Modelling of $Ar/H_2/CH_4$ microwave discharges used for nanocrystalline diamond growth

F. Mohasseb, K. Hassouni, F. Bénédic, G. Lombardi, A. Gicquel

Laboratoire d'Ingénierie des Matériaux et des Hautes Pressions, UPR 1311 CNRS, Université Paris Nord, France

This work deals with the modelling of $Ar/H_2/CH_4$ discharges ignited in microwave cavity systems and used for nanocrystalline diamond film deposition. These microwave discharges are characterized by a strong thermal and chemical non-equilibrium and the gas mixture is typically composed of an argon amount greater than 90% and a CH_4 concentration of around 1 %. Plasma models were developed and used in order to describe the considered discharges under quasi-homogeneous plasma assumption. They allowed the determination of the plasma composition, gas temperature and electron energy in the bulk of the discharge.

As far as chemistry is concerned, the discharges used for nanocrystalline diamond growth are characterized by H/C ratio ranging between 8 and 18. For these H/C values, heavy hydrocarbons and soot particles may form for some discharge conditions, depending on pressure and input power values. Thus, in order to describe the plasma chemistry various thermochemical models were developed.

The description of the kinetics of the discharges was first focused on conditions where the formation of heavy hydrocarbons and soot particles is limited and may be neglected. In these situations the gas temperature is higher than 2000 K, which corresponds to the conditions met in the plasma bulk. Consequently, only species containing up to 2 carbon-atoms were considered in a first numerical model (2C model) that permitted to understand the main energetic characteristics of the investigated plasma and to evaluate the population of active species in growth conditions. In particular, the gas temperature inside the discharge was estimated to be higher than 4000 K. The validity of the numerical and kinetic schemes was partially checked by experimental spectroscopic measurements.

In order to probe the soot particle sources, the numerical model was extended to take into account Poly-Aromatic Hydrocarbons (PAHs) growth, following several mechanisms.

The first one took into account large neutral PAHs up to 4 aromatic rings (A4 model) from which the particle nucleation was assumed to take place. This study was performed in such a way to investigate the whole temperature domain that characterize both the plasma bulk, the plasma-substrate boundary layer and the regions outside the discharge (plasma edges and post-discharge regions). This was achieved by exploring a large domain of input microwave power which includes conditions that do not correspond to those used for NCD deposition. The soot formation is obtained for gas temperature values below 1500 K with a nucleation rate as high as 10^8 part./cm^3/h. At high gas temperature, the 2C and A4 models predicted the same species evolutions, and we concluded that the 2C model is accurate enough to describe such a discharge under deposition conditions. Thus, taking into account the formation of PAHs and soot nucleation is necessary only for temperature values less than 1500 K, which correspond to the boundary layer between the plasma and the substrate surface or reactor walls.

In the second mechanism, we studied the kinetic that leads to the formation of PAHs up to 9 aromatic rings (A9 model). The purpose was to investigate how the assumption on the size of the PAHs that lead to soot nucleation affects the nucleation rate. Results showed that the values found for this rate by the A4 and A9 models are quite similar. It was therefore concluded that the A4 model is adequate for studying PAHs formation and soot nucleation in $Ar/H_2/CH_4$ microwave discharges.

Then the chemistry of the model was extended in order to take into account the formation of ionic PAHs. Ions with up to four aromatic rings were considered (A4+ model). We showed that the growth of PAHs and nucleation of soot through this ionic mechanism is significant especially at high temperatures (>1500K). This means that soot particles may also nucleate in the bulk of the discharge where temperature is quite high (~4000K).

The last part of this work dealt with the investigation of the particle population dynamic. This was performed using the method of moment where we took into account the nucleation from PAHs molecules, growth by PAHs and small hydrocarbon condensation, coagulation and transport through diffusion, thermophoresis and drag forces, as well.