Application Note: CHEMKIN / CHEMKIN-PRO

Fluorocarbon Plasma Etching of Silicon Dioxide

APP-Plasma-3 (v2.0) August 30, 2010

Summary

This application note is an example of modeling a low-pressure plasma reactor as a steady-state Perfectly Stirred Reactor.

Project Description

This application is representative of a high-density plasma, with a plasma power of 3000 Watts and a pressure of 10 mtorr. Pure hexafluoroethane is the inlet gas. The energy equation and the electron energy equation are solved, and a heat-transfer correlation is used to account for heat loss through the wall of the reactor. This example illustrates the use of multiple materials, each with a different set of surface reactions, as well as the use of continuations with varying flow rate and ion impact energy.

This chemistry set is for a fluorocarbon plasma (C_2F_6) used for etching silicon dioxide films, a process that is used in the fabrication of microelectronic and MEMS devices. The chemistry set includes detailed surface reactions, including multiple materials with different reaction sets. Although it is quite complex, this mechanism is actually a small, early version of a more complete mechanism developed by Meeks and coworkers for etching several fluorocarbon precursors. Detailed descriptions of the full mechanisms, including information on the sources of rate parameters, can be found in their publications.[1, 2, 3]

The gas-phase chemistry described in the chemistry input file, *chem.inp* file involves 6 elements, 36 species, of which there are 9 positive ions, 3 negative ions, the electron, and 23 neutral species. There are 149 gas-phase reactions. Of these, 75 are electron-impact reactions leading to dissociation, dissociative ionization, attachment, vibrational and electronic excitation. Such reactions are included for the starting reactant C_2F_6, dissociation fragments such as CF_3 and CF_2, as well as etching products such as O_2 and SiF_4. The electron-impact reactions are all irreversible, and the rates depend on the electron energy, rather than the neutral gas temperature. There are 22 irreversible reactions describing the neutralization between positive and negative ions in the gas phase. Such reactions have high

---

[1] "Modeling the Plasma Chemistry of C_2F_6 and CHF_3 Etching of Silicon Dioxide, with Comparisons to Etch Rate and Diagnostic Data", P. Ho, J. E. Johannes, R. J. Buss, and E. Meeks, *J. Vac. Sci. Technol. A* **19**:2344 (2001).

[2] "Plasma Modeling", E. Meeks and P. Ho, Chapter 3 in "Advanced Plasma Processing Technologies", edited by R. J. Shul and S. J. Pearton, Springer-Verlag, Heidelberg, (2000).

[3] "Chemical Reaction Mechanisms for Modeling the Fluorocarbon Plasma Etch of Silicon Oxide and Related Materials", P. Ho, J. E. Johannes, R. J. Buss and E. Meeks, Sandia National Laboratories Technical Report No. SAND2001-1292.

A-factors and are not energy dependent. The remaining 46 reactions are reactions of neutral gas-phase species, mostly reversible, some with explicitly specified reverse reaction rates. Many of the reactions include the participation of new specific collision partners (M), and a number of the unimolecular decomposition/bimolecular recombination reactions have detailed descriptions of the pressure dependence of the rate parameters.

The surface chemistry described in the surface input file, surf.inp, involves three materials with different reaction sets. The different materials in the model correspond to different physical parts of a plasma reactor that are all exposed to the plasma, but are affected by the plasma in different ways. The material called `SIDEWALL` and the material called `WAFER` are both silicon dioxide. The wafer is expected to have an applied electrical bias, resulting in higher ion energies. It thus has a more extensive set of reactions, especially ion-enhanced chemical reactions that result in etching. Although both sets of reactions describe the chemical species in the plasma interacting with silicon dioxide, the mechanism description needs to have unique names for the two sets of materials, surface sites, surface species, and bulk species to allow for different reaction sets. The material `SIDEWALL` has a surface site called `GLASS` with species SIO2(S) and SIO2_F2(S), and a bulk phase `QUARTZ` with a bulk species SIO2(B). The material `WAFER` has a surface site called `AMOXIDE` (for amorphous oxide) with species WSIO2(S), WSIO2_F2(S), and WSIO2_CF2(S), and a bulk phase `OXIDE` with a bulk species WSIO2(B). In the species names, the (S) is a convention often used to indicate a surface species, the _F2 and the _CF2 indicate a surface silicon oxide site with two F atoms or a C atom and two F atoms bonded to it, respectively, and the (B) indicates a bulk species. All the surface reactions are irreversible. All ion-surface reactions are subject to the Bohm flux criterion.

There are 31 surface reactions for the material `WAFER`. First there is a reaction describing the spontaneous etching of silicon dioxide by F atoms, and a reaction describing the adsorption reaction of F atoms with an open-site surface species to form a fluorinated surface species. There are five reactions describing the ion-enhanced etching of SiO_2 from the fluorinated surface species, producing SiF_4 and O_2 as etch products, and regenerating the open SIO2(S) species. These reactions have yields (number of surface sites converted per ion) that depend on the ion energy, as well as overrides of the default order of the reaction. More details about these features are provided in the *CHEMKIN Input Manual*. Next are reactions describing the adsorption of CF_x radicals to form the WSIO2_CF2(S) species, and five reactions describing the ion-enhanced etching of SiO_2 from the fluorocarbon-covered surface species, producing SiF_4 and CO as etch products, and regenerating the open SIO2(S) species. These reactions also have ion-energy–dependent yields and overrides of the default order of the reaction. There are nine reactions describing ion-neutralization with electrons on the surface, plus seven reactions describing the direct sputtering of SiO_2 by ions.

The reaction set for the material `SIDEWALL` is a 16-reaction subset of that for the material `WAFER`, but with the appropriate species names. The material called `TOPWALL` is defined as silicon with two surface species. However, the reactions consist only of non-site–specific neutralization reactions of positive ions with electrons.

Project Setup

The project file is called ***plasma_psr__c2f6_etch.ckprj***. The data files used for this sample are located in the *samples\plasma_psr__c2f6_etch* directory. This reactor diagram contains a gas inlet and a plasma PSR.

You input the reactant gas mixture, which is pure C_2F_6 in this case, on the Species-specific Property tab of the C1_Inlet1 panel. The Stream Property tab of the R1_IN1 panel has fields for the input of the gas flow rate (30 sccm), inlet gas temperature and inlet electron temperature, but.although the latter is required, it has little impact on the solution unless there are electrons in the input gas mixture.

You input most of the parameters on the C1_Plasma PSR panel. Its Reactor Physical Property tab allows selection of problem type, as well as places to enter parameters such as the plasma power, pressure (10 mTorr), volume, internal area, heat loss parameters, cross-section for electron momentum loss, and initial guesses for the electron, neutral, and ion temperatures. The Species-specific Data tab allows input of initial guesses for the steady-state gas composition, surface site fractions, and bulk activities, on the corresponding sub-tabs, as well as species-specific values for electron-momentum loss cross-sections. Make a good initial guess for the gas and surface compositions (one that is close to the steady-state solution) to gain fast convergence; a poor initial guess can lead to failure of the simulation. The Bulk-phase-specific Data tab allows you to indicate that all the bulk materials are being etched, which affects some of the equations. The Material-specific Properties tab is for specifying properties like surface temperature (if different from the neutral gas temperature), ion energy or bias power, Bohm factor, sheath energy loss factor, area fraction, or heat loss, either for all materials, or on a per-material basis. For this non-parameter-study problem, you use the bottom part of the panel to set up values that are dependent on the material. Material-independent properties can be set on the Reactor Physical Properties panel. In this example, the `WAFER` is held at a temperature near room temperature (consistent with active cooling), while the `TOPWALL` is held at an elevated temperature (consistent with active heating), while the `SIDEWALL` temperature is allowed to float with the gas temperature (the default). A relatively high ion energy (in electron Volts) is specified for the `WAFER`, reflecting that this material substrate has an applied electrical bias, separate from the main power, for this system. The low ion energy for the `SIDEWALL` is consistent with the plasma self-bias, rather than active biasing of this surface. Do not specify a temperature for the `TOPWALL`, as no ion-energy–dependent reactions occur on this material.

On the Solver panel, a number of parameters on both the Basic and Advanced tabs have been altered from the defaults in order to help get a good solution. Skipping the intermediate fixed-temperature solution is the default for plasma simulations and is recommended. The Output Control panel allows you to specify whether sensitivities should be calculated and printed in the output and solution files, and whether ROPs should be printed and saved. In this case, sensitivities for temperature, growth (etch) rate, F atoms and SiF_4 will be calculated. ROPs for six species will be included. The Continuations panel specifies two continuations. First, the ion energy for the wafer is changed from 200 to 300 V, and the flow rate is increased from 30 to 50 sccm. Second, the flow rate is returned to the initial lower value, while leaving the ion energy at the higher value. In this example, the plasma power is entered on both continuation panels, although it is not changed. This is not necessary, but will not cause any problems and may serve as a useful reminder.

Project Results

In *Figure 1*, the SiO_2 etch rates for variations of C_2F_6 flow rate and Wafer ion energy are: 1) 30 sccm, 200 V. 2) 50 sccm, 300 V. 3) 30 sccm, 300 V. This shows that oxide etch rates (negative growth rates) on the Wafer are much larger than those on the Sidewall, in accord with the higher ion energy for that material. Comparing solutions 1 and 3 shows that increasing the Wafer ion energy increases the etch rate, as expected. But comparing solutions 2 and 3 shows that increasing the reactant flow rate also increases the etch rate, indicating that the etching system may be reagent-supply limited. This is consistent with the results shown in Figure 2, which shows the 10 neutral species with the highest mole fractions. C_2F_6, the reactant species, does not appear, as it is mostly decomposed to smaller fragments in the plasma. The species with the highest mole fraction, F atoms, is a reactant fragment that can contribute to etching, as are CF and CF_3, which are also present in relatively high concentrations. These species have higher mole fractions in solution 2, which has the highest flow rate, whereas etch-product species, such as CO and SiF_3, have lower mole fractions at the shorter residence time. Figure 3 Fluorocarbon Plasma Etching of Silicon Dioxide—Positive Ion Mole Fractions shows that CF^+ is the most prevalent positive ion, with F^+, CF_2^+ and CF_3^+ about a factor of 2 lower. There is less F^+ than CF^+, even though there is more F than CF, and the major pathways producing F^+ and CF^+ are ionization of F and CF, respectively. This reflects a higher rate for the CF ionization reaction than the F ionization reaction. Although not shown, the electron is the most prevalent negatively charged species, with CF_3^- roughly a factor of 6 lower. Negative ions stay in the body of the plasma and do not participate in reactions at the surface due to the presence of an electronegative sheath.

Figure 1 Fluorocarbon Plasma Etching of Silicon Dioxide—SiO_2 Etch Rates Variations

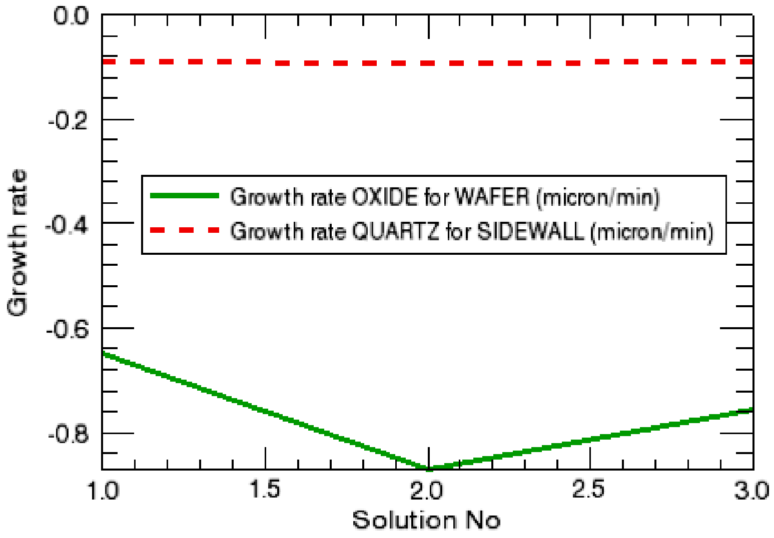


Figure 2 Fluorocarbon Plasma Etching of Silicon Dioxide—10 Highest Mole Fractions

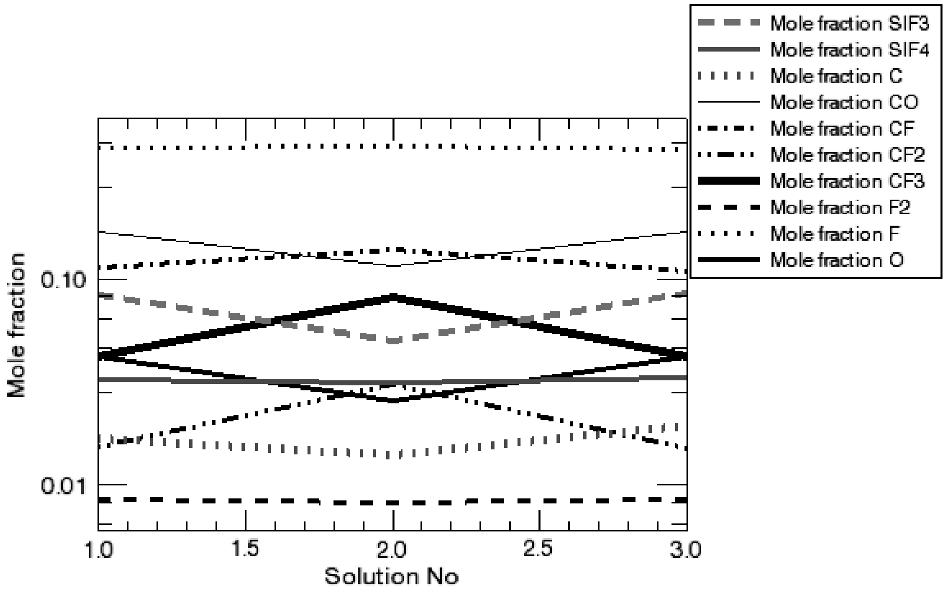
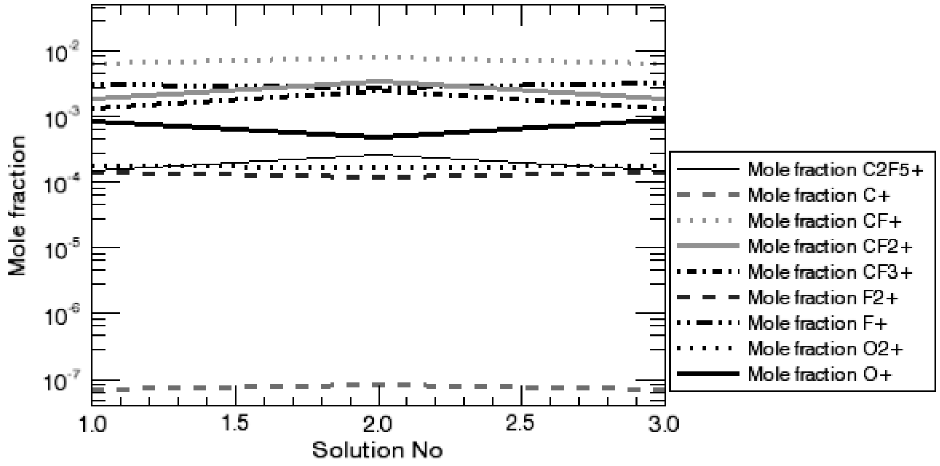


Figure 3 Fluorocarbon Plasma Etching of Silicon Dioxide—Positive Ion Mole Fractions



The surface site fractions shown in *Figure 4* show minor changes with conditions. Comparing solutions 1 and 3 shows that increasing the Wafer ion energy increases the fraction of open sites and decreases the fraction of fluorocarbon-covered sites. This is consistent with the increased ion energy causing an increase in yield for the ion-enhanced etching reactions. Comparing solutions 3 and 2 shows that increasing the C_2F_6 flow rate decreases the fraction of open sites and increases the fraction of fluorocarbon-covered sites. This is consistent with an increased supply of fluorocarbon radicals that can react with the open sites. Figure 5 shows the 5 reactions with the largest contribution to the loss of silicon dioxide from the wafer. In order of decreasing importance, surface reactions 13, 14, 11, and 12 are etching of WSIO2_CF2(S) sites assisted by CF^+, F^+, CF_2^+, and CF_3^+, respectively. Reaction 5 is the

F^+ ion-assisted etching reaction of the WSIO2_F2(S) site. These five reactions are responsible for most of the etching, but a number of other reactions contribute to the total etch rate.

Figure 4 Fluorocarbon Plasma Etching of Silicon Dioxide—Surface Site Fractions

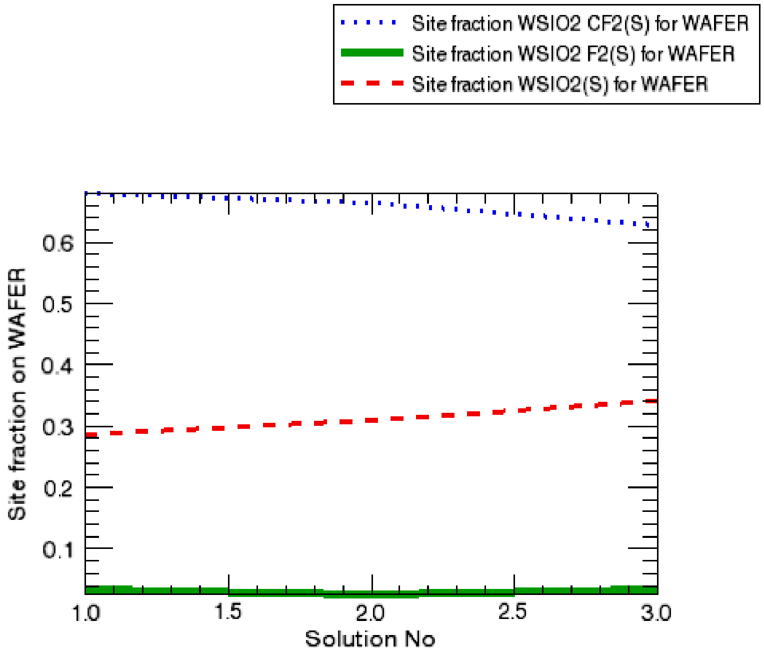
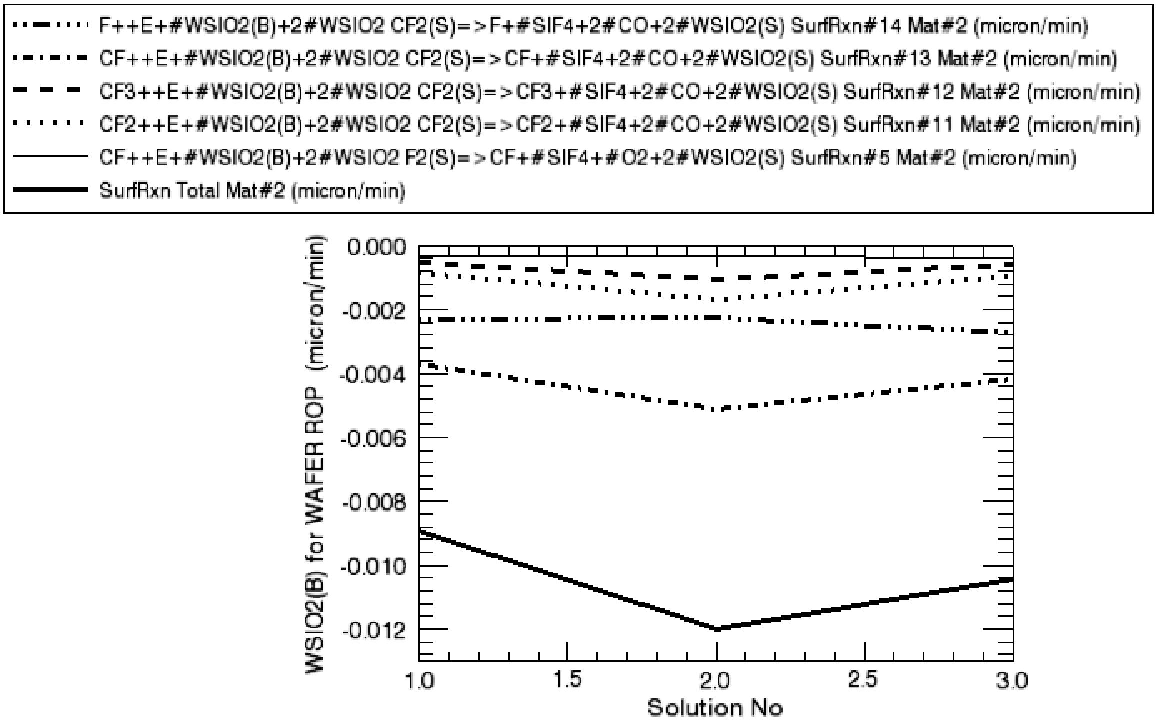


Figure 5 Fluorocarbon Plasma Etching of Silicon Dioxide—Highest ROP



About Reaction Design

Reaction Design helps transportation manufacturers and energy companies rapidly achieve their Clean Technology goals by automating the analysis of chemical processes via simulation and modeling solutions. Reaction Design is the exclusive developer and distributor of CHEMKIN, the *de facto* standard for modeling gas-phase and surface chemistry that provides engineers ultra-fast access to reliable answers that save time and money in the development process. Reaction Design also offers the KINetics software module, which brings detailed kinetics modeling to other engineering applications, such as Computational Fluid Dynamics (CFD) programs. Reaction Design's world-class engineers, chemists and programmers have expertise that spans multi-scale engineering from the molecule to the plant. Reaction Design serves more than 350 customers in the commercial, government and academic markets.

Reaction Design can be found online at www.reactiondesign.com.