Chapter 1

Introduction

Over the past decades, plasma etching has been widely used in the fabrication of silicon-based integrated circuits. However, due to complex physical and chemical effects during etching, issues of reproducibility and control of the interaction processes ultimately limit its widespread application and further progress. In plasma etching, reactive neutral and ionic species strike the surfaces that are in contact with plasma and form products as illustrated in figure 1. An electron-free space-charge region designated as a "sheath" forms between a plasma and a contacting solid surface. Sheaths are of critical importance for plasma etching, since positive ions are accelerated toward the surface when entering a sheath. The accelerated ions bombard the surface with energies that are much greater than thermal energies. This results in non-thermal interactions that are in many instances dominant in controlling the outcome of a plasma-surface process. The consequences of plasma-surface interactions are to a significant extent controlled by the incident ion fluxes and their energies. A number of theoretical studies have indicated that nearly all incident ions will be neutralized within a few angstroms of the surface, as a result of Auger or resonant processes. Thus, the majority of the particles actually striking surface atoms are not positive ions, but neutral species.

In order to fully understand etching processes, a fundamental knowledge of plasma-surface interactions is needed. Establishing and quantitatively describing a plasma-induced surface reaction mechanism in the plasma environment requires, (a) characterization of the incident species fluxes, e.g., as a function of composition, energy, angle, and so forth; (b) determination of the surface processes, e.g., adsorption, reflection, direct reaction behavior of the incident species, the surface coverage, composition of the reaction layer, and so forth; (c) determination of the reaction products ejected from the surface (their chemical identity, energy content, desorption mechanism, angular distribution etc.). Ideally we would like to characterize and quantify the importance of each of the elementary surface processes for important plasma and surface species, and relate these to measured etching or deposition rates, film properties, etc.

For analysis of the incident flux and the ejected reaction products, many techniques are applicable for in-situ analysis. Laser-induced fluorescence, line-of-sight plasma sampling by mass spectrometry, Fourier transform infrared (IR) spectroscopy or IR diode laser absorption spectroscopy and UV absorption spectroscopy. Using these techniques, the incident flux can be relatively precisely characterized. Many powerful surface science tools are used to for post-exposure characterization of surfaces, such as X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES) and scanning electron microscopy (SEM). However, the measurements of these tools are performed under ultra-high vacuum (UHV) conditions. Therefore, the treated sample must be transferred to a UHV chamber and an assumption of stability of the plasma-modified surface must be made.
In order to overcome deficiencies of conventional surface analytical tools, in our laboratory a new low energy, grazing-incidence ion scattering apparatus was introduced to investigate plasma surface interactions. This technique can monitor real-time and in-situ surface reactions occurring during plasma processing. It has the following advantages: (1) monolayer or subsurface sensitivity by adjusting the primary ion and angles involved. (2) element-specific and sensitive to all elements, including hydrogen, in the outermost layers. (3) surface structure analysis. In addition, in order to avoid strong coupling between plasma and surface, a cascaded arc source introduces plasma to the UHV chamber through three differentially pumped stages. Combining these two sources in one chamber, plasma strikes the surface at normal incidence. At the same time, a low ion energy beam scatters from the surface at grazing incidence to monitor reactions occurring.

Typically experimental results from plasma/ion surface interaction are complex because of the wide range of processes occurring. Identifying the relative importance of individual events from the measured ensemble can be very important. In order to better interpret the experimental data and to get insight into the interactions of low energy ions with surfaces, we adopted molecular dynamics (MD) simulations to model the processes. In terms of the functions of the new setup, our simulations are divided into two parts. One part is the simulation of grazing scattering of projectiles (Ar and CF) from the surface. The other part deals with plasma surface interactions. This thesis details the functions of the experiment apparatus and the results from the complementary MD simulations.

MD is an atomic simulation method for studying equilibrium and transport properties of classical many-body systems. The basic idea in an MD simulation is simply to set up the system and to solve Newton’s equations of motion for the collection of mutually interacting particles. Newton’s equations are used to derive the dynamics of the system; we obtain the following set of $6N$ equations:

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\begin{align*}
  r_i &= p_i / m_i \\
  p_i &= F_i
\end{align*}
\]
where $p_i$ is the momentum of the particle, $r_i$ and $m_i$ are the position and mass of the particle $i$, $F_i$ is the total force exerting on it derived from the interatomic potential. These two equations can be solved by finite difference methods using a time interval $\Delta t$ which must be made sufficiently small for accurate results. In MD simulations, the dynamics of the system are obtained by following trajectories of the individual atoms. The course of a trajectory is dictated by the interatomic potential. This means that we are able to address time-dependent properties of the system, such as ion scattering from a surface, ion implantation, sputtering of surface atoms and thin film growth.

It is important to note that the purpose of an MD simulation is not to predict precisely what will happen to a system that is initially in a well-defined state. In fact, for almost all systems, the trajectory of the system through phase space is sensitively dependent on the initial conditions. This means that the trajectories of two systems which were initially very close to one another may diverge exponentially as time progresses. Therefore, the aim of the simulation is to predict the average behavior of the system in a statistical sense.

By using MD simulations, much work has been performed on particle interaction with surfaces (at normal and grazing incidence), cluster beam deposition, annealing processes and structure of thin films and the mechanical properties of multilayer films. In this thesis, we examine grazing scattering geometry relevant to the new setup. In addition, deposition and etching modeling, related to plasma-surface interactions, are done using MD methods. Therefore, this thesis can be clearly divided into two main parts, based on the incidence geometry.

(1) Grazing scattering

In this part, we simulated projectiles (Ar, CF) scattering from un-reconstructed Si and defected Si (100) surfaces at grazing incidence. The incidence energy is more than 1 keV. The normal incidence energy is related to the total energy, according to the equation: $E_n = E_T \sin(\theta)^2$, where $E_n$ is the normal incident energy, $E_T$ is the total energy and $\theta$ is the incidence angle with respect to the surface plane. At grazing incidence, the normal incidence energy is only several eV while the parallel energy is much larger than the normal incidence. This means that the incidence particles cannot penetrate the surface into the bulk. Therefore, scattering under this geometry is very sensitive to the surface structure and is suitable as a surface probe. Given the small normal incidence energy, in this section a Molière potential is used to describe the interaction between projectiles and Si atoms. A spring potential is used for Si-Si interactions. For the C-F interaction, the Morse potential is adopted.

(2) Interaction with surface at normal incidence (deposition and etching)

In the second part, plasma-surface interactions are simulated. As mentioned before, ion interactions play an important role in plasma-surface interaction. When reactive ions from plasmas interact with surface atoms many chemical reactions (bond breaking and formation) occur. In order to relatively precisely describe this behavior under classic MD, reactive empirical bond order (REBO) potential is adopted. This type of potential allows for covalent bond breaking and formation with associated changes in atomic hybridization within a classical potential, producing a powerful method for modeling complex chemistry in large many-body systems. The incidence energy ranges from 2-200 eV, comparable to ion energies in plasma processes.

This thesis

This thesis consists of several chapters representing the particle-surface modeling that was done by MD simulations. Each chapter can be read separately and since they are inter-
related some overlap of content is inevitable. Together they describe physical and chemical processes that may occur in our new instrumentation.

**Chapter 2** describes the new time-of-flight (TOF) instrument for studying the dynamics of plasma-surface interactions. Some experimental results for Ar$^+$ scattering from Si (100) surfaces subject to different pre-treatments are shown.

In **chapters 3-5**, modeling of grazing scattering in the new setup is shown. In **chapter 3**, grazing scattering of 3 keV Ar along the [100] direction of an ideal (unreconstructed) Si (100) surface is simulated. A detailed analysis of the scattering trajectories is performed. The dependence of the energy loss, scattering angle on the surface structure is shown. In **chapter 4**, the MD simulations of Ar scattering from perfect and point-defected Si(100) surfaces at grazing incidence are shown. The simulated results demonstrate that the angular and energy distributions of the scattered particles are extremely sensitive to small adatom coverages. An electron-stopping model is included in the simulations to model the available experimental data in which the energy loss is mainly contributed by inelastic loss processes. The results produce simulated energy losses that are in good agreement with experimental measurements. In **chapter 5**, we have simulated CF scattering from Si (100) using the molecular dynamics method. Translational energy loss spectra are presented and the stereodynamics of CF scattering is discussed.

**Chapters 6-8** show modeling of plasma-surface interactions. In **chapter 6**, the interaction of CF with the clean Si(100)-(2x1) surface at normal incidence and room temperature was investigated using molecular dynamics simulation. Some simulated results are in good agreement with available experimental data. The level of agreement between the simulated and experimental results and the limitation of MD simulation are discussed. In **chapter 7**, molecular dynamics simulations of the CH$_3$ interaction with Si (100) were performed using the Brenner potential. The results show that H atoms preferentially react with Si. SiH is the dominant form of SiH$_x$ generated. The amount of hydrogen that reacts with silicon is essentially energy-independent. H atoms do not react with adsorbed carbon atoms. The presence of C-H bonds on the surface is attributed to molecular adsorption. In **chapter 8**, a general discussion is presented to show how the potential, some important parameters (heat bath, relaxation time and cell size) and the surface temperature affect etching of Si by fluorocarbon. **Chapter 8** can be regarded as a primer on some of the technical consideration involved in MD simulations.