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学 位 論 文 題 目	Development of Etching Process Simulator Based on Tight-Binding Quantum Chemical Molecular Dynamics Theory and Its Application to Design of MEMS and Semiconductor Processes (強結合量子分子動力学法に基づくエッチングプロセスシミュレータの開発と MEMS・半導体プロセス設計への応用)
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論文内容要約

Microelectromechanical system (MEMS) is widely employed and applied in various fields such as electronics engineering, mechanical engineering, and medical engineering. Generally, MEMS consists of complicated structures such as holes and pillars, and its fabrication processes are actively studied. In particular, the patterning technique on semiconductor materials in micro- and nano-scales with a high accuracy is one of the hottest topics. In the MEMS processes, the plasma etching is frequently used to pattern on a substrate surface. In the plasma etching, etchant gases are activated by a plasma system, and generated etchant species including ions, radicals, and molecules are emitted onto a substrate surface. Those etchant species cause chemical reactions with a substrate surface, and generate etching products. By the vaporization of etching products, etching proceeds. The plasma etching is developed in the semiconductor technology, and then the miniaturization of a fabrication scale contributes to the developments of both the MEMS and semiconductor processes. However, in the plasma etching for a very small scale fabrication, there are serious problems such as the decrease in etching rate, the decrease in selectivity, and the deformation of etching holes. In fact, bombardments of etchant species and chemical reactions during the plasma etching occur in an atomic scale. Moreover, the combination of them makes etching reactions complicated. In other words, to develop the plasma etching technique, the elucidation of etching reactions is necessary. However, in experiments, the investigations of an etching process in an atomic scale is difficult. In particular, SiO_2 and SiC etching processes include complicated chemical reactions because each element shows a different chemical reactivity and these materials have strong chemical bonds of Si-O and Si-C. In order to elucidate the etching mechanisms in an atomic scale, several simulation methods have been used. Classical molecular dynamics simulations are performed for the investigations of the atomic behavior. The etching processes with different conditions in the surface temperature, the irradiation energy, the etchant species, and so on have been studied. To calculate chemical reactions, quantum chemical methods have been employed. Static first principles calculations were previously used to reveal chemical reaction paths and its energy barriers. However, these methods focus on only dynamics or chemical reactions. For the design of optimal etching processes, the elucidation of chemical reaction dynamics is essential. Here, to reveal chemical reaction dynamics during the etching processes, a new approach which can calculate both dynamics and chemical reactions is required. In

this study, a new etching process simulator is developed by using the quantum chemical molecular dynamics theory. Employing the developed simulator, optimal etching processes are designed for promoting the chemical reactions, controlling the surface structure, and improving the effects of additional etchant species in the etching with two different etchant species. Contents of the thesis are described as follows.

Chapter 1: General Introduction

Backgrounds of the study are described. Outlines of the MEMS and semiconductor processes, the problems of those processes, and the experimental studies of them are introduced. Additionally, the previous simulation studies of etching processes are also reviewed. Objectives of the study are described as the development of the etching simulator and the design of optimal etching processes.

Chapter 2: Computational Methods and Development of Etching Simulator

In Chapter 2, the simulation methods and the outline of the developed etching simulator are described. Quantum chemical theory and molecular dynamics theory for the development of the etching simulator are shown. The functions for representing etching system are implemented in the tight-binding quantum chemical molecular dynamics (TB-QCMD) theory, and then the TB-QCMD etching process simulator is developed. The developed simulator also has the function to solve the problem occurring in conventional methods: When an etchant species and substrate models are located at very far positions and have odd numbers of electrons respectively, electrons can unexpectedly transfer to other energy level. Thus, the original etching simulator is successfully developed.

Chapter 3: Dynamics in SiO_2 Etching by Fluorocarbon Radicals

In the experimental SiO_2 etching, the etching mechanisms in an atomic scale are still unclear. Therefore, the elucidation of chemical reaction dynamics is required. In this chapter, the SiO_2 etching simulations are performed by CF_2 radical, which is one of the dominant etchant species in most of fluorocarbon plasma, in order to reveal chemical reaction dynamics and the etching mechanisms. In the SiO_2 etching simulations, the dissociation of Si-O bonds, the formation of Si-F and C-O bonds, and the vaporization of CO_y and COF_y (y = 1-2) molecules, which are the experimental etching products, are observed. The increase in the irradiation energy of CF_2 radical affects the formation of deep etching hole on the SiO_2. Moreover, during the etching simulations, penetrating C and F atoms are observed. As the increase in the irradiation energy of CF_2 radical, both penetration depth and width increase. In particular, the penetration depth increases more rapidly than the penetration width. Therefore, the increase in the irradiation energy affects not only etching rate but also the aspect ratio of the etching hole. The elementary reactions in the SiO_2 etching and the etching mechanisms are revealed.

Chapter 4: Comparison of SiO_2 Etching Processes in Different Etchant Species

For the design of an optimal SiO_2 etching process, the elucidation of the etching mechanisms depending on experimental parameters such as the etchant species and the irradiation energy of them are required. Therefore, the SiO_2 etching simulations are performed by CF_2 and CF_3 radicals with the different irradiation energies from 10 to 150 eV. In the SiO_2 etching simulations, the vaporization of SiF_x (x = 1-4) and CO_y (y = 1-2) molecules are frequently observed, especially in the etching at 150 eV. In the etching with the low irradiation energy, di-radical CF_2 shows an advantage in the chemical reactivity. On the other hand, in the etching with the high irradiation energy, CF_3 radical promotes etching more rapidly than CF_2 radical. This is because a large number of F atoms contributes to efficient etching by the generation of many Si-F bonds after C-F bonds of etchant species are dissociated by the high irradiation energy. Moreover, to investigate the balance between the etching and the deposition of etchant species, etching simulations are performed with the CF_x-covered SiO_2 surface. In the etching with the low irradiation energy, etchant CF_3 radical mainly reacts with the CF_x-layer. In this case, the CF_x-layer prevents SiO_2 layers from the etching, and then the deposition is more dominant than the etching. In the etching with the high irradiation energy, C and F atoms of the CF_x-layer are dissociated by the bombardments of CF_3 radicals and cause chemical reactions with SiO_2 layers. Then, the etching is more dominant than the deposition. The threshold energy between the etching- and deposition-dominant processes are successfully suggested. Thus, the etching process is designed to promote chemical reactions on the SiO_2.

Chapter 5: Dynamics in SiC Etching by SF_x and O Radicals

In SiC etching, the dissociation of Si-C bonds requires high energy, and then that makes etching difficult. Moreover, to improve SiC etching efficiency, the vaporization of both Si and C atoms with the same speeds is necessary. However, the atomistic SiC etching mechanisms are still unclear, and then the experimental etching is difficult to solve those problems. In this chapter, at the beginning, the SiC etching simulations are performed to reveal chemical reaction dynamics. In the SiC etching by SF_3 and SF_5 radicals which are the dominant etchant species in the SF_6 plasma, the vaporization of SiF_x, CF_x (x = 1-4), SiS, and CS_y (y = 1-2) molecules are observed. In particular, SiF_x is the most generated species among them. Although many Si atoms vapor, C atoms are likely to remain on the SiC surface. Remaining C atoms make C-C bonds on the SiC. A C-C bond has a high binding energy, and then the growth of C-C bonds can decrease etching rate. Next, in order to remove Si and C atoms from the SiC efficiently, the SiC etching simulations by both SF_5 radicals and O atoms are performed. O atoms contribute to the vaporization of C atoms by the generation of CO_y molecules. Then, the addition of O atoms to etchant species is good for the etching progress. However, very high O concentrations generates many C-C and Si-Si bonds which decrease etching rate. This is because in the etching with the high O concentrations, there are less F and O atoms to terminate Si and C atoms after Si-C bonds are dissociated. Then, the best O concentration is suggested for reducing C-C and Si-Si bonds and getting high etching rate. The etching process is successfully designed to control the

surface structure.

Chapter 6: Comparison of SiC etching Processes by F-, Cl-, or Br-Containing Etchant Species

In the experimental SiC etching, halogen atoms of F, Cl, and Br are frequently used in etchant species, and show different results in etching rate and the surface structure. For the design of optimal SiC etching processes, the effects of additional O atoms on the SiC etching processes should be revealed in an atomic scale. In this chapter, to design the SiC etching process for improving the effects of additional O atoms, the etching simulations by F, Cl, and Br atoms with the different O concentrations are performed. During the etching simulations, the penetration of etchant atoms is observed. O and F atoms show the deepest penetration depths, and the penetration depth is in the order of O, F, Cl, and Br atoms. In the SiC etching with F/O system, both F and O atoms penetrate deep SiC layers, and form a thick reaction layer on the SiC. In the etching with Cl/O and Br/O systems, Cl and Br atoms do not penetrate deep SiC layers, and two different reaction layers form: The reaction layer for both Cl/Br and O atoms forms near the SiC surface, and that for only O atoms forms at deep SiC layers. The reaction layer for only O atoms includes many Si-O bonds. Then, that reaction layer has a probability to decrease etching rate and deform etching hole. This is because Si-O bond has a high binding energy, and then the dissociation of them is difficult. Comparing numbers of vaporized Si and C atoms in the etching by F/O, Cl/O, and Br/O systems, it is understood that Si and C atoms are likely to vapor by generating bonds with halogen and O atoms, respectively. This means that the O addition to etchant species improves the vaporization of C atoms. In particular, the etching with F/O system has the largest advantage in the improvement of the etching progress. This is because O atom is used for the generation of etching products in the thick reaction layer for both F and O atoms. Thus, the etching processes are designed to enhance an effect of the additional etchant species.

Chapter 7: Summary and Conclusions

The results and discussions are summarized. The original etching simulator shows the breakthrough in the investigation of the etching mechanisms and the design of the etching processes.

Thus, the development of the etching simulator and the design of the etching processes are successfully performed. Moreover, this study expands the application field of the computational chemistry. These achievements are significantly meaningful to the developments of both the computational simulations and atomistic fabrication techniques.