optimized by a combination of two or more gas components designed, for example, to provide the best effective combination of electron attaching and electron slowing down gases. Knowledge of the electron attachment cross sections of many gases not only led to the discovery of many excellent insulating gases (such as SF_6, c-C_4F_8), but also to the appropriate choice of electronegative components for dielectric gas mixtures. Similar knowledge on electron scattering at low energies [2,3,11] guided the choice of buffer gases for mixtures containing electronegative gas additives.

Of unique practical significance are mixtures of the strongly electron attaching gas SF_6 with the inert, inexpensive, and environmentally acceptable non-electron attaching gas N_2 because the two gases act synergistically: the non-electron attaching gas N_2 scatters the electrons (indirectly, principally through the negative ion state at 2.3eV, Fig. 3b) into the low-energy region where the electron

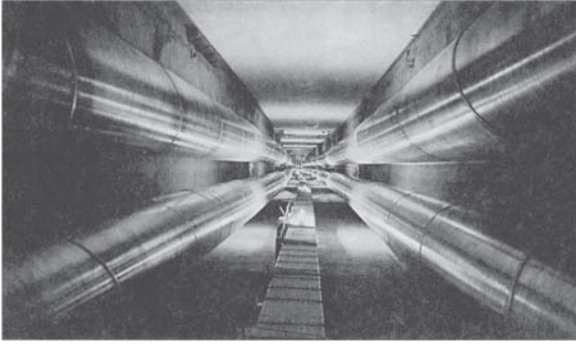


Fig. 7. 300-kV gas-insulated lines (GIL) for electric power transmission, located in a tunnel and insulated with 80%N_2 + 20%SF_6 gas mixture [13], as suggested by basic research results [11,12].

attaching gas SF_6 removes them efficiently. Such mixtures [11,12] are currently in use (see Fig. 7, Ref. [13]) in electric power transmission. The SF_6 gas is best suited for substation and circuit breaker insulation, and also in gas–insulated power transformers. It, and its mixtures with N_2, are also used in insulating high energy research equipment such as the Van de Graaff accelerators.

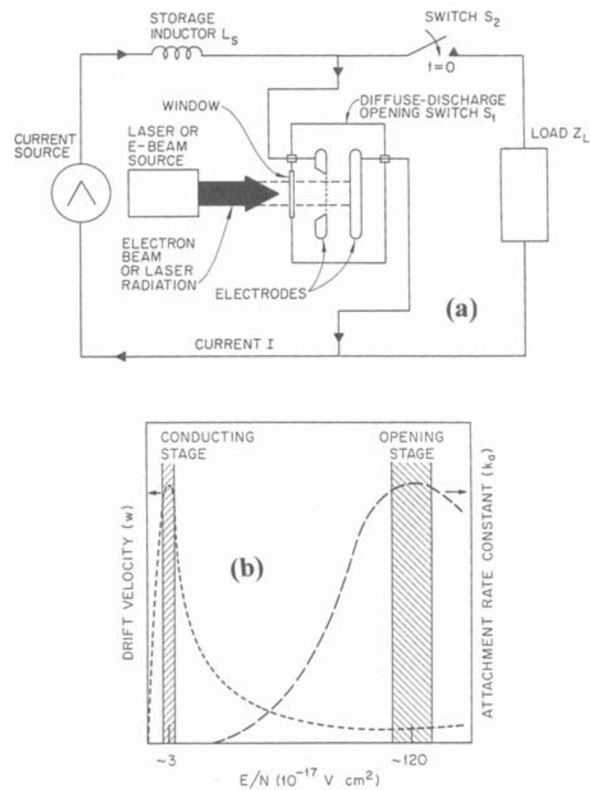


Fig. 8. (a) Inductive energy discharge circuit (see text and Refs. [2,14]). (b) Schematic illustration of the desirable characteristics of the $w(E/N)$ and $k_a(E/N)$ functions of the gaseous medium in an externally (electron-beam sustained) diffuse-discharge opening switch. Indicated in the figure are rough estimates of the E/N values for the conducting and opening stages of the switch [2].

2.4. Pulsed power technologies, diffuse-discharge switches, and optical switching of the dielectric properties of matter

Today, pulsed power is an integral part of many advanced technologies such as controlled fusion, electromagnetic propulsion, charged-particle beams, and high-power microwave and laser pulse devices. In these technologies energy is stored at a low power level and at a given desired time it is released as very powerful short pulses of energy. In these technologies inductive energy storage is often considered for storing and transferring energy because in inductive energy storage the energy density is about 100 to1000 times larger than in capacitive systems, and also because the time for transferring the stored energy to the load can be very short (submicroseconds).

Functional materials for the crucial switching devices of such technologies are required which are capable of switching their properties from conductors to insulators and from insulators to conductors in very short times (< μs). Let us briefly see how such materials can be identified for diffuse discharge opening switches and optical switches.

In Fig. 8a is shown the operating principle of a fast, repetitive pulsed power switch, namely, the externally sustained diffuse discharge opening switch operating at gas pressures of one to several atmospheres. There are two stages of this switch as used in inductive storage: *the conducting (energy storing) stage* and *the opening (energy transferring) stage*. During the conducting stage, the switch S_2 is open and the switch S_1 conducts by means of a diffuse discharge between the electrodes, which is sustained by ionization of the gas using either an electron beam or a laser. The E/N during this stage

is low. During the opening stage, the external ionization source is removed, thus opening S_1, and the switch S_2 is closed to allow the energy stored in the inductor L_S to be transferred to the load Z_L. It is known, however, that in an inductive system when one attempts to rapidly open the conducting switch, a very large voltage is induced across the switch due to the term $V_i = - L\, di/dt$ (L is the inductance of L_S in Fig. 8a and i is the current). This induced voltage tends to maintain a conducting arc between the electrodes of the switch S_1, and 'how to interrupt the conduction process against a high driving voltage is the essence of an opening switch' [14]. Thus, a gaseous medium is needed, which, while in the energy storing stage is a good conductor, in the energy transferring stage is a good insulator.

In Fig. 8b are shown the basic requirements for a gaseous medium to function as a good conductor in the storing stage and as a good insulator in the transferring stage. In the storing stage *E/N* is small (~ $3 \cdot 10^{-17}$ V cm^2) and conduction must be maximum. Thus, the gas must have a large electron drift velocity *w* and a negligible attachment (low electron attachment rate constant, k_a). In the energy transferring stage *E/N* is large, (~ $120 \cdot 10^{-17}$ V cm^2) and the breakdown strength of the gas must be large to avoid gas breakdown. Thus, the electron drift velocity *w* must be small and the electron attachment rate constant k_a must be large. Basic knowledge on electron-atom/molecule interactions identified such functional materials for those technologies. Among them, Ar/C_2F_6 mixtures have the desirable properties shown in Fig. 8b [2].

It is also possible to have a switching medium which is a good conductor in the conducting stage, and in the transferring stage becomes an insulator by firing a laser beam through the gas concomitantly with the opening of the switch so that a large number of the gas molecules become electronically excited. Here, then, use is made of the discovery that electronically excited molecules attach slow electrons with much larger cross sections than unexcited molecules [15]. In this mode, the diffuse discharge switch operates as an externally sustained optical switch.

Generally, knowledge of the electron attachment (and detachment) properties of materials and the use of laser light pulses enable changing and/or modulating the impedance characteristics of materials to fit many applied needs.

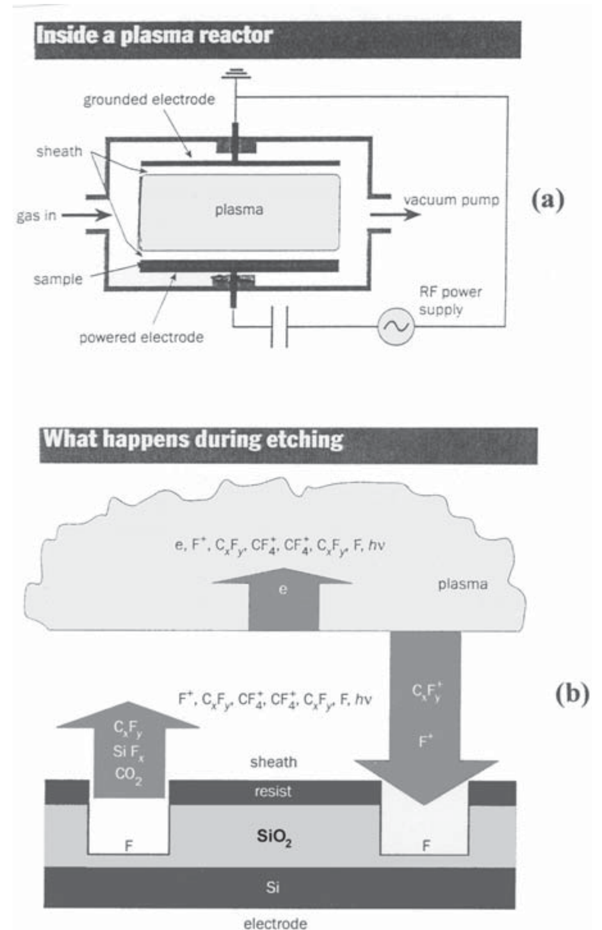


Fig. 9. (a) Schematic diagram of a capacitively coupled parallel-plate reactor. (b) Schematic diagram of the plasma etching of a silicon dioxide (SiO_2) layer on a silicon surface. The regions to be etched are defined by the resist (see text, and [16]).

2.5. Low-temperature non-equilibrium plasmas (for use in the semiconductor industry)

Technological plasmas play a key role in many modern industries, including the lighting and semiconductor industries. The plasmas used in these and other applications, are partially ionized, and partially dissociated gases. Fundamental electron-molecule interactions are basic to understanding the properties of industrial plasmas. To illustrate the role of these processes in the development of functional materials for the specific needs of these industries we focus on low-temperature, low-density,

non-equilibrium collision-dominated plasmas commonly employed for plasma processing in the semiconductor industry [3]. By low temperature we mean 'cold' plasmas with temperatures normally in the range 300 to 600K, by low density we mean plasmas with neutral gas number densities of ~ 10^{13} to 10^{16} molecules cm^{-3} (pressures between ~ 0.1 and 10^3 Pa) which are weakly ionized (charge-carrier densities ~ 10^8 to 10^{11} cm^{-3} and degree of ionization 10^{-6} to 10^{-1}), and by non-equilibrium we mean media for which the mean energy of the electrons is much higher than that of the neutral gas molecules. In such media, the electrons have a distribution of kinetic energies whose mean value is typically in the range of 0.5 to 5 eV, far in excess of the mean energy of the ions which is typically below 0.05 eV.

Fig. 9a shows schematically [16] the radiofrequency, capacitively coupled, parallel-plate reactor used in the microelectronics industry. Many of the features of this device are common to all technological plasmas. The device consists of two parallel-plate electrodes separated by a few centimeters, and mounted in a grounded vacuum chamber. The plasma constituents – electrons, ions and neutrals – are not in thermal equilibrium with one another; the input energy is essentially transferred to the electrons. After ignition of the plasma, the capacitively coupled electrode acquires a negative charge because the electron mobility is much larger than that of the ions. The material on the electrode is thus exposed to the bombardment of energetic positive ions, and the bulk of the plasma is exposed to energetic electrons. Both of these charged species obtain their energies by acceleration through the sheath that forms between the plasma glow and the electrode surfaces. This sheath is usually a fraction of a millimeter, and visually manifests itself as the dark region between the surface and the glow. It is the nearly collisionless acceleration across this space that enables the anisotropic etching that is so important in many plasma processes.

Chemical reactions between the radicals and the neutral species and the material being etched occur at the surface and produce either volatile species or their precursors. The positive ion bombardment of the surface removes materials by sputtering and produces chemically active sites on the solid. The combination of chemical activity of species and sputtering can result in much higher erosion rates in the vertical than in the lateral direction, which makes reactive-ion etching an essential tool for replicating device patterns in the fabrication of very-large scale integrated circuits. The goals of any plasma etch process are [17] high etch rates, uniformity (same etch characteristics), selectivity (relative rate of etching of one material with respect to another), controlled shape of the microscopic features etched into the film (anisotropy), and no radiation damage. These goals are realized by suitable control of key plasma properties such as the electron energy distribution function, the space and time variation of electron, ion, and neutral species densities as well as the control of the flux energy, and angular distribution of ions and neutrals bombarding the electrodes and their uniformity across the electrodes.

In controlling the above plasma characteristics, it should be noted that the interactions of low-energy electrons in these plasmas occur under different conditions depending on the plasma region. Three regions can be identified: the bulk plasma, the plasma-surface interface (sheath) and the solid. From a plasma processing perspective, the most important processes are those occurring at the surfaces, since they drive the etching and deposition of material. However, those processes are all initiated by species generated in the gas phase (or the glow) of the plasma. The generic primary reactions of elastic and inelastic electron scattering, electron impact ionization, electron impact dissociation, and electron attachment occurring in the bulk plasma are thus the most important parameters defining the plasma reactor characteristics. Table 2 lists some of the important plasma parameters in low-temperature, low-density, non-equilibrium plasmas and the corresponding major electron interaction processes on which they depend. Knowledge on such processes (and also on the secondary reactions between the products of the primary reactions) is crucial for optimizing the performance of plasma reactors and their diagnostics, for establishing realistic models designed to emulate various aspects of reactive plasmas and predict the properties of plasma reactors (e.g., see Refs. [3,17] and references cited therein), and for selecting appropriate functional materials for etching and deposition.

One of the plasma etching gases employed in the semiconductor industry is CF_4. Partly for this reason, this gas has been extensively studied [3]. The known electron collision cross sections for CF_4 have been shown in Fig. 1. The use of CF_4 to selectively remove areas of a silicon dioxide (SiO_2) layer on a silicon wafer helps demonstrate the general principles involved. The 'etching' of patterns in an insulating SiO_2 layer to expose parts of the silicon layer below, is one of the most important processes

Table 2. Plasma parameters and basic electron interaction cross section needs
(Plasma modeling requires the calculation of basic parameters describing plasma conditions in the reactor. Calculation of each parameter *requires knowledge of specific electron interaction cross sections).*#

Plasma Parameter	*Electron Interaction Cross Section Need*
Electron energy distributions	- Momentum transfer - Elastic scattering - Inelastic scattering
Electron densities	- Total ionization - Total attachment
Positive ion densities	- Partial ionization
Negative ion densities	- Attachment - Dissociative attachment
Radical densities	- Neutral dissociation - Dissociative attachment - Partial ionization
Excited species densities	- Vibrational excitation - Electronic excitation

#Also needed is knowledge of the electron attachment and ionization coefficients, electron drift velocities and electron diffusion coefficients, and electron interaction cross sections for energy rich species (vibrationally and/or electronically excited) and radicals.

in the entire microelectronics industry (Fig. 9b, [16]). The SiO_2-coated silicon wafer is placed on the driven electrode of the plasma reactor. A resist layer (acting like a stencil) is placed on top of the SiO_2 layer; it exposes those parts of the surface to be etched away and covers the rest areas. The ionization and dissociation of the CF_4 molecules in the plasma produce a multiplicity of products, among them fluorine atoms and various CF_x radicals both of which diffuse to the surface creating other products such as SiF_x and CO_2. These leave the surface either after formation or assisted by ion bombardment. The fluorine atoms, however, etch the SiO_2 layer; they combine with the silicon atoms in the SiO_2 layer forming volatile compounds which evaporate from the surface and are pumped away. When the exposed SiO_2 areas have been etched away to reveal the silicon underneath, polymer builds up at the bottom of the trench, which can be removed by exposure to an oxygen plasma [16].

3. CONCLUDING REMARKS

The examples discussed in this presentation concern technological applications driven by basic knowledge on low-energy electron-molecule interactions. The transition from basic research to application was purposely limited to the gaseous and the plasma states of matter. The basic nature of electron-atom/molecule interactions is of generic significance in many other modern technologies such as environmental clean up and pollutant detection, extra sensitive analytical instrumentation, particle beams, radiation and health effects, surface modification, light sources, and so on. The same knowledge can also be applied to the other two phases of matter, namely, the liquid and solid phases. There, however, profound changes can occur in both the energetics and the cross sections of the interactions due to the delicate effects of the nature and density of the medium on such processes (e.g., see Ref. [4]).

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