On the role of surface processes and dust in plasma processing and in astro-chemistry

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1. Introduction
For optimization of plasma processing as molecule formation, deposition and etching a full understanding of the processes as dissociation, radical formation, the role of ions and electrons, surface processes and the role of energy have to be studied. In this contribution a summary will be given on advances on these physical processes. In particular the effects of dissociation by charged particles, radical interactions and of formation of new molecules together with the influence of charged particles are discussed, as well as their impact for cluster growth. In recent years the emphasis, given previously to volume processes, has shifted to include the role of surface processes.
2. Plasma structure and processes
A more general picture is developed of chemical plasmas, which include spatial (and/or temporal) structure.
1. In this picture at some place (or time), where power is dissipated plasma is created, the plasma is ionizing: around this hot plasma (or later in time), in a larger volume, a colder recombining and more passive plasma develops. In other words plasma is at first a dissociating medium: molecules injected or formed are being dissociated in the active plasma by electron induced dissociation and in the recombining plasma by dissociative recombination of molecular ions; association takes place primarily at the surface; molecular ions in turn can be formed from atomic ions by charge transfer between molecules and atomic ions. These processes are important for molecular plasmas, and cause these to recombine faster than purely atomic plasmas. At low pressure produced radicals can commonly not associate to molecules in the plasma volume, as then commonly a third body reaction is necessary.
2. Hence most radicals (probably transformed in other radicals by two body reactions) will arrive at surfaces of the experiment and/ or surfaces of clusters and dust particles formed in the plasma. In plasmas the incoming flux of radicals is much larger than the thermal Langmuir Hinshelwood desorption flux and thus chemically active surfaces get saturated with radicals and become passivated. This differs thus from the situation in CVD and catalysis when the incoming flux of radicals is much smaller than the LH desorption flux as a hot surface and weak fragmentation. In the first few ms of a discharge surfaces change when surfaces are covered and other (“hot”) association reactions may produce new and excited molecules. This in turn may give rise to dissociative attachment and formation of negative ions. These may play a role in the formation of small clusters in plasmas with silanes & oxygen or hydrocarbons. The question is then: which is first: new molecules or cluster formation. In this framework surface reactions are discussed which lead to deposition and the possible role of radicals, charged particles and clusters.

Keywords: processes in plasmas, surface reactions, radicals, charged particles, clusters

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