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## 論文内容要旨

### Chapter 1 General Introduction

Silicon- and carbon-based amorphous materials show excellent electronic, optical, and mechanical properties and are expected for a broad range of industrial applications. They are often prepared by the plasma-enhanced chemical vapor deposition (PECVD) technique. However, the growth mechanisms and microstructures have not been understood so far. The lack of microscopic information about CVD processes gives rise to the difficulties in controlling the microstructures. Several problems arising from atomic-scale structural defects such as degradation remain unsolved. In this dissertation, the growth mechanisms and microstructures of silicon- and carbon-based amorphous materials have been studied by using different-scale computational calculation techniques. One of the objectives of this study is to develop a CVD simulator based on a quantum chemistry method. The second one is to achieve the theoretical design of CVD processes for circumventing the problems.

### Chapter 2 Development of Chemical Vapor Deposition Simulator Based on Tight-Binding Molecular Dynamics

A CVD simulator based on a nonorthogonal extended-Hückel type tight-binding molecular dynamics (EH-TBMD) method has been developed. Original algorithms have been implemented into an EH-TBMD program, which allows the continuous impingement of deposition precursors and removal of vaporized or reflected particles. TB parameters for the Hamiltonian matrix elements and two-body repulsive energy are determined from the first-principles calculation results. The accuracy and effectiveness have been validated by applying it to CVD simulations of hydrogenated amorphous silicon (a-Si:H). The developed CVD simulator allows us to optimize various growth conditions, i.e. substrate temperatures, types of source gases, and gas ratios.

### **Chapter 3 Different Growth Mechanisms of Si(001)-(2×1):H during Plasma-Enhanced Chemical Vapor Deposition of SiH<sub>3</sub> and SiH<sub>2</sub> radicals**

Experimental results revealed different contribution of SiH<sub>3</sub> and SiH<sub>2</sub> radicals, which are primary and secondary species in the plasma, respectively, to the film growth during a-Si:H PECVD processes. However, the different growth mechanisms and effects on the microscopic structures have not been understood due to the difficulty of *in situ* observation of chemical reactions. In this chapter, CVD simulations of a-Si:H have been carried out using the CVD simulator developed in Chapter 2. The differences in the growth mechanisms between SiH<sub>3</sub> and SiH<sub>2</sub> radical deposition and the effects on the microscopic structures have been studied. SiH<sub>3</sub> radical deposition consists of the “abstraction-adsorption” mechanism, where a SiH<sub>3</sub> radical firstly abstracts a surface H atom and secondly another impinging SiH<sub>3</sub> radical can be adsorbed on the generated dangling bond (DB). It means that at least two SiH<sub>3</sub> radicals are necessary to form a new Si-Si bond. On the other hand, a SiH<sub>2</sub> radical can be directly adsorbed on a hydrogenated surface. Interestingly, a SiH<sub>2</sub> radical alone has two different roles of the H abstraction and adsorption. One SiH<sub>2</sub> radical is sufficient for generating a new Si-Si bond. Therefore, the direct adsorption of SiH<sub>2</sub> radicals results in higher deposition rate of SiH<sub>2</sub> radical deposition than SiH<sub>3</sub> radical deposition. However, in SiH<sub>2</sub> radical deposition, DB defect densities increase as the film growth proceeds. It is also found that although SiH<sub>2</sub> radical deposition forms defective films with polymer-like structures and high DB defect densities, SiH<sub>3</sub> radical deposition produces energetically stable films with many ring structures. SiH<sub>3</sub> radicals are hence suitable for obtaining high-quality a-Si:H films.

### **Chapter 4 Development of Large-Scale Density-Functional Tight-Binding Molecular Dynamics Program and Its Expansion to Chemical Vapor Deposition Simulator**

A density-functional tight-binding (DFTB) MD program has been developed and expanded to a CVD simulator. The DFTB method is a semi-empirical density functional theory (DFT) and overcomes several problems that the EH-TB method suffers from, i.e. transferability of TB parameters, long-range interactions, and unphysical electron transfer. Furthermore, a linear-scaling DFTB technique based on conjugate-gradient density-matrix search (CG-DMS) scheme has been constructed and implemented into the original DFTB code. In the CG-DMS scheme, a neglect threshold for determining surviving matrix elements is introduced and the sparse matrix technique is used, which reduce the computational efforts drastically from  $O(N^3)$  to  $O(N)$ . Benchmark calculations for polyethylene molecules and bulk water have been carried out. The CG-DMS-based DFTB scheme exhibits almost linear scaling for both polyethylene molecules and bulk water. The linear scaling technique has also been applied to MD calculations for bulk water. The CG-DMS scheme shows good energy conservation properties during MD calculations even when a loose threshold is employed. Therefore, the CG-DMS-based

DFTB technique is effective in large-scale quantum chemical (QC) MD calculations not only for sparse one-dimensional systems but also for three-dimensional condensed systems.

## **Chapter 5 The Reason Why Thin-Film Silicon Grows Layer by Layer in Plasma-Enhanced Chemical Vapor Deposition**

In a-Si:H, surface morphologies are key parameters to determine the physical properties and device performance because rough surface morphologies induce surface or interface defects. Experimental investigations suggested that atomically flat surfaces can be obtained under an optimized PECVD conditions. However, the understanding of layer-by-layer growth mechanisms of a-Si:H has been lacking. Therefore, a layer-by-layer growth mechanism of a-Si:H during PECVD has been investigated using the DFTB MD simulations. The DFTB MD simulations have suggested the DB-diffusion mechanism as an alternative to a previously suggested SiH<sub>3</sub> radical diffusion model, which is in conflict with experimental and theoretical results. In the DB-diffusion mechanism, a DB diffuses rapidly on the upper layer consisting of SiH<sub>3</sub>-island and then migrates to the lower layer consisting of Si-H site. The migration from the upper to lower layers produces the two-dimensional growth of the films. Additional DFT calculation results support the proposed DB-diffusion mechanism. Furthermore, based on the obtained DB-diffusion mechanism, an atomistic kinetic model has been developed using the reaction rates obtained by DFT calculations. Numerically solving the obtained microscopic master equations, the theoretical model demonstrates the macroscopic diffusion phenomena for DB. The kinetic model calculations have revealed that the average diffusion length of DBs is about 5.0 to 10.0 nm, which is in good agreement with experimental results. The numerical calculations have also suggested that substrate temperatures in the range of 500 to 700 K are suitable for obtaining atomically smooth surfaces during PECVD processes.

## **Chapter 6 Origin of Chemical Order in Hydrogenated Amorphous Silicon Carbide**

Hydrogenated amorphous silicon carbide (a-Si<sub>x</sub>C<sub>y</sub>H<sub>z</sub>) is one of the most promising wide bandgap materials. As in any binary or ternary compounds, chemical order is an important factor to determine the microstructures and physical properties. However, the origin of chemical order has not been solved yet because the atomic mixing leads to much complicated structures. In this chapter, the origin of chemical order in a-Si<sub>x</sub>C<sub>y</sub>H<sub>z</sub> and furthermore effects of the chemical composition on the degree of chemical order during PECVD processes have been studied using DFTB MD and statistical thermodynamics (ST) calculations. CVD simulations using DFTB MD have been performed by the impingement of CH<sub>3</sub> and SiH<sub>3</sub> radicals with different [CH<sub>3</sub>]/([CH<sub>3</sub>] + [SiH<sub>3</sub>]) fractions. The DFTB MD simulations have revealed that the initial growth process consists of the “abstraction-adsorption” mechanism and the “bond-rearrangement and DB-transfer” mechanism explains the preferential formation of heteronuclear Si-C bond during PECVD processes. Based on the obtained microscopic growth mechanisms, a statistical thermodynamics model for a-Si<sub>x</sub>C<sub>y</sub>H<sub>z</sub> based on a quasi-chemical approximation has been

developed. To obtain the bonding fractions for the H atom fractions of 0.54 and 0.20, the non-linear simultaneous equations are numerically solved using the Newton-Raphson method. The bonding fractions for the H atom fraction of 0.54 obtained by the ST calculations show excellent agreement with those obtained by SCC-DFTB MD simulations. The ST model has revealed that there is a suitable composition with highest degree of chemical order with respect to each H atom fraction and the highest degree of chemical order increases with decreasing the H atom fraction.

## **Chapter 7 Formation Rule for $sp^3$ -Carbon in Hydrogenated Amorphous Carbon**

Hydrogenated amorphous carbon (a-C:H) is attractive for use as a protective coating. Forming a-C:H coatings with a high  $sp^3$ -C fraction by a PECVD technique is a challenging issue for industrial applications because a  $sp^3$ -C fraction drastically affects the hardness. However, the growth mechanisms, especially how  $sp^3$  bonding states are formed during CVD processes, have not been revealed yet. Therefore, the formation mechanisms of  $sp^3$ -C have been studied using DFTB MD. CVD simulations have been carried out by impingement of  $CH_3$  radicals with different kinetic energies in the range of 1.0 to 100.0 eV. The time evolution of the depth profiles of mass densities and  $sp^3$ -C fractions has been analyzed. At low incident energies of less than 40.0 eV, C atoms are deposited on the growing surfaces. The “abstraction-adsorption” mechanism produces  $sp^3$  bonding states. At high kinetic energies of more than 70.0 eV, the penetration of impinging C atoms produces  $sp^3$  bonding. The a-C:H film growth consists of the “ $sp$ - $sp^2$ - $sp^3$  transition” mechanism. Near the growing surfaces,  $sp$ - and  $sp^2$ -rich structures are formed via the etching. Polyene chains are preferentially removed from the surfaces. On the other hand, in the subsurface layer at about 1 nm below the surfaces, the nucleation of diamond-like structures occurs by converting  $sp^2$ - to  $sp^3$ -C. The kinetic energy of 70.0 eV has a suitable valance between the nucleation and etching.

## **Chapter 8 Conclusion**

The objectives of this study is (I) to develop CVD simulators based on fast QCMD techniques and (II) to achieve the theoretical design of CVD processes for silicon- and carbon-based amorphous materials by understanding the growth mechanisms and microstructures. The developed CVD simulators based on EH-TB and DFTB MD methods allow us to demonstrate CVD processes. The CVD simulations have revealed the growth mechanisms and microstructures. The atomistic simulations therefore give us the microscopic information that cannot be obtained by experimental measurements. Furthermore, theoretical models have been constructed based on the growth mechanisms obtained by atomistic simulations. The numerical calculations provide us with the macroscopic information that can be directly compared with experimental data. Finally, design principles for forming high-quality silicon- and carbon-based amorphous materials have been successfully obtained.

# 論文審査結果の要旨

近年、地球規模で環境問題への取り組みが求められている中、クリーンかつ高エネルギー変換効率を有する太陽光発電システムの開発及び機械システムの作動環境下での摩擦によるエネルギー損失の低減が急務である。シリコン及びカーボン系材料は、優れた機械的・熱的・化学的安定性を有し、それらの問題を解決するための材料として注目されている。しかし、成膜プロセスに依存する原子レベルの欠陥がもたらす性能劣化などの問題は解決されていない。故に、原子レベルで膜構造を制御可能な成膜技術の確立が急務である。一方で、現在まで原子レベルの構造制御が実現できていない原因は、成長機構及び原子レベルの膜構造が十分に理解されていないことにある。そこで本論文では、シリコン及びカーボン系材料の CVD プロセスの成長機構及び原子レベルの膜構造の解明、さらに得られた知見に基づく CVD プロセスの理論設計を目的として、計算科学的手法を用いた研究を行っている。

第 1 章では、シリコン及びカーボン系アモルファス材料とその CVD プロセスに関する背景と計算科学手法を用いることの必要性について述べられている。

第 2 章では、拡張ヒュッケル近似に基づく CVD シミュレータの開発及び水素化アモルファスシリコン(a-Si:H)の CVD プロセスへの応用について述べられている。これまで不可能であった量子論に基づく CVD シミュレータの開発に成功しており、重要な成果である。

第 3 章では、2 章で開発したシミュレータを用いた CVD シミュレーションを行うことにより、 $\text{SiH}_3$  と  $\text{SiH}_2$  ラジカルの表面化学反応の違い及び膜構造へ及びす影響が明らかにされている。 $\text{SiH}_2$  ラジカルは欠陥を生成するのに対し、 $\text{SiH}_3$  ラジカルは高品質膜の生成において重要であることを提案しており、重要な成果である。

第 4 章では、密度汎関数強結合近似(DFTB)に基づく大規模量子分子動力学シミュレータの開発と CVD シミュレータへの拡張に関して述べられている。また、DFTB 法とオーダー N 法を組み合わせることで、計算時間を大幅に減少させることに成功している。数千原子の量子分子動力学計算が実現可能になることから、重要な成果である。

第 5 章では、CVD プロセスにおける a-Si:H の Layer-by-Layer 成長機構の解明を目的として、DFTB 法を用いた CVD シミュレーションを行っている。その結果、ダングリングボンドの拡散機構が明らかにされている。また、得られた知見を基にダングリングボンドの拡散に関するマスター方程式を構築している。数値解析の結果、原子レベルで平坦な表面を作る最適な温度を提案しており、CVD プロセスの最適化において重要な知見を得ている。

第 6 章では、水素化アモルファスシリコンカーバイドの CVD プロセスにおける化学的秩序の発現機構について、DFTB 法を用いた CVD シミュレーションにより検討している。さらに、統計熱力学計算を行うことにより、化学的秩序の程度と組成比の関係が明らかにされている。これは、原子レベルの構造設計において、重要な知見である。

第 7 章では、水素アモルファスカーボン(a-C:H)の CVD プロセスにおける硬質化メカニズムについて、DFTB 法を用いた CVD シミュレーションにより検討している。 $\text{CH}_3$  ラジカルの入射エネルギーをパラメータとし、密度及び  $\text{sp}^3$  結合の時間変化を解析することにより、70 eV 以上のエネルギー域におけるサブサーフェスでの高密度化プロセスが明らかにされている。これは、高硬度を有する a-C:H 膜の形成において、重要な成果である。

第 8 章は、本論文の総括である。

以上、本論文では、開発した CVD シミュレータを用いることにより、シリコン及びカーボン系材料の CVD プロセスにおける成長機構及びマイクロ構造の解明に成功した。また、得られた知見を基に反応速度論及び統計熱力学モデルを構築し、数値解析を行うことで、成膜温度及び原料ガス比といった成膜パラメータの最適化に成功した。それらの知見は、シリコン及びカーボン系材料の CVD プロセスにおけるマイクロ構造の制御指針を提案するものであり、材料科学の発展への貢献は多大である。

よって、本論文は博士(工学)の学位論文として合格と認める。