くわはら　たくや
氏　　名　桑　原　卓　哉
研究科，専攻の名称　東北大学大学院工学研究科（博士課程）知能デバイス材料学専攻
学 位 論 文 題 目　Development of Large-Scale Density-Functional Tight-Binding Molecular Dynamics Simulator and Theoretical Design of Chemical Vapor Deposition Processes for Silicon- and Carbon-based Materials (大規模密度汎関数強結合分子動力学シミュレータの開発とシリコン及びカーボン系材料の化学気相成長プロセスの理論設計)
論 文 審 査 委 員　主査　東北大学教授　久保　百司　東北大学教授　毛利　哲夫
東北大学教授　大谷　博司

論文内容要約

Chapter 1 General Introduction

Silicon- and carbon-based amorphous materials show excellent electronic, optical, and mechanical properties a are expected for a broad range of industrial applications. They are often prepared by the plasma-enhanced chemical vap deposition (PECVD) technique. However, the growth mechanisms and microstructures have not been understood so far. T lack of microscopic information about CVD processes gives rise to the difficulties in controlling the microstructures. Seve problems arising from atomic-scale structural defects such as degradation remain unsolved. In this dissertation, the grow mechanisms and microstructures of silicon- and carbon-based amorphous materials have been studied by using different-sc computational calculation techniques. One of the objectives of this study is to develop a CVD simulator based on a quantu 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_3 and SiH_2 radicals

Experimental results revealed different contribution of SiH_3 and SiH_2 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_3 and SiH_2 radical deposition and the effects on the microscopic structures have been studied. SiH_3 radical deposition consists of the "abstraction-adsorption" mechanism, where a SiH_3 radical firstly abstracts a surface H atom and secondly another impinging SiH_3 radical can be adsorbed on the generated dangling bond (DB). It means that at least two SiH_3 radicals are necessary to form a new Si-Si bond. On the other hand, a SiH_2 radical can be directly adsorbed on a hydrogenated surface. Interestingly, a SiH_2 radical alone has two different roles of the H abstraction and adsorption. One SiH_2 radical is sufficient for generating a new Si-Si bond. Therefore, the direct adsorption of SiH_2 radicals results in higher deposition rate of SiH_2 radical deposition than SiH_3 radical deposition. However, in SiH_2 radical deposition, DB defect densities increase as the film growth proceeds. It is also found that although SiH_2 radical deposition forms defective films with polymer-like structures and high DB defect densities, SiH_3 radical deposition produces energetically stable films with many ring structures. SiH_3 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 (CC-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_3 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_3-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-$Si_xC_yH_z$) 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-$Si_xC_yH_z$ 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_3 and SiH_3 radicals with different $[CH_3]/([CH_3] + [SiH_3])$ 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-$Si_xC_yH_z$ 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. Polyyne 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.