Modeling of the plasma chemistry and plasma-surface interactions in reactive plasmas

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Abstract: In this paper, an overview is given of modeling activities going on in our research group, for describing the plasma chemistry and plasma-surface interactions in reactive plasmas. The plasma chemistry is calculated by a fluid approach or by hybrid Monte Carlo – fluid modeling, while the plasma-surface interactions are described either with Monte Carlo or with molecular dynamics simulations.

Keywords: modeling, plasma chemistry, plasma-surface interactions, fluid, Monte Carlo, MD

1. Introduction

Plasmas in reactive gas mixtures are used in a growing number of application fields. For environmental applications, the plasma can be used as a chemical reactor, to destroy e.g., volatile organic compounds, or to convert e.g., greenhouse gases into value-added chemicals. Chemical reactions in the plasma also give rise to the formation of species which can react at a substrate, resulting in important applications in materials technology, such as plasma-etching and deposition of thin films.

To improve these applications, a good insight in the underlying plasma chemistry and plasma-surface interactions is of uttermost importance. We try to obtain this insight by computer simulations.

2. Modeling the plasma chemistry

For detailed modeling of the plasma chemistry, a fluid approach is the most appropriate, because many different species and chemical reactions can be included without too much computational effort.

For each species (i.e., electrons, various ions, molecules and radicals) a continuity equation (based on different production and loss processes, defined by the chemical reactions) and a flux equation (based on diffusion and by migration in the electric field, for the charged species) is constructed. Furthermore, the average electron energy is calculated with an energy balance equation, accounting for the gain of energy due to the electric field, and the loss of energy due to collisions. Based on this average electron energy, the electron impact collision rates can be calculated. For the so-called heavy particles (i.e., ions, molecules, radicals) no energy balance equation needs to be solved, as they are considered in equilibrium with the gas temperature. These equations are coupled to Poisson equation, to obtain a self-consistent electric field distribution in the plasma.

An alternative is to use a hybrid model, consisting of the fluid approach for the heavy particles and a Monte Carlo (MC) module for the electrons. In this way, the electron energy, and hence the electron impact collision rates, can be calculated in a more explicit and accurate way. However, the hybrid approach typically results in a longer calculation time.

The first example presented here is for fluid modeling of the gas conversion in dielectric barrier discharges used as a chemical reactor for gas treatment. Indeed, we are investigating the possibilities of greenhouse gas conversion to value-added chemicals, such as methanol and formaldehyde. More specifically, the partial oxidation of methane with CO₂ is investigated.

Table 1. Overview of the species taken into account in the CH₄/CO₂ gas mixture, besides electrons.

<table>
<thead>
<tr>
<th>Molecules</th>
<th>Ions</th>
<th>Radicals</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₄</td>
<td>CH⁺, CH₃⁺, CH₂⁺, CH⁺, C⁺</td>
<td>CH₂, CH₂, CH, C</td>
</tr>
<tr>
<td>C₂H₆, C₂H₅, C₂H₂, C₂H₈</td>
<td>C₂H₆⁺, C₂H₅⁺, C₂H₂⁺, C₂H⁺, C₂⁺</td>
<td>C₂H₅, C₂H₆, C₂H, C₂, C₂H₇</td>
</tr>
<tr>
<td>H₂</td>
<td>H⁻, H₂⁺, H⁺</td>
<td>H</td>
</tr>
<tr>
<td>O₂⁻, O₂</td>
<td>O₂⁺, O⁻, O₂⁺, O⁻, O₂⁻, O⁻</td>
<td>O</td>
</tr>
<tr>
<td>CO₂, CO</td>
<td>OH, HO₂</td>
<td></td>
</tr>
<tr>
<td>H₂O, H₂O₂</td>
<td>CHO, CH₂OH, CH₂O, C₂H₂O, C₂H₂O, C₂H₂O, CH₂CHO, CH₂CHO, CH₂O₂, C₂H₂O₂</td>
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To describe the chemistry in a CH$_4$/CO$_2$ mixture, 65 different species (including molecules, radicals, ions and electrons) are taken into account in the model, as is outlined in Table 1. In total, 112 different electron-neutral collisions, 39 different electron-ion, 328 different neutral-neutral, 166 different ion-neutral and 14 different ion-ion reactions are taken into account at this stage (the model is still under development).

The calculations are performed for a cylindrical DBD reactor, consisting of two concentric electrodes. Typical results obtained with this model include the densities of the various plasma species, as well as the relative importance of their various production and loss processes. Moreover, information can be obtained about conversion of the gases and the yields and selectivities of the various reaction products, for different values of gas flow and length of the reactor (or in other words: residence time).

The second example presented here is for studying the plasma chemistry in a (1%) CH$_4$ / (3-7%) H$_2$ / Ar gas mixture, in a microwave reactor used for the growth of nanocrystalline diamond thin films. In this model, 51 different species, including electrons, various molecules, radicals, positive ions and one negative ion (H$^-$), were taken into account, as is summarized in Table 2. About 60 different electron impact collisions, 110 different ion-neutral and 180 neutral-neutral reactions are included. For this application, a hybrid MC-fluid model is applied, more specifically the “hybrid plasma equipment model”, developed by Kushner [1], in order to accurately account for the electron energy as a result of microwave coupling.

Finally, the third example is for modeling the plasma chemistry in an Ar/Cl$_2$/O$_2$ inductively coupled plasma (ICP) reactor used for the etching of Si films. In this case, again the hybrid MC-fluid model (HPEM) is used, because the ICP reactor operates at pressures in the mTorr range, and under these conditions, the electron energy balance equation in the pure fluid model is too much of an approximation. In this model, the species taken into account are the following: electrons, Ar, Ar$^+$, Ar$^{++}$, Cl$_2$, Cl$_2^+$, Cl, Cl$^+$, Cl$^-$, O$_2$, O$_2^+$, O, O$^+$, O$^-$, O$^{++}$ and ClO. In total, approximately 120 different electron impact collisions, 26 different ion-neutral, 10 neutral-neutral and 80 plasma-surface reactions are included.

In both cases, typical results of this model include again, among others, the densities (and energies) of the various plasma species and the importance of their production and loss processes, as well as the electric field distribution in the plasma. Furthermore, also the fluxes of the various plasma species to the substrate are obtained, which is important for the applications, i.e., to describe the growth of the diamond film or the etching of the silicon wafer, respectively. The latter results form the input for the description of the plasma-surface interactions, as discussed in the next section.

### 3. Modeling the plasma-surface interactions

We investigate plasma-surface interactions on two different levels, i.e., (i) with MC simulations and (ii) with molecular dynamics (MD) simulations.

MC simulations can be used for predicting etch profiles. This is illustrated here with a MC module as part of the HPEM code [1,2]. Indeed, with the hybrid model, fluxes of the species bombarding the wafer can be calculated, as mentioned above. However, for accurately describing their interactions at the surface of the wafer (giving rise to etch profiles), it is important to know also their energy and angular distributions when arriving at the wafer. The latter are calculated by means of MC simulations for the ions and radicals in the sheath in front of the wafer. Subsequently, another MC model is used to describe the surface reactions (i.e., etching, sputtering, deposition), based on predefined reaction probabilities. We have applied this method to investigate the etching of a Si wafer by means of an Ar/Cl$_2$/O$_2$ plasma. Typically, the Cl atoms give rise to etching, and the O$_2$ is added to the discharge gas to protect the side walls by forming SiO$_2$, in order to ensure anisotropic etching. However, if too much O$_2$ is added, protecting SiO$_2$ layers are also formed on the bottom of the trench, preventing the Cl$_2$ plasma from further etching.

![Etch rate vs. Oxygen flow and Pressure](image_url)
We have numerically investigated this so-called “etch stop” behavior by varying the O₂ fraction as well as the total gas pressure, electric power and bias voltage at the wafer [2]. Figure 1 presents the effect of O₂ fraction (left) and total gas pressure (right) on the calculated etch rate. The model predictions are in good agreement with experimental observations (see dashed lines), indicating that the model can be used to predict under which conditions the etch stop behavior can be avoided.

It should be noted that the above calculation results depend critically on the assumed reaction probabilities of the various plasma species with the surface of the wafer, and the latter are not always known. They can be obtained from experiments, or from MD simulations.

In MD simulations, the interactions of the plasma species at the surface can be described in full detail, without predefined reaction probabilities. Indeed, the latter follow automatically from the calculations. The behavior of all atoms within the system is followed as a function of time by solving Newton’s laws, where the force is obtained from the interatomic interaction potential between all atoms. In this way, the system is simulated in a fully self-consistent and deterministic way, without making a priori assumptions. The greatest disadvantage of this method is that it is very time-consuming. Moreover, the reliability of the calculation results depend critically on the accuracy of the assumed interatomic interaction potential. We will present in the talk several examples of MD simulations.

The first example is for the interaction of Cl and O radicals on Si surfaces, in order to obtain reaction probabilities for etching and deposition, as needed in the MC etch profile simulations, described above. In our simulations, the Tersoff-Brenner potential form is used for the Si-Cl system, as originally developed by Humbird and Graves [3]. For the Si-O system, the interactions between Si-O and O-O are described by the Tersoff model parametrized by Munetoh et al. [4].

The second example is for the growth of nanocrystalline and ultrananocrystalline diamond ((U)NCD) thin films by means of microwave PE-CVD. From the fluxes calculated in a plasma model as outlined above, or obtained from experimental measurements, we know the relative importance of hydrocarbon radicals arriving at the substrate. In this case the Brenner potential [5] is used as the interatomic interaction potential. With the MD simulations we were able to predict sticking coefficients of the various hydrocarbon radicals on different diamond surfaces, as is explained in detail in [6,7]. This enables us to predict which are the most important growth species for (U)NCD thin films.

On the other hand, modeling the real growth process of the films is not possible, because of the limited time and length scales of the MD simulations, i.e., typically up to 4 ns and for a surface of 4 nm² (to maintain acceptable calculation times). The latter does not allow us to observe diamond nanocrystals (of typical diameter of 50-100 nm for NCD and of 2-5 nm for UNCD) in an amorphous matrix. The problem of the limited calculation time of the MD simulations implies that the real growth process cannot be simulated. Indeed, the typical integration time per hydrocarbon impact is in the order of 5 ps in the simulations. When starting immediately afterwards the next impact, there is not enough time for surface relaxation, which is very important for pursuing the diamond structure. Therefore, we have coupled the MD model with a Metropolis Monte Carlo (MMC) method, which accounts for the slower adatom surface processes. A detailed description of this procedure, as well as the calculation results, are presented in [8]. It is illustrated how the MMC simulation predicts the formation of diamond six-rings, therefore pursuing the diamond crystal structure. To verify the results, additional longer time-scale MD simulations have also been carried out. The resulting structures were found to be very similar to those obtained by the MMC simulations, but the MMC simulation time is typically one order of magnitude shorter than the MD simulation time, or in other words, a boost factor of one order of magnitude was achieved.

A similar (combined MD-MMC) approach can also be used to simulate the growth of carbon nanotubes (CNTs) by PE-CVD. It is well-known that the growth of CNTs by PE-CVD is catalyzed by metal nanoclusters (e.g. Ni). The hydrocarbon source gas (e.g., C₂H₆, C₂H₂, CO₂, CH₃OH,…) is assumed to dissociate immediately upon impact on the nanoparticle, so that MD simulations can be used to describe the interaction of C atoms with the Ni nanocluster. The interatomic interaction potential used for these simulations is the Shibuta potential [9].

Fig. 2. Simulated configuration after 295 ns, as a result of MD/MMC trajectories of consecutive C “impacts” on a Ni₁₀₀₈ nanocluster at 1200 K. Ni is blue; the C network is yellow.

The growth process is simulated by consecutive “impacts” of C atoms on the nanocluster, consisting of about 100 Ni atoms. The timestep in such MD simulations is in the order of fs, and the integration time per impact is in the order of ps. Because in reality, the time between two C
“impacts” (as defined by the flux) is much longer (typically in the order of microseconds), the MD method needs to be combined again with MMC simulations to account for diffusion and relaxation effects between two impacts.

Figure 2 presents the results of MD/MMC simulations of consecutive C atoms impacting on a Ni108 nanocluster, after a growth time of 295 ns. Obviously, this time is still too short for CNT growth, but the start of a CNT cap is already visible.

Finally, the last example given here is for metal oxide thin film growth due to magnetron sputter-deposition. Figure 3 illustrates the simulated microscopic structure (a) and the calculated Mg-O radial distribution functions (RDFs) (b) of thin Mg, Cr, O films, deposited on an amorphous Al2O3 substrate for different ratios of Mg/Cr.

Fig. 4. Snapshots of simulated Mg, Cr, O films at different Mg/Cr metal ratio (a) and calculated Mg-O RDFs (b) for the presented films. For comparison, the RDF of a MgO crystal is also presented. The RDFs show a clear transition from a crystalline MgO phase to a more amorphous film.

The film is grown to a thickness of approximately 6-7 nm. The simulation time per impact is 2-4 ps, followed by 2-6 ps of relaxation before the next impact takes place. Again, this yields far too high deposition rates and does not allow sufficient time for surface diffusion and other relaxation processes. However, in the case of magnetron sputter-deposition where the growth process is assisted by energetic ion bombardment, thermal surface diffusion probably does not play a significant role in the simulation of film growth, if the surface temperature is low compared to the activation energy barrier for surface diffusion.

As is clear from Figure 3, the growing film appears to be crystalline with MgO structure and Cr in between at high Mg content, and it gradually becomes amorphous when more Cr is added. The Cr2O3 film is a mixture of polycrystalline and amorphous phases. Similar results were also obtained for Mg, Al, O films, and were confirmed by X-ray diffraction and transmission electron microscopy, as is explained in detail in [10].

4. Conclusions

We have shown several examples of computer simulations, both for describing the plasma chemistry and plasma-surface interactions. The plasma chemistry is modeled by means of a fluid or a hybrid MC-fluid approach, whereas the plasma-surface interactions (more specifically for plasma-etching or deposition of thin films or CNT growth) are described by either MC or MD simulations. The output of the plasma models can be used as input in the plasma-surface simulations and vice versa (e.g., to define the boundary conditions for the plasma modeling). Therefore, we believe that by combined effort of simulations of both the plasma behavior and plasma-surface interactions, a more complete picture of reactive plasmas can be obtained.

References