Simultaneous Measurement of Electron Density and Electron Temperature in Highly Reactive Capacitively-Coupled Plasmas

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- Capacitively-coupled discharges of BCl_3 and Cl_2 are used to etch GaN, GaP, GaAs.
- Methods of Plasma Analysis:
  - Spatially resolved LANGMUIR probe measurements.
  - Optical emission spectroscopy (OES).
  - Self-excited electron resonance spectroscopy (SEERS).
- Range:
  - From pure Cl_2 to pure BCl_3.
  - Discharge pressure: one order of magnitude (7.5 – 75 mTorr).
  - RF power: $1/2$ order of magnitude (100 – 400 W).
- Plasma Parameters:
  - Actual RF power coupled into the discharge.
  - Plasma density.
  - Plasma potential.
  - Electron temperature (low- and high-energy tail).
  - Electron collision rate with neutrals.
  - Bulk Plasma Temperature.

1 Experimental Setup

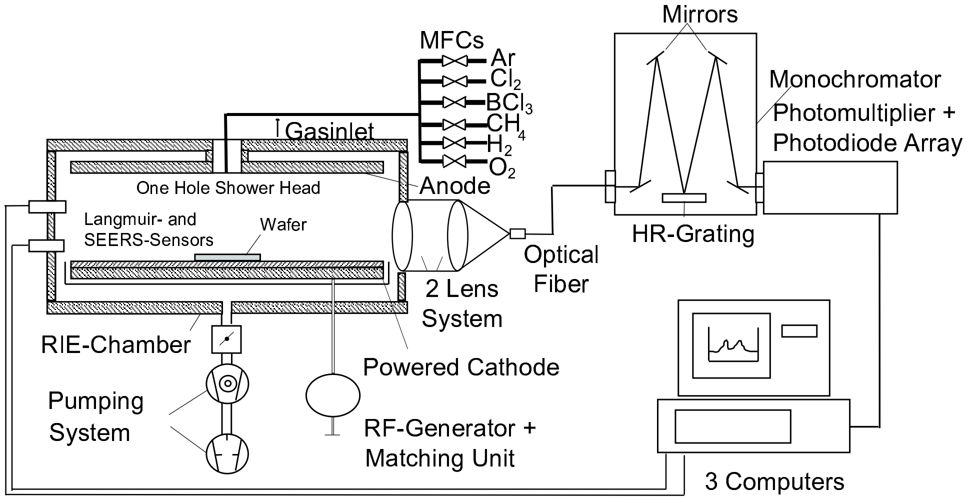

Figure 1. The experimental setup consists of a parallel-plate reactor (Plasma Lab 90 of Oxford Plasma Technology) and three plasma sensors. They are all connected via KF 40 ports. Not shown is the mass spectrometer for RGA.

2 Mutual Interference Between the Plasma Probes

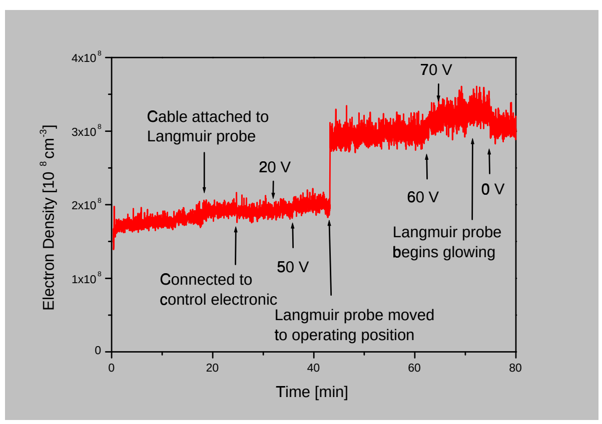

Figure 2. The value for the electron density as measured with SEERS is influenced by the Langmuir probe. Already the movement into the bulk plasma causes an irratation which is even enhanced during current drawing. The second, even higher influence can be seen during the glowing of the wire. Other probes, like optical emission spectroscopy, are very robust against the wire glow.

⇒ Drawing a current out of the plasma does have an influence at least on electrical properties like the electron plasma density.

⇒ All the data points which are reported here have been recorded just before the Langmuir probe was driven.

3 Actually Absorbed RF Power

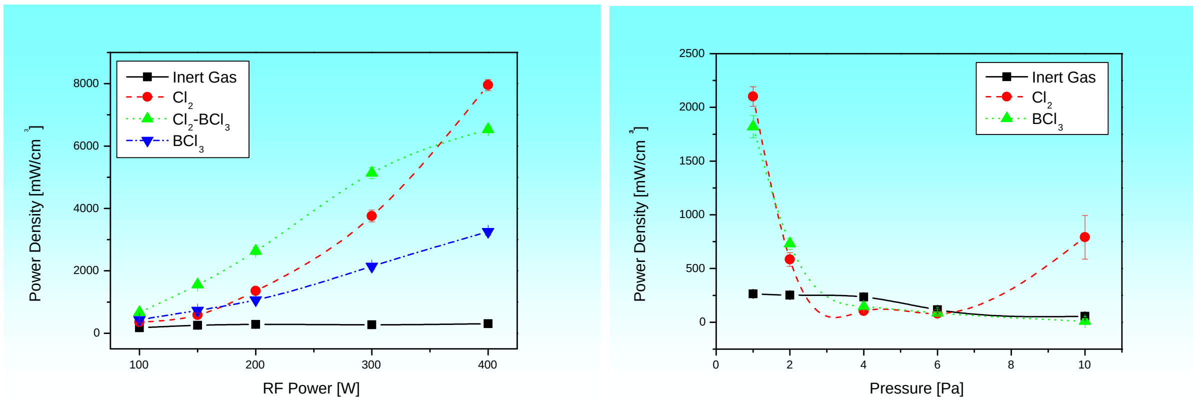

Figure 3. Actual RF power (as calculated by the SEERS algorithm) which is coupled into the plasma (parameter list for an electropositive gas like argon).
Inert gas (Ar:Kr = 10:10 sccm): there is nearly no higher input when the emitted power is enlarged by a factor of 4.
BCl_3, Cl_2, and BCl_3:Cl_2 as mixture 1:1: nearly the same behavior up to 200 W emitted power. BCl_3 resembles argon even for higher values. Cl_2-containing gases (treated with the same evaluation parameter set): For high emitted powers beyond 300 W sharp increase of the absorbed power which is even larger than the emitted power.
⇒ Model breaks down here, perhaps due to a homolytic or heterolytic dissociation of Cl_2 or to the onset of the electronegative behavior.

From first principles

[M.A. Lieberman, A.J. Lichtenberg: *Principles of Plasma Discharges and Materials Processing*, J. Wiley, New York, N.Y., 1994]:

$$P_{\text{abs}} = e_0 n_{\text{s}} v_{\text{B}} A_{\text{eff}} \sum_i E_i$$

n_{s}: the ion density at the plasma sheath edge,
v_{B}: the Bohm velocity,
A_{eff}: the effective area for particle loss (in the simplest case the surface of the cylinder containing the plasma),
$\sum_i E_i$: the total energy loss of the wave per ion, which is composed of at least the three independent parts:

- E_{ion} the collisional energy lost by creation per electron-ion pair;
- E_{diss} the kinetic energy lost by the carriers when they suffer wall collisions (for MB electrons, this part equals 2 $k_{\text{B}}T_{\text{e}}$);
- E_{DC} the energy gained by a carrier during the fall across the sheath (to account for the total kinetic energy of an ion, the plasma potential V_{p} has to be added)

4 Plasma Potential

$$V = V_{\mathrm{P}} - V_{\mathrm{F}} = \frac{k_{\mathrm{B}} T_{\mathrm{e}}}{2 e_0} \ln \frac{e m_{\mathrm{i}}}{2 \pi m_{\mathrm{e}}},$$

In plasma theory of zero order, the difference between plasma potential V_{P} and the floating potential V_{F} is independent of the applied RF power [J.D. Swift, M.J.R. Schwar: *Electrical Probes for Plasma Diagnostics,* ILIFFE Books Ltd., London, England. 1970, eq. 1.16, p. 15].

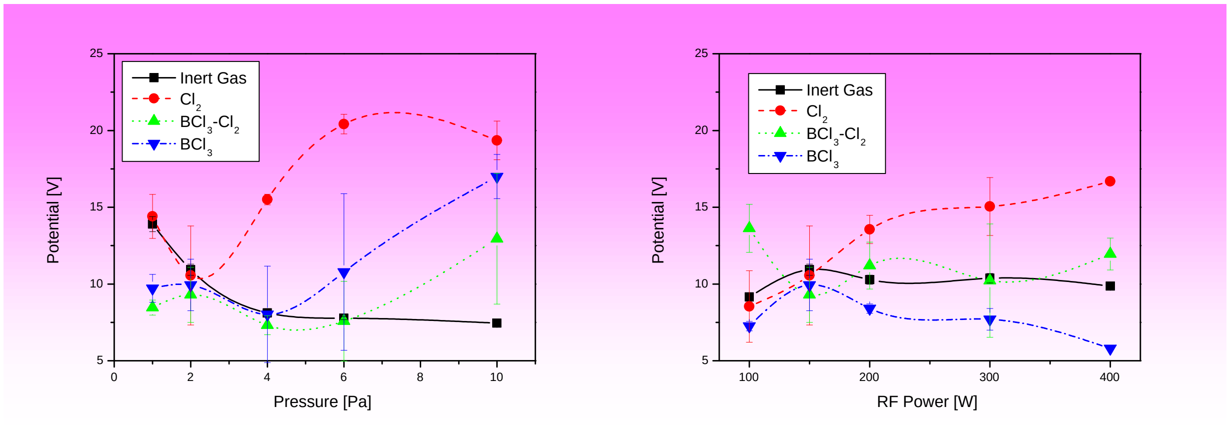

Figure 4. The difference *V* of plasma potential V_{P} and floating potential V_{F} as function of emitted RF power and discharge pressure should be proportional to T_{e}.
Discharge pressure inert gas (Ar:Kr = 10:10 sccm) and BCl_3: nearly constant or **$1/p$ dependence (inert gas)**.
Discharge pressure Cl_2: increase.
RF power: Above 300 W, V in Ar drops significantly.
RF power: continuous increase. Since the total amount of energy which can be gained in the plasma is the sum of the potentials of plasma and the sheath, this has consequences for the production of carriers (see electron plasma density).

5 Radial Uniformity of the Plasma

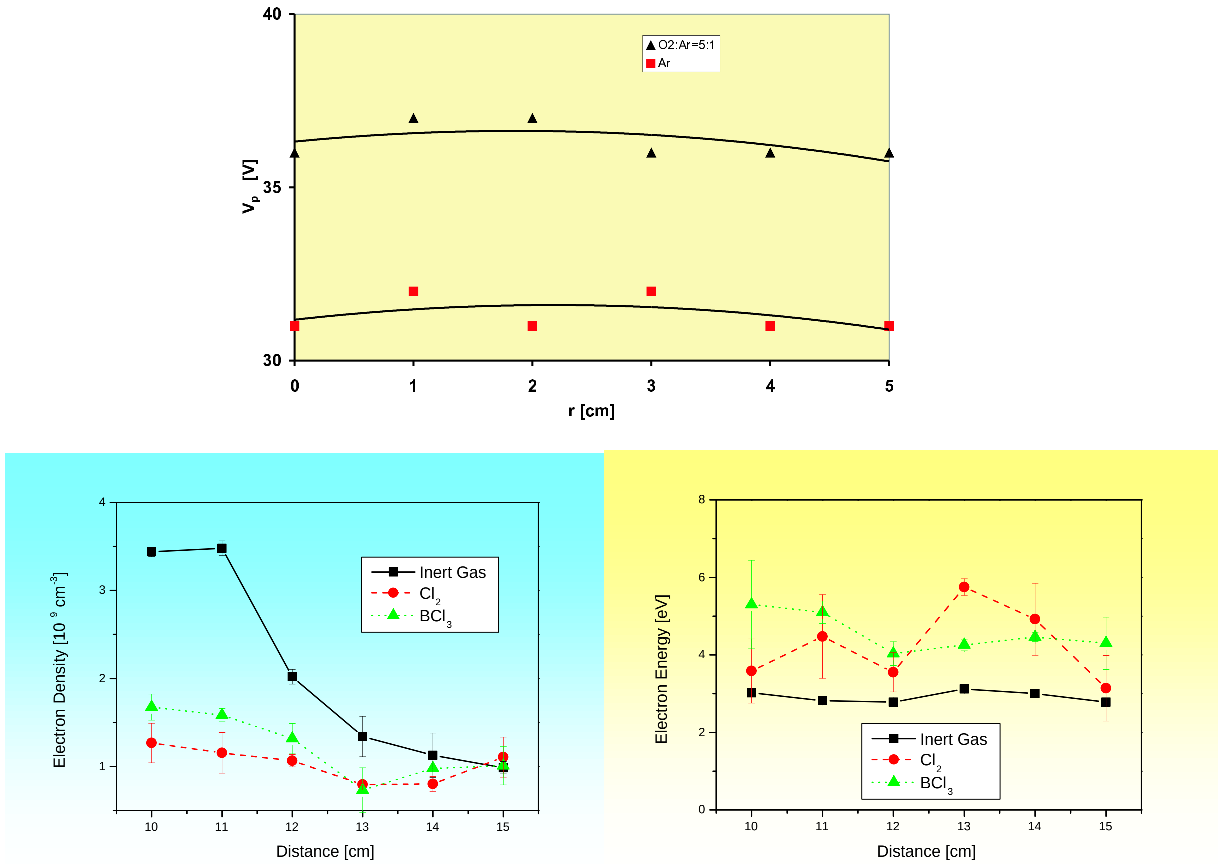

Figure 5. In a parallel-plate reactor (distance between the electrodes is small against the diameter of the electrodes), the radial uniformity of the plasma density is merely constant, until the (radial) edge of the electrode is reached. This is shown here for discharges of argon and oxygen/argon (center, top, plasma potential) and argon, chlorine and boron trichloride for the plasma parameters electron temperature and electron density as measured for the marginal part of the reactor (edge of the electrode at 12.5 cm, center = 0 cm, bottom). Conditions: p: 2 Pa, P_{RF}: 150 W

6 Plasma Electron Density n_e

Plasma density is determined by the equilibrium between generation and loss of carriers (in low pressure discharges, mainly due to diffusion to the walls). For every transfer reaction, its cross section is extremely energy-sensitive ⇒ Nonlinearity of the energy dependence of n_e even in argon.

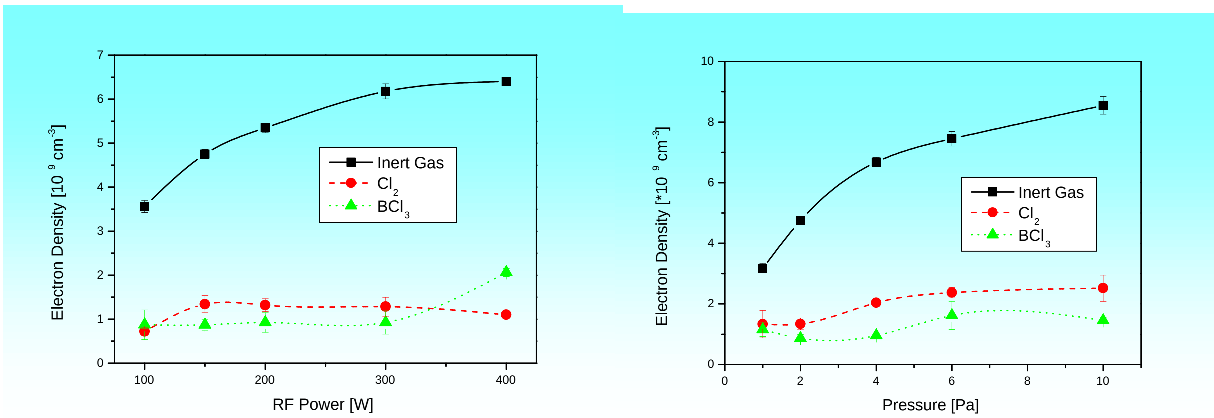

Figure 6. The electron plasma density n_e as function of emitted RF power and discharge pressure (Langmuir).

- n_e remains nearly unchanged for the reactive gases, their density is very similar.

- **n_e in argon is significantly higher and a square-root dependence is observed.**

1) the most important mechanism for energy gain is the fall through the plasma sheath, since V_{DC} is proportional to the square root of the RF power,

2) the loss mechanisms are even constant with respect to RF power.

- The pressure dependence of the reactive gases follows perfectly the straight-line behavior, which is expected from the crudest theory.

Ionization potentials are all of the same order of magnitude (Ar: 15.755 eV, Cl_2: 11.48 eV, BCl_3: 12.0 eV) ⇒ **this must be due to an effective, additional loss mechanism (electron attachment).**

7 Comparison between Langmuir and SEERS

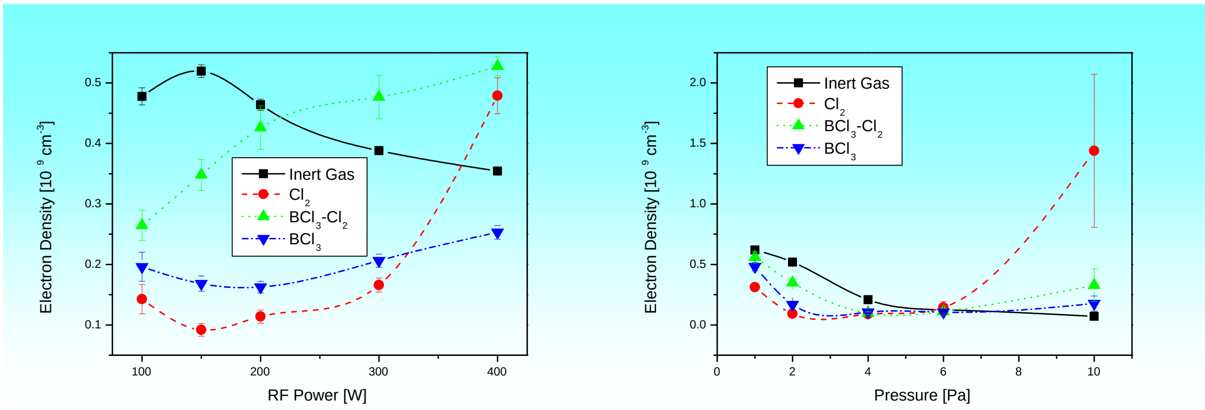

Figure 7. The electron plasma density n_e as function of emitted RF power and pressure (SEERS):
- the densities are less by a factor of 5 to 10 compared to the LANGMUIR probe data.
- n_e remains nearly unchanged for the reactive gases up to 300 W emitted RF power.
- n_e in Cl_2 increases sharply beyond 300 W RF power and 6 Pa (45 mTorr).

Compared to LANGMUIR, the SEERS data are lower by a factor of $4-6$ but roughly exhibit the same habitus (cf. Figs. 7). This attenuation is mainly due to the integration over space, by which the sheath with a very low or zero electron density contributes to the overall result.
At high RF powers, the main difference is a decrease of n_e for Ar, a slight increase for BCl_3, and a steep increase for Cl_2, which reminds of the increase for absorbed power in Fig. 3. **These effects are likely to be referred to processes in the electrode sheath,** *i. e.* to effects associated with energy gain at higher RF powers: lower efficiency for Ar, higher efficiency in Cl_2. From Fig. 4 (LHS), it is evident that only the change in V_P (and hence the energy gain) is the reason for this behavior (the DC bias potential exhibits the normal $\sqrt{P_{RF}}$ behavior).

8 Electron Energy (Temperature) T_e (Low-Energy Tail)

Due to its specific characteristics of drawing the current, with a Langmuir probe the low-energetic tail of the electrons will be measured
[V.M. DONNELLY; J. Vac. Sci. Technol. **A 14**, 1076 (1996)].

T_e is determined by the ratio of ionization in the volume (bulk plasma) and the losses at the surface and is expected to depend

- mainly and inversely on discharge pressure in inert gases,
- linearly on $V = V_P - V_F$ [SWIFT AND SCHWAR].

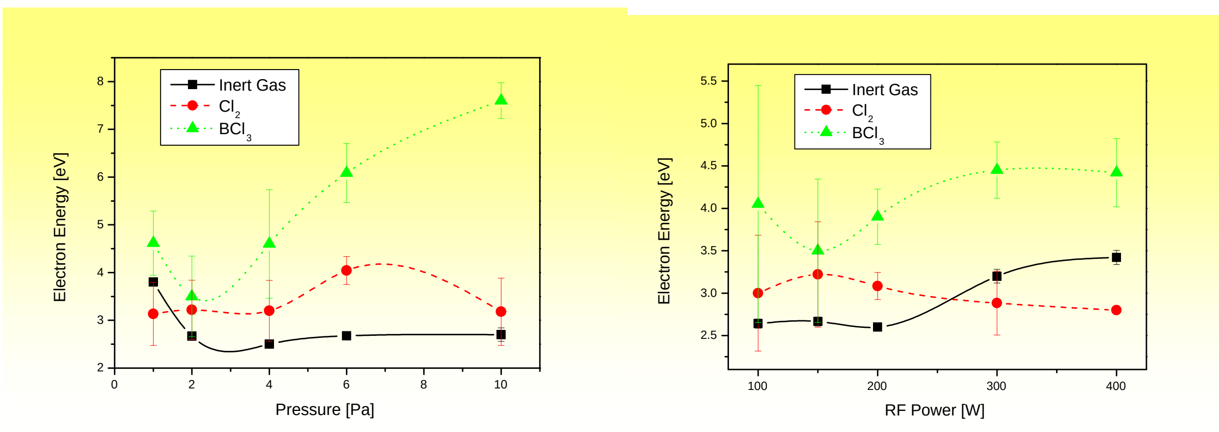

Figure 8. Electron energy (Langmuir) as a function of discharge pressure (LHS, at constant emitted RF power of 150 W = 0.3 W/cm^2) and RF power (RHS, at constant discharge pressure of 2 Pa = 15 mTorr), in discharges of an inert gas (Ar:Kr = 10:10 sccm), pure chlorine, and pure boron trichloride.
pressure-dependence: **$1/p$ dependence for the inert gas,** distinct drop between 1 and 2 Pa for chlorine, whereas T_e of BCl_3 and Ar remains constant over nearly the whole pressure range.
power-dependence: distinct increase between 100 and 200 W for the inert gas and chlorine, whereas T_e of BCl_3 remains constant over nearly the whole power range. **On the low-energy branch of the $\mathcal{EEDF}$, BCl_3 reminds much more an inert gas than Cl_2.**

9 Electron Energy (Temperature) T_e (High-Energy Tail)

OES with small amount of actinometrical gases

[P. Awakowicz; Mat. Sci. Forum **287 - 288**, 3 (1998), M.V. Malyshev, V.M. Donnelly; J. Vac. Sci. Technol. **A 15**, 550 (1997)].

Modelling the rate coefficients (corona balance, $\mathcal{EEDF}$: MB? or D? or in between?):

$$k_{\rm ij} = \int_{E_{\rm j}}^{\infty} v_{\rm e}\sigma(E)\,\mathcal{EEDF}\,{\rm d}E.$$

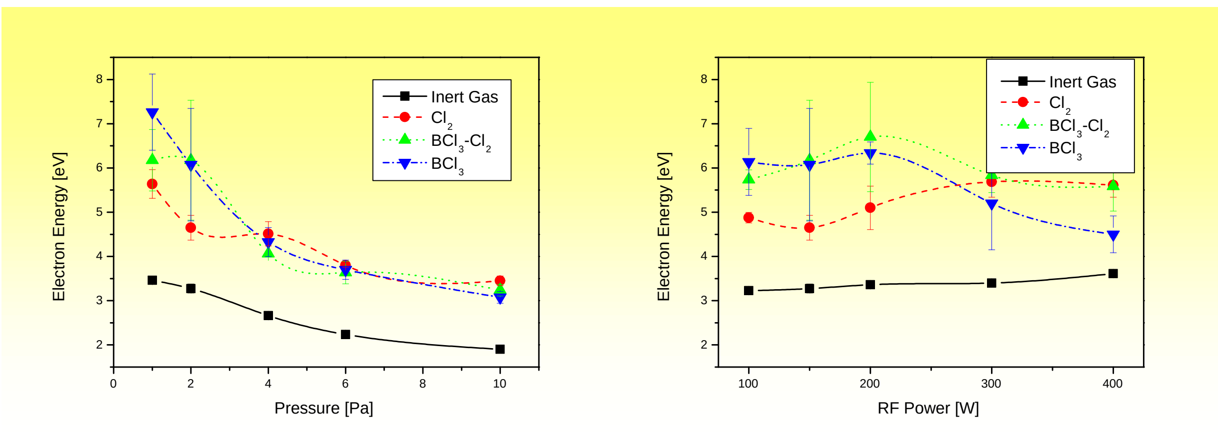

Figure 9. Electron energy (OES) as function of discharge pressure at constant emitted RF power (150 W = 0.3 W/cm^2, LHS) and of emitted RF power at constant discharge pressure (15 mTorr or 2 Pa) in discharges of an inert gas (Ar:Kr =10:10 sccm), pure chlorine, pure boron trichloride, and a mixture of BCl_3 and Cl_2 (10:10 sccm).
The electron energy is highest in the BCl_3 containing atmospheres, followed by chlorine, but significantly lowest in argon. $\mathcal{EDF}$ is assumed Maxwellian.
Pressure dependence for all gases follow an inverse density law.

Main advantage: small perturbation of the plasma. Limitation: consideration of the high-energy tail of the $\mathcal{EEDF}$.

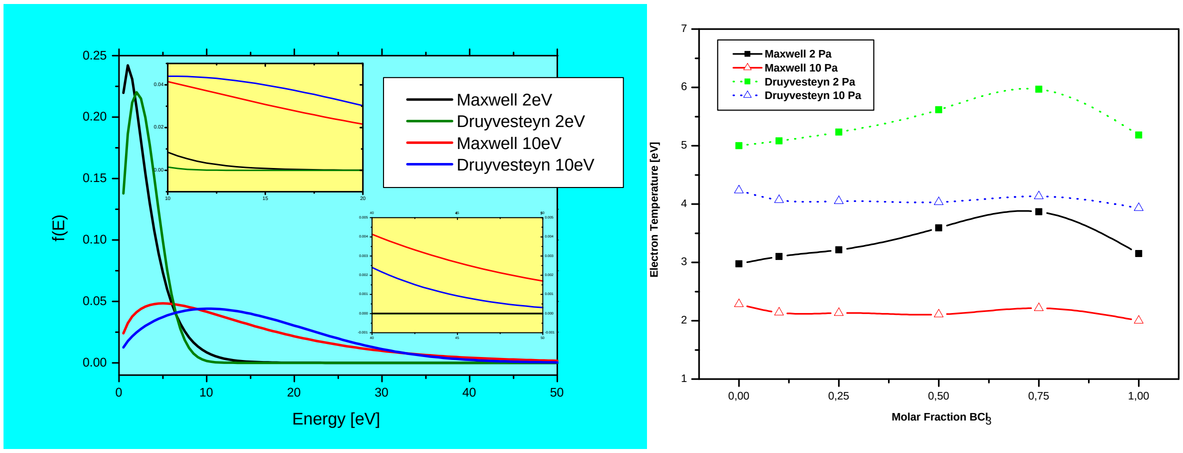

Figure 10. LHS: Comparison of the distributions according to MAXWELL-BOLTZMANN (MB) and DRUYVESTEYN (D) for same mean energy $<E>$ 2 and 10 eV
M.J. DRYUVESTEYN, F.M. PENNING; Rev. Mod. Phys. **12**, 87 (1040).
$f(v)(MB) \propto \exp(-E/kT) \wedge f(v)(D) \propto \exp(-E/<E>)^2$:
For same mean energy, the D-distributed electrons are depleted in the high-energy region. The most probable energy of the D-electrons is slightly higher than for the MB-electrons.
RHS: As consequence, **the calculated electron temperatures are definitely higher for a D distribution compared to a MB distribution, but exhibit nearly the same shape!**

Low-Energy Tail, Langmuir.

- $T_e(\mathrm{Ar}) < T_e(\mathrm{BCl_3}) < T_e(\mathrm{Cl_2})$
- For increasing neutral density (increasing discharge pressure), the electron energy drops in the low-density range between $1 - 2$ Pa ($7^1\!/_2 - 15$ mTorr) and remains constant up to 10 Pa (Fig. 8, LHS).
- For increasing power, no increase is expected. Works perfectly for Ar, but not for molecular gases (Fig. 8, RHS).
- Steep increase for Cl_2? Change in the chemical nature of Cl_2? Change in density of the neutrals? Dissociation?

High-Energy Tail, OES.

- Pressure dependence: All the four gases behave normally vs. pressure (Fig. 9, LHS). Inert gases are significantly cooler than Cl_2/BCl_3-containing atmospheres.
- Power dependence (Fig. 9, RHS):
  - Ar: no dependence
  - molecular gases: no clear trend.

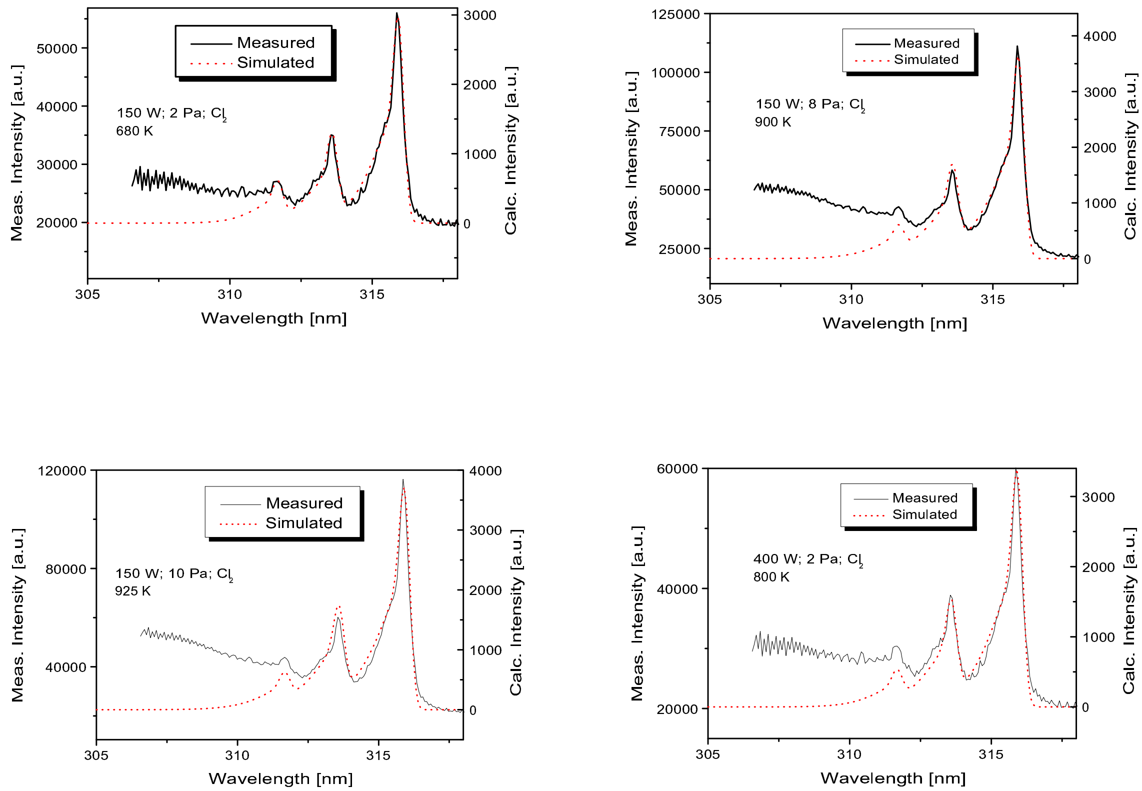

Figure 11. Determination of the gas temperature with rotational spectroscopy of nitrogen bands and their simulation: [K. Behringer; Plasma Phys. Control. Fusion **33**, 997 (1991)]; [P. Awakowicz; Mat. Sci. Forum **287 - 288**, 3 (1998)]. It is evident that the gas temperature at 10 Pa has been increased by a factor of 1.4 compared to 2 Pa. Since the discharge pressure is downstream-controlled, the effective number density is reduced by the inverted factor according to ideal gas law.

10 Temperature of the Bulk Plasma

The increase of T_e (low-energy branch) for chlorine with increasing discharge pressure diametrally contradicts simple plasma theory. This can be at least partly made understood with evaluation of the gas temperature (rotational spectrum of N_2);

K. Behringer; Plasma Phys. Control. Fusion **33**, 997 (1991).

Applying the transition $C^3\Pi \rightarrow B^3\Pi$ (315.93 nm: v': 1, v'': 0; 313.6 nm: v': 2, v'': 1), we measured an increase of T_{gas} from

- 680 K at 2 Pa and 150 W to
- 900 K at 150 W and 8 Pa (Δ: 40 %) or
- 925 K at 150 W and 10 Pa (Δ: 40 %) or
- 800 K at 400 W and 2 Pa (Δ: 20 %).

According to ideal gas law, the number density is reduced by the inverted factor, and since the pressure is downstream-controlled, we should correct the indicated pressure by this factor. Upheating is more "effective" at higher pressures than for higher power input.

11 Electron Collision Frequency ν_m

ν_m describes the dissipative effects during the transfer of kinetic energy into the plasma. In inert gases, T_e decreases with increasing discharge pressure (number density) to become eventually constant, ν_m is merely constant. Deviations in ν_m vs. discharge pressure from this straight-line behavior are due to changes from this behavior.

In the pressure dependence for the molecular gases, the enlargement of the electron energy is manifested at low pressures (between 1 and 2 Pa) and high pressures beyond 6 Pa (only for Cl_2) which is reflected in the steep increase in T_e. Since n_e does not show any unusual features (cf. Fig. 6), and T_e is correlated to the net ionization, this increase is a further clear hint that Cl_2 acts as an electronegative molecule beyond a threshold of $5-6$ Pa. Furthermore, this change in T_e, low-energy branch (i. e. Langmuir), is reflected in a physical property associated with the electron resonance.

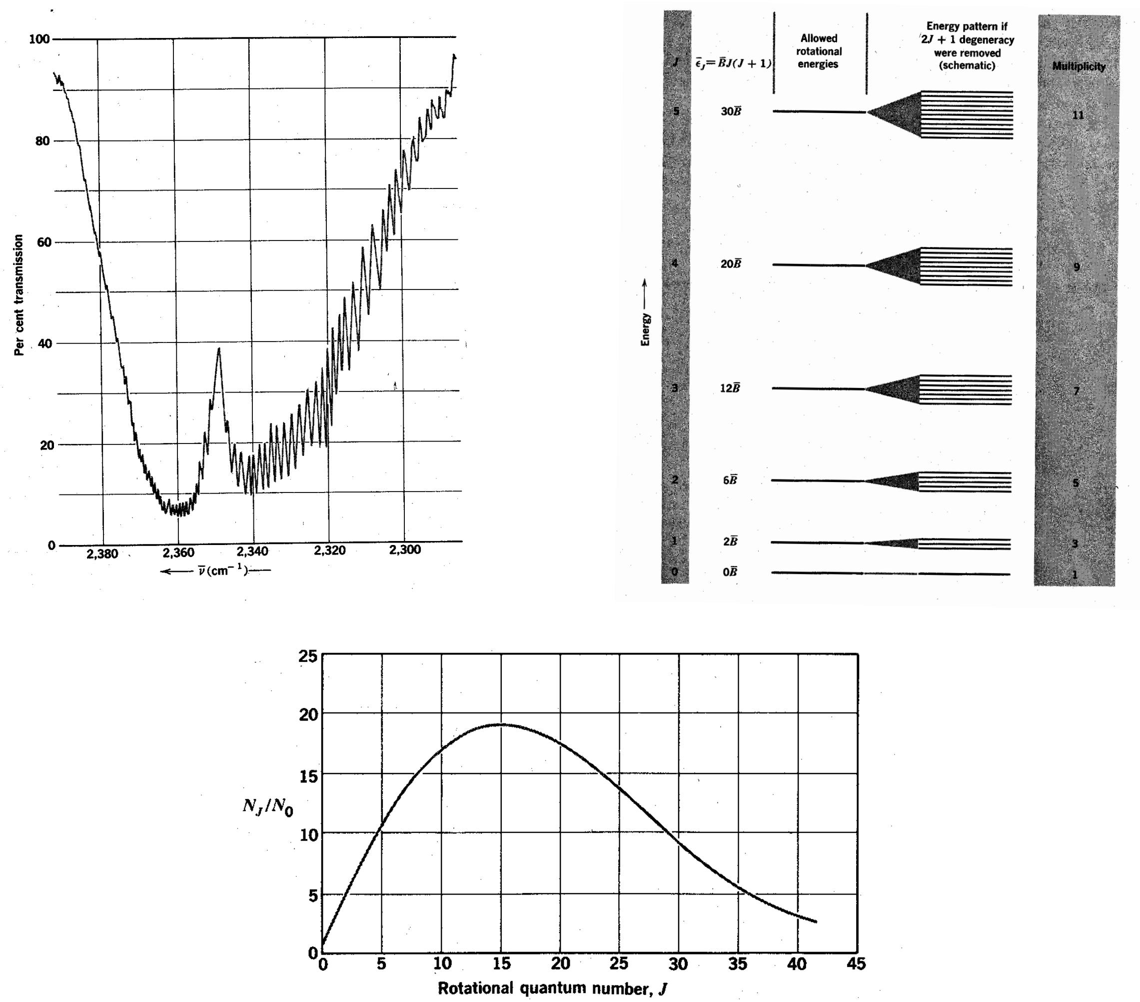

Figure 12. The intensity of a vibronic rotational spectrum (CO_2, top, left) is determined by the occupancy of the ground state. This is determined by the degeneracy $2J+1$ of the state J (top, right, increasing) and a BOLTZMANN term (decreasing). As a result, we obtain a maximum for medium J (bottom).

12 Conclusion

- Only the radial uniformity and the electron plasma density of the bulk plasma behave the way which is expected using the simplest plasma approach. Most remarkable are **"Islands of Stability":** for certain regions of RF power and discharge pressure, a plasma property like n_e or **pressure dependence of the collision frequency** ν_m is constant over nearly the whole range, except for high-pressure discharges of Cl_2. This deviation can clearly be referred to the onset of electronegative behavior of Cl_2.

- Most prominent differences between molecular gases vs. inert gases:

  – n_e is significantly lower and almost the same for BCl_3 and Cl_2,

  – T_e, (LP and OES) are definitely higher for the molecular gases.
  $\Rightarrow$
  Attachment of low-energy electrons by the electronegative molecules. For BCl_3 over the whole range, onset for Cl_2 at about 4 – 6 Pa (30 – 40 mTorr) and 300 W RF power.
  Increase in ν_m at relatively hard conditions can also be due to **higher a degree of dissociation of Cl_2.**

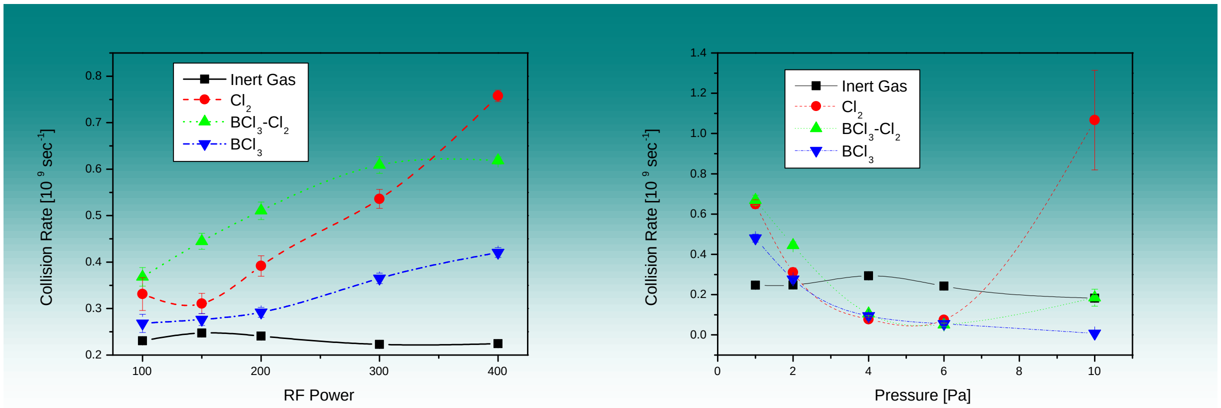

Figure 13. ν_m as function of emitted RF power at constant discharge pressure of 15 mTorr (2 Pa) and of discharge pressure at constant RF power of 150 W in discharges of an inert gas (Ar:Kr =10:10 sccm), pure chlorine, pure boron trichloride, and a mixture of BCl_3 and Cl_2 (10:10 sccm).
- **For increasing RF power, the molecular gases behave different to Ar.**
- The high electron energy in Cl_2 at high discharge pressure is reflected in the steep increase of ν_m.

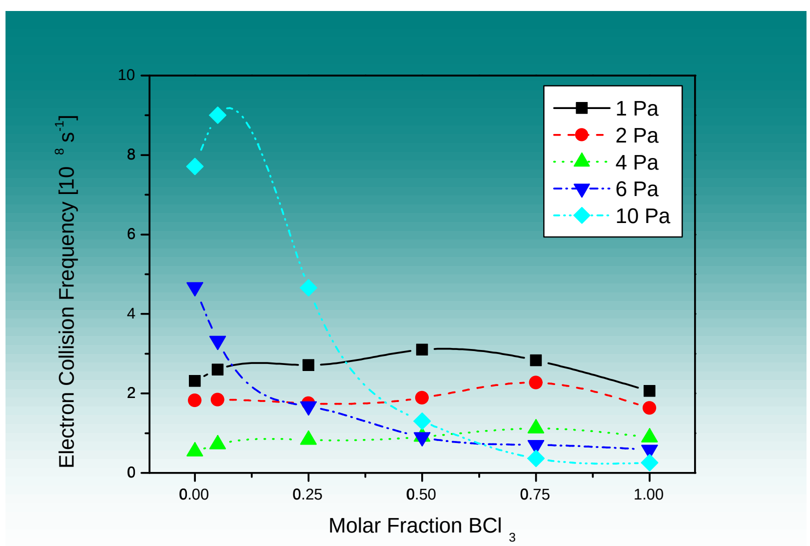

Figure 14. The collision frequency of electrons with neutrals, ν_m, in Cl_2/BCl_3 plasmas as function of discharge pressure. Parameter is the composition of the discharge at constant RF power of 150 W (0.3 W/cm^2). In BCl_3, ν_m is proportional to the mean free path ($1/p$), in Cl_2, we observe a minimum at about 4 Pa. For 10 Pa, the highest value is higher by a factor of 15 than the lowest.