Non-equilibrium Plasma Chemistry

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Abstract: Plasma processing represents an electrically-driven and sustainable technology that can strongly contribute to the transition to a Green Economy. While it is already in use in many industries as e.g. for plasma cleaning and deposition, some basic concepts should still be further developed to fully use the potential of non-equilibrium plasma chemistry and to support process optimization, treatment of sensitive substrates, costs and up-scaling.

1. Introduction

In an electrically excited plasma, energy supplying and energy dissipating processes are typically dominant over energy exchange processes. The plasma thus is in a non-equilibrium state with high electron temperature, T_e, and lower gas temperature, T_{gas}. In a low pressure plasma, electron impact excitation is the predominant way to transfer energy to molecules, which allows an effective conversion of even inert molecules such as e.g. methane at T_{gas} close to room temperature (Figure 1).

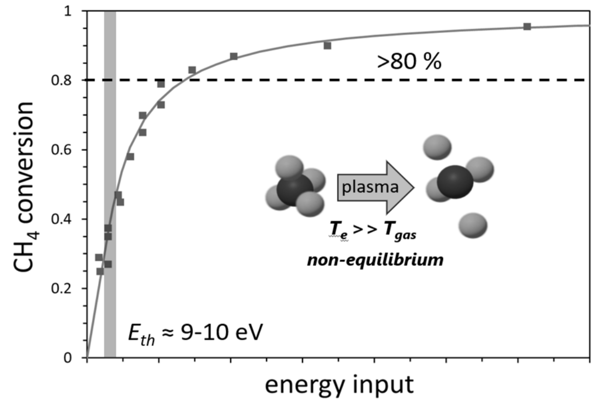

Fig. 1. Decomposition of methane in a low pressure plasma allows high conversion when the energy input surpasses the threshold energy, E_{th}.

2. Results and Discussion

The energy of the electrons follows an electron energy distribution function (EEDF) resulting in a low ionization degree, just sufficient to maintain the plasma (Figure 2). Thus energy is provided to promote any chemical reaction in the plasma, however, low conversion (far below the observed >80%) might be expected for direct electron-impact. Since molecules can already be excited at lower energies, several inelastic collisions during their residence time, τ_{pl}, in the plasma support dissociation, which thus occurs via intermediates enhancing overall conversion. Hence, not electron energy but the energy available per molecules, the specific energy input (SEI), governs chemical reactions in a plasma. Microscopically, SEI is related to parameters depending on the EEDF but also on τ_{pl}. Macroscopically, it is given by absorbed power per (molecular) gas flow rate. Recently, we could show by applying thermodynamic principles that SEI is also given by $T_e \bullet \Delta S_{m,e}$ regarding the change in entropy per molecule by electron-induced chemical reactions [1]. Since T_e is constant by changing absorbed power or gas flow rate, plasma chemistry is driven by entropy change in non-equilibrium conditions, whereas conventional chemistry is temperature-driven at thermodynamic equilibrium.

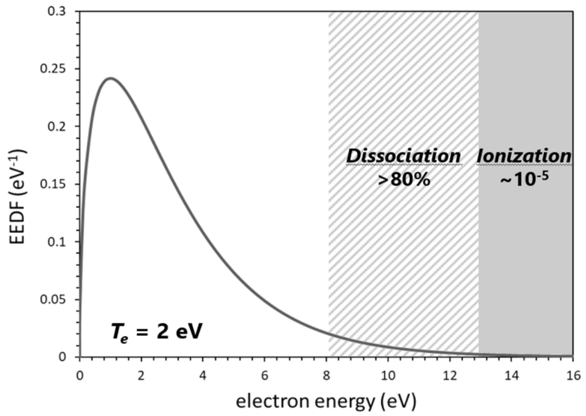

Fig. 2. Only the tail of the EEDF provides sufficient energy for direct electron-impact ionization yielding a weakly ionized plasma. Plasma chemistry, however, occurs with much higher conversion.

Different examples are presented considering plasma polymer film growth in siloxane- and hydrocarbon-based plasmas. Since film growth also involves plasma-surface interaction, methods are introduced to reduce its detrimental impact and to obtain a more defined film chemistry for the treatment of sensitive materials [2]. Thus, surface functionalization can be tailored, while upscaling is facilitated.

3. Conclusion

Plasma processing is a dry and sustainable technology that can be used to modify even sensitive materials at low temperature by adjusting energy input in the gas phase as well as in plasma-surface interactions.

References

[1] D. Hegemann, P. Navascués, R. Snoeckx, Int. J. Hydrogen Energy **100**, 548-555 (2025).
[2] P. Navascués, U. Schütz, B. Hanselmann, D. Hegemann, Nanomaterials, **14**, 195 (2024).