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HETEROGENEOUS REACTIONS IN NON-ISOTHERMAL LOW PRESSURE PLASMAS: PREPARATIVE ASPECTS AND APPLICATIONS

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Abstract—Non-equilibrium properties of low pressure plasmas open new ways to preparative solid state chemistry since they enable strongly endothermic reactions, as well as reactions requiring high activation energies, to take place at low temperatures. For example, the plasma techniques are now replacing many conventional methods in semiconductor technology such as thin film deposition, removal of photoresists and etching, and significant progress is expected in the application of low pressure plasmas to chemical vapour deposition (CVD). Chemical transport appears to be a simple method for investigating the behaviour of heterogeneous systems, solid/gas, under plasma conditions, as well as a promising technique for crystal growth. The unique features of plasma chemistry are demonstrated by two examples along with a description of adequate diagnostic investigations. Several significant aspects of plasma production and characterization are discussed from a plasma chemist's point of view. A number of heterogeneous systems are described to illustrate the variety of plasma syntheses and of the interactions between low pressure plasmas and solid surfaces.

INTRODUCTION

Ten years ago, heterogeneous reactions in low pressure plasmas were an underdeveloped field of plasma chemistry.[1,2] On the other hand, the major part of the recent book by Hollahan and Bell is devoted to the applications of the plasma to heterogeneous systems—solid/gas.[3] There are several reasons for this fast development: (a) The high internal energy of the plasma as well as a high activation energy, which is available at low temperatures, offer unique possibilities for chemical synthesis. (b) A large variety of the different types of discharges allows one to choose the most suitable experimental arrangement for a particular problem, etc. (c) The most important reason is, however, the high reaction yields obtained by this technique.

The low yields arising from the low pressure used makes the application of these plasmas to homogeneous systems in industrial processes unfavorable when a conventional method is available. However, this consideration does not apply to heterogeneous processes such as crystal growth and deposition of thin films. In such processes the growth rate is limited by the rate of build-up of crystal lattice. The rate of lattice growth is a function of temperature and the processes which control the nucleation. In many systems the activation energy of nucleation can be supplied by the plasma. Moreover, linear growth rates of the order of 10^{-3}–10^{-2} cm hr^{-1}, which are usually obtained by the conventional technique below 1000°C,[4] can also be reached in the plasma.

Let us consider a simple example: a deposition temperature of 100–1000°C, a concentration of the particular monomer $n_M \approx 5\times10^{14}$–$10^{16}$ cm^{-3} (i.e. partial pressure $p_M < 1$ torr) and a sticking probability $\alpha \approx 10^{-1}$–10^{-3}. The Hertz–Knudsen equation[4,5] leads to deposition rates between 6×10^{15} and 2.5×10^{19} species cm^{-2} sec^{-1}; i.e. a linear deposition rate of the order of 10^{-4}–1 cm hr^{-1}.

Table 1 shows the growth rates of several solid materials experimentally obtained in low pressure plasmas. It can be seen that the theoretically expected rates are reached in the experiments. In some cases, the use of plasma allows a faster rate of solid growth than obtained by the conventional technique. This is especially valid for systems such as the transport of red phosphorus (see Section 5) and the deposition of cadmium sulfide, which involve some kinetically hindered steps in either the evaporation or in the deposition. If, for example, cadmium sulfide were deposited at the rate of 3×10^{-4} cm hr^{-1} by the thermal evaporation, the layers would show very low resistivity due to the sulfur deficiency.[7]

Table 1. Linear deposition rates of solid materials obtained in low pressure plasmas

Solid	Temperature (°C)	Linear deposition rate (cm hr^{-1})	Ref.
AlN		5×10^{-3}	
crystals	1000		
TiN		2×10^{-2}	6
CdS	100–300	3×10^{-3}	7
P(red)	150	5×10^{-2}	8
P_3N_5	265	10^{-4}–10^{-3}	9
SiO_2			
Al_2O_3	100–500	10^{-4}–10^{-3}	10, 11
Si_3N_4			
SiO_2/GeO_2	$\lesssim 1000$	$\lesssim 0.6$	12, 13

The electrical and optical properties of conventionally deposited cadmium sulfide films are usually improved by long term annealing. Kassing and Deppe have shown that annealing in a H_2S-plasma for about 2 min leads to the same effect.[14] Further examples of enhanced deposition rate by discharge applications can be found elsewhere.[15,16]

The transport of phosphorus demonstrates a purification effect. If one can reach the desirable high degree of purity, an apparatus with a 2 kW high frequency generator could supply several hundred kilograms of pure phosphorus per year. Today's annual world production is a few tons.

The deposition and properties of various oxides and nitrides will be described in the next section together with some further examples of plasma applications. The present paper is intended as a short introduction into this field rather than a detailed review of the previous work (see e.g. Refs 1, 3, 10, 17–20). However, we shall try to show, with use of several selected examples, "what can be done" and "how to do it". The choice of the particular systems considered reflects the philosophy of the author

rather than an attempt to evaluate their importance in the general concepts.

The topics of the title include three types of reactions: (a) chemical evaporation and deposition of solids in which only gaseous reactants appear on the right hand side of the eqn (1):

$$A(s) + B(g) \rightleftharpoons C(g) + D(g) + \cdots\cdots \quad (1)$$

(b) modification of the solids and/or their surfaces such as oxidation and nitridation (2a), changes in the properties of the solid and/or surface (2b) and reduction of oxides, halides, etc. (2c):

$$A(s) + B(g) \longrightarrow C(s) \quad (2a)$$
$$A(s) + B(g) \longrightarrow A'(s) + B(g) \quad (2b)$$
$$A(s) + B(g) \longrightarrow C(s) + D(g) \quad (2c)$$

(c) reactions in which the solid is involved as a "third body" e.g. surface recombination of atoms and ions, de-excitation of various excited states, and surface catalysis.

The main part of this paper will be devoted to type (a) reactions. Although some reactions of type (b) and (c) will also be mentioned, the reader should consult the above mentioned general literature as well as some specialized articles for more details; e.g. plasma anodization[21] and ion plating,[22] morphology changes,[23] plasma treatment of polymers,[24] surface recombination,[25] thermal accommodation and molecular beam scattering from solid surfaces.[26]

In fact, the plasma can influence a heterogeneous system described by reaction (1) in two different ways, which will be called "the kinetic"—and "the thermodynamic effects" (Refs. 6, 27, 28). In the first case, the necessary activation energy for a thermodynamically possible reaction is supplied by the plasma, without which the reaction would not occur due to a kinetic barrier. A weak discharge, which is used to catalyze such a reaction, changes the energy content of the system only slightly.[2,27]

On the other hand, the high energy of an intense low pressure discharge (discharge current $\approx 10^{-1}$ to several ampères, pressure $\approx 10^{-1}$ to several torr) changes drastically the chemistry of such systems as compared with the conventional chemistry at the same pressure and temperature.

Usually, both of these effects take place more or less simultaneously. We shall give, later in this paper, two examples in which these effects can be quite clearly distinguished (transport of carbon according to Boudouard's reaction and with hydrogen, Section 3).

The last part of this paper deals with some preparative applications of the plasma. The chemical transport of solids in low pressure plasma which has been used in these studies appears to be a promising preparative method as well as a simple tool for the investigation of the behaviour of heterogeneous systems under plasma conditions. We shall try to illustrate this point with several examples.

Any theoretical treatment of heterogeneous systems under plasma conditions is very difficult because of the large number of elementary processes involved and the lack of data on the reaction rates. A simple, phenomenological theoretical approach was developed previously by the author in order to obtain some fundamental ideas on the behaviour of such systems.[2] Any substantial progress of the theory requires an accumulation of more experimental and preparative experience, a better and more detailed diagnostic approach and, last but not least, more data on the elementary processes, both in the gas phase as well as on the surface of the solid.

1. APPLICATIONS

Considering the high deposition rate indicated in Table 1 one may ask about the quality of the deposited films. Table 2 shows the dielectric properties of various materials obtained by the plasma technique. For comparison, the deposition temperatures necessary for conventional and plasma techniques are also given. Of principal importance for *semiconductor technology* is the low temperature which can be used in plasma as compared with the high temperature necessary for the conventional technique. Such high temperatures cause technological difficulties due to an enhanced diffusion of doping materials in the semiconductors. The dielectric properties of the plasma deposited films—which are given on the right hand side of the table—are excellent.

A typical method for the preparation of *inorganic oxides* is the low temperature pyrolysis of organometallic compounds. Several methods of *nitride* deposition will be described later.

Thin films of *organic polymers* are obtained by polymerization of a suitable monomer gas in electric discharge at low pressure.[31-33] The possible fields of application of the polymer films are in semiconductor technology,[11,32] integrated optics,[34] semipermeable membranes[35] and protective coatings.

Removal of photoresists and *etching* are among the several important steps in the fabrication of semiconduc-

Table 2. Dielectric properties of plasma deposited thin films

Compound	Deposition temperature (°C)		Properties of plasma deposited films				Ref.
	Conventional	Plasma	Dielectric constant	tan δ	Dielectric strength (V cm^{-1})	Surface charge density (cm^{-2} eV^{-1})	
Si_3N_4	700–900	250–500	6–10	$\leq 10^{-4}$	$0.5–1 \cdot 10^7$	10^{11}	10, 11
SiO_2	900–1200	200–300	4.5–5.5	$\leq 10^{-4}$	$0.5–1 \cdot 10^7$	10^{10}–10^{11}	10, 11, 14
Al_2O_3	700–1000	100–500	7.5–8.5	$\leq 10^{-2}$	$0.7 \cdot 10^7$	$>2 \cdot 10^{10}$	10, 11, 29, 30
Organic polymers		100	2.5–6.2	$\leq 10^{-2}$	$0.1–1 \cdot 10^7$	10^{12}	10, 31, 32, 33
P_3N_5		200–300	4.4	$\leq 10^{-2}$	$0.1–0.9 \cdot 10^7$	?	9

tor devices. The photoresists are photosensitive organic polymers which are used by the photolithographic technique for masking the device during fabrication. At the end of the particular process the photoresist has to be removed. The conventional technique involves several wet steps and requires the use of highest grade chemicals. On the other hand, the photoresist can easily be removed by oxidation in a low pressure discharge.[11,36]

In a similar way silicon, silicon oxide and nitride can be etched using CF_4-plasma[37] which is fast, simpler, cleaner and cheaper than the conventional technique. The etching rate can be significantly enhanced if a combined r.f. sputtering/etching technique is used.[38]

A comparison of the two techniques for the manufacture of semiconductor devices has recently been given by Kirk.[11]

The success of plasma technology in this field is well known. A more recent example will now be described, i.e. the application of the plasma for fabrication of low loss optical fibres.

Optical fibres will be an important part of future communication systems. The fibre consists of a core with a high refractive index and a sleeving with a low one, providing total reflexion of light at the boundary. A definite radial index profile and low attenuation—i.e. extremely high purity of the glass—is desirable for the application of fibres to communication purposes. Although the main problems in the preparation of low loss optical fibres have already been solved some problems, such as the achieving the definite radial index profile remain to be overcome. One way to achieve the definite profile is to approximate the desired profile by repeated layer deposition followed by diffusion equalization. This means that layers of thickness less than 1 μm are required. Such layers are deposited in a microwave discharge as shown in Fig. 1 (for more details see Refs. 12, 13).

Gaseous starting substances, e.g. $SiCl_4/GeCl_4/O_2$ are introduced into a quartz tube where they pass a microwave cavity. In the discharge region, the transformation of chlorides to oxides takes place. Oxide layers of a uniform thickness are obtained by moving the microwave cavity along the enclosing tube. The typical experimental conditions are as follows: total pressure 10–30 torr, frequency 2.450 GHz, inner diameter of the surrounding tube 6 mm; a deposition rate of about 0.3–0.6 cm hr^{-1} is obtained at a temperature of about 1000°C.

Optical fibres of an outer diameter of 100 μm are drawn from such preforms. Optical losses below 10 dB km^{-1} in the spectral region 740–920 nm with a minimum of 3.6 dB km^{-1} at about 1040 nm have been obtained so far. These losses are quite comparable with those of fibres produced by the conventional technique, but the use of a plasma allows much better control of the radial refractive index profile. Geittner *et al.* expect, that after elimination of some impurities (e.g. Fe^{2+} from stainless steel components in the experimental equipment) the total losses will become even less.[12]

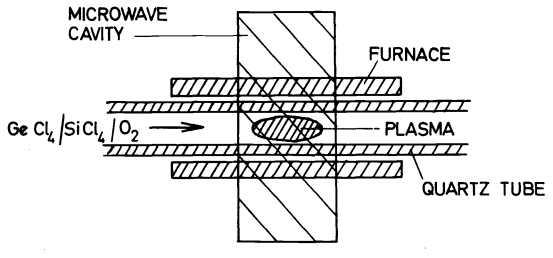


Fig. 1. Experimental set up for deposition of optical fibres.[12,13]

The last example we shall mention in this introduction is the *continuous wave* HCN-*laser*.[40,41] Due to the long wave length, 337 μm and 311 μm, this laser is suitable for a variety of applications including plasma diagnostics, direct mixing of the far i.r. light with electromagnetic radiation produced by klystrons, study of nonlinear phenomena, etc.

The strongest radiation at 337 μm corresponds to the vibrational-rotational transition (11′0) J = 10 → (04°0) J = 9 of the HCN molecule. This transition is allowed because of a strong Coriolis coupling between these levels and the population inversion is obtained due to the high de-excitation probability of the lower lasing level (04°0). For the operation, HCN molecules must be formed and/or excited into the (11′0) state.

The mechanism of the formation of vibrationally excited HCN molecules remained unresolved for a long time. Recently, Schötzau and the author have shown that the excited HCN-molecules are formed by both volume and wall processes, the latter contributing apparently more to the total power emitted by the laser.[42]

Shortly after first switching on the discharge in an optimal gas mixture, the inner wall of the discharge tube becomes covered with a polymer corresponding to approximately stoichiometric paracyanogen $(CN)_x$. If a pure, stoichiometric paracyanogen is first deposited by discharge activated polymerization of cyanogen $(CN)_2$, and, afterwards, the discharge is maintained in hydrogen only, the highest lasing power is obtained from the particular laser.[43]

A high degree of dissociation is found in the discharge even near the tube wall.[42] Hydrogen atoms impinging on the surface of the polymer are adsorbed there and HCN molecules are formed:

$$(CN)_x + 2H \longrightarrow (CN)_{x-1} \cdots\cdots\cdots (HCN)_2$$

$$(CN)_{x-1} \cdots\cdots (HCN)_2 \longrightarrow (CN)_{x-1} + 2HCN^+(g) \qquad (3)$$

The desorption can occur either directly, or there may be some intermediate steps involved. In any case, the HCN molecules are most probably vibrationally excited when leaving the surface. For the particular laser we have studied, the total number of HCN molecules formed per second on the wall is almost two orders of magnitude larger than the number of the stimulated transitions which give the measured laser gain. The experimentally observed gain of the HCN laser, which is constant over the cross section of the resonator tube, is then explained in terms of the combined effects of volume processes and reactions on the wall of the discharge tube (for further details see Ref. 42). Quite recently, Kunstreich and Lesieur have been able to distinguish experimentally between these two processes by measuring the relaxation time for the onset of the stimulated emission.[44,45]

It is surely very encouraging to see the application of low pressure plasmas to a variety of practical problems. However, we must realize, that we still know only very little about the basic processes taking place in the plasma. We shall therefore discuss these processes as far as is possible in the light of our present understanding of the problem.

Experience has taught us that it is often very difficult or almost impossible to compare results of various authors

due to insufficient data on the experimental arrangement and, especially, on the discharge conditions. For this reason, we shall pay attention to these problems in the following section.

2. APPARATUS AND CHARACTERIZATION OF DISCHARGE PARAMETERS

A variety of apparatus for chemical syntheses in low pressure plasmas has been described in the literature (e.g. Refs. 1, 3, 17). A typical apparatus consists of a vacuum pump, gas sampler, a properly designed discharge tube (reaction vessel), a generator of electric power for maintaining the discharge and necessary instruments for monitoring discharge conditions. Since most of these items are standard laboratory equipment we shall select only a few problems concerning the production and characterization of the plasma which are important for choosing particular instruments. Let us recall that we are considering low pressure plasmas (pressure $\approx 10^{-2}$ to several torr, with an electrical power dissipated in the discharge 10^{0}–10^{4} W).

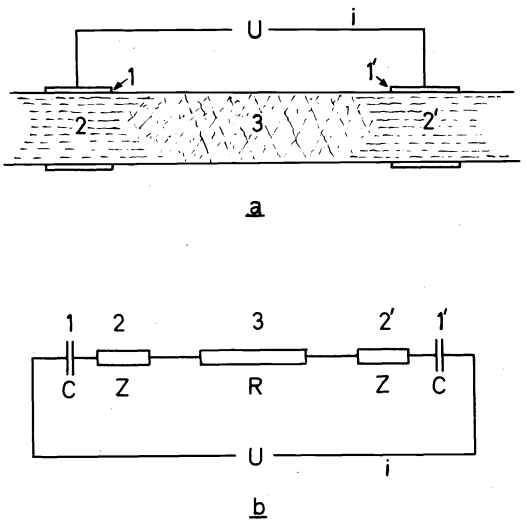


Fig. 2. (a) Discharge tube; (1) capacitance of the glass wall; (2) electrode regions; (3) plasma column. (b) Equivalent high frequency circuit.

2.1. *Generation of the plasma*

With a few exceptions such as deposition of solid on thin wires in a corona discharge, plasmas which are more or less homogeneous over a region of at least several centimetres are desirable for application to preparative solid state chemistry. It turns out, that a *radio frequency, electrodeless discharge* is most suitable for these purposes (e.g. Ref. 3, chap. 1 and 10). The discharge is maintained in a quartz or pyrex tube between two external electrodes ("capacitive coupling"). At a power of more than several hundred watts, these electrodes must be water cooled in order to avoid damage to the tube. It should be pointed out that if the so called "inductive coupling" (see e.g. Ref. 1, p. 39) is used to produce plasma at lower power and a frequency greater than 10 MHz, the discharge is maintained due to the r.f. electric field between both ends of the coil, and the coupling is in fact a capacitive one.

In principle, any *frequency* from 50 Hz up to GHz can be used to excite gas at low pressure, but for our purposes, a frequency of 20–100 MHz is most convenient.

At lower frequencies the *voltage*, which has to be applied to the external electrodes to maintain the discharge at a given value of the discharge current, increases significantly. Figure 2 shows schematically the discharge tube and the equivalent high frequency circuit. At a discharge current **i**, the applied voltage **U** is given by

$$\mathbf{U} = \mathbf{i}\left(\frac{2}{j\omega C} + 2\mathbf{Z} + R\right). \qquad (2.1)$$

Here, $\omega = 2\pi f$, f is the frequency, C denotes the capacity of the condenser consisting of the external electrode, discharge tube wall and conducting layer of the plasma near the inner wall, **Z** is the impedance of the electrode regions and R is the ohmic resistance of the plasma column. The imaginary part of the plasma conductivity is zero in the frequency region considered here.[46]

The impedance **Z** increases with decreasing frequency due to increasing losses of charged particles during one period of the h.f. field. This means, that with decreasing frequency f, the term $(2/j\omega C + 2\mathbf{Z})$ increases. In order to keep the power dissipated in the plasma column (which is being used for the plasma chemistry work) constant, this increase must be compensated by an adequate increase in the voltage **U**.

This is illustrated in the following example:[47] An h.f. discharge in nitrogen was maintained in a tube of diameter 10 cm; the separation of the water cooled electrodes was about 25 cm (arrangement as in Fig. 2a) and the pressure was 1 torr. At a discharge current of between 4–7 A a power of about 1–2 kW is dissipated in the discharge. The value of the h.f. voltage applied to the electrodes is between 1 and 1.5 kV at 27 MHz, but is as much as 9–14 kV at 1 MHz. It is evident that the impedance matching is much more complicated at 1 MHz than at 27 MHz. Moreover, a power of up to 3 kW can be dissipated in a pyrex tube at 27 MHz and the discharge can be maintained for several thousand hours without damaging the glass. On the other hand, the same pyrex or quartz tubes only survived a few hours when the discharge was run at 1 MHz.

Nevertheless, the frequency of 1 MHz can be used if internal, water cooled electrodes are applied. Several arrangements have been developed in our laboratory by E. Wirz.[48,49] Figure 3 shows as an example a quartz *discharge tube and the impedance matching* for the synthesis of nitrides. For the preparation of a particular nitride an insert made from the same metal is used to protect the inner wall of the electrodes and to avoid a contamination of the plasma. Although the 1 MHz generator was successfully used for preparative plasma chemistry,[48,49] the experimental design, as well as the handling of the apparatus itself, appears to be much more complicated than in our earlier work at a frequency of 80 MHz.[6]

The upper frequency limit is determined mostly by the decreasing efficiency of electron tubes above 100 MHz. In addition, sophisticated experimental arrangements must be used to produce a homogeneous plasma in large volumes at very high frequencies, for then the wavelength is comparable to, or shorter than the dimensions of the discharge tube.

A d.c. discharge is to be preferred when measurements on plasmas have to be done using sensitive electronic instruments (e.g. mass spectrometry, optical and i.r. spectrometry, etc.). The equivalence between plasma of the positive column of a d.c. discharge and that of a h.f.

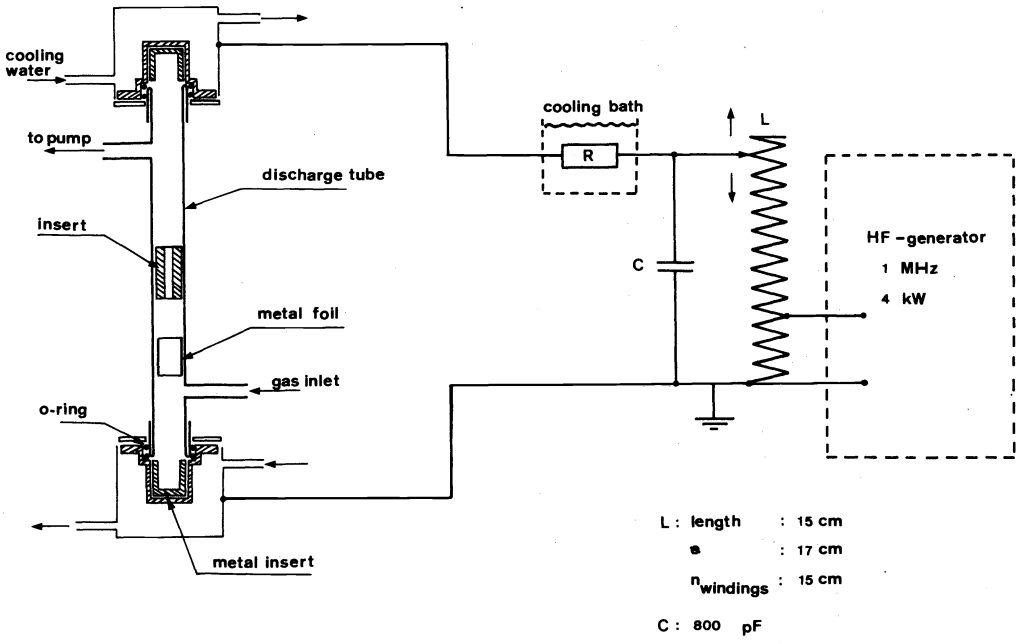


Fig. 3. Discharge tube and impedance matching for synthesis of nitrides at a frequency of 1 MHz.

one allows one to correlate the results of measurements in a d.c. discharge with those of capacitive coupled discharges at frequencies 10–100 MHz.[46,50,51]

2.2. *Characterization of the plasma*

A comparison of experimental findings of different authors who have worked with the same systems is frequently very difficult or impossible due to insufficient data on plasma parameters. As a minimum the following *macroscopic parameters of the discharge* are needed: diameter of the discharge tube, distance between the electrodes, frequency, discharge current, gas pressure and flow rate, and, of course, all data on chemical compounds used. In addition, the neutral gas temperature and the axial field strength should be measured. A knowledge of these parameters allows one to calculate or to estimate from literature data the important *microscopic parameters* such as electron concentration and temperature, degree of dissociation, etc.

Many authors used to give as a discharge parameter the *power dissipated* in the whole discharge and/or the h.f. voltage applied to the electrodes. It is evident, that due to the frequency dependence of the usually unknown values of the first two terms in eqn (2.1), (i.e. $1/j\omega C$ and $\mathbf{Z}$) these parameters do not characterize the plasma of the discharge column.

We shall pay attention to the *measurement of the electric parameters* at the frequencies considered, since most chemists are not quite familiar with them.

A modern *oscilloscope* with high voltage probes for the frequency range of up to 100 or 200 MHz (at least up to the third harmonic of the generator frequency) and with a corresponding current and range is the most suitable and versatile instrument for such measurements. The current probe has to be placed next to the earthed electrode and the capacitive current is subtracted from the measured value. The capacitive current is measured either with a discharge tube evacuated below 10^{-4} torr or filled with an inert gas at high pressure (no discharge).

The *axial electric field strength E* can be found by measuring the voltage U applied to the discharge tube at constant current and varying electrode distance (see Fig. 2 and Ref. 52, p. 238). The power dissipated in the plasma column of length L is then equal to ELi_{ef} · (i_{ef} denotes the effective value of the h.f. current). One notices again, that the plasma conductance of the column (see (3) in Fig. 2) contains only the real term at the frequencies considered.[46]

The relatively high costs of the oscilloscope including the probes may prevent many plasma chemists from buying them. Use of a *high frequency voltmeter* instead of the oscilloscope can significantly reduce the total cost of the facilities, but information on the actual time dependence of the current and voltage during one period of the h.f. field will be missing. The latter is very important, especially if the discharge tube is placed in a screening box ("Faraday cage") where intense standing waves at high harmonics are induced. These oscillations may interfere with the instruments and cause significant errors in the measurements.

For the "every day" characterization of a discharge in plasma chemistry work, simple, self-made instruments which can be set up in any laboratory can be used. It may be helpful to describe them here.

The simplest *h.f. ammeter* consists of two thin, metallic foils and of a thermometer filled with a non-conductive liquid (e.g. petroleum, up to 270°C). The chosen thickness of the foil must be much less than the electric skin depth at the given frequency. For example, zirconium foil of thickness $\lesssim 0.02$ mm or platinum foil of thickness $\lesssim 0.01$ mm can be used up to 80 MHz.[53] The mechanical construction is shown schematically in Fig. 4. The thermometer and foils must be rigidly secured (using teflon), and the whole ammeter has to be thermostatted (e.g. by surrounding it with a coil of plastic pipe containing water or oil at constant temperature). Since the resistivity of the foil does not depend on frequency up to several hundred MHz, the thermometer can be calibrated using either d.c. or a.c. (50 Hz) current. The current range of the ammeter depends on the width of the foil. For example, an h.f. current

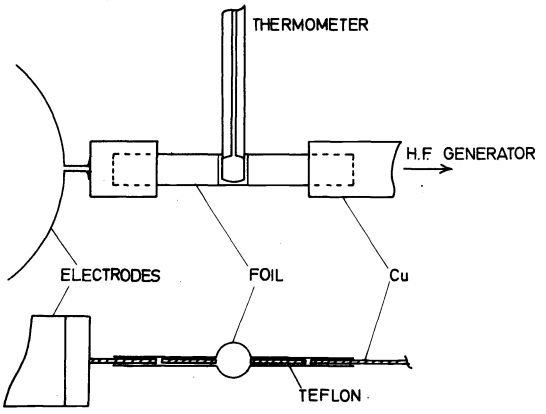


Fig. 4. Schematic design of h.f. ammeter.

of up to 10 A can be measured when a foil width of 10 mm is used. This ammeter can also be used for measurement by a "symmetrical arrangement", i.e. with no electrode earthed.

The *h.f. voltmeter* consists of a voltage divider (e.g. two condensers), a rectifier and d.c. voltmeter. The arrangement can be found in any standard textbook, and the instruments necessary for the calibration are available in most physics departments.

A small *gas thermometer* made of quartz appears to be the most suitable instrument for measuring the neutral gas temperature.[53] It is filled with nitrogen at ~250 torr (hydrogen diffuses through quartz at high temperatures) and the pressure differences which are proportional to the temperature are measured by a "U"-manometer using a gallium/indium alloy (liquid at room temperature, negligible pressure up to 1000°C).

The actual temperature measured by the thermometer in a particular discharge depends on the catalytic efficiency and on the emissivity of the surface of the thermometer top. Figure 5 shows the temperature measured by the thermometer when the top was covered with various solid materials. The reproducibility of these measurements is illustrated by the curve for platinum. The individual points were obtained with three different gas thermometers and two different ammeters in two discharge tubes over a period of six months.

The temperature of the particular solids measured at the same value of h.f. current depends predominantly on the catalytic efficiency of these materials for the surface recombination of atoms (Refs. 53, 54, pp. 170–200, 25, 25a). The temperature of quartz poisoned with HPO_3 is roughly equal to the neutral gas temperature. An exact determination of the latter value would include a detailed consideration of the radial gradient of temperature, emissivity of the surface and plasma, concentration of atoms, mestastables and ions. However, neglecting these effects is quite tolerable within the limits of accuracy of usual plasma chemical work. It is also evident from Fig. 5, that the temperature measured by a simple thermocouple can differ significantly from the neutral gas temperature.

The temperature difference found for platinum and quartz/HPO_3 surfaces can be employed for an approximate determination of the *degree of dissociation*.[55] The Wrede–Harteck gauge is suitable for more exact measurements (e.g. Ref. 1). A particular construction of a W-H. gauge for measurements in intense molecular discharges at higher temperatures can be found in our

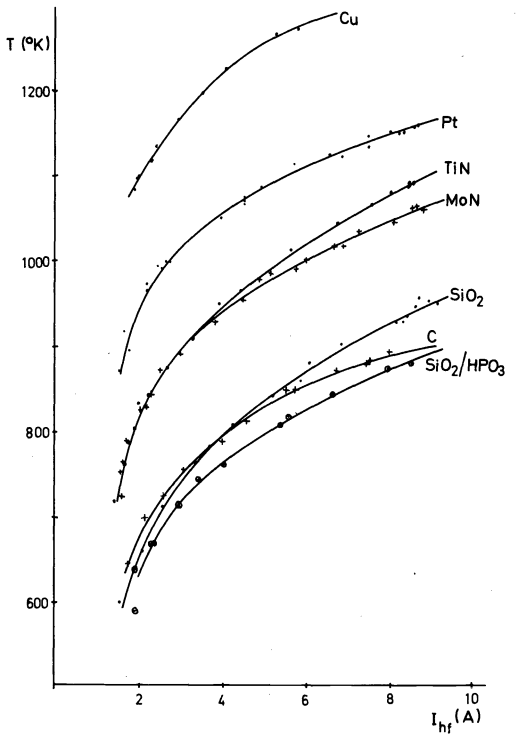


Fig. 5. Dependence of the temperature of various solids in nitrogen discharge on h.f. current. Pressure 1.35 torr, frequency 80 MHz, discharge tube diameter 10 cm.

previous paper.[42] The gradient of the degree of dissociation in the vicinity of the quartz gauge is negligible and produces no significant errors (for the calculations see Ref. 56).

3. CHEMICAL TRANSPORT OF SOLIDS IN PLASMA (GENERAL ASPECTS)

Theoretical as well as preparative aspects of chemical transport of solids in low pressure plasmas have been discussed in our previous papers.[2,6,27,28,57–60] In this section we shall only consider transport of carbon by Boudouard's reaction in a weak CO/CO_2-discharge and in an intense hydrogen discharge. As pointed out in the introduction, the first case displays a kinetic effect and the second one illustrates a thermodynamic effect of the plasma. In order to compare conventional and plasma chemistry we shall pay attention to the mechanism of transport in the light of some recent diagnostic investigations into these systems. It will be seen, that reactions of neutral atoms and radicals predominate in intense discharges, whereas ion-molecule reactions are more dominant in weak plasmas at low temperatures.

3.1. *The Boudouard's reaction* (3.1)

This was presented by Schäfer[61] as an example of a system where transport ($T_2 \rightarrow T_1$), which should be possible thermodynamically, does not take place due to the high activation energy of the reverse reaction.

$$C(s) + CO_2(g) \rightleftharpoons 2CO(g). \qquad (3.1)$$

We have shown earlier, that this activation energy can be supplied to the system by a weak discharge (for the experiments see Ref. 27). The mechanism of the reverse

reaction $2CO(g) \rightarrow CO_2(g) + C(s)$ remained unresolved at that time.

This problem was recently clarified in a mass spectrometric study of the system[62,63] using a double focussing instrument (CEC 21-110) which was modified for a collision-less extraction of a molecular beam of neutral particles from the discharge tube. The experimental arrangement is shown in Fig. 6. More details on the apparatus and on the construction of the orifices into the wall of the discharge tube will be published elsewhere.[63] Three different discharge tubes with conical orifices of minimal diameter 60, 100 and 200 μm, and of wall thickness less than 100 and 200 μm respectively, were used in this study. Carbon monoxide of greater than 99.995% purity was introduced into the discharge tube. At a total pressure chosen between 0.5 and 6 torr, the steady state concentration of CO and CO_2 in the discharge, under gas flow conditions, was monitored by the mass spectrometer. The mean residence time τ_{res} of the gaseous species in the discharge plasma between 0.1 and 200 sec could be established by varying the flow rate. τ_{res} is equal to the time period which is available to the system to reach the particular steady state concentration ratio of CO_2/CO at the position of the orifice.

The reverse, plasma catalyzed reaction (3.1) involves several elementary processes. The overall rate of this reaction, which is predominantly affected by the slowest elementary process, can be expressed in terms of an overall relaxation time, τ_{rel}. At a given pressure and discharge current, the ratio CO_2/CO does not depend on τ_{res} (i.e. on the flow rate) as long as $\tau_{res} \gg \tau_{rel}$, but it should decrease for $\tau_{res} \lesssim \tau_{rel}$. Thus, the relaxation time τ_{rel} can be determined experimentally by measuring the dependence of the CO_2/CO-ratio on τ_{res}, provided, of course, that the relaxation time of electrons $\tau_{el} \ll \tau_{res}$.

The reverse reaction (3.1) can take place via three different mechanisms (see Refs. 27, 62, 63):

$$\left.\begin{array}{l} \nearrow O^- + C_\downarrow \longrightarrow O^- + CO \longrightarrow CO_2 + e \qquad (3.2a) \\ CO + e \rightarrow CO^* + e \longrightarrow CO^* + CO \rightarrow \\ \qquad \cdots \longrightarrow C_3O_2 \longrightarrow 2C_\downarrow + CO_2 \qquad (3.2b) \\ \searrow C_\downarrow + O + e \longrightarrow O + CO \longrightarrow \cdots \longrightarrow CO_2 \qquad (3.2c) \end{array}\right.$$

Detailed calculations show[62,63] that the three possible reaction mechanisms are characterized by different overall relaxation times:

$$\tau_a \gtrsim 0.4 \text{ sec}, \quad \tau_b \gtrsim 500 \text{ sec}, \quad \tau_c \gtrsim 20 \text{ sec}. \qquad (3.3)$$

Consequently, the reaction path (3.2a) involving the ion-molecule process should predominate and the ratio CO_2/CO should decrease for $\tau_{res} \gtrsim 1$ sec. Figure 7 shows the measured dependence of the CO_2/CO ratio on τ_{res} at constant pressure and discharge current. The agreement of the measured value $\tau_{rel} \approx 0.36$ sec with the calculated value $\tau_a \gtrsim 0.4$ sec is excellent and we can conclude that the ion–molecule reaction mechanism (3.2a) is most probably predominant in the weak discharge.

To be sure that the change of the CO_2/CO ratio was not due to any effects other than those discussed above, the measurements were also checked by switching the

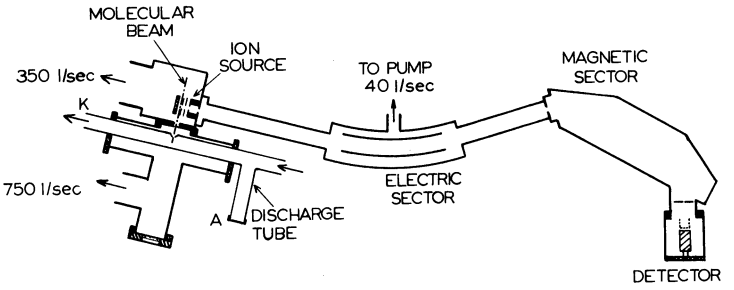


Fig. 6. Experimental arrangement for mass spectrometric study of the low pressure plasmas.

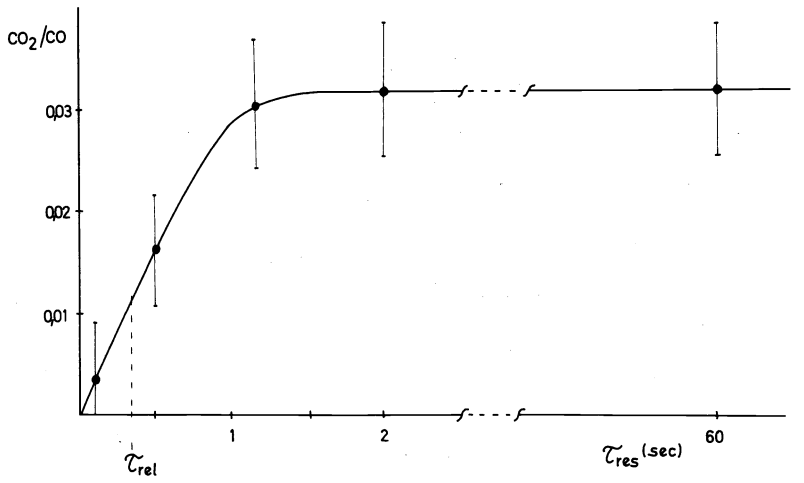


Fig. 7. Dependence of the CO_2/CO-ratio on the mean residence time. Total pressure 3 torr, discharge current 15 mA, inner diameter of the discharge tube 1.2 cm.

discharge on and off and following the approach of the ratio to the steady state value. However, this measurement was limited due to the response time of the recording equipment being about 0.8 sec. Nevertheless, it has been proved that the relaxation time of the CO_2/CO ratio is less than this value.

Brown and Bell studied the oxidation of CO and the dissociation of CO_2 in an intense h.f. discharge.[64] They showed that the contribution of the ion–molecule reaction to the overall reaction rate was small and that the reactions of electrically neutral radicals and atoms predominate in such plasmas. We have found similar results in previous work on chemical transport.[27,28,57,60,65]

3.2. *The transport of carbon with hydrogen*

In an intense low pressure discharge the transport of carbon with hydrogen displays the thermodynamic effect of the plasma. The experiments and theoretical considerations of this system can be found elsewhere.[2,27,65] In the present paper we shall report some recent work on a diagnostic investigation[66] which has allowed an explanation of the transport mechanism. Matrix isolation spectroscopy, used in this work, appears to be a suitable tool for the diagnostics of low pressure plasmas in chemically reacting systems. In addition, some new aspects of the carbon/hydrogen system will be discussed in view of the possible use of carbon in the next generation of Tokamak devices for controlled thermonuclear fusion.[56]

The transport of carbon in hydrogen plasma has been attributed to the formation and subsequent decomposition of simple hydrocarbon radicals. A discussion of the elementary processes occurring in the plasma has brought forth many arguments in support of this mechanism.[27,65]

However, there has been some doubt regarding the validity of this explanation because another equally plausible argument could be suggested: in the thermodynamic equilibrium, the gas phase of this system contains a number of species, i.e. CH_4, H_2, H, C_2H_2, C_2H, CH_3, CH_2, CH, C_3, C_2, C_1.[67,68] At a given pressure, the concentration of each particular species strongly depends on temperature (see Fig. 13 in Ref. 68). The total amount of carbon in the gas phase, expressed by the ratio C:H reaches a minimum around 1300°K at a pressure of 1 torr (see Fig. 14 in Ref. 68). Therefore, the chemical transport of carbon in the direction of increasing temperature (e.g. $900 \rightarrow 1300$°K[27]) could also be attributed to the decreasing "solubility" of carbon in the gas phase with increasing temperature. In such a case, the plasma would merely be catalysing this "thermodynamically possible" reaction. However, the solubility of carbon decreases within this temperature range due to decreasing concentration of methane, i.e. a significant concentration of methane should be found in the plasma.

To determine which of these two possible transport mechanisms is correct, one has to devise a proper diagnostic method for investigation of the gas phase composition under the given experimental conditions. Mass and optical spectroscopy are the most frequently used tools for such investigations. However, both these techniques require the species under consideration to be "activated" by electron impact, which can, however, also lead to their dissociation. Consequently, determination of the true chemical composition of the active discharge plasma by these methods is difficult. In addition, use of absorption spectroscopy (in visible and i.r. region) is frequently hindered by the plasma's own radiation.

In view of these difficulties, matrix isolation spectroscopy appeared to be an attractive tool for the plasma diagnostics in such systems. By this method, species effusing from the plasma, through a small orifice, are trapped and isolated in a solid matrix of an inert gas at cryogenic temperatures (4–15°K) and are subsequently identified by absorption spectroscopy. The problem of plasma radiation is avoided and the whole spectral region from u.v. to i.r. can be utilized for spectoscopic measurements. A large number of papers demonstrate that free radicals, atoms, as well as ions can be isolated and stored in the matrices.[69,70] The problem of fragmentation by electron impact is avoided by the application of this method.

The matrix isolation apparatus used for the study of the C/H_2-system is schematically shown in Fig. 8 (for more details see[66]). The high frequency discharge took place in a quartz tube (1) which is shown in cross section. The construction of the metal "double" Dewar is similar to that described elsewhere.[70–72] The molecular beam effuses from a part of the discharge tube which contains graphite insert (6) through a small orifice (2) ($\phi \approx 150$–$200\ \mu$). It is trapped on a liquid helium cooled, optically polished copper block (3) simultaneously with a suitably chosen matrix gas M (e.g. Ar, Kr, Xe, N_2). After the required matrix has been deposited, the copper block, together with the reservoirs for the liquefied gases, is rotated through 180° and the absorption spectrum of the matrix is scanned through the KBr window (5).

A series of experiments has shown that there is no significant concentration of methane in the plasma under the conditions of carbon transport.[66] Since no fragmentation could take place by this method, the second of the above mentioned mechanisms was ruled out and the mechanism originally suggested was supported.

Hence, the transport of carbon in hydrogen discharge involves the following steps. In the charge region, H-atoms react rapidly with carbon and simple hydrocarbon radicals are formed.

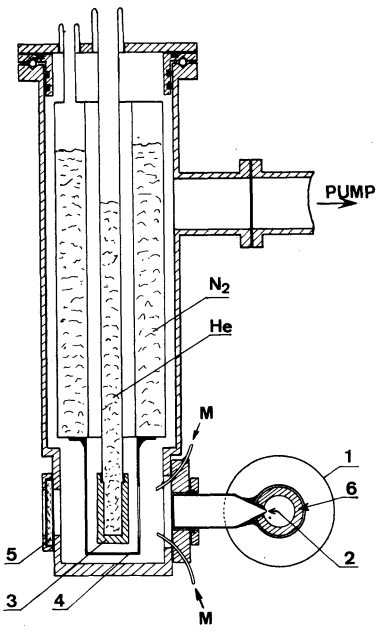


Fig. 8. Dewar assembly for diagnostic investigation of the low pressure plasmas by means of the matrix isolation spectroscopy. (1) discharge tube; (2) orifice; (3) copper block at ≈10°K; (4) heat shield at ≈77°K; (5) KBr window; (6) graphite insert.

Due to the gas flow, the hydrocarbons reach the zone of high plasma energy where they are decomposed by the dissociative de-excitation of the hydrogen metastables.[65] Solid carbon is deposited since its equilibrium pressure is too low at the neutral gas temperature of 1300°K which is found in the deposition zone.

Coulon and Bonnetain have recently shown, that the reactivity of H-atoms towards solid carbon has a local maximum around 900°K (charge zone) and a minimum around 1300°K (deposition zone) (Ref. 73, for further Refs. see also 56). Therefore, the higher temperature in the deposition zone is favourable for the transport to take place and the necessary concentration of hydrogen metastables can be lower than the upper limit estimated earlier.[65] The very interesting questions about the nature of species leaving the carbon surface as well as about the radial distribution of the hydrocarbons in the discharge remain, however, still unresolved.†

The interaction of solid carbon with hydrogen, deuterium, tritium and other particles within a wide energy range (10^{-2}–10^{5} eV) is now being studied in several laboratories because of its importance in further progress towards controlled fusion (e.g. Ref. 74). It has been recently reported that the presence of relatively small amounts of impurity ions in a hot plasma (energy about 10 keV) constitutes one of the most severe impediments to achieving ignition conditions.[75–79] These impurities are released from the first wall of the reactor and from the limiter by plasma-wall interactions such as sputtering, blistering, thermal shocks and chemical reactions. Since low z impurities are more desirable than high z ones, various carbon materials, carbides and nitrides of light elements are proposed as construction materials for the first wall and limiter, in the large Tokamak machines which are now being planned.

Some recent, preliminary investigations[56] have shown, that the chemical erosion of silicon carbide and of a properly chosen graphite (e.g. pyrolytical graphite attack along the c-axis) should not inhibit ignition, provided that the reaction probability of hydrogen atoms with the particular material is not increased as a result of radiation damage to the surface. It is possible, however, that radiation damage to the surface due to a bombardment by high energy particles (above 10^{2} eV) will enhance the reaction probability and then chemical erosion could produce serious problems (for further discussion see Ref. 56). These questions are now being investigated in many laboratories including our own.‡

The control of impurities appears to be the most serious obstacle in the development of the next generation of Tokamaks and consequently the present research activity is very intense. By the time this article is published a large amount of new information will probably be available and hopefully, some suitable material will have been found. Nevertheless, future progress towards controlled thermonuclear reactors will give rise to many new problems for plasma chemists. Let us bear in mind that, in view of the present state of science and technology, controlled fusion appears to be the only way to solve the energy demands of the not-too-distant future, even within the scope of a reasonably limited economic growth.[80]

4. SYNTHESIS OF NITRIDES

The high dissociation energy of nitrogen causes serious problems in the preparation of nitrides at low temperatures. For example, a number of heterogeneous systems involving solid nitrides and HCl or iodine possess quite suitable equilibrium compositions below 1000°C but the deposition of nitride does not take place because of the high activation energy for the reaction of molecular nitrogen with the particular metal.[61] A low pressure plasma with a high degree of dissociation is an ideal means of achieving such a synthesis.

A number of papers on the preparation of thin nitride films by chemical vapour deposition (CVD) or by a direct nitridation of metals in low pressure plasmas is available (e.g. Refs. 3, 19, 54, 81).

By means of a typical CVD technique, volatile compounds of the particular metal are mixed with nitrogen or a nitrogen containing gas (NH_3, $Ar + N_2$) and introduced into the reaction vessel where a discharge takes place. In this way *nitrides of boron*,[19] *aluminum and gallium*[81] were deposited from metal halides and nitrogen. Silane-ammonia mixture is preferred to silicium halides if *silicon nitride* films are deposited for semiconductor devices.[10,11,82] In a given system, better conditions for nitride deposition are to be expected if iodide is used instead of chloride, since the former is generally less stable.[2]

4.1. *Growth of crystals*

Chemical transport of metal with a simultaneous nitridation appears to be a suitable method for the growth of crystals.[6,48] The experimental arrangement is shown in Fig. 9. The discharge took place in a quartz tube (1) between two outer electrodes (4) which were not water cooled in this particular case. The typical discharge parameters were: frequency 80 MHz, discharge current 2–3 A, pressure 1–2 torr, gas flow around 100 torr $cm^3\ sec^{-1}$ and a $N:Cl_2$-molar ratio about 12:1.

Metal chlorides are formed by a reaction of chlorine with the metal sheet (5) in the zone of a low plasma energy at a temperature of about 500°C. They are transported into the insert (2) where a high plasma energy is obtained (high

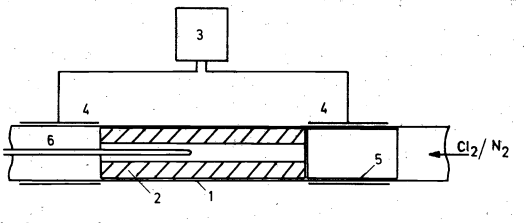


Fig. 9. Experimental arrangement for growth of nitride crystals. (1) quartz discharge tube, $\phi \approx 30$ cm; (2) insert (Al_2O_3, AlN, BN, etc.); (3) h.f. generator (80 MHz, 1.2 kW); (4) electrodes; (5) metal sheet; (6) corundum tube.

†Remark added in proof. More recent measurements utilizing beams of thermally produced H-atoms[103,104] have revealed the decreasing reaction probability at higher temperatures (above about 800°K) under these conditions. In an active discharge, however, no such decrease could be observed, but the reactivity increases monotonically in the temperature region measured so far.[105] Two effects may be responsible for this discrepancy:[105] (a) Since the surface chemistry involves nonlinear processes of different orders[104] the overall mechanism can be different at the high densities of the primary fluxes of H-atoms under plasma conditions, from that at the low densities in the molecular beams. (b) The high energy which is transformed to the chemisorbed layer due to the recombination of ions and atoms, and due to the de-excitation of various species can enhance the surface diffusion (see Ref. 105).

‡Remark added in proof. The effect of the radiation damage has been demonstrated in several papers presented at the recent "Conf. on Surf. Effects in Controlled Fusion Devices" (San Francisco, February 1976) (see Refs. 105–108).

density of the discharge current). Due to this high energy and a relatively low neutral gas temperature (≈1000°C), the chlorides are dissociated and the corresponding nitride is deposited on tube (6) as well as on the inner wall of insert (2). A theoretical discussion of the AlN/Cl_2 and TiN/Cl_2 systems was given in Ref. 2.

Worth mentioning is the purification effect taking place during the synthesis: if aluminum containing zinc, iron, silicon, lead, magnesium and copper is used in the charge zone, only very small traces of silicon and magnesium can be found in the *aluminum nitride*.

A growth rate of about 0.05 mm/hr and 0.2 mm/hr was observed for aluminum and titanium nitride respectively. The aluminum nitride crystals show a mosaic structure with some disorientation in the direction of the a-axis. In some cases twin growth was also observed. Crystals grown near the tube axis apparently have a better stoichiometry and fewer lattice defects than those grown near the wall. This is probably due to radial gradients of plasma parameters such as concentration of electrons and excited species, degree of dissociation, temperature, etc. and to a possible contamination of the growing crystal by the material of the insert.

In a similar way, the radial plasma gradients also influence the growth of *titanium nitride* crystals. The contamination can be avoided by using a titantium sheet as a substrate for deposition. Crystals of a cubic shape with singular faces, shown to be smooth at a magnification of up to 60,000 times, were obtained.

If the plasma energy in the deposition zone was rather less (either a smaller discharge current or a larger internal diameter of the insert) the growing crystals were simultaneously dissolved on the side adjacent to the substrate. This effect was more pronounced if the titanium sheet was placed only in the insert, i.e. there was no metal sheet (5) (see Fig. 9).

The transformation of titanium sheet in the high energy zone into nitride took place due to a short-range transport which has been described for the recrystallization of molybdenum in our recent paper.[2]

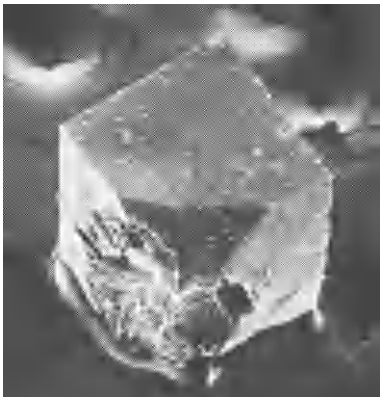
Figure 10a shows such a crystal fixed on the probe holder of the electron scanning microscope. Figure 10b illustrates the position of the crystal during the growth in plasma.

This effect can be explained in terms of the short-range gradients of plasma energy which appear in the vicinity of solid surfaces possessing a high catalytic efficiency for the recombination of atoms and de-excitation of various excited species.[2,28] Without a plasma, the TiN/Cl_2-system is strongly exothermic and the chemical equilibrium is shifted far towards gaseous titanium chloride. Therefore, a high plasma energy is necessary for deposition of TiN to take place.

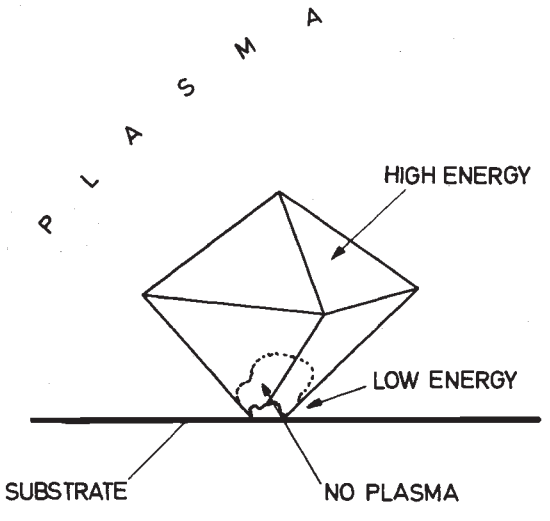
Due to its metallic character, titanium nitride possesses a relatively high catalytic efficiency for surface recombination of atoms and de-excitation of excited species as can be seen in Fig. 5. Consequently, the plasma energy decreases in the space which is screened from the active discharge and there is no plasma inside the hollow of the crystals (Fig. 10b). We have recently calculated the gradients of the degree of dissociation which appear in the vicinity of a flat, i.e. not screened, surface placed in a hydrogen plasma.[56] Similar calculations for the titanium chloride/nitrogen system show that the degree of dissociation decreases by 10% at a distance of about 0.1 mm if the total probability of loss of atoms on the surface, i.e. recombination and reaction, is of the order of 10^{-1} or larger. This means that the degree of dissociation and of excitation decreases strongly at a distance of a few tenths of a millimetre in regions which are screened from the active discharge but, at the same time, a high degree of dissociation is obtained on surfaces which are directly exposed to the active plasma. Thus, the chemical equilibrium is shifted to the chloride on the side adjacent to the substrate, especially in the plasma free hollow, and the crystal is dissolved there whilst it simultaneously grows on the outer surfaces. Figures 10a and b illustrate this interesting transition from plasma chemistry to ordinary chemistry near the thermodynamic equilibrium. One notices, that the attack of the crystal appears within a distance of a few tenths of a millimetre which is in agreement with the estimation given above.

E. Wirz has recently obtained crystals of the high temperature β-modification of *silicon nitride*, using the experimental arrangement shown in Fig. 3.[48,49]

In conclusion it may be said, that, in view of the results obtained so far with these systems, chemical transport in plasma is a promising method for growth of nitride crystals



(a)



(b)

Fig. 10. Titaniumnitride crystal which was, during the growth, attacked on the side adjacent to the substrate. (a) microphotograph (electron scanning microscope) (b) schematic view.

at relatively low temperatures. In order to obtain better crystals a frequency higher than ≈30 MHz and h.f. power ≈4 kW or more should be used. In addition, the plasma energy necessary for the deposition of nitrides should be less if iodine or bromine is employed instead of chlorine.[2]

4.2. *The synthesis of phosphorus nitride*

This is another example which illustrates the advantage of plasma chemistry. Recent thermodynamic calculations have shown that the formation of phosphorus nitride requires the use of high temperatures.[83] On the other hand, nitrogen reacts with phosphorus at a low temperature under plasma conditions and solid phosphorus nitride of various compositions between P_3N_3 and P_3N_5 can be obtained.[84–86] This compound is used for doping of semiconductors (e.g. silicon). Our recent study of thin films of phosphorus nitride P_3N_5 has revealed the excellent dielectric properties of this compound.[9]

The films have been prepared by a direct synthesis from the elements in a high frequency low pressure nitrogen discharge (for further details see Ref. 9). At a temperature of about 265°C, X-ray amorphous thin layers could be deposited on various substrates. They are transparent in the visible and near i.r. regions. An absorption edge around 350 nm and two strong, broad absorption bands with maxima at 8.2 μ and 11.2 μm have been found.

Permittivity of 4.4 (±0.4) at room temperature is independent of frequency within the limits of accuracy of measurement between 1 kHz and 20 MHz and increases linearly with temperatures between 77 and 525°K. The corresponding temperature coefficient is 3.6×10^{-4} deg^{-1}. The films show relatively low dielectric losses, $\tan\delta \lessapprox 10^{-2}$ at 1 kHz, and a high dielectric strength of up to 1×10^7 V cm^{-1}.

All these values are quite comparable with those of typical dielectric films such as SiO_2 (see Table 2) and possibly they can still be improved by further preparative work. Phosphorus nitride might therefore find some applications in semiconductor technology, especially for compound semiconductors (e.g. gallium phosphide). Further work on the preparation and relevant characterization of this material is now being done in our laboratory.

5. TRANSPORT WITH HYDROGEN

A number of binary compounds—commonly called "hydrides"—are formed by reactions of discharge activated hydrogen with corresponding elements or compounds.[1,87,88] Many of these hydrides are volatile and they decompose at higher temperatures. In such systems chemical transport of the element can take place.

This phenomenon was first described around the year 1920 and, since it appeared as an anomalous strong cathode sputtering of some elements by hydrogen, it was called "chemical cathode sputtering".[89,90] However, Güntherschulze had already shown that "sputtering" of As, Sb and Bi took place even if they were not electrically connected with the cathode, but only placed in the positive column of glow discharge at floating potential.

Güntherschulze originally thought that this phenomenon was due to an interaction of hydrogen ions with the solid,[80,90] but later work of other authors showed that the formation of volatile hydrides can take place by reactions of H-atoms at thermal energies (e.g. Refs. 1, 88). Whatever the particular mechanism of the process may be, one has to distinguish between real *sputtering* and *chemical interactions* with the surface. In the former case the primary particle penetrates into the solid and an atom of the solid is sputtered due to a momentum transfer from the primary particle to the crystal lattice. This phenomenon is observed at high energies and does not take place below some threshold energy which depends on the particular system. The ion energy in the low pressure plasmas of the positive column of a glow discharge is far below these threshold energies even if ambipolar diffusion is considered (e.g. Ref. 56). Moreover one can calculate that the total flux of ions towards the surface of the solid is too small to be able to cause the observed rate of the reaction (e.g. Refs. 27, 66).

High energy sputtering is theoretically well understood at the present time,[91] but only very little is known about the interactions of gaseous particles with solid surfaces at energies below 100 eV.[26,109] The transport phenomena which will be discussed in this section occur at thermal energies.

The transport of a number of elements with hydrogen plasma have been described previously: As, Sb, Bi, Se, Te,[89,92] C,[27,89] Ge, Si,[93] P.[8] The *carbon transport* has already been discussed in Section 3.2. There is no doubt that this transport takes place due to the formation and subsequent decomposition of volatile hydrocarbon compounds, and that the reaction of electrically neutral species dominate.

The *transport of germanium and silicon* took place only in the direction of increasing neutral gas temperature $T_1 \longrightarrow T_2$, but the discharge current density was nearly constant between the charge and the deposition zone.[93] The experimental arrangement was similar to that shown in Fig. 11, but the deposition of germanium and silicon took place only if the deposition zone was heated up to 400 and 600°C respectively. In view of the very low deposition rate of about 20–50 nm hr^{-1}, a reaction mechanism involving ions cannot be completely ruled out in this case. However, experimental findings of other authors indicate that the hydrides are formed rather by reactions of H-atoms.[110]

For example, Radford observed formation of gaseous monohydride radicals like SeH, TeH, etc. during a reaction of the corresponding element with hydrogen

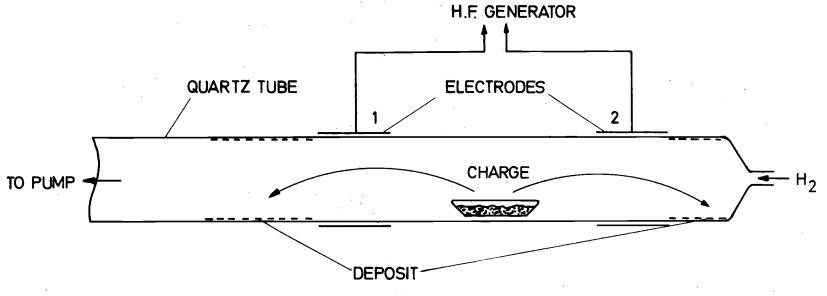


Fig. 11. Experimental arrangement for transport of red phosphorus with hydrogen.

afterglow.[94] The high concentration which was found—about 5 and 1% for SeH and TeH respectively—excludes any significant role of ions. SiH was observed by optical spectroscopy in an arc discharge taking place between two silicon electrodes (Ref. 95, p. 227). If silane is introduced into a weak low pressure discharge, a solid of the composition SiH_x ($x = 1.2$–1.7) is deposited, which again indicates that hydride radicals SiH_x ($x = 1.2$) are formed in the plasma. The solid decomposes at higher temperature with the formation of solid silicon and hydrogen (Ref. 95, p. 229).

All these findings indicate, that the transport of silicon and germanium involves the formation and subsequent decomposition of volatile hydride radicals. Participation of ions in this process cannot be completely excluded, but it seems to be improbable.

5.1. *The transport of phosphorus*

This has been studied only recently.[8] Since it involves some very interesting surface processes, we shall discuss it in more detail.

The experimental arrangement is shown in Fig. 11. The high frequency discharge took place in a quartz tube of an inner diameter of 40 mm between two external, water cooled electrodes. The typical discharge parameters were as follows: frequency, 24 MHz; total pressure, 1 torr; gas flow rate, about 140 torr $cm^3\,sec^{-1}$; discharge current, between 0.5 and 1 A and distance between the electrodes, 150 mm. X-ray amorphous, red phosphorus (Merck, techn. qual., Art. 7270 Lab) and hydrogen of purity better than 99.995% were used. A phosphorus charge in a quartz boat was inserted into the zone between the two electrodes and carefully outgassed (see Ref. 8).

Under the above specified discharge conditions, several grams of phosphorus could be transported in an hour, as indicated by the arrows in Fig. 11. The neutral gas temperature reached a value between 250 and 370°C at the charge and a value between 150 and 200°C in the deposition zone. A linear growth rate of phosphorus layers around 0.5 mm hr^{-1} was observed. Due to the high deposition rate, glass-like, X-ray amorphous, red phosphorus is formed (density 2.09 g cm^{-3}, specific resistivity $\gtrsim 10^8\,\Omega$cm).

When the discharge tube on the left of electrode 1 was externally heated above 250°C, no phosphorus was deposited there. The deposition took place further to the left where a temperature around 150°C prevailed.

If, on the other hand, the discharge tube was cooled by means of flowing water between the two electrodes, deposition of red phosphorus occurred in that region within a few seconds after the beginning of cooling.

Little transport was observed when pure argon was used instead of hydrogen. The transport rate was more than two orders of magnitude less than that with hydrogen, and this could be due to traces of hydrogen since it is impossible to completely remove moisture from the technical phosphorus and from the quartz tube.

A strong purification effect which appears during the transport can be of practical interests. Preliminary investigations have shown that impurity content of elements like B, Na, Mg, Ca, Cl, Mn, Fe is diminished by several orders of magnitude up to the ppm level. Some problems arise from the contamination of phosphorus with silicon from the discharge tube (up to several ppm). Nevertheless, there is a good possibility of avoiding this contamination by a proper design of the discharge tube. The advantage of plasma transport as a purification method could be the simplicity of the procedure. Pure hydrogen, which is the only chemical used, is cheap and simple to handle. Also, no white phosphorus, which is dangerous, is involved in the process. The purification aspects of the transport are now being investigated in our laboratory.

Let us now discuss the possible transport mechanisms. Red phosphorus is thermodynamically more stable than the white one, and it can exist in a number of crystallographic modifications.[86,96] For evaporation, several P–P lattice bonds must be broken and a P_4-tetrahedral gaseous molecule formed. This requires a large activation energy and, consequently, the evaporation is kinetically slow ($E^*_{evap}(P_\infty, \text{red}) = 52$ kcal mol^{-1}). An evaporation coefficient less than 10^{-6} has been found.[84,97,98]

The equilibrium vapor of the heterogeneous system consists of the P_4 tetrahedra. If solid phosphorus is deposited at near equilibrium conditions, only the metastable modification, the white phosphorus, is formed, having a molecular crystal lattice composed of these P_4 species. The evaporation of this modification involves a low activation energy and the evaporation coefficient is one.[84,97,98]

It is seen, therefore, that in the plasma transport of red phosphorus two effects are involved: First, the high activation energy for the evaporation of red phosphorus is circumvented by some surface process and, second, the deposition of red phosphorus is made kinetically possible due to the absence of P_4 molecules in the gas phase.[8]

Let us consider the evaporation. One may ask whether the observed high rate of evaporation could be due to some surface melting. Such a possibility cannot be excluded without conclusive proof since H atoms are impinging on the surface at a rate of 5×10^{20}–10^{21} $sec^{-1}\,cm^{-2}$. This gives at least 10^3–10^4 recombination events, $2H \rightarrow H_2$, occurring on each surface site per sec. Figure 12 shows a microphotograph of the surface of the red phosphorus layer which has been exposed to the hydrogen discharge at about 320°C for 13 min. There is no indication of surface melting, even with the highest resolution obtainable on this material (about 30,000x). In addition, careful measurements of the temperature have been done, but no significant overheating of phosphorus was found. Therefore, surface melting can be

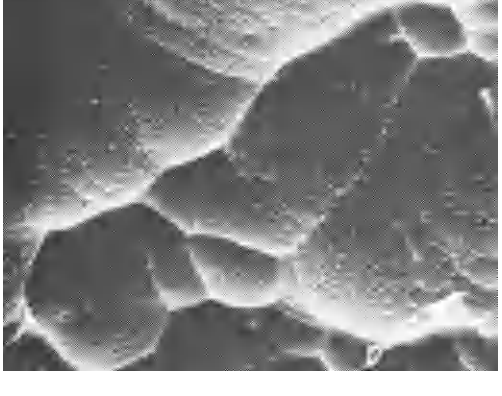


Fig. 12. Surface of the red phosphorus layers which has been exposed to hydrogen discharge at 320°C for about 13 min (electron scanning microscope, 360×).

excluded and some surface chemical processes must be involved in the transport mechanism.

A detailed analysis of surface processes belongs to the most difficult problems in chemistry and one is not able to give a final solution of this problem now. However, a step by step discussion of all possible processes, which will lead to an interesting model of the chemical evaporation of phosphorus will be given.

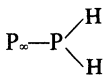
The primary flux of H atoms between 5×10^{20} and 10^{21} cm^{-2} sec^{-1} corresponds to about 5×10^{5}–10^{6} atoms impinging every second on each surface site. It is evident, that a PH species strongly bonded to the phosphorus surface will be immediately formed with any P surface atom possessing a free electron (e.g. atom No. 21 in Fig. 2 of Ref. 99):

$$P_{\cdot} = P\cdot + H \longrightarrow P_{\infty} = P\text{–}H \qquad (5.1)$$

The desorption frequency, ν_{des}, of the PH species is extremely low at a temperature of about 250 to 315°C as can be calculated from the formula $\nu_{des} = \nu_0 \cdot \exp(-E^*_{des}/RT)$.[100] Assuming $\nu_0 = 10^{12}$–10^{13} sec^{-1}, and that $E^*_{des}(P\text{–}H) \approx E^*_{vap}(P,\ red) \approx 50$ kcal mol^{-1}, $\nu_{des} \lessapprox 10^{-7}$ sec^{-1}.

The overall surface density of H-atoms which are adsorbed on the surface can be estimated only roughly. In analogy with other systems (e.g. Ref. 101) one can expect a desorption energy $E^*_{des}(H) \gtrapprox 20$ kcal mol^{-1} which gives a desorption frequency of about 10^{3}–10^{4} sec^{-1}. This is equal to, or smaller than the number of H-atoms sorbed on one site per second if a sticking probability larger than, or equal to 10^{-2} is assumed for the impinging H-species (c.f. Ref 102). Thus, the phosphorus surface is almost completely covered with a chemisorbed layer of atomic hydrogen.

Two H-atoms adsorbed on adjacent sites can break the corresponding P–P bond with either the formation of two P_∞=P–H groups (e.g. atoms No. 19 and 20 in Fig. 2 of Ref. 99), or one P_∞=P–H and one

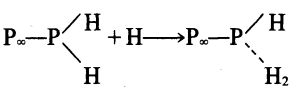


(5.2)

group (e.g. atoms No. 21 and 17 or 21 and 18 in Fig. 2 of Ref. 99). The latter process occurs if a P–P bond between a PH-group (see eqn 5.1) and a neighbouring P-atom is attacked. Considering the energies of P–H and P–P bonds (about 77 kcal mol^{-1} and 48–58 kcal mol^{-1} respectively[84–86]) it is evident that both those steps are strongly exothermic. Due to the low desorption frequency of the PH species, each formation of a PH group is probably followed by the formation of (5.2).

Also the PH_2-species are chemisorbed relatively strongly to the phosphorus surface as shown by the following consideration: A desorption frequency of the PH_2 species equal to the lowest value of the sticking rate of H atoms, $\nu_{des} \approx 5\times10^{3}$ sec^{-1}, is obtained if a desorption energy $E^*_{des}(PH_2) \approx 20$ kcal mol^{-1} is assumed. Since this value is much less than the bonding energy (E(P–P) ≈ 48–58 kcal mol^{-1}) a direct desorption of PH_2 is much slower than the sticking rate of H-atoms.†

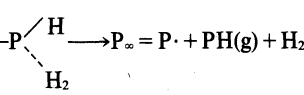
Therefore, another H-atom will probably impinge on the strongly chemisorbed PH_2-group (5.2) and recombine with one of the H-atoms there:



(5.3)

The H-atom can come either directly from the gas phase, or from a weakly bonded, mobile ("liquid") layer which is adsorbed on the first one.

The step (5.3) is then followed by the formation either of gaseous PH and H_2 species (5.4),



(5.4)

$$\Delta H \approx 26 \pm 5 \text{ kcal mol}^{-1}$$

or of the PH_3 molecule

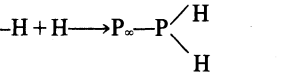
$$P_\infty\text{—}P\text{—}3H \longrightarrow P_\infty = P\cdot + PH_3 \qquad (5.5)$$
$$\Delta H \approx -24 \pm 5 \text{ kcal mol}^{-1}$$

The latter process, although exothermic, seems to be less likely because of steric reasons. In addition, if the transport were to take place by the formation and subsequent decomposition of the PH_3 species, the deposition of phosphorus should be enhanced at a higher temperature (see eqn 5.5). However, the opposite effect has been observed experimentally and an insignificant amount of gaseous products was condensed in a cold trap (77°K) attached to the outlet of the discharge tube.

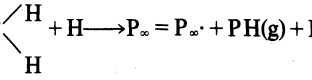
In conclusion, the proposed mechanism of the chemical evaporation of red phosphorus can be summarized as follows:

$$P_\infty + H \longrightarrow P\cdots H \qquad (5.6a)$$

$$P_\infty\cdots H \longrightarrow P_\infty = P\text{–}H \qquad (5.6b)$$



(5.6c)



(6d)

Considering the known crystal structures of red and black phosphorus,[86,96,99] it is easy to see, that this mechanism produces more and more active sites $P_\infty = P\cdot$. Therefore, the overall reaction rate (which might be very low for an ideal surface) will increase up to a steady state value corresponding to a surface with a high density of the active sites.

The previous estimations indicate that the rate limiting step should be the desorption of PH and H_2, (5.4). An activation energy for this process of $E^*_{des}(PH + H_2) \gtrapprox \Delta H$ (5.4) ≈ 26 kcal mol^{-1} along with a surface site density of the order of 10^{15} cm^{-2} gives a total evaporation rate of $\lessapprox 5\times10^{17}$ P-atoms cm^{-2} sec^{-1}.

An experimental value between about 5×10^{16} and 5×10^{17} cm^{-2} sec^{-1} has been estimated from the weight loss of the phosphorus charge. The uncertaintity is due to the unknown ratio of the active surface and the geometric area of the phosphorus powder used.

†Remark added in proof. As pointed out by Olander (D. R. Olander, Univ. of Berkley, Private communications), the rate of formation and desorption of the PH_2 group could be enhanced by a high activation entropy (increase of the number of rotational degrees of freedom). Such an effect was reported recently by Madix *et al.* (see also Ref. 26a) for Co desorption from Nickel.[111]

A better estimation could be obtained from the linear deposition rate of about 5×10^{-2} cm hr^{-1} when the discharge tube was cooled by flowing water at a place close to the charge (see above). The absolute temperature of such a layer during deposition is about half that of phosphorus charge, which results in a decrease of the factor $\exp(-E^{\ddagger}_{es}$ (5.4)/RT) by orders of magnitude. It means that the evaporation from this layer is negligible, and the deposition rate at the cooled place is equal to the evaporation rate at the charge providing, that diffusion limitations can be omitted. The latter is approximately valid if the cooled surface is small. The deposited layers of red phosphorus are glass like and the ratio of active surface : geometric area estimated from microphotographs is between 1 and 3. Thus, the calculated deposition rate of about $2\text{–}6 \times 10^{17}$ cm^{-2} sec^{-1} can be directly compared with the theoretically estimsted evaporation rate of $\lesssim 5 \times 10^{17}$ cm^{-2} sec^{-1}.

The agreement supports the proposed mechanism. Moreover, the considerations of the last paragraph also show why the transport takes place in the direction of decreasing temperature even at a constant concentration of H atoms.

Such an agreement, of course, gives no conclusive evidence for the correctness of the proposed model. Only further experiments will allow a better understanding of the transport mechanism. The actual significance of the model consists in the fact that it allows one to formulate the problems to be studied and enables experiments to be done more precisely.

6. CONCLUSIONS

Plasma chemistry is being developed in a region somewhere between physics and chemistry. The choice, generation and characterization of a suitable plasma presume a deep knowledge of plasma physics but their application to interesting and important chemical problems requires the experience and imagination of chemists.

The success of plasma technique in various fields such as semiconductor technology, deposition of organic polymer films, plasma spraying, preparation and modification of powder materials, justifies the efforts of many scientists and technologists in this field. In contrast to these results, there has been relatively little progress towards the understanding of the basic processes occurring in the plasma. The present article summarizes part of the recent investigation of these latter problems.

Low pressure plasma chemistry is a method "par excellence" for doing "high temperature chemistry" at low temperatures. It is especially suitable for deposition of thin films and crystal growth since the reaction yield is not limited by the low pressure, as it is in many homogeneous systems.

An energy of reaction, as well as an activation energy of up to 100 kcal mol^{-1}, can be supplied by the plasma at temperatures of less than 1000°C for both the neutral gas and solid. Thus, strongly endothermic reactions can take place at low temperatures and the rates of many processes, including the evaporation and deposition of solids, which involve some kinetically hindered steps, can be significantly enhanced by using plasma.

There are many basic problems to be solved in the future work. Particularly, more attention has to be paid to the interactions of plasmas with solid surfaces, which also involves a detailed study of surface chemistry. A better understanding of the basic processes will surely open new possibilities for plasma applications.

The erosion of solids by atoms, radicals, excited species and ions, with energy varying over a wide range, is now being investigated because of the impurity problems in the Tokamak devices for controlled thermonuclear fusion. This appears to be one of the most serious impediments towards achieving ignition conditions. Similar kinds of erosion also arise in the exhaust of rockets and during the entry of satellites and spacecraft into the atmosphere of the earth and other planets.

Chemical transport of solids in low pressure plasmas is a promising preparative method, as well as a simple diagnostic technique for studying the behaviour of heterogeneous systems under plasma conditions. The possible use of plasma transport for solid purification requires further investigation into this effect.

It has not been possible in this article to cover the whole field of heterogeneous reactions under plasma conditions. We have attempted rather to illustrate with several selected examples the unique properties of low pressure plasmas and the feasibility of their applications to preparative solid state chemistry.

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