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

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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.

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Abstract

In this thesis, the influence of atomic hydrogen on the surface passivation of Si-SiO_2 interface was mainly investigated. The effect of corona charging, humidity, UV exposure and mineral acid on Si-SiO_2 interface was compared to the effect of atomic hydrogen. The electrical properties of thin (~20nm), low temperature (750-900^oC) 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^oC). 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-SiO_2 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-SiO_2 interface in both cases was investigated. The effect of atomic hydrogen exposure and the post-atomic hydrogen exposure thermal anneal on the Si-SiO_2 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^oC.

Surface orientation had a large effect on achievable surface passivation. (111) surfaces displayed high recombination rates even at an oxidation temperature of 850^oC 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-SiO_2 interface. These defects were efficient carrier recombination centres, were thermally unstable and could be effectively removed by a short RTA anneal at 300^oC or above. The annealing of this thermally unstable defect was not characterized by a single activation energy but rather by a spread of activations 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^{o}C during atomic H plasma exposure. In particular, at all sample temperatures in the range 25-600^{o}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-SiO_2 interface and these defects could be subsequently removed by an RTA treatment, which were consistent with effects of atomic hydrogen on the Si-SiO_2 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-SiO_2 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-SiO_2 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-SiO_2 interface.

Immersion of oxidised silicon samples in mineral acids resulted in a modification to the Si-SiO_2 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%H2 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

$C_{hf}(C_{lf})$	High (Low) frequency capacitance
$C_i(C_s)$	Capacitance of insulator(semiconductor)
$D_{it}(D_{itm})$	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

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