ON A POSSIBLE CONTRIBUTION OF THE RECOMBINATION ENERGY OF ATOMS TO THE OCCURENCE OF HETEROGENEOUS REACTION IN MOLECULAR GLOW DISCHARGES.

V. Hermoch
Institute of Physics Czech. Acad. of Sciences, 180 40
Prague 8, Na Slovance 2, Czechoslovakia

Keywords: Heterogeneous processes

Compounds: Atom recombination energy and heterogeneous reactions

ABSTRACT

Qualitative discussion on the transformation of recombination energy into a solid and the contribution of this energy to the occurence of heterogeneous plasma reactions is presented.

1. INTRODUCTION

There is a well known fact, that the heterogeneous reactions /reduction, oxidation, nitridation ets [1,2]/ occuring under nonisothermal plasma condition procede at higher rates in comparison with the reaction under thermal condition. This effect is explained by an active role of atoms of the glow discharge molecular plasma in the above mentioned processes.

The aim of the present paper is to point out another possible effect[3] influencing the rates of reactions, namely that of the recombination energy of atoms.

2. ON THE TRANSFER OF RECOMBINATION ENERGY TO THE SOLID

The degree of dissociation of molecular plasma depends on respective molecular gas and on the discharge type and its parameters. It ranges from some fraction of per cent to several tens of per cent[4,5,6,7]. Most of these atoms do not participate immediately in the described reactions, but they recombine on the surface of discharge vessel or on that of the substrate.

The surface recombination is basically a three-body reaction, that can be characterized by the equation

$$A + A + M \quad A_2 + M + (E_R) \qquad (1)$$

where A, A_2 denotes atoms or molecules resp., M - the surface and E_R - the recombination energy /4,48 eV, 5,08 eV, 9,7 eV for H, O and N atoms resp./. The presence of the surface makes possible a simultaneous energy and momentum conservation, leading thus to the stabilization of the resulting molecule. Whereas in the case of volume recombination the formation of electronically or vibrationally excited molecules occures very often, the same process for surface recombination is just rarely[8,9] observed.(Even a thorough cleaning of the experimental system avoided production of excited molecules[10]). However this means that the entire recombination energy (or at least its great part) has to be absorbed by the solid. This effect is currently used in a method for measurement of atom concentration in a low pressure plasma. With the exception of the papers[11,12,13], the mechanism of the recombination energy transfer into the solid has not been solved yet.

The transfer of the energy of the magnitude below 1 eV was solved with the help of the classical as well as quantum mechanical theory in a number of papers[14,15]. From these papers it follows that the efficiency of a transfer into solids is energetically limited. This is described by means of an accomodation coefficient, which expresses the fraction of imparted energy absorbed by the solid. The authors[11,12,13] used this mechanism to explain their results. As the magnitude of the recombination energy as well as accomodation coefficients are very high the conception of the mentioned authors seems to be not without problems.

Neither the results of the energy transfer studies for energies higher than 25 eV[16,17] are immediately applicable to the energy region, that important for the studied effect. Nevertheless, these results may be used to present at least a qualitative model of energy transfer mechanism, connected with surface atomic recombination.

The first idea, originally elaborated for the elucidation of the effect of radiation and ion bombardement inside the volume of a solid is based on the existence of the so called thermal spike[17], defined as a limited volume with most of its atoms temporarilly in motion. According to the authors[16], spike effects may became important when the spike lifetime is larger than the duration of its initiation. In the following a modification of the above mentioned concept for the solid state surface of solid will be used.

As the interatomic spacings of most solids[18] are considerably larger than those of diatomic molecules it can be supposed, that the recombination energy will be transmitted to only one of the surface atoms. Formally, this is equivalent to the application of a pointlike, instanteneous acting heat source of magnitude E_R at the surface of the solid. Volume/time temperature distribution around the source is given by the equation

$$T_0 + T(r,t) = \frac{2E_R}{c\varrho(4\pi a t)^{\frac{3}{2}}} \exp\left(-\frac{r^2}{4at}\right) \qquad (2)$$

where T_0 is the ambient temperature, $r^2=x^2 + y^2 + z^2$ - square of the distance from the source, t - time, c - specific heat, ρ - mass density, $a=\lambda/c\varrho$, λ - thermal conductivity. Applicability of the above equation is restricted mainly by uncertainty in the appropriate value of λ . (According to the calculation[19] carried out under thermal spike condition the thermal diffusivity for Cu has been found to be an order of magnitude lower than the experimental value.

Therefore we use another approach, suggested by the author[20]. We can suppose, in accordance with the spike definition, that all the particles within a semisperical volume, the centre of which concides with the recombination event, will be set in motion as a result of the recombination.

If we suppose that the mean increase of the energy of particles inside the spike is equal to 0,1 eV and the recombination energy of the atom is 5 eV, we get the number of particles as 5/0, 1 i.e. 50. (0,1 eV corresponds to 800K in the E=3/2 kT model). From this the radius of semispherical volume containing the calculated 50 particles may be determined. Its average value is about $(6 - 10) \cdot 10^{-10}$ m.

The validity of this procedure may be verified by comparing the velocity at that the energy is propagating within the spike with the time over that the local equilibrium in the spike is established.

According to the classical theory of heat conduction the heated region of radius r_s is cooled within the characteristic relaxation time of the order τr_s^2 , where $\tau = c\varrho/4\lambda$ In our case, as we are interested in the processes on the insulators, the appropriate value for λ_1 is that of glass and glasslike materials ($\sim 10^{-1}$ W m^{-1} K^{-1}). The relaxation time is then of the order of 10^{-12} s.

The recombination energy is transferred to the central particle of the spike in time 10^{-13} s[8]. Inside the spike the released energy will be transferred by two-body collisions of the type ion-ion, electron-electron and electron-

-ion. The first type of collision is the most efficient one, its characteristic time of the energy exchange being of the order of 10^{-13} s. As we see, the relaxation time τr_s^2 is an order of magnitude higher than the collision time so that can be assumed, that the local equilibrium will be established almost completely.

3. INFLUENCE OF THE SPIKES TO THE OCCURENCE OF THE HETEROGENEOUS REACTIONS

It follows, that the surface atomic recombination event results in a local energy increase of about 50 particles of the hemisperical spike; from these about 20 particles are situated at the surface. It is clear that the number of spike particles, their energy increase and spike dimension depend on the type of recombining atoms and on the properties of solid surface.

Even though the energy increase of spike particles is not sufficient to produce some material defects (intersticials, vacancy ets) it is nevertheless high enough to accellerate surface processes[21] (surface migration of adsorbed particles, chemisorption processes, place-exchange processes, nucleation ets.) and increase the rate coefficient of chemical reactions under plasma condition. As the influence of the spike effect is bounded to the this surface layer the diffusion does not lose its importance for growing thick layers by plasmochemistry.

We can mentioned another group of results, showing the possible role of the spike effects. Many papers[5,7] concerned with the atomic particles concentration measurements refer to the change or the increase of the atomic recombination coefficient γ on the glass walls, in the case of an interaction of the walls with molecular plasma. In comparison with the recombination coefficient, gained from measurement with the plasma outside the active zone, the values of γ are by several orders of magnitude higher. The increase corresponds to the value of several hundred of K in the vicinity of glass walls. Because such a high temperature is hardly possible to admit, the only reasonable explanation is due to the influence of the spikes. Similar argument may be applied for explanation of permanent or temporary changes in the glass walls composition[7,24] of the tube in which the discharge of the molecular gas burns.

As a last example the methods of plasma etching of polymers[25] may be mentioned. In this case the polymer may be chemically changed or demaged by an enormous increase in the energetically active particles due to the spikes. It is to a certain degree similar to the ion etching of metallic or unmetallic materials.

4. CONCLUSION

The direct verification of the above hypotheses is difficult. Nevertheless we feel that the role which the recombination energy of atoms plays for heterogeneous reactions inside the plasma discharge tube, is substantial.

Further study of this effect is necessary to elucidate not only the rate of plasmachemical reaction but also the nature of the recombination coefficient itself.

REFERENCES

(1) F.K. Mc Taggart, "Plasma Chemistry in Electrical Discharges" (Elsevier, Amsterdam 1967).
(2) J.R. Hollahan, A.T. Bell, "Techniques and Application of Plasma Chemistry" (A. Willey Interscience Public., 1974).
(3) V. Hermoch, Proc. V. Conf. Czech. Phys., Košice 1977, 433.
(4) H.D. Beckey, K.P. Warneck, Z. Naturfschg 10a, 62 (1955).
(5) H. Sabadil, L. Biborosch, G. Koebe, Beitr. Plasmaphys. 15, 319 (1975).
(6) V. Hermoch, Proc. IV Conf. Czech. Phys., Liberec 1975, 369.
(7) D.I. Sloveckij, P.D. Todesajte, Chimija vysokich energij 7, 291 (1973).
(8) S.H. Baumford, C.F.H. Tipper, "Vozbužděnyje častici v chimič. kinetike" (Mir, Moskva 1973)(Rus. transl.).
(9) P. Harteck, R.R. Reeves, Disc. Faraday Soc. 37, 82 (1964).
(10) T.R. Rolfes, R.R. Reeves, P. Harteck, J. Chem Phys. 69, 849 (1965).
(11) B.J. Wood, J.S. Mills, H. Wise, J. Phys. Chem. 67, 1402 (1963).
(12) G.A. Melin, R.J. Madix, Trans. Faraday Soc. 67, 198 (1971).
(13) G.A. Melin, R.J. Madix, Trans. Faraday Soc. 67, 2711 (1971).
(14) R. Zwanzig, J. Chem. Phys. 32, 1173 (1960).
(15) J.D. Doll, L.E. Myers, J. Chem. Phys. 63, 4908 (1975).
(16) P. Sigmund, Appl. Phys. Lett. 25, 169 (1974).
(17) F. Seitz, D. Turnbull, "Solid State Physics", V 2, (1956 (Acad. Press, New York).
(18) G. Ehrlich, J. Chem. Phys. 31, 1111 (1951).
(19) G.H. Vineyard, Disc. Faraday Soc. 31, 7 (1961).
(20) M.W. Thompson, "Defects and Radiation Demage in Metals (Univ. Press, Cambridge, 1969).
(21) S.J.R. Saunders, Sci. Prog., Oxf., 63, 163 (1976).
(22) V. Hermoch, Proc. 13. ICPIG, Berlin 1977, P.I., 251
(23) K. Mašek, L. Láska, Acta Slovaca Physica, 2, 172 (1979).
(24) H. Dunken, H.J. Tiller, Zeitst. Phys. Chem. 244, 305 (1970).
(25) Z. Pelzbauer, Faserfschg. Textiltechnik 29, 71 (1978).