Hydrogen atom sources; hydrogen kinetics, anomalous recombination and possible relevance to deposition

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Hydrogen atom sources; hydrogen kinetics, anomalous recombination and possible relevance to deposition

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The kinetics of hydrogen is an important subject for plasmachemistry for several reasons. Atomic hydrogen is used for treatment of semi–conductor layers. Hydrogen is used as a selective etching agent in plasma deposition of crystalline carbon layers as diamond[1] and graphite[2]. Also it is a constituant in plasmas used for the deposition of amorphous hydrogenated carbon [1] and silicon layers[3]. On a more fundamental level hydrogen discharge can be seen as one of the most simple plasma chemical systems.

The present study was aimed at the production of intense atomic hydrogen beams. To this end the expanding beam method was employed, described in an other contribution to this conference[3]. In this method the plasma is produced in a flowing subatmospheric cascaded arc plasma with plasma currents up to I=100A. This plasma flows from the cathodes to the anode, which serves as the nozzle to the expansion chamber. This latter is pumped to a pressure of 1–20 mbar. In the arc the ionization degree is typically 2–10% and the dissociation is above 50%. The dissociation of the emanating arc plasma has been obtained[4] by measuring the heat loss from the arc and comparing the loss with the power input to the arc. The dissociation degree at I=50A varies between near to 90% to 60% if the flow is varied from 50–100 scc/s H_2. Hence, at a specific current the dissociation degree decreases slightly with increasing flow; the total amount of hydrogen atoms increases and reaches fluences of 4.10^{21} atoms/s.

Form the nozzle the partially ionized plasma flows into the pumped expansion chamber, first supersonically, then after a shock subsonically. In pure argon the total ion fluence (typically 10^{20}/s) remains constant as atomic ion recombination has shown[5] to be negligable. This situation changes drastically when hydrogen is admixed in the arc to the argon flow. At a few percentage H_2 (in 100scc/s argon) the ionization degree in the expansion plasma changes drastically. At 10% H_2 the ionization loss amounts already to more than two orders of magnitude as compared to the pure argon case at a distance of Z = 20 cm from the nozzle[6]. With full hydrogen this is even further reduced. The explanation of this anomalous recombination of Ar^+ and H^+ ions emanating from the arc in hydrogen containing plasmas is a two step process: first the atomic ions (for which atomic recombination is negligable) are charge exchanged with H_2 molecules to molecular ions (ArH^+ and H_2^+). These molecular ions are subsequently recombined by the process of dissociative recombination (in the case of hydrogen, possibly through intermediate H_3^+ formation).
This anomolous recombination in hydrogen containing plasmas may have serious implications for deposition experiments. Hydrogen is usually present either by admixture or by dissociation of the monomers (CH_4, C_2H_2 etc.) used for deposition. If ions play a role in the deposition process, then this secondary effect of hydrogen admixture may have a negative effect on the deposition rate.

Hence it is useful to investigate the origin of the H_2 molecules which are essential in the first step: the charge exchange process. To this end two methods were employed; RF–probe excited actinometry[4] and depolarization Rayleigh scattering[7]. In the first method the (in the expansion cooled) electrons are heated locally, so that they can excite H–Balmer and H_2–Fulcher lines. From the ratio of the two, the dissociation degree of the plasma in the expansion chamber has been determined to be 10–15%

now increasing with flow. This dissociation degree is much lower than that of the plasma emanating from the arc and it increases with flow rather than decreases as the arc plasma. The conclusion is that the hydrogen molecules in the expansion chamber result from wall association of hydrogen atoms which come from the arc source. The dissociation degree increases with flow at constant chamber pressure, as higher flow means stronger pumping to maintain the same pressure and thus shorter residence time.

If the above mentioned loss of ionization is to be avoided one has to go to low pressures and short residence time to avoid the built up of H_2–abundance due to wall association. A magnetic field has then to be added to confine the plasma beam.

A more general conclusion of the present study is that the abundance of a molecular radical is more a consequence of wall processes than the result of the plasma source. In the present case the molecular abundance will be high even if the arc source emits only atomic hydrogen. The plasma acts mainly dissociating, whereas association takes place primarily at the wall. It is likely that similar processes take place in the more complicated situations of plasma deposition. The study of detailed kinetics of "simple" hydrogen plasmas, which have been investigated extensively in the framework of negative hydrogen ion sources[8], may therefore serve as an important example for studies of more complicated plasma chemical systems. At the same time the present study shows feasibility of the plasma production of intense atomic hydrogen beams for plasma chemical applications.

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