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Passivation of TiO_2/Si by Interlayer SiO_x studied with Scanning Zone Annealing and Atomistic Modelling for Perovskite/Si Tandem Solar Cells

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Thesis outline

In this thesis, the passivation of the TiO_2/Si interface using a natively formed SiO_x interlayer was studied using experimental and atomistic modeling approaches for application in perovskite/Si tandem solar cells.

Chapter 1: Introduction

In Chapter 1, an overview of the current state of solar cells was described. Here, it was pointed out that among different solar cell technologies, crystalline Si solar cells are the most adopted in real-world applications. To surpass the theoretical efficiency limit of the c-Si solar cells, tandem solar cells that combine metal organo-halide perovskite as the top cell and c-Si as the bottom cell has attracted much attention as they promise high theoretical energy conversion efficiency combined with low fabrication cost potential. However, the current efficiency of these devices is almost equivalent to the single-junction Si and perovskite solar cells. Thus, perovskite/Si tandem solar cells (PSTSCs) do not present economic benefits today.

To further improve upon the PSTSCs technology, the importance of the interface between the perovskite top cell and Si bottom cell, and Si passivation technologies were introduced. Here, it was pointed out that, although Si passivation technologies have been thoroughly studied, the lack of band alignment between the current state-of-the-art Si surface passivation materials such as Al_2O_3 and SiO_2 with perovskite materials leads to the need for a new material passivation method that accommodates electron transport in PSTSCs.

The electron transporting layer made of TiO_2 has been known to achieve high energy conversion efficiency for single-junction perovskite solar cells. Therefore, perovskite/Si tandem solar cells with a TiO_2 layer as the interface between the top and bottom subcells might

offer high energy conversion efficiency as well as high heat stability. However, carrier recombination at TiO_2/Si interface is notoriously high. For this reason, methods to passivate the TiO_2/Si interface that is suitable for perovskite top cells and Si bottom cells are required for future PSTSCs with high efficiency.

Moreover, the concepts of Scanning Zone Annealing (SZA), Density Functional Theory (DFT), and Density Functional Tight Binding (DFTB) were introduced. Scanning Zone Annealing is a unique heating treatment developed by our research group that can be used to selectively treat the surface of a sample. DFT is based on the idea that the behavior of a material can be sufficiently described by its electron density, that is, a measure of the number of electrons per unit volume. By calculating the electron density, DFT can provide information about the distribution and energies of electrons in a material, which can then be used to predict its chemical and physical properties. DFTB is a variant of the Tight Binding (TB) method that combines TB with the principles of DFT. By using DFT to calculate the electron density followed by TB to model the behavior of the electrons, DFTB is able to accurately predict the electronic structure and properties of materials with much less computation resources than the full DFT calculations. However, DFTB requires parameterization of all pair-wise atoms of the model of interest. This limit the applicability of this method significantly. For example, models that consist of Si, Ti, O atoms cannot be directly modeled using the DFTB method.

Chapter 2: The scope of the thesis

The scope of the thesis was introduced in Chapter 2. Here, the study aims to maximize the efficiency of perovskite/Si tandem solar cells based on a new way to treat metal oxide/Si interface (Scanning Zone Annealing) and to better the understanding of the Si/TiO_2 interface using atomistic modeling approaches.

To achieve this goal, the following questions were investigated:

1. What bottlenecks significantly affect the efficiency of the perovskite/Si tandem solar cell?
2. What is the state (structure and electronic properties relevant for cell performance) of the TiO_2/Si interface and how does it affect the efficiency of perovskite/Si tandem solar cells?
3. What is the importance of the amorphous SiO_x interlayer at the TiO_2/Si interface? How do the properties of this interlayer alter the recombination dynamics at the TiO_2/Si interface?
4. How to control the properties of the amorphous SiO_x interlayer following the deposition of TiO_2 layer on Si surface?
5. What is the effect of the change in properties of the amorphous SiO_x interlayer on the carrier lifetime at the TiO_2/Si interface and the performance of the perovskite/Si tandem solar cell?
6. How can we calculate a large-scale material model such as TiO_2/amorphous SiO_x/Si at a low cost with high accuracy?

Chapter 3: Methodology

Chapter 3 describes the methodologies used in the experimental and calculation parts of the study. In the experimental part, the followings are described: the fabrication of perovskite solar cell and perovskite-on-silicon solar cell, Scanning Zone Annealing to passivate the TiO_2/Si interface, and estimation of the change in solar cell efficiency using solar cells simulation software PC1D. In the calculation part, the following are described: an overview of Density Functional Theory (DFT) and Density Functional Tight Binding (DFTB). Development flow for DFTB/MM, a novel approach that allows DFTB calculation of models

with a missing pair-wise parameterization was described. Calculations of TiO_2, SiO_x, and Si interfaces using the above methods are described. DFT was used for the separated models of TiO_2, SiO_x, and Si. Full DFTB was used to model SiO_x/Si interface. DFTB/MM was used to model the TiO_2/SiO_x/Si interfaces.

Chapter 4: The study of perovskite/Si tandem solar cell by perovskite-on-silicon device

In Chapter 4, the bottleneck of the perovskite/Si tandem solar cell using single-junction perovskite solar cells grown on Si substrate (PoSiSC) is addressed. Here, it was found that although the correct open circuit voltage of around 1.1 V was achieved, the short circuit current density for the PoSiSC devices was very low. Two main reasons for this were proposed: the lack of transparency of the electrode used in our PoSiSC device and high carrier recombination at the TiO_2/Si interface. Here, we found that the latter significantly reduced the carrier lifetime of the carriers and therefore limit the number of extractable carriers.

Furthermore, a very thin SiO_x interlayer was found at the TiO_2/Si interface. This interlayer is unavoidable for most metal oxide/Si interfaces. As crystalline SiO_2 is one of the most well-known Si passivating material, a reasonable argument can be made that an increase in carrier lifetime might be achievable by changing the properties of the interlayer SiO_x.

Chapter 5: Proposal to increase the efficiency of perovskite/Si tandem solar cell using the insight from first-principle calculations

The idea of using unavoidable natively formed interlayer SiO_x was then explored using DFT and DFTB in Chapter 5. Using DFT, separated slab models of TiO_2, SiO_x with different stoichiometry, and c-Si were optimized and their pdos were calculated. After appropriate adjustment of the level of the electro potential of the vacuum on each model was

performed, the position of the conduction and valence band edges of each model was compared. Here, it was found that, indeed, TiO_2 and c-Si possess high conduction band edges alignment. Furthermore, it was confirmed that the change in band gap can be achievable with the change of the O ratio to the Si of the SiO_x models.

From the SiO_x/Si interface modeling using DFTB, it was found that reducing the thickness of the layer and increasing the oxygen content of the SiO_x interlayer led to the expansion of its band gap. As the capacitance of metal oxide materials can be approximately calculated from the band gap, here it was argued that the increase in SiO_x layer thickness might increase the capacitance of the layer. This led to a possible increase in passivation effectiveness, especially field-effect passivation.

Chapter 6: Effective passivation of TiO_2/Si by interlayer SiO_x controlled by scanning zone annealing for perovskite/Si tandem solar cell

Based on the result above, Scanning Zone Annealing (SZA) was proposed to alter the properties of the SiO_x interlayer at TiO_2/Si interface in Chapter 6. Here, a significant increase in carrier lifetime from less than 5 μs to up to 355 μs was observed on TiO_2/Si interface using p-type and n-type Si wafers. This improvement allows the perovskite/Si tandem solar cell to achieve an efficiency of up to 29.7% based on the simulation using PC1D software. Furthermore, different SZA conditions (scanning rate and lamp output) led to a different level of improvement in carrier lifetime. To investigate this phenomenon further the thickness of the SiO_x interlayer was directly observed using Tunneling Electron Microscope. Here, it was found that an optimum SiO_x interlayer thickness that maximizes carrier lifetime was 2.4-2.6 nm. Furthermore, as the SiO_x interlayer thickness increases, increasing then decreasing trends were observed on the carrier lifetime. While the increasing trend can be explained based on the calculation in Chapter 5 as well as the literature, the decreasing trend was specific to the TiO_2/a-

SiO_x/Si system. The decreasing trend was then investigated further by atomistic modeling of the TiO_2/a-SiO_x/Si interface directly in the following chapter.

Chapter 7: Development of Hybrid DFTB/MM method for large-scale material simulation

In Chapter 7, the change in trap-states with the increase in SiO_x thickness was investigated using novel atomistic modeling of TiO_2/a-SiO_x/Si interface models. Here, DFT calculation of the models was found to be too costly. Moreover, DFTB cannot be directly implemented as a suitable parametrization for Si and Ti pair-wise interaction is currently missing. To solve this problem, a novel hybrid approach that combines DFTB and force-field-based molecular mechanics was developed. Moreover, using TiO_2-C3N4 models and Si-Ti-O systems such as $SiTiO_4$, Si_5TiO_{13}, and $Ti(SiO_3)_2$, it was shown that the accuracy of the DFTB/MM was comparable to the original DFTB (for TiO_2-C3N4 system) and DFT (for Si-Ti-O systems) on both structural optimization as well as electronic properties.

This novel DFTB/MM approach was then used to calculate the TiO_2/a-SiO_x/Si interface. Here, it was found that the number of trap states at TiO_2/a-SiO_x and a-SiO_x/Si interfaces was increased with the increase in a-SiO_x interlayer thickness. Thus, the declining trend in carrier lifetime observed in the experiment can be explained by the increase in the number of the recombination centers, in other words, the reduction in chemical passivation as the thickness of the interlayer increases.

Chapter 8: Conclusion

In summary, this thesis explored the possibility of using a natively formed SiO_x interlayer to passivate the TiO_2/Si.

Using DFTB calculations, it was expected that an increase in SiO_x layer thickness can lead to an increase in field-effect passivation. This inspire the utilization of SZA to adjust the thickness of SiO_x layer after the deposition of TiO_2 layer. Adjustment on SiO_x layer thickness led to significant improvement in carrier lifetime from 5 µs to up to 355 µs. However, an unexpected reduction in carrier lifetime was observed with the increase of the SiO_x layer thickness after a certain point. This was not expected based on the calculation of SiO_x/Si and literature.

To explain this phenomenon, the TiO_2/SiO_x/Si interfaces were modeled. A novel DFTB/MM method was developed to allow the calculation of the TiO_2/SiO/Si models as a suitable Ti-Si parameterization is currently does not available. From the calculation, it was found that, due to the nature of amorphous SiO_x used in the investigation, the increase in layer thickness leads to an increase in the number of recombination centers, therefore reducing the chemical passivation of the layer. The interaction between these two passivation effects, the increasing field-effect passivation and the reduction of the chemical passivation create a peculiar pattern in which an optimum SiO_x interlayer that maximizes carrier lifetime was observed at around 2.5 nm.