Contents

CONTENTS ... 7

LIST OF FIGURES ... 10

1 INTRODUCTION ... 15

2 THE CRYSTALLINE SILICON THIN-FILM SOLAR CELL ... 17

2.1 THE LOW-TEMPERATURE APPROACH ... 18

2.2 THE HIGH-TEMPERATURE APPROACH ... 18

2.2.1 General ... 19

2.2.2 Concepts of high-temperature CSiTF solar cells ... 22

3 THE CSITF SOLAR CELL ON FOREIGN SUBSTRATE ... 25

3.1 OVERVIEW OF THE PREPARATION STEPS ... 25

3.2 THE SUBSTRATE ... 26

3.3 DIFFUSION BARRIER LAYERS ... 27

3.4 SILICON DEPOSITION BY ATMOSPHERIC PRESSURE CVD ... 28

3.5 GRAIN ENLARGEMENT BY ZONE-MELTING RECRYSTALLISATION ... 29

3.6 CELL PROCESS FOR ONE-SIDE CONTACTED CSITF SOLAR CELLS ... 30

3.7 MAIN TOPICS OF THIS RESEARCH WORK ... 31

3.7.1 The intermediate layer as barrier against impurities ... 32

3.7.2 Zone-melting recrystallisation and solar cell processing ... 34

4 DIFFUSION BARRIER PROPERTIES OF SILICON DIOXIDE AND SILICON NITRIDE INTERMEDIATE LAYERS ... 39

4.1 RELEVANT ASPECTS OF DIFFUSION ... 39

4.2 PREPARATION AND GENERAL PROPERTIES OF INTERMEDIATE LAYERS USED FOR CSITF SOLAR CELLS ... 44

4.2.1 Deposition of intermediate layers ... 44

4.2.2 Mechanical and chemical properties ... 45

4.3 INVESTIGATED IMPURITY METALS ... 47

4.4 KNOWN DIFFUSION BARRIER PROPERTIES ... 48

4.4.1 Properties of impurity diffusion in SiO_2 ... 48

4.4.2 Properties of impurity diffusion in Si_3N_4 .... *49*
4.4.3 Properties of impurity diffusion in SiC *52*
4.5 OVERVIEW OF EXPERIMENTS DONE ON DIFFUSION BARRIER PROPERTIES 52
4.6 INDIRECT INVESTIGATION METHOD 54
4.6.1 Investigations on metal – barrier – silicon structure *54*
4.6.2 Investigations on metal – µc-silicon – barrier – silicon structures *55*
4.6.3 Investigations on metal – silicon – barrier – Si structures *59*
4.7 THE DIRECT INVESTIGATION METHOD – ION IMPLANTATION 67
4.7.1 Experimental approach *67*
4.7.2 Experiment *68*
4.7.3 Results and analysis *70*
4.8 APPLICATION OF DIFFUSION BARRIER RESULTS ON A TYPICAL MANUFACTURING PROCESS OF CSITF SOLAR CELLS 73
4.8.1 Simulation tool *74*
4.8.2 Influence of uncertainties of experimental values *75*
4.8.3 Influence of diffusivity in substrate *76*
4.8.4 Influence of intermediate layer thickness *77*
4.9 SUMMARY 78

5 ZONE-MELTING RECRYSTALLISATION OF THIN SILICON LAYERS AND PREPARATION OF CSITF SOLAR CELLS 81
5.1 EXPERIMENTAL SET-UP FOR ZONE-MELTING RECRYSTALLISATION 82
5.2 THE ONE-SIDE CONTACT SOLAR CELL PROCESS 85
5.3 MULTICRYSTALLINE SILICON WAFERS AS IDEAL SUBSTRATE 88
5.3.1 Particularities of crystal growth using ZMR *88*
5.3.2 Parameters influencing the supercooled zone *91*
5.3.3 Influence of substrate base temperature *93*
5.3.4 Influence of the intensity profile of the focussed lamp *97*
5.3.5 CSiTF solar cells on optimised ZMR layers *101*
5.3.6 Summary *104*
5.4 SSP RIBBON AS SUBSTRATE 104
5.4.1 Preparation of the silicon layer *105*
5.4.2 Solar cell results and electrical properties *107*
5.4.3 Summary *109*
5.5 SILICON NITRIDE CERAMICS AS SUBSTRATE 110

5.5.1 Sample structure and preparation *110*
5.5.2 Crystallographic properties *113*
5.5.3 Solar cell results and electric properties *120*
5.5.4 Summary *124*
5.6 SILICON-INFILTRATED SILICON CARBIDE CERAMICS AS SUBSTRATE 126
5.6.1 SiSiC substrates with SiO_2/SiN_x *intermediate layers* *126*
5.6.2 SiSiC substrates with SiC intermediate layer *134*
5.7 FURTHER SUBSTRATES 140
5.7.1 SiAlON ceramics as substrate *140*
5.7.2 Mullite ceramics as substrate *143*
5.8 SUMMARY 145

6 SUMMARY 149

APPENDIX A ABBREVIATIONS 153

APPENDIX B METHODS FOR MEASUREMENT AND ANALYSIS 155
B.1 GLOW DISCHARGE MASS SPECTROSCOPY (GDMS) 155
B.2 SPECTRALLY RESOLVED LIGHT BEAM INDUCED CURRENT (SR-LBIC) 156
B.3 DEEP LEVEL TRANSIENT SPECTROSCOPY (DLTS) 158

APPENDIX C ELECTRICAL MODELLING OF THE SILICON SOLAR CELL 161
C.1 CURRENT/VOLTAGE CHARACTERISTICS 161
C.2 LOSS MECHANISMS 164

BIBLIOGRAPHY 167

ACKNOWLEDGEMENTS 180

CURRICULUM VITAE 183

List of Figures

Fig. 1.1: Cost breakdown for a commercial silicon PV module 15

Fig. 2.1: Top view of a simox cell textured by inverted pyramids. 20

Fig. 2.2: Scheme of a) backside contacted cell (upper part) and b) frontside contacted cell (lower part). 20

Fig. 2.3: Important technology paths for the different cell concepts pursued in the high temperature approach. 23

Fig. 3.1: Scheme of preparation steps to fabricate a CSiTF sample which can be processed to a CSiTF solar cell. 26

Fig. 3.2: Seeding layer on a SiO_2 intermediate layer in different states. 30

Fig. 3.3: Degradation of solar cell efficiency with impurity concentration. 33

Fig. 3.4: Simulated diffusion of fast and slow diffusing metals out of the substrate into the epi layer during a rapid thermal CVD epitaxy 33

Fig. 4.1: Schematic of an impurity concentration profile in a CSiTF sample. 43

Fig. 4.2: Cross section of a SiSiC substrate with SiO_2-SiN_x-SiO_2 intermediate layer after ZMR. 46

Fig. 4.3: Effect of transition metals on the minority carrier diffusion length in silicon. 48

Fig. 4.4: Sample structure with sole iron layer as impurity source 54

Fig. 4.5: Large area heater (LAH) with linear halogen lamps as heating elements. 55

Fig. 4.6: Structure of the samples used for the diffusion experiments 56

Fig. 4.7: Secco etched cross section of a sample treated at 1200°C for 30min. 57

Fig. 4.8: Iron concentration profiles as measured by GDMS, at two different temperatures and duration. 58

Fig. 4.9: Secco etched cross section of a sample treated at 1350°C for 30min. 58

Fig. 4.10: Sample structure with monocrystalline silicon source layer and mono- or multicrystalline silicon sink. 59

Fig. 4.11: Measured iron concentrations in the sink layer for bonded samples with SiO_2 and SiN_x/SiO_2 diffusion barrier, respectively. 63

Fig. 4.12: Arrhenius plot of diffusion coefficient of iron in SiO_2 (left) and SiN_x (right) at different parameter values of m. 65

Fig. 4.13: Arrhenius plot of diffusion coefficient of chromium in SiO_2 and SiN_x at different parameter values of m. 66

Fig. 4.14: Measured vanadium concentrations in the sink layer for bonded samples with SiO_2 and SiN_x/SiO_2 diffusion barrier, respectively, as well as upper and lower limits of literature data for the solid solubility of vanadium in silicon. 67

Fig. 4.15: Sample structure used for the diffusion experiments with ion implanted impurity source. 68

Fig. 4.16: Comparison of vanadium profiles as simulated with SRIM and as measured by SIMS for SiO_2 (left) and SiN_x (right). 70

Fig. 4.17: Vanadium profiles in SiO_2 measured by SIMS after different annealing times at 1000°C, 1200°C and 1350°C, respectively. 71

Fig. 4.18: Vanadium profiles in SiN_x measured by SIMS after different annealing times at 1000°C, 1200°C and 1350°C, respectively. 72

Fig. 4.19: Simulation with different values of the diffusion coefficient of iron calculated after DLTS analysis for SiO_2 and for SiN_x intermediate layer. 75

Fig. 4.20: Simulation of different diffusivities in the substrate for SiO_2 and for SiN_x intermediate layer. 76

Fig. 4.21: Simulation of iron diffusion with different values of SiO_2 intermediate layer thickness, a) for silicon substrate and b) for silicon nitride substrate. 77

Fig. 4.22: Simulation of iron diffusion with different values of SiN_x intermediate layer thickness, a) for silicon substrate and b) for silicon nitride substrate. 78

Fig. 5.1: Set-up of the 'old' ZMH. 82

Fig. 5.2: Set-up of the modified zone-melting heater. 83

Fig. 5.3: Power course of a typical ZMR process. 84

Fig. 5.4: Process sequence of the solar cell process and resulting cell structure of CSiTF solar cells on foreign substrates. 86

Fig. 5.5: Typical structure of subgrain boundaries. 89

Fig. 5.6: Formation of subgrain boundaries at the inner edges of the solidification front. 89

Fig. 5.7: Mechanism of constitutional supercooling. 90

Fig. 5.8: Relationship of ZMR parameters and width of the supercooled zone, which affect the distance between the subgrain boundaries. 92

Fig. 5.9: Lateral temperature distribution in the substrate (a) and related temperature gradient. 95

Fig. 5.10: Nomarski images of Secco-etched cross sections and polished surfaces of samples recrystallised at 910°C and 1060°C. 95

Fig. 5.11: Mean values of solar cell parameters of samples processed at different ZMR base temperature. 97

Fig. 5.12: Diffusion length topography of samples type L and M and corresponding frequency of diffusion length values. 97

Fig. 5.13: Correlation of morphology of melt zone and topography of epi layer. 99

Fig. 5.14: Surface and cross sections corresponding to the regions I and II of Fig. 5.13. 100

Fig. 5.15: Internal quantum efficiency of a textured and non-textured solar cell processed on optimised silicon layers on mc-S/SiO_2 – substrate. 103

Fig. 5.16: Principle of the SSP manufacturing process and a sample of a SSP ribbon. 105

Fig. 5.17: Surface topography of 'rough' and 'smooth' regions of an impure SSP substrate on macroscopic and microscopic scale. 106

Fig. 5.18: Comparison of external quantum efficiency of cells with one and with two RPHP passivation steps. 108

Fig. 5.19: Effective diffusion length of samples with two RPHP treatments, but with extremely different L_{eff} values. 108

Fig. 5.20: Pictures of the melt zone during ZMR. 111

Fig. 5.21: Surface of a silicon layer on an insulating Si_3N_4 ceramics without intermediate layer after ZMR.. 112

Fig. 5.22: Cross sections of the solar cell DF52.1 (non-conductive substrate type A): interface and dislocated silicon layer and crack in silicon layer; excess acid has corroded the vicinity of the crack. 114

Fig. 5.23: Surface of the solar cell DF52.1: surface with clearly visible cracks and a metallisation finger which crosses a crack without causing a short circuit. 114

Fig. 5.24: Cross sections of the solar cell DF52.9 (type D): interface and dislocated silicon layer and loose Si_3N_4 structure with filled pores. 115

Fig. 5.25: Typical region of the surface of the solar cell DF52.9 (type D). 116

Fig. 5.26: Cross section of the solar cell DF52.11 (type B): interface with thermal SiO_2 intermediate layer and crack in the silicon layer. 117

Fig. 5.27: Surface of the solar cell DF52.11 (type B): highly defective surface structure with cracks and crack network filled with silver. 117

Fig. 5.28: Glow discharge mass spectroscopy of sample types A and B. 118

Fig. 5.29: Glow discharge mass spectroscopy of sample types C and D. 119

Fig. 5.30: Dark characteristic curves of solar cells on Si_3N_4 ceramic of type A and D after remote plasma hydrogen passivation and antireflection coating . 122

Fig. 5.31: Integral external quantum efficiency of solar cells on samples of type A. 123

Fig. 5.32: Mappings of the effective diffusion length of the solar cells on non-conductive ceramics (type A) and conductive ceramics (type D). 125

Fig. 5.33: Cross section of a CSiTF sample on SiSiC substrate. 127

Fig. 5.34: SEM image of an ONO layer on top of a SiSiC ceramics. 128

Fig. 5.35: Impurity concentration profile of a CSiTF solar cell structure after all process steps. 128

Fig. 5.36: CSiTF solar cells on SiSiC substrate. 130

Fig. 5.37: Nomarski photograph of a polished and Secco etched epi layer. 131

Fig. 5.38: Comparison of BEI and EBIC images of unpolished and polished samples. 132

Fig. 5.39: Carrier concentration profile of the silicon layer of a thin-film solar cell on SiSiC, as obtained by spreading resistance measurement. 132

Fig. 5.40: Diffusion length mapping of the CSiTF solar cell on SiSiC with the highest efficiency. 133

Fig. 5.41: Absolute spectral response of the cell with maximum efficiency. 134

Fig. 5.42: Cross section of SiSiC ceramics coated with SiC a) by LPCVD, b) by APCVD. 135

Fig. 5.43: Cross section of a SiSiC substrate with seeding layer and epitaxial layer of good quality and with high defect density. 137

Fig. 5.44: Top view of a zone-melting recrystallised and epitaxially thickened silicon layer on SiC intermediate layer. 137

Fig. 5.45: Glow discharge mass spectroscopy analysis of samples with APCVD and LPCVD SiC layers. 138

Fig. 5.46: Diffusion length topography obtained from SR-LBIC measurement of the cell with the best performance and a cell with reduced solar cell parameters. 139

Fig. 5.47: Cross section of a recrystallised silicon layer on top of a SiAlON substrate. 141

Fig. 5.48: Dark characteristics of CSiTF solar cells on SiAlON substrates. 142

Fig. 5.49: LBIC map of the best solar cell (13-1) on SiAlON substrate. 143

Fig. 5.50: Zone-melting recrystallised silicon layers on top of mullite substrates a) without and b) with ONO intermediate layer. 144

Fig. 5.51: Dark current of CSiTF solar cells on mullite substrate with and without ONO intermediate layer. 145

Fig. B.3.1: Time lapse of bias voltage and corresponding capacity change. 159

Fig. C.1.2: Geometry factor G_F at various ratios of surface to bulk recombination velocities. 163

Fig. C.1.3: Equivalent circuit of the two-diode model of a solar cell. 163