

Assessment of 2D materials and transition metal oxides as carrier selective contacts for silicon solar cells

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Assessment of 2D Materials and Transition Metal Oxides as Carrier Selective Contacts for Silicon Solar Cells

by

Jing Zhao

Supervised by

Stephen P. Bremner, Anita Ho-Baillie and Fa-Jun Ma

A thesis submitted to UNSW in fulfilment of the requirements for the degree of Doctor of Philosophy



School of Photovoltaic and Renewable Energy Engineering

University of New South Wales

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| Surname/Family Name | : | Zhao |
|--|---|---|
| Given Name/s | : | Jing |
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Although amorphous silicon as carrier selective contacts (CSCs) has been widely used for hetero-junction cell (p-aSi:H/*i*-aSi:H/*a*-Si

Extensive characterization of the fabricated graphene/Si solar cells was performed to establish a full heterojunction model. In comparison with the simple Schottky junction models, the heterojunction model allows for thorough investigation on the sensitivity of solar cell performance to graphene properties like doping level.

The full heterojunction model was also extended to simulate TMDs/Si heterojunction and investigate the origin of the widely reported 'kink' in the light J-V curves. Simulation results indicate that the kink is attributable to interface charge building up due to the TMD/Si band alignment, which leads to high recombination. More importantly, it was shown that selection of Si substrate type is critical for the function of TMD as a CSC. Results demonstrate that 2D materials (graphene and TMDs) /Si solar cells show immense potential in achieving over 20% efficiency.

Spin coated NiOx and VOx as CSCs for Si was also investigated with results showing an additional buffer layer is required to provide surface passivation. In this work, a-Si was used, but the anneal temperature of 350 °C required for NiOx makes it incompatible with a-Si. In contrast, VOx/a-Si showed excellent potential performance when applied to both *p* and *n* type substrate.

An alternate method for NiOx Pulsed Laser Deposition was investigated. Results for deposition on p Si under at temperatures of 300 - 900 °C indicate increasing crystallinity with temperature up to 500 °C. However, amorphous NiOx obtained for 700 °C and 900 °C gave better results both in terms of surface passivation and contact resistance. The results can help explain the relatively poor performance of the spin-coated NiOx, where greater crystallinity was seen, with these results suggesting amorphous material provide better CSCs for silicon.

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Abstract

Although amorphous silicon as carrier selective contacts (CSCs) has been widely used for hetero-junction cell (*p*-aSi:H/*i*-aSi:H/*c*-Si/*i*-aSi:H/*n*-aSi:H) producing excellent device performance, the drawbacks like low doping efficiency and optical losses associated with a-Si are limitations that may be overcome by the alternate CSCs. In this thesis, the suitability of some alternative CSCs such as Graphene, Transition Metal Dichalcogenide (TMDs), Nickel Oxide (NiOx) and Vanadium Oxide (VOx) was investigated.

Extensive characterization of the fabricated graphene/Si solar cells was performed to establish a full heterojunction model. In comparison with the simple Schottky junction models, the heterojunction model allows for thorough investigation on the sensitivity of solar cell performance to graphene properties like doping level.

The full heterojunction model was also extended to simulate TMDs/Si heterojunction and investigate the origin of the widely reported 'kink' in the light J-V curves. Simulation results indicate that the kink is attributable to interface charge building up due to the TMD/Si band alignment, which leads to high recombination. More importantly, it was shown that selection of Si substrate type is critical for the function of TMD as a CSC. Results demonstrate that 2D materials (graphene and TMDs) /Si solar cells show immense potential in achieving over 20% efficiency.

Spin coated NiOx and VOx as CSCs for Si was also investigated with results showing an additional buffer layer is required to provide surface passivation. In this work, a-Si was used, but the anneal temperature of $350 \,^{\circ}$ C required for NiOx makes it incompatible with a-Si. In contrast, VOx/a-Si showed excellent potential performance when applied to both *p* and *n* type substrate.

An alternate method for NiOx Pulsed Laser Deposition was investigated. Results for deposition on p Si under at temperatures of 300–900 °C indicate increasing crystallinity with temperature up to 500 °C. However, amorphous NiOx obtained for 700 °C and 900 °C gave better results both in terms of surface passivation and contact resistance. The results can help explain the relatively poor performance of the spin-coated NiOx, where greater crystallinity was seen, with these results suggesting amorphous material provide better CSCs for silicon.

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| Chapter 1. Introduction 1 |
|---|
| 1.1 Problems of the Energy Economy 1 |
| 1.2 Overview of today's solar cell market |
| 1.3 Basic concept of silicon solar cells |
| 1.4 Heterojunction silicon solar cells |
| 1.5 Alternative concept: Carrier Selective Contact materials |
| 1.6 Previous work on Carrier Selective Contact/Si solar cells |
| 1.7 Organization of this thesis14 |
| Chapter 2 . Methodology |
| 2.1 Wafer cleaning 15 |
| 2.2 Sentaurus 15 |
| 2.3 Density functional Theory 17 |
| 2.4 Spin-coating 17 |
| 2.5 Pulsed Laser Deposition |
| 2.6 Material Characterization |
| 2.6.1 Ellipsometry |
| 2.6.2 Ultraviolet Photoelectron Spectroscopy |
| 2.6.3 X-ray Diffraction |
| 2.6.4 Atomic Force Microscopy |
| 2.6.5 Hall Effect |
| 2.6.6 Reflective High Energy Electron Diffraction |
| 2.6.7 Photoluminescence Imaging |
| 2.7 Contact and Device Characterization |
| 2.7.1 Capacitance-Voltage |
| 2.7.2 Transfer Length Method |
| 2.7.3 Lifetime Tester |
| 2.7.4 I-V Tester |

| 2.7.5 Quantum Efficiency Measurement System |
|---|
| Chapter 3 . Full Heterojunction Modelling of Graphene/Si solar cells35 |
| 3.1 Introduction |
| 3.2 Results and Discussion |
| 3.2.1 Graphene/Silicon solar cell fabrication |
| 3.2.2 Characterization of graphene sheets |
| 3.2.3 Simplified Schottky junction model |
| 3.2.4 Graphene-silicon heterojunction model |
| 3.3 Optimization of graphene sheets, ARC and the rear of Graphene-Si solar cells . 43 |
| 3.4 Conclusion |
| Chapter 4 . Full Heterojunction of Transition Metal Dichalcogenides/Si |
| solar cell |
| 4.1 Introduction |
| 4.2 Electronic and optical properties of monolayer TMDs 49 |
| 4.3 Influence of Si doping type and the origin of J-V kink |
| 4.4 Potential efficiency of TMDs/Si solar cell 60 |
| 4.4.1 Influence of doping concentration of TMDs on the solar cell performance |
| 4.4.2 Influence of surface recombination at the TMDs/Si interface on the solar cell performance64 |
| 4.4.3 Influence of Si substrate on the solar cell performance |
| 4.5 Improvement of TMDs/Si solar cells |
| 4.6 Conclusion |
| Chapter 5 . Application of Solution processed Transition Metal Oxide |
| layers on Silicon solar cell |
| 5.1 TMOs on <i>n</i> -Si70 |
| 5.1.1 Introduction |
| 5.1.2 Experiment and Simulation |
| 5.1.2.1 Characterization of Spin-Coated NiOx and VOx sheets |
| 5.1.2.2 Characterization of TMO/ <i>n</i> -Si Contacts |

| | .77 |
|---|---|
| 5.1.2.4 Advanced Models for TMOs/ <i>n</i> -Si Solar Cells | . 80 |
| 5.2 TMOs on <i>p</i> -Si | 83 |
| 5.2.1 Characterization of TMO/p-Si Contacts | . 83 |
| 5.2.2 Characterization of TMO/ <i>i</i> -aSi:H/ <i>p</i> -Si Contacts | . 85 |
| 5.2.3 Advanced Models for CSC/p-Si Solar Cells | . 87 |
| 5.3 Improvement | 88 |
| 5.4 Conclusion | 89 |
| Chapter 6 . Pulsed Laser Deposition Nickel Oxide on crystalline Silicon | as |
| hole selective contacts | 90 |
| 6.1 Introduction | 90 |
| | / 0 |
| 6.3 Results and Discussion | 91 |
| 6.3 Results and Discussion6.4 Discussion | 91 96 |
| 6.3 Results and Discussion6.4 Discussion6.5 Conclusion | 91 96 97 |
| 6.3 Results and Discussion 6.4 Discussion 6.5 Conclusion Chapter 7 . Conclusion and Future work | 91 96 97 98 |
| 6.3 Results and Discussion 6.4 Discussion 6.5 Conclusion Chapter 7 . Conclusion and Future work 7.1 Conclusion of the Thesis | 91 96 97 98 98 |
| 6.3 Results and Discussion 6.4 Discussion 6.5 Conclusion Chapter 7 . Conclusion and Future work 7.1 Conclusion of the Thesis 7.2 Future work | 91 96 97 98 98 99 |
| 6.3 Results and Discussion 6.4 Discussion 6.5 Conclusion Chapter 7 . Conclusion and Future work 7.1 Conclusion of the Thesis 7.2 Future work 7.3 List of publications resulted from this work | 91 96 97 98 98 99 101 |

List of tables

| Table 3.1 TCAD heterojunction model parameters and their values (For their sources, |
|--|
| Exp. denotes experiment; Cal. calculation; Ref. reference)42 |
| Table 3.2 Parameters and modelling results of the optimized GSJ solar cells under |
| Heterojunction junction (other input parameters of graphene not listed below remain the |
| same as Table 3.1)46 |
| Table 4. 1 Electronic and optical parameters calculated by DFT 53 |
| Table 4. 2 TCAD heterojunction model parameters and their values |
| Table 4. 3 TCAD heterojunction model parameters and their values |
| Table 4. 4 Modelling results of the TMDs/ Si solar cells with PERC |
| Table 5.1 Electrical parameters of NiOx and VOx films |
| Table 5.2 TCAD heterojunction model parameters and their values (for their sources, |
| Exp. denotes experiment; Ref. reference)80 |
| Table 5. 3 Simulated and experimental output parameters of CSC solar cells |
| Table 5.4 Modelling results of the solar cells with/without hole transporting layer (p- |
| aSi:H, NiOx or VOx) |
| Table 6 .1 Specific contact resistivity of TLM samples (the order follows the increasing |
| trend of the specific contact resistivity) |

List of figures

| Figure 1.1 Average surface temperature of the earth [1]1 |
|--|
| Figure 1.2 The energy band diagram (a) of a p - n diode (solar cell) in the equilibrium (b) |
| under illumination [5] |
| Figure 1.3 A typical I-V curve of a silicon solar cell, where the Jsc, Voc, maximum |
| power voltage, maximum power current and the maximum power point are indicated [6] |
| |
| Figure 1.4 Schematic band diagram of heterojunction solar cell [5]5 |
| Figure 1.5 Schematic band diagram of HIT structure on <i>n</i> type Si [11]6 |
| Figure 1.6 The energy level diagram of CSC candidates7 |
| Figure 1.7 Schematic band diagram of the heterojunction between NiOx and <i>n</i> -Si [18].8 |
| Figure 1.8 Schematic band diagram of the heterojunction between MoOx and n -Si [19]8 |
| Figure 1.9 (a) Representative schematic of MoOx local rear contact cell structure and |
| (b) Light J-V characteristic of CSC solar cells [47]11 |
| Figure 1.10 Current-voltage measurements and ρ_c extractions for (a) p Si / MoOx, (b) p^+ |
| Si / MoOx, and (c) n Si/MoOx contact strucures with a fixed MoOx interlayer thickness |
| of ~10nm [48] |
| Figure 1.11 HR-TEM micrograph of the c-Si / <i>i</i> a-Si:H / MoOx / IO:H interfaces [49]12 |
| Figure 1.12 Proposed band diagram for the TMO/c-Si heterojunctions [50]12 |
| Figure 1.13 Schematic of three groups of 2 um thick ultrathin c-Si solar cells; double |
| sided, with both NiOx and TiOx carrier-selective contact on p contact and n contact, |
| respectively [53]13 |
| Figure 2.1 Simulated J-V characteristic of the heterojunction silicon wafer solar cells [4] |
| |
| Figure 2.2 Electronic band structure of doped graphene calculated by DFT17 |
| Figure 2.3 three stages of spin-coating: spin-up, spin-off and evaporation [55]18 |
| Figure 2.4 Schematic of Pulsed Laser Deposition system [56]19 |
| Figure 2.5 Schematic view of the spectra ellipsometry [57]20 |
| Figure 2.6 Plots of $(\alpha hv)^2$ and hv for the NiOx grown by atomic layer deposition [58].21 |
| Figure 2.7 UPS spectra of the ZnO [61] |
| Figure 2.8 Schematic view of the XRD geometry [62] |
| Figure 2.9 Schematic view of the AFM geometry [63] |
| Figure 2.10 Geometry of fields in Hall effect experiment [64]25 |
| Figure 2.11 Schematic view of the RHEED geometry [65]25 |

| Figure 2.12 PL image for a Si based solar cell [66]26 |
|--|
| Figure 2.13 $1/C^2$ -V plot of a heterojunction for differently doped substrates [67] |
| Figure 2.14 Plot of total resistance as a function of contact spacing d [68]28 |
| Figure 2.15 Schematic of the contact resistivity test structure |
| Figure 2.16 QSSPC setup for effective lifetime measurement [69] |
| Figure 2.17 Schematic of Light J-V curve of silicon solar cell and the characteristic |
| parameters calculated from it: <i>Voc</i> , <i>Jsc</i> , <i>FF</i> and η [6] |
| Figure 2.18 Schematic of dark I-V curve of silicon solar cells [70]33 |
| Figure 2.19 The quantum efficiency (EQE (λ) and IQE (λ)) of a silicon solar cell [71] 34 |
| Figure 3.1 (a) Schematic view (b) cross-sectional view and (c) photograph (top view) of |
| the graphene/silicon solar cell. The central grey zone is the active area of the device |
| where graphene contacts silicon and the dark zone is SiO ₂ /Si |
| Figure 3.2 (a) complex refractive index and (b) $1/C^2-V$ plot for a graphene (3-layer) |
| /silicon test structure |
| Figure 3.3 UPS spectra of three-layer graphene sheets on silicon substrate (Inset: |
| Secondary electron cut-off where the work function was derived) |
| Figure 3.4 Schematic of band diagram for an ideal Schottky junction between graphene |
| and silicon under thermal equilibrium condition |
| Figure 3.5 (a) External quantum efficiency curves and (b) light J-V curves measured |
| and simulated using the simplified Schottky junction approach for three scenarios (i) the |
| ideal Schottky contact (ii) the Schottky contact with barrier lowering or (iii) Fermi-level |
| pinning, were simulated. Simulated results for scenario (i) is in good agreement with |
| measured results |
| Figure 3.6 Schematic band diagram of the p - n heterojunction between graphene and |
| silicon under thermal equilibrium condition |
| Figure 3.7 (a) EQE and (b) light J-V characteristic measured and simulated using a |
| heterojunction model |
| Figure 3.8 Dependence of PCE on the (a) bandgap (b) work function (c) electron |
| affinity and (d) effective density of states of graphene sheets as predicted by the TCAD |
| heterojunction model |
| Figure 3.9 Schematic of graphene/silicon solar cell with DLARC and PERC45 |
| Figure 3.10 Efficiency comparison of various graphene/silicon solar cells [20-24, 26] 47 |
| Figure 4.1 The top and side views of monolayer (a) MoS_2 (b) $MoSe_2$ (c) WS_2 (d) WSe_2 . |
| The areas circled by red dashed rhombus and blue dashed rectangle lines represent the |

| hexagonal primitive and the orthogonal supercell respectively. The purple, yellow, grey |
|--|
| and green balls represent Mo, S, W, and Se atoms respectively5 |
| Figure 4.2 Electronic band structure of monolayer (a) MoS ₂ (b) MoSe ₂ (c) WS ₂ (c |
| WSe ₂ |
| Figure 4.3 Schematic of the proposed 2D-Si heterojunction solar cell |
| Figure 4.4 Light current density –voltage curves simulated of (a) MoS_2 / Si (b) WSe_2/Si |
| (c) MoSe ₂ /Si and (d) WS ₂ /Si heterojunction solar cells (black line: n -Si; red line: p -Si |
| |
| Figure 4.5 Schematic of band diagram under (a) thermal equilibrium condition (b) 0.3 V |
| |

bias voltage (c) 0.5V bias voltage (d) recombination (Auger, Radiative, Shockley Read Hall and Surface recombination) under bias voltage from 0.3 V to 0.6 V (e) zoom in view of the band diagram of p-MoS₂/n-Si contact under different doping concentration Figure 4.6 Schematic of band diagram for (a) $p-MoS_2/n-Si$ and (b) $n-MoS_2/p-Si$ Figure 4.7 Schematic of band diagram for (a) p-WSe₂/n-Si and (b) n-WSe₂/p-Si Figure 4.8 Schematic of band diagram under (a) thermal equilibrium condition (b) 0.3V bias voltage (c) 0.5V bias voltage (d) Interface carrier density (black line: electron; red line: hole) (e) recombination under bias voltage from 0.3 V to 0.6 V and (f) light current density-voltage curves under different surface recombination velocity of p-WSe₂/n-Si Figure 4.9 Schematic of band diagram for (a) n-MoSe₂/p-Si (b) p-MoSe₂/n-Si (c) n-Figure 4.10 Dependence of PCE on the doping concentration of TMD layers for (a) n-MoS₂/p-Si (b) n-WSe₂/p-Si (c) p-MoSe₂/n-Si (d) p-WS₂/n-Si heterojunction solar cells (Inset: the corresponding Light J-V curves under different doping concentration of TMD layers)......63 Figure 4.11 Schematic of band diagram for (a) n-MoS₂/p-Si heterojunction (b) p-WS₂/n-Figure 4.12 Dependence of PCE on the surface recombination velocity of the carriers at the contacts for (a) n-MoS₂/p-Si (b) n-WSe₂/p-Si (c) p-MoSe₂/n-Si (d) p-WS₂/n-Si heterojunction solar cells (Inset: the corresponding Light J-V curves under different

| Figure 4.13 Dependence of PCE on the doping concentration of Si for (a) $n-MoS_2/p-Si$ |
|---|
| (b) n-WSe ₂ /p-Si (c) p-MoSe ₂ /n-Si (d) p-WS ₂ /n-Si heterojunction solar cells (Inset: the |
| corresponding Light J-V curves under different doping concentration of Si)66 |
| Figure 4.14 (a) Schematic of band diagram for MoS_2 / p-Si heterojunction under |
| different doping concentration of Si (b) dependence of EQE on the doping concentration |
| of Si |
| Figure 4.15 Dependence of EQE on the thickness of Si wafer67 |
| Figure 4.16 Current loss analysis for TMDs / Si solar cell |
| Figure 4.17 Schematic of (a) n-MoS ₂ or n-WSe ₂ /p-Si solar cell and (b) p-MoSe ₂ or p- |
| WS ₂ / <i>n</i> -Si solar cell with PERC |
| Figure 5.1 AFM images of NiOx $$ under annealing temperature of (a) 350 $^{\circ}C$ (b) 450 $^{\circ}C$ |
| (c) 550 °C and (b) VOx under annealing temperature of (d) 100 °C (e) 200 °C (f) 300 |
| °C |
| Figure 5.2 X-Ray Diffraction patterns of (a) NiOx and (b) VOx73 |
| Figure 5.3 Plots of $(\alpha hv)^2$ and hv (Inset: Complex refractive index $n \& k$) of (a) NiOx |
| and (b) VOx73 |
| Figure 5.4 Dark J-V measurements of TLM array for (a) Al/NiOx/Si and (b) Au/VOx/Si |
| contacts75 |
| Figure 5.5 Dark J-V measurements of TLM array for (a) Al/NiOx (30-40nm)/Si and (b) |
| Au/VOx (30-40nm)/Si contacts |
| Figure 5.6 Dark J-V measurements of TLM array for (a) Al/NiOx (<5nm)/Si and (b) |
| Au/VOx (<5nm)/Si |
| Figure 5.7 Effective carrier lifetime of TMO/ <i>n</i> -Si/ TMO structures |
| Figure 5.8 carrier lifetimes for TMO/i-aSi:H/n-Si/ i-aSi:H /TMO structures as a function |
| of minority carrier injection level obtained using steady state photo-conductance |
| measurements structure |
| Figure 5.9 Dark J-V measurements of TLM array for (a) Al/NiOx/i-aSi:H/Si and (b) |
| Au/VOx/ <i>i</i> -aSi:H/Si contacts |
| Figure 5.10 <i>1/C</i> ² - <i>V</i> plot for a TMO/ <i>i</i> -aSi:H/ <i>n</i> -Si test |
| Figure 5.11 (a) Schematic of the simulated heterojunction solar cell (b) simulated Light |
| J-V characteristic of HIT, NiOx and VOx-Si solar cells |
| Figure 5.12 Schematic band diagram of the heterojunction between (a) p -aSi:H (b) |
| NiOx or (c) VOx and <i>n</i> -Si under thermal equilibrium condition |

| Figure 5.13 Hole density distribution at the interface of TMO/i-aSi:H/Si contacts (a) |
|--|
| NiOx (b) VOx |
| Figure 5.14 Dark J-V measurements of TLM array for (a) Al/p-Si (b) Au/p-Si (c) |
| Al/NiOx/p-Si and (d) Au/VOx/p-Si contacts |
| Figure 5.15 Effective carrier lifetime of TMO/ <i>p</i> -Si/ TMO structures |
| Figure 5.16 Effective carrier lifetime of TMO/ <i>i</i> -aSi:H/ <i>p</i> -Si/ <i>i</i> -aSi:H/TMO structures86 |
| Figure 5.17 Dark J-V measurements of TLM array for (a) Al/NiOx/ <i>i</i> -aSi:H/ <i>p</i> -Si and (b) |
| Au/VOx/ <i>i</i> -aSi:H/ <i>p</i> -Si contacts |
| Figure 5.18 Schematic of the proposed solar cell with hole transporting layer (<i>p</i> -aSi:H, |
| NiOx or VOx) |
| Figure 5.19 (a) Simulated Light J-V characteristic and (b) schematic band diagram of |
| the front side of the solar cells with/without hole transporting layer (p-aSi:H, NiOx or |
| VOx) |
| Figure 6.1 In-situ Reflective high energy electron diffraction (RHEED) patterns of PLD |
| NiOx taken at the end of each deposition at temperatures of 300 °C, 500 °C, 700 °C and |
| 900 °C. (a) The bright streaks as highlighted indicate planar crystalline growth while (c) |
| the diffuse pattern as highlighted indicates an amorphous layer, suggesting 500 $^{\circ}\mathrm{C}$ |
| deposition results in the most crystalline material92 |
| Figure 6.2 Atomic force microscopy tapping mode surface scan of PLD NiO deposited |
| at (a) 300 °C, (b) 500 °C, (c) 700 °C, and (d) 900 °C93 |
| Figure 6.3 Current voltage characteristic curves measured for different contact spacing |
| for Al/NiOx/p-Si contact with PLD NiOx deposited at (a) 300 $^{\circ}$ C (b) 500 $^{\circ}$ C, (c) 700 $^{\circ}$ C, |
| d) 900 °C and (e) direct Al/Si contact |
| Figure 6.4 PL images of the NiOx films under the growth temperature of (a) 300 $^{\circ}$ C (b) |
| 500 °C (c) 700 °C and (d) 900 °C95 |
| Figure 7.1 Current voltage characteristic curves for different contact spacing for a |
| sample with SrO between NiOx/Si |
| Figure 7.2 PL images of the NiOx films under the growth temperature of 900 C with |
| SrO between NiOx/Si |

Chapter 1. Introduction

1.1 Problems of the Energy Economy

In the recent past, the energy economy has been mainly based on the use of fossil fuel energy in the form of natural gas, coal as well as oil. Satisfying our energy needs from reserves results in two problems: resource depletion and environmental issues. The former limits long-term economic development. While the later introduces unpleasant side effects such as the rapid release of carbon dioxide into air and water hence causing greenhouse effect; or radioactive substance into the environment from inappropriate waste management or nuclear meltdowns. The environmental pollution and greenhouse effect have a subsequent effect on increasing the frequency of natural disasters. The disadvantages push us to develop alternatives for fossil energy.

Among all the problems mentioned above (energy shortage, environmental pollution and greenhouse effect), greenhouse effect is the most series topic all over the world. The earth's temperature is a result of an equilibrium established between the incoming radiation from the sun and the energy radiated into space by the earth which is strongly affected by the presence and composition of the earth's atmosphere. Human activities are increasingly releasing 'greenhouse gases' like carbon dioxide, ozone and nitrous into the atmosphere. These gases prevent the normal escape of energy and potentially will lead to an increase in terrestrial temperature as shown in Figure 1.1.



Figure 1.1 Average surface temperature of the earth [1]

Since the energy sector is the main producer of 'greenhouse gases', seeking for renewable green energy is attracting more and more attention. There are various renewable energy sources: hydro energy, wind energy, geothermal energy, solar energy and bio-fuel energy, while solar energy is the most ideal alternative energy source. Solar energy is renewable with unlimited supply, clean and widely available. Under the current technical conditions, Photovoltaics (PV) is a simple and efficient method that directly converts solar radiation into electricity based on the photovoltaic effect.

1.2 Overview of today's solar cell market

The first practical photovoltaic devices were demonstrated in the 1950s [2]. Research and development of photovoltaics received its first major boost from the space industry in the 1960s [2]. In the 1980s research into silicon solar cells paid off and solar cells began to increase their efficiency. In 1985 silicon solar cells achieved the milestone of 20% efficiency [2]. Today solar cells are recognized not only as a way to provide green energy, but also significantly diminish the impact of environmental damage caused by fossil energy. With the development of photovoltaics production facilities and the decrease of the manufacturing cost, photovoltaics show great potential in competing with conventional electricity generation.

Silicon-based solar cells have always been the dominant technology of PV market. Crystalline silicon solar cell has taken up 90% market share for terrestrial applications [3]. The main reason is that silicon technology has already been highly developed and high-quality material is being produced in large quantities for the PV market. Silicon solar cells are mainly *p*-*n* homo-junctions fabricated with solid-state diffusion method, which are also called 'First generation' solar cells. So for, the highest efficiency for mono-crystalline Si solar cells is ~25.7% and for multi-crystalline Si is ~21.25% at laboratory scale. Industrially produced solar modules currently achieve efficiencies ranging from 18%–22% [4] under standard test conditions.

1.3 Basic concept of silicon solar cells

Photovoltaics effect which converts solar energy to electricity in solar cells consists of two essential steps. First, absorption of light generates an electron-hole pair. The electron and hole are then separated by the structure of the device - electrons to the negative terminal and holes to the positive terminal - thus generating electrical power.



Figure 1.2 The energy band diagram (a) of a p-n diode (solar cell) in the equilibrium (b) under illumination [5]

The efficiency of a solar cell denotes the fraction of solar energy converted into electrical energy, which is given as:

$$\eta = \frac{P_{out}}{P_{in}} = \frac{FF \cdot Jsc \cdot Voc}{Psun}$$
(1.1)

, where P_{in} is the input power density of the radiation, P_{out} is the maximum electrical output power density of the solar cell, *Jsc* is the short-circuit current, *Voc* is the opencircuit voltage and *FF* is the fill factor of solar cell's J-V curve. A typical currentvoltage characteristic of a solar cell is shown in Figure 1.3. Solar cell J-V characteristic are usually measured under standard test conditions (STC) where P_{in} is set to 0.1 W/cm² using AM1.5 solar spectrum and the solar cell temperature is 25 °C.



Figure 1.3 A typical I-V curve of a silicon solar cell, where the *Jsc*, *Voc*, maximum power voltage, maximum power current and the maximum power point are indicated [6]

1.4 Heterojunction silicon solar cells

The selective extraction of holes and electrons is largely defined by the conductivity of the device regions which form the hole and electron selective contacts of a solar cell. These device regions provide a high conductivity to the collected carrier to guarantee a lossless carrier transport; and a much lower conductivity to the blocked carrier. Experimentally, such an asymmetric conductivity for carriers is mainly achieved by sufficient doping and/or an induced junction, which results in a strong asymmetry of the local hole and electron densities. Both doping and the induced junction must be designed to make the local p+ or n+ regions for which p >> n and n >> p are maintained for all working conditions, respectively. For the classical homojunction silicon solar cell, heavy doping can obtain a preferred hole/electron transport but it always come at the cost of an increased carrier recombination. Depending on the actual junction design, major losses arise from (1) the high recombination caused by the un-passivated metallized regions contacting the doped c-Si regions and (2) the increased Auger recombination and band gap narrowing caused by the heavy doping effects of the doped p+ and n+ c-Si regions. These limitations have prompted the development of heterojunction solar cells which simultaneously fulfils the passivation and contacting roles.

For heterojunction, band discontinuity, if chosen properly, can dramatically increases the contact resistivity of the minority carrier while keeping the contact resistivity of the majority carrier unchanged or lower. This asymmetric carrier selectivity enables low contact resistance without the necessity of high doping as shown in Figure 1.4.



Figure 1.4 Schematic band diagram of heterojunction solar cell [5]

The most standard type of heterojunction solar cell is based on hydrogenated amorphous silicon (a-Si:H) to create a-Si:H (n or p type)/Si (p or n type) structure. In 1983, Hamakawa and co-workers reported the first solar cell using a Si-based heterojunction [7, 8]. In the late 1980s, Sanyo incorporated heterojunctions into Si wafer-based solar cells [9]. The first devices by Sanyo had cell efficiencies around 12% [9]. The subsequent development of the Heterojunction with Intrinsic Thin-layer (HIT) structure reduced the interface defect density, allowing a cell efficiency of 14.5% in 1990 [10]. Further improvements in the HIT solar cell technology, by addressing the key loss mechanisms, have allowed many research institutes and companies to improve on HIT cell efficiency over the years. In particular, Kaneka holds the record of 25.1% efficiency for the bifacial heterojunction silicon solar cell structure till date. At the rear of HIT solar cell, high valance band discontinuity prevents holes from moving through *n* type Si to *n* type a-Si:H. The barrier in the conduction band is much smaller than the barrier in the valence band and hence electrons can transport through n type a-Si:H to the metal contact. But on the front side of HIT as shown in Figure 1.5, it's worth noting there is a high band discontinuity ΔEv due to different bandgaps, work functions and electron affinities of Si and p type a-Si:H, which might supress the holes collection and hence is detrimental to the solar cell performance.



Figure 1.5 Schematic band diagram of HIT structure on *n* type Si [11]

There are some other inherent challenges coming along with the application of a-Si:H. (1) The band gap of a-Si:H is around 1.75eV, just slightly larger than the value of Si substrate (~1.17eV). The parasitic photon absorption in the doped a-Si:H lowers the carrier generation in the absorber. (2) The doping efficiency of a-Si:H is rather low, particularly to the *p*-doped films. Their low doping concentration and high defect density make the optimization of the hole contact more challenging. (3) The complex fabrication process of HIT solar cells is also another limitation that are sought to be overcome. These disadvantages are the main drivers for research in alternative carrier selective contacts.

1.5 Alternative concept: Carrier Selective Contact materials

One alternative is the application of carrier selective contact (CSC) materials which provide an asymmetry in carrier conductivity. CSC materials which are standard in other photovoltaic technologies like dye-sensitized and organic solar cells, has recently been demonstrated on c-Si. CSC materials include the hole transporting layers (HTL) which facilitate the hole transporting but block the electrons; and oppositely, electron transporting layers (ETL). In this work, a few CSC materials including 2D materials and transition metal oxides (TMOs) were studied in detail. 2D materials have excellent electrical conductivity [12, 13], outstanding mechanical strength [14, 15], super thermal

conductivity [16], remarkable resilience to high temperature and humidity [16], high optical transmittance in the visible-infrared region [17] and tunable electronic structure. Thanks to the exceptional properties mentioned above, 2D materials like graphene and transition metal dichalcogenides (TMDs) shows great potentials in many electrical devices such as transparent electrodes, displays and solar cells. For TMOs, the most important properties of TMOs that can be useful for this purpose are (1) ability to be doped from defects or extrinsic dopant species, (2) usually wide bandgap that is transparent to the visible spectrum of sunlight and (3) widely varying band line-up with Si.



Figure 1.6 The energy level diagram of CSC candidates

One kind of CSC materials like NiOx and graphene achieves the high carrier selectivity based on the asymmetric hetero-barriers at the interface between CSC and Si. HTLs have high conduction band discontinuity and low valence band discontinuity while the ETLs have high valence band discontinuity and low conduction band discontinuity with Si as illustrated as Figure 1.7. Due to high band discontinuity for the minority carrier, the diode injection current in the forward bias will be completely blocked. The low band discontinuity for the majority carrier will ensure no significant barrier to the photogenerated current.



Figure 1.7 Schematic band diagram of the heterojunction between NiOx and *n*-Si [18]

The other kind of CSC materials like MoOx and VOx, builds up sufficient electric field and induces the up-forward band bending at the Si interface based on their extreme high work function (over 5 eV) to achieve carrier selectivity. The electrons are blocked by the large barrier resulting from the band bending, but the way that holes transport through them is still not conclusive. One possible mechanism is that holes transit through the oxygen vacancy- derived defect states in these CSC materials.



Figure 1.8 Schematic band diagram of the heterojunction between MoOx and n-Si [19]

In this work, the suitability of CSC materials (Graphene, TMDs, NiOx and VOx) to either (i) be used as a p type layer and inducing an inversion layer upon n-Si (i.e., a p-n heterojunction), or (ii) act as a transporting layer to improve the work function matching

between p-Si substrate and metal (i.e., inducing an accumulation layer upon p-Si) were investigated.

1.6 Previous work on Carrier Selective Contact/Si solar cells

Graphene, a two dimensional material, has attracted tremendous research interest in the past decade. Thanks to its exceptional properties like excellent electrical conductivity [12, 13] and high optical transmittance in the visible-infrared region [17], graphene shows great potentials in many electrical devices such as transparent electrodes, displays and solar cells. Graphene has been used as transparent electrodes, antireflection coating, electron/hole accepting layers or active layers for carrier separation in graphene solar cells [16, 20-29]. The latter is particularly attractive as the p-n junction can be replaced by the simplified processing graphene/silicon junction (GSJ). The first GSJ solar cell was fabricated by Li et al. in 2010 and showed 1.5% power efficiency [20]. Since then, many strategies have been used to improve the power conversion efficiency up to nearly 10%. They include the use of Si nano-array [30-32], optimization of silicon dioxide interlayer, the use of poly (3-hexylthiophene) (P₃HT) [31, 33] or graphene oxide (GO) interlayer [34] to suppress GSJ interface recombination, the use of chemical dopant such as SOCl₂ [35, 36], bis (trifluoromethanesulfonyl) amide (TFSA) [21, 22], HNO₃ [23, 30, 32] and AuCl₃ [37]. In addition, Song et al. recently demonstrated that the efficiency of graphene/silicon solar cells can be enhanced to 15.6% by optimising the interfacial oxide thickness and antireflection coating [24].

TMDs can display metallic, semimetallic, semiconducting, and superconducting behaviors depending on the polytype and the strained structure, which renders them promising applications as interlayers or active layers in photovoltaic devices [38]. Meng et al. demonstrated photovoltaic operation in large-scale MoS₂ monolayers by the formation of a type-II heterojunction with *p*-type silicon (*p*-Si). Such a heterojunction photovoltaic device achieves a power conversion efficiency of 5.23%, which is the highest efficiency among all monolayer TMD-based solar cells [39]. Sanjay et al. reported a transfer-free chemical vapor deposition (CVD) process for the growth of WS₂ on *p*-Si substrates to build WS₂/*p*-Si heterojunction solar cells. The device exhibites a J_{SC} of 8.4 μ A/cm², a V_{OC} of 16.34 mV, and a *FF* of 26% when tested under AM 1.5G illumination [40]. The demonstrated results of monolayer TMDs/Si-based solar cells hold the promise for integration of 2D materials with commercially available Si-based electronics in highly efficient devices. Recently, Quanrong et al. modelled $n-MoS_2/p-Si$ heterojunction solar cells and the optimized option for ideal devices yielded the highest efficiency over 19.0% [41]. Pranjala et al. simulated the structure for $n-WSe_2/p-Si$ heterojunction solar cell and the simulated PCE of nearly 13.09% has been achieved [42]. These experimental and simulation results make TMDs worthwhile to be further explored in the application of photovoltaics.

Stoichiometric TMOs are ideal insulators, while nonstoichiometric TMOs display semimetallic properties [43, 44]. The electrical properties of TMOs can be tuned when their stoichiometry is altered by oxygen defects [43-45]. Oxygen vacancies acting as *n*-type dopants raise the Fermi level and reduce the work function [46]. Conversely, oxygen interstitials acting as *p*-type donants reduce the Fermi level and increase the work function [2]. The effects can be used to tune the energy alignment of an oxide. NiOx is known to form oxygen interstitial defects, whereas MoOx, WOx and VOx which have extreme high work function (over 5 eV) are known to form oxygen vacancy defects [46].

For TMOs, Bullock et al. explored the application of thermally evaporated transparent MoOx (x<3) films as hole-collecting contacts on the rear side of crystalline silicon solar cells. The simple *p*-type cells featuring a \sim 5% rear fraction MoOx contact attain a conversion efficiency of 20.4%, a promising result, given the early stage of development for this technology [47].



Figure 1.9 (a) Representative schematic of MoOx local rear contact cell structure and (b) Light J-V characteristic of CSC solar cells [47]

Bullock et al. also examines the application of thermally evaporated MoOx (x<3) films directly onto crystalline silicon to create hole-conducting contacts for silicon solar cells. The carrier-selectivity of MoOx based contacts on both *n*- and *p*-type surfaces is evaluated via simultaneous consideration of the contact recombination parameter J_{0C} and the contact resistivity ρ_c [48]. The results demonstrate that MoOx films can play a significant role in the development of selective-contacts both in terms of versatility and performance.



Figure 1.10 Current-voltage measurements and ρ_c extractions for (a) p Si / MoOx, (b) p^+ Si / MoOx, and (c) n Si/MoOx contact strucures with a fixed MoOx interlayer thickness of ~10nm [48]

Geissbühler et al. substituted p-type amorphous silicon films at the front of silicon heterojunction solar cells with wide-bandgap thermally evaporated MoOx films, featuring a fill factor value higher than 80% and certified energy conversion efficiency of 22.5% [49]. These results therefore demonstrate that metal oxide layers can be used as a replacement for p-doped amorphous silicon layers in highly efficient HIT cells, improving optical performance while maintaining excellent passivation and high fill factors.



Figure 1.11 HR-TEM micrograph of the c-Si / i a-Si:H / MoOx / IO:H interfaces [49]

Gerling et al. reported on a comparative study comprising three transition metal oxides, MoOx, WOx and VOx, acting as front *p*-type contacts for *n*-type crystalline silicon heterojunction solar cells. Of all three devices, the VOx/Si heterojunction performed the best with a conversion efficiency of 15.7% and an open circuit voltage of 606 mV, followed by MoOx (13.6%) and WOx (12.5%). The wide bandgap of these transition metal oxide resulted in an estimated *Jsc* gain of ~1.2 mA/cm² (300-600 nm wavelength range) when compared to the a-Si:H reference [50].



Figure 1.12 Proposed band diagram for the TMO/c-Si heterojunctions [50]

Compared with *n* type TMOs mentioned above, less work has been done on NiOx, which is one of the very few wide band gap *p*-type oxide semiconductors. Recently Hassan et al. investigated the performance of c-Si heterojunction with NiOx/c-Si (front)

and TiO₂/c-Si (back), which demonstrates a theoretical efficiency up to ~28% [51]. Islam et al. demonstrated a single MIS solar cell using NiOx as a hole selective contact and the insertion of NiOx results in an improvement of Voc by 20 mV [18]. Islam et al. also reported the experimental demonstration of Fermi level depinning using nickel oxide (NiOx) as the insulator material in metal-insulator-semiconductor (M-I-S) contacts. Using this contact, it showed less than 0.1 eV barrier height for holes in platinum/NiOx/silicon (Pt/NiOx/p-Si) contact and the pinning factor was improved from 0.08 (metal/Si) to 0.26 (metal/NiOx/Si) [52].

Xue et al. demonstrated and ultrathin c-Si solar cell with a metal oxide-selective contact that shows an efficiency of 10.8% [53]. Nickel oxide has been shown to block the electrons while working as a hole contact, and titanium oxide has been demonstrated to block holes while working as an electron contact. The asymmetric band discontinuity in each contact improves the open-circuit voltage significantly. The work also shows the importance of contact improvement in ultrathin silicon solar cells.



Figure 1.13 Schematic of three groups of 2 um thick ultrathin c-Si solar cells; double sided, with both NiOx and TiOx carrier-selective contact on p contact and n contact, respectively [53]

1.7 Organization of this thesis

This thesis consists of 7 chapters. Chapter 2 summarises the methods for fabrication, characterisation and simulation used in this thesis. An advanced full heterojunction model based on extensive characterization was established to study the transport mechanism and evaluate the efficiency potential of CSCs/Si solar cells. Chapter 3 provided a detailed comparison of simplified Schottky model and full heterojunction model for simulating graphene/Si solar cell, demonstrating that it is physically more accurate to model graphene/Si junction as a heterojunction, and the heterojunction model paves the way for thorough investigation on the sensitivity of solar cell performance to graphene properties like band gap, which is impossible for Schottky model. Chapter 4 investigated the mechanism behind the kink shown in the simulated Light J-V curves for TMDs/Si heterojunction solar cells and the methods how to reduce the kink. The dependence of TMDs/Si heterojunction solar cell performance on the doping concentration of TMDs, the interface of TMDs/Si contact, as well as the properties of Si wafer (doping concentration, bulk lifetime and thickness) were also studied in detail. Chapter 5 examined the suitability of solution processed transition metal oxide (Nickel Oxide and Vanadium Oxide) as the hole transporting layer for n-Si or p-Si based on a series of material and contact characterization techniques. The TCAD model was also used to gain insight into carrier transport and the optimization of NiOx-Si and VOx-Si CSC solar cells. In chapter 6, Pulsed laser deposition NiO was studied to assess the suitability for use as a hole transporting layer on p-Si. Layers of 10 nm thickness were deposited at temperatures between 300 °C and 900 °C. A series of material and contact characterizations were carried out to find the optimum growth condition. Finally, possible future direction of this research was discussed along with a summary of the thesis in chapter 7.

Chapter 2 . Methodology

2.1 Wafer cleaning

The silicon wafers were cleaned by the RCA standard cleaning process. It consists of two processes: RCA 1 and RCA 2. RCA 1 can remove organic contamination from the sample surface by dissolving organics in NH₄OH. H₂O₂ is added to oxidise the sample surface to protect it from corrosion by NH₄OH. RCA 2 is to remove metal contamination from the sample surface by dissolving metals in HCl. H₂O₂ is added to oxidise the sample surface to protect it from corrosion by HCl. HF dip process followed by RCA is used to remove the native oxide layer formed at the surface of silicon wafers.

2.2 Sentaurus

To investigate carrier transport mechanism in Graphene/Si solar cells and TMDs/Si solar cells, the heterojunctions between graphene or TMDs and Si were modelled using Sentaurus technology computer-aided design (TCAD). Based on the band diagram, recombination, carrier density distribution etc., the mechanism behind the kink occurred in the simulated Light J-V characteristic was investigated. The full heterojunction model was also used to study the TMOs/Si CSC solar cells. Carrier density distribution, etc. were conducted for a better understanding of the characterization results.

In the model, optical modelling is decoupled and its solution is fed to the subsequent electrical simulation. In the heterojunction approach, thermionic emission model is used to compute currents and energy fluxes [54], where currents and energy fluxes at the abrupt interface are better defined.

Thermionic emission is the flow of carriers over some electrical potential barrier, caused by thermal vibrational energy overcoming the electrostatic forces. The carriers can be electrons or ions, and sometimes are referred to as 'thermions'. In thermionic emission, the interface is treated as a boundary. Conditions for potential and for the electron/hole currents on both sides of the interface are stated. The total charge of the emitted carriers (either positive or negative) will be equal in magnitude and opposite in sign to the charge left in the emitting region. In Sentaurus Device, the definition of thermionic current and thermionic energy flux follows the literature. The hetero-interface model has also been considered.

When Graphene, TMD or TMO films are brought into an intimate contact with *n*-Si substrate, they form a conventional p-n heterojunction. When the heterojunction is illuminated, electron-hole pairs generate and then get separated due to the built-in voltage (V_{bi}). These free minority carriers move to the opposite sides of barrier and get collected at the respective electrodes. Due to discontinuities in the energy band diagram, the carrier transport, currents and energy fluxes, across the heterojunction can be explained by the thermionic emission model across the barrier. For a hetero-interface between CSCs and Si with appreciable band discontinuities, the Neumann boundary condition is applied to establish the relation for the current density Jc (c refers to either electrons n or holes p according to the context) and energy flux density Sc as follows [68],

$$J_{c,2} = J_{c,l} = 2q[u_{c,2}c_2 - \frac{m_{c,2}}{m_{c,l}}u_{c,l}c_lexp(-\frac{E_{bo}}{kT_{c,l}})]$$
(2.1)

$$S_{c,2} = S_{c,I} + \frac{J_{c,2}E_{bo}}{q} = -4[u_{c,2}c_2kT_{c,2} - \frac{m_{c,2}}{m_{c,I}}u_{c,I}c_IkT_{c,I}exp(-\frac{E_{bo}}{kT_{c,I}})]$$
(2.2)

, where *m* represents the effective mass, E_{bo} the band discontinuity, *T* the temperature and v_c the emission velocity.



Figure 2.1 Simulated J-V characteristic of the heterojunction silicon wafer solar cells [4]

2.3 Density functional Theory

Density functional theory is an approach for the description of ground state properties of metals, semiconductors, and insulators. The main idea of DFT is to describe an interacting system of fermions via its density and not via its many-body wave function. For N electrons in a solid, which obey the Pauli principle and repulse each other via the Coulomb potential, this means that the basic variable of the system depends only on three - the spatial coordinates x, y, and z – rather than 3N degrees of freedom. The success of density functional theory (DFT) not only encompasses standard bulk materials but also complex materials such as proteins and carbon nanotubes. It's used for instance in: (1) structural prediction of chemical compounds; (2) simulation of chemical reactions; (3) high precision molecular dynamics; (4) predicting /validating spectroscopic data, etc.

In this work, DFT was used to calculate the band structure and the related physical properties of TMDs.



Figure 2.2 Electronic band structure of doped graphene calculated by DFT

2.4 Spin-coating

In this work, spin coated NiOx and VOx were studied as potential candidate of hole transporting layers. It's the first time that spin coated NiOx and VOx were used in Si solar cells for carrier selective purposes. Spin coating is a popular method for applying thin uniform films onto flat surfaces, and is used widely in polymer photovoltaic research, due to its low cost, simple, and fast fabrication process. In spin coating, a

solution drop of the coating material dissolved in an appropriate solvent is dispensed onto the substrate surface, which is made to rotate at high velocity. The spinning motion spreads out the solution and, as the solvent evaporates away, a thin film of coating is left on the surface.

The basic spin-coating process can be divided into three stages, as illustrated in Figure 2.3.



Figure 2.3 three stages of spin-coating: spin-up, spin-off and evaporation [55]

The thickness of the spin-coated films is controlled by the spin speed, the cycles of spin-coating process and solution concentration. In this work, different solution concentration of NiOx and VOx precursors were spin coated under the spin speed of 3000 rpm and 10000 rpm for single or multi cycles to study the influence of the film thickness on the contact resistance. The quality of the film is also dependent on solvent properties like the solubility of the polymer in the solvent. In this work, the optimization of the solvent (e.g. add HCl to NiOx precursor to increase the solubility) was also investigated.

2.5 Pulsed Laser Deposition

Figure 2.4 below is a schematic illustration of a typical pulsed laser deposition (PLD) system; the major components include a laser source, a high vacuum deposition chamber, and pumping systems.



Figure 2.4 Schematic of Pulsed Laser Deposition system [56]

For PLD, an intense laser pulse is focused onto the target material which is placed inside a vacuum chamber. When the power density is above a threshold, the target materials eject out as luminous plasma and then the plasma is deposited onto the substrate. In this work, it's the first time PLD deposited NiO was studied as the potential HTL for Si-based devices. The stoichiometry of NiOx can be tuned by the growth conditions like deposition temperature; and the thickness of NiOx can be precisely controlled by the number of laser pulses.

2.6 Material Characterization

2.6.1 Ellipsometry


Figure 2.5 Schematic view of the spectra ellipsometry [57]

Ellipsometry is a purely optical technique that monitors changes in the elliptical polarization of light after it has interacted with a material. The most common application for ellipsometry is the measurement of thin film thickness and optical constants. It has also proven to be the primary technique for determining optical constants in the UV, visible, and IR wavelength ranges.

The complex refractive index or the dielectric function tensor in the corresponding spectral region can be extracted by spectra ellipsometry, which gives access to large number of fundamental physical properties. The optical bandgap of the samples can also be extracted based on measured complex refractive index. The absorption coefficient α of sample can be obtained via $\alpha = \frac{4\pi k}{\lambda}$, where λ is wavelength of the incident light. The spectral variation of α as a function of the photon energy is shown. It is observed that α abruptly rises, which is attributable to band gap absorption in the measured sample. Based on the optical absorption spectra, the nature of optical transition can be determined. The optical band gap E_g can be calculated using the following:

$$(\alpha h v)^{2} = A(h v - E_{g})^{1/2}$$
(2.3)

, where A is a constant and hv is the incident photon energy. The variation of $(\alpha hv)^2$ versus hv for samples is shown in Figure 2.6. The E_g values are determined from the energy intercept by extrapolating the linear portion of the plot of $(\alpha hv)^2$ versus hv to $\alpha=0$. In this work, optical constants of graphene and TMO sheets were measured using an ellipsometry (M-2000VI) in the wavelength range of 350-1680 nm and the accompanying software WVASE from J.A. Woollam Co. was used for data analysis.



Figure 2.6 Plots of $(\alpha hv)^2$ and hv for the NiOx grown by atomic layer deposition [58]

2.6.2 Ultraviolet Photoelectron Spectroscopy

Ultraviolet photoelectron spectroscopy (UPS) probes valence electrons in solids and at surfaces. It relies on the process of photoemission, in which an incident photon provides enough energy to release bound valence electrons into vacuum. Their energy *E*, momentum $\hbar k$, and spin σ provide the full information about the quantum numbers of the original valence electron based on conservation laws.

The sharp emission threshold at high-binding energy in the UPS is identified as the cutoff energy $E_{cut-off}$. The work function of the measured material can be determined by:

$$\phi = h\nu - E_{cut-off} \tag{2.4}$$

, where hv is the incident photon energy from HeI irradiation of 21.23 eV [59, 60]. The work function of graphene sheets was evaluated by the custom-built UPS spectra in chapter 3.



Figure 2.7 UPS spectra of the ZnO [61]

2.6.3 X-ray Diffraction

X-ray diffraction (XRD) is an analytical technique which reveals information about the crystal structure, chemical composition, and physical properties of materials. This method is based on observing the diffraction intensity of characteristic X-ray irritating a substance. The 4 circular ranges of motion are the 2θ - θ , ω , φ and χ planes.



Figure 2.8 Schematic view of the XRD geometry [62]

The combined motions in the 2θ - θ plane and ω plane produce a scan commonly called a 2θ - ω scan which indicates all crystalline peaks of the grown material and the substrate. From the 2θ - ω scan, the positions of peaks are noted to characterize the crystallinity of the measured materials. The crystal structure of TMOs was characterised by PANalytical Empyrean Thin-Film XRD.

2.6.4 Atomic Force Microscopy

Atomic force microscope (AFM) is a very high-resolution type of scanning probe microscope, much better than the optical diffraction limit. Depending on the application, AFM can be operated in a number of modes, and in our study the tapping mode was used.



Figure 2.9 Schematic view of the AFM geometry [63]

Essential components of an atomic force microscope include an atomically sharp tip/stylus for sensing the topography of the sample surface, a scanner for precisely positioning the probe on the sample surface, and a feedback system (Z Feedback) for ensuring the tip accurately tracks the surface topography. In most cases a feedback mechanism is employed to adjust the tip-to sample distance to maintain a constant force between the tip and the sample. Traditionally, the sample is mounted on a piezoelectric tube, which can move the sample in the Z direction for maintaining a constant force, and the x and y directions for scanning the sample. The resulting map of the area represents the topography of the sample. In this work, the topography of TMO sheets was measured by Atomic Force Microscope (AFM, The Bruker BioScope CatalystTM).

2.6.5 Hall Effect

Hall Effect measurement system can actually be used to determine quite a few material parameters such as carrier mobility, carrier concentration (n), resistivity and the conductivity type (n or p type).

The first step in determining carrier mobility is to measure the Hall voltage (V_H) by forcing both a magnetic field perpendicular to the sample and a current through the sample. The combination of the current flow (I) and the magnetic field (B) causes a transverse current. The resulting potential (V_H) is measured across the device. Accurate measurements of both the sample thickness (t) and its resistivity (ρ) are also required. The resistivity can be determined using a four-point probe technique. With just these five parameters (B, I, V_H , t, and resistivity), the Hall mobility can be calculated using this formula:

$$\mu H = \frac{|V_H t|}{BI\rho} \tag{2.5}$$

The conductivity of a semiconductor depends upon both the carrier densities and their mobilities and can be determined by: $\sigma = \frac{1}{\rho} = q\mu_n n + q\mu_p p$. The Hall effect yields a direct measure of the majority carrier density.

The sheet resistance of the measured material can be deduced from the resistivity, namely the reciprocal of the conductivity: $\rho = R_s t$

In this work, it's the first time the electrical properties like carrier mobility and sheet resistance of these spin coated TMOs were extracted by Hall Effect Measurement System (HMS-5000).



Figure 2.10 Geometry of fields in Hall effect experiment [64]

2.6.6 Reflective High Energy Electron Diffraction

In this work, Reflective High Energy Electron Diffraction (RHEED) was used to reveal information about the PLD deposited NiOx which cannot be seen just by looking through a view port. RHEED enables us to analyse structures of crystal surfaces at atomic levels and also to in situ monitor growth processes of thin films. From the arrangement, intensity and profile of the diffraction spots in RHEED patterns, the following information can be obtained: (1) parameters characterizing structural phase transitions; (2) the periodicity (unit cells) in atomic arrangements; (3) epitaxial relation between the grown films/islands with respect to the substrate; (4) growth styles of thin films and numbers of atomic layers grown and (5) flat-ness of surfaces, etc.

The geometry of the system is shown in Figure 2.11. The electron gun and screen are placed on opposite ports of the chamber so that a grazing incidence of the electron beam on the sample surface can be achieved. The diffracted electrons from the substrate surface provide information about the top layer and produces a real-time picture of the growth of the crystal. The low angle of incidence results in a small penetration depth of only a few atomic layers before total external reflection occurs and the electron is diffracted out of the crystal.



Figure 2.11 Schematic view of the RHEED geometry [65]

2.6.7 Photoluminescence Imaging

The photoluminescence (PL) method provides valuable information on the states occupied by recombining electrons and holes. In PL imaging of silicon samples, the surface of the sample is photo-excited in order to emit luminescence signal and a camera is used to obtain a spatially-resolved image of the luminescent emission. PL imaging enables a quantitative analysis of spatially resolved calibrated minority carrier lifetime and series resistance measurements. The high resolution and the short measurement time enable PL imaging to become a useful tool for inline process monitoring.

In this work, PLD deposited NiO under different deposition temperature was characterized for the passivation quality by PL imaging technique (BT imaging LIS-R1) with a 1025nm short-pass filter.



Figure 2.12 PL image for a Si based solar cell [66]

2.7 Contact and Device Characterization

2.7.1 Capacitance-Voltage

The capacitance-voltage (C-V) of graphene/Si heterojunction and TMO/Si contacts was characterised by the impedance/gain-phase analyser (Hewlett Packard 4194A) to extract the built-in potential between graphene or TMOs and Si.

In the C-V measurements a differential capacitance is measured by a small modulation of a DC bias voltage applied to a material stack. The DC voltage is biasing the semiconductor surface potential. In the equilibrium state of the MIS capacitor, the change of the gate charge is balanced by a change of the charge presented in the semiconductor surface and interface. During C-V measurements, the semiconductor is first driven into the state of accumulation, then depletion and inversion. C-V measurements can provide several information of the MIS contacts, for instance: doping type of the semiconductor, the equivalent thickness of the insulator, the k-value of the insulator, the doping concentration and built in potential of the contact.

Figure 2.13 shows the inverse of the capacitance squared as a function of voltage for the GSJ device. In the negative bias voltage, C-V measures the junction capacitance of the TMOs/Si contact; then the junction capacitance turns to a combination of junction capacitance and diffusion capacitance when the bias voltage grows over 0V. Thus in the reverse bias (negative bias voltage), according to Anderson's model, the junction capacitance of the device is described by,

$$\frac{1}{C^2} = \frac{2(\frac{kT}{q} - V_{bi} - V)}{qA^2 \varepsilon_0 \varepsilon_{si} N_D}$$
(2.7)

, where *C* is the capacitance; *k* the Boltzmann constant; *T* the temperature; V_{bi} the builtin potential; *V* the applied voltage; *q* the unit charge; *A* the diode area; $\varepsilon_0\varepsilon_{Si}$ the permittivity of silicon and N_D the dopant concentration of silicon. V_{bi} and N_D can be determined from the x-intercept and the slope of the extrapolated linear part of the measurement under the reverse bias, respectively [67].



Figure 2.13 I/C^2 -V plot of a heterojunction for differently doped substrates [67]

2.7.2 Transfer Length Method

Transfer length method (TLM) means measuring the current-voltage characteristic between two contacts at different contact spacing on a semiconductor device to extract the specific contact resistance. The basis of a standard TLM array is a series of contacts of width Z and length L, unequally spaced, aligned in an isolated area of width W of the semiconductor layer, all fabricated simultaneously and therefore presumed identical. In the measurement, the total resistance R_t is measured for each pair of adjacent contacts, and plotted as a function of the various spacing d. A linear approximation of the measured resistance values is then extrapolated. This yields a linear function $R_t = A + B^*d$, A being the intercept at d=0, and B being the slope.



Figure 2.14 Plot of total resistance as a function of contact spacing d [68]

 R_{sh} and ρ_c are extracted by:

$$R_{sh} = B \cdot W \tag{2.8}$$

$$\rho_c = \frac{W \cdot A^2}{4B} \tag{2.9}$$

 R_{sh} means the semiconductor sheet resistance, and ρ_c means the specific contact resistance. The structure of TLM samples fabricated in this work is shown in Figure 2.15. The specific contact resistance of TMOs/Si contacts were measured based on TLM means to characterize the carrier selectivity of TMOs.



Figure 2.15 Schematic of the contact resistivity test structure

2.7.3 Lifetime Tester

The effective lifetime (τ_{eff}) measures how long the minority carriers generated in the bulk is likely to persist before recombining and is one of the most important parameters for the characterization of semiconductor wafers. The effective lifetime value which depends on the bulk lifetime (τ_b) and surface recombination velocity is given by:

$$\frac{1}{\tau_{eff}} = \frac{1}{\tau_{Bulk}} + \frac{1}{\tau_{SRV}}$$
(2.10)

At the surface of a semiconductor, the atoms lack neighbours to bond to, hence being left with unsatisfied 'dangling' bonds (unpaired outer-shell electrons). Surface states introduced by these dangling bonds greatly increase electron-hole recombination at the surface. Surface recombination velocity (SRV) is used to specify the recombination at a surface.

In the bulk of the material the carriers recombine by either Radiative recombination, Auger recombination or Shockley-Read-Hall (SRH) recombination. The lifetime of carriers in the material bulk τ_b is composed of radiative lifetime (τ_{rad}), Auger lifetime (τ_A) and a SRH lifetime (τ_{SRH}) with the relation:

$$\frac{1}{\tau_{Bulk}} = \frac{1}{\tau_{Band}} + \frac{1}{\tau_{Auger}} + \frac{1}{\tau_{SRH}}$$
(2.11)

Radiative (band-to-band) recombination is the recombination that an electron directly combines with a hole in the conduction band and releases a photon. For Auger Recombination, an electron and a hole recombine and the emitted energy is given to a third carrier, an electron in the conduction band. Auger recombination is most important in heavily doped or heavily excited material. SRH recombination is the recombination through defects, occurs only in defected material.

For the lifetime tester, the light stimulation leads to the generating of electron-hole pairs (excess carriers) in the solar cells. The continuity equation for excess carrier is given by:

$$\frac{\partial \Delta n(t)}{\partial t} = G(t) - R(t)$$
(2.12)

, where G is the generation rate, R is recombination rate in the bulk, $\Delta n(t)$ is the excess minority carrier density. In the QSSPC mode the flash lamp is used to produce a slowly varying illumination and the resulting time dependence of the excess photo conductance of the sample is measured. Under QSSPC mode, the photo generated excess carrier density, $\Delta n = \Delta p$, results in an increase in wafer conductance given by:

$$\Delta \sigma_L = (\mu_n \Delta n + \mu_p \Delta p) q W = q \Delta n (\mu_n + \mu_p) W$$
(2.13)

, where *W* is the wafer width, μ_n and μ_p are the carriers mobilities. Also, the generation and the recombination rates must be balanced, leading to:

$$J_{photogeneration} = J_{recombination}$$
(2.14)

In terms of effective minority carrier lifetime:

$$J_{ph} = q \Delta n W / \tau_{eff} \tag{2.15}$$

Combining equation (2.14) and (2.15), an expression for determining the effective lifetime of the minority carriers can be obtained:

$$\tau_{eff} = \sigma_L / [J_{ph}(\mu_n + \mu_p)]$$
(2.16)

Figure 2.16 displays the sketch of the measurement set up.



Figure 2.16 QSSPC setup for effective lifetime measurement [69]

In this thesis, the effective lifetime testing under QSSPC mode (Sinton Instrument, S/N 13-128197) was carrier out as an indicator of the passivation quality of TMO/Si contact.

2.7.4 I-V Tester

For light J-V testing, the measurement of current as a function of voltage is the most valuable tool for characterization of a solar cell. An artificial light source that simulated the sunlight shines on the solar cell. As scanning the voltage, the current between the probes is recorded for each applied voltage. Figure 2.17 shows a typical I-V curve of a solar cell under illumination.



Figure 2.17 Schematic of Light J-V curve of silicon solar cell and the characteristic parameters calculated from it: *Voc*, *Jsc*, *FF* and η [6]

In this work, the I-V data were recorded using a Keithley 2612 Source Meter. For graphene/Si solar cell, the photovoltaic properties were tested using a solar simulator (Newport 91160) under AM 1.5 conditions. The irradiation intensity is 100 mW/cm², which was calibrated by a Newport standard Si solar cell 91150.

The specific contact resistance of TMO/Si was examined by Dark I-V testing. Dark I-V measurements are widely used in examining the diode properties. Dark I-V measurement is based on the inject carriers into the circuit with electrical means rather than with light generated carriers. A solar cell in the dark is a large flat diode as shown in Figure 2.18.



Figure 2.18 Schematic of dark I-V curve of silicon solar cells [70]

2.7.5 Quantum Efficiency Measurement System

Quantum efficiency (QE) is defined as the ratio of the number of electrons in the external circuit produced by an incident photon of a given wavelength. For the external quantum efficiency (IQE (λ)), all photons impinging on the cell surface are taken into account; for the internal quantum efficiency (EQE (λ)), only photons that are not reflected are considered.

If the internal quantum efficiency is known, the total photo generated current is given by

$$I_{ph} = q \int_{(\lambda)} \phi(\lambda) (1 - R(\lambda)) I Q E(\lambda) d\lambda$$
(2.17)

, where $\Phi(\lambda)$ is the photon flux incident on the cell at the wavelength λ , $R(\lambda)$ is the reflection coefficient from the top surface, and the integration is carried out over all wavelength λ of light absorbed by the solar cell. The value of the internal and external quantum efficiency is routinely measured to assess the performance of a solar cell by interference filters or monochromators. In this work, the EQE (λ) of graphene/Si solar cells was characterized by PV measurement QX7.



Figure 2.19 The quantum efficiency (EQE (λ) and IQE (λ)) of a silicon solar cell [71]

Chapter 3 . Full Heterojunction Modelling of Graphene/Si solar cells

2D materials have numerous unique properties which make them alternative candidates as the active layer in silicon solar cells. In this work, the transporting mechanism of graphene/silicon solar cell and the potential efficiency of TMDs/silicon solar cells have been discussed in detail. According to our results, 2D materials would be a useful contribution for the improvement in solar energy harvesting.

As a member of 2D materials, graphene has achieved multifunctional applications in photovoltaic devices. In graphene/silicon solar cells, it is crucial to understand the transport mechanism of the graphene/silicon interface to further improve power conversion efficiency. Until now, the transport mechanism has been predominantly simplified as an ideal Schottky junction. However, such an ideal Schottky contact is never realised experimentally. According to literature, doped graphene shows the properties of a semiconductor, therefore, it is physically more accurate to model graphene/silicon junction as a Heterojunction. In this work, extensive characterization was implemented to establish an advanced technology computer-aided design (TCAD) model, where *p*-doped graphene forms a straddling heterojunction with the *n*-type silicon. In comparison with the simple Schottky junction models, our TCAD model paves the way for thorough investigation on the sensitivity of solar cell performance to graphene properties.

3.1 Introduction

In this chapter GSJ solar cells were fabricated with a PCE of 9.45% (without any antireflection coating (ARC)). Extensive characterization was performed to extract optical and electrical properties of the graphene sheets prepared by chemical vapour deposition (CVD) method. Based on the measurement as well as theoretical calculations, a sophisticated heterojunction model was built, which successfully reproduces the characteristic behaviour of the 9.45% GSJ solar cell. For comparison, the simple model of Schottky junction was used as well with optional models of barrier lowering and Fermi level pinning. Results show that the model offers an advantage over the predominant Schottky simplification for thorough investigation on the sensitivity of

solar cell performance to graphene properties like band gap and work function, which is critical for the improvement of graphene/Si solar cells.

3.2 Results and Discussion

3.2.1 Graphene/Silicon solar cell fabrication

300 nm SiO₂ layer was prepared on lightly doped *n*-type Si wafers (resistivity of 1-3 Ω cm) and was later patterned by photolithography and wet etched by hydrofluoric acid solution, leaving an almost square window around 0.071 cm². Three-layer graphene sheets, synthesized by CVD, were transferred to this opening and formed GSJ as shown in Figure 3.1. Typically the transferred graphene size was 1-2 cm and the Ag paste was applied on top of graphene sheets around the opening for an electrical contact which also serves as an aperture mask. The eutectic gallium-indium (E-GaIn) paste was applied on the bottom side of silicon to form an ohmic back contact. Doping treatment of graphene was carried out by exposing the cells with the graphene side down to the vapour of nitric acid for several minutes.



Figure 3.1 (a) Schematic view (b) cross-sectional view and (c) photograph (top view) of the graphene/silicon solar cell. The central grey zone is the active area of the device where graphene contacts silicon and the dark zone is SiO₂/Si

3.2.2 Characterization of graphene sheets



Figure 3.2 (a) complex refractive index and (b) $1/C^2-V$ plot for a graphene (3-layer) /silicon test structure

Figure 3.2(a) shows the complex refractive index of the 3 monolayer Graphene which agrees with values reported in the literature [72-75]. These were extracted with a Lorentz-Drude-Gaussian oscillator model. The thickness of single layer graphene was found to be 0.399 nm and in agreement with the reported value (~0.35 nm [76]).

Capacitance-Voltage measurements were performed with the voltage and corresponding $1/C^2$ as shown in Figure 3.2(b) to estimate the work function of graphene. In this experiment, V_{bi} was found to be 0.63 eV and N_D 2.85×10¹⁵ cm⁻³, consistent with the value of 2.36×10¹⁵ cm⁻³ calculated from the substrate resistivity. The work function of graphene sheets can be deduced from the built-in potential V_{bi} ,

$$\phi = V_{bi} + \frac{kT}{q} \ln \frac{Nc}{N_D} + \chi_s \tag{3.1}$$

, where N_C is the effective density of states in the conduction band and χs the electron affinity of silicon substrate. The work function for measured graphene sheets was calculated to be 4.86 eV. This is within the range of the reported results (4.60-5.00 eV) [77-79].

Figure 3.3 shows the UPS spectra of the graphene/Si test structure, which can be used to evaluate the work function of graphene sheets.

The work function of our graphene sheets is determined to be 4.83 eV, which is qualitatively consistent with 4.86 eV extracted from Figure 3.2(b).



Figure 3.3 UPS spectra of three-layer graphene sheets on silicon substrate (Inset: Secondary electron cut-off where the work function was derived)

3.2.3 Simplified Schottky junction model

In addition to the thickness and doping concentration obtained from the Si substrate used in the graphene/Si solar cells, state-of-the-art models reported by Altermatt [80] and the latest Auger model [81] were applied to predict silicon characteristic for both Schottky junction model and heterojunction model. In the Schottky barrier approach, the Schottky-Mott model was applied [5]. In addition, barrier lowering model and Fermi level pinning [82] were also studied as they are typically associated with a Schottky contact. Despite the experimentally observed [83-86] of HNO₃-doped graphene sheets, in the simplified Schottky junction approach that is commonly taken, graphene is still treated simply as a metal. According to the Schottky contact theory, a space charge region forms as electrons flow from silicon to graphene to establish a flat Fermi level under thermal equilibrium condition, as illustrated in Figure 3.4. The Schottky barrier height ϕ_B plays a key role in determining the solar cell PCE [87]. With the measured graphene work function $\phi_M = 4.86$ eV, the silicon surface is under strong inversion. For an ideal Schottky contact, ϕ_B is simply the difference between the graphene work function ϕ_M and the silicon electron affinity χs .



Figure 3.4 Schematic of band diagram for an ideal Schottky junction between graphene and silicon under thermal equilibrium condition

In practice, however, such an ideal Schottky contact is never realised experimentally [5]. Two phenomena, barrier lowering and Fermi-level pinning, are always observed on a realistic Schottky contact [52, 88]. For the barrier-lowering effect, one physical mechanism that is responsible for this is the image force in the presence of an electric field [88], which make the observed ϕ_B lower than expected and sometimes even independent of the metal work function [52]. For the Fermi-level pinning effect, the interface states in the semiconductor bandgap are responsible. The energy level in the bandgap at which the dominant character of the interface states changes from donor-like to acceptor-like is called the charge neutrality level (E_{CNL}). Due to the charge transfer between the metal and the interface states, ϕ_B may be effectively pinned towards E_{CNL} , depending on a pinning factor (S)

$$\phi_B = S(\phi_M - E_{CNL}) + (E_{CNL} - \chi_s) \tag{3.2}$$

The following three scenarios were considered in simulating external quantum efficiency (EQE) and light current density-voltage (J-V) curves, (i) the ideal Schottky contact; (ii) the Schottky contact with barrier lowering and (iii) Fermi-level pinning. For scenario (iii), a very strong pinning effect was examined where S was presumed to be zero and E_{CNL} 4.78 eV (According to Mead's rule, the barrier height for Schottky contact formed on *n* type semiconductor is roughly equal to two thirds of semiconductor bandgap energy due to pinning [89]) in Eq. 3.2. In order to check the effect of the different mechanisms, the experimentally obtained EQE against modelled EQE curves

under Schottky model with different approaches were plotted. As shown in Figure 3.5(a), the measured EQE curve has a similar shape to a typical silicon wafer solar cell [90]. All simulated EQE curves agree well with the measured values with almost no difference. This is expected as the variation of ϕ_B is supposed to have big impact on carrier separation instead of carrier recombination [91]. As shown in Figure 3.5(b), scenario (i) provides a reasonable match with the measured J-V curve. In scenario (ii), barrier lowering significantly reduces open circuit voltage *Voc* from 0.55 to 0.50 V, pulling down PCE from 9.01 to 8.00%. In scenario (iii), Fermi-level pinning is even more detrimental to the Schottky junction solar cell, lowering *Voc* to 0.47 V and PCE to 6.87%. From these scenarios, it is noteworthy that an ideal Schottky junction is very different from a realistic Schottky junction when undertaking the simplified Schottky junction approach.



Figure 3.5 (a) External quantum efficiency curves and (b) light J–V curves measured and simulated using the simplified Schottky junction approach for three scenarios (i) the ideal Schottky contact (ii) the Schottky contact with barrier lowering or (iii) Fermi-level pinning, were simulated. Simulated results for scenario (i) is in good agreement with measured results

3.2.4 Graphene-silicon heterojunction model

With HNO₃ doping, multilayer graphene sheets behave like a p-type semiconductor material. When graphene sheets are brought into an intimate contact with n-type silicon substrate, they form a conventional p-n heterojunction as graphene has a small bandgap. Discontinuities in the energy band diagram are also expected due to their different bandgaps, work functions and electron affinities. As illustrated in Figure 3.6, graphene

and silicon forms a straddling gap to establish a flat Fermi level at thermal equilibrium condition. Notable energy discontinuities are present for both the conduction band and valence band, which can be quantified by band discontinuity ΔE_C and ΔE_V , respectively. A large ΔE_C leads to a strong upward band bending beneath the silicon surface and the build-in potential is similar to that in Figure 3.6. The band alignment exhibits a hole-selective behaviour without any *p*-type doping in the silicon substrate.



Figure 3.6 Schematic band diagram of the p-n heterojunction between graphene and silicon under thermal equilibrium condition

Unlike the simplified Schottky junction approach, more parameters are required to establish an accurate TCAD model for the *p*-*n* heterojunction between graphene and silicon. The key optical and electrical parameters such as graphene thickness, work function, and complex refractive index were determined by the measurement results. In this work, graphene was input as a *p* type semiconductor with a bandgap varying from 0.01eV to 0.80eV [78, 83, 92-97] and the corresponding J (V) & EQE curves were found. The simulation results are most consistent with the measured curves when a bandgap of 0.26eV is assumed for graphene. This value agrees well with the measured bandgap opening of graphene reported in several studies (~0.25eV [83-86]). Additional parameters such as relative permittivity, hole/electron mobility and conduction/valence band density of states were taken from the literature values.

Table 3.1 TCAD heterojunction model parameters and their values (For their sources, Exp. denotes experiment; Cal. calculation; Ref. reference)

| Description | Symbol | Unit | TCAD model | Literature value |
|--------------------|----------------|---|------------------------------|---|
| | | | value (source) | |
| Three-layer | Т | nm | 1.65 (Exp.) | single layer: 0.35 [76] |
| thickness | | | | |
| Bandgap | Eg | eV | 0.26 | Below 0.8 [78, 83, 92- |
| | | | | 97] |
| Work function | ϕ | eV | 4.86 (Exp.) | 4.60-5.00 [77-79] |
| Complex refractive | n & k | NA | Figure 3.2(b) | NA |
| index | | | (Exp.) | |
| Relative | E _r | NA | 6 (Ref.) | 6 [98] |
| permittivity | | | | |
| | χ | eV | 4.61 (Ref.) | 3.4-4.8 [78] |
| Electron affinity | | | | |
| Conduction band | N _C | cm ⁻³ | 1.00×10^{21} (Ref.) | 1.00×10^{19} - 3.00 × 10 ²² |
| density of states | | | | [78, 98] |
| Valence band | N_V | cm ⁻³ | 1.04×10^{21} (Ref.) | 1.00×10^{19} - 3.00×10^{22} |
| density of states | | | | [78, 98] |
| Hole mobility | μ_p | $cm^2V^{-1}s^{-1}$ | 15000 (Ref.) | 15000 [16, 78, 93] |
| Electron mobility | μ_n | $\mathrm{cm}^{2}\mathrm{V}^{-1}\mathrm{s}^{-1}$ | 15000 (Ref.) | 15000 [16, 78, 93] |

With above model parameters, the validity of our TCAD model was checked against the measured characteristic. As shown in Figure 3.7, there is a satisfactory match between simulated and measured EQE and light J-V curves.



Figure 3.7 (a) EQE and (b) light J-V characteristic measured and simulated using a heterojunction model

3.3 Optimization of graphene sheets, ARC and the rear of Graphene-Si solar cells Compared with the simplified Schottky junction approach, the established TCAD heterojunction model gives more insight on the sensitivity of solar cell performance to the optical and electrical properties of graphene. Figure 3.8 shows the PCE of the solar cell as a function of graphene bandgap, work function, electron affinity and the effective density of states with the other parameters set at values listed in Table 3.1. It is observed that cell performance generally improves with graphene bandgap, work function, electron affinity but decreases with effective density of states. The increase in bandgap, work function and electron affinity of graphene induces a higher built-in potential, resulting in higher Voc for the graphene/Si solar cells. However, the increase in effective density of states reduces the band bending at the graphene/silicon interface, which causes the drop of PCE. The properties of graphene can be modulated by the doping process (doping concentration [92, 99, 100], dopant types [21, 79, 92, 94-96, 99-101], external electrical field [26, 92, 99], etc.) and the number of graphene layers [85, 99, 102]. In this chapter, HNO₃ was used as the dopant and HNO₃ doping concentration can be modified by the HNO₃ treatment time [30] and the concentration of HNO₃ solutions [103]. The doping concentration is related to the properties of graphene like bandgap, work function, electron affinity and effective density of states [37, 59, 79, 95, 96, 100, 101, 104-106] and deserves further investigation. To optimize graphene/silicon heterojunction, all tunable parameters of graphene (bandgap, work function, electron affinity and effective density of states) were swept in the range of literature values (Table 3.1) and the corresponding PCE was calculated. As shown in Table 3.2, a maximal theoretical PCE of 12.1% is predicted when modulation of graphene sheets is employed. The optimization of graphene sheets induces a relatively large band bending at the interface of graphene/silicon, facilitating carrier flow, as well as increasing V_{bi} between graphene and silicon. Since V_{bi} is directly proportional to *Voc*, enhanced *Voc* and *FF* would be expected, as compared with our experimental results. The results show the great potential of graphene/silicon solar cells, particularly when the bandgap opening is stable and the impacts of the graphene on device performance is no longer negligible.



Figure 3.8 Dependence of PCE on the (a) bandgap (b) work function (c) electron affinity and (d) effective density of states of graphene sheets as predicted by the TCAD heterojunction model

The addition of an ARC can significantly attenuate the optical reflection and further improve the cell performance [77, 107]. Double layer anti-reflection coating (DLARC) is an option to minimize the reflection especially for a wide range of wavelengths. [77, 107]. In this work, the MgF₂/ZnS were chosen as the DLARC [107] and the standard

weighted reflectance (SWR) under different thicknesses of MgF_2 and ZnS was calculated for the optimum design. Theoretical calculation predicts a reduction of reflection to below 6% by introducing the 110nm MgF_2 / 50nm ZnS DLARC.

The presence of an aiding Passivated Emitter and Rear Cell (PERC) at the back surface of a conventional silicon solar cell minimises the impact of rear surface recombination, improving short-circuit current density and open-circuit voltage [108]. The optimization of the rear surface of graphene/silicon solar cell by inclusion of a PERC was also studied. The input parameters of the PERC were taken from the previous report [109]. As shown in Table 3.2, the PCE can be enhanced to reach the theoretical maximum up to 22.5% (with DLARC and PERC optimization), much higher than reported values [20-24, 26]. Importantly this level of efficiency compares favourably with those for current conventional screen-printed PERC solar cell [110], highlighting the potential for graphene / silicon solar cells to achieve comparable PCE using a highly simplified fabrication process.



Figure 3.9 Schematic of graphene/silicon solar cell with DLARC and PERC

Table 3.2 Parameters and modelling results of the optimized GSJ solar cells under Heterojunction junction (other input parameters of graphene not listed below remain the same as Table 3.1)

| | Without | With | With | Conventional |
|----------------------------|-----------------------|-------|----------|--------------|
| | ARC | DLARC | DLARC | PERC solar |
| | | | and PERC | cell [110] |
| Bandgap (eV) | 0.3 | · | | |
| Work function (eV) | 5.0 | | | |
| Electron affinity (eV) | 4.8 | | | |
| Effective density of | 1.00×10^{19} | | | |
| states (cm ⁻³) | | | | |
| SWR (%) | 40.0 | 5.7 | 5.7 | |
| Jsc (mA/cm ⁻²) | 25.1 | 38.9 | 39.1 | 39.1 |
| Voc (V) | 0.65 | 0.65 | 0.72 | 0.69 |
| FF (%) | 72.6 | 74.8 | 78.2 | 77.4 |
| PCE (%) | 12.1 | 19.3 | 22.5 | 21.0 |

Figure 3.10 compares the theoretical and experimental efficiencies of graphene/silicon solar cells in this study with the reported efficiencies. It is encouraging to notice that the cell performance can be improved further to reach the theoretical maximum with the modification of graphene sheets and optimization of antireflection films and the rear structure.



Figure 3.10 Efficiency comparison of various graphene/silicon solar cells [20-24, 26]

3.4 Conclusion

In this chapter, extensive characterization techniques were carried out to extract key optical and electrical parameters of graphene sheets to facilitate the establishment of a detailed TCAD heterojunction model. Compared with the current predominant Schottky junction approach, a heterojunction junction model simulated by TCAD is physically more accurate and provides advantages for a more detailed material property study. These advantages were highlighted by investigating the impact of the graphene bandgap, work function, electron affinity and effective density of states on the device performance. This was not previously feasible using the Schottky junction approach. According to the TCAD model, the maximum conversion efficiency can be enhanced to 22.5% based on the modification of graphene layers and optimizations of the antireflection coatings and the rear structure. The results are encouraging for fabricating high efficiency graphene/silicon solar cells and other optoelectronic devices.

Chapter 4 . Full Heterojunction of Transition Metal Dichalcogenides/Si solar cell

Transition metal dichalcogenides (TMDs) with graphene-like structure have garnered immense interest in recent years. As compared to graphene, the successful translation of 2D MX₂ in photovoltaics still remains at an early stage. In this chapter, based on the electrical and optical properties of transition metal dichalcogenides (TMDs) calculated from first principle calculations, TMDs/Si heterojunction solar cells were theoretically investigated by the TCAD model. The origin of the widely reported 'kink' in the Light J-V curves, which appears in the simulated Light J-V curves for TMDs/Si heterojunction solar cell, was analysed in detail based on the simulated band diagram, recombination, carrier density distribution, etc. under different bias voltages. Simulation demonstrates this is attributable to the interface charge building up at the interface, which results in high recombination. To overcome this effect, high doping of the TMD and a passivation layer between TMD and Si are necessary. Simulation also indicates the best way to proceed is to avoid the band alignment issues, namely the selection of substrate type: p-Si is more likely to be recommended for MoS₂ and WSe₂; and oppositely, n-Si for MoSe₂ and WS₂. And the dependence of solar cell performance on the doping concentration of TMDs, the interface of TMDs/Si contact, as well as the properties of Si wafer (doping concentration, bulk lifetime and thickness) were also studied in detail. The cell performance is found to achieve over 20% with the rear optimization. The results demonstrate the great potential of TMD materials in fabricating high-efficiency silicon solar cells.

4.1 Introduction

TMDs are a class of materials with the generalized formula of MX₂, whereby M represents a transition metal element from group IV, V or VI and X represents a chalcogen. Monolayer MX₂ consists of three atomic layers where the transition metal layer is sandwiched by two chalcogens layers. Each atomic layer is stacked via covalent forces [111]. Individual layers of TMDs can be isolated from the bulk form via mechanical exfoliation, liquid exfoliation or ion intercalation methods [39, 40, 112-114], since the TMD monolayers in the bulk form are connected by weak van der Waals force. TMDs materials possess remarkable properties in their ability to be exceptionally strong, lightweight, flexible, and excellent conductors of heat and electricity [115]. In this work,

the group-IV semiconductor dichalcogenides MoX_2 and WX_2 , namely Molybdenum disulfide (MoS₂), Molybdenum diselenide (MoSe₂), Tungsten disulfide (WS₂) and Tungsten diselenide (WSe₂) were studied in detail.

A detailed modelling work which can establish the practical limits of the structures and guide experimentalists beyond the idealized model for TMDs/Si heterojuncion solar cells is still lacking. Since all the optical and electrical parameters of TMDs can vary as a function of process/deposition methods and so on, their role in cell characteristic needs to be well assessed. In this work, first principle calculations were carried out to obtain the necessary physical properties of TMDs. The effects of the doping type of Si, the mechanism behind the kink, the doping concentration of TMDs, the interface of TMDs/Si contact, as well as the properties of Si wafer (doping concentration, bulk lifetime and thickness) were investigated to further improve the efficiency.

4.2 Electronic and optical properties of monolayer TMDs

The band structure and the related physical properties were calculated by the Vienna abinitio simulation package (VASP) based on density functional theory (DFT) [116]. Ionelectron interactions were calculated by the projector augmented-wave (PAW) pseudo potential method with a plane wave basis set with a kinetic energy cut-off of 600 eV. Exchange and correlation interactions were calculated by the generalized gradient approximation (GGA) using the Perdew-Burke-Ernzerhof (PBE) function. When optimizing atomic positions using this k mesh, the energy convergence value between two consecutive steps were chosen as 10^{-5} eV and the maximum Hellmann-Feynman force acting on each atom was less than 10^{-3} eV/ Å. To avoid the artificial interaction between atom layers, the separation between layers from the nearest supercell was set to be 30 Å for monolayer MoS₂, MoSe₂, WS₂ and WSe₂. For geometry optimization and self-consistent electronic structure calculations, a Monkhorst-Pack scheme was performed for the Brillouin zone integration with k-point meshes of $15 \times 15 \times 1$ for the two-dimensional (2D) structures. The optical properties of these monolayers were investigated by calculating complex dielectric constants using PBE method on the grid of $31 \times 31 \times 1$ *k*-points mesh.

Based on first principle calculations, the geometric and electronic band structures of

TMDs: MX₂ (M = Mo, W; X = S, Se) were systematically investigated. The top and side views of the optimized structure of monolayer MoS₂, MoSe₂, WS₂, WSe₂ are shown in Figure 4.1. Monolayer MoS₂ has a hexagonal primitive cell (the red dashed rhombus) contains one M atom and two X atoms, as the other three materials. The values of the optimized lattice parameters for monolayer MX₂ are: a=3.18 Å (MoS₂), a=3.31 Å (MoSe₂), a=3.18 Å (WS₂), a=3.32 Å (WSe₂), which are in good agreement with the reported theoretical results [117, 118]. The buckling height (h) of these four materials was also presented in Table 4.1.

In Figure 4.2, the band structures with the valence band maximum (VBM) and conduction band minimum (CBM) for MoS₂, MoSe₂, WS₂, WSe₂ were calculated using PBE function. The results show these four materials are all direct-bandgap semiconductors with VBM and CBM located at the K high-symmetry point. The calculated band gap of MoS₂, MoSe₂, WS₂ and WSe₂ are 1.68 eV, 1.49 eV, 1.81 eV and 1.53 eV respectively. These values agree well with the reported PBE functional results of 1.59 eV [117], 1.47 eV [118], 1.80 eV [118, 119] and 1.63 eV [117], respectively.

The work function of monolayer 2H-MX₂ is obtained by the equation: $\Phi = E_{vacuum} - E_F$, where E_{vacuum} is the vacuum energy of monolayer, E_F represents the Fermi level. The calculated work function of MoS₂ is 5.09 eV, which is consistent with the reported value of 5.1 eV [120].

The calculated electron affinity of MoS₂, MoSe₂, WS₂, WSe₂ given by $E_a = E_{vacuum} - E_{CBM}$ are 4.25 eV, 3.86 eV, 3.90 eV and 3.58 eV respectively, which are in consistent with the reported PBE functional results of 4.25 eV, 3.87 eV, 3.84 eV and 3.53 eV respectively.

As shown in Figure 4.1 (a), the orthogonal supercell is enclosed with blue dashed lines of the atomic structure of monolayer MoS_2 , together with hexagonal primitive cell for comparison. The supercell built in this way allows for an intuitive demonstration of carrier conduction along the armchair 'a' and zigzag 'b' directions. The effective mass m_e^* tensor for charge transport along a and b directions are given by $m_{a/b}^* = \hbar^2 (\partial^2 E(k)/\partial k^2)^{-1}(k \text{ is wave-vector, and } E(k) \text{ denotes the energy}), m_d \text{ is the average effective mass defined by } m_d = \sqrt{m_a^* m_b^*}$. The calculated values are 0.50 m₀ for electrons and 0.63 m₀ for holes, which are consistent with the reported values of 0.48 m₀ for electrons and 0.64 m₀ for holes [118, 122]. The same method was applied to three other materials.

The effective density of states for electrons in the conduction band is calculated by $N_c = 2 \left[\frac{2\pi m_d^e k_B T}{h^2} \right]^{3/2}$, where m_d^e is the electron effective mass along the transport direction, *h* is the Planck's constant, and the effective density of states for holes in the valence band is obtained by $N_v = 2 \left[\frac{2\pi m_d^h k_B T}{h^2} \right]^{3/2}$, where m_d^h is the hole effective mass. The intrinsic carrier density is then extracted based on

$$n_i = \sqrt{N_c N_v} e^{-(E_c - E_v)/2k_B T}$$
(4.1)

The optical properties of monolayer MoS₂, MoSe₂, WS₂, WSe₂ are obtained based on the results of complex dielectric function: $\varepsilon(w) = \varepsilon_1(w) + i\varepsilon_1(w)$. The imaginary part of dielectric tensor $\varepsilon_2(w)$ is determined by a summation over empty band states as follows [123],

$$\varepsilon_2(w) = \frac{2\pi e^2}{\Omega \varepsilon_0} \sum_{k,\nu,c} \delta(E_k^c - E_k^\nu - \hbar w) |\langle \Psi_k^c | \boldsymbol{u}. \boldsymbol{r} | \Psi_k^\nu \rangle|^2$$
(4.2)

, where ε_0 is the vacuum dielectric constant, Ω is the crystal volume, v and c represent the valence and conduction bands respectively, $\hbar w$ is the energy of the incident photon, u is the vector defining the polarization of the incident electric field, u^*r is the momentum operator, Ψ_k^c and Ψ_k^v are the wave functions of the conduction and valence band at the k point, respectively. The real part of dielectric tensor $\varepsilon_1(w)$ is obtained by the Kramers-Kronig relation [124],

$$\varepsilon_1(w) = 1 + \frac{2}{\pi} P \int_0^\infty \frac{\epsilon_2(w')w'}{w'^2 - w^2 - i\eta} dw'$$
(4.3)

, where *P* denotes the principle value. When the incident phonon energy ($\hbar w$) is 0 eV, the dielectric constant of monolayers in the long wavelength limit, $\bar{\varepsilon}$ can be obtained. The calculated dielectric constant $\bar{\varepsilon}$ of monolayer MoS₂ is 2.94, which is consistent with the reported value of 2.8 eV [125]. The dielectric constant $\bar{\varepsilon}$ of monolayer MoSe₂, WS₂ and WSe₂ are also listed in Table 4.1.

The refractive index n(w) and extinction coefficient k(w) can be subsequently given by [126, 127]

$$n(w) = \frac{1}{\sqrt{2}} \left\{ [\epsilon_1^2(w) + \epsilon_2^2(w)]^{1/2} + \epsilon_1(w) \right\}^{\frac{1}{2}}$$
(4.4)

$$k(w) = \frac{1}{\sqrt{2}} \left\{ [\epsilon_1^2(w) + \epsilon_2^2(w)]^{1/2} - \epsilon_1(w) \right\}^{\frac{1}{2}}$$
(4.5)



Figure 4.1 The top and side views of monolayer (a) MoS_2 (b) $MoSe_2$ (c) WS_2 (d) WSe_2 . The areas circled by red dashed rhombus and blue dashed rectangle lines represent the hexagonal primitive and the orthogonal supercell respectively. The purple, yellow, grey, and green balls represent Mo, S, W, and Se atoms respectively



Figure 4.2 Electronic band structure of monolayer (a) MoS_2 (b) $MoSe_2$ (c) WS_2 (d) WSe_2

Table 4.1 shows the electronic and optical parameters calculated by DFT. It is worth noting that these values are consistent with the previous reports as mentioned before.

| Properties | MoS_2 | MoSe ₂ | WS_2 | WSe ₂ |
|---|------------|-------------------|-----------|------------------|
| Lattice- <i>a</i> [Å] | 3.18 | 3.31 | 3.18 | 3.32 |
| <i>h</i> [Å] | 3.13 | 3.34 | 3.14 | 3.35 |
| $E_g[eV]$ | 1.68 | 1.46 | 1.81 | 1.53 |
| Work function ϕ [eV] | 5.09 | 4.59 | 4.79 | 4.35 |
| Electron affinity E_a [eV] | 4.25 | 3.86 | 3.90 | 3.58 |
| Average effective mass | 0.50/0.63 | 0.59/0.71 | 0.32/0.44 | 0.35/0.47 |
| (m_{de}/m_{dh}) [m ₀] | | | | |
| $Nc/Nv (\times 10^{18}) [cm^{-3}]$ | 8.91/12.58 | 11.42/15.16 | 4.63/7.47 | 5.32/8.21 |
| $n_i (\times 10^5) [\text{cm}^{-3}]$ | 9.06 | 78.14 | 0.46 | 11.08 |
| Dielectric constant $\bar{\varepsilon}$ | 2.94 | 2.75 | 2.43 | 2.64 |

Table 4. 1 Electronic and optical parameters calculated by DFT

4.3 Influence of Si doping type and the origin of J-V kink

The simulated structure of TMDs/Si heterojunction solar cell with 80nm ITO as the anti-reflection coating is shown as Figure 4.3. The parameters of TMDs calculated by

DFT are given in Table 4.1. The comparison of Light J-V curves for TMD on *n*-Si and *p*-Si wafers was studied and a detailed investigation of the kink in the Light J-V curves was given.



Figure 4.3 Schematic of the proposed 2D-Si heterojunction solar cell

All the input values as listed in Table 4.2 (TMDs doping concentration, surface recombination velocity, Si doping concentration, Si bulk lifetime, as well as Si thickness) are typical of the Si solar cells [109, 128-130] operating at Air Mass 1.5 spectra.

Table 4. 2 TCAD heterojunction model parameters and their values

| Description | Unit | Input Value |
|---------------------------|------------------|-------------------------|
| TMDs doping concentration | cm ⁻³ | 1.00×10 ¹⁵ |
| Surface Recombination | cm/s | 1×10 ³ |
| Velocity | | |
| Si doping concentration | cm ⁻³ | 1.00×10^{16} |
| Si bulk lifetime | S | e: 2.1×10 ⁻³ |
| | | h: 2.1×10 ⁻² |
| Si thickness | μm | 200 |

In the context of 2D layered materials, dopant atoms may intercalate between layers or alter the structure to create a new phase. Doping can be useful in controlling p- or n-type semiconducting behaviour. For example, p-type conduction has been realized in MoS₂ by substituting Mo with Nb or S with N while strong n-type conduction has been reported when S is substituted by Cl [131]. Hence the solar cell performance based on

the same doping concentration of TMDs and Si was studied on both p-Si and n-Si to form the heterojunction for comparison.

Figure 4.4 (a) (b) shows a S-shaped kink in Light J-V characteristic for p-MoS₂/n-Si and p-WSe₂/n-Si heterojunction solar cells. The S-shaped kinks are often observed for Si heterojunction solar cells on both p and n-Si wafers. The origin for the kink is still non-conclusive. Several possible mechanisms have been proposed to explain this S-shaped concavity. Charge transport restrictions caused by band mismatch and imbalanced carrier mobilities which alter the distribution of the internal electric field are generally regarded to be mainly responsible for the occurrence of the S-shaped kink for organic solar cells [132-135]. Song et al. proposed that the recombination of the native silicon oxide layer dominates over tunnelling is the possible reason for the kink occurred in graphene-silicon solar cells [24]. But there is still a lack of detailed study on the occurrence of kink for Si heterojunction solar cells.

To reveal the mechanism behind the kink, the band diagram, recombination and also carrier density under bias voltage in the range of 0.3V to 0.6V were studied, and results demonstrate the kink is likely attributable to the band mismatch (p-MoS₂/n-Si) and surface recombination (p-WSe₂/n-Si) at the interface of TMDs/Si contact. The methods to reduce the kink are also discussed to further improve the performance of the heterojunction solar cells.




Figure 4.4 Light current density –voltage curves simulated of (a) MoS_2 / Si (b) WSe_2/Si (c) $MoSe_2/Si$ and (d) WS_2/Si heterojunction solar cells (black line: *n*-Si; red line: *p*-Si)

The band diagrams of p-MoS₂/n-Si under thermal equilibrium condition, 0.3 V bias voltage (the start of the kink) and 0.5 V bias voltage (the middle of the kink) waplotted as shown in Figure 4.5(a)-(c). The band diagrams show a large ΔEv at the p-MoS₂/n-Si contact, which are due to the different bandgaps, work functions and electron affinities of MoS₂ and Si. The valence band discontinuity supresses the holes collection, resulting in holes accumulation in the c-Si. With the increase of bias voltage, the electric field at the p-MoS₂/n-Si junction decreases hence resulting in an insufficient c-Si band bending to ensure asymmetric selectivity of carriers. This insufficient carrier selectivity plus the large valence band discontinuity cause holes to pile up at the interface of $p-MoS_2/n-Si$ interface, and these non-extracted holes recombine with electrons at the interface, hence causing the current loss as shown in Figure 4.5(d) (in this case, Auger Recombination dominates among all the recombination types). To verify the assumption, the solar cell performance under different doping concentration of MoS₂ (namely different band discontinuity at the p-MoS₂/n-Si interface) was investigated. As shown in Figure 4.5(e), the low doping concentration of MoS₂ induces a high band discontinuity ΔEv at the interface of p-MoS₂/n-Si, which leads to an obvious kink in Light J-V curve. The kink becomes smaller until disappears with the increase of MoS₂ doping, indicating the doping concentration of MoS₂ needs to be carefully adjusted for a higher fill factor of the heterojunction solar cells.



Figure 4.5 Schematic of band diagram under (a) thermal equilibrium condition (b) 0.3 V bias voltage (c) 0.5V bias voltage (d) recombination (Auger, Radiative, Shockley Read Hall and Surface recombination) under bias voltage from 0.3 V to 0.6 V (e) zoom in view of the band diagram of p-MoS₂/n-Si contact under different doping concentration of MoS₂ and (f) the corresponding light J–V curves

Compared with p-MoS₂/n-Si as shown in Figure 4.6(a), there is no obvious band mismatch of n-MoS₂/p-Si contact, which explains why n-MoS₂/p-Si demonstrates a better solar cell performance.



Figure 4.6 Schematic of band diagram for (a) p-MoS₂/n-Si and (b) n-MoS₂/p-Si heterojunction (Inset: zoom in view of band diagram at the interface)

The simulated band diagrams at the interface of p-WSe₂/n-Si as illustrated in Figure 4.7 demonstrate the large band bending near the n-Si or p-Si surface towards WSe₂, which facilitates the separation of holes-electrons and shows good carrier selectivity. But Figure 4.4(b) demonstrates a S-shaped kink in Light J-V characteristic for p-WSe₂/n-Si heterojunction solar cells.



Figure 4.7 Schematic of band diagram for (a) p-WSe₂/n-Si and (b) n-WSe₂/p-Si heterojunction

To investigate the mechanism behind the kink, band diagrams under thermal equilibrium, 0.4 V bias voltage (the start of the kink) and 0.5 V bias voltage (the middle of the kink) were also plotted as shown in Figure 4.8(a)-(c). It's worth noting that the distance between E_{Fn} and E_C , and the distance between E_{Fp} and E_V indicate the carrier density of electrons and holes, respectively. The band diagrams show at the p-WSe₂/n-Si interface as highlighted, the electron density increases until approaching the level of the hole density with the increase of bias voltage, which's also verified by the simulated surface carrier density under the bias voltage of 0.3 V-0.6 V as shown in Figure 4.8(d). The hole density remains relatively unchanged, while the electron density increases exponentially with the bias voltage, leading to a large growth of surface recombination. Figure 4.8(e) indicates Surface Recombination dominates among all the recombination types, which is the possible reason for the current losses as observed in Figure 4.4(b). The Light JV curves under different surface recombination velocity was also plotted to verify our assumption as shown in Figure 4.8(f). It demonstrates the kink gets larger with the growth of surface recombination velocity. To overcome the efficiency limitation, a pssivation layer like SiO₂ or intrinsic amorphous silicon which reduces the surface recombination should be considered.



Figure 4.8 Schematic of band diagram under (a) thermal equilibrium condition (b) 0.3V bias voltage (c) 0.5V bias voltage (d) Interface carrier density (black line: electron; red line: hole) (e) recombination under bias voltage from 0.3 V to 0.6 V and (f) light current density-voltage curves under different surface recombination velocity of *p*-WSe₂/*n*-Si heterojunction solar cells

Indirect contrast, MoSe₂ and WS₂ show a better solar cell performance on *n*-Si as compared to *p*-Si as shown in Figure 4.4(c)(d) because of the higher built-in potential (V_{bi}) induced by MoSe₂ and WS₂ when contact with *n*-Si substrate. The built-in potential is defined as the difference between the Fermi levels in both the *n* type and *p* type semiconductor of a heterojunction. It can be expressed as:

$$V_{b_i} = \frac{\Delta E_c - \Delta E_v}{2} + kT ln \frac{N_D N_A}{n_{i,n} n_{i,p}} + \frac{kT}{2} ln \frac{N_{v,n} N_{c,p}}{N_{c,n} N_{v,p}}$$
(4.6)

, where $n_{i,n}$ and $n_{i,p}$ are the intrinsic carrier concentrations of the *n* type and *p* type semiconductor respectively; ΔEc and ΔEv are the band discontinuity of the conduction band and valence band between *n* and *p* type semiconductor respectively; N_D and N_A are the doping concentration of *n* type and *p* type semiconductor respectively; $N_{v,n}$ and $N_{v,p}$ are the effective density of states in the valence band for *n* type and *p* type semiconductor respectively and $N_{c,n}$ and $N_{c,p}$ are the effective density of states in the conduction band for *n* type and *p* type semiconductor respectively [136]. Since V_{bi} is directly related to *Voc*, it explains a slightly higher *Voc* on *n*-Si than *p*-Si solar cells. And as shown in Figure 4.9, band diagrams for both *n*-Si and *p*-Si show the sufficient asymmetry of the conductivities for holes and electrons. It is worth noting that *p*-WS₂/*n*-Si presents a similar band diagram with *p*-MoS₂/*n*-Si, the possible reason for the high *FF* of *p*-WS₂/*n*-Si solar cell is the smaller valence band discontinuity.



Figure 4.9 Schematic of band diagram for (a) n-MoSe₂/p-Si (b) p-MoSe₂/n-Si (c) n-WS₂/p-Si and (d) p-WS₂/n-Si heterojunction

The MoS₂ and WSe₂ demonstrate a higher efficiency on p-Si, thus these two materials can be called as '*n* type TMDs', and the following discussion on the sensitivity to different parameters of MoS₂ or WSe₂ and Si is based on p-Si. Similarly, *n*-Si is more likely to be recommended in achieving higher efficiency as compared with p-Si for MoSe₂ and WS₂, so the dependence of efficiency on the parameters of MoSe₂ or WS₂ and Si is discussed based on *n*-Si.

4.4 Potential efficiency of TMDs/Si solar cell

Section 4.4.1 to 4.4.3 discuss the solar cell performance as a function of the doping concentration of TMD, the interface of TMDs/Si contact and the Si substrate (doping concentration, bulk lifetime and thickness) respectively with the other parameters set at values listed in Table 4.2 (Input Values). The results were used for the optimization of TMDs/Si heterojunction solar cells as discussed in Section 4.5. The current loss of TMD/Si heterojunction solar cells was also studied to further improve the cell

performance.

Doping concentration for TMDs may range anywhere from 10^8 cm^{-3} to 10^{18} cm^{-3} [137-140]. Typical concentration values fall somewhere in this range and are tailored to produce the desired properties in the device that the TMD is intended for.

In a surface with no recombination, the movement of carriers towards the surface is zero, and hence the surface recombination velocity is zero. In a surface with infinitely fast recombination, the movement of carriers towards this surface is limited by the maximum velocity they can attain. The unpassivated side with $S_{n0}=S_{p0}=10^5$ cm/s is a worst-case scenario for typical industrial solar cells [141]. Thus the surface recombination velocity was discussed in the range of $1 \times 10^1 - 1 \times 10^5$ cm/s.

For Si substrate, the typical doping level is from 1.00×10^{13} — 1.00×10^{18} cm⁻³ [130]. As shown in Table 4.3, the sensitivity of PCE on Si doping concentration was discussed in the range as mentioned above.

The bulk lifetime of Si is quite unpredictable and difficult to control. It can vary by several orders of magnitude, from approximately 1 ns to 1 ms in the common Si solar cell materials. The highest value ever measured is 32ms for undoped Si, and the lowest 10^{-9} s for heavily doped Si [142]. In this work, a feasible range $(2.1 \times 10^{-1} - 2.1 \times 10^{-5} \text{ s})$ was chosen to study the influence of Si bulk lifetime on TMDs/Si solar cell performance.

An optimum Si solar cell with very good surface passivation is about 100 μ m thick. However, thickness between 200 and 500 μ m are typically used, partly for practical fabrication issues, and partly for light absorption reasons. The amount of light absorbed depends on the optical path length and the absorption coefficient, which means thick wafer can absorb more light in solar cell. In this work, the dependence of PCE on Si thickness was discussed in the range of 100—500 μ m.

The ranges of the parameters discussed are listed in Table 4.3 as shown below:

Table 4. 3 TCAD heterojunction model parameters and their values

| Description | Unit | Range of input value for |
|---------------------------|------------------|--|
| | | discussion |
| TMDs doping concentration | cm ⁻³ | 1.00×10^{8} - 1.00 × 10 ¹⁸ |
| Surface Recombination | cm/s | $1 \times 10^{1} - 1 \times 10^{5}$ |
| Velocity | | |
| Si doping concentration | cm ⁻³ | 1.00×10^{13} -1.00×10^{18} |
| Si bulk lifetime | S | e: 2.1×10^{-1} — 2.1×10^{-5} |
| | | h: 2.1×10^{-1} - 2.1×10^{-5} |
| Si thickness | μm | 100—500 |

4.4.1 Influence of doping concentration of TMDs on the solar cell performance

In Figure 4.10 the dependence of solar cell quality on doping concentration of TMDs was plotted. It shows that the light J-V characteristic develop an S-shape for lower doping concentration of MoS₂ and WS₂. As illustrated in Figure 4.11, for MoS₂ or WS₂ /Si solar cells, low doping concentration of MoS₂ or WS₂ indicates that a lower electrical field on the side towards c-Si wafers, which leads to an insufficient c-Si band bending that violates the asymmetric conductivities of carriers as discussed in Figure 4.5. Modelling indicates that for improved performance of *n*-MoS₂/*p*-Si heterojunction solar cells, the doping of MoS₂ has to be over than 10^{12} cm⁻³, unless the kink in JV exists. For *p*-WS₂/*n*-Si heterojunction solar cells, the kink disappears when the doping concentration of MoS₂ is over 10^{11} cm⁻³. Another salient feature is that J_{SC} , V_{OC} and *FF* are almost saturate when the doping concentration of MoS₂ is higher than 10^{14} cm⁻³ and 10^{13} cm⁻³ for WS₂. The possible reason is that under high doping concentration of MoS₂ or WS₂, the majority of the photo-generated carriers inside the c-Si wafer can surmount the field barrier and get collected at the front metal contact. At this stage, no improvement of PCE is observed.

For MoSe₂ or WSe₂/ Si solar cell, JV curves with increasing doping concentration of MoSe₂ or WSe₂ are likely to have higher *Voc* because of a more advantageous band diagram leading to higher built-in potential (V_{bi}). And the solar cell parameters reach saturation when the doping concentration is over 10¹⁵ cm⁻³ for MoSe₂ and 10¹² cm⁻³ for

WSe₂. Based on the simulation results, a sufficient doping concentration of 2D materials is an essential requirement for good carrier selectivity.



Figure 4.10 Dependence of PCE on the doping concentration of TMD layers for (a) n-MoS₂/p-Si (b) n-WSe₂/p-Si (c) p-MoSe₂/n-Si (d) p-WS₂/n-Si heterojunction solar cells (Inset: the corresponding Light J-V curves under different doping concentration of TMD layers)



Figure 4.11 Schematic of band diagram for (a) n-MoS₂/p-Si heterojunction (b) p-WS₂/n-Si heterojunction under different doping concentration of TMDs

4.4.2 Influence of surface recombination at the TMDs/Si interface on the solar cell performance

The dependence of PCE on the interface of TMDs/Si was studied by the surface recombination velocity of the carriers. At the surface of a semiconductor, the atomic lattice is abruptly interrupted. Surface atoms lack neighbours bond to, and are left with unsatisfied 'dangling' bonds (unpaired outer-shell electrons). These dangling bonds introduce electronic energy levels inside the normally forbidden semiconductor bandgap, referred to as surface or interface states. Such states greatly enhance electron–hole recombination at the surface by acting as stepping stones for carriers transition between the conduction band and valence band.A parameter called the 'surface recombination velocity' (SRV) is used to specify the recombination at a surface [143, 144].



Figure 4.12 Dependence of PCE on the surface recombination velocity of the carriers at the contacts for (a) n-MoS₂/p-Si (b) n-WSe₂/p-Si (c) p-MoSe₂/n-Si (d) p-WS₂/n-Si heterojunction solar cells (Inset: the corresponding Light J-V curves under different surface recombination velocity)

The SRV does not affect cell performance up to a value of 10^3 cm/s as shown in Figure 4.12. For WS₂ or WSe₂/Si solar cells, SRV has only a small influence when it is over 10^4 cm/s. For MoS₂ or MoSe₂/Si solar cells, hole collection is already somewhat

impeded by the valence band mismatch at the TMDs/Si interface; hence a high value of SRV is expected to have a disastrous influence on carriers collection. Figure 4.12 (a)(c) also proves that surface recombination is the possible reason to cause the kink as discussed in Figure 4.8.

4.4.3 Influence of Si substrate on the solar cell performance

The Light J-V curves under different doping concentration of Si for these four TMDs have the same trend, hence MoS₂-Si was taken as the example to shed light on the relation between Si doping and solar cell performance (the electrical resistance, recombination rate, etc. relative to the change of Si doping are not considered in this model). For a better understanding, the corresponding EQE under different Si doping concentration for MoS₂-Si heterojunction solar cells was also plotted as shown in Figure 4.14 (b). For the quantum efficiency (QE) of the simulated structure, the illumination conditions taken are monochromatic light signal intensity (photon flux) of 1 x 10^{-3} Wcm⁻² with 2 µm spectral width in the range of 300 - 1200 nm.

For MoS_2/p -Si heterojunction solar cells, the Fermi level shifts downward and starts overlapping the valence band with the increase of Si doping concentration. This facilitates carriers flowing across the load as well as increasing the built-in potential between MoS_2 and Si, thus the V_{OC} and FF enhance. However, the enhancement of doping concentration results in a lower EQE, particularly in the long-wavelength region; less photons are absorbed and less electron-hole pairs are generated, which causes the decrease of Jsc. These two opposite effects from increase of Si doping concentration at which the efficiency peaks. The optimum value is around 10^{16} cm⁻³ for MoSe₂, and around 10^{17} cm⁻³ for the other three 2D materials.



Figure 4.13 Dependence of PCE on the doping concentration of Si for (a) n-MoS₂/p-Si (b) n-WSe₂/p-Si (c) p-MoSe₂/n-Si (d) p-WS₂/n-Si heterojunction solar cells (Inset: the corresponding Light J-V curves under different doping concentration of Si)



Figure 4.14 (a) Schematic of band diagram for MoS_2 / p -Si heterojunction under different doping concentration of Si (b) dependence of EQE on the doping concentration of Si

Impact of bulk lifetime of Si on the solar cell performance was also studied. The bulk lifetime of Si is varied in the range of 10^{-1} — 10^{-5} s and the results show both *Jsc* and *Voc* improve slightly with the increasing bulk lifetime of Si.

To study the effect of thickness variation, the thickness of Si is varied from 100 μ m to 500 μ m and the result shows an increase in all the performance parameters of the cell. The increase of Si thickness enhances the EQE especially for long wavelength area as shown in Figure 4.15. It results in a growth of electron-hole pairs generation and as a consequence, *Jsc* as well as *Voc* increase. According to the simulation results, around 3% improvement of PCE is achieved with the increase of the wafer thickness.



Figure 4.15 Dependence of EQE on the thickness of Si wafer

4.5 Improvement of TMDs/Si solar cells

The current loss for TMD/Si heterojunction solar cells are given in Figure 4.16. The current loss in the back contact dominates among all the losses for the solar cells. The current loss analysis demonstrates the efficiency of TMDs/Si solar cells can be further improved by the optimizations of the rear structure. The presence of an aiding Passivated Emitter and Rear Cell (PERC) at the back surface minimises the impact of rear surface recombination, improving the solar cell performance [108]. Thus the optimization of the rear of TMDs/Si solar cell by inclusion of a PERC was also studied. The input parameters of the PERC are taken from previous report [109]. As shown in Table 4.4, the PCE can be enhanced to reach over 20% based on the optimization of the discussed parameters (the doping concentration of TMDs, SRV of TMDs/Si contact and the properties of Si substrate) and the rear.



Figure 4.16 Current loss analysis for TMDs / Si solar cell



Figure 4.17 Schematic of (a) n-MoS₂ or n-WSe₂/p-Si solar cell and (b) p-MoSe₂ or p-WS₂/n-Si solar cell with PERC

Table 4. 4 Modelling results of the TMDs/ Si solar cells with PERC

| | <i>n</i> -MoS ₂ / <i>p</i> -Si | <i>n</i> -WSe ₂ / <i>p</i> - | p-MoSe ₂ /n- | <i>p</i> -WS ₂ / <i>n</i> -Si | |
|----------------------------|---|---|-------------------------|--|--|
| | solar cell | Si | Si solar cell | solar cell | |
| | | solar cell | | | |
| TMDs | 10 ¹⁵ | 10 ¹⁵ | 10 ¹⁵ | 10 ¹⁵ | |
| Doping (cm ⁻³) | | | | | |
| SRV (cm/s) | 10 ¹ | | | | |
| Si Doping | 5 ¹⁷ | 10 ¹⁸ | 10 ¹⁶ | 10 ¹⁷ | |
| (cm^{-3}) | | | | | |
| Si Bulk | e: 2.1×10^{-3} | | | | |
| Lifetime (s) | h: 2.1×10 ⁻² | | | | |

| Si thickness | 500 | | | |
|----------------------------|------|------|------|------|
| (µm) | | | | |
| Jsc (mA/cm ⁻²) | 33.1 | 33.2 | 33.1 | 33.1 |
| Voc (V) | 0.67 | 0.67 | 0.68 | 0.69 |
| FF (%) | 86.3 | 86.9 | 87.3 | 87.4 |
| PCE (%) | 19.2 | 19.3 | 20.0 | 20.2 |

4.6 Conclusion

In this work, DFT calculations were carried out to extract key optical and electrical parameters of TMDs sheets to facilitate the establishment of a detailed TCAD heterojunction model for TMDs/Si solar cells. The results demonstrate the origin of the kink in Light J-V curves is due to the band alignment at the interface of TMDs and Si, which leads to the interface charge building up thus resulting in high recombination. It can be overcome by heavily doping TMDs and inserting a passivation layer between TMDs and Si. Simulation also indicates the best way to proceed is to avoid the band alignment issues, namely the selection of substrate type: *p*-Si is more likely to be recommended for MoS₂ and WSe₂; and oppositely, *n*-Si for MoSe₂ and WS₂. The influence of the doping concentration of TMDs, surface recombination, bulk lifetime and thickness) were also investigated on the solar cell performance of TMDs/Si solar cells show immense potential in achieving over 20%, which is encouraging for fabricating high efficiency TMDs/Si solar cells and other optoelectronic devices.

Chapter 5. Application of Solution processed Transition Metal Oxide layers on Silicon solar cell

In this chapter, the suitability of alternative carrier selective contact layers based on two kinds of transition metal oxide (TMO), namely nickel oxide (NiOx) and vanadium oxide (VOx) to form hole selective contacts with both *n* type and *p* type silicon was evaluated. Depending on the doping character of the c-Si substrate (*n*- or *p*-type), TMOs can form a hole selective contact by: (i) inducing an inversion layer upon *n*-Si (i.e., a *p*-n junction), or (ii) inducing an accumulation layer upon *p*-Si (i.e., a *p*⁺-*p* contact) [145].

5.1 TMOs on *n*-Si

5.1.1 Introduction

TMOs are of great interest since they are cheap, abundant and provide new low-cost deposition methods. A distinctive feature of TMOs is their preferential conductivity for one kind of charge carrier (i.e. holes) while blocking the other kind (electrons), aiding in the separation of photo-generated carriers. TMOs have been widely used in dye-sensitized and organic photovoltaics as hole transporting layer (HTL) or electron transporting layer (ETL) [46]. Thermally evaporated MoO₃ has also been used for c-Si hetero-junction cell (MoOx/ *i*-aSi:H/ c-Si/ *i*-aSi:H/*n*-aSi:H) reaching a power conversion efficiency as high as 22.5% [49]. Compared with MoOx, less work has been done on NiOx and VOx for silicon solar cells though encouraging results have been reported.

This work looks at the suitability of NiOx and VOx layers, deposited by spin coating, as CSCs for silicon solar cells. The spin-coated layers of NiOx and VOx were deposited on *n*-Si substrates for detail material and electrical characterizations. Results from the measurements were used as inputs into an advanced TCAD model, which simulates a hetero-junction with intrinsic thin layer (HIT) solar cell (*p*-aSi:H/ i-aSi:H/ *n*-Si/ i-aSi:H/*n*-aSi:H) but with the *p*-type a-Si:H replaced by NiOx or VOx. Results of these simulations provide insights into the carrier transport properties and the operation of the NiOx-Si and VOx-Si CSC solar cells. The potential performance of these devices can also be estimated, and consequently pathways for improvement are identified.

5.1.2 Experiment and Simulation

5.1.2.1 Characterization of Spin-Coated NiOx and VOx sheets

In this chapter, NiOx and VOx films were prepared by the sol-gel dip coating method. The thickness of TMOs films were controlled by the concentration of TMOs solution, spinning speed and the spin coating cycles. The impact of the annealing process on the film quality was also investigated. Nickel acetate tetrahydrate was dissolved in ethanolamine (0.1 mol·L–1) and doped by 1at% copper acetate to make the 1wt% or 4wt% NiO precursor solution. A drop of HCl (\approx 50µL) was also added to enhance the solubility. The solution was stirred at 60° for 12h to obtain the sol-gel. NiOx film was coated on silicon substrate at a withdrawal speed of 3000 rpm/s or 10000 rpm/s for 30s, as well as VOx film. Finally the NiOx film was annealed for 1h at 350 °C— 550 °C to remove organics species after the spin coating process. Vanadium Oxide was spin-coated from isopropanol solution of vanadium oxitriisopropoxide at 1:10 or 1:70 volume ratio. The VOx film was annealed for 20 mins at 100 °C — 300 °C to remove organics species.

Atomic force microscopy (AFM) was used to characterize the surface morphology of the TMO films. The AFM root mean square roughness (RMS) values were obtained by NanoScope Analysis. Figure 5.1 shows that these films are uniformly deposited and smooth after spin coating and annealing process of the sol–gel precursor. The roughness for NiOx films under annealing temperature of 350 °C, 450 °C and 550 °C is around 0.298 nm, 0.572 nm and 0.631 nm, respectively. And the roughness for VOx films under annealing temperature of 100 °C, 200 °C and 300 °C is about 0.169 nm, 0.488 nm and 0.779 nm, respectively. AFM characterization shows the roughness of films increases with the annealing process, which is likely attributable to the increase in crystallinity of the spin-coated films. Considering the roughness of the films, the NiOx film was annealed under 350 °C and VOx film was annealed under 100 °C for the following study.



Figure 5.1 AFM images of NiOx under annealing temperature of (a) 350 °C (b) 450 °C (c) 550 °C and (b) VOx under annealing temperature of (d) 100 °C (e) 200 °C (f) 300 °C

Grazing Incidence X-ray Diffraction (GIXRD) analysis (with a grazing angle of 2°) was used to determine the crystal structure of NiOx and VOx. The diffraction patterns of films recorded by varying the diffraction angle (2 θ) in the range of 30-50°. Results for NiOx and VOx are presented on Figure 5.2. From Figure 5.2 (a), two peaks are observed at 2θ =37.290°, 43.270° in XRD pattern. The observed pattern matches the standard XRD pattern reported for Rhombohedral NiO (ICDD: 04-011-2340). These peaks are attributable to cubic crystalline structure with preferred orientation along (111) and (200) plane. The absence of impurity peaks in all XRD patterns suggests the high purity of the nickel oxide. The XRD pattern of VOx shows no well-defined sharp peaks. This indicates VOx annealed at 100 °C is amorphous in this work.



Figure 5.2 X-Ray Diffraction patterns of (a) NiOx and (b) VOx

Optical constants (complex refractive index n & k) in the wavelengths range of 380-168 Onm measured by Spectra Ellipsometry were extracted with double Tauc-Lorentz oscillators model for NiOx and triple Lorentz oscillators model for VOx [58, 146]. The optical bandgap was determined from the energy intercept by extrapolating the linear portion of the plot (the square of absorption coefficient multiply photon energy versus photon energy hv) to the zero of absorption coefficient. The optical bandgap for these NiOx layers is estimated to be 3.6 eV and for VOx layers is 2.7 eV. The band gap values are in good agreement with the previous reports [147-149]. The larger bandgap of NiOx and VOx mean there will be lower optical losses when these layers are used on the front side of the solar cells compared with p-aSi:H (bandgap:1.75 eV). Finally, the extracted thickness for the spin coated NiOx or VOx film was ~15 nm.



Figure 5.3 Plots of $(\alpha hv)^2$ and hv (Inset: Complex refractive index n & k) of (a) NiOx and (b) VOx

Hall effect measurements were performed in order to obtain electrical parameters of the NiOx and VOx layers, with a summary of results shown in Table 5.1. For the Hall Effect measurements, the spin-coating process was repeated for 10 cycles to achieved thickness of ~150 nm for NiOx and VOx. Al was evaporated to form a contact for NiOx, whilst Au was evaporated to contact the VOx layer. Both metals were evaporated on the four corners of the sample using a shadow mask. As can be seen in Table 5.1, the signs of the bulk concentrations (+: *p* type; -: *n* type) confirm that spin-coated NiOx is a *p* type semiconductor, whilst VOx is *n* type. The measured conductivities of the NiOx and VOx layers both fall in the medium of the ranges reported in the literature ($10^{-8} - 10^{0} \Omega^{-1}$ cm⁻¹ for NiOx [150-154] and $10^{-5} - 10^{-1} \Omega^{-1}$ cm⁻¹ for VOx [155-157]).

| | Carrier | Conductivity o | Carrier Density | Sheet |
|------|-------------------------|----------------------------------|-----------------------|------------------|
| | mobility μ | $(\Omega^{-1} \mathrm{cm}^{-1})$ | (cm ⁻³) | Resistance R_s |
| | (cm ² /Vsec) | | | $(M\Omega/sq)$ |
| NiOx | 11.3 | 1.0×10 ⁻³ | $+4.9 \times 10^{14}$ | 64.1 |
| VOx | 4.2 | 3.4×10 ⁻³ | -4.8×10^{15} | 19.7 |

Table 5.1 Electrical parameters of NiOx and VOx films

5.1.2.2 Characterization of TMO/n-Si Contacts

The passivation quality of the carrier selective contact structure towards electrons can be evaluated via its effective carrier lifetime. And the equally important contact selectivity toward holes can be evaluated via its specific contact resistivity (ρ_c) [158]. In this work, ρ_c was measured by Transmission Line Method (TLM) and effective carrier lifetime was characterized by lifetime tester [158, 159].

For a TLM structure consisting of an array of ~1um Al contacts for NiOx or ~100nm Au contacts for VOx with different spacing was evaporated on the front of the test structures via a shadow mask. Dark current–voltage (J–V) measurements were taken at room temperature. With all samples exhibiting an ohmic J-V response for each contact spacing, it allows for a precise linear fit to the data. The extracted ρ_c values are 39.4 m Ω cm² for NiOx and 47.8 m Ω cm² for VOx.



Figure 5.4 Dark J-V measurements of TLM array for (a) Al/NiOx/Si and (b) Au/VOx/Si contacts

The TLM samples with multi-cycle spin-coated TMOs were also measured. All the samples with 2 or 3 cycles of TMOs (thickness is estimated to be over 30nm) show the rectifying behavior, indicating the formation of a Schottky contact between TMOs and Si as shown in Figure 5.5. The rectifying behavior is likely due to the large resistance of the thick TMOs films, suppressing the holes transporting through TMOs.



Figure 5.5 Dark J-V measurements of TLM array for (a) Al/NiOx (30-40nm)/Si and (b) Au/VOx (30-40nm)/Si contacts

The dark J-V measurements of TLM samples with a thinner TMO layer (below 5nm) were also carried out as shown in Figure 5.6. 1wt% NiO precursor solution and 1:70 volume ratio VO isopropanol solution were coated on Si at a withdrawal speed of 10000 rpm/s for 30s.Other processes remained the same as mentioned above. The thickness of TMO films were found to be below 5 nm by ellipsometry. The rectifying behavior of

the TLM samples is likely attributable to the non-uniformity of the TMO thin films, which induces a large interface defect states between TMOs and Si hence causing Fermi-level pinning.



Figure 5.6 Dark J-V measurements of TLM array for (a) Al/NiOx (<5nm)/Si and (b) Au/VOx (<5nm)/Si

According to the measurement results of TLM samples with different thickness of TMOs, the following discussion is based on ~15 nm TMOs which show ohmic contact behavior with Si.

The recombination at the interface between *n*-Si and the deposited films was evaluated via effective carrier lifetime measurements under quasi-steady-state photo-conductance (QSSPC) mode [160]. The lifetime test structures were coated with TMO symmetrically on both sides of silicon. The implied open-circuit voltage (*iVoc*) at one sun was extracted using the method of Kane and Swanson [161]. Though TMOs/Metal stacks provide good Ohmic contact to *n*-Si (that is a low ρ_c), it provides little passivation to the silicon surface, as evidenced by a low effective carrier lifetime of 5.79 µs for NiOx and 12.76 µs for VOx respectively (at an injection level of 1×10^{15} cm⁻³), corresponding to an *iVoc* of 0.515V for NiOx and 0.553V for VOx, respectively.



Figure 5.7 Effective carrier lifetime of TMO/ n-Si/ TMO structures

5.1.2.3 Characterization of TMO/i-aSi:H/n-Si Contacts

To improve the passivation quality of TMO/Si contacts, an insertion of a thin a-Si:H film (6-7nm) between TMO and *n*-Si which has already been proven effective for molybdenum oxide based hole-selective contacts was explored [47]. Si surface can be passivated by chemical passivation or field-effect passivation [158]. Attributable to a very low defect concentration (~10-20% atomic) of hydrogen incorporated into the thin interfacial *i*-aSi:H layer, it can provide chemical passivation of the c-Si dangling bonds.

Figure 5.8 depicts the effective lifetime of symmetric TMO/ *i*-aSi:H /*n*-Si/ *i*-aSi:H /TMO test structures as a function of minority carrier injection level. As shown in Figure 5.8, upon the insertion of *i*-aSi:H layer between TMO and Si, the surface passivation quality is greatly enhanced, yielding around 30 times improvement in carrier lifetime. The measured τ_{eff} at one sun illumination are 188.92µs for NiOx and 299.87µs for VOx respectively (at an injection level of 1×10^{15} cm⁻³). Though the values are in the low range of typical passivated wafers, the measured *iVoc* values of 0.632 V for NiOx and 0.657 V for VOx show that TMOs/i-aSi:H can provide an accepted level of surface passivation. It's worth noting that NiOx was annealed under 350 °C after the spin coating process, and the annealing would be expected to degrade the passivation quality of the *i-aSi*:H layer. But the measured *iVoc* values of 632 mV for NiOx suggest

the TMOs/*i*-aSi:H layers still can provide an acceptable level of surface passivation after the annealing.



Figure 5.8 carrier lifetimes for TMO/*i*-aSi:H/*n*-Si/*i*-aSi:H /TMO structures as a function of minority carrier injection level obtained using steady state photo-conductance measurements structure

The extracted ρ_c values are 93.1 m Ω cm² for NiOx and 63.3 m Ω cm² for VOx. The samples with *i*-*aSi*:H show a slightly higher ρ_c than those of samples without *i*-*aSi*:H, which could be attributable to the bulk resistivity of the *i*-*aSi*:H, introducing an additional hindrance to current transport. Additionally, the sheet resistance of the conduction channel between TLM contacts are 51.7 k Ω /sq for NiOx sample and 41.3 k Ω /sq for VOx sample, over three orders of magnitude lower than the sheet resistance of TMO film (64.10 M Ω /sq for NiOx and 19.67 M Ω /sq for VOx extracted by Hall effect), much lower than the sheet resistance of *i*-*aSi*:H layer (over 10⁴ M Ω /sq [162]) and three orders of magnitude higher than the sheet resistance of Si bulk (~30 Ω /sq), which confirms that carrier transport is confined, at least partially, to the inversion layer by the carrier depletion region formed between TMO and Si. The similar behavior has also been observed in the previous reports using MoOx or aluminum oxide in silicon solar cells [48, 141].



Figure 5.9 Dark J-V measurements of TLM array for (a) Al/NiOx/*i*-aSi:H/Si and (b) Au/VOx/*i*-aSi:H/Si contacts

Capacitance-Voltage measurements were performed with the voltage and corresponding $1/C^2$ to estimate the built-in voltage (V_{bi}) of TMO/i-aSi:H/n-Si contacts. Figure 5.10 shows the inverse of the capacitance squared as a function of voltage for the GSJ device. In this experiment, V_{bi} is found to be 0.64 V for NiOx and 0.69 V for VOx. It is worth noting that the extracted V_{bi} values are similar to those of standard c-Si solar cells, where 0.60-0.75 V is distributed between the two sides of the homojunction. The difference is that V_{bi} for NiOx or VOx is restricted to the Si side, indicating the formation of an inversion layer at zero bias [163].



Figure 5.10 $1/C^2$ -V plot for a TMO/i-aSi:H/n-Si test

5.1.2.4 Advanced Models for TMOs/n-Si Solar Cells

A predictive model for NiOx-Si and VOx-Si CSC solar cell using electrical and optical properties of NiOx and VOx as inputs was developed by adapting a full heterojunction CSC model in Sentaurus technology computer-aided design (TCAD). More details about the model can be found in a previous report using the model for graphene/silicon solar cells [54].

Key optical and electrical parameters, such as bandgap and V_{bi} , were taken to be the measured results. The values used for key inputs to the heterojunction model are summarised in Table 5.2. With these model parameters, simulated Light J-V, band diagram of HIT and TMO/Si solar cells were calculated.

| Tabl | e 5.2 TCAI |) heterojuncti | on model | parameters | and | their | values | (for | their | sources |
|------|-------------|----------------|-----------|------------|-----|-------|--------|------|-------|---------|
| Exp. | denotes exp | periment; Ref. | reference | e) | | | | | | |

| Description | Symbol | Unit | Nickel Oxide | Vanadium Oxide | |
|--------------------|----------|--------------------|---------------|----------------|--|
| Band gap | E_g | eV | 3.6 (Exp.) | 2.7 (Exp.) | |
| Complex refractive | n & k | NA | Figure 5.3(a) | Figure 5.3(b) | |
| index | | | (Exp.) | (Exp.) | |
| Carrier mobility | μ | $cm^2V^{-1}s^{-1}$ | 11.25 (Exp.) | 4.17 (Exp.) | |
| Built in potential | V_{bi} | V | 0.64 (Exp.) | 0.69 (Exp.) | |
| Specific Contact | $ ho_c$ | $m\Omega cm^2$ | 93.1 (Exp.) | 63.3(Exp.) | |
| Resistivity | | | | | |

It is worth noting that although VOx is *n*-type, its high work function induces large band bending when combined with *n*-Si, creating an electric field sufficient to transport photo-generated holes into the VOx film. One possible mechanism suggests that holes transit through the oxygen vacancy-derived defect states in VOx, allowing them to be extracted through the metal contact [19, 164]. The large leakage currents, which are often observed for TMO/Si diodes [165-167], make the determination of the defect states distribution challenging with the extracted values often being unreliable. In light of these difficulties mentioned, VOx was input as a high work function metal forming a Schottky junction with Si in this work.

The structure of the model is shown as Figure 5.11(a). The input parameters of the HIT solar cell (p-aSi:H/ i-aSi:H/ n-Si/ i-aSi:H/n-aSi:H) were taken from a previous simulation study [1]. A comparison between experimental and simulated HIT solar cell (p-aSi:H/ i-aSi:H/ n-Si/ i-aSi:H/ n-aSi:H) performance was used to check the validity of the model. As shown in Table 5.3, there is a good agreement between the simulated and experimental output parameters of HIT solar cell.

According to the TCAD heterojunction model used here, the conversion efficiency can reach up to 16.9 % and 20.6 % for NiOx and VOx solar cells respectively as listed in Table 5.3. Importantly this level of efficiency compares favourably with those for current conventional HIT solar cell [168], highlighting the potential for TMO/Si solar cells to achieve comparable efficiency using a highly simplified fabrication process. As shown in Figure 5.11(b), the J_{SC} values for the NiOx-Si, VOx-Si CSC solar cells and the HIT solar cell are very similar. The possible reason is that the *p* type layers (*p*-aSi:H, NiOx or VOx) are thin (below 20 nm) for each design, meaning optical losses associated with the *p* type layers are negligible. The possible reason for the lower *Voc* of NiOx-Si CSC solar cell as compared with the *Voc* of VOx-Si CSC solar cell and HIT solar cell is the high recombination of the NiOx-Si contact, which is also observed in the lifetime measurement as shown in Figure 5.8. The lower *Voc* and *FF* of NiOx-Si CSC solar cell as compared with the *Voc* and *FF* of NiOx-Si CSC solar cell and HIT solar cell are likely attributable to the high recombination of the NiOx-Si CSC solar cell and HIT solar cell are likely attributable to the high recombination of the NiOx-Si CSC solar cell and HIT



Figure 5.11 (a) Schematic of the simulated heterojunction solar cell (b) simulated Light J-V characteristic of HIT, NiOx and VOx-Si solar cells

| | HIT | NiOx-Si | VOx-Si |
|---------------------------|------|---------|--------|
| Jsc (mA/cm ²) | 35.0 | 35.1 | 34.9 |
| Voc (V) | 0.72 | 0.69 | 0.75 |
| FF (%) | 78.2 | 70.0 | 79.0 |
| Efficiency (%) | 19.6 | 16.9 | 20.6 |

Table 5. 3 Simulated and experimental output parameters of CSC solar cells

To further understand the predicted behavior of the CSCs, band diagrams were calculated with the results for HIT, NiOx and VOx displayed in Figure 5.12 (a)-(c), respectively. A salient feature is the asymmetry of conduction band discontinuity and valence band discontinuity at the interface between p-aSi:H, NiOx or VOx and n-Si, which makes it possible to achieve high conversion efficiency without the use of heavy doping in the silicon. The large barrier for electrons resulting from the band bending in n-Si and the conduction band discontinuity at the conduction band edges effectively blocks the transport of electrons. And the comparatively small valence band discontinuity facilitates holes to transit through p-aSi:H or NiOx, or the oxygen vacancy-derived defect states in VOx to the front contact [19, 159], suggesting both TMOs are well suited as CSCs as designed.

The band diagrams also support the previous assumption of the presence of a p type inversion layer in the *n*-Si in the vicinity of the TMO interface. TMOs under study tend to induce an inversion layer, forming the selective contact for holes extraction under illumination. The transition from *n* doping in the Si bulk to *p* type character near the surface is a result of the band bending whose magnitude is V_{bi} of the heterojunction.





Figure 5.12 Schematic band diagram of the heterojunction between (a) p-aSi:H (b) NiOx or (c) VOx and n-Si under thermal equilibrium condition

Hole density distribution for TMO/Si solar cells was also plotted. As shown in Figure 5.13, the hole concentration at the interface of TMO/*i*-aSi:H/Si is $\sim 10^{14}$ cm⁻³ for NiOx and $\sim 10^{15}$ cm⁻³ for VOx, lower than the reported hole density for MoOx-Si contact as mentioned before ($\sim 8.6 \times 10^{19}$ cm⁻³ [48]), which explains the larger sheet resistance of the conduction channel between TLM contacts in this work.



Figure 5.13 Hole density distribution at the interface of TMO/i-aSi:H/Si contacts (a) NiOx (b) VOx

5.2 TMOs on p-Si

5.2.1 Characterization of TMO/p-Si Contacts

Since TMOs can provide asymmetry in contact resistivity between electrons and holes, they can also be used as the interfacial layer on *p*-Si to facilitate the holes transporting, thus reduce the ρ_c of the *p* type contact. To characterize the holes selectivity of NiOx and VOx, the ρ_c for Metal/*p*-Si contacts with and without TMOs were measured, respectively. As shown in Figure 5.14, the ρ_c for Al/*p*-Si contact is 50.9 m Ω cm², and the value reduces to 32.4 m Ω cm² after the insertion of NiOx. This shows the contact selectivity of Si can be improved with the integration of NiO. The extracted ρ_c values are 28.6 m Ω cm² for Au/*p*-Si and 51.2 m Ω cm² for Au/VOx/*p*-Si, respectively. The slightly higher ρ_c might be related to the bulk resistivity of the VOx; or comparatively low work function of VOx, which can't build up enough electric field to transport holes.



Figure 5.14 Dark J-V measurements of TLM array for (a) Al/p-Si (b) Au/p-Si (c) Al/NiOx/p-Si and (d) Au/VOx/p-Si contacts

The lifetime test structures were coated with TMO symmetrically on both sides of *p*-Si. Same with what's observed for the samples on *n*-Si, both TMO (NiOx or VOx)/*p*-Si contacts demonstrate a low effective carrier lifetime of 26.49 μ s for NiOx and 45.10 μ s

for VOx (at an injection level of 1×10^{15} cm⁻³), corresponding to an iVoc of 0.565V for NiOx and 0.611V for VOx, respectively.



Figure 5.15 Effective carrier lifetime of TMO/ p-Si/ TMO structures

5.2.2 Characterization of TMO/i-aSi:H/p-Si Contacts

To enhance the passivation quality, a thin layer of *i* a-Si:H (6-7 nm) was also inserted between TMO and *p*-Si. The measured τ_{eff} at one sun illumination are 308.96µs for Al/NiOx/i-aSi:H/*p*-Si contact and 340.46µs for Au/VOx/*i*-aSi:H/*p*-Si contact (at an injection level of 1×10¹⁵ cm⁻³), corresponding to *iVoc* values of 0.651 V for NiOx contact and 0.653 V for VOx contact, respectively. The results show with the i aSi:H passivating interlayer, TMOs contacts can provide a decent level of surface passivation to *p*-Si.



Figure 5.16 Effective carrier lifetime of TMO/i-aSi:H/p-Si/i-aSi:H/TMO structures

Same with what's observed for samples on *n*-Si, ρ_c increases after the insertion of *i*-aSi:H as shown in Figure 5.17, but all samples demonstrate highly ohmic behavior.



Figure 5.17 Dark J-V measurements of TLM array for (a) Al/NiOx/*i*-aSi:H/*p*-Si and (b) Au/VOx/i-aSi:H/*p*-Si contacts

5.2.3 Advanced Models for CSC/p-Si Solar Cells



Figure 5.18 Schematic of the proposed solar cell with hole transporting layer (*p*-aSi:H, NiOx or VOx)

The solar cell with and without hole transporting layer between front contact and p type Si were also simulated by TCAD model, respectively as shown in Figure 5.18. Compared with the simulated Si solar cell without hole transporting layer, the efficiency improves ~ 1% for the cell with NiOx, ~ 4% for the cell with *p*-aSi:H and ~ 5% for the cell with VOx as shown in Table 5.4. Band diagrams were calculated with the results for solar cells with/without hole transporting layer (*p*-aSi:H, NiOx or VOx) displayed in Figure 5.19 (b), respectively to understand the mechanism behind these hole transporting materials. For p-aSi:H and NiOx, a relevant feature is the asymmetry of conduction band discontinuity and valence band discontinuity compared with the Si solar cell without any hole transporting layer. The large barrier for electrons effectively blocks the transport of electrons; and the comparatively small valence band discontinuity facilitates holes to transit to the front contact [19, 159]. For VOx, its high work function induces large band bending and creates a sufficient electric field to facilitate the hole transporting. The improved carrier selectivity is the possible reason for the better solar cell performance. The results demonstrate NiOx and VOx can also be used as a hole transporting layer for silicon solar cells to improve the carrier selectivity.



Figure 5.19 (a) Simulated Light J-V characteristic and (b) schematic band diagram of the front side of the solar cells with/without hole transporting layer (*p*-aSi:H, NiOx or VOx)

Table 5.4 Modelling results of the solar cells with/without hole transporting layer (*p*-aSi:H, NiOx or VOx)

| | Without TMO | <i>p</i> -aSi:H | NiOx | VOx |
|-----------------|-------------|-----------------|------|------|
| | or aSi | | | |
| $Jsc (mA/cm^2)$ | 31.3 | 34.5 | 33.1 | 34.5 |
| Voc (V) | 0.62 | 0.72 | 0.66 | 0.73 |
| FF (%) | 76.2 | 77.7 | 71.5 | 78.5 |
| PCE (%) | 14.7 | 19.3 | 15.5 | 19.5 |

5.3 Improvement

To further reduce the contact resistance and improve the passivation quality of TMOs/Si contacts, the following alternatives are expected to enhance the non-ideal TMO/Si (n or p type) contacts performance. The TMO layers can be modulated by the doping process (dopant types [169-171], doping concentration [170-172]), deposition method (such as sputtering or atomic layer deposition which potentially provides better control over the stoichiometry and thickness of TMO), post deposition treatments (such as UV/Ozone treatment for NiOx [173], or vacuum annealing for VOx [174]), etc. The passivation layer can also be optimized by the thickness and the deposition process [4].

5.4 Conclusion

The feasibility of nickel oxide and vanadium oxide as CSCs for silicon has been examined. Nickel oxide and vanadium oxide layers on silicon were fabricated by spincoating and characterized to obtain the input parameters for the heterojunction model. It was found that both NiOx and VOx required an additional buffer layer to provide surface passivation. In this work, a-Si was used as the passivaiton layer for TMOs/Si contact, but limitations were found for NiOx due to the incompatibility of the anneal temperature of 350 °C with a-Si stability. In contrast, VOx/a-Si showed excellent potential performance when applied to both p and n type Si substrate. The contacts performance can be further improved by heavier doping or work function manipulation of the TMO films to strengthen inversion or accumulation at the surface of TMOs/Si contacts; and also optimization of the passivation layer.

Chapter 6. Pulsed Laser Deposition Nickel Oxide on crystalline Silicon as hole selective contacts

The solution processed TMOs have proved to be good candidates for carrier selective materials in chapter 5; in chapter 6, Pulsed laser deposition NiO was also studied to assess the suitability for use as a carrier selective contact (other TMOs like MoOx and VOx were not considered for our PLD system because of the material contamination issue). Pulsed laser deposition was used to fabricate Nickel Oxide/Si heterostructure and suitability of this structure as a hole selective contact was assessed. Films were deposited at temperatures of 300 °C, 500 °C, 700 °C, and 900 °C. Results from reflective high energy electron diffraction patterns indicate increasing crystallinity with temperature up to 500 °C. However, layers deposited over 700 °C are amorphous. Nevertheless, results from atomic force microscopy, contact resistance measurements and photoluminescence lifetime imaging indicate that films deposited at 900 °C have the best film smoothness, lowest specific contact resistivity, and highest lifetime and therefore are best suited for hole selective contact applications.

6.1 Introduction

NiOx has been prepared by different techniques: chemical deposition, sputtering, vacuum evaporation, reactive-sputtering, sol-gel process and recently, pulsed laser deposition (PLD). The synthesis method and conditions of deposition methods are essential for determining the microstructure, stoichiometry and morphology and finally the properties and performance of synthesized structures. In this chapter, the feasibility of NiOx layers deposited by Pulsed Laser Deposition (PLD), for use as a hole transporting layer has been investigated. 10 nm thick NiOx layers were deposited at temperatures between 300 °C and 900 °C. In-situ monitoring of the surface during deposition and ex-situ surface studies by atomic force microscopy indicate deposition at 900 °C gives the smoothest layer of amorphous NiOx. This deposition temperature also gives the best specific contact resistivity when Al metal is deposited, and the best passivation quality.

6.2 Experiment

Nickel Oxide films were deposited on $1 \text{ cm} \times 1 \text{ cm} p$ -type float zone c-Si (100) substrates with a resistivity of ~2.5 Ω ·cm and a thickness of 200 µm, in a PASCAL Mobile- Combinatorial Laser MBE System. All wafers were cleaned using the RCA procedure and dipped in a 1% diluted hydrofluoric acid (HF) acid solution to remove any remaining oxide prior to film depositions. A NiO target (99.99% purity, Hefei Ke Jing Materials Technology Co., Ltd) was used for NiOx thin film deposition. The target, ~25 mm in diameter, was rotated at 5 rpm and the laser pulses were swept cyclically across the target radius to prevent localized heating. NiO was ablated using a Q-switched second harmonic generation SHG Nd-YAG laser of 532 nm wavelength (repetition frequency 6 Hz, pulse width 7 nsec).

The films were prepared under vacuum pressure of $\sim 5 \times 10^{-8}$ mbar with the substrate heated at constant temperatures 300 °C, 500 °C, 700 °C, 900 °C using a halogen lamp with 1000 laser pulses. Thicknesses of the deposited films (~10nm) were determined by analyzing results from Spectra Ellipsometry measurements using the double Tauc-Lorentz oscillators model [58]. The surface of the substrate was monitored in-situ using reflective high energy electron diffraction (RHEED) during deposition. After removal from the system the samples surfaces were studied using atomic force microscopy.

For transmission line measurement (TLM), an array of metal (~500nm Al) contacts with different spacing was evaporated via a shadow mask on NiOx (deposited at different temperatures for each sample). Current–voltage (I–V) measurements were taken at room temperature using a Keithley 2425 source-meter.

6.3 Results and Discussion

A selection of the RHEED patterns taken during deposition is presented in Figure 6.1. Streaks are observed on films deposited at 300 °C (Figure 6.1a), which become sharper at 500 °C (Figure 6.1b). This suggests the best crystalline material is obtained when deposition temperature equals 500 °C. When the deposition temperature was increased further to 700 °C a diffused pattern is seen (Figure 6.1c), indicating an amorphous layer has been deposited. A similar pattern was seen at 900 °C (Figure 6.1d).


Figure 6.1 *In-situ* Reflective high energy electron diffraction (RHEED) patterns of PLD NiOx taken at the end of each deposition at temperatures of 300 °C, 500 °C, 700 °C and 900 °C. (a) The bright streaks as highlighted indicate planar crystalline growth while (c) the diffuse pattern as highlighted indicates an amorphous layer, suggesting 500 °C deposition results in the most crystalline material

After the samples were removed the deposition system, AFM tapping mode scans were performed and results are presented in Figure 6.2. Using the software NanoScope Analysis included with the AFM, root mean square roughness values were obtained for NiOx deposited 300 °C, 500 °C, 700 °C, and 900 °C, which were around 0.848 nm, 0.811 nm, 0.399 nm and 0.231 nm, respectively. These results suggest that deposition at 900 °C gives the best result, in terms of surface smoothness.



Figure 6.2 Atomic force microscopy tapping mode surface scan of PLD NiO deposited at (a) 300 °C, (b) 500 °C, (c) 700 °C, and (d) 900 °C

The specific contact resistivity ρc was measured using the transfer length method (TLM). Figure 6.4 shows a series of J-V measurements of a sample with a ~10nm PLD deposited NiOx film under different deposition temperature, and one representative I-V measurement of a sample with Al directly on *p*-Si. The resistance versus contact spacing trend is fitted with a spreading resistance model, allowing accurate extraction of ρc .



Figure 6.3 Current voltage characteristic curves measured for different contact spacing for Al/NiOx/*p*-Si contact with PLD NiOx deposited at (a) 300 °C (b) 500 °C, (c) 700 °C, d) 900 °C and (e) direct Al/Si contact

Figure 6.3c and 3d show that Al/NiOx/*p*-Si ohmic contact can be formed when the ~10nm PLD NiOx is deposited at 700 °C or 900 °C and with much lower specific contact resistivity compared to the Al/*p*-Si contact (Figure 6.3e). The low resistance for hole transport provided by the Al/NiOx/*p*-Si structure is likely attributable to (1) a reduction in the work function, compared to that of Al, and/or (2) electron tunnelling

through a reduced barrier width, which is likely similar to the mechanism of the Ohmic contact between the heavily phosphorus doped p+ c-Si and a direct Al contact [158].

The I-V characteristic for the samples with NiOx deposited at 300 °C (Figure 6.3a) and 500 °C (Figure 6.3b) exhibited rectifying behavior, indicating the presence of a Schottky contact. This rectifying behavior is likely attributable to the presence of a large surface potential barrier known to exist at this surface, or Fermi-level pinning caused by a large defect density of states [87].

To further study the passivation quality of PLD deposited NiOx, the effective minority carrier lifetime was assessed by photoluminescence (PL) as shown in Figure 6.4. Note that the PL imaging was performed in an uncalibrated mode and therefore the PL counts presented here only gave an indication of the relative change in recombination at the silicon surfaces. However, this technique is effective for comparison when samples are imaged at the same time. The relative minority carrier lifetime is quantified by PL intensity as the steady-state PL intensity scales linearly with the lifetime. Figure 6.4 shows the average PL intensity over the whole area which increases for NiOx deposited at higher temperatures. The possible reasons for improved passivation with deposition temperature are less defects states within NiOx since the defects act as electron hopping paths through NiOx increasing recombination velocity; or less interface defect states between NiOx and Si [18].



Figure 6.4 PL images of the NiOx films under the growth temperature of (a) 300 $^{\circ}$ C (b) 500 $^{\circ}$ C (c) 700 $^{\circ}$ C and (d) 900 $^{\circ}$ C

According to results, PLD thin NiOx deposited at 700 °C and 900 °C are best for Al/NiOx/Si contact in terms of specific contact resistivity providing an even better ohmic contact compared to the Al/*p*-Si contact. The average PL intensity over the whole area, which is an indicator of the passivation quality, also increases for films deposited at 900 °C. These films also show best results in terms of surface smoothness.

For comparison, the specific contact resistivity for PLD-NiOx or spin coated NiOx on p-Si TLM samples was summarized as listed in Table 6.1. The samples with PLD-NiOx or spin coated NiOx directly on p-Si demonstrate a much lower specific contact resistivity than the samples without NiOx (Al/Si contact), which indicates the asymmetrical carrier selectivity of NiOx. The specific contact resistivity of PLD-NiOx samples deposited at 900 °C and 700 °C is lower than spin-coated ones. The TLM samples with a-Si between spin coated NiOx and p-Si shows a slightly higher specific contact resistivity than Al/Si TLM samples, which is likely attributable to the large sheet resistance of a-Si passivation layer.

Table 6 .1 Specific contact resistivity of TLM samples based on *p*-Si (the order follows the increasing trend of the specific contact resistivity)

| | PLD- | PLD- | Spin | Without | <i>i</i> -aSi:H / |
|------------------|----------|----------|---------|---------|-------------------|
| | NiOx | NiOx | coated- | NiOx | Spin |
| | (900 °C) | (700 °C) | NiOx | | coated- |
| | | | | | NiOx |
| ρc | 15.7 | 26.5 | 32.4 | 50.9 | 60.7 |
| $(m\Omega cm^2)$ | | | | | |

6.4 Discussion

Results indicate increasing crystallinity of PLD NiOx with temperature up to 500 °C. Amorphous NiOx samples deposited over 700 °C gave better results in terms of contact resistance and surface passivation. This is also the possible reason for the comparatively poor behaviour of spin-coated NiOx, which shows the cubic crystalline structure. To improve the carrier selectivity of PLD NiOx: (1) utilise a deposition that allows better control the growth rate and stoichiometry of NiOx, such as atomic layer deposition [175]. (2) Perform post deposition treatments, such as oxygen plasma which could decrease the Fermi-level pinning between NiOx and Si [18]. (3) And for the better passivation quality, incorporation of passivation layers like SiO₂ could reduce the carrier recombination at the interface [175].

6.5 Conclusion

NiO layers have been deposited on p type silicon wafers by pulsed laser deposition at temperatures between 300 °C and 900 °C. RHEED results indicate 500 °C deposited layers are most crystalline. Photoluminescence imaging results suggest improved passivation with increasing deposition temperature with 900 °C deposited layers giving the best result. Similar trend is also seen in terms of specific contact resistivity. The best is achieved for amorphous NiOx deposited at high temperatures in terms of contact resistance, passivation quality as well as the film smoothness. These results can help explain the relatively poor performance of the spin coated NiOx where greater crystallinity was seen, with these results suggesting amorphous materials provide better CSCs for silicon. Notably the materials parameters of spin-coated NiOx (band gap and work function) are similar to PLD NiOx.

Chapter 7. Conclusion and Future work

7.1 Conclusion of the Thesis

In this work, a full heterojunction model for 2D materials on Si was developed, which allowed for analysis of the impact of doping of 2D materials, etc. on the solar cell performance. For graphene/Si solar cells, the transport mechanism has been predominantly simplified as an ideal Schottky junction, which is never realized experimentally. According to literature, doped graphene shows the properties of a semiconductor, therefore, it is physically more accurate to model graphene/silicon junction as a Heterojunction. In comparison with the simple Schottky junction models, the heterojunction model paves the way for thorough investigation on the sensitivity of solar cell performance to graphene properties like bandgap and work function. Simulation indicates that suitable doping of graphene plus antireflection coating (ARC) and rear Si structure should allow efficiency over 20%.

The model was also used to model 2D Transition metal dichalcogenides /Si solar cells and analyze the origin of the widely reported kink in the Light J-V. Simulation indicates the most likely reason for the origin of the kink which appears in the simulated light J-V curves is that the interface charges build up due to the band alignment between TMDs and Si, which leads to high recombination. To overcome this effect, high doping of the TMDs and the passivation layer of TMDs/Si contacts are necessary. More importantly, simulation also indicates the best way to proceed is to avoid the band alignment issues, namely the selection of substrate type: *p*-Si is more likely to be recommended for MoS₂ and WSe₂; and oppositely, *n*-Si for MoSe₂ and WS₂. The cell performance of TMDs/Si heterojunction solar cells is found to achieve over 20% with the rear optimization. Results demonstrate 2D materials (graphene, TMDs studied in this work) would be a useful contribution for the improvement in solar energy harvesting.

TMOs like VOx and NiOx were also investigated as CSCs. Spin coating of TMOs on Si allowed for assessment of potential by characterizing TMO films and TMOs/Si contacts. It was found that both NiOx and VOx required an additional buffer layer to provide surface passivation. In this work, a-Si was used, but limitations were found for NiOx due to the incompatibility of the anneal temperature of 350 °C with a-Si stability. In contrast, VOx/a-Si showed excellent potential performance when applied to both *p* and *n* type substrate. Simulation using the full heterojunction model with typical silicon solar cell

paramters suggest VOx offers a pathway for devices that can outperform conventional a-Si based CSC solar cells. The carrier selectivity of TMOs can be further enhanced by heavier doping or work function manipulation of the TMOs to strengthen inversion/accumulation of the surface. And the interface between TMOs and Si can be improved by inserting a passivation layer like SiO₂ or Al₂O₃.

Finally, PLD deposited NiOx on Si under the deposition temperature of 300 °C, 500 °C, 700 °C and 900 °C was fabricated. Results indicate increasing crystallinity with temperature up to 500 °C. However, the samples with NiOx deposited below 500 °C exhibited rectifying behavior and poor passivation. Amorphous NiOx samples which were deposited over 700 °C gave better results both in terms of surface passivation and contact resistance. These results can help explain the relatively poor performance of the spin coated NiOx where greater crystallinity was seen, with these results suggesting amorphous materials provide better CSCs for silicon. Notably the materials parameters of spin-coated NiOx (band gap and work function) are similar to PLD NiOx.

7.2 Future work

Based on the 2D materials (graphene or TMDs) /Si heterojunction modelling results, one of the future work directions is to fabricate high efficiency 2D materials/Si heterojunction solar cells with the optimization of ARC and the rear. And because the properties of 2D materials like band gap and work function, which can be tuned by the doping process, have a large impact on the solar cell performance, the doping process (dopant, doping concentration, etc.) needs to be further investigated to better control the properties of 2D materials.

To further reduce the contact resistance and improve the passivation quality of spin coated TMOs/Si contacts, the TMO layers can be modulated by the doping process (dopant types [169-171], doping concentration [170-172]), deposition method (such as sputtering or atomic layer deposition which potentially provides better control over the stoichiometry and thickness of TMO), post deposition treatments (such as UV/Ozone treatment for NiOx [173]), etc. The passivation layer like SiO₂ or Al₂O₃ could also be considered to improve the interface of TMOs/Si contacts. [4].

The high deposition temperature of PLD NiOx might not be suitable for the fabrication of silicon solar cells but it may be a pathway for assessing alternate methods for intermediate buffer layers. As an example of this, we have employed SrO to enhance the interface between NiOx and Si with some preliminary results presented. Figure 7.1 demonstrates the ρ_c of the sample with ~2nm SrO, showing a higher ρ_c (41.4 m Ω cm²) than the sample without SrO under the same growth temperature (15.7 m Ω cm²). This is likely due to the bulk resistivity of the SrO interlayer, introducing an additional hindrance to current transport. Nevertheless, it is encouraging that the insertion of a thin SrO layer increases the contact resistivity only moderately.



Figure 7.1 Current voltage characteristic curves for different contact spacing for a sample with SrO between NiOx/Si

Figure 7.2 shows the average PL intensity over the whole area increases with the growth temperature, with SrO layers showing the best passivation. After inserting a thin film of SrO, the PL intensity significantly increases by around 20%, indicating an equivalent increase in effective lifetime. This can be attributable to the native-oxide free surface for NiO growth induced by SrO, which reduce the interface defect density thus improve the passivation.



Figure 7.2 PL images of the NiOx films under the growth temperature of 900 C with SrO between NiOx/Si

The results illustrate SrO as a buffer can enhance the passivation quality for PLD NiOx/p-Si contacts. One possible extension is to make SrO/NiOx/Al samples under different deposition temperature (300 °C, 500 °C and 700 °C) and compare with the samples without SrO, which is possible to shed light on the mechanism behind the trend of passivation quality and contact resistance. Other passivation layers like SiO₂, Al₂O₃ also need to be studied to further improve the TMOs/Si contacts.

Results of PLD NiOx indicate the NiOx which has crystalline structure on *p*-Si exhibit rectifying behavior and poor passivation. Amorphous NiOx samples gave better results both in terms of surface passivation and contact resistance. These results can help explain the relatively poor performance of the spin coated NiOx where greater crystallinity was seen, with these results suggesting amorphous materials provide better CSCs for silicon. Hence one possible extension is to find the alternate NiOx precursors and improve the spin coating and annealing process to make the spin coated amorphous NiOx, which is possible to enhance the contact performance.

7.3 List of publications resulted from this work Published article:

Jing Zhao, Fa-Jun Ma, Ke Ding, Hao Zhang, Jiansheng Jie, Anita Ho-Baillie and Stephen P. Bremner, "Advanced interface modelling of n-Si/HNO₃ doped graphene solar cells to identify pathways to high efficiency", Applied Surface Science, 2018, p.102-111

In preparation:

Jing Zhao, Yuan-Feng Xu, Fa-Jun Ma, Hao Zhang, Anita Ho-Baillie, Stephen P. Bremner, "Numerical analysis of Transition Metal dichalcogenides/Si contacts for silicon heterojunction solar cells", in preparation

Submitted:

Jing Zhao, Anita Ho-Baillie, Fa-Jun Ma and Stephen P. Bremner, "Assessment of Spin Coated Transition Metal Oxide Layers on Silicon for a Carrier Selective Contact Solar Cell solution process", physica status solidi (RRL) – Rapid Research Letters, under revision

Jing Zhao, Anita Ho-Baillie, and Stephen P. Bremner, "Pulsed Laser Deposition Nickel Oxide on crystalline Silicon as hole selective contacts", Applied Physics Letters, under review

Conference:

Jing Zhao, Fa-Jun Ma, Anita Ho-Baillie and Stephen P. Bremner, "Spin Coated Nickel and Vanadium Oxide Layers on Silicon for a Carrier Selective Contact Solar Cell", 44th IEEE Photovoltaic Specialist Conference, Washington, DC, Jun. 2017

Jing Zhao, Yuan-Feng Xu, Fa-Jun Ma, Hao Zhang, Anita Ho-Baillie and Stephen P. Bremner, "Simulation of Solar Cells Employing 2 Dimensional Transition Metal Dichalcogenide – Silicon Front Surfaces", World Conference on Photovoltaic Energy Conversion (WCPEC-7), Waikoloa, Hawaii, Jun.2018

Jing Zhao, Anita Ho-Baillie and Stephen P. Bremner, "Pulsed Laser Deposition Nickel Oxide on crystalline Silicon as hole selective contacts", World Conference on Photovoltaic Energy Conversion (WCPEC-7), Waikoloa, Hawaii, Jun.2018

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