

Analysis of Chlorine-Containing Plasmas Etching Ga-Containing III/V Semiconductors

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Abstract

Capacitively coupled discharges of strongly reactive atmospheres containing mixtures of boron trichloride and chlorine are investigated with optical emission spectroscopy and advanced measurements of the discharge current (self-excited electron resonance spectroscopy) which is the first time to analyze the whole area spanned by these gases and their impact on important plasma parameters like plasma density, electron temperature, and electron collision rate with neutrals. Using these data, roughly calculated cross sections for these gases are obtained in the low-energy region. Molecular chlorine ions, Cl_2^+ , are evidently present to a preponderant amount as main agent, which are accompanied by chlorine radicals, $\text{Cl}(\text{I})$, in mixtures with chlorine. Absolutely no chlorine ions could be found in the plasma which is referred rather to the effective cooling of the Cl-containing species than to the nonexistence of these species.

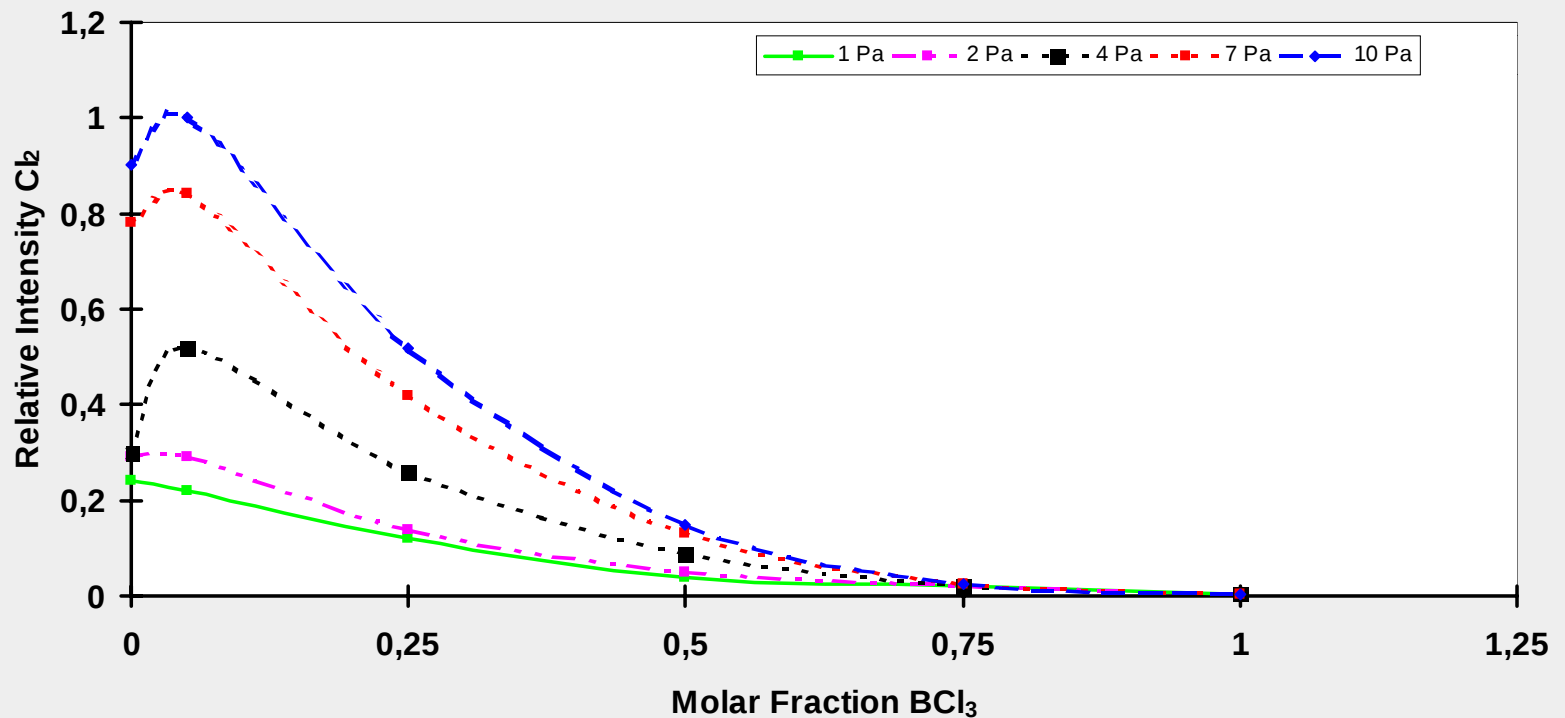
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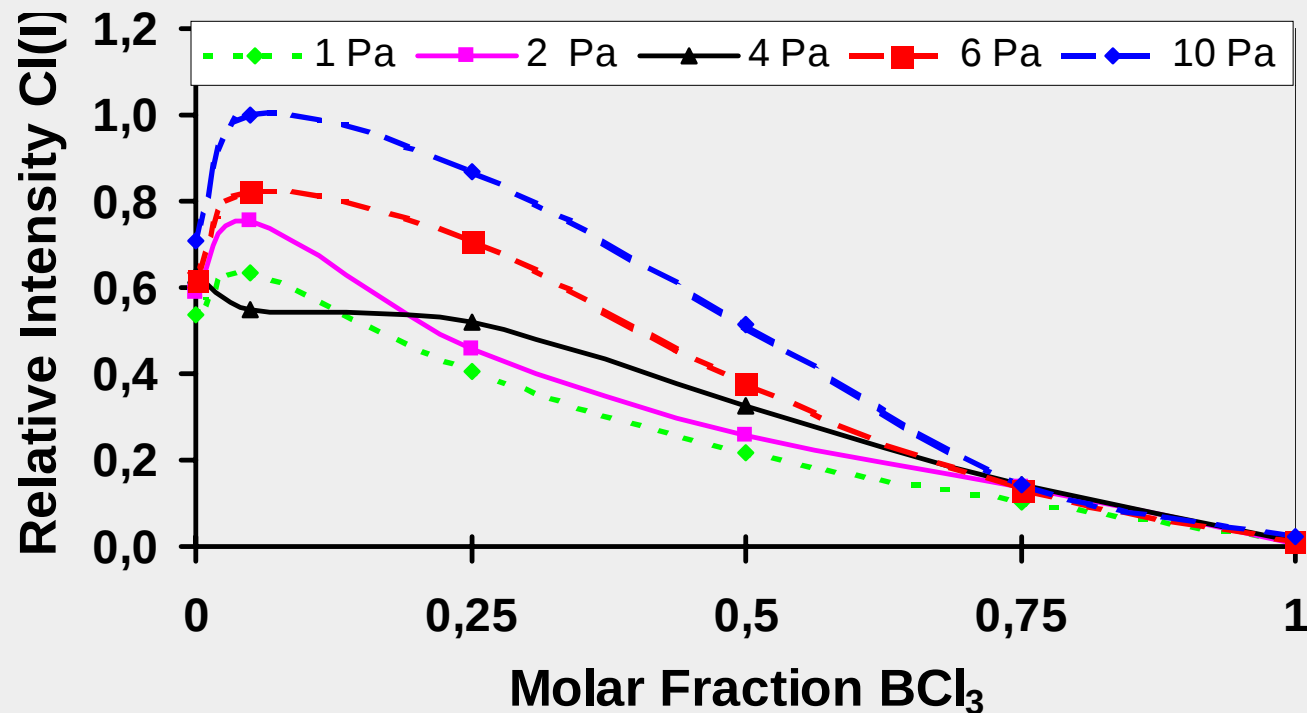
OES: Cl_2 Intensity vs. Molar Fraction BCl_3

OES: Cl_2 Intensity vs. Molar Fraction BCl_3
Parameter: Discharge Pressure at 150 W RF-Power



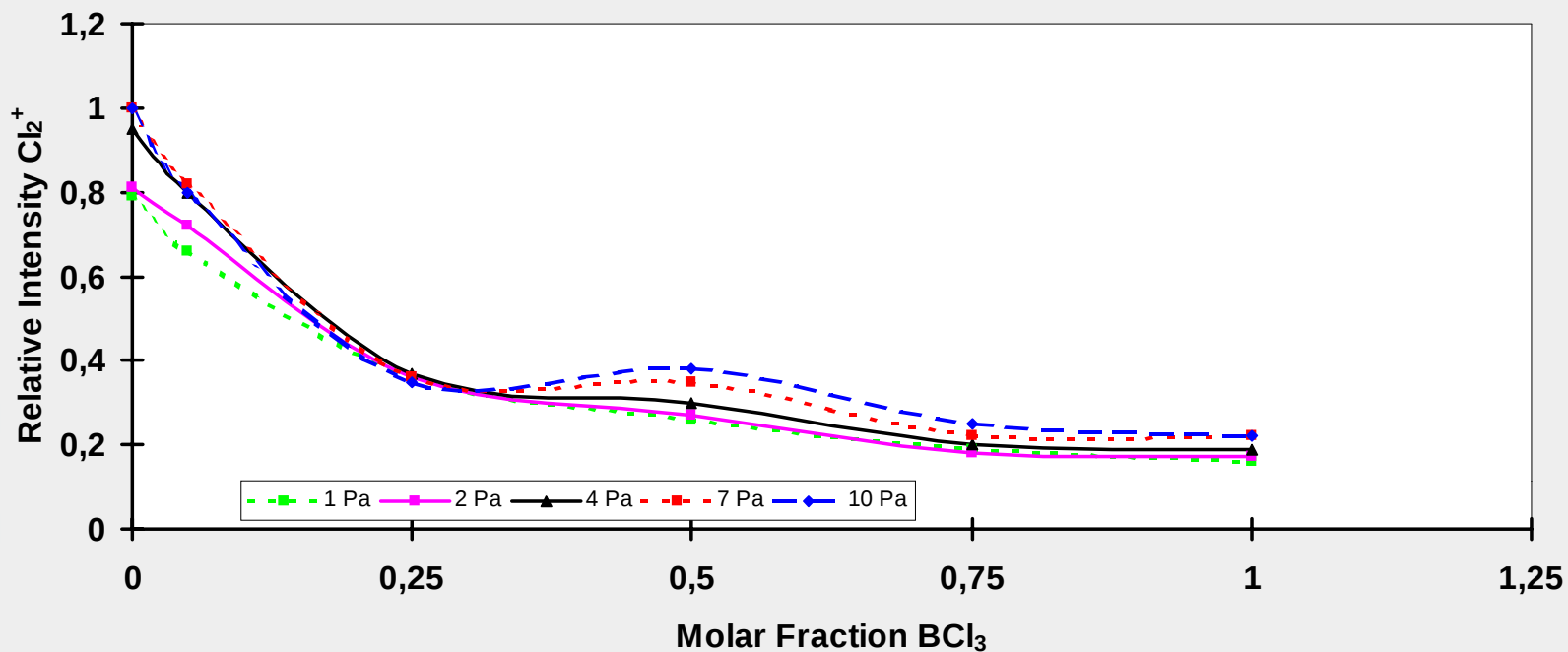
OES: Cl(I) at 725.7 nm vs. Molar Fraction of BCl_3

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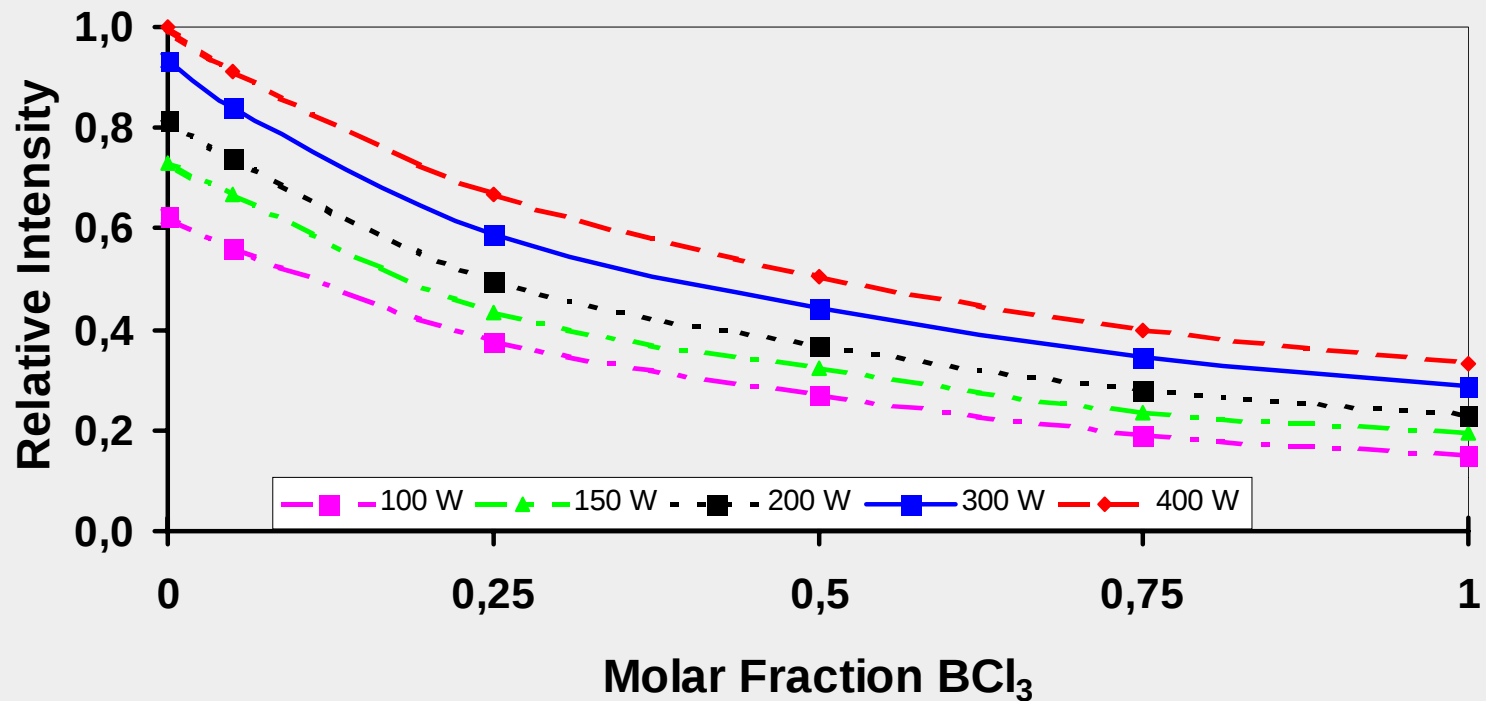
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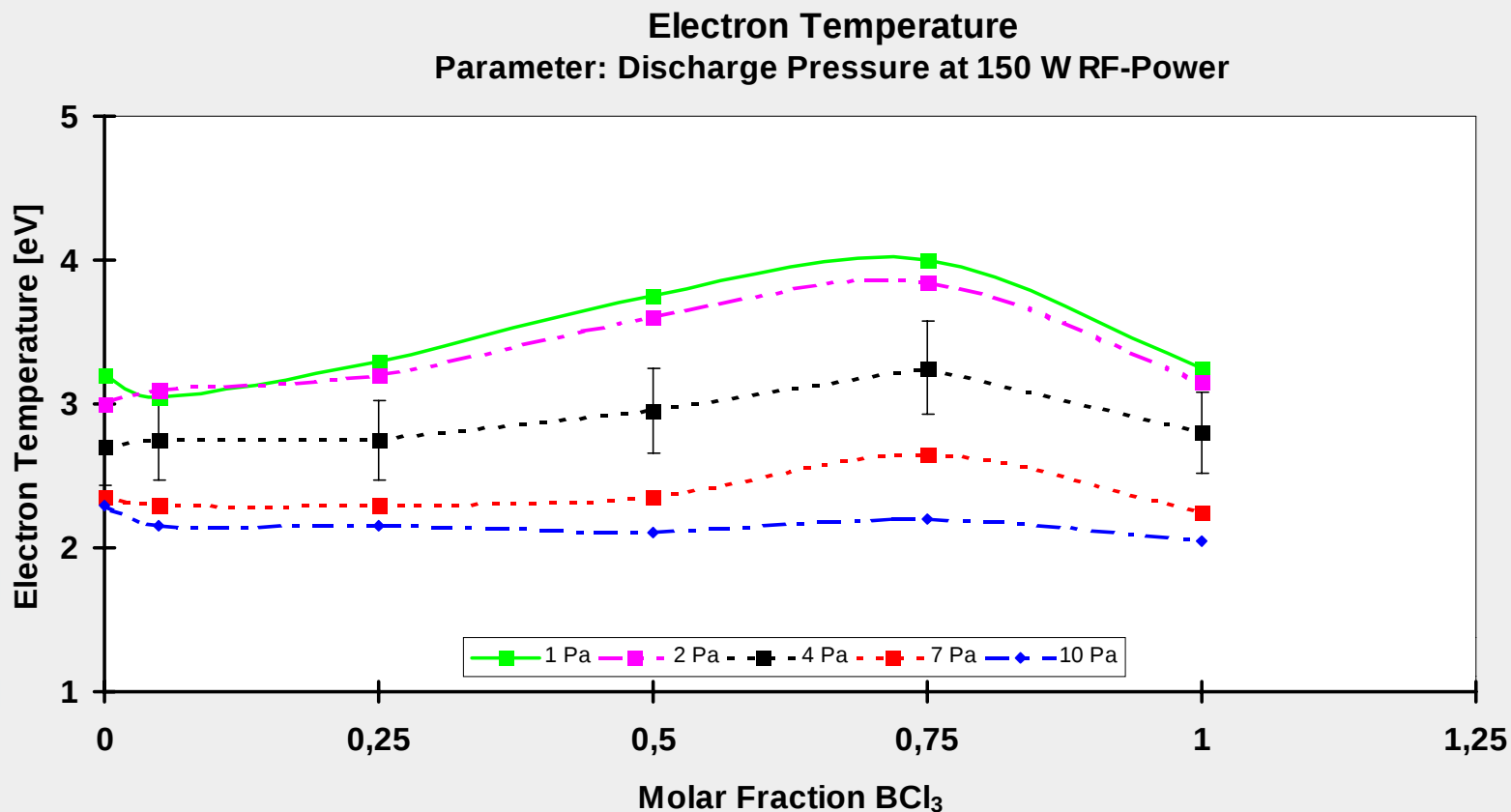
Ar(I) at 750.4 nm vs. Molar Fraction of BCl_3

Ar(I) at 750.4 nm vs. Molar Fraction of BCl_3
p: 2 Pa (15 mTorr)



Electron Temperature

Parameter: Discharge Pressure at 150 W RF-Power



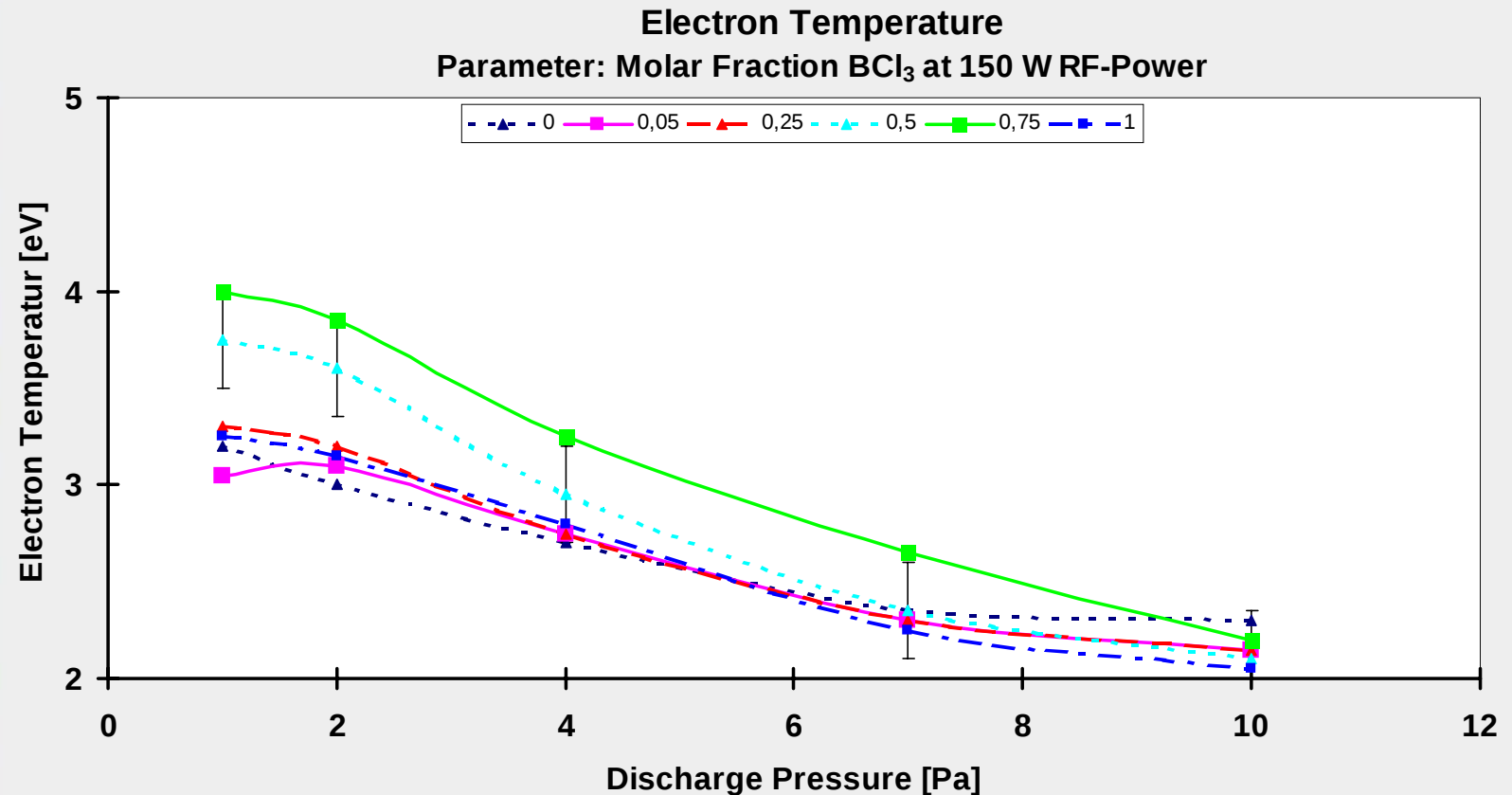
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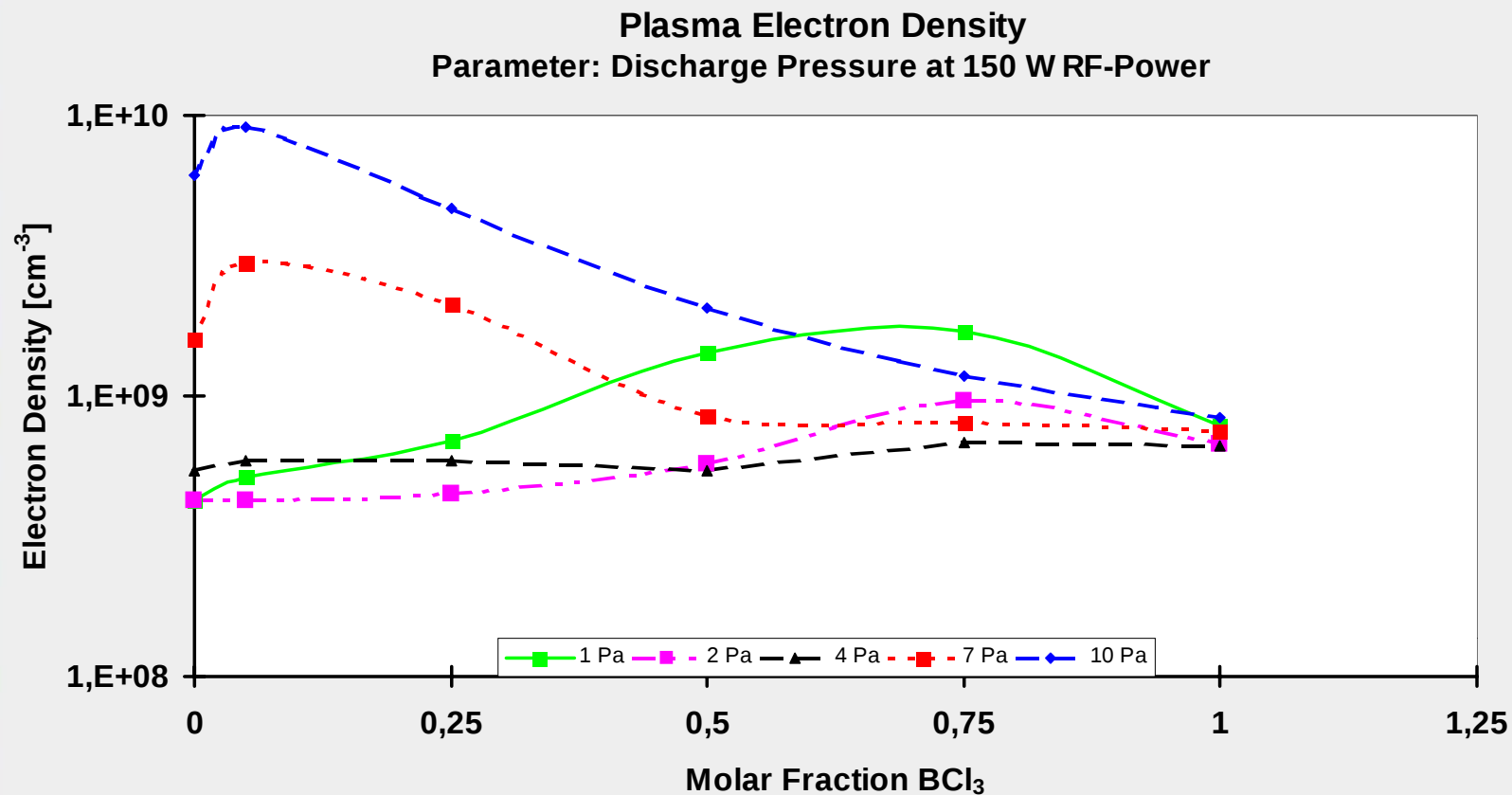
Electron Temperature

Parameter: Molar Fraction BCl_3 at 150 W RF-Power



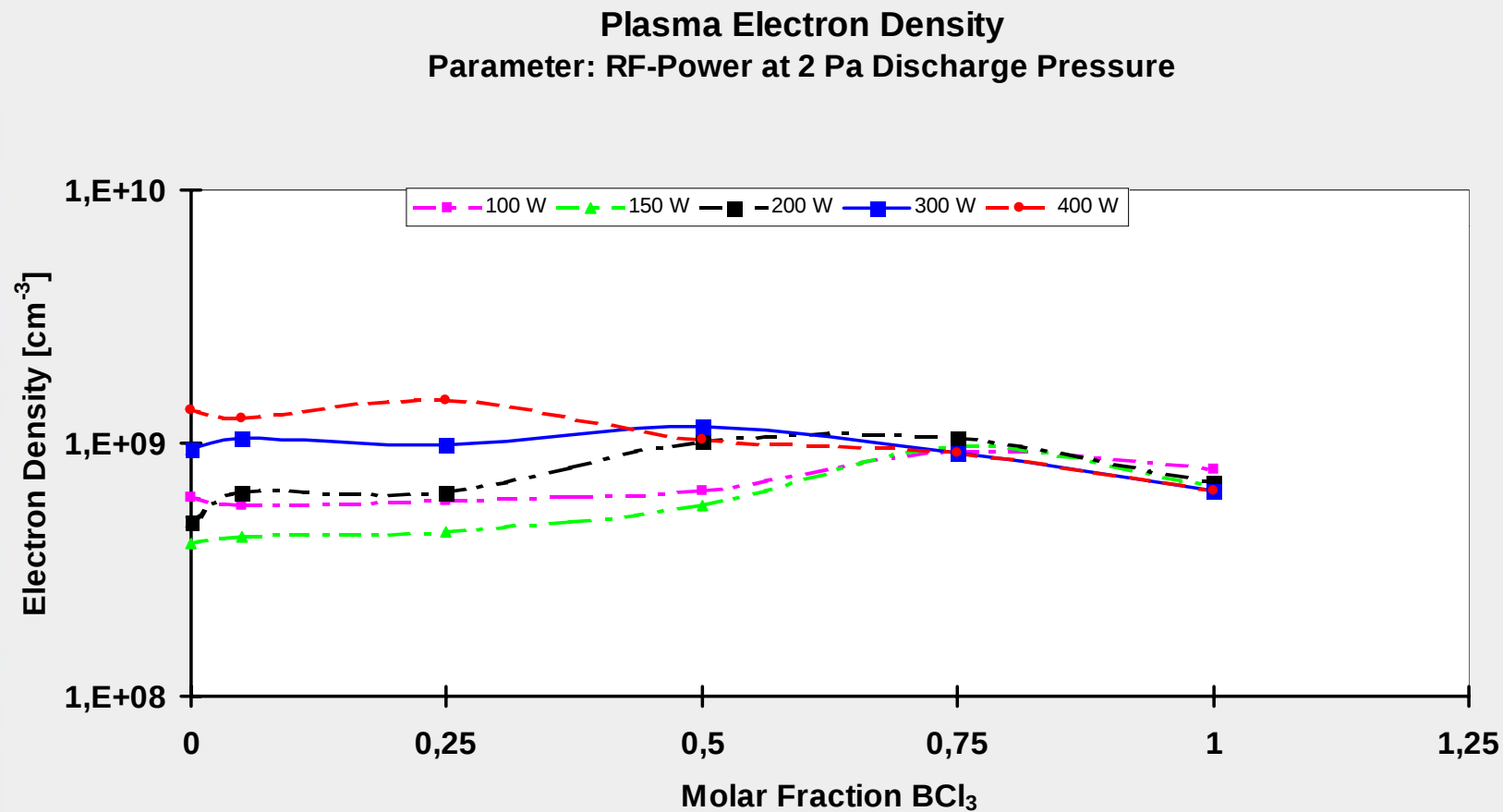
Plasma Electron Density

Parameter: Discharge Pressure at 150 W RF-Power



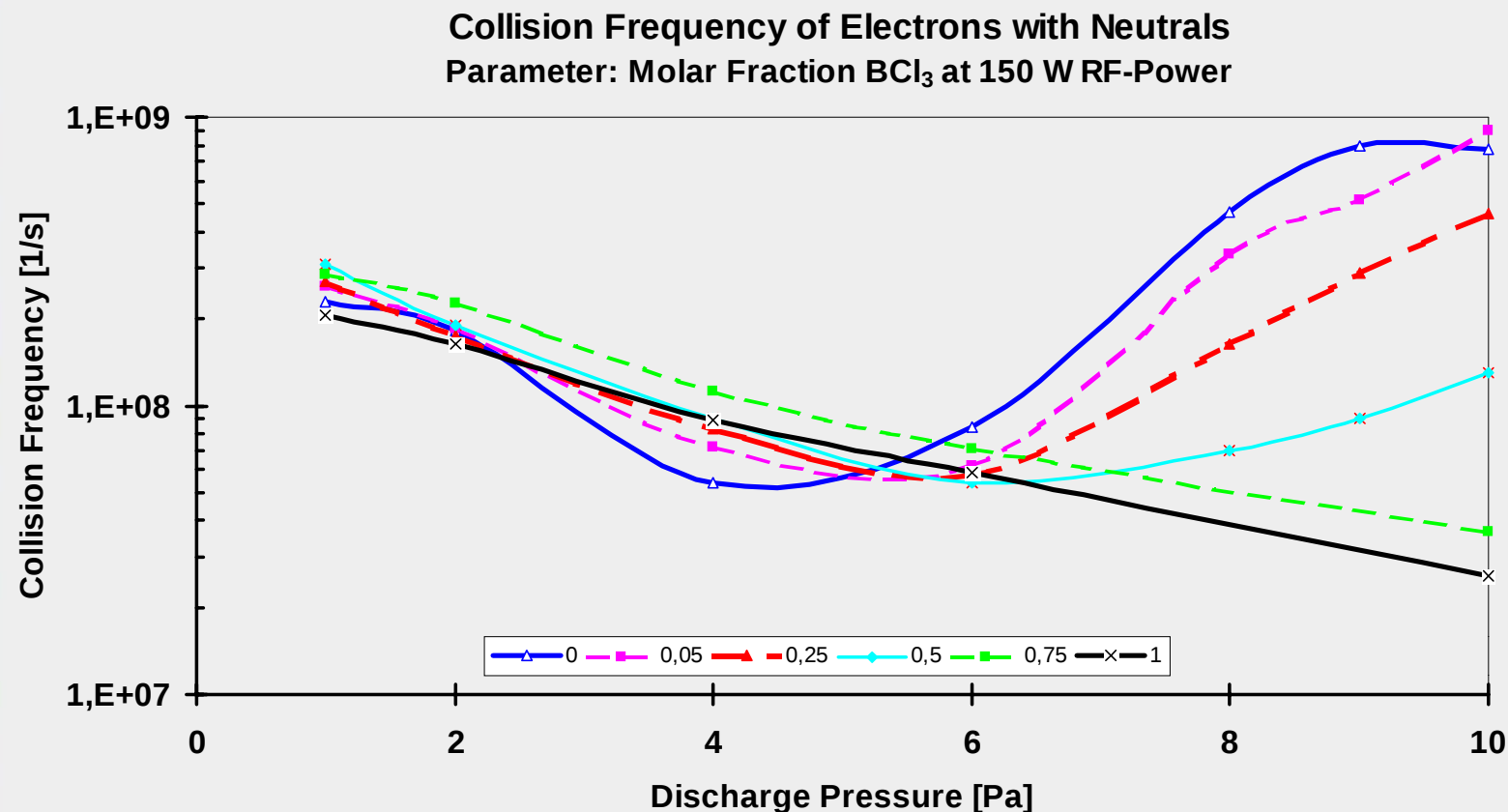
Plasma Electron Density

Parameter: RF-Power at 2 Pa Discharge Pressure



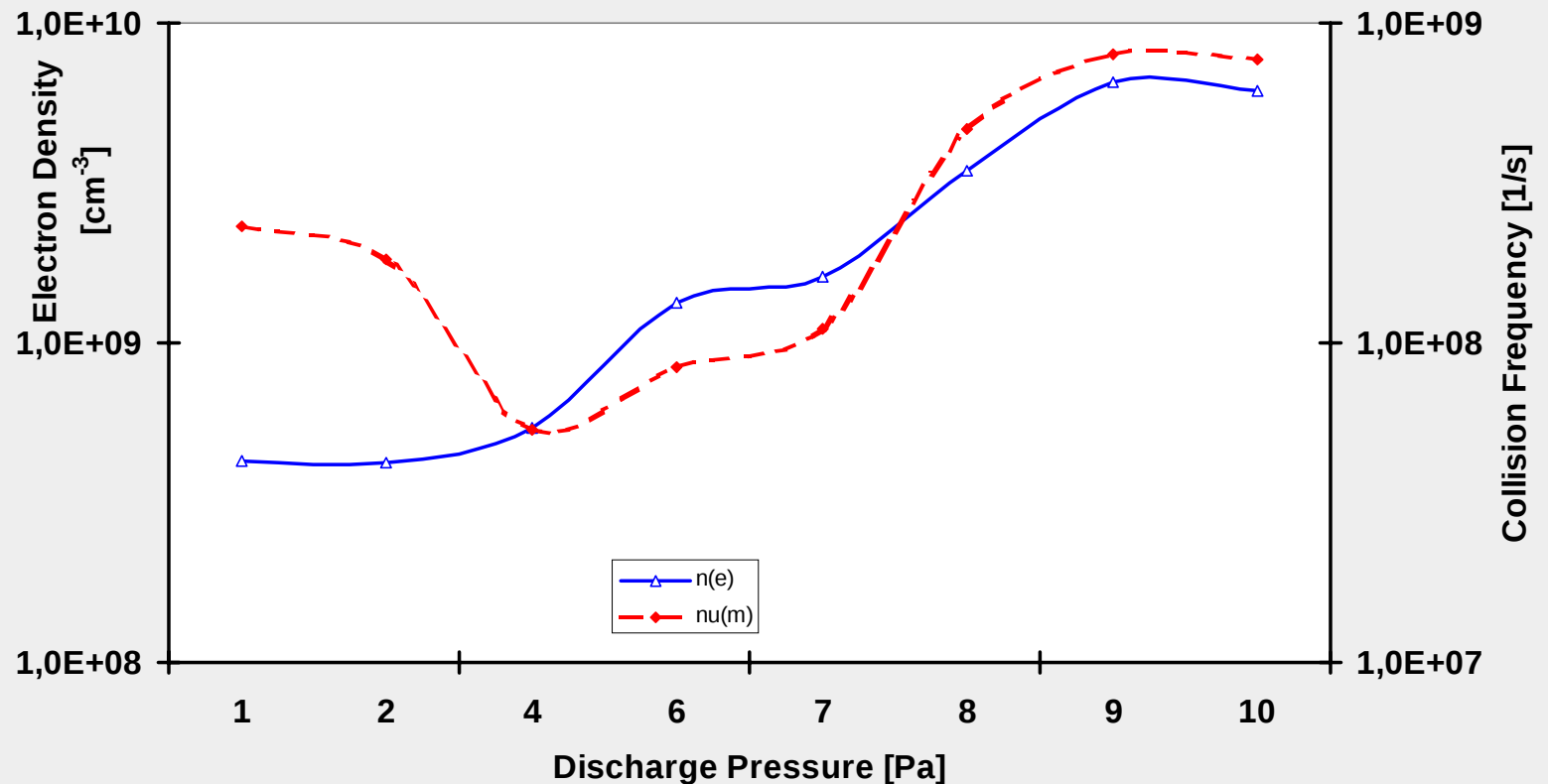
Collision Frequency of Electrons with Neutrals

Parameter: Molar Fraction BCl_3 at 150 W RF-Power



Cl₂: Electron Plasma Density and Collision Frequency

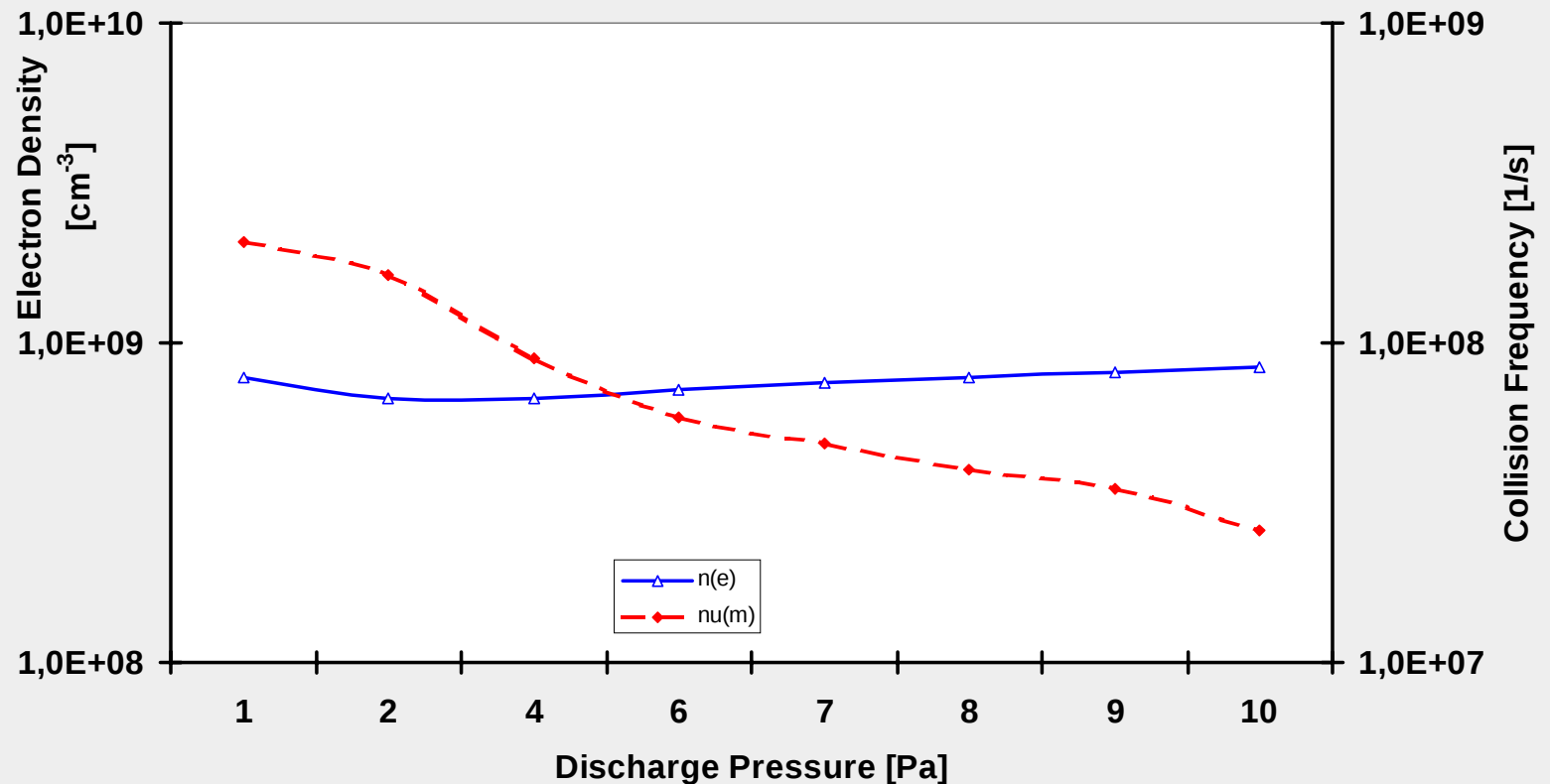
Cl₂: Electron Plasma Density and Collision Frequency



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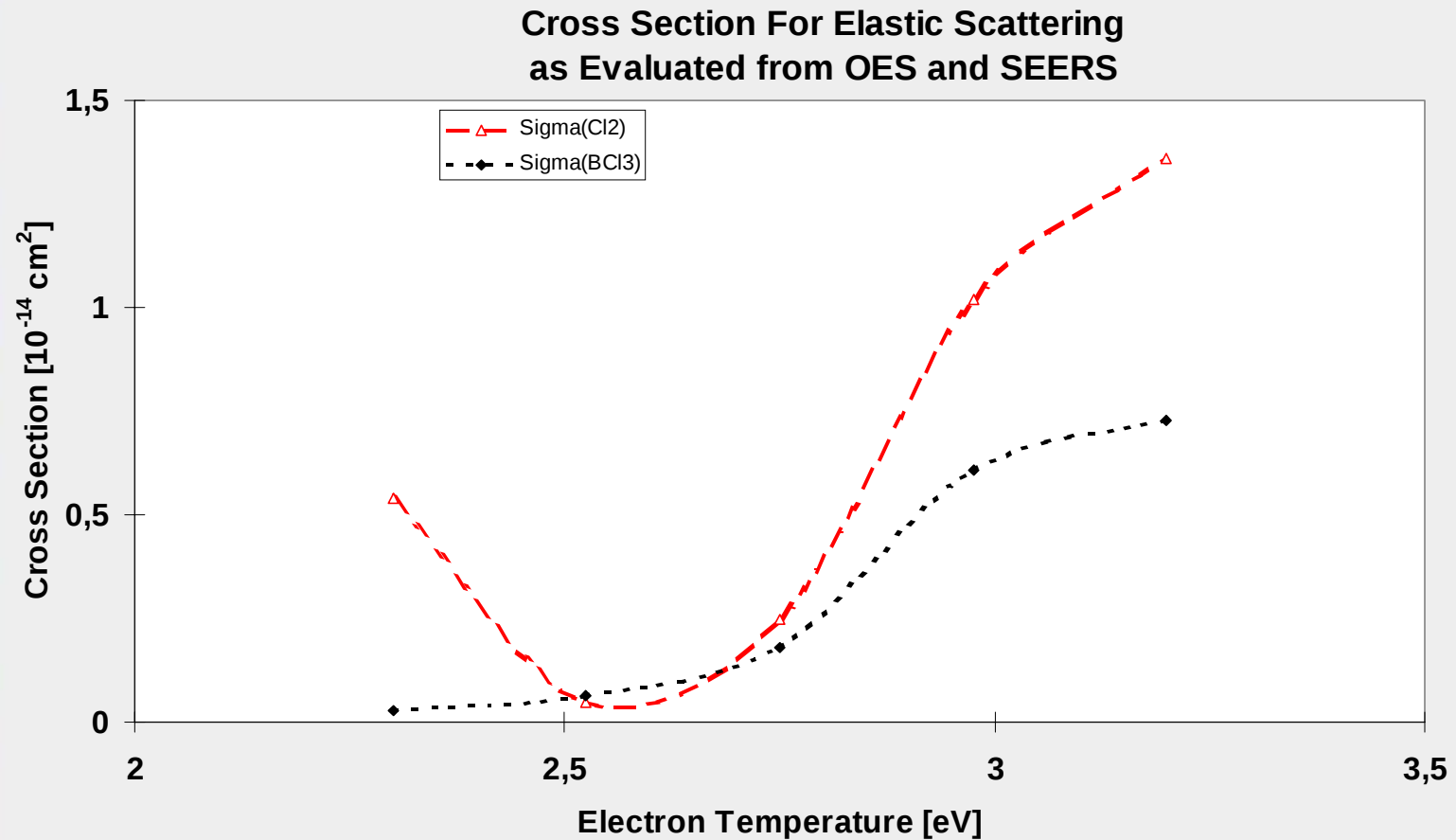
BCl₃: Electron Plasma Density and Collision Frequency

BCl₃: Electron Plasma Density and Collision Frequency



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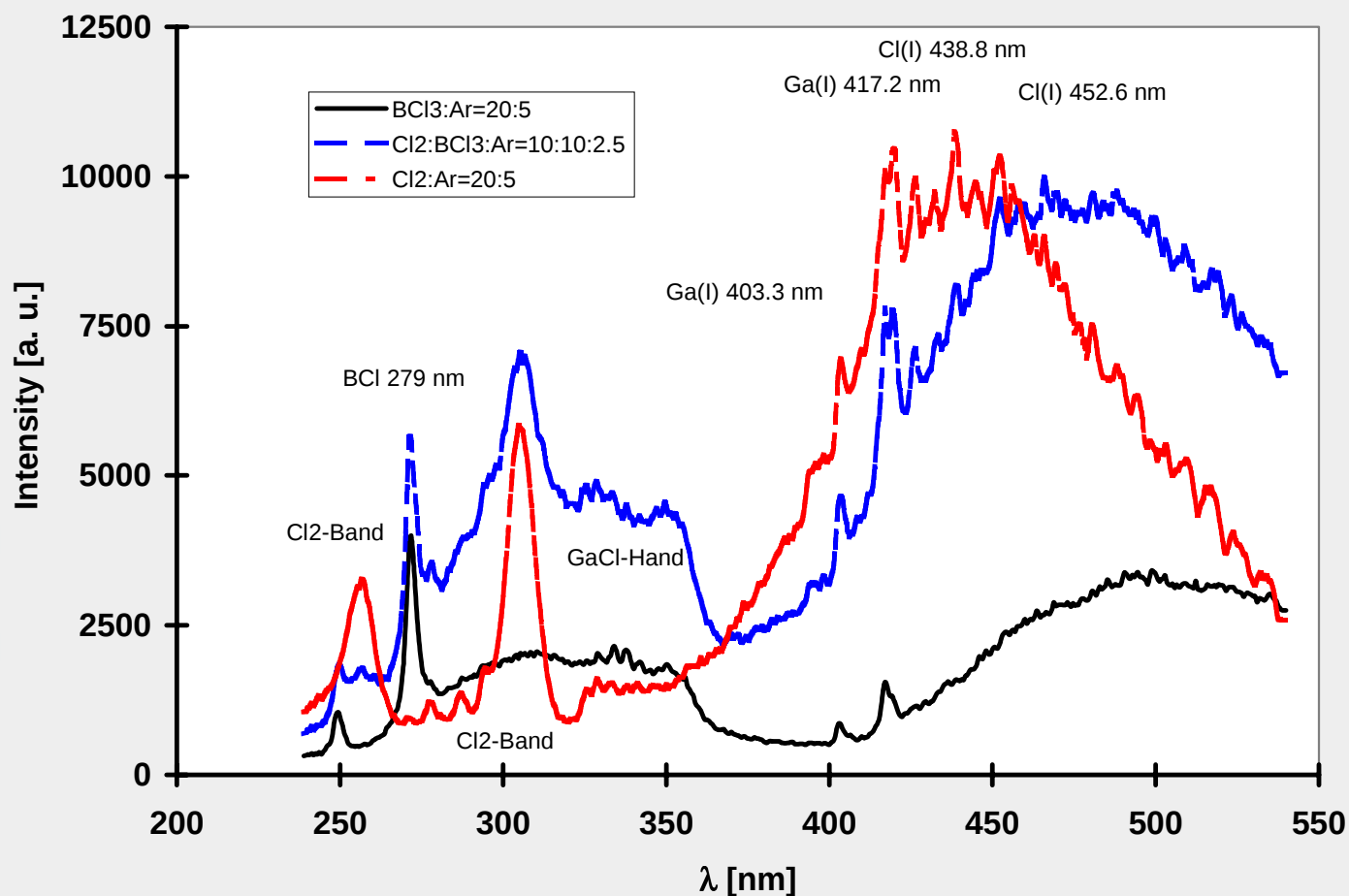
Cross Section For Elastic Scattering as Evaluated from OES and SEERS



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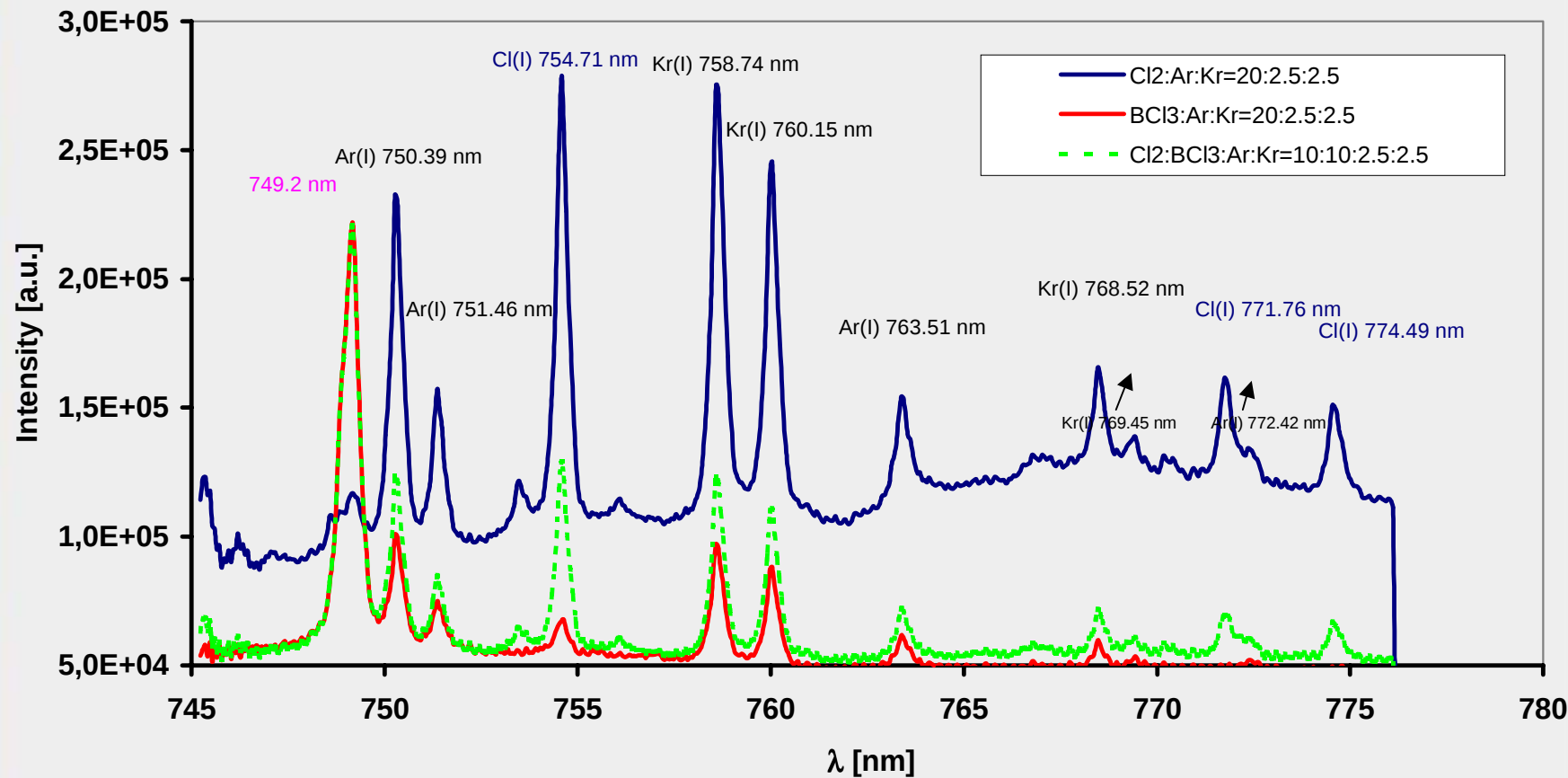
CCP-RIE of GaAs in Chlorine-Containing Atmospheres

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Optical Emission Spectroscopy Long- Wavelength Range for Advanced Actinometry (AA)

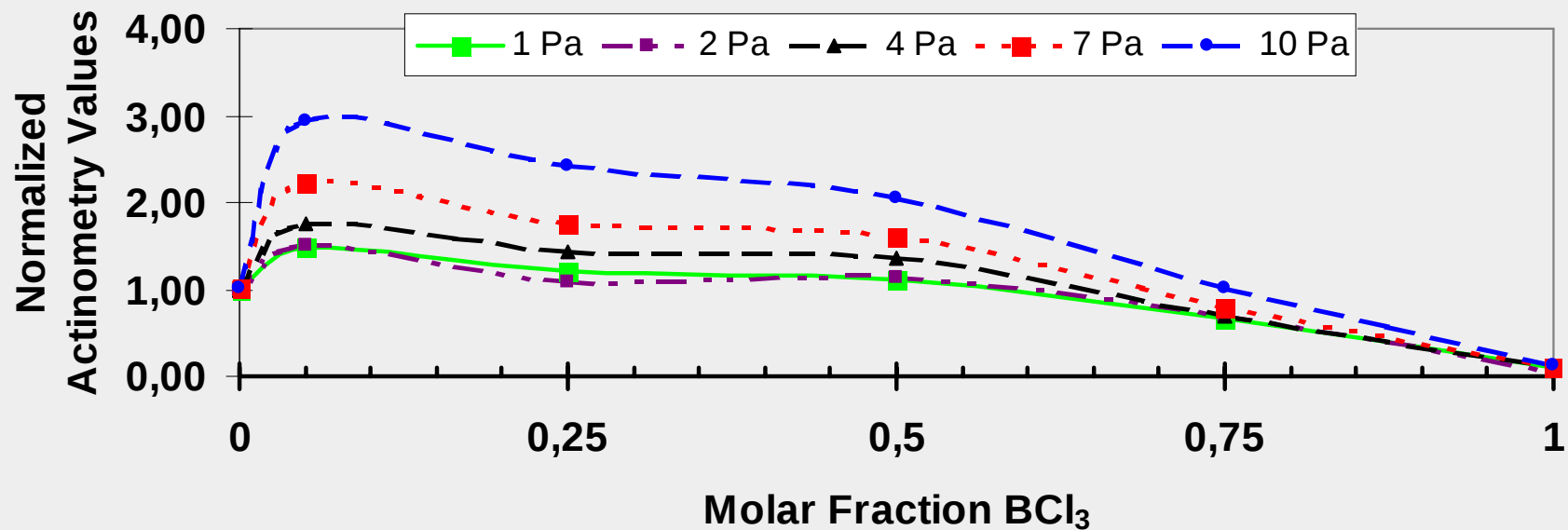
Optical Emission Spectroscopy
Long-Wavelength Range for Advanced Actinometry (AA)



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Normalized and Averaged Actinometry

Normalized and Averaged Actinometry
Cl(I): 725.66 nm and 741.41 nm; Ar(I): 750.39 nm and 751.46 nm



Conclusions I

The whole area of the BCl_3/Cl_2 CCP-plasma was measured using optical emission spectroscopy and electrical measurements to obtain non-spatial resolved data for the electron plasma density n_e , the electron temperature T_e , and the collision frequency ν_m of electrons with neutrals. Both the gases, Cl_2 and BCl_3 , act as effective coolants for the plasma. This leads to the complete extinction of Ar(II) lines. Therefore, it is impossible to evaluate T_e by measuring the optical intensities of Ar(I) and Ar(II), and measuring of various lines of at least two inert gases is required.

Conclusions II

The electron temperature increases with decreasing discharge pressure. Whereas at 10 Pa, over the whole range of mixing T_e remains constant at approximately 2 eV, at the lowest pressures between 1 and 2 Pa, a maximum of T_e is observed. Here, the electron temperature peaks at 4 eV. Remarkably, this will occur at a BCl_3 molar fraction of 0.75.

The electron density spans over more than 1 order of magnitude in pure chlorine (from $5 \times 10^8 \text{ cm}^{-3}$ to $1 \times 10^{10} \text{ cm}^{-3}$). Normally, it increases with increasing pressure except for the very low pressure of 1 Pa. Here again, the maximum is reached at a BCl_3 molar fraction of 0.75. The gap of one order of magnitude shrinks to undistinguishable differences in pure boron trichloride. This holds also true for the pressure range between 2 - 4 Pa.

The shape of variation for plasma density and electron temperature does not vary monotonically, but exhibits two more or less pronounced maxima: one at a mixing ratio of 95:5 for chlorine and one at equal gas flows. As it was shown in the introduction, the early maximum can be correlated to a maximum in spectral intensity of Cl_2 and Cl(I) .

Conclusions III

The active species in discharges of the pure compounds is the singly ionized chlorine molecule, which is accompanied by the chlorine radical in discharges of chlorine. Spectroscopically, there is absolutely no evidence for atomic chlorine in discharges of BCl_3 . For mixtures, we evidently observe a synergetic mechanism which is caused by the conduct of BCl_3 as a Lewis acid: the addition of chlorine to a discharge of boron trichloride leads to a little, but not a significant enhancement of the concentration of Cl(I) . By this effect, the etch rate not only of GaP and GaAs, but also of the aluminum-containing compounds like AlGaAs can be dramatically enhanced. Etch rates will peak when chlorine is doped with boron trichloride to reach a second (local) maximum when the flows equal each other.

The working window for a stable process which is robust or at least not very sensitive to deviations of process parameters pressure or composition of the atmosphere of the discharge can now be opened or closed using scientific plasma parameters. A process engineer is not interested in a very high electron density itself, but rather in constant process conditions. In fact, these are narrower, when fundamental process parameters tend to vary to a larger extent.