Fractional Dissociation Measurements of H_2 and D_2 in Molecular Gas Mixtures in RF Discharges

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High fractional dissociation of H_2 and D_2 in a helical resonator discharge, operated in inductive mode, has been measured using two-photon allowed laser induced fluorescence of H and D atoms in H_2/D_2 and $\%H_2$-$\%N_2$ and $\%D_2$-$\%N_2$ gas mixtures. Absolute H and D atom density measurements yield 11% dissociation efficiency in H_2 (13.5% in D_2) at 1 Torr. The fractional dissociation efficiency of both H_2 and D_2 was found to increase (approaching 100%) with an increase in $\%N_2$ in H_2/D_2-N_2 gas mixtures leading to a nearly constant H and D atom density over a wide range of $\%H_2$-$\%N_2$ and $\%D_2$-$\%N_2$ gas compositions.

Microelectronics manufacturing processes require large area plasma sources which can provide high density plasma and radicals with controllable low ion energies for etching selectivity, surface cleaning and surface passivation without inducing ion impact surface damage. The optimization of the fluxes of ions, atoms and radicals is strongly dependent on the electron energy distribution function (EEDF) and the heavy particle collisional energy transfer. It is well known that the EEDF can be significantly modified with gas mixtures and particularly with molecular gas mixtures. The operation of a plasma source with a gas mixture can thus provide an additional parameter to optimize the plasma processing steps. The dissociation efficiency measurement of pure hydrogen and gas mixtures such as H_2-N_2 and D_2-N_2 in an inductive discharge is, therefore, of considerable interest. The H_2-N_2 gas mixture discharge is also useful as N atom source for dielectric and diffusion barrier coatings. Although pure hydrogen and pure nitrogen dc

and rf discharges have been extensively investigated both experimentally [1,2,3] and theoretically [4,5], gas mixtures have only recently been the subject of such investigations [6,7]. We report the measurement of hydrogen and deuterium dissociation efficiency in pure H_2, D_2 and $\%H_2$ - $\%N_2$, $\%D_2$ - N_2 gas mixtures in a helical resonator discharge operated in the inductive mode. The absolute H and D atom densities have been measured by a two-photon allowed laser induced fluorescence (TALIF) technique [2].

The fractional dissociation measurements have been conducted in a 2 inch diameter discharge tube with a 4.5 inch diameter helical resonator operating in inductive mode [8] at 83 MHz excitation frequency. The TALIF measurement was performed with the discharge operating over the 0.5 Torr to 4 Torr pressure range and at 20 sccm (80 sccm for gas mixtures with 5% or less hydrogen) total gas flow rate. The rf power varied from 30 Watt at 0.5 Torr to 90 Watt at 4 Torr pressure.

When using the TALIF method to make quantitative H or D atom density measurements, the signals may have to be corrected for collisional quenching effects. In our measurements estimates of the quenching coefficients for hydrogen, deuterium and nitrogen were obtained in-situ from the temporal response of the TALIF signals. The figures 1a and 1b show the temporal variation of the H_α TALIF emission at 0.5 Torr and 2 Torr pressures respectively, for 100% H_2 and 5% H_2 - 95% N_2 gas discharges. These data show a very significant impact of collisional quenching of the H atom TALIF signal by H_2 and 95% N_2 + 5% H_2 along with the discharge produced products (H, N atoms and NH radicals) at pressures as low as 2 Torr. The effective radiative lifetime of 3s and 3d states was found to vary from 17 ± 3 nsec at 0.5 Torr to 8 ± 3 nsec at 2 Torr pressures for both 100% H_2 and 5% H_2 - 95% N_2 gas discharges. The pressure dependent variation of the inverse effective radiative lifetime of H_α fluorescence emission is plotted in figure 2. These measurements yield a collisional quenching rate of $\sim 2.5*10^{-9} cm^3 sec^{-1}$ for both H_2 and N_2 discharges which is in good agreement with the previous measurements [9,10]. Quenching coefficients for D atoms are the same as those for H atoms, within the accuracy of our measurements. The absolute accuracy of these effective lifetime measurements is limited to ± 3 nsec due to the photomultiplier signal risetime and the shot to shot laser pulse jitter.

We have calibrated the H and D atom TALIF signals by NO_2 titration [2] to correlate the fluorescence signal with the H and D atom ground state density. In the calibration measurement the H_2 or D_2 is dissociated by a microwave discharge and the TALIF signal is measured with the identical optical layout as used for the discharge measurements. The plot of a calibration TALIF signal amplitude (quenching corrected) with the NO_2 flow rate is shown in figure 3. The microwave discharge power and the H_2 gas flow rate (42 sccm) are adjusted to obtain a TALIF signal amplitude comparable to that from the helical resonator discharge. The H and D atom densities are obtained from the NO_2 flow rate value when the TALIF signal goes to zero (baseline). The NO_2 flow rate was calibrated by measuring the pressure rise in a known volume. The atom density is given by

$$[H] \text{ or } [D] = [NO_2] = (3.3 \times 10^{16} cm^{-3} Torr^{-1}) * (F(NO_2))/\Sigma F * P$$

where $F(NO_2)$ is the flow rate for zero TALIF signal, ΣF is the total gas flow rate and P is the pressure in Torr. A comparison of this calibration signal with the 1 Torr pure H_2 discharge measurement, shown in figure 4, yields H atom number density, $[H] = 3.7 \times 10^{15} cm^{-3}$, i.e. 11 percent dissociation efficiency for 1 Torr 52 watt inductive mode helical resonator discharge. Similarly, the D atom number density measurement for 1 Torr discharge pressure with 60 Watt rf input power leads to a 13.5 percent dissociation efficiency. Under our measurement conditions (20 sccm flow rate, 1 Torr pressure, 5 cm I.D.) 11 percent dissociation efficiency corresponds to an atomic hydrogen flux of $\approx 1*10^{20}$ atoms/sec which implies that nearly 80 percent of the input energy goes into the H_2 dissociation process [11]. The probable reason for this high H atom flux is that inductively coupled discharges operate at an E/N (where E is the electric field and N is the gas number density) of ≈100 Td [12] which is at or near the optimum E/N value [4] for dissociation of H_2.

The variation of the H and D-atom TALIF signals with the change in $\%H_2$-$\%N_2$ and $\%D_2$-$\%N_2$ gas composition are shown in figure 4 and figure 5 for discharge pressures from 0.5 Torr up to 4 Torr. It should be noted that the TALIF signal amplitude for H atoms has been corrected for collisional quenching.

The H atom TALIF data in figure 4 show that for a discharge pressure of 1 Torr and above, the H atom density changed by only 30% or less as the percentage of H_2 was varied from 100% to 10%, i.e. the fractional dissociation of H_2 increased by a factor of

3-4. The D atom TALIF data in figure 5 show similar behavior. Since the optimum condition for the dissociation rate due to direct electron impact is already achieved for pure H_2 and D_2 discharges, the observed enhanced dissociation efficiency with N_2 dilution cannot be due to a change in E/N.

Very high H_2 and D_2 dissociation rates are obtained over the entire discharge pressure range measured, as shown by the data in fig.4 and fig.5. These results indicate that the H_2 and D_2 dissociation processes in $\%H_2$-$\%N_2$ and $\%D_2$-$\%N_2$ gas mixtures are not very sensitive to the E/N values. Therefore, the direct electron impact dissociation process can not be solely responsible for the observed behavior [4,7]. Similarly, the heavy particle collisional energy from the N_2 electronic states also cannot by itself lead to the observed enhanced dissociation of H_2 and D_2 in N_2 gas mixture discharges. These results suggest that both the electronic and the vibrationally excited N_2 interactions with H_2 and D_2 may be required to explain the observed high fractional dissociation of H_2 and D_2 in discharges with N_2 gas mixtures.

In summary we have demonstrated that a large area inductively coupled helical resonator is a very efficient radical source as compared to some other plasma sources [3]. Also it was shown that the interaction of heavy particle and electron kinetics in $\%H_2$-$\%N_2$ and $\%D_2$-$\%N_2$ gas mixtures are responsible for achieving the high fractional dissociation in these gas mixtures.

References

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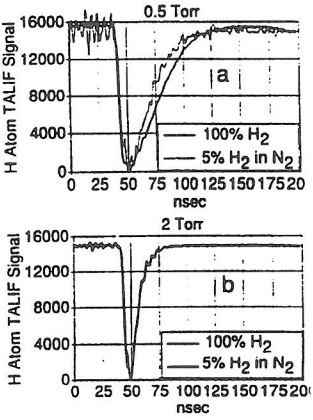

Figure 1. Temporal waveforms of the H atom TALIF signals in pure hydrogen and in 5% H_2 95% N_2 discharge. a) 0.5 Torr, b) 2 Torr.

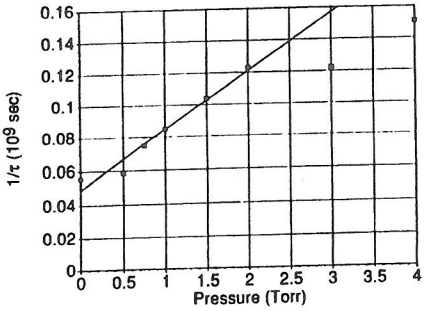

Figure 2. Inverse effective lifetime of H_α fluorescence emission vs. discharge gas pressure.

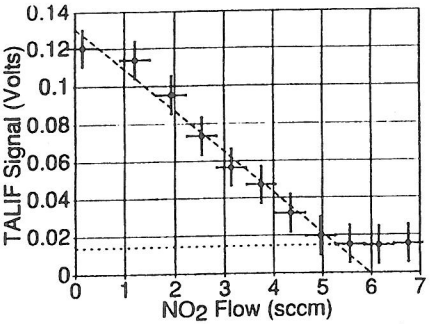

Figure 3. H atom TALIF signal calibration by NO_2 titration.

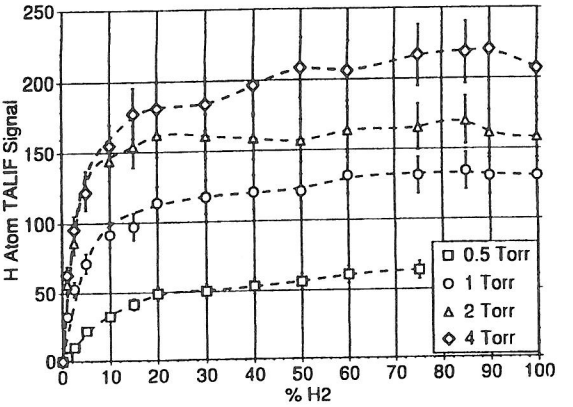

Figure 4. Effect of variation of $\%H_2$ - $\%N_2$ gas composition on H atom TALIF signal with total gas pressure as parameter. The lines drawn through the data points are spline fit to the data.

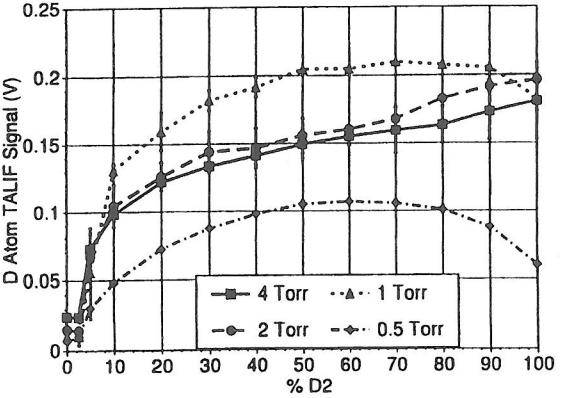

Figure 5. Effect of variation of $\%D_2$ - $\%N_2$ gas composition on D atom TALIF signal with total gas pressure as parameter. This data has not been corrected for collisional quenching.