

Mid-infrared laser absorption spectroscopy for the detection of transient species in plasmas

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1. Introduction

Many industrial processes, such as the deposition and etching of thin films, involve the application of molecular plasmas. To improve the efficiency of these processes, more insight into the plasma chemistry is required. Therefore, the detection and quantitative measurement of transient species is a major challenge in industrial plasma applications. We will discuss three examples of transient species detection in varying types of plasmas applying laser-based diagnostics in the mid-infrared using lead salt diode lasers and quantum cascade lasers (QCLs).

2. Examples of transient species detection

2.1. Atomic chlorine

Inductively coupled radio frequency chlorine based gas mixture plasmas (ICPs) are frequently used to etch silicon thin films for the fabrication of microelectronic circuits. To improve the knowledge of the etching process, we monitored the atomic Cl density by measuring the ${}^2P_{1/2}(F=2) \leftarrow {}^2P_{3/2}(F=3)$ spin-orbit transition at 882.36 cm^{-1} ($11.3 \text{ }\mu\text{m}$) in a pure Cl_2 ICP by tunable diode laser absorption spectroscopy (TDLAS). The Cl density and translational temperature (from the Doppler width) were determined as a function of the gas pressure (20 – 200 mTorr) and the RF power (50 – 500 W).

2.2. CF_2 radical

The optimization of the dielectric etching process of ultra low-k porous SiCOH by fluorocarbon plasmas requires a deeper understanding of the density of the CF_2 radical, which acts as precursor in the polymerization of the etch sample surfaces. In an industrial plasma reactor, the CF_2 radical density was measured in-situ using a continuous wave QCL around 1106.2 cm^{-1} . We measured Doppler-resolved rovibrational absorption lines and determined absolute densities by probing transitions in the ν_3 fundamental band of CF_2 with the aid of an improved simulation of the spectrum and the line strength values. We found that the CF_2 radical concentration during the

etching plasma processes directly correlates to the layer structure of the etched wafer [1]. Hence, this correlation can serve as a diagnostic tool of dielectric etching plasma processes.

2.3. SiH_3 radical

The last example will address our current experiments, the detection of the silyl radical, SiH_3 , which is considered to be the most relevant radical in silane based plasma processes. The SiH_3 radical is detected in its ν_3 band around 2185 cm^{-1} which is more than a factor of three stronger than the well-known ν_2 band at 707 cm^{-1} . However, in this region also transitions from the ν_3 band of SiH_4 absorb and as a result the positions and line strengths of the SiH_3 transitions are not well known. We already quantified the silane line positions and line strengths in this region in the last year [2]. As far as we are aware, we now present the first measurements of SiH_3 radicals in a silane plasma (10% SiH_4 in H_2) using the external-cavity QCL absorption technique, providing a new and reliable method for measuring quantitatively the silyl radical in industrial plasmas.

This work was supported by the DFG via the SFB-TR24 “Fundamentals of Complex Plasmas”, project B2; the French-German PROCOPE Collaboration Programme, Project No. 154366449; funding from the European Union Seventh Framework Programme (FP7/2007-2013) under grant agreement No. 316216; funding from the technology funding for regional development (ERDF) of the European Union and by funds of the Free State of Saxony, Germany

References

- [1] M. Hübner, N. Lang, S. Zimmermann, S.E. Schulz, W. Buchholtz, J. Röpcke and J.H. van Helden 2015 *Applied Physics Letters* **106** pp 031102
- [2] J.H. van Helden, D. Lopatik, A. Nave, N. Lang, P.B. Davies, J. Röpcke 2015 *Journal of Quantitative Spectroscopy & Radiative Transfer* **151** pp 287