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Gas-phase characterization in diamond hot-filament CVD by infrared tunable diode laser absorption spectroscopy

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Abstract

In hot-filament CVD the gas-phase composition is a vital parameter for diamond coating results. Concentrations of carbon-containing species have significant influence on growth rate, quality and morphology of deposited diamond. To learn more about the correlations between process parameters and gas species concentrations we applied the highly sensitive infrared tunable diode laser absorption spectroscopy (IR-TDLAS) technique. With a sophisticated compact IR-TDLAS unit, relative and absolute concentrations of CH_4, C_2H_2 and CO were simultaneously measured. Also, the absolute concentration of the methyl radical was determined in dependence on process parameters. Concentrations of CO_2, C_2H_6 and HCN were investigated but found to be lower than the detection limit. The influence of the typical diamond CVD-process parameters on various species concentrations is discussed. The applicability of IR-TDLAS for hot-filament process monitoring is evaluated. In context with diamond growth results, information for CVD process refinement was deducted from the IR-TDLAS measurements.

Keywords: CVD; Diamond; Hot filament; Gas-phase; Methyl concentration; Absorption spectroscopy; IR-TDLAS

1. Introduction

In CVD diamond coating, hot-filament reactors are the most suitable ones when it comes to growing layers on complex geometries or up-scaled industrial coating processes with high numbers of substrates to be coated. Even though the precursor gases are often solely hydrogen and methane, the gas composition within the active coating zone becomes abundant on species. Therefore many works have been done for characterizing the gas-phase conditions and kinetics by numerous interdependent gas-phase reactions. Theoretical modeling, such as in [1–6] has been done to reveal gas-phase processes. Modeling results are dependent on input border conditions, being different for every reactor and filament–substrate arrangement. For experimental gas-phase diagnostics, sumptuous optical techniques such as REMPI, CRDS, CARS, LIF have been applied [7–10]. Each of these techniques has its advantages and drawbacks, as e.g. elucidated in Ref. [11]. Mostly, though, only one single species of the gas-phase can be measured at a time.

The improvement of process effectiveness, reliability and reproducibility in our hot-filament reactors requires investigation of process parameter effects on as many gas species as possible. For this purpose a compact infrared tunable diode laser absorption spectroscopy (IR-TDLAS) system has been used, that is capable of measuring absolute molecular gas concentrations of up to 8 species simultaneously in real time. IR-TDLAS is on one hand a very sensitive and non-invasive in-situ gas-phase characterization technique. On the other hand, when realized in a compact mobile system, the applicability for process refinement or even industrial on-line monitoring arises. The experiments at our hot-filament unit have been conducted with the following aims:

- Identification of carbon-containing species which are present in a sufficiently high concentration for being considered to act as growth precursors.

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- Characterization of species concentrations in dependence on process parameters.
- Determination of the role of oxygen- and nitrogen-containing species which might be present in our standard processes due to leakage influence.
- Evaluation of IR-TDLAS as an industrially applicable on-line gas-phase monitoring diagnostic.

For a comprehensive HFCVD gas-phase characterization, the role of atomic hydrogen, which could not be measured, is crucial. Therefore, gas-phase reactions involving this species are discussed taking into account the aspects of works on hydrogen diagnostics such as [12–14]. Additionally, former work on our reactors described dependencies of hydrogen dissociation processes and atomic hydrogen concentration from process parameters [15,16].

Experimental results of this work showing carbon-containing species concentrations are discussed comprising experience in diagnostics and gas-phase kinetics of low-pressure, low-temperature environments such as plasma discharges [17,18] and measurements in a diamond CVD bell jar reactor [19].

The choice of species to be analyzed was based on following aspects: former experimental work and modeling studies in literature had identified CH_3 and C_2H_2 as the only two species being sufficiently reactive and present at high enough concentrations to serve as precursor of diamond carbon [7,9–11,20–22]. According to widely accepted theories, CH_3 is the most likely growth species for diamond [20,22–24]. Other models [25] consider C_2H_2 as predominant growth species. In any case, acetylene is one of the most abundant carbon-containing species in diamond CVD gas mixtures besides undissoziated CH_4 and effects diamond growth [21,23]. Further, C_2H_6 was presumed as a product from recombination of CH_3 and as a link in the chain of forming longer carbon molecules. Oxygen present in Diamond CVD environments is mostly converted into CO [9,26], HCN has been identified as one of the most abundant stable species in low pressure methane- and nitrogen-containing HF-CVD atmospheres [27] of microwave discharges [28].

As a consequence, in this work species concentrations of CH_4, C_2H_2, CH_3, C_2H_6, CO, CO_2 and HCN have been examined. The results are analyzed with respect to the influence on CVD process parameter, related to diamond growth characteristics such as growth rate and morphology and further compared to experimental results found in literature.

2. Experimental

2.1. The CVD reactor

The IR-TDLAS measurements have been carried out in a new designed hot-filament plant at the WTM institute. This CVD reactor features all components that are state of the art for industrial diamond CVD coating plants and is operated by an SPS process control unit. Fig. 1 shows the geometry and dimensions of the reactor chamber. A filament–substrate arrangement similar to industrial coating plant set-ups was applied. The infrared laser beam entered the reaction chamber through KBr windows and was positioned parallel to the filament rows directly striving above the substrate surface. Using a retro-mirror, two passes inside the chamber were realized, leading to an optical length of 960 mm inside the chamber. Measurements were conducted employing one of the two possible rows of tungsten filaments (Fig. 1) on one side of the laser beam, representing industrial-like coating conditions in hot-filament diamond CVD. The feed gas was supplied from the top side of the chamber. The vacuum connection was located in the chamber's bottom plate. Species concentration measurements were performed at typical diamond coating conditions in the range of 7–30 mbar process pressure using hydrogen with an admixture of 0.3–2% methane as precursor gas at total gas flows between 300 and 2000 sccm. The filaments were operated at temperatures between 2000 and 2400 K.

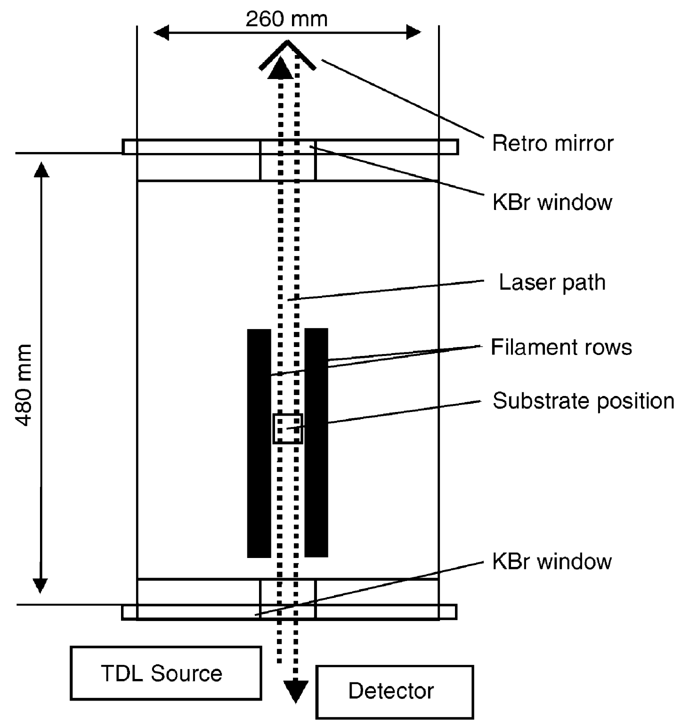

Fig. 1. Top view of the CVD reactor chamber with filament substrate arrangement and position of the laser beam path striving directly above the substrates surface. The shown set up with two paths of the laser through the chamber results in an absorption length of 960 mm window to window.

2.2. The IR-TDLAS system

For the infrared laser absorption measurements the compact and transportable IRMA (infrared multi-component acquisition) system [29] was employed. It features