Theoretical Study of Hydrogenated Amorphous Silicon with Quantum Simulations(Abstract_要旨)

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論文題目	Theoretical Study of Hydrogenated Amorphous Silicon with Quantum Simulations （量子シミュレーションによる水素化アモルファスシリコンの理論的研究）		

（論文内容の要旨）

This thesis focuses on hydrogenated amorphous silicon (a-Si:H) as solar cell materials. The nano-scale structure and physical properties of a-Si:H were studied with quantum simulations based on the density functional tight binding (DFTB) model. The main purpose is to investigate the relation among the nano-scale structures, electronic properties, and the optical response, attempting to address the improvement of photovoltaic efficiency and stability. The thesis consists of seven chapters as follows.

Chapter 1 describes the background of a-Si:H material research with survey of various types of solar cells and presents the motivation, objectives, and outline of this thesis.

Chapter 2 gives the description on the methodology used in this thesis. The main scheme is the DFTB method to evaluate the electronic states, combined with the molecular dynamics (MD) method to trace the nano-scale structural change. The theoretical framework of DFTB method is explained in detail. The non-equilibrium Green's function (NEGF) method is also described, which is utilized to investigate the electron transport mechanism.

Chapter 3 is devoted to validating the methodology and the modeling of a-Si:H samples. The samples were fabricated with a continuous random substitution network model, and a series of DFTB simulations were performed to investigate their structural and electronic properties. Excellent structural properties were obtained by adjusting the hydrogen concentration C_H and the cooling rate. The results indicated that C_H strongly affects the structure. The sample with 14% C_H has the best structural properties. The cooling rate has also much effect on the structure. Upon comparison with experimental results, it was confirmed that this random substitution network model enables the author to theoretically investigate the properties of a-Si:H.

Chapter 4 describes the electronic properties studied by varying C_H and using different metal electrodes. The electron transport properties of a-Si:H were investigated with the NEGF method combined with DFTB simulations. Comparison of a-Si:H with crystalline (c-Si) and amorphous silicon (a-Si) systems confirms that passivation of defects by hydrogen atoms generally improves electronic transmission, by generating defect states in the bandgap and mitigating charge localization. Contents of 3-6 % hydrogen gives the largest transmission due to the defect states resonance. By comparing copper electrode systems and aluminum ones, the interface between a-Si:H and electrodes is found to affect the electron transport, although general trend of C_H dependence is similar. Due to the electronegativity difference, clearly discernible electric double layers are generated on the Al/a-Si:H interface. These findings provide important guidelines for the use of hydrogenated amorphous silicon devices.

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Chapter 5 gives the investigation of light absorption and photo-induced charge transfer properties of a-Si:H. A time-dependent DFTB simulations combined with MD calculations were adopted to investigate the light absorption spectrum and the dynamic process of charge separation under photon irradiation. In the first part, it was shown that the absorbance increases with higher C_H. It was revealed that the structural disorder, such as floating and dangling bonds, has a major contribution to this behavior. The optical bandgap E_g of a-Si:H is strongly influenced by its structural properties. Several methods proposed to evaluate E_g based on the absorption spectrum were compared, and it was concluded that the conventional Tauc plot gives the most reasonable value of E_g. In the second part, the charge separation dynamics was examined by exertion of oscillating electric field mimicking photons with energy close to the bandgap. Hydrogen atoms act as electron donors in general. More charge is transferred with larger C_H. The dynamic charge transfer continues for 100 – 300 fs after the irradiation stops, suggesting that some irreversible structural change is brought by the irradiation. These findings suggest the way of improving efficiency and stability of amorphous based photovoltaic materials.

In Chapter 6, a-Si:H/c-Si heterojunctions were investigated. Based on the above single (bulk) material studies, the photo-induced charge separation and transfer behaviors in a-Si:H/c-Si heterojunctions were examined. It was found that hydrogen plays an important role in the charge separation-transfer mechanism in a-Si:H/c-Si heterojunctions. At higher C_H, the net charge transfer on hydrogen increases significantly with time, but no increment is observed for the whole system, suggesting that the H effect on the charge behavior in inter-material is related to structural differences. The carrier-type modifications with aluminum (Al) or phosphorus (P) doping in c-Si were examined and it was revealed that the doping in c-Si has important effects on the charge behavior in a-Si:H/c-Si. Al doping generally results in more favorable charge separation-transfer behavior over longer time period while P doping brings surprisingly excellent charge behavior at higher C_H. It was noted that electron-phonon coupling leads to this charge behavior. Doping of a-Si:H with Al or P was also investigated, and it was found that the doping in a-Si:H restricts inter-material charge recombination to some extent. a-Si:H contributes mainly to defect passivation and carrier-selective transporting, but the charge separation and transfer are significantly affected as well. Finally it was found that significant correlation exists between photo absorption spectrum and inter-material charge behavior. A large and stable charge separation-transfer occurs at the peaks of absorption spectrum, while the absorption valleys seemingly correspond to strong carrier recombination.

Chapter 7 summarizes the whole research in this thesis, and provides suggestions for possible future extensions of the present study.

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（論文審査の結果の要旨）

本論文は，太陽電池材料として重要な水素化アモルファスシリコン (a-Si:H) について，量子シミュレーションと理論解析により，そのミクロ構造や物性を調べた研究の成果をまとめたものであり，得られた主な成果は以下の通りである．

1. ランダム置換ネットワークモデルによりアモルファス構造の原子配置を構築した後，強結合密度汎関数 (DFTB) 法に基づく分子動力学計算により急冷と構造緩和を行い，a-Si:H のモデル系を作成した．水素濃度や冷却速度の異なるさまざまなサンプルについて，結晶構造や電子物性を調べ，実験との比較を行った結果，この方法で作成したモデル系が現実に用いられる a-Si:H 材料とよく対応することを示した．

2. a-Si:H 材料を金属電極と接触させた系に対して，DFTB 法と非平衡グリーン関数法による電子輸送解析を行った．電子透過係数にはバンドギャップ内の欠陥準位の存在と水素による欠陥低減が大きく寄与していることを明らかにした．また，電極界面近傍に電気二重層が形成されることを示し，その原因と電子輸送への影響を解明した．

3. フォトンに相当する振動電場下での量子シミュレーションにより，a-Si:H 材料の光吸収特性と電荷分離ダイナミクスを調べた．a-Si:H 材料のバンドギャップ (E_g) を光吸収スペクトルから定量的に見積もるさまざまな方法を比較検討し，信頼性の高い E_g を与える方法を提案した．

4. 結晶シリコン (c-Si) と a-Si:H のヘテロ接合を模擬したモデル系を構築し，フォトン照射による電荷分離・移動過程の量子シミュレーションを行った．c-Si あるいは a-Si:H へのドーピングの影響を詳細に調べ，Al ドープによる p 型半導体，P ドープによる n 型半導体のいずれも，ドープのない真性半導体に比べて電荷分離性能が向上することを明らかにした．さらに，これらのドーパントは電荷の再結合を阻害する効果があることを示した．

以上，本論文は a-Si:H について，ミクロスケールのモデル構築と量子シミュレーションの手法を確立し，電子輸送への水素の役割を明らかにするとともに，フォトン照射下での電荷分離や再結合過程を調べる理論的方法を提示し，その有効性を検証したものであり，学術上，実際上寄与するところが少なくない．よって，出願者が博士後期課程学位取得基準を満たし，本論文が博士（工学）の学位審査の請求に値するものと認める．また，令和４年１２月１６日，論文内容とそれに関連した事項について試問を行って，申請者が博士後期課程学位取得基準を満たしていることを確認し，合格と認めた．