Spectroscopic study of low pressure, low temperature H_2-CH_4-CO_2 microwave plasmas used for large area deposition of nanocrystalline diamond films

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In a distributed antenna array (DAA) reactor, microwave H_2 plasmas with admixtures of 2.5% CH_4 and 1% CO_2 used for the deposition of nanocrystalline diamond films have been studied by infrared absorption and optical emission spectroscopy techniques.

1. General

Although already more than two decades ago the feasibility of the deposition of nanocrystalline diamond (NCD) has been shown [1], the further development of this technology is still of great importance, in particular, as far the treatment of large substrates at relatively low temperatures is concerned. The physical properties of NCD are comparable to polycrystalline diamond (PCD), however, compared to PCD, NCD films are characterized by a very low roughness, which is independent on the thickness of the layers. A wider commercial use of NCD films has been limited so far (i) by insufficient adhesion properties to substrates and (ii) by the requirement of high substrate temperatures above 800 °C damaging sensitive substrates in the deposition process.

2. Experimental

In 2007 Latrasse and co-workers developed a new approach to provide high density microwave plasma sources for large area depositions while ensuring relatively low substrate temperatures below 400 °C. This new concept to realize a planar reactor comprises a 2-dimensional matrix of several single microwave plasma source elements without using magnetic fields [2]. Based on this 2-dimensional matrix approach of microwave antennas a 4 x 4 configuration has been successfully used to deposit uniform NCD films with very low surface roughness between 5 – 10 nm and a grain size in the range of 10 – 20 nm on a 4 inch wafer in 2014 [3].

The deeper understanding of the complex chemistry in H_2-CH_4-CO_2 microwave plasmas will be a crucial step for the further improvement of large scale NCD deposition at low substrate temperatures. In the present contribution optical emission spectroscopy in the visible spectral range has been combined with absorption spectroscopy (AS) in the mid-infrared spectral. For the latter one two different radiation sources have been used. Firstly, traditional lead salt lasers, since several decades employed in tunable diode laser absorption spectroscopy. Secondly, a new laser class, external cavity quantum cascade lasers (EC-QCLs), which up to now have only been used in limited cases in plasma diagnostics. In contrast to lead salt lasers EC-QCLs can be tuned over a spectral range greater than 100 cm^{-1} with a mode-hop free tuning range of the order of 80 cm^{-1}.

3. Results

Using AS the absolute concentrations of the methyl radical and of five stable molecules, CH_4, CO_2, CO, C_2H_2 and C_2H_6, were monitored in the reactor. Reliable information about the neutral gas temperature is a crucial precondition for the determination of concentrations of molecular species. Monitoring a variety of CO lines in the ground state and in three hot bands enabled an extensive temperature analysis providing novel insights into energetic aspects of the multi component plasma. An additional target was to derive fragmentation rates of the CH_4 and CO_2 precursors and their conversion rates to the reaction products. The influence of the discharge parameters power and pressure on the molecular concentrations was another focus of interest.

3. References

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