

Heterogeneous Reactions in Nonisothermal Low Pressure Plasmas.  
Preparative Aspects and Applications

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The topics include three types of chemical reactions: 1) Chemical evaporation and deposition of solids:  $A(s) + B(g) \rightleftharpoons C(g) + D(g) + \dots$  2) Modification of the solid and/or its surface:  $A(s) + B(g) \rightarrow C(s)$  (e.g. anodization and nitridation of metals, etc.) 3) Reactions in which the solid is involved as a "third body" (e.g. heterogeneous recombination of atoms). The main part of this talk will be devoted to the first type of the reactions.

In fact, there are two ways for a plasma to influence a particular heterogeneous system. a) Kinetic effect: A weak discharge can catalyze a reaction which is favourable thermodynamically ( $\Delta G^r < 0$ ), but which does not take place without the plasma due to a high activation energy. For example, thin films of oxides, nitrides and other technically important materials can be deposited at a low temperature ( $200-400^\circ C$ ) which is advantageous for the fabrication of semiconductor devices. b) Thermodynamic effect: The high internal energy of the intense low pressure discharges can significantly change the chemistry of a particular heterogeneous system and allow for strongly endothermic reactions between a gas and a solid to take place at a temperature of the solid below  $1000^\circ C$ . The growth of crystals of nitrides and the recrystallization of refractory metals should be mentioned as an example.

In the wide region of the existence of the low pressure plasmas (discharge current between  $10^{-3}$  and several amperes) both these effects appear more or less simultaneously. Theoretical considerations of such systems are very difficult because of the large number of the elementary processes involved and the lack of data on the reaction rates. Any substantial progress of the theory requires an accumulation of

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more experimental and preparative experience, a better and more detailed diagnostic and, last but not least, more data on the elementary processes.

The chemical transport of solids in low pressure plasma has appeared to be a promising preparative method as well as a simple tool for the investigation of the behaviour of heterogeneous systems under plasma conditions. Several transporting system will be discussed together with the results of the recent diagnostic investigations by means of the matrix isolation spectroscopy. Of particular practical as well as theoretical interests is the plasma catalyzed sublimation of the red phosphorus in a hydrogen plasma. In addition, the formation of the excited HCN molecules in a cw HCN laser will be mentioned among other applications of the heterogeneous reactions in the low pressure discharges.

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