

The Impact of Atomic Hydrogen on the Properties of the Silicon/ Silicon Dioxide Interface

Chun Zhang

October 2010

A thesis submitted for the degree of
Doctor of Philosophy
of The Australian National University

Declaration

I certify that this thesis does not incorporate without acknowledgement any material previously submitted for a degree or diploma in any university, and that, to the best of my knowledge, it does not contain any material previously published or written by another person except where due reference is made in the text. The work in this thesis is my own, except for the contributions made by others as described in the Acknowledgements.

Chun Zhang

Acknowledgment

I would like to express my deepest gratitude to my primary supervisor, Associate Prof. Klaus Weber, for his enormous support and earnest teachings. Without his consistent and illuminating instruction, positive encouragement, and generous financial support, this thesis would certainly not have reached its present form. His enthusiastic approach to research, patient instructions and meticulous scholarship benefited me a great deal.

I would also like to thank Dr. Keith McIntosh for forming part of my supervisor panel, for a wealth of insightful and helpful discussions. I am also grateful to Prof. Andres Cuevas as a member of my supervisory panel and his warm encouragement. I would also like to thank Prof. Andrew Blakers for giving me the ANU Miscellaneous Scholarship.

I am very appreciative of Dr. Jin Hao for his energetic assistance in the laboratories, especially in the first year of my study, and for his help with lifetime, CV and EPR measurements. I would like to thank Dr. Wendy Jellett for explaining techniques of Boron diffusion and Kelvin Probe measurements. I would also like to thank Dr Paul Smith, from the department of Chemistry, ANU, for his great help with EPR measurements.

I am also grateful to Dr. Daniel Macdonald for cheerful help with the PECVD system. Thanks to Dr. Jason Tan for wise and friendly help with the PECVD and the RTA system.

I would like to thank the people in the CSES at ANU for making it such a great place to work. In particular, I would like to thank Sonita Singh and Nina de Caritat who trained me with the necessary skills to prepare my samples safely in the clean room. I am especially thankful to Chris Samundsett for his patient tutelage in the intricacies of photolithography work. I also would like to thank Neil Kaines and Bruce Condon for generosity of their time and skills whenever I had a technical problem. Thanks to James Cotsell for help with flash tester operation and John Musladin for constructing the jigs for electroplating.

For many other forms of assistance throughout my time as a student at ANU, I am very grateful to the following people: Soe Zin Ngwe (thanks for the fabrication of solar cell), Andrew Li (thanks for the PECVD system), Sieu-Pheng Phang (thanks for proofreading help), Dr. Andrew Thomson (thanks for calculation of the activation

energy), Dr. Bijaya Paudal (thanks for the TIDLS operation), Fiona Beck (thanks for the EPR references), Simeon Baker-finch (thanks for proofreading chapter 6), Yongling Ren (thanks for compute issues), Natalita Nursam, Nicholas Grant, Kean Chern Fong, Fiacre Rougieux, Erin Davies for many interesting discussions. I would like to express my gratitude to all those who helped me during the writing of this thesis.

Finally, my thanks would go to my beloved parents, my sister, my wife, my son and my niece for their loving considerations and great confidence in me all through these years.

Abstract

In this thesis, the influence of atomic hydrogen on the surface passivation of Si-SiO₂ interface was mainly investigated. The effect of corona charging, humidity, UV exposure and mineral acid on Si-SiO₂ interface was compared to the effect of atomic hydrogen. The electrical properties of thin (~20nm), low temperature (750-900°C) oxides, and in particular the degree of surface passivation achievable with such oxides, was also investigated and compared with the properties of oxides grown at higher temperatures (1000°C). Both wet and dry oxidations were used.

Inductively coupled photoconductivity decay and Capacitance-voltage (CV) techniques were used to characterize the electronic properties of Si-SiO₂ interface. A Plasma enhanced chemical vapour deposition (PECVD) system was used for atomic hydrogen exposure. This system is equipped with both a radio frequency (RF) and the microwave (MW) power source, both of which can be used to create a hydrogen plasma. The effect of atomic hydrogen plasma exposure parameters, such as power, pressure, and time, on the Si-SiO₂ interface in both cases was investigated. The effect of atomic hydrogen exposure and the post-atomic hydrogen exposure thermal anneal on the Si-SiO₂ interface has been studied.

It was found that generally, higher oxidation temperatures resulted in better surface passivation, as expected. A significant increase in emitter saturation current density (J_{0e}) and interface defect density (D_{it}) was observed when the oxidation temperature was decreased below 850°C.

Surface orientation had a large effect on achievable surface passivation. (111) surfaces displayed high recombination rates even at an oxidation temperature of 850°C and following an FGA.

The diffusion of phosphorous into the oxide resulted in a significant improvement in surface passivation. However, this improvement appeared to be related to a slight increase in positive charge density in the oxide rather than to a decrease in the unpassivated interface defect density.

Atomic H exposure at room temperature was observed to result in the generation of additional defects at the Si-SiO₂ interface. These defects were efficient carrier recombination centres, were thermally unstable and could be effectively removed by a short RTA anneal at 300°C or above. The annealing of this thermally unstable defect was not characterized by a single activation energy but rather by a spread of activation energies.

Following sufficiently long atomic H exposure times, the fraction of unpassivated P_{bx} centres reached a steady-state value which was independent of the initial passivation state of the interface. The degree of steady-state passivation showed no discernible dependence on temperature in the range 25-600°C during atomic H plasma exposure. In particular, at all sample temperatures in the range 25-600°C, the efficiency of defect passivation by H was lower than that afforded by H_2 . A similar behaviour was observed between phosphorous diffused and undiffused samples and also for (100) planar, (111) planar and (100) textured samples.

For oxide/nitride stacks in particular, there is no conclusive evidence that atomic hydrogen is actually diffusing through nitride film.

A sufficiently high electric field created by corona charging resulted in the introduction of additional defects to the Si-SiO₂ interface and these defects could be subsequently removed by an RTA treatment, which were consistent with effects of atomic hydrogen on the Si-SiO₂ interface. Following identical low temperature annealing, both corona charging and atomic hydrogen exposed samples showed similar but not identical improvement behaviour. This suggested that, while the underlying cause of the degradation was likely to be the same in both cases (atomic H), there were some differences in the generated defects, perhaps as a result of different H fluxes or other factors.

Humidity and UV exposure resulted in the degradation of Si-SiO₂ stack. For humidity exposed samples, the general trend of the interface modification, both after humidity exposure and subsequent thermal anneal, was largely consistent with the effect of atomic hydrogen on the Si-SiO₂ interface. For UV exposed samples, the general trend of the interface modification was largely consistent with the hydrogen redistribution model in which the atomic H in the oxide film is mainly responsible for the change of the Si-SiO₂ interface.

Immersion of oxidised silicon samples in mineral acids resulted in a modification to the Si-SiO₂ interface properties. Care therefore needed to be taken when such treatments were employed for the preparation of samples for characterisation. However, acid immersion could also provide a very cheap, alternative means of surface passivation due to hydrogen or a hydrogen complex diffusing into the oxide layer and affecting the interface properties.

LIST OF ACRONYMS AND SYMBOLS

Acronyms	Description
ALNEAL	Aluminium Anneal
APC	Anomalous Positive Charge
ARC	Antireflection coating
CV	Capacitance Voltage
CZ	Czochralski growth method for crystalline silicon
EPR	Electron Paramagnetic Resonance
FGA	Forming Gas (5%H ₂ in 95% Ar) Anneal
FZ	Float-zone
HFCV	High Frequency Capacitance Voltage
IPA	Isopropanol
LPCVD	Low Pressure Chemical Vapor Deposition
MIS	Metal Insulator Semiconductor
MOS	Metal Oxide Semiconductor
MOSFET	Metal Oxide Semiconductor Field Effect Transistor
MW	Microwave
PCD	Photo Conductance Decay
PECVD	Plasma Enhanced Chemical Vapour Deposition
QSCV	Quasi Static Capacitance Voltage
QSSPC	Quasi Steady State Photo conductance
RTA	Rapid Thermal Anneal
RF	Radio Frequency
SCCM	Standard Cubic Centimeters per Minutesute
SIMS	Secondary Ion Mass Spectroscopy
SRH	Shockley-Read-Hall
SRV	Surface Recombination Velocity
TCA	Trichloroethane
TIDLS	Temperature and injection dependent lifetime spectroscopy system
TMAH	Tetramethyl Ammonium Hydroxide
UV	Ultraviolet
Symbols	Description

$C_{\text{hf}}(C_{\text{lf}})$	High (Low) frequency capacitance
$C_i(C_s)$	Capacitance of insulator(semiconductor)
$D_{\text{it}}(D_{\text{itm}})$	Interface (midgap) state density
E_F	Fermi level energy
E_i	Intrinsic Fermi level energy
J_{0e}	Emitter saturation current density
q	Magnitude of the elementary charge
Q_f	Fixed charge
Q_m	Mobile charge
Q_o	Oxide charge
Q_{ot}	Oxide trapped charge
R_s	Sheet resistance
S	Surface recombination velocity
U_s	Net recombination rate via surface states
V_{fb}	Flat Band voltage
V_g	Gate voltage
Φ_{ms}	Work function difference between metal and semiconductor
ψ_s	Surface potential
τ_b	Bulk lifetime
τ_{eff}	Effective lifetime

Table of Contents

CHAPTER 1: Introduction.....	1
CHAPTER 2: The role of hydrogen in Si-SiO₂ interface.....	7
2.1 Configurations of Hydrogen in Silicon	8
2.2 Effect of molecular hydrogen on the Si-SiO ₂ interface	9
2.3 Oxide grown at different temperatures.....	12
2.4 Effect of atomic hydrogen on the Si-SiO ₂ interface.....	12
2.4.1 Passivation and depassivation of existing P _b centres	13
2.4.2 Generation of new defects.....	14
2.4.3 Formation of anomalous positive charge	16
2.4.4 Effect of hot electrons on Si-SiO ₂ interface.....	16
2.4.5 Effect of Ultraviolet light on Si-SiO ₂ interface.....	18
2.5 Effect of post-oxidation thermal annealing on Si-SiO ₂ interface.....	21
2.6 Simple model for atomic hydrogen.....	21
2.7 Summary	23
CHAPTER 3: Quantifying and measuring of Si surface electrical properties.....	25
3.1 Measurement of minority carrier lifetime	26
3.1.1 Recombination mechanics	26
3.1.1.1 Bulk recombination.....	27
3.1.1.2 Surface recombination	28
3.1.2 Emitter recombination.....	29
3.1.3 Effective lifetime.....	31
3.1.4 Lifetime measurement techniques.....	32
3.1.4.1 Photo-conductance decay (PCD)	33
3.1.4.2 Quasi Steady State photo-conductance (QSSPC)	35
3.2 Measurement of Si interface properties by the Capacitance-Voltage method.....	36
3.2.1 Structure and theory of ideal Metal Insulator Semiconductor	36
3.2.2 Calculation of the overall electrical characteristics of silicon surfaces	39
3.2.2.1 Calculation of insulator thickness	41

3.2.2.2 Calculation of doping level	41
3.2.2.3 Calculation of Flat band voltage	41
3.2.2.4 Calculation of fixed oxide charge density.....	42
3.2.2.5 Calculation of interface defect density and surface potential	43
3.3 Measurement of paramagnetic interface defects by Electron Paramagnetic Resonance	44
3.3.1 Paramagnetic point defects at the Si-SiO ₂ interface	44
3.3.2 EPR operation and calculation of P _b -type defect density	45
3.4 Summary	47
CHAPTER 4: Experimental.....	49
4.1 Hydrogenation Systems	49
4.2 Hydrogenation Plasma Exposure	50
4.3 Rapid thermal annealing	52
4.4 Temperature and injection dependent lifetime spectroscopy system.....	54
4.5 General sample processing.....	55
4.6 Summary	57
CHAPTER 5: Passivation effect of wet oxidation, and with oxide/LPCVD nitride stacks on the Si-SiO₂ interface.....	59
5.1 Introduction.....	60
5.2 Effect of low temperature oxides on the passivation of Si-SiO ₂ interface.....	61
5.2.1 Experimental details.....	61
5.2.2 Effect of oxidation temperature on the passivation of Si-SiO ₂ interface.....	62
5.2.3 The influence of exact processing conditions on the passivation quality of 750°C oxide.....	64
5.3 Effect of a phosphorous diffusion on the passivation quality of the oxide.....	66
5.3.1 Experimental details.....	66
5.3.2 Effect of a phosphorous diffusion into the thin oxide on surface recombination	66
5.3.2.1 Effect on planar sample.....	66
5.3.2.2 Effect on textured sample	70
5.4 Comparison of passivation effect of low temperature wet oxidation on (100) and (111) Si-SiO ₂ interface.....	71
5.4.1 Experimental details.....	72
5.4.2 Effect of surface orientation and oxidation temperature.....	72

5.4.3 Thermal stability of low temperature wet oxidation (100) and (111) Si-SiO ₂ stack.....	73
5.4.3.1 Experimental details.....	73
5.4.3.2 Stability of lifetime and J _{0e} of samples following FGA.....	74
5.4.3.3 Stability of lifetime and J _{0e} of samples following RTA.....	75
5.5 Passivation effect of oxide/nitride stacks on Si-SiO ₂ interface.....	76
5.5.1 Effect of LPCVD nitride deposition temperature on surface passivation of Si-SiO ₂ stack.....	76
5.5.2 Effect of LPCVD nitride deposition on surface passivation of Si-SiO ₂ stack..	78
5.5.3 Effect of subsequent LPCVD nitride deposition treatments on surface passivation of (100) and (111) samples	79
5.5.4 Thermal stability of samples with oxide/LPCVD nitride stacks.....	83
5.6 Summary	86
CHAPTER 6: Influence of atomic hydrogen exposure on the Si-SiO₂ interface.....	89
6.1 Experimental details.....	90
6.2 Background tests	91
6.2.1 Effect of molecular H ₂ on the Si-SiO ₂ interface	91
6.2.2 Effect of illumination during RTA.....	91
6.3 Effect of RTA on the Si-SiO ₂ interface following atomic hydrogen plasma exposure	95
6.3.1 RF power.....	95
6.3.2 MW power	101
6.3.3 Comparing of RTA results between at 300°C and 400°C	105
6.4 Effect of atomic hydrogen plasma exposure parameters on the Si-SiO ₂ interface	109
6.4.1 Influence of hydrogen plasma exposure power on Si-SiO ₂ interface defect distribution	109
6.4.1.1 RF power.....	109
6.4.1.2 MW power	111
6.4.2 Influence of hydrogen plasma exposure time on Si-SiO ₂ interface defect distribution	115
6.4.2.1 RF power plasma hydrogen exposure	115
6.4.2.2 MW power plasma hydrogen exposure.....	119

6.4.3 Influence of hydrogen plasma exposure pressure on Si-SiO ₂ interface defect distribution.....	122
6.4.4 Optimization of the atomic hydrogen plasma exposure parameters	124
6.5 Effect of MW hydrogen plasma exposure and following thermal anneal on the Si-SiO ₂ interface	124
6.5.1 Effect of MW hydrogen plasma exposure and following thermal anneal on the Si-SiO ₂ interface	125
6.5.2 Influence of hydrogen plasma exposure temperature on Si-SiO ₂ interface passivation.....	131
6.6 Effect of hydrogen plasma exposure and following thermal anneal treatments on Si-SiO ₂ interface of planar (111) and textured (100) samples	133
6.6.1 Effect of hydrogen plasma exposure and following thermal anneal treatments on Si-SiO ₂ interface of planar (111) Si-SiO ₂ interface	133
6.6.2 Effect of hydrogen plasma exposure and following thermal anneal treatments on Si-SiO ₂ interface of textured (100) Si interface properties	135
6.7 Effect of atomic hydrogen and subsequent thermal annealing treatments on LPCVD Si ₃ N ₄ /SiO ₂ /Si stacks.....	137
6.8 Effect of low temperature thermal annealing on Si-SiO ₂ stack following MW hydrogen plasma exposure.....	140
6.9 Summary	148
CHAPTER 7: Effect of corona charging, humidity, UV exposure and mineral acid on the Si-SiO₂ interface.....	151
7.1 Effect of corona charging and following thermal anneal on Si-SiO ₂ stacks.....	152
7.1.1 Effect of corona charging and post corona RTA on the Si-SiO ₂ surface passivation.....	152
7.1.2 Detailed investigation of annealing behaviour of defects introduced by corona charging.....	156
7.2 Effect of humidity on the properties of the Si-SiO ₂ interface.....	159
7.3 Effect of UV illumination on the Si-SiO ₂ surface passivation.....	162
7.4 Effect of mineral acid solution on the Si-SiO ₂ surface passivation	166
7.4.1 Experimental details.....	167
7.4.2 Effect of hydrogen introduction by acid solution on Si-SiO ₂ interface	167
7.4.3 Effect of temperature and time of acid immersion on Si-SiO ₂ interface	171
7.5 Summary	174

Summary and further work.....	177
List of Publications.....	181
Bibliography.....	183

