Hydrogen and Surface Passivation of Thin-film Crystalline Silicon Solar Cells on Graphite Substrates

Wasserstoff- und Oberflächenpassivierung von kristallinen Silicium-Dünnschichtsolarzellen auf Graphitsubstraten

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“Never, never, never give up.” — Winston Churchill

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Abstract

Silicon substrates can be replaced by foreign substrates for crystalline silicon thin-film (CSiTF) solar cells, which is an effective strategy to reduce both the cost of cell production and the consumption of silicon. Graphite is a foreign substrate widely known for its high purity and high temperature resistance (>1300°C). The purposes of this work are to develop cell concepts, to characterize and furthermore to improve the performance of CSiTF solar cells on graphite substrates. Three new strategies with low-temperature processing (<350°C) are presented: laser single side contact (LSSC) formation, the hydrogen passivation process (HP), and surface passivation using hydrogenated intrinsic amorphous silicon [a-Si:H(i)].

Due to the application of LSSC and HP, cell performance is improved by increasing the open circuit voltage and fill factor. This leads to an increase in cell efficiency of 3.4 percentage points for a 40 μm thick, 4 cm² aperture area, CSiTF solar cell on graphite substrates. Based on the above findings, a-Si:H(i) was further applied to reduce surface recombination of the sun-facing side of solar cells. The optical properties of the SiNx/a-Si:H(i) stack were also taken into account and investigated using spectroscopic ellipsometer techniques. In addition, scanning transmission electron microscopy inside a scanning electron microscope was applied to characterize the cross section of the SiNx/a-Si:H(i) stack using focus ion beam preparation. An increase in cell efficiency of 0.6 percentage points to 10.8% was finally achieved due to the application of a-Si:H(i) surface passivation.

Besides the conventional characterization methods, i.e., current density-voltage measurement, quantum efficiency (QE), Raman spectrometry, and light beam induced current. The recently emerging methods of spatially resolved lock-in thermography techniques were also explored to characterize the cells on graphite substrates. Moreover, the simulation software PC1D was used to fit QE results and to further analyze the cell performance in detail.

Those three cell concepts, i.e., LSSC, HP and a-Si:H(i), were successfully combined and developed for the CSiTF cells on graphite substrates, thus, achieving new efficiency record. However, many advanced concepts of cell processing are not included in this work, including optimum design of metal grids, light trapping, rear side passivation or local diffusion. Thus, there is still room for further improvement.
Zusammenfassung

Bei kristallinen Silizium-Dünnschicht (CSiTF) Solarzellen können Fremdsubstrate verwendet werden, um Siliziumsubstrate zu ersetzen. Dies ist eine wirksame Strategie, um sowohl die Kosten für die Zellproduktion als auch den Verbrauch von Silizium zu reduzieren. Graphit ist ein Fremdsubstrat, das für seine hohe Reinheit und seine hohe Temperaturbeständigkeit (>1300°C) gut bekannt ist. Die Ziele dieser Arbeit sind es, Zellkonzepte zu entwickeln, zu charakterisieren, und die Leistung der CSiTF Solarzellen auf Graphitsubstraten zu verbessern. Drei Strategien mit niedriger Prozesstemperatur (<350°C) werden dargestellt: die einseitig Laserkontaktbildung (LSSC), das Wasserstoff-Passivierungsverfahren (HP), und die Oberflächenpassivierung mit hydriertem eigenleitendem, amorphem Silicium [a-Si:H(i)].

Durch die Anwendung der LSSC und HP wurden die Zellleistung, die Leerlaufspannung und der Füllfaktor verbessert. Es zeigt sich eine Erhöhung des absoluten Zellwirkungsgrades um 3,4 Prozentpunkte für eine 40 µm dicke CSiTF Solarzelle auf Graphitsubstrat mit 4 cm² Aperturfäche. Basierend hierauf wurde außerdem a-Si:H(i) angewandt, um die Oberflächenrekombinationsgeschwindigkeit der Sonnenseite der Solarzellen zu reduzieren. Die optischen Eigenschaften des SiN_x/a-Si:H(i) Stapels wurden unter Verwendung von spektroskopischen Ellipsometer-Techniken untersucht. Zusätzlich wurde Rastertransmissions-Elektronenmikroskopie in einem Rasterelektronenmikroskop angewendet, um den Querschnitt des SiN_x/a-Si:H(i) Stapels mittels fokussiertem Ionenstrahl zu untersuchen. Schließlich wurde eine Erhöhung des absoluten Zellwirkungsgrades um 0,6 Prozentpunkte auf 10,8% durch die Anwendung von der a-Si:H(i) Oberflächenpassivierung erzielt.

Neben den herkömmlichen Charakterisierungsmethoden, d.h. Stromdichte-SpannungsMESSung, Quanteneffizienz (QE), Raman-Spektroskopie und lichtstrahlinduziertem Strom, wurde die in jüngster Zeit entwickelte Methode der ortsaufgelösten Lock-in-Thermographie angewandt, um die Zellen auf Graphitsubstraten zu erforschen. Darüber hinaus wurde die Simulationsoftware PC1D verwendet, um QE Ergebnisse zu fitten und die Zellenleistung detailliert zu analysieren.

Diese drei Zellkonzepte, d.h. LSSC, HP und a-Si:H(i), wurden erfolgreich zusammengeführt und für die CSiTF Zellen auf Graphitsubstraten optimiert — wodurch der neue Rekordwirkungsgrad erreicht wurde. Viele fortschrittliche Konzepte der Zellprozessierung sind noch nicht in dieser Arbeit enthalten, somit gibt es, zum Beispiel hinsichtlich der
optimalen Gestaltung von Metallgittern, dem Lichtfang, der Rückseitenpassivierung oder der lokalen Diffusion immer noch Raum für weitere Verbesserungen.
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1 Introduction

Abstract

Nowadays, the development of photovoltaics is highly dependent on supply/demand market forces and global economic policies. This chapter offers some background on the ZAE Bayern and on thin-film silicon photovoltaic research in general. My studies will be also introduced in brief. In addition, the main contents of each chapter are listed at the end.
1.1 Research at the ZAE Bayern

The work of this thesis in the last several years was accomplished at the Bavarian Center for Applied Energy Research (ZAE Bayern), which was founded as a non-profit association in December 1991. The ZAE Bayern widely promotes energy research in the fields of energy efficiency, energy storage, and renewable energies. The association has scientific divisions in Würzburg, Garching, Erlangen, Nuremberg, and Hof. The ZAE Bayern cooperates with several universities, and it also is a member of the Renewable Energy Research Association (FVEE), a strategic partnership between non-university German research institutes working in the field of renewable energy. Moreover, the ZAE Bayern is a founding member of the Energy Campus Nuremberg (EnCN). The EnCN is an energy research cooperation between the FAU, the TH Nuremberg and the Fraunhofer-Gesellschaft zur Förderung der angewandten Forschung e.V., and ZAE Bayern’s division in Nuremberg. Furthermore, the ZAE Bayern is a partner in the network Renewable Energies of the research initiative “TUM.Energy”.

The scope of work at the ZAE Bayern in Erlangen includes developing its own concepts and manufacturing processes for solar cells based on printed semiconductors (e.g. organic and other new materials). In addition, imaging techniques for the characterization of solar cells and modules (e.g. infrared thermography and electroluminescence) are developed and applied with high spatial and temporal resolution. Furthermore, the site in Erlangen has an accredited test laboratory for photovoltaic modules. The ZAE Bayern in Erlangen works in close cooperation with the Friedrich-Alexander Universität Erlangen-Nürnberg (FAU), especially with the Department of Materials for Electronics and Energy Technology (i-MEET). The research cooperation between the ZAE Bayern and the i-MEET is focused on the aspects of materials for electronics and energy technology, as well as on all aspects of printable semiconductors and conductors (e.g. organic, inorganic, and hybrid). In the division Erlangen, ZAE Bayern has established a laboratory with its own cell fabrication equipment for the production of silicon solar cells, including a heated wet chemical bench to etch and clean samples, three chemical vapor deposition systems for layer deposition and recrystallization, and test and measurement equipment for characterization (e.g. current-voltage simulator and light beam induced current measurement systems.). As a member of photovoltaic-systems group, since 2010
I have participated several projects in cooperation with the divisions at the ZAE Bayern, the i-MEET, other universities, and industrial partners.

1.2 Thesis motivation

Renewable energy sources include solar energy, biofuel, biomass, geothermal, hydropower, ocean power (tidal and wave), and wind power. They are clean, sustainable and environmentally friendly. Development of renewable energy can not only meet a population’s daily needs and reduce environmental pollution, but can also reduce a nation’s dependency on the influential exporters of traditional energy sources (crude oil, coal or natural gas), helping to keep the country's economy stable.

Photovoltaic (PV) devices, such as silicon solar cells, can convert the solar radiation directly to electricity. Most of the energy on Earth derives from solar radiation, and moreover, the sun is still supposed to have a 5-billion-year life span. When oil, coal, and other traditional energy sources are depleted, solar energy will remain and meet the requirements of human beings. As shown in Fig. 1.1, the latest statistics show that the global power generation from renewable energies is increasing. In particular, the power generated from solar energy has been steadily increasing between 2007 and 2013, reaching 150 Billion (Bn) kWh in 2013. With the needs of

![Fig. 1.1 Global total and photovoltaics electricity generation in 2007-2013. The power generated from solar energy has been steadily increasing. Status: August 2014 [1].](image)
Introduction

The world's population growing and economies developing in countries all over the world, energy demand in 2015 is expected to reach 57 GW [16].

In Germany, the share of renewable energies increased in 2014. In Fig. 1.2, the latest data from Bundesverband der Energie- und Wasserwirtschaft (BDEW) shows that renewable energy makes up 25.8% of the gross electricity generation, thus making renewable energy the single largest contributor to total electricity generation. The contribution of photovoltaics shows an increase of from 30.0 Bn kWh to 35.2 Bn kWh, increasing its share from 4.7% to 5.8%. In line with the increase in energy consumption, it is essential to explore new cell concepts to steadily increase the energy conversion efficiency, promoting the popularization and the residential application of PV products.

PV electricity generation is based on solar cells with semiconductor materials. The most widespread inorganic material in PV is silicon, and silicon has the advantage of non-toxic and abundant in the earth. The typical silicon materials applied in photovoltaics include mono- and polycrystalline silicon (i.e., c-Si and mc-Si), and amorphous silicon (i.e., a-Si). The nomenclature of silicon depends on their different grain sizes, as introduced in Section A.3. Thin-film crystalline silicon solar cell technologies have been rapidly developed in the past two decades. Various substrates (flexible or rigid, glass or graphite) can be used for deposition of different layers.
(absorber, anti-reflector, or passivation), in order to realize wide application with less high-purity silicon consumption and simple fabrication process [17].

The focuses of this thesis are the cell concepts of crystalline silicon thin-film (CSiTF) solar cells, developed for less material consumption and higher efficiency. Typical CSiTF cell concepts can be divided into silicon-based and foreign substrates.

Since the first publication on foreign substrates was published in 1997 [18], the scientists at the ZAE Bayern have devoted at least 18 years to the studies of CSiTF solar cells on foreign substrates. Many cell concepts and characterization methods have been developed for and applied to solar cells on foreign substrates. Fig. 1.3 gives the research and design route map of the cells on foreign substrates at the ZAE Bayern. The related cell concepts are introduced in Appendix A. Originally, research at the ZAE Bayern mainly focused on comparing different materials of foreign substrates and barrier layers, developing layer deposition techniques using CoCVD, and applying new methods in characterization, e.g. Raman spectrometer, EBSD and EBIC.

However, the scientists at the ZAE Bayern have not intensively researched on contact formation, hydrogen passivation, or surface passivation until a project —

![Fig. 1.3 Progress in the concepts and cell efficiencies of thin-film silicon solar cells on graphite substrate. The important milestone are: the SiC barrier layer in 2003 [2]; the large-scale convection-assisted CVD (CoCVD) technique in 2004 [3]; zone melting recrystallization (ZMR), graphite and ceramic substrates in 2006 [4-7]; plasma etching with the cell efficiency with a 11.1% on 1.7 cm² in 2008 [8]; laser edge isolation in 2009 [9]; Raman spectrometry in 2010 [10], with a cell efficiency of 6.8% on 4 cm² in 2011 [11]; electron beam induced current (EBIC) and electron backscatter diffraction (EBSD) in 2012 [12, 13]; laser single side contact (LSSC) formation and hydrogen passivation in 2013 [14]; a-Si:H(i) surface passivation in 2014 [15].]
HELIOS, i.e., Herstellung kristalliner Silicium-Dünnschicht-Solarzellen auf biologisch abgeleiteten Substraten [19]. The research of this project is based on foreign substrates. As part of HELIOS, my thesis motivation is that the developed and developing cell concepts were intended to be applied to CSiTF solar cells on foreign substrates, in order to improve their performance.

There are two approaches to increasing the competitiveness of the CSiTF solar cells on foreign substrates:

- To reduce the cost of high-purity foreign substrates;
- To improve cell efficiency while simplifying the cell fabrication process.

For these purposes, several primarily studies have been carried out at the ZAE Bayern based on plasma enhanced chemical vapor deposition (PECVD) system. The graphite samples were supplied by our project partner Schunk Kohlenstofftechnik GmbH, Gießen. In this work, laser single side contact (LSSC) formation, hydrogen bulk passivation (HP) process, and a-Si:H(i) surface passivation are applied to CSiTF solar cells on graphite substrate. The greatest efficiency of solar cells on graphite substrate was achieved with hydrogen passivation and laser single side contact formation, with an increase from 6.8% to 10.2% on a 4 cm² active area. Finally, the cell efficiency achieved 10.8% with an a-Si:H(i) layer for surface passivation.

1.3 Thesis outline

The work of this thesis provides preliminary studies for the application of LSSC, HP and surface passivation using a-Si:H(i) layers to CSiTF silicon solar cells on graphite substrate.

Chapter 2: Fundamentals provides the underlying physical mechanisms (light absorption and recombination), reviews the state-of-the-art bulk and surface passivation of CSiTF solar cells on different substrates, and reviews of the state-of-the-art single and double layer(s) antireflection coatings techniques.

Chapter 3: Overview of characterization techniques provides the background to the experimental results presented in this thesis by describing the characterization techniques used in this work.

Chapter 4: Hydrogen passivation and laser single side contact analyses the PECVD system for hydrogen passivation. The best hydrogen passivation process was investigated, highlighting the physical characteristics that are likely to influence the bulk passivation that is achieved.
Chapter 5: a-Si:H(i) surface passivation introduces the fabrication and applicability of a-Si:H(i) layers to CSiTF solar cells. This chapter analyses a-Si:H(i) films using thin-film characterization techniques.

Chapter 6: Solar cells on graphite substrates provides the experimental details and results of the effects of LSSC, HP, and surface passivation on CSiTF solar cells on graphite.

A summary of the main conclusions from this thesis is presented in Chapter 7: Summary and outlook, which also outlines the direction for further work on the cell concepts. Appendix A: Cell concepts introduces the developed cell concepts which have been applied in the cell fabrication processing in this work.
1 Introduction
2 Fundamentals

Abstract

The basic principles of absorption, generation and passivation are introduced in this chapter. Moreover, the reviews of the state-of-the-art bulk and surface passivation are detailed in the tables, which were used as essential reference to investigate the bulk and surface passivation techniques for CSiTF solar cells on graphite substrates.
2 fundamentals

2.1 Light absorption of silicon solar cells

Semiconductors are materials with a conductivity of $10^4$–$10^8$ Ωcm⁻¹. For light absorption, an absorber semiconductor material should have a bandgap of 1–1.5 eV with a high solar optical absorption ($10^4$–$10^5$ cm⁻¹) in the wavelength region of 350–1000 nm [20], since this region is close to the range of solar radiation on Earth. Therefore high conversion efficiency from solar energy to electrical energy can be expected using this kind of materials. The photovoltaic phenomenon can be explained using the energy band theory. Only when the photon energy ($h\nu$) is no less than the forbidden bandgap ($E_g$) of a semiconductor can the electrons be excited from valence band ($E_v$) to reach a higher energy level in conductive band ($E_c$); meanwhile, holes are created in valence band. This is a fundamental process of photovoltaics, i.e., the light-generated electron-hole ($e$-$h$) pair. The prior condition can be described as a formula:

$$h\nu \geq (E_c - E_v) = E_g$$

2-1

The bandgaps of c-Si and a-Si at 300 K are 1.1 eV and 1.7 eV. In 2013, the theoretical efficiency limit for a 110 µm thick undoped c-Si solar cell was presented to be 29.4% [21]. Si is an indirect semiconductor. This means that the minimum of the Si conduction band and the maximum of the Si valence band lie at different crystal momentums. The electron transition from the valence band to the conduction band requires a higher energy than $E_g$. Moreover, c-Si has a lower absorption coefficient than a-Si and the direct semiconductor GaAs. (i.e., c-Si needs a thicker layer than a-Si and GaAs to absorb the same energy.) [22], p. 29. However, a-Si has a higher absorption coefficient than c-Si (< 700 nm at 300 K), which is likely to be a good candidate as a bulk (absorber) material. However, it is critical for a-Si to be directly used as a sun-facing surface passivation layer, whose thickness must be well-considered, as described in Section 5.1.1.

An intrinsic silicon has a low intrinsic carrier concentration ($n_i$) at 300 K of $1.0 \times 10^{10}$ cm⁻³, corresponding to a high resistivity of $3.0 \times 10^5$ Ωcm [23], p. 24. In order to increase the charge carriers concentration in silicon and thus to increase its conductivity, a silicon atom in its crystal structure can be replaced with an element from the fifth group of the periodic table (e.g. phosphorus and arsenic). These elements can easily donate one more valence electron to be a free charge carrier in silicon. The silicon doped with the donor atoms is called n-type silicon, whereas the
silicon doped with the acceptor atoms (e.g. boron and aluminum) is called p-type silicon. For a p-type silicon, its resistivity will decrease to 0.5 Ωcm when the acceptor concentration \( (N_A) \) is \( 3.25 \times 10^{16} \text{ cm}^{-3} \) at 300 K. Although a heavy doping concentration induces a large conductivity, every semiconductor has a maximum solubility of the impurity dopants. Where a reasonable range of the resistivity of silicon is 0.01 Ωcm to 100 Ωcm, this corresponds to a doped range of

\[
7.3 \times 10^{18} > N_D > 1.3 \times 10^{14} \text{ cm}^{-3} \quad \text{for n-type silicon,}
\]

\[
3.6 \times 10^{18} > N_A > 4.4 \times 10^{13} \text{ cm}^{-3} \quad \text{for p-type silicon,}
\]

where \( N_D \) is the donor concentration.

At thermal equilibrium the concentrations of electrons \( (n_0) \) and holes \( (p_0) \) are related to intrinsic carrier concentration \( (n_i) \), by the equations:

\[
n_0 \times p_0 = n_i^2 \quad 2-2
\]

for n-type Si

\[
n_0 = N_D, p_0 = n_i^2 / N_D \quad 2-3
\]

for p-type Si

\[
p_0 = N_A, n_0 = n_i^2 / N_A \quad 2-4
\]

When silicon is under illumination, two excess concentrations \( (\Delta n, \Delta p) \) are generated by incident photons. Therefore, the total concentrations of electrons \( (n) \) and holes \( (p) \) are

\[
n = \Delta n + n_0 \quad 2-5
\]

\[
p = \Delta p + p_0 \quad 2-6
\]

Carrier generation is always accompanied by carrier recombination. The average time for an \( e\)-\( h \) pair to recombine after generation is defined as the charge carrier lifetime \( (\tau) \):

\[
\tau = \Delta n / R \quad 2-7
\]

where \( R \) is the recombination rate. The value of \( \tau \) is an important parameter in evaluating the electrical property of materials. A charge carrier with a high \( \tau \) is able to be effectively collect and then generate electricity.

### 2.2 Bulk recombination

Currently, the highest efficiency for thin-film silicon solar cells is 25.6\%, achieved using a Heterojunction with Intrinsic Thin Layer (HIT) cell concept [24] — the culmination of developments which have brought solar cells ever close to their
Fundamentals

Any remaining inefficiencies are a result of electrical and optical losses [23], p. 89.

The focus of this work is carrier recombination in bulk and surface. In order to improve cell performance, it is essential to reduce the bulk and surface recombination.

There are three main recombination mechanisms occurring in the silicon solar cells:

- Radiative recombination ($R_{\text{rad}}$),
- Auger recombination ($R_{\text{Aug}}$),
- Recombination via defect levels in the bandgap ($R_{\text{SRH}}$).

Radiative recombination is the inverse process to the $e$-$h$ pair generation. An electron in the conduction band moves back to the valence band, combines with a hole, and releases a phonon as the excess energy, i.e., 3-particle process. The radiative recombination rate is:

$$R_{\text{rad}} = B(n_0 + p_0 + \Delta n)$$ \hfill (2-8)

the corresponding carrier lifetime is

$$\tau_{\text{rad}} = \frac{1}{B(n_0 + p_0 + \Delta n)}$$ \hfill (2-9)

where $B$ is the material constant, which has a small value in c-Si of $1.0 \times 10^{14}$ cm$^3$/s at 300 K. Since silicon is an indirect semiconductor which requires an additional phonon to finish a 4-particle process, radiative recombination is negligible compared to the other two recombination mechanisms in silicon. Nevertheless, the radiative recombination is applied to characterize surface recombination using the photoluminescence (PL) and the lock-in thermography (LIT) techniques (Section 3.2.2 and 3.2.6, respectively).
As shown in Fig. 1.1 (c)–(d), Auger recombination is different from radiative recombination in the way an electron releases its energy. When the electron leaves the conduction band to the valance band, the electron gives its energy to another electron or hole (a third particle). Finally, the excited third particle will lose its additional energy in a series of collisions in the lattice. As shown in Fig. 2.1, Auger recombination includes two possible processes: electron-electron-hole (eeh) and electron-hole-hole (ehh). $R_{\text{Aug}}$ is given by

$$R_{\text{Aug}} = C_n(n^2p - n_0^2p_0) + C_p(np^2 - n_0p_0^2) \quad (2-10)$$

where $C_n$ and $C_p$ are the electron and hole Auger coefficients, respectively. For $\Delta n = \Delta p$, the Auger recombination lifetimes are given by

$$\tau_{\text{Aug},n} = 1/(C_n n^2 + C_p n \Delta n) \quad \text{for n-type material}, \quad (2-11)$$

$$\tau_{\text{Aug},p} = 1/(C_p p^2 + C_n p \Delta n) \quad \text{for p-type material}. \quad (2-12)$$

Equations 2-11 and 2-12 show that the $\tau_{\text{Aug}}$ highly depends greatly on the doping concentration and injection level. Hence, in the highly doped emitters of silicon solar cells, Auger recombination plays a dominant role [25].

Defects, such as impurities and dislocations, generate defect energy levels in the bandgap of a semiconductor. The related concept was developed by Shockley and Read [26], as well as Hall [27], therefore recombination through defects is also called SRH recombination. As shown in Fig. 2.1, given two trap types (donor and acceptor) in defect levels located at $E_{\text{trap}}$, there are four possible interactions of SRH recombination, i.e., (e) electron capture by an empty defect level, (f) electron emission by a filled defect level, (g) hole emission by an empty defect level, (h) hole capture by a filled defect level. The SRH recombination rate is given by

$$R_{\text{SRH}} = (np - n_t^2)/[\tau_{p_0}(n + n_t) + \tau_{n_0}(p + p_t)] \quad (2-13)$$

with $n_t = n_t \exp(E_{\text{trap}} - E_i)/kT$, $p_t = n_t \exp(E_i - E_{\text{trap}})/kT$, $n_t p_t = n_t^2$, where $\tau_{p_0}$ and $\tau_{n_0}$ are the capture time constants of electrons and holes, and the values of $\tau_{p_0}$ and $\tau_{n_0}$ depend on the capture cross-sections of electrons and holes, the thermal velocity of the charge carriers, and the concentration of the defects.

Assuming $\Delta n = \Delta p$, the corresponding SRH lifetime depends greatly on the injection level, and is defined by

$$\tau_{\text{SRH}}(\Delta n) = \tau_{p_0} \frac{n_0 + n_t + \Delta n}{n_0 + n_t + \Delta n} + \tau_{n_0} \frac{p_0 + p_t + \Delta n}{p_0 + p_t + \Delta n} \quad (2-14)$$

Finally, the total recombination rate in bulk material of silicon is:
\[ R_{Bulk} = R_{Rad} + R_{Aug} + R_{SRH} \]  \hspace{1cm} 2-15

The corresponding total carrier lifetime in bulk is:

\[ \frac{1}{\tau_{Bulk}} = \frac{1}{\tau_{Rad}} + \frac{1}{\tau_{Aug}} + \frac{1}{\tau_{SRH}} \]  \hspace{1cm} 2-16

which shows that \( \tau_{Bulk} \) depends on the smallest value of the three recombinations.

The approach of this work is to diminish the SRH recombination using bulk passivation techniques, in order to increase the \( \tau_{Bulk} \) and finally to improve the cell performance.

### 2.3 Surface recombination

In addition to the recombination in bulk, there are a number of surface defects, i.e., dangling bonds, impurities, and dislocations, also present in the bandgap at the surface and the interface of solar cells. Therefore, surface recombination through defects \( R_{SRH} \) is most noticeable than the other two recombination mechanisms \( R_{Rad} \) and \( R_{Aug} \).

In analogy to \textbf{Equation 2-7}, an important parameter, surface recombination velocity \( (S) \), is defined by

\[ S = \frac{R_{surface}}{\Delta n_s} \]  \hspace{1cm} 2-17

where \( R_{surface} \) is the recombination rate through one surface defect state, \( \Delta n_s \) is the excess minority carrier concentration at surface. It is necessary to note that the surface defect states are heavily affected by the doping concentration, which will further induce related surface band-bending conditions. The corresponding conditions and calculations can be found in Aberle [25], pp. 26-43 and Li [28], pp. 12-28.

There are two strategies to reduce surface recombination:

1. To reduce the \( R_{SRH} \) using a-Si, SiO\(_2\) or SiN\(_x\) layer, or some acids (e.g. HF, H\(_2\)SO\(_4\)) due to the reduction of the density of surface states. More details will be discussed in \textbf{Section 2.5}.

2. To implement a doping profile, i.e., a high-low junction \((p^+p \text{ or } n^+n)\), which is widely-known as back surface field (BSF). This is a well-developed technique and has been applied to former generations of CSiTF solar cells on graphite substrates.

### 2.4 Bulk passivation: state-of-the-art

The history of bulk passivation using hydrogen, which can effectively suppress recombination via defects \( R_{SRH} \), can be traced back to the 1970s. Originally, many efforts were developed in hydrogen passivation for amorphous silicon [29, 30], until
the first application of hydrogen treatment of grain boundaries in multi-Si solar cells on native substrate was reported by Seager et al. at Sandia National Laboratories in 1979 [31]. Chu et al. presented the first hydrogen passivation application in poly-Si solar cells, especially, on foreign substrates [32]. In 1980s, a remarkable reduction in both the states of defect density and grain-boundary potential barriers was achieved [33, 34]. Pearton et al. [35] reported that hydrogen can be applied to passivate both donor and acceptor impurities.

Since the 1990s, the hydrogen treatment has been commonly used in the CSiTF solar cells on native substrates. Hydrogen has been proven to be able to diffuse into Si and can also bond to dangling bonds [36]. In addition, at the Fraunhofer Institute for Solar Energy Systems (ISE), Ralf Lüdemann evaluated three kinds of hydrogen passivation methods for mc-Si solar cells on nine different silicon bulk materials with accompanying different qualities [37]. These hydrogen passivation methods include a SiN-layer (SiN:H), low-energy hydrogen ion implantation (HII), and remote plasma hydrogen passivation (RPHP). Both SiN:H and RPHP are still widely in use nowadays, whereas there is less implementation of HII in photovoltaics due to ion bombardment damage to bulk materials. SiN:H, combined with rapid thermal process (RTP), is attractive to industries because it is a much quicker process than RPHP [38]. Lüdemann’s results also demonstrate that the hydrogen concentration largely dependent on the power of microwave, the process duration, and the gas flow rate. Moreover, the effective minority carrier diffusion length is proven to be improved after hydrogenation. Since the 2000s, hydrogen has been used to reduce the defect concentration in poly-Si [39]. Darwiche et al. proved that the hydrogen passivation can cost-efficiently increase the minority carrier diffusion length and improve the chemical and electrical properties of poly-Si surfaces [40].

For industrial bulk passivation of wafer based Si solar cells, hydrogen passivation is done by firing (i.e., annealing) of SiN:H at temperatures of around 750°C. During the firing the hydrogen is driven into the material for a few seconds [41]. However, in the case of poly-Si thin-film solar cells, a hydrogen plasma treatment below 400°C for 30 minutes is able to supply a larger amount of hydrogen [42]. Compared to SiN:H firing, plasma hydrogenation consistently leads to better solar cell results [43]. Note that, during a high temperature process without any capping layer, most of the hydrogen will escape from the poly-Si layers. Therefore, there are usually two strategies for the process of bulk hydrogen passivation:
1. At low temperature (< 400°C) for 30 min to 60 min, or
2. At high temperature (600°C to 700°C) for a few seconds.

Additionally, a post-deposition process, i.e., annealing in atomic hydrogen atmosphere, is applied to maintain the hydrogen content in solar cells. The quality of hydrogen passivation depends on the quality of bulk materials, the quality of substrates, and on layer deposition techniques (epitaxy, chemical vapor, ion-assisted, sputtering, etc.). Based on their different substrate materials, solar cells can be categorized into two main groups: native and foreign substrates. Although they both respond similarly to the hydrogen passivation process, the next section reviews current techniques for both substrate types and lists their results in reference tables.

2.4.1 Native substrates

The state-of-the-art literature reviews of hydrogen passivation on CSiTF solar cells on native substrates are shown in Table 2.1 and Table 2.2. Both tables induce several important experiences:

1. **Performance:** a CSiTF solar cell with an active layer of approximately 40 µm can achieve a cell efficiency of approximately 19% [44]. The thickness of an active layer can be reduced to a few microns using epitaxy techniques [45]. The values of the following electrical parameters ($V_{oc} = 630–660$ mV, $J_{sc} \sim 37$ mA/cm$^2$, $FF = 79–82\%$, and $\eta \sim 19\%$) can be expected for a solar cell with the best performance.

2. **Process temperature:** The value of $250°C < T < 450°C$ and $t < 60$ min are widely used as the temperature and duration of the hydrogen passivation process in laboratory settings. In industry, $T > 750°C$ for a few seconds is popular. The effusion of hydrogen out of silicon was observed and discussed when $T > 500°C$ [37, 46]. The high process temperature (1100°C) at sea-level pressure is applied for hydrogen passivation during the growth of a Si layer, whereas the low process temperature $T < 300°C$ in a vacuum is applied for the individual hydrogen passivation process.

3. The **process pressure** value of 1 mbar is commonly used for hydrogen passivation. Less pressure than 1 mbar will induce less hydrogen diffusion into silicon, whereas higher pressure induces low quality passivation, especially decreasing $V_{oc}$. 
(4) Characterization: several parameters are used to evaluate the passivation quality, i.e., potential barrier height, forward and reverse leakage current, trapping state density [47], diffusion length and resistivity.

Table 2.1 Literature review of hydrogen passivation of thin-film silicon solar cells on native substrates with lift-off techniques, including the best reported electrical parameters of the corresponding technology. Note that these best parameters were not necessarily obtained on the same solar cell.

<table>
<thead>
<tr>
<th>Substrates:</th>
<th>Epitaxy</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>EpiWE</td>
<td>Porous Si lift-off</td>
</tr>
<tr>
<td>η record:</td>
<td>ISE</td>
<td>Solexel</td>
</tr>
<tr>
<td>Inst. &amp; Comp.</td>
<td>1999</td>
<td>2012</td>
</tr>
<tr>
<td>Year</td>
<td>[48]</td>
<td>[49]</td>
</tr>
<tr>
<td>Thickness</td>
<td>20 [51]</td>
<td>43 [44]</td>
</tr>
<tr>
<td></td>
<td>37 [48]</td>
<td></td>
</tr>
<tr>
<td>Electrical</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Voc (ΔV&lt;sub&gt;oc&lt;/sub&gt;)</td>
<td>661 [48]</td>
<td>650 [44]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>J&lt;sub&gt;sc&lt;/sub&gt; (ΔJ&lt;sub&gt;sc&lt;/sub&gt;)</td>
<td>32.5 [48]</td>
<td>37.8 [44]</td>
</tr>
<tr>
<td>FF (ΔFF)</td>
<td>82.2 [48]</td>
<td>77.6 [44]</td>
</tr>
<tr>
<td>η (Δη)</td>
<td>17.6 [48]</td>
<td>20.6 [49]</td>
</tr>
<tr>
<td>Temperature (Duration)</td>
<td>1100 [48]</td>
<td>250 (30) [53]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>280 (10) [54]</td>
</tr>
<tr>
<td>Pressure</td>
<td>1013 [48, 51]</td>
<td>0.0013 [55]</td>
</tr>
<tr>
<td>Hydrogenation</td>
<td>CVD-Grown</td>
<td>HII [53]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>RF-PIII [54]</td>
</tr>
<tr>
<td>Notes</td>
<td>Safety [56]</td>
<td>PSI [44]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>VEST [58]</td>
</tr>
<tr>
<td>Inst. &amp; Comp.</td>
<td>IMEC-UKN</td>
<td>IMEC, IPV, ISFH, Mitsubishi, VTT, ZAE</td>
</tr>
<tr>
<td>Characterizations</td>
<td>IV, IQE, LBIC, QSSPC, Suns-Voc, Hall [61], X-TEM [54]</td>
<td></td>
</tr>
</tbody>
</table>

Substrates: Silicon layers are grown epitaxially on a low-cost crystalline silicon substrate, i.e., epitaxial wafer equivalent (EpiWE), lift-off and epitaxy on porous Si (Porous Si lift-off), liquid phase epitaxy on low-cost silicon substrate (LPE lift-off).

Units: Active layer thickness (µm), diffusion length <i>L</i><sub>diff</sub> (µm), <i>V</i><sub>oc</sub> (mV), <i>J</i><sub>sc</sub> (mA/m²), <i>FF</i> (%), η (%), passivation temperature (°C), duration (min), and pressure (mbar).

Hydrogenation: Gas mixture in CVD when a layer is grown (CVD-Grown), Hydrogen Ion Implantation (HII), Inductively Coupled Plasma (ICP), Plasma Immersion Ion Implanter (PIII), and radio frequency (RF).

Notes: Discussion of the process safety for large area solar cells (Safety). Porous Si lift-off techniques include porous-silicon (PSI) process, Quasi-Monocrystalline Si process (QMS), and Via-hole Etching for the Separation of Thin Films (VEST).

Institutes and Companies (Inst. & Comp.): Australian National University (ANU), Institute for Photovoltaics at Stuttgart University (IPV), Fraunhofer Institute for Solar Energy Systems (ISE), Institute for Solar Energy Research Hamelin (ISFH), Laboratory for Advanced Research in Microelectronics (IMEC), Mitsubishi Electric Corporation (Mitsubishi), University of Constance (UKN), University of Iceland (HIIS), Technical Research Centre of Finland (VTT), and Bavarian Center for Applied Energy Research (ZAE).

Characterizations: Current-Voltage (IV), internal quantum efficiency (IQE), light beam induced current (LBIC), Quasi-steady state photo-conductance (QSSPC), Hall Effect for the carrier concentration and the electrical conductivity (Hall), and cross-section transmission electron microscopy (X-TEM) measurements,
Table 2.2  Literature review of hydrogen passivation of thin-film silicon solar cells on native substrates with ribbon growth techniques, including the best reported electrical parameters of the corresponding technology. Note that these best parameters were not necessarily obtained on the same solar cell.

<table>
<thead>
<tr>
<th>Substrates</th>
<th>Ribbon growth</th>
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</thead>
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<td></td>
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</tr>
<tr>
<td>η record:</td>
<td></td>
</tr>
<tr>
<td>Inst. &amp; Comp.</td>
<td>UKN, ISE,</td>
</tr>
<tr>
<td>Year</td>
<td>ECN</td>
</tr>
<tr>
<td>[Reference]</td>
<td>[62]</td>
</tr>
<tr>
<td>Thickness</td>
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</tr>
<tr>
<td></td>
<td>[62]</td>
</tr>
<tr>
<td></td>
<td>350</td>
</tr>
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<td></td>
<td>[62]</td>
</tr>
<tr>
<td>Electrical</td>
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<tr>
<td>L\text{eff}</td>
<td>92</td>
</tr>
<tr>
<td>(D L\text{eff})</td>
<td>[62]</td>
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<tr>
<td>Voc (V\text{oc})</td>
<td>596</td>
</tr>
<tr>
<td></td>
<td>(12)</td>
</tr>
<tr>
<td>Jsc (A\text{sc})</td>
<td>30.6</td>
</tr>
<tr>
<td></td>
<td>(2.4)</td>
</tr>
<tr>
<td>FF (AFF)</td>
<td>79.1</td>
</tr>
<tr>
<td></td>
<td>(3.2)</td>
</tr>
<tr>
<td>η (η)</td>
<td>14.4</td>
</tr>
<tr>
<td></td>
<td>[62]</td>
</tr>
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<td></td>
<td></td>
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<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>Temperature</td>
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<tr>
<td>(Duration)</td>
<td>(60)</td>
</tr>
<tr>
<td></td>
<td>[37]</td>
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<td>(210)</td>
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<tr>
<td></td>
<td>(30)</td>
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<td></td>
<td>[75]</td>
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</tr>
<tr>
<td></td>
<td>[37]</td>
</tr>
<tr>
<td>Inst. &amp; Comp.</td>
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</tr>
<tr>
<td>Status</td>
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<tr>
<td></td>
<td>End in 2009 [84]</td>
</tr>
<tr>
<td>Notes</td>
<td>Bayer AG [87]</td>
</tr>
<tr>
<td>Hydrogenation</td>
<td>HII</td>
</tr>
<tr>
<td>Characteristics</td>
<td>PL [46], IV, QSSPC, IQE, LBIC, Suns-Voc</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Substrates:** Ribbon Growth on Silicon (RGS), Silicon Sheets from Powder (SSP), Edge-defined Film-fed Growth (EFG), String Ribbon (SR), and Dendritic-Web Growth (D-Web).

**Electrical units:** Active layer thickness (µm), diffusion length L\text{eff} (µm), V\text{oc} (mV), J\text{sc} (mA/m²), FF (%), η (%), passivation temperature (°C), duration (min, ex., h = hours), and pressure (mbar).

**Institutes and Companies (Inst. & Comp.):** ASE Americas Inc. (ASE), Energy Research Centre of the Netherslands (ECN), Evergreen Solar Inc. (Evergreen), Fraunhofer Institute for Solar Energy Systems (ISE), Georgia Institute of Technology (GaTech), Institute for Solar Energy Research Hamelin (IFSH), Laboratory for Advanced Research in Microelectronics (IMEC), Paul Scherrer Institute (PSI), Sandia National Laboratory (Sandia), University of Constance (UKN), University of Leuven (KU Leuven), University of New Mexico (UNM), Ebara Corporation (EBARA), and Westinghouse R&D Center (Westinghouse).

**Notes:** RGS was first applied in commercial production by Bayer AG. Effusion of hydrogen (Effusion). Several chemical vapor deposition systems were compared (CVDs). Rapid thermal process (RTP). Aluminum as back surface field (Al-BSF), oxygen affected cell performance (Oxygen), process temperature profile (T. Profile), and no available (NA).

**Hydrogenation:** Hydrogen Ion Implantation (HII), Remote Plasma Hydrogen Plasma (RPHP), and Hydrogen diffusion out of a silicon nitride layer deposited by PECVD (SiN:H).
2.4.2 Foreign substrates

Both Table 2.3 and Table 2.4 are the literature reviews of hydrogen passivation on CSiTF solar cells on foreign substrates. Table 2.3 is presented the data for the solar cells on graphite [32], oxidized Si wafer [90], and ceramic substrates [91, 92]. Brendel et al. [93], Beaucarne et al. [94], and Bhopal et al. [95] reviewed thin-film solar cells on foreign substrates. The properties of graphite are discussed in Section A.1, like oxidized Si wafer and ceramic substrates, only finds wide application on a laboratory scale. However, high-temperature borosilicate glass (BSG, Schott Borofloat® 33) has been successfully developed as a substrate for commercial production. A detailed literature review is shown in Table 2.4. In 2004, CSG Solar AG (ex. Pacific Sola) developed the Crystalline Silicon on Glass (CSG) technique. Subsequently, a research group was formed comprising the University of New South Wales (UNSW), Suntech R&D Australia, and CSG Solar AG. They have been focusing on CSG for over 10 years [96]. Note that Schillinger et al. [97, 98] introduced his research on recrystallized thin-film solar cells on zircon ceramics, including the informative fabrication processing.

For the research on graphite substrates, Chu et al. [32] registered a patent about solar cells on graphite substrates at Southern Methodist University since 1970s; Rand et al. [99] at AstroPower Inc. produced approximately 100 μm thick solar cells on graphite cloth around 1993; Pauli et al. [100] reported a low-cost fabrication method for mc-Si layers on graphite substrates at the Max Planck Institute for Solid State Research (MPG-FKF) in 1996, forming seed layers by ZMR and thickening the layers using PECVD; Reehal et al. [101] reported thin-film poly-Si solar cells prepared by RF plasma-assisted CVD; Lüdemann et al. [102] realized single side contact formation using a photolithographic grid for thin-film silicon solar cells at the ISE; At the Technical University of Hamburg (TUHH), Kunze et al. [103] described thin recrystallized silicon seed layers on graphite substrates; Hauttmann et al. [104] introduced SiC formed on graphite substrates due to ZMR process. Note that their active area of the solar cells is lower than 2 cm², as an important development, 4 cm² active area solar cells are investigated in this work. Larger active area means closer to apply the cell concepts in industry, but it also means more challenges in high-quality fabrication processing.

The following points also deserve to be noted from both Table 2.3 and Table 2.4:
(1) **Performance:** The minimum thickness of the active layer on foreign substrate is approximately 1 µm to 3 µm on oxidized Si wafer and on ceramic substrates. So far, the best cell efficiency on foreign substrates is 11.8% [105]. The electrical parameters ($V_{oc} \sim 630$ mV, $J_{sc} \sim 27$ mA/cm$^2$, $FF \sim 76\%$) can be achieved.

(2) **Remote hydrogen plasma source** is commonly used for the passivation. It is thought to be able to passivate deep level defects associated with dangling bonds, to charge metal impurities at grain boundaries and/or dislocations [96], and to result in a large absolute increase in $V_{oc}$ values of approximately 50 mV.

(3) **Pre- and post-passivation:** For foreign substrates, much effort worldwide is focused on BSG, which is widely applied as a superstrate for CSiTF solar cells in commercial products. Not only the temperature and duration of the passivation process, but the conditions of the pre-passivation (warm up) and post-passivation (cooling) are also taken into account. In addition, Qiu et al. [91] mentioned that the plasma was running during the cooling process as part of the post-passivation process for cells on ceramic substrates.

(4) **Process temperature:** The proper substrate temperatures during hydrogen passivation have been widely investigated [38, 106-111], with most concentrating on the CSG cell concept. The results demonstrate that hydrogenation is most effective at high temperatures of above 600°C with a plateau time of less than 10 minutes, which results in a strong improvement of open circuit voltage. Research by Focsa et al. [112] and Carnel et al. [113] investigated the temperature dependence at temperatures of below 550°C. The authors found an optimum temperature range of 420°C to 450°C, albeit with slight improvements to $V_{oc}$ at low temperatures [25]. Carnel et al. pointed out a dependence of $V_{oc}$ on pressure, with an optimum at approximately 2 mbar [113]. In particular, $V_{oc}$ will decrease sharply when the process pressures is below 0.5 mbar. **Fig. 2.2** shows the processing duration versus average open circuit voltage curves of poly-Si solar cells in the dependence of substrate temperatures (350–600°C) [114].

(5) **Contact formation:** Beaucarne et al. [94] introduced the concept of contact formation of CSiTF solar cells on foreign substrates. The single side contact formation was schematized and formed using photolithography. Stocks et al. [115] presented the concept of CSiTF solar cells with base front-contacts.
Hebling et al. [116] realized the concept by using photolithography. Meanwhile, Lüdemann et al. [102] realized base front-contacts silicon solar cells on a SiC intermediate layer with a graphite substrate. Furthermore, Rachow et al. [117] named the concept as single side contact formation. Different microstructures of single side concepts can be formed using photolithography [115] or reactive ion etching (RIE) [118]. However, the photolithography is an expensive technology, whereas a typical RIE system consists of a vacuum chamber and a plasma generation system. Due to the development of laser techniques, laser processes are nowadays widely used in thin-film solar cell fabric processing. Such techniques can now be used to complete a solar cell with single side contact formation in fewer steps.

According to the reviews above, the RPHP method is well-suited to obtaining optimum hydrogen passivation levels, as practiced in the laboratory at the ZAE Bayern. Unlike the SiN:H method, the process of RPHP is independent from other cell fabrication processes. Therefore, the best RPHP process for CSiTF silicon solar cells on graphite substrates can be determined with regard to the following factors important in PECVD: sample positions on the sample stage, substrate temperature, process duration, process sequences, etc. The investigations in detail are shown in Section 4.1. The PECVD system is described in Section A.4.

![Fig. 2.2 Processing duration versus average open circuit voltage curves of poly-Si solar cells. The cells were passivated at different temperatures (350 °C, 400 °C, 500 °C, and 600 °C). For 500 °C and 600 °C, the average V_{oc} achieved the maximum value in 10 min.](image-url)
Table 2.3 Literature review of hydrogen passivation of thin-film silicon solar cells on foreign substrates, including the best reported electrical parameters of the corresponding technology. Note that these best parameters were not necessarily obtained on the same solar cell.

<table>
<thead>
<tr>
<th>Substrates:</th>
<th>Graphite</th>
<th>Oxidized Si wafer</th>
<th>Ceramic</th>
</tr>
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<td>ZAE 2008 [8]</td>
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<td></td>
</tr>
<tr>
<td>Inst. &amp; Comp. Year [Reference]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Active layer</td>
<td>30 [102]</td>
<td>1 to 3 [90]</td>
<td>2 [91]</td>
</tr>
<tr>
<td>Active area</td>
<td>1 [99, 102]</td>
<td>NA NA</td>
<td>1.033 [119]</td>
</tr>
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<td>Electrical</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Log</td>
<td>NA NA</td>
<td>3 [91]</td>
</tr>
<tr>
<td></td>
<td>Voc (AV)</td>
<td>570 [102]</td>
<td>520 (200) [90] ([442])</td>
</tr>
<tr>
<td></td>
<td>Jsc</td>
<td>32.3 [8]</td>
<td>14.3 [90]</td>
</tr>
<tr>
<td></td>
<td>FF</td>
<td>75.7 [102]</td>
<td>68.8 [90]</td>
</tr>
<tr>
<td></td>
<td>η</td>
<td>11.1 [8]</td>
<td>5.00 [90]</td>
</tr>
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<td>Passivation temperature (Duration)</td>
<td>400 (60) [102, 121]</td>
<td>400 (30)</td>
<td>420 (10)</td>
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<td>Lab</td>
<td>Lab</td>
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<td>Characterizations</td>
<td>Suns-Voc, 4-point probe [42], CFD [114], EBSD [129], LIBC [98], SEM [130]</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Substrates: Graphite (“FP479”, Schunk Kohlenstofftechnik GmbH), Alumina ceramic (Fox 25 smoothed). Other ceramic substrates include: mullite (Al2Si2O5), and Glass-Ceramic [94].

Units: Active layer thickness (µm), diffusion length Ldiff (µm), Voc (mV), Jsc (mA/m²), FF (%), η (%), temperature (°C), duration (min), and pressure (mbar).

Hydrogenation: Inductive Coupled Remote Plasma (ICRP), Electron Cyclotron Resonance (ECR), Remote and Direct Plasma Hydrogen Passivation (RPHP and DPHP)

Institutes and Companies (Inst. & Comp.): AstroPower Inc. (Astro), Energy Research Centre of the Netherlands (ECN), Institute of Physics of the Academy of Sciences of the Czech Republic (FZU), ICube Laboratory [ICube (ex. InESS, PHASE France)], Laboratory for Advanced Research in Microelectronics (IMEC), Fraunhofer Institute for Solar Energy Systems (ISE), Max Planck Institute for Solid State Research (MPG-FKF), Shanghai Institute of Microsystem and Information Technology (SIMIT), Technische Universität Hamburg-Harburg (TUHH), Institute National des Sciences Appliquées Lyon (INSA, includes GEMPPM), University of New South Wales (UNSW), Bavarian Center for Applied Energy Research (ZAE), and no available (NA).

Contacts: single side contact (SSC).

Characterizations: Computational Fluid Dynamics (CFD), Electron Backscatter Diffraction (EBSD), and Light Beam Induced Current (LIBC).
Table 2.4 Literature review of hydrogen passivation of poly-Si solar cells on borosilicate glass substrates, including the best reported electrical parameters of the corresponding technology. Note that these best parameters were not necessarily obtained on the same solar cell.

<table>
<thead>
<tr>
<th>Substrate:</th>
<th>Borosilicate glass</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inst. &amp; Comp.</td>
<td>Year</td>
</tr>
<tr>
<td>HZB</td>
<td>2014</td>
</tr>
</tbody>
</table>

**Active layer thickness**
- 1.4 - 2.2 [109, 132, 133]
- 10-20 [105]

**Active area**
- 0.6 [105]
- 35 [132]

**Electrical**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$L_{d_{ff}}$</td>
<td>0.6±2 [134]</td>
</tr>
<tr>
<td>$V_{oc}$</td>
<td>632 [105]</td>
</tr>
<tr>
<td>($AV_{oc}$)</td>
<td>(300) [107]</td>
</tr>
<tr>
<td>$J_{sc}$</td>
<td>27.8 [105]</td>
</tr>
<tr>
<td>($AJ_{sc}$)</td>
<td>(10) [107]</td>
</tr>
<tr>
<td>$FF$</td>
<td>67.0 [105]</td>
</tr>
<tr>
<td>$\eta$</td>
<td>11.8 [105]</td>
</tr>
</tbody>
</table>

**Warm up temperature**
- 350–480 in N Plasma (17) [135, 136]

**Passivation temperature**
- 480 (°C), (75) [135, 137]
- 600 (10), (15), (25) [114], [105], [110]
- 610 (4), (15) [106, 138], [108]
- 620 (-), (10), (15) [139], [140], [107]
- 650 (-), (20) [141], [109]
- 800 (8, 16) [136]

**Cooling temperature**
- 325 (14) [107]
- 350 (3) [109, 141] ([106, 139])
- 740 (20), 800 on [136, 138]

**Pressure (mbar)**
- 0.09 [136]
- 0.1–1.0 [139]
- 25 [110]

**Hydrogenation techniques**
- ICRP [106-108, 135, 136]
- hc-RF [139-142]
- RF-PECVD [108]
- ICRP-LPCVD [109]

**Inst. & Comp.**
- UNSW [106, 107, 109, 132, 135, 136, 143], Suntech R&D and CSG Solar AG [106, 132, 133, 138, 144], HZB [114, 132, 139, 141, 142], CSP [132], IPHT [110, 132], MPG-FKF [134]
- BSG SLG [132]

**Notes**
- BSG SLG [132]

**Status**
- Factory

**Characterizations**
- SIMS, IV, Suns-Voc, QE, PC1D [106, 107]

**Substrate**: Borosilicate glass (BSG, Schott Borofloat® 33). Most of them are used as superstrates.

**Units**: Active layer thickness (µm), active area (cm²), $L_{d_{ff}}$ (µm), $V_{oc}$ (mV), $J_{sc}$ (mA/cm²), FF (%), $\eta$ (%), temperature (°C), duration (min), and pressure (mbar).

**Hydrogenation techniques**: Inductive Coupled Remote Plasma (ICRP), Hollow-cathode Radio Frequency plasma source 13.56 MHz (hc-RF).

**Institutes and Companies (Inst. & Comp.)**: Fraunhofer - Centre for Silicon Photovoltaics (CSP), Helmholtz-Zentrum Berlin (HZB) für Materialien und Energie, Laboratory for Advanced Research in Microelectronics (IMEC), Institute of Photonic Technology (IPHT), Max Planck Institute for Solid State Research (MPG-FKF), University of New South Wales (UNSW).

**Notes**: the difference between Borosilicate Glass (BSG) and Soda-Lime Glass (SLG) was introduced in the reference.

**Characterizations**: Secondary ion mass spectrometry (SIMS).
2.5 Surface passivation: state-of-the-art

2.5.1 Single layer coating

As early as 1934, Bauer [145] reported that an accurate determination of the thickness of a crystal layer has related optical absorption characteristics. Since the 1970s, many studies have been published about the antireflection coating on silicon solar cells [146, 147]. Besides the chemical method of HF [148], several dielectric materials are widely applied as surface passivation coatings, such as hydrogenated amorphous silicon (a-Si:H) [29, 149, 150], silicon nitride (SiN$_x$) [78, 151, 152], thermal silicon oxide (SiO$_2$) [153-155], aluminum oxide (Al$_2$O$_3$) [156-159], and amorphous silicon carbide (a-SiC$_x$:H) [160-162].

High-quality surface passivation is essential for a cell to suppress surface recombination ($R_{\text{surface}}$) and to achieve high conversion efficiencies [25]. The surface recombination velocities ($S_{\text{eff}}$) and minority carrier lifetime ($\tau_{\text{eff}}$) are mainly used to evaluate the quality of surface passivation.

As demonstrated in Table 2.5, it is important to note that:

1. **Suitable methods for p- or n-Si**: The a-Si:H($i$), Al$_2$O$_3$, and SiO$_2$ are suitable dielectric films to passivate the surface of p-Si ($S_{\text{eff}} < 3$ cm/s, when the p-Si resistivity is 1–2 $\Omega$cm). Al$_2$O$_3$ is mainly applied in p-Si rear surface passivation to aluminum back-surface field (Al-BSF) cells. All four dielectric films listed in Table 2.5 are suitable for n-Si with a resistivity of 2–4 $\Omega$cm.

2. **Pros and cons**: The deposition process of SiO$_2$ has two shortcomings, i.e., high deposition process and slow deposition rate. The deposition rate of SiN$_x$ (approximately 600 nm/min) is the highest one among them. A thin a-Si:H($i$) or Al$_2$O$_3$ layer (< 10 nm) can achieve high-quality surface passivation, and therefore, in recent decades many researchers have focused on a-Si:H($i$) for the HIT n-Si cell concept and Al$_2$O$_3$ for Al-BSF on p-Si.

In this work, the a-Si:H($i$) layer is applied to passivate the surfaces of n-Si solar cells. In addition, a capping layer, i.e., the SiN$_x$ layer, is combined with the a-Si:H($i$) layer as a double-layer stack offers better cell performance than a single layer. The optical properties of a SiN$_x$ layer has also been taken in account thanks to their usefulness as an antireflection coating, as described in **Section 5.1.3**. More details about double layer coatings follow in the next section.
Table 2.5  Literature review of typical single layer coatings, including the best reported electrical parameters of the corresponding technology. Note that these best parameters were not necessarily obtained on the same solar cell.

<table>
<thead>
<tr>
<th>Dielectric Film</th>
<th>a-Si:H</th>
<th>Al₂O₃</th>
<th>SiNₓ</th>
<th>SiO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Techniques</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CatCVD [163]</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PECVD [164]</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sputtering [165]</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Deposition</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>p-Si</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>≤ 1.0 μm</td>
<td>5.8 (1.7) [164]</td>
<td>4 (2) [159]</td>
<td>1.6 [182]</td>
<td>45.8 (0.3) [155]</td>
</tr>
<tr>
<td>1-2 μm</td>
<td>3 [183]</td>
<td>2.9 (4.7) [167]</td>
<td>5 [25, 184]</td>
<td>2.4 (6.0) [185]</td>
</tr>
<tr>
<td>≥ 10 μm</td>
<td>NA [186]</td>
<td>4.2 (4.7) [180]</td>
<td>4 [181]</td>
<td>1.4 (13) [185]</td>
</tr>
<tr>
<td>n-Si</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1-2 μm</td>
<td>2.1 (3.5) [165]</td>
<td>5 (1.8) [156, 173]</td>
<td>5.2 [184]</td>
<td>2.4 (6.0) [185]</td>
</tr>
<tr>
<td>≥ 2-4 μm</td>
<td>1.5 [178]</td>
<td>0.8 (18) [167]</td>
<td>2 [174]</td>
<td>2.4 [187]</td>
</tr>
<tr>
<td>≥ 10 μm</td>
<td>NA NA</td>
<td>3.8 (5.2) [180]</td>
<td>5 (2) [188]</td>
<td>0.46 (29) [185]</td>
</tr>
<tr>
<td>Refractive indices</td>
<td>5 [189]</td>
<td>1.6 [180]</td>
<td>1.8-2.8 [174]</td>
<td>1.5 [25]</td>
</tr>
<tr>
<td>Rate</td>
<td>60 [193]</td>
<td>30 [194]</td>
<td>600 [25]</td>
<td>0.5 [195]</td>
</tr>
<tr>
<td>Pressure</td>
<td>0.003 [165]</td>
<td>0.02 [167]</td>
<td>0.2 [174, 175]</td>
<td>0.15 [174]</td>
</tr>
<tr>
<td>Post-deposition temperature (Duration)</td>
<td>200 (&gt;60) [196]</td>
<td>350 (5) [180]</td>
<td>850 (5s) [174]</td>
<td>1050 [185]</td>
</tr>
<tr>
<td>p-Si</td>
<td>300 (15) [165]</td>
<td>425 (5) [180]</td>
<td>450 (30) [173]</td>
<td></td>
</tr>
<tr>
<td>n-Si</td>
<td>400 (10) [167]</td>
<td>500 (45s) [197]</td>
<td>850 (3s) [179]</td>
<td></td>
</tr>
<tr>
<td>Classic references</td>
<td>[29, 150, 198]</td>
<td>[159, 166]</td>
<td>[78, 199, 200]</td>
<td>[153-155, 201]</td>
</tr>
</tbody>
</table>

Notes: HIT [24, 202], Calculation [203], Industry [163, 204, 205]

Techniques: Atmospheric pressure chemical vapor deposition (APCVD), Catalysis chemical vapor deposition (Cat-CVD), Plasma enhanced chemical vapor deposition (PECVD), Thermal assisted atomic layer deposition (TAALD), Plasma assisted atomic layer deposition (PAALD), Sputter deposition (Sputtering).

Units: Active layer thickness (nm), Surface recombination velocity ($S_{sr}$) (cm/s), Minority carrier lifetime ($\tau_{mr}$) (ms), Temperature (Temp. °C), Duration (min), Pressure (mbar), Rate (nm/min), and Thermal stability (°C).

Notes: related topics of HIT (HIT), the calculation of $\tau_{sr}$ (calculation), the applications in industry (Industry), and no available (NA).
2.5.2 Double layer coatings

Several combinations for double layer antireflection coating (DLARC) have been developed in recent years [206], such as SiN_x/SiO_2 [207-210], SiN_x/SiN [211, 212] SiN_x/a-Si:H(i) [213-215], and SiO_x/ITO [216]. Among these various concepts, the a-Si:H(i)/c-Si(n) hetero-interface has a high passivation quality and can be fabricated at low temperature (< 250°C). This stack is successfully applied in the HIT cell concept [217-220].

Table 2.6 reveals the following helpful information regarding SiN_x/a-Si:H(i) stack. For the thermal stability of SiN_x/a-Si:H(i), the highest process temperature tolerance was estimated at below 500°C [214, 221-223], whereas Schüttauf et al. reported the well-passivated surface working at no less than 255°C [224]. Koyama et al. [225] suggested that it is better to decrease process duration, in order to prevent the degradation of passivation quality. Mews et al. [226] introduced post-deposition hydrogen plasma treatments to improve the surface passivation (V_{oc} ~ 725 mV [227, 228]) at the a-Si:H/c-Si interface.

So far, the highest conversion efficiency of a crystalline silicon solar cell has been reported to be 25.6% (cell area: 143.7 cm²) using the HIT cell concept developed by Panasonic [24]. The usage of high-quality surface passivating films suppresses the S_{eff} at both surfaces of the HIT devices to as low as 1.5 cm/s [225].

All the experimental parameters in Table 2.6 are given with regard to high-quality double layer coatings. In addition, these parameters had to be investigated and adjusted according to the conditions of our laboratory. The details are described in Chapter 5.

2.6 Chapter summary

The fundamental principles of absorption, recombination and passivation are introduced in this chapter. The detailed reviews of bulk and surface passivation provide an overview of the corresponding state-of-the-art techniques. Previous research serves as an important reference. Moreover, the process parameters of bulk and surface passivation are investigated and developed in the context of the actual conditions in our laboratory, as shown in Chapters 4–6.
Table 2.6 Literature review of surface passivation of thin-film silicon solar cells on foreign substrates. Also shown is the best reported electrical parameters of the corresponding technology (note that these best parameters were not necessarily obtained on the same solar cell).

<table>
<thead>
<tr>
<th>Dielectric Film</th>
<th>SiNx/a-Si:H</th>
<th>SiNx/AIox</th>
<th>SiNx/SiNx</th>
<th>SiNx/SiOx</th>
</tr>
</thead>
<tbody>
<tr>
<td>Techniques</td>
<td>PECVD</td>
<td>PECVD</td>
<td>PECVD</td>
<td>PECVD</td>
</tr>
<tr>
<td></td>
<td>CatCVD</td>
<td>CatCVD</td>
<td>[211]</td>
<td>[211]</td>
</tr>
<tr>
<td>[230]</td>
<td>[231]</td>
<td>[232]</td>
<td>[231]</td>
<td>[231]</td>
</tr>
<tr>
<td>Thickness</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>100/10 [230]</td>
<td>70/30 [231]</td>
<td>65/15 [211]</td>
<td>70/15 [174]</td>
<td></td>
</tr>
<tr>
<td>70/30 [231]</td>
<td>70/15 [232]</td>
<td>70/15 [174]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.9 (5.1) [211]</td>
<td>11 (1.3) [233]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6 (2.3) [233]</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Refractive indices</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.0/3.2 [225]</td>
<td>2.0/1.61 [174]</td>
<td>1.9/2.3 [211]</td>
<td>2.0/1.47 [174]</td>
<td></td>
</tr>
<tr>
<td>2.0/1.61 [235]</td>
<td>2.0/1.47 [174]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rate</td>
<td>0.7/0.5 [225]</td>
<td>4/6 [237]</td>
<td>1.1/0.7 [211]</td>
<td>NA/1 [233]</td>
</tr>
<tr>
<td>Pressure</td>
<td>0.1/0.0055 [225]</td>
<td>0.2/0.1 [231]</td>
<td>NA/0.1 [232]</td>
<td>0.2/0.15 [174]</td>
</tr>
<tr>
<td>Post-deposition temperature</td>
<td>250 (24) [225]</td>
<td>750 (&lt;10s) [238]</td>
<td>350 (30) [232]</td>
<td>840 (60) [239]</td>
</tr>
<tr>
<td>(Duration)</td>
<td>350 (10) [214]</td>
<td>800 (&lt;10s) [231]</td>
<td>880 (25) [211]</td>
<td>800 (&lt;10s) [233]</td>
</tr>
</tbody>
</table>

Techniques: Catalysis (Cat) and Plasma enhanced (PE) CVD.

Units: Active layer thickness (nm), Surface recombination velocity (S_{off}, cm/s), Minority carrier lifetime (\tau_{off}, ms), Temperature (Temp., °C), Duration (min), Pressure (mbar), Rate (nm/min), Thermal stability (°C).

Notes: Plagwitz et al. has much helpful experience (Plagwitz), Effusion of hydrogen (Effusion), Industry CVD applications (Industrial CVD), calculation of the optical parameters (Calculation), some classical references (Classic), and no available (NA).
3 Overview of characterization techniques

Abstract

This chapter presents the optical and electrical characterization methods, discussed in greater detail in the following chapters, in order to analyze the performance of CSiTF solar cells. The resulting advantages and disadvantages for thin-film silicon cell concepts are also described in this chapter.
Typical optical and electrical characterization methods are listed in Table 3.1 [242], which shows the specific methods applied in this work, and the other important methods applied in other related works. The ZAE Bayern and i-MEET provide me with access to most of characterization methods used in this thesis; meanwhile some other institutes kindly allowed us the use of their high-precision instruments.

Table 3.1 Characterization methods for CSiTF solar cells.

<table>
<thead>
<tr>
<th>Classes</th>
<th>Methods</th>
<th>Applications</th>
<th>Loc.</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raman</td>
<td>Composition</td>
<td>ZAE [243, 244]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SE</td>
<td>Composition, roughness, thickness, refractive index</td>
<td>ZAE [245, 246]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>FIB-STEM</td>
<td>Topography and composition</td>
<td>WW1 [247, 248]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4T sensing</td>
<td>Sheet resistance</td>
<td>ZAE [249]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>J-V curve</td>
<td>$V_{oc}$, $J_{sc}$, FF, $R_s$, $R_p$, $\eta$</td>
<td>ZAE [260]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>In this work:</td>
<td>QSSPC &amp; $\mu$PCD</td>
<td>Carrier lifetime</td>
<td>ZAE [250, 251]</td>
<td></td>
</tr>
<tr>
<td>PL</td>
<td>Carrier lifetime, diffusion length, voltage, series resistance, $I_{dark}$</td>
<td>ZAE [252]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>EL</td>
<td>Defects, recombination centers, resistance and shunt</td>
<td>ZAE [253]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>LBIC</td>
<td>Recombination centers, electrical defects</td>
<td>ZAE [254]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>QE</td>
<td>energy dependence of the photocurrent loss</td>
<td>ZAE i-MEET [23], p.210</td>
<td></td>
<td></td>
</tr>
<tr>
<td>LIT</td>
<td>Shunts</td>
<td>ZAE [255, 256]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C-V</td>
<td>Doping profile, electrically active defect densities</td>
<td>ZAE [257, 258]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>DLTS</td>
<td>Defects, e.g. charge carrier traps</td>
<td>LAP [259]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>EBSD</td>
<td>Crystal orientation mapping, defect studies, phase identification, grain boundary, morphology studies</td>
<td>WW1 [260]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>FTIR</td>
<td>Absorption, emission, photoconductivity, Raman scattering</td>
<td>ZAE [261]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SIMS</td>
<td>Composition of solid surfaces</td>
<td>LKO [262]</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Abbreviations of measurement methods in this work: Electroluminescence Lock-in (ELLI), Photoconduction (PC), Photoluminescence (PL), 4-point probes method (4T sensing), Raman spectrometry (Raman), Spectroscopic ellipsometer (SE).

Other methods in related work: they are NOT included in this work but in related scientific research. Capacitance-Voltage profiling (C-V), Deep Level Transient Spectroscopy (DLTS), Electron Backscatter Diffraction (EBSD), Fourier Transform Infrared spectroscopy (FTIR), Secondary Ion Mass Spectroscopy (SIMS).

Locations: Chair of Applied Physics at FAU (LAP), Chair for Surface Science and Corrosion at FAU (LKO), University of Konstanz (UNK), Materials Science and Engineering at FAU, Institute I (WW1) and Institute IV (i-MEET), ZAE Bayern (ZAE).
3 Overview of characterization techniques

3.1 Optical characterization

3.1.1 Raman spectrometry

Raman spectrometry is used to identify the compositions in silicon solar cells. A composition with a crystal structure will be easily to be identified due to its characteristic Raman peaks. A confocal Raman imaging microscope (alpha 500AR, manufactured by WITec GmbH) was used for the Raman measurements. For excitation a frequency doubled Nd:YAG laser at 532 nm was used, which resulted in a penetration depth in silicon of approximately 0.5 µm [10, 263]. Raman spectrometry is applied in this work to distinguish between crystalline and amorphous silicon.

3.1.2 Spectroscopic ellipsometer

Ellipsometry is a non-destructive and precise technique for the characterization of nm-scale layers on silicon solar cells to determine film thickness and optical constants. An ellipsometer measures a change in polarization as light reflects or transmits from a material structure. The polarization change is represented as an amplitude ratio and the phase difference. The measured response depends on optical properties and the thickness of individual materials. Thus, for a multi-layer solar cell, it is necessary to identify and determine the thickness and optical constants film by film.

There are two ellipsometers used in this work. As shown in Section 5.1.2, the optical parameters, such as the refractive index and the film thickness of a-Si:H(i) on float-zone (FZ) Si wafers, were measured using the variable angle spectroscopic ellipsometer (VASE, J. A. Woollam Co. Inc.), i.e., SE-VASE. For the SiNx/a-Si:H(i) stacks on graphite-based solar cells, the optical parameters of the SiNx/a-Si:H(i) stacks were characterized using the other SE (EL X-04, DRE-Dr. Riss Ellipsometerbau GmbH), i.e., SE-ELX04, at the Department of Glass and Ceramics at FAU.

3.1.3 Focused ion beam - scanning transmission electron microscope

In order to attain sufficient resolution for imaging the thin-film cross-sections, electron transparent lamellae were prepared by means of the focused ion beam (FIB) lift-out technique and investigated by scanning transmission electron microscopy (STEM) inside the SEM. The preparation as well as the imaging was conducted inside the Dual Beam FIB Helios NanoLab 600i (FEI, Hillsboro, OR, USA) equipped with a Schottky field emitter. The access of FIB-STEM measurement was provided by Prof. Mathias Göken at the Materials Science and Engineering, Institute I, at the FAU.
The sample preparation steps are: After locating a flat and homogeneous area on the sample surface, a protective platinum layer of 400 nm was deposited via electron-beam-induced CVD which was grown to about 3 µm by subsequent ion-beam-deposition. From the protected area a 1.5 µm thick lamella was isolated and transferred to a copper grid by the standard in-situ lift-out procedure using a micromanipulator [247]. As described in M. Schaffer et al. [248], the thinning of the lamella was carried out in a wedge shaped manner using low beam currents and gradually decreasing the acceleration voltage from 30 kV to 8 kV. After reaching a thickness of about 200 nm, low-kV-cleaning at 5 kV, 2 kV and finally 1 kV at sample tilts of 6 to 9 degrees was applied in order to reduce damage and artifacts introduced by the FIB. The final lamella with a thickness of approximately 65 nm was investigated in transmission at an electron acceleration voltage of 30 kV using a retractable STEM-detector.

In this work, the cross section of the lamella of the CSiTF solar cells was prepared and characterized by FIB-STEM, and those results were compared with the results from SE, as presented in Section 6.2.2.

3.2 Electrical characterizations

3.2.1 Photoconduction techniques

Quasi-steady state photo-conductance (QSSPC) was applied to measure carrier lifetime using Sinton WCT-100. Charge carriers can be excited by a flash lamp whose light intensity and decay time are adjustable for different applications.

As the light decay time is larger than the carrier lifetime, the sample is in a quasi-steady state and the absolute carrier lifetime can be measured. The following points must be taken into account when measuring with a Sinton WCT-100:

1. The measurement result is not a high resolution carrier lifetime mapping.
2. Sample must be not thicker than 2 mm. However, in our case, a graphite substrate is already 2 mm thick.
3. It is not suitable to measure finished devices.

On the other hand, the microwave-detected photo conductance decay (µPCD) method typically operates at very high injections with a very short light pulse of only 200 ns. Effective minority carrier lifetime mappings are measured via the photoconductive decay using a SemiLab WT2000. The µPCD detects the photoconductivity by measuring the reflection of a microwave at the sample. This
method can measure parameters of not only a wafer but also a completed solar cell, and therefore it is frequently used in laboratory.

However, due to the extreme difference in thickness between the substrate (2 mm) and the active cell (40 μm), it is hard to characterize the carrier lifetime and the surface recombination velocity using the photoconductive techniques. Furthermore, both the graphite and the SiC intermediate layer are electrically conductive. Consequently, the signals from the experiments, i.e., QSSPC and μPCD, were severely disturbed [15].

### 3.2.2 Photoluminescence techniques

An Equus 327k NM infrared (IR) camera (IRCAM GmbH, Erlangen, Germany) was used to capture the photoluminescence (PL), which is excited from samples using a light source. The camera is equipped with a cooled indium-gallium-arsenide (InGaAs) FPA detector (Resolution: 640 × 512 pixels, spectral response: 0.8 ~ 1.8 μm, frame rate: 60 Hz, and standard lock-in detection was applied). Two kinds of light sources were applied for PL:

1. White light LED array (Citizen Electronics Co., Ltd.) in the range from 410 to 780 nm. The LEDs can illuminate a large area of 40 × 40 cm at a power of 30 W/m² [264]. Its drawback is that its power is not high enough to fulfil the AM1.5G standard (IEC 60904-3:2008 and/or ASTM G-173-03 global) requiring a power of 1000 W/m². PL imaging was supposed to evaluate the passivation quality in the value of effective carrier lifetime [265, 266]. This

---

**Fig. 3.1** The μPCD imaging (left) and PL imaging with weight LED (right) of the back side of a 1.5 Ωcm 4 inch FZ Si wafer, i.e., sample P033b, on which an a-Si:H(i) layer was deposited at 350 °C for 90 sec.
technology is still in its early stages at the ZAE Bayern. As shown in Fig. 3.1, so far, the challenge is this: it is difficult to find any correlation between the two sets of test results.

(2) LED arrays (Future LED GmbH, 700 LEDs with 22 different wavelengths between 400 nm ~ 1050 nm, duration of exposure between 2 ms and 10 min) were used as an AM1.5G spectrum light source or quasi monochrome light source [267]. Its drawback is that the effects of the light source must be filtered from PL mapping. Fig. 3.2 shows that the PL system is working and samples are illuminated under a quasi-blue light source.

3.2.3 Electroluminescence techniques

Spatially resolved electroluminescence (EL, i.e., ELLI) imaging was developed as a standard tool for the quality control of finished CSiTF solar cells. Defects (e.g. a crack or a broken finger) and recombination centers (e.g. low \( L_{\text{diff}} \) areas due to dislocation or grain boundaries) [253] can be observed. For EL imaging in this work, the same IR-camera was used as for PL. During the measurement the finished devices were biased with 1.5 V in forward direction [268].

3.2.4 Light beam induced current

Spatially resolved efficiency of a complete solar cell is determined by measuring current induced by light (LBIC). High resolution mapping allows the visualization

![Fig. 3.2 Photograph and schematic of PL Setup with LEDs light source at the ZAE Bayern. The system was working under quasi-blue light.](image-url)
and localization of shunts and other defects that decrease cell efficiency and cell lifetime. LBIC can provide information critical for successful cell processing.

LBIC measurement is carried out using a SemiLab WT2000, which has four light sources (976 nm, 951 nm, 846 nm, and 662 nm). The diffusion length mapping is calculated by the instrument itself from the LBIC measurements at various wavelengths.

### 3.2.5 Quantum efficiency

External quantum efficiency ($E_QE$) measurements are performed on an Enlitech solar cell analysis system QE-R in the range of 300 nm to 1200 nm, which includes a spectrometer with integrating spheres used to measure $R(\lambda)$ of the cell. $E_QE(\lambda)$, the measure of electron flow under short-circuit conditions into the external circuit per photon incident onto the solar cell, can be converted to internal quantum efficiency $I_QE(\lambda)$ if the total hemispherical reflectance $R(\lambda)$ and transmittance $T(\lambda)$ are known. $I_QE(\lambda)$ is then given by

$$I_QE(\lambda) = E_QE(\lambda) / [1 - R(\lambda) - T(\lambda)]$$  \hspace{1cm} (3-1)

The measured $E_QE$ data are then used to calculate the corresponding $J_{sc}$ of the solar cell under AM1.5G illumination. In 1997 Clugston et al. [269] at the Research Centre at the University of New South Wales developed the computer program PC1D for

![Fig. 3.3 IQE features and the corresponding cell parameters of crystalline silicon in PC1D. (a) Surface recombination, (b) Emitter, (c) Space charge region and bulk, (d) $L_{diff}$, (e) Rear recombination, (f) Rear reflection, and (g) Layer thickness.](image)

35
personal computers, which can solve the coupled nonlinear equations for the quasi-one-dimensional transport of electrons and holes in crystalline semiconductor devices. The IQE curves can be fitted by the PC1D program, which can predict the performance of each part and obtain the corresponding values of e.g. diffusion length, effective front and rear surface recombination. More details will be given in Sections 6.1.3 and 6.2.4. The measured IQE and fitting by PC1D are used to analyze the cell performance as shown in Fig. 3.3, which shows the response of each part of a solar cell, e.g. emitter, space charge region and the bulk. They correspond to the wavelength of incident.

3.2.6 Lock-in thermography

Lock-in thermography (LIT) techniques fall mainly into one of two categories: dark lock-in thermography (DLIT) and illuminated lock-in thermography (ILIT) [256], p.214. Various reverse biases are applied in DLIT for locating the electrical loss positions, while small surface temperature differences are measured using a high spatial and thermal resolution infrared (IR) camera. Then, the measured temperature differences can be interpreted to give the values of shunt, saturation current, or resistivity. The lock-in components minimizes the noise-signal rate, which is effective at detecting defects with a weak response to excitation.

ILIT was introduced since 2004 [270-272]. In ILIT, a solar cell is excited by a pulsed light source. Under both the $V_{oc}$-condition (i.e., the solar cell or module is not externally connected) and the $J_{sc}$-condition (i.e., the cathode and anode of solar cells are directly connected), ILIT displays considerable advantages, being time-efficient, contactless, and non-destructive. Furthermore, ILIT can measure solar cells and modules when they are in operation.

At the ZAE Bayern, Adams et al. [273] established an LIT imaging system with an Equus 327k IR-camera (IRCAM GmbH, Erlangen, Germany), which is controlled by a computer for real-time lock-in calculations for the $V_{oc}$-DLIT, $J_{sc}$-DLIT, $V_{oc}$-ILIT and $J_{sc}$-ILIT measurements. The camera uses an InSb (indium antimonite) focal plane array detector ($640 \times 512$ pixels) cooled by a stirling engine and is highly responsive in the wavelength range between 1.5 $\mu$m and 5 $\mu$m. The typical frame rate is 100 Hz and the noise equivalent temperature difference is less than 20 mK. White LEDs (Citizen Electronics) were used for periodic excitation of the solar modules. Each LED had an electric power of 7 W and a spectral range from 410 nm to 780 nm with a spectral peak at 440 nm. More details will be given in Section 6.2.5.
3.3 Chapter summary

The common methods of optical and electrical characterization and simulation methods used for CSiTF solar cells in this work have been introduced. The spatially resolved techniques, such as EL, PL, and LIT, are time-efficient, simple, and swift, which meet the requirements both in laboratory and in industry. The resolution of the resulting images depends on the resolution of the camera. These techniques are alternatives to LBIC. The measurement duration of an EL imaging is approximately two orders of magnitude shorter than an LBIC mapping (tens of micrometer scale). In addition, these techniques, i.e., EL, PL and LIT, can be used to inspect entire cells or modules but also to visualize microscopic defects on the micrometer scale.
3 Overview of characterization techniques
4 Hydrogen passivation and laser single side contact

Abstract

The PECVD system in our laboratory was tested and adjusted to run under the best working conditions, in order to achieve high-quality bulk hydrogen passivation, and furthermore to increase cell performance.

The cell structures, including laser single side contact formation, and the fabrication sequences were designed and prepared on reference silicon wafers. Via a comparison of those results, the best process sequences of hydrogen passivation and properly experimental parameters were determined, which were finally applied in the production of CSiTF solar cells on graphite substrates.

Results given here have, in part, been published elsewhere (reproduced with permissions):

As described in Section 2.4, PECVD systems with a remote plasma source have been widely applied in performing high-quality passivation and depositing uniform thin films. Under laboratory conditions, a PECVD system with a small-scale chamber, e.g. Oxford Instruments PlasmaPro 800 (approximately 3 Liters), is easier to be operated precisely than a large-scale chamber, e.g. a Roth & Rau AK1000 system at the ZAE Bayern (approximately 250 Liters), which was set up around 2001 [275]. Earlier publication regarding the operation of the AK1000 system are valuable references [8], however, it is essential at the outset of this work to re-investigate the system under current conditions. The investigation of the AK1000 system is introduced in Section A.4 in details.

4.1 Hydrogen bulk passivation

The experimental conditions were designed to deliver high-quality hydrogen passivation. The homogeneity of the hydrogen passivation effect and the best processing sequence were the focus of this work, and were realized using the two strategies:

(1) to explore the structure and the function of PECVD,
(2) to prepare the samples for hydrogen passivation on reference silicon wafers, in order to optimize their parameters, e.g. position, duration, and temperature.

In this case, hydrogen passivation was carried out using a PECVD system (the AK1000 system) with microwave excitation frequency at 2.45 GHz and hydrogen used as the precursor. Unless explicitly stated otherwise, the parameters in this chapter for hydrogen passivation are as the same as shown in Table 4.1.

<table>
<thead>
<tr>
<th>Table 4.1 PECVD and references’ parameters.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Items</strong></td>
</tr>
<tr>
<td><strong>PECVD</strong></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td><strong>Glass reference</strong></td>
</tr>
<tr>
<td><em>(Borofloat® 33)</em></td>
</tr>
<tr>
<td></td>
</tr>
</tbody>
</table>
4.1.1 Heating stage

In order to investigate the temperature distribution on the sample stage, the graphite plate on the top of the heating stage was removed. As shown in Fig. 4.1, two flat heating elements inside can be observed. Subsequently, the heating element was recovered with the graphite plate and five measurement positions were chosen, where samples are frequently placed. Fig. 4.1(a) shows the setup of the heating stage and gives these five measurement points (#1 to #5).

In Fig. 4.2 the temperature curves were measured for 2000 sec at these four positions (#1 to #4) on the graphite plate using the Thermal Barrier TB7400A system at atmospheric pressure. The actual average temperature on the sample stage was...
measured at a value of 350°C with a deviation of ±25°C, when the temperature was set at 500°C in the controlling program. The #5 is the most used position in our cell fabrication processing. At this position the temperature curve was measured by non-contact infrared thermometer (optris® Laser Sight MSPlus, working range of -32°C to 530°C) at atmospheric pressure. Fig. 4.3 shows the preset and measured temperature curves. The related difference between preset and measured temperature must be taken into account in experiment designs. Nevertheless, for high-quality passivation, the temperature-increasing decay and the temperature limit of the PECVD cannot be neglected in the following research. The decay is probably due to the large chamber, which is hard to warm up or cool down rapidly.

Note that the substrate temperature will change with the pressure in the chamber. Thus, each fabrication process can only be started once the temperature and pressure have become stable. It also means that the cell performance is affected by the time for warming up and cooling down. In an ideal situation, the durations for warming up and cooling down would be controlled and minimized.

4.1.2 Position

In Fig. 4.4 two wafers (7.8 cm × 7.8 cm) were used for the investigation of the best position of the hydrogen passivation process. In order to ensure the comparability, both wafers are cut from a standard mc-Si wafer (15.6 cm × 15.6 cm).

Fig. 4.3 Preset and measured temperatures at the position #5 on the heating stage in the PECVD Chamber.
Wafer 1 was under microwave source 2. There were two rectangular boron glasses on the wafer, in order to stop the sample being blown away. The wafers were put into the PECVD chamber at 350°C for 30 minutes.

Wafer 2 was on the edge of the stage, in order to demonstrate the passivation effect at different substrate temperatures. The part of the wafer was out of the range of the heating stage, resulting in a lower temperature.

After the hydrogen process, the wafers’ surfaces have the same color as before the process. Therefore, they were characterized using µPCD measurement. As shown in Fig. 4.4 (a), the part of Wafer 2 without hydrogen is brown, which corresponds to a carrier lifetime with a value of approximately 0.68 µs, whereas the lifetime of the passivated part in deep blue is approximately 1.2 µs.

The results demonstrate that the hydrogen plasma can pass through the gaps at the edges of the boron glass and enter the covered area. Moreover, the quality of the passivation is highly dependent on the position on the heating stage and the substrate temperature.

4.1.3 Duration

The next investigation is focused on the duration of the hydrogen passivation process. Eight wafers (7.8 cm × 7.8 cm) were passivated with four different durations
(a) Top view of heating stage

Position 1

Position 2

(b) Carrier lifetime mappings

30 min 45 min 60 min 75 min

30 min 45 min 60 min 75 min

1.4 us 2.8 us

Fig. 4.5  Carrier lifetime mapping (Raster: 1 mm) of the wafers after hydrogen passivation with different durations (30 min, 45 min, 60 min, and 75 min).

(30 min, 45 min, 60 min, and 75 min). During each passivation process, two wafers were placed on two positions simultaneously under the microwave sources 1 and 2 (Position 2 and 1, respectively).

As shown in Fig. 4.5, at Position 1 the wafer achieves the highest value for carrier lifetime and the passivation is also homogeneous. Otherwise, at Position 2 the wafers have lower values in lifetime and are not uniform, probably due both to more microwave (MW) reflection back to the MW generator and to the non-uniform temperature distribution of the heating stage. The results prove that the hydrogen passivation duration is ideally set up within a range of 45–75 min, which induces optimum and homogeneous distributions of the hydrogen passivation results.

4.2 Laser single side contact

There are two contact formations widely applied in solar cells: both-sided contact and single-side contact. For both-sided (front and back) contact, an aluminum base contact can be evaporated on the back as a back side contact. Based on the development of laser technology, the back base contacts can be fabricated on the front using a laser process, i.e., laser single side contacts (LSSC) instead of the Al back base contacts. Here a Nd:YVO₄ laser system (Rofin Power Line LP20, wavelength 1064 nm) was used at a power of 5.1 W to make approximately 30 µm deep trenches into the samples down to the $p^+$-Si layer and to obtain 3 mm wide contact strips around the cells. After the laser trenching and LEI process, the emitter contacts and
the base contacts were evaporated on the front at the same time and with the same metals Ti, Pd, and Ag (30 nm, 30 nm and 5 μm thick, respectively).

4.3 Solar cells on Si-wafer substrates

As shown in Table 4.2, there are five batches (Waf.A–E) of the finished cells used for comparing of the effects of LSSC, hydrogen passivation, and the process sequence of hydrogen passivation. Here, Waf. denotes that a batch is based on Si-wafer substrates. Fig. 4.6 shows the reference batch Waf.A on mc-Si wafer with the epitaxial layer in the thickness of 20 nm, without LSSC but with the standard both-sided contact formation, whereas the LSSC formation is applied in Waf.B. Fig. 4.6 (a) and Fig. 4.7 (a) illustrate that nine cells are fabricated on each wafer.

In order to confirm the improvements conferred by LSSC formation and hydrogen passivation, the results of the reference batches (Waf.A-C) were further compared. As shown in Table 4.3, the reference (Waf.) batches exhibit similar variations in $V_{oc}$ and $FF$, which can be described by:

$$V_{oc} (Waf.A) < V_{oc} (Waf.B) < V_{oc} (Waf.C)$$
$$FF (Waf.A) < FF (Waf.B) < FF (Waf.C)$$

those inequalities indicate that the batches with LSSC formation have better

![Image](image_url)

Fig. 4.6 (a) Top view of Waf.A. (b)–(c) Structure and fabrication process sequence of Waf.A with both-sided contact without HP process.
performance than the batches with both-sided contact formation. Moreover, hydrogen passivation reduced the bulk recombination, and therefore the batches with both LSSC formation and hydrogen passivation applied have the best performance in $V_{oc}$.

In addition, Fig. 4.8 illustrates the $J$-$V$ and IQE curves of the best cells in Waf.$B$ and Waf.$C$, which also indicates that hydrogen passivation can greatly improve cell performance.

### Table 4.2 Sample list on $p$-Si wafer substrates in this chapter.

<table>
<thead>
<tr>
<th>No.</th>
<th>Names in Chapter</th>
<th>Names in Record</th>
<th>H$^+$ pass</th>
<th>Formation</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Waf.$A$</td>
<td>ALZ514</td>
<td>Both-sided</td>
<td>ALZmcSi$_n$</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Waf.$B$</td>
<td>ALZ513</td>
<td>LSSC</td>
<td>ALZmcSi$_LSSC$</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Waf.$C$</td>
<td>ALZ511</td>
<td>50</td>
<td>LSSC</td>
<td>ALZmcSi$_LSSC_H$</td>
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<td>4</td>
<td>Waf.$D$</td>
<td>ALZ496</td>
<td>50</td>
<td>LSSC</td>
<td>Waf.process</td>
</tr>
<tr>
<td>5</td>
<td>Waf.$E$</td>
<td>ALZ497</td>
<td>50</td>
<td>LSSC</td>
<td>Waf.process</td>
</tr>
</tbody>
</table>

Fig. 4.7 Hydrogen passivation for the solar cells based on the mc-Si wafers with epitaxial $p^+$ layer. (a) Top view of the Waf.$B$. The top views of Waf.$B$–$E$ are similar. The white square frames around the nine cells are the LSSC covered by metal grid. (b) Schematic of the cell structure. The structures of Waf.$B$–$E$ are similar. (c) Fabrication process.
Hydrogen passivation and laser single side contact

Subsequently, the LSSC formation and hydrogen passivation with different process sequences was applied to batches $Waf.C-E$. This is the preliminary study for the fabrication of cells on graphite substrates. The process sequence is critical for hydrogen passivation. As shown in Fig. 4.9 (a), in order to determine the best fabrication sequence for hydrogen passivation, three different process sequences were prepared and compared. For this study, the reference system on wafer substrates was used in order to exclude influences from varying defect structures, as they may result from the recrystallization process. As shown in Fig. 4.9 (a), the hydrogen passivation process was included after

- SOD diffusion processing ($Waf.C$);
- laser trenching and LEI ($Waf.D$);
- metallization processing ($Waf.E$).

Comparing the results of these three batches ($Waf.C-E$) in Fig. 4.9 (b) and Table 4.3, the best hydrogen passivation sequence is the hydrogen bulk passivation process of $Waf.C$. This batch has the highest average values of parallel resistance $R_p$ ($\overline{R_p}$), open circuit voltage $V_{oc}$ ($\overline{V_{oc}}$) and fill factor $FF$ ($\overline{FF}$) among the three batches.

In the case of $Waf.D$, the hydrogen passivation was applied after the laser trenching and LEI process. This process sequence resulted in lower cell performance than $Waf.C$, which is most probably due to laser induced defects. Slaoui et al. [276] reported the hydrogen passivation of laser induced defects, which demonstrated that

![Fig. 4.8 J–V curves (left) and IQE curves (right) of the best cells in Batches Waf.B–C. The cell performance was improved using the hydrogen passivation process.](image)
the quality of hydrogen passivation highly depends on the temperature of the passivation process.

In the case of \textit{Waf.E}, the contacts were already evaporated before the hydrogen passivation process. As described above, hydrogen bulk passivation was not applied in \textit{Waf.A}. Comparing \textit{Waf.A} and \textit{Waf.E}, \(V_{oc}\) and \(J_{sc}\) of \textit{Waf.E} increased slightly due to the hydrogen bulk passivation. However, this process sequence resulted in a much lower \(R_p\) than \textit{Waf.C}, which further resulted in a low \(FF\). This was presumably due to the fact that the front contacts (Ag/Pd/Ti) penetrated through the thin emitter layer into the base layer during the passivation process at 350°C [277].

Accordingly, the best hydrogen passivation sequence was made directly after the phosphor diffusion process, which was also applied to fabricate the cells on graphite substrates as shown in \textbf{Section 6.1}.
Table 4.3  Cell parameters. Open circuit Voltage \( (V_{oc}) \), parallel resistance \( (R_p) \), series resistance \( (R_s) \), current density \( (J_{sc}) \), fill factor \( (FF) \), and efficiency \( (\eta) \). The highest efficiency is highlighted in bold.

<table>
<thead>
<tr>
<th>Batches</th>
<th>Contacts</th>
<th>( H^+ ) (min)</th>
<th>( R_p ) (( \Omega \text{m}^2 ))</th>
<th>( R_s ) (( \Omega \text{cm}^2 ))</th>
<th>( V_{oc} ) (mV)</th>
<th>( J_{sc} ) (mA/cm(^2))</th>
<th>( FF ) (%)</th>
<th>( \bar{\eta} ) (%)</th>
<th>Best ( \eta ) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Waf. A</td>
<td>Both-sided</td>
<td>-</td>
<td>1.08</td>
<td>2.22</td>
<td>450</td>
<td>25.5</td>
<td>49.0</td>
<td>5.74</td>
<td>7.68</td>
</tr>
<tr>
<td>Waf. B</td>
<td>LSSC</td>
<td>-</td>
<td>2.51</td>
<td>2.77</td>
<td>501</td>
<td>25.0</td>
<td>57.0</td>
<td>7.18</td>
<td>8.19</td>
</tr>
<tr>
<td>Waf. C</td>
<td>LSSC</td>
<td>50</td>
<td>3.18</td>
<td>2.85</td>
<td>534</td>
<td>26.3</td>
<td>58.7</td>
<td>8.29</td>
<td>10.1</td>
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<tr>
<td>Waf. D</td>
<td>LSSC</td>
<td>50</td>
<td>0.33</td>
<td>3.24</td>
<td>465</td>
<td>23.9</td>
<td>49.2</td>
<td>5.52</td>
<td>7.77</td>
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<tr>
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<td>LSSC</td>
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<td>0.03</td>
<td>2.21</td>
<td>467</td>
<td>26.7</td>
<td>47.7</td>
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<td>7.14</td>
</tr>
</tbody>
</table>

4.4 Chapter summary

Hydrogen passivation and LSSC formation are investigated and introduced in this chapter for CSiTF solar cells on the epitaxial layers on Si-wafer substrates. The optimum experimental conditions and the best hydrogen passivation sequence are studied to determine further applications for silicon solar cells on graphite substrates.

The \( J-V \) and QE results demonstrate that the two new strategies, i.e., LSSC formation and the hydrogen bulk passivation process, can improve CSiTF solar cell performance at a low process temperature. Both methods result in an increase of \( V_{oc} \) and \( FF \). 10.2\% cell efficiency was achieved on an aperture area of 4 cm\(^2\) on the reference cells. Therefore, these two new concepts were applied in the solar cells on graphite substrates, as described in Chapter 6.
Section 4: Hydrogen passivation and laser single side contact
5 a-Si:H(i) surface passivation

Abstract

Hydrogenated intrinsic amorphous silicon [a-Si:H(i)] was investigated as a surface passivation method for crystalline silicon thin-film solar cells on glass substrates and reference silicon wafers.

The optical and electrical parameters of the thin intrinsic a-Si:H(i) films were characterized using a Raman spectrometer, a µPCD and spectroscopic ellipsometers. Moreover, the SiNx/a-Si:H(i) stack was designed with double-layer antireflection coatings, which were applied in the finished solar cells on the reference silicon wafers. The characterization results demonstrated the improvements in cell performance due to the application of a-Si:H(i) layers as the surface passivation method.

Results given here have, in part, been published elsewhere (reproduced with permissions):

At the ZAE Bayern, this is the first time that SiN$_x$/a-Si:H(i) stacks for CSiTF solar cells on foreign substrates have been thoroughly studied using the Roth & Rau AK1000 system. As given in Section 2.5, the optimal thickness of an a-Si:H(i) layer is approximately 10 nm [218, 278], however, in this work related, optimal experiment conditions must be investigated for optimal passivation, refractive index ratio, and thickness ratio of SiN$_x$/a-Si:H(i) stacks under our conditions. The strategies of the studies include:

1. verifying the existence of a-Si:H(i) via Raman spectrometry;
2. verifying the passivation effect of a-Si:H(i) via µPCD;
3. simulating the optimal refractive index and thickness ratios for further research.

Because from now on a-Si:H(i) is introduced, the nomenclature of Si layers will be changed to avoiding confusion, while contents include a-Si:H(i). For example: c-Si(p), c-Si(n), and c-Si(n$^+$) correspond to p-Si, n-Si, and n$^+$-Si, respectively.

5.1 Experimental details and results

5.1.1 SiN$_x$/a-Si:H(i) stacks on glass substrates

At the beginning of the investigation of the SiN$_x$/a-Si:H(i) stacks, the different thickness combinations of SiN$_x$/a-Si:H(i) stacks were deposited on the glass substrates (Schott Borofloat® 33) as the preliminary study. The samples and the references are shown in Fig. 5.1, meanwhile the corresponding parameters are listed in Table 5.1. These stacks were afterwards surveyed using a Raman spectrometer to identify whether any crystalline silicon exists in these stacks.

The results of the Raman spectrometer were acquired using a 20× objective lens (numerical aperture 0.4), as shown in Fig. 5.2. No typical Raman peak of crystalline silicon (520 cm$^{-1}$) can be observed in the samples with SiN$_x$/a-Si:H(i) stacks. Therefore, the deposited layers are verified to be amorphous silicon layers. For a-Si:H(i) layers, the gas flow ratio of the precursor H$_2$:SiH$_4$ was 240:50 sccm:sccm; for SiN$_x$ layers, the gas flow ratio of the precursor for NH$_3$:SiH$_4$ was 81:69 sccm:sccm. The deposition rate of the a-Si:H(i) layer is approximately 90 nm/min. The typical broad peak below 500 cm$^{-1}$ and small peaks between 750 cm$^{-1}$ and 1250 cm$^{-1}$ belong to the glass substrate (SiO$_2$). The curves (a)–(d) in Fig. 5.2 indicate that the signals of a-Si are too weak to be observed when the a-Si:H(i) thickness is below 350 nm. The curves (e)–(f) demonstrate when the duration of a-Si layer deposition is more than 300 sec, a large board peak can be observed from 1500 cm$^{-1}$ to 3500 cm$^{-1}$. The curve
(g) shows when the duration of SiN\(_x\) layer deposition is more than 300 sec, the signals from a-Si will be hidden.

![Image](image.png)

**Fig. 5.1** Top views of the samples on glasses and the references for Raman spectrometer. The sample names and the corresponding parameters are listed in Table 5.1.

<table>
<thead>
<tr>
<th>Process duration (sec)</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>a-Si:H(i)</td>
<td>SiN(_x)</td>
</tr>
<tr>
<td>(a) 15</td>
<td>0</td>
</tr>
<tr>
<td>(b) 30</td>
<td>100</td>
</tr>
<tr>
<td>(c) 120</td>
<td>120</td>
</tr>
<tr>
<td>(d) 300</td>
<td>120</td>
</tr>
<tr>
<td>(e) 600</td>
<td>120</td>
</tr>
<tr>
<td>(f) 600</td>
<td>0</td>
</tr>
<tr>
<td>(g) 600</td>
<td>300</td>
</tr>
<tr>
<td>(h) 0</td>
<td>0</td>
</tr>
<tr>
<td>(i) 0</td>
<td>0</td>
</tr>
</tbody>
</table>

### Table 5.1 The parameters of the a-Si and SiN\(_x\). The duration of depositions is to be considered as corresponding directly to the thickness of the films.

5.1.2 Carrier lifetime of a-Si:H(i) on silicon substrates

It is difficult to characterize the a-Si:H(i) coatings on the CSiTF solar cells based on graphite substrates, due not only to the thin a-Si:H(i) layer, but also the rough and irregular shaped a-Si:H(i)/c-Si\((n^+)\) interface [15]. As mentioned in **Section 3.2.1**, because of the extreme difference in thickness between the substrate (2 mm) and the active cell (40 µm), it is hard to characterize the carrier lifetime and the surface
a-Si:H(i) surface passivation

recombination velocity using the photoconductive techniques. Therefore, the a-Si:H(i) layers were deposited on Si-wafer reference wafers, and then they were characterized using μPCD method.

Therefore, the optical and carrier lifetime properties of the a-Si:H(i) layers on the planar FZ p-type c-Si reference wafers (single-side polished, boron-doped, 0.5 Ωcm resistivity and 280±15 μm thick) were investigated. For each parameter study in this work, small pieces were used cut from one and the same 5-inch reference wafer. The a-Si:H(i) coatings were prepared on the polished side of these small pieces. The optical parameters, such as the refractive index and the film thickness of a-Si:H(i), were measured using the SE-VASE at λ₁ = 600 nm. The deposition conditions are listed in Table 5.2. The effective carrier lifetime of a-Si:H(i) coatings show the quality of surface passivation using the μPCD technique with SemiLab WT2000.

Corresponding to the deposition conditions in Table 5.2, Fig. 5.3 gives the measured dependence of the effective carrier lifetime on the gas flow ratio of the precursors (H₂:SiH₄) and the substrate temperature (Tₘₙₐₓ), whereby every a-Si:H(i) layer was deposited within 100 sec. The result demonstrates that the samples have been passivated. The best effective carrier lifetime is close to 20 μs, when the gas
flow ratio is in the range of 1 to 5 and $T_{\text{sub}}$ is between 250°C and 350°C, as shown (red dash rectangles) in Fig. 5.3.

Otherwise, where the flow ratio is in excess of 3.5 and the $T_{\text{sub}}$ is lower than 150°C, the effective carrier lifetime is less than 9 µs or even 5 µs, which indicates that those samples were not surface passivated.

Fig. 5.4 shows the measured dependence of the reflective index $n_{600}$ ($\lambda_1 = 600$ nm) of the a-Si:H(i) layer on the layer thickness, the gas flow ratio, and the substrate temperature using the SE-VASE. The results demonstrate that:

(1) The dependence of $n_{600}$ - Layer thickness indicates that the layer thickness and the refractive index of an a-Si:H(i) layer are independent;

(2) The dependence of $n_{600}$ - Flow ratio shows that for a flow ratio between 1.4 and 4, the refractive index decreases sharply and the deposition rate hardly changes, whereas at a flow ratio in excess of 4, the refractive index and the deposition rate slowly decrease. The results demonstrate that the refractive index and the gas flow ratio have a high dependence. A higher gas flow ratio has a lower refractive index;
(3) The samples were prepared for the $n_{600} - T_{\text{sub}}$ dependence with a flow ratio = 2 and $t_{\text{dep}} = 100$ sec. The dependence shows that for a $T_{\text{sub}}$ between 0°C and 350°C, the refractive index hardly increases and the deposition rate hardly decreases.

From these experiments, the optimal experiment conditions were identified. For further research, a thickness of 15 to 20 nm and a refractive index of approximately 2.2 were derived for the a-Si:H(i) layers on the crystalline thin-film cells on graphite substrates (Flow ratio = 2, $T_{\text{sub}} = 250$°C, and $t_{\text{dep}} = 1$ sec.).

Fig. 5.4 Measured dependence of the refractive index at 600 nm and the layer thickness of a-Si:H(i) layers on planar FZ c-Si(p) wafers as a function of (a) the deposition time, (b) the gas flow ratio, and (c) the substrate temperature.
Table 5.2 Summary of deposition conditions used for the parameter study of a-Si:H(i), as compared in Fig. 5.3 and Fig. 5.4. There are three parameters in the study (deposition time, gas flow ratio, and substrate temperature). For the dependence study on each parameter, the other two parameters remain constants.

<table>
<thead>
<tr>
<th>Dependence of</th>
<th>Deposition time</th>
<th>Gas flow ratio</th>
<th>Substrate temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>n_{600} and thickness on:</td>
<td>(sec)</td>
<td>(H\textsubscript{2}:SiH\textsubscript{4})</td>
<td>(°C)</td>
</tr>
<tr>
<td>(a) Deposition time</td>
<td>From 20 to 140</td>
<td>2</td>
<td>350</td>
</tr>
<tr>
<td>(b) Gas flow ratio</td>
<td>100</td>
<td>From 1.4 to 10</td>
<td>350</td>
</tr>
<tr>
<td>(c) Substrate temperature</td>
<td>100</td>
<td>2</td>
<td>From 0 to 350</td>
</tr>
</tbody>
</table>

5.1.3 Optical properties of SiN\textsubscript{x}/a-Si:H(i)

Here, the best range of the reflectivity of the SiN\textsubscript{x}/a-Si:H(i) stack was simulated using the formulas [146, 279]:

\[
\begin{align*}
r_1 &= \frac{n_0 - n_1}{n_0 + n_1} \\
r_2 &= \frac{n_1 - n_2}{n_1 + n_2} \\
r_3 &= \frac{n_2 - n_3}{n_2 + n_3} \\
\theta_1 &= \frac{2\pi n_1 t_1}{\lambda} \\
\theta_2 &= \frac{2\pi n_2 t_2}{\lambda}
\end{align*}
\]

where \(n_0\) is the refractive index of air, equal to 1. The SiN\textsubscript{x} layer has a refractive index of \(n_1\) and a thickness of \(t_1\). The a-Si:H(i) layer has \(n_2\) and \(t_2\). The refractive index of the c-Si(n\textsuperscript{+}) is 3.87 at \(\lambda_2 = 632\) nm [280]. Hence, the reflectivity of the SiN\textsubscript{x}/a-Si:H(i) stack is given by:

\[
R = \frac{r_1^2 + r_2^2 + r_3^2 + r_1^2 r_2^2 r_3^2 + 2 r_1 r_2 (1 + r_1^2) \cos 2 \theta_1 + 2 r_2 r_3 (1 + r_2^2) \cos 2 \theta_2 + 2 r_1 r_3 (1 + r_3^2) \cos 2 \theta_3 + 2 r_1 r_2^2 r_3^2 \cos 2 (\theta_1 + \theta_2) + 2 r_1 r_2 r_3^2 \cos 2 (\theta_1 + \theta_3) + 2 r_1 r_2^2 r_3 \cos 2 (\theta_2 + \theta_3) + 2 r_1 r_2 r_3^2 \cos 2 (\theta_1 - \theta_2) + 2 r_1 r_2^2 r_3 \cos 2 (\theta_1 - \theta_3) + 2 r_1 r_2 r_3^2 \cos 2 (\theta_2 - \theta_3)}{1 + r_1^2 r_2^2 + r_2^2 r_3^2 + r_1^2 r_3^2 + 2 r_1 r_2 (1 + r_1^2) \cos 2 \theta_1 + 2 r_2 r_3 (1 + r_2^2) \cos 2 \theta_2 + 2 r_1 r_3 (1 + r_3^2) \cos 2 \theta_3 + 2 r_1 r_2^2 r_3^2 \cos 2 (\theta_1 + \theta_2) + 2 r_1 r_2 r_3^2 \cos 2 (\theta_1 + \theta_3) + 2 r_1 r_2^2 r_3 \cos 2 (\theta_2 + \theta_3) + 2 r_1 r_2 r_3^2 \cos 2 (\theta_1 - \theta_2) + 2 r_1 r_2^2 r_3 \cos 2 (\theta_1 - \theta_3) + 2 r_1 r_2 r_3^2 \cos 2 (\theta_2 - \theta_3)}
\]

We fabricated the SiN\textsubscript{x} layer at low temperature (250°C) with a gas flow ratio (NH\textsubscript{3}:SiH\textsubscript{4}) of approximately 0.85, the refractive index of SiN\textsubscript{x} was measured in the range between 1.5 and 1.8 using SE-ELX04 at \(\lambda_2 = 632\) nm.
**Fig. 5.5** Calculated dependence of the reflectance of SiN$_x$/a-Si:H(i) stacks as a function of (a) the layer thickness ($t_1$, $t_2$) when $n_1 = 1.7$ nm and $n_2 = 2.2$ nm and (b) the refractive index ($n_1$, $n_2$) when $t_1 = 90$ nm and $t_2 = 20$ nm.
**Fig. 5.5 (a)** shows the contours of the reflectance at 632 nm \(R_{632}\) for the SiN\(_x/a\)-Si:H(i) stack as a function of their thickness \(t_1, t_2\) at \(\lambda_2 = 632\) nm, where \(n_1 = 1.7\) and \(n_2 = 2.2\). **Fig. 5.5 (b)** shows the contours of the reflectance for the SiN\(_x/a\)-Si:H(i) stack as a function of their refractive indices of them \((n_1, n_2)\), where \(t_1\) is 90 nm and \(t_2\) is 20 nm. Bare silicon has a high surface reflection of approximately 34%. Lower reflectance for the stacks, the solar cells will be able to absorb more light (energy). Both contours show the \(R_{632}\) of the SiN\(_x/a\)-Si:H(i) stack, which has low values (<3.5%), if:

\[
1.6 < n_1(SiN_x) < 1.7 \\
2.1 < n_2[\text{a-Si:H(i)}] < 2.3 \\
75 nm < t_1(SiN_x) < 90 nm \\
10 nm < t_2[\text{a-Si:H(i)}] < 30 nm
\]

whereby the reflectance from the metal contacts was not taken into account in the simulation.

**5.2 Chapter summary**

In this chapter the investigation of the properties of a-Si:H(i) has been introduced. In order to develop the cell concept on graphite substrates, the study was focused on surface passivation using a SiN\(_x/a\)-Si:H(i) stack. A primary study on FZ c-Si wafers was conducted to find optimized process parameters and optimal thickness values for low optical losses. Subsequently, the optimized SiN\(_x/a\)-Si:H(i) stacks were used to fabricate crystalline silicon thin-film solar cells on graphite substrates.

The precise thickness of the SiN\(_x/a\)-Si:H(i) stacks was then measured using the FIB-STEM technique, which will be described in next chapter.
5 a-Si:H(i) surface passivation
6 Solar cells on graphite substrates

Abstract

In line with the results of the experiments described in the preceding chapters, bulk hydrogen passivation and a-Si:H(i) surface passivation were applied to the CSiTF solar cells on graphite substrates. Quantum efficiency, light beam induced current and current density-voltage measurements are used as characterization methods. Scanning transmission electron microscopy was applied to characterize the cross section of the SiN_x/a-Si:H(i) stack using focus ion beam preparation. Lock-in thermography techniques revealed the electrical characteristics of the cells.

Finally, an absolute increase of 3.4% cell efficiency to 10.8% was achieved for a 40 µm thick 4 cm² aperture area silicon thin-film solar cell on graphite substrate.

Results given here have, in part, been published elsewhere (reproduced with permissions):
Fig. 6.1 (a) shows the schematic of a CSiTF solar cell at the ZAE Bayern, which includes the previous cell concepts, e.g. both-sided contact formation and laser edge isolation. Whereas, Fig. 6.1 (b) shows the new cell concepts developed in this work, e.g. LSSC formation. The application (LSSC, HP, and surface passivation) of cell concepts on graphite-based solar cells will be introduced into two parts: bulk passivation and surface passivation.

Table 6.1 Sample list of the cells on graphite substrates for bulk passivation.

<table>
<thead>
<tr>
<th>No.</th>
<th>Names in Chapters</th>
<th>Names in Record</th>
<th>Substrates</th>
<th>H pass</th>
<th>Contacts</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Gra.A</td>
<td>ALZ368</td>
<td>Graphite</td>
<td>Both-sided</td>
<td>ALZG_Null</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Gra.B</td>
<td>ALZ445</td>
<td>Graphite</td>
<td>LSSC</td>
<td>ALZG_LSSC</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Gra.C</td>
<td>ALZ429</td>
<td>Graphite</td>
<td>50</td>
<td>LSSC</td>
<td>ALZG_LSSC_H30</td>
</tr>
<tr>
<td>4</td>
<td>Gra.D</td>
<td>ALZ432</td>
<td>Graphite</td>
<td>30</td>
<td>LSSC</td>
<td>ALZG_LSSC_H50</td>
</tr>
</tbody>
</table>

6.1 Bulk passivation

6.1.1 Experimental details

Table 6.1 gives the sample list for the investigation of bulk passivation. Here, Gra. denotes that a batch is based on graphite-based substrates. The cell concepts were based on high purity graphite substrates (“FP479”, Schunk Kohlenstofftechnik GmbH) with a size of 100 mm × 100 mm × 2 mm.

![Figure 6.1](image.png)

Fig. 6.1 The two different Si thin-film solar cell designs were studied. (a) Gra.A: the cell of a developed model is based on front and back contacts. (b) Gra.B–C: the new design in this work is based on laser single side front contacts (LSSC). The layers are not to scale.
As shown in Fig. 6.2, the batches denoted by different capital letters correspond to the different processing sequences:

1) **Gra.A** and **Waf.A** are the samples with base contacts on the back of the solar cells. They are based on the design of Fig. 6.1 (a). The base contact is formed by a 5 µm thick aluminum layer, which was deposited on the back of the substrate. Hydrogen passivation is not used in these batches.

2) **Gra.B** and **Waf.B**’s base contacts were formed from the front using LSSC. They are based on the design of Fig. 6.1 (b), but without the hydrogen passivation process.

3) **Gra.C** and **Waf.C** are with LSSC and the hydrogen passivation process. **Gra.C** is based on the design of Fig. 6.1 (b).
The reference batches (Waf.A-C) have been detailed discussed in Chapter 4; therefore in this chapter the graphite-based substrate batches (Gra.A-D) will be introduced. In order to prevent impurity diffusion from the foreign substrate, a SiC layer was deposited as an intermediate layer on both-sided of the substrate using hot wall chemical vapor deposition. Afterwards, a $p^+$-Si layer, which served as a seed and back surface field layer (approximately 20 $\mu$m thick and with an acceptor concentration of $4 \times 10^{18}$ cm$^{-3}$), was deposited on top of the SiC layer using CoCVD. The subsequent ZMR process yielded a large size of silicon grain. A 20 $\mu$m thick epitaxial $p$-Si base layer was applied over the $p^+$-Si layer and was grown using CoCVD. This $p$-Si layer had a boron doping concentration of about $2 \times 10^{16}$ cm$^{-3}$. The $n^+$-Si emitter was formed by spin on doping (SOD) of a phosphorous solution followed by RTP in a furnace. It was essential to reduce bulk recombination using a hydrogen passivation process, which was applied directly after the removal of the phosphorous glass. As described in Chapter 4, the hydrogen passivation process was carried out at a low temperature (< 350°C) for 50 minutes with the PECVD system at the ZAE Bayern. The PECVD system has an 88 cm $\times$ 96.5 cm $\times$ 35 cm volume.

![Graph showing $V_{oc}$, FF, and $J_{sc}$ for Gra.A, Gra.B, and Gra.C batches](image)

**Fig. 6.3** $V_{oc}$ (top), FF (middle) and $J_{sc}$ (bottom) resulting from the both-sided contact, LSSC formation (i.e., Gra.B and C), and hydrogen passivation processes (i.e., Gra.C).
chamber containing a 42 × 42 cm² heating stage.

Due to recent rapid developments in laser technology, the LEI process and LSSC formations were applied in our cell concepts. Trenches approximately 30 μm deep (down into the c-Si(p⁺) layer) and 3 mm wide were fabricated for contact strips around the cells using a Nd:YVO₄ laser (Rofin Power Line LP20, λ_laser = 1064 nm).

Afterwards, the emitter contacts and the base contacts were simultaneously evaporated on the front. The grid metallization was formed by electron beam evaporation of Ti, Pd, and Ag (30 nm, 30 nm, and 5 μm thick, respectively). Finally, a silicon nitride layer serving as a single layer antireflection coating (80 nm thick, refractive index between 1.5 and 1.8) was deposited using plasma enhanced chemical vapor deposition (PECVD). The PECVD system was kept at a pressure of 0.035 mbar, a work frequency of 2.45 GHz and microwave power of 1000 W. The total thickness of the silicon layers was approximately 40 μm.

### 6.1.2 J–V characterization

Table 6.2 lists the parameters obtained from the illuminated and dark J-V measurements. In Fig. 6.3, the V_{oc}, FF, and J_{sc} data of all the samples was arranged in the form of a box chart; moreover, both the graphite-based (Gra.) batches exhibit similar variations in J_{sc}, FF, and V_{oc}, which can be described by:

\[ V_{oc} (Gra.A) < V_{oc} (Gra.B) < V_{oc} (Gra.C) \]
\[ FF (Gra.A) < FF (Gra.B) < FF (Gra.C) \]
\[ J_{sc} (Gra.A) < J_{sc} (Gra.B) < J_{sc} (Gra.C) \]

those inequalities indicate that the batches with LSSC formation perform better than the batches with both-sided contact formation. Moreover, the hydrogen passivation reduced the bulk recombination. The same trend of the reference cells based on the p–Si wafer substrates was also observed as shown in the following equations:

\[ V_{oc} (Waf.A) < V_{oc} (Waf.B) < V_{oc} (Waf.C) \]
\[ FF (Waf.A) < FF (Waf.B) < FF (Waf.C) \]

Fig. 6.4 shows illuminated J-V curves of the best cells from Gra.B–C. The best cell in Gra.C (cell No.5) i.e., Gra.C-5, has 3.17 Ωm² parallel resistance, 502 mV V_{oc} and a fill factor of 67.2%. In contrast, the best cell in Gra.B, i.e., Gra.B-8, without the hydrogen bulk passivation, has less V_{oc} and J_{sc} mainly due to the defects in the bulk. In addition, hydrogen passivation for Gra.D was fabricated at the same condition as Gra.C, except the duration was 20 min less than Gra.C, and hence Gra.D has worse
Solar cells on graphite substrates

To date, a cell efficiency of 10.2% was achieved, which is the highest ever efficiency of a 40 µm thick crystalline silicon solar cell on graphite substrate with a 4 cm² aperture area.

Table 6.2 Cell parameters on graphite substrates. Open circuit parallel resistance ($R_p$), series resistance ($R_s$) Voltage ($V_{oc}$), current density ($J_{sc}$), fill factor ($FF$), and efficiency ($\eta$). The best efficiencies are highlighted in bold.

<table>
<thead>
<tr>
<th>Batches</th>
<th>Contacts</th>
<th>$H^+$ (min)</th>
<th>$R_p$ (Ωm²)</th>
<th>$R_s$ (Ωcm²)</th>
<th>$V_{oc}$ (mV)</th>
<th>$J_{sc}$ (mA/cm²)</th>
<th>$FF$ (%)</th>
<th>$\eta$ (%)</th>
<th>Best $\eta$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gra.A</td>
<td>Both-sided</td>
<td>-</td>
<td>1.53</td>
<td>1.52</td>
<td>426</td>
<td>21.3</td>
<td>56.7</td>
<td>5.18</td>
<td>6.79</td>
</tr>
<tr>
<td>Gra.B</td>
<td>LSSC</td>
<td>-</td>
<td>1.97</td>
<td>1.06</td>
<td>469</td>
<td>23.4</td>
<td>66.5</td>
<td>7.33</td>
<td>7.81</td>
</tr>
<tr>
<td>Gra.C</td>
<td>LSSC</td>
<td>50</td>
<td>2.47</td>
<td>1.05</td>
<td>499</td>
<td>26.2</td>
<td>67.7</td>
<td>8.86</td>
<td>10.2</td>
</tr>
<tr>
<td>Gra.D</td>
<td>LSSC</td>
<td>30</td>
<td>3.58</td>
<td>1.46</td>
<td>490</td>
<td>26.2</td>
<td>65.4</td>
<td>8.39</td>
<td>9.10</td>
</tr>
</tbody>
</table>

6.1.3 Quantum efficiency

Fig. 6.5 shows the measured IQE of Gra.B-8 and Gra.C-5, the simulated IQE using PC1D, and the reflectance of Gra.C-5. Gra.B-8 had the shorter diffusion length and lower quantum efficiency than Gra.C-5 due to the surface and bulk recombination without the hydrogen bulk passivation. The simulation parameters are shown in Table 6.3. The simulation results correlate significantly with the measured curve. The main

![Graph showing J-V curves of the cells Gra.B-8 and Gra.C-5.](image)

Fig. 6.4 J-V curves of the cells Gra.B-8 and Gra.C-5. (i.e., LSSC formation without (Gra.B) and with (Gra.C) hydrogen passivation).
difference is that the simulated $V_{oc}$ is about 50 mV higher than the measured one. This may be a result of spatial non-uniformities due to various crystal grains, which cannot be accounted for in 1-dimensional simulations using PC1D.

The antireflection coating layers made of silicon nitride with a thickness of 75 nm. The refractive index of the layer is approximately 2. Fig. 6.5 shows that the minimum reflection of the reflectance curve is close to 600 nm, since it was fabricated close to the maximum of the number of incident photons. The SiN$_x$ layers were formed at a low temperature without optimized passivation properties, which cannot reduce the surface recombination in the emitter. Therefore, as shown in the IQE curves, this was assumed to be the main reason why the cell has a spectral response below 90% in the range from 400 nm to 550 nm. In the range from 550 nm to 1000 nm, the IQE goes down gradually due to bulk and rear recombination loss. In addition, the QE results also reveal that there are some possibilities for improving cell performance further, such as by lowering the surface recombination and by optimizing the bulk passivation process.

Fig. 6.5 The reflectance measured and simulated IQE curves of the cell Gra.C-5. The measured IQE of the cell Gra.B-8 is plotted for comparison. The bulk lifetime was varied for fitting. The IQE is simulated by PC1D for diffusion lengths with 15 µm, 22 µm, 40 µm, and 100 µm.
Table 6.3  PC1D parameters and simulation results. The parameters device area, base contact, thickness, p-type background doping and first rear diffusion were chosen according to cell No.5 in batch Gra. C. *The parameters were varied for fitting IQE.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Results</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Input</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Device area</td>
<td>4</td>
<td>cm²</td>
</tr>
<tr>
<td>Base contact</td>
<td>0.7125</td>
<td>Ω</td>
</tr>
<tr>
<td>Thickness</td>
<td>40</td>
<td>µm</td>
</tr>
<tr>
<td>p-type background doping</td>
<td>2×10¹⁶</td>
<td>cm⁻³</td>
</tr>
<tr>
<td>Sheet Resistance</td>
<td>112</td>
<td>Ω/square</td>
</tr>
<tr>
<td>1st rear diffusion</td>
<td>4×10¹⁸</td>
<td>cm⁻³</td>
</tr>
<tr>
<td>Bulk recombination*</td>
<td>0.2</td>
<td>µs</td>
</tr>
<tr>
<td>Front surface recombination*</td>
<td>8×10⁵</td>
<td>cm/s</td>
</tr>
<tr>
<td><strong>Output</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$I_{sc}$</td>
<td>0.103</td>
<td>A</td>
</tr>
<tr>
<td>$V_{oc}$</td>
<td>567.9</td>
<td>mV</td>
</tr>
<tr>
<td>Efficiency</td>
<td>10.15</td>
<td>%</td>
</tr>
</tbody>
</table>

6.1.4 LBIC and PC1D

Fig. 6.6 (a) is a photograph of Gra.C, on which are the nine cells with the graphite substrate. The cell No.5 is in the center as shown in Fig. 6.6 (b). The $L_{diff}$ mapping of the cell No.5 is shown in Fig. 6.6 (c). The patterns of the grain boundaries on the surface are revealed in the $L_{diff}$ mapping. However, the resulting average $L_{diff}$ is about 120 µm, since these three wavelengths (976 nm, 951 nm, and 846 nm) have the longer penetration lengths than the 40 µm thick active layers of the cells. In Fig. 6.6 (d) the LBIC mapping shows the distribution of the electricity generation. Levels of low to high electricity generation correspond to red to blue area, respectively. The brown area around the busbar is due to surface defects after many measurements.

The effective diffusion length of the CSiTF solar cell was obtained by using PC1D. The real thickness of the cell was included in the PC1D model. This model was used to fit the measured IQE. As shown in Fig. 6.5, the simulated IQE characteristic curves for diffusion lengths were 15 µm, 22 µm, 40 µm, and 100 µm, respectively. The effective diffusion length was varied for the fitting and is approximately 22 µm. This result again demonstrates that a surface passivation process and a higher layer quality are necessary for further increasing cell efficiency.
6.2 Surface passivation

In crystalline silicon thin-film (CSiTF) (< 40 μm) solar cells, the electron-hole generation is close to the surface and thus the surface recombination plays an extremely important role in the cell performance. Therefore, in order to improve our cell concepts further, we focused our effort on front surface passivation to reduce the surface recombination using an a-Si:H(i) layer. In order to implement DLARC and surface passivation for SiNx/a-Si:H(i) stacks on graphite-based solar cells, the dependence of the reflectance of the SiNx/a-Si:H(i) stack was simulated with regard to their refractive indices and thicknesses, as described in Section 5.1.3. Under the same fabrication process conditions, the thicknesses of SiNx and a-Si:H(i) were expected to be prepared to the values of 70–90 nm and 10–20 nm, respectively.

![Fig. 6.6](image)

(a) Top view of batch Gra.C (cell No.5, i.e., Gra.C-5). (b) Top view of batch Gra.C-5. (c) The $L_{diff}$ mapping of the best cell in batch Gra.C (cell No.5), resolution: 125 μm spot size. The average $L_{diff}$ is about 120 μm. The mapping shows the patterns of front contacts and crystalline silicon orientations, which is parallel to the busbar in the middle (d) The LBIC mapping of Gra.C-5 with arbitrary units.
6 Solar cells on graphite substrates

Table 6.4 Sample list of the cells on graphite substrates for the investigation of a-Si:H(i) surface passivation. Note that Batch D was used for LIT imaging.

<table>
<thead>
<tr>
<th>No.</th>
<th>Names in Chapters</th>
<th>Names in Record</th>
<th>a-Si:H(i)</th>
<th>Substrates</th>
<th>H⁺ pass.</th>
<th>LSSC</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Batch A</td>
<td>ALZ442</td>
<td>Yes</td>
<td>Graphite</td>
<td>50</td>
<td>Yes</td>
<td>a-Si process sequence 01</td>
</tr>
<tr>
<td></td>
<td></td>
<td>ALZ460</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>ALZ466</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Batch B</td>
<td>ALZ450</td>
<td>Yes</td>
<td>Graphite</td>
<td>50</td>
<td>Yes</td>
<td>a-Si process sequence 02</td>
</tr>
<tr>
<td></td>
<td></td>
<td>ALZ462</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>ALZ465</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Batch C</td>
<td>ALZ437</td>
<td>no</td>
<td>Graphite</td>
<td>50</td>
<td>Yes</td>
<td>Reference</td>
</tr>
<tr>
<td></td>
<td></td>
<td>ALZ459</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Batch D</td>
<td>ALZ464</td>
<td>no</td>
<td>Graphite</td>
<td>50</td>
<td>Yes</td>
<td>Ref. for LIT</td>
</tr>
</tbody>
</table>

Fig. 6.7 Processing sequence of the cells. Three solar cell batches were prepared. Batch A was passivated by the depositing using the a-Si:H(i) layer after the hydrogen bulk passivation. The surface passivation layer of Batch B was applied before the SiNx layer. Batch C–D were the reference batches without surface passivation process.
6.2.1 Experimental details

The samples are listed in Table 6.4 for the investigation of the a-Si:H(i) surface passivation. For Batch D, especial use was made of LIT imaging to observe the un-recrystallized Si area. As shown in Fig. 6.7 and Fig. 6.8, we divided the samples into four batches corresponding to the three different cell concepts. For Batch C–D all steps of the process sequence of Gra.C, which is described in Section 6.1.1, were followed, with the exception of surface passivation, as shown in Fig. 6.8 (c).

As shown in Fig. 6.8 (a)–(b), two strategies were investigated to find the best surface passivation process sequence using the a-Si:H(i) layer. As shown in Fig. 6.7, the samples of one strategy were named as Batch A, and in these samples a-Si:H(i) layers were fabricated before the laser trenching and the LEI process. Moreover, the a-Si:H(i) layer was deposited directly after the hydrogen passivation in the same PECVD chamber, which may have advantages for the a-Si:H(i)/c-Si(n+) interface characteristics. Table 6.5 gives the experiment conditions of SiNx/a-Si:H(i) stacks deposition.

The alternative strategy was to fabricate the a-Si:H(i) layers (applied in Batch B) after the laser processing and the grid metallization. The a-Si:H(i) and SiNx layers were formed stepwise at the same temperature and in the same PECVD chamber, which may have advantages as for the SiNx/a-Si:H(i) interface quality.

In addition, Fig. 6.8 (a)–(b) indicate a small difference between Batch A and Batch B with regard to their cell structures. The isolated edges and the sides of Batch A were not covered by the a-Si:H(i) coating, because they were removed by the subsequent laser process. In contrast, the a-Si:H(i) coatings of Batch B covered the full surface area including the laser isolated edge and the sides.

Finally, the SiNx coatings were identically deposited on the front of all the batches, forming the SiNx/a-Si:H(i) stacks in Batch A–B. The optical and electrical properties of the stacks will be discussed in the next sections.

Table 6.5 The experiment conditions of SiNx/a-Si:H(i) stacks deposition. Note that here is the real temperature on the stage, not the preset temperature.

<table>
<thead>
<tr>
<th>Precursors</th>
<th>Gas flow rate</th>
<th>Temperature</th>
<th>Duration</th>
<th>Thickness</th>
</tr>
</thead>
<tbody>
<tr>
<td>a-Si:H(i)</td>
<td>H₂:SiH₄</td>
<td>200:100</td>
<td>250</td>
<td>15</td>
</tr>
<tr>
<td>SiNx</td>
<td>NH₃:SiH₄</td>
<td>81:69</td>
<td>250</td>
<td>105</td>
</tr>
</tbody>
</table>
Fig. 6.8 Schematic of the three different CSiTF solar cell concepts. All concepts are based on graphite substrates. The surface passivation is achieved depositing the SiN$_x$/a-Si:H(i) stack (a) before the laser process and (b) after grid metallization process, respectively. (c) The SiN$_x$/a-Si:H(i) stack was not applied in the reference cell concept. The layers are not to scale.
Fig. 6.9  FIB preparation process. (a) Platinum protective layer lies at the top. (b)–(c) A specimen of approximately 1µm was milled by FIB. (d)–(e) The specimen was cut to be removed from the solar cell. (f) The specimen was welded to the STEM holder. (g) The specimen was finally polished to approximately 50 nm. (h) The side view of the specimen. It is ready to be characterized using STEM.
6.2.2 FIB-STEM

A cell (\textit{A-18}) from \textit{Batch A} was chosen for the FIB-STEM micrographs. A small part was taken from the surface of \textit{A-18} and prepared into a 65-nm thick FIB lamella.

Fig. 6.9 illustrates the FIB preparation process. Fig. 6.10 shows the cross section of \textit{A-18} after FIB preparation. As shown in Fig. 6.10, the platinum (Pt) protective layer lies at the top, with the \textit{SiN}_x layer (approximately 90 nm) beneath. Beneath that lies the approximately 20-nm thick a-Si:H(i) layer, with the lowest c-Si layer beneath that. \textit{A-18} was also characterized using the SE-ELX04 as a comparison, and the optical parameters of \textit{A-18} were obtained \((t_1 = 84.7 \text{ nm}, \ t_2 = 19.0 \text{ nm}, \ n_1 = 1.72 \text{ and } n_2 = 2.20\)). Thus the measured parameters using the FIB-STEM are in agreement with those measured using the SE, as described in Inequalities 5-1 to 5-4.

Fig. 6.11 shows that the measured \(R_{632}\) of \textit{A-18} is approximately 6.1\%. As a comparison, the \(R_{632}\) of the cells \textit{A-26} and \textit{B-26} have blue shifts, which is predominately due to a thinner \textit{SiN}_x layer or a thinner a-Si:H(i) layer. Both \textit{A-26} and \textit{B-26} seemed promising candidates for better cell performance than \textit{A-18}, since the related wavelengths of their minimum reflectances are close to the peak intensity of the solar spectrum. However, the result demonstrates that, even in the same deposition condition, the minimum reflectances of this \textit{SiN}_x/a-Si:H(i) stack were at different

![Fig. 6.10 STEM picture of the cross section of the SiN_x/a-Si:H(i) stack of a finished solar cell on graphite substrate.](image-url)
6 Solar cells on graphite substrates

The SiN/a-Si:H(i) layers of these batches were not uniform. This was mainly due to the inhomogeneous ambient in the large PECVD chamber and the rough surfaces of the cells.

6.2.3 J-V characterization

As shown in Table 6.6, the performance of all batches are listed with respect to parallel resistance (R_p), series resistance (R_s), J_sc, V_oc, FF, and cell efficiency. A-18 was used to characterize the cross section of the SiN/a-Si:H(i) stack. The cells A-26, B-26, and C-05 had the highest cell efficiencies in each batch, respectively. In addition, Fig. 6.12 shows the J-V curves of these three cells.

Compared to C-05, both A-26 and B-26 have approximately 20 mV increased V_oc, which is due to the passivated surfaces of A-26 and B-26 using a-Si:H(i) layers.

The a-Si:H(i) layer was fabricated for Batch A before the metallization process. Table 6.6 shows that Batch A has the lowest average value in R_p among the three batches due to the leak current at the edges, where the a-Si:H(i) layer was not covered or removed by the subsequent laser process.
Table 6.6  Cell parameters. Parallel resistance ($R_p$), series resistance ($R_s$), open  
circuit voltage ($V_{oc}$), current density ($J_{sc}$), fill factor ($FF$) and efficiency ($\eta$). The  
extreme values are highlighted in bold.

<table>
<thead>
<tr>
<th>Batches</th>
<th>$R_p$</th>
<th>$R_s$</th>
<th>$V_{oc}$</th>
<th>$J_{sc}$</th>
<th>$FF$</th>
<th>$\eta$</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ohm∙m²</td>
<td>Ohm∙cm²</td>
<td>mV</td>
<td>mA/cm²</td>
<td>%</td>
<td>%</td>
<td></td>
</tr>
<tr>
<td>Best cell A-26</td>
<td>1.04</td>
<td>0.679</td>
<td>521</td>
<td>29.1</td>
<td>71.4</td>
<td>10.82</td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>Average</td>
<td>1.02</td>
<td>0.843</td>
<td>492</td>
<td>25.7</td>
<td>65.9</td>
<td>8.36</td>
</tr>
<tr>
<td></td>
<td>A-18</td>
<td>0.76</td>
<td>0.950</td>
<td>506</td>
<td>26.0</td>
<td>65.4</td>
<td>8.64</td>
</tr>
<tr>
<td>Best cell B-26</td>
<td>2.45</td>
<td>1.085</td>
<td>525</td>
<td>29.9</td>
<td>68.5</td>
<td>10.77</td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>Average</td>
<td>1.93</td>
<td>0.943</td>
<td>502</td>
<td>26.4</td>
<td>66.6</td>
<td>8.84</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>3.09</td>
<td>0.883</td>
<td>499</td>
<td>29.8</td>
<td>67.2</td>
<td>9.99</td>
</tr>
<tr>
<td></td>
<td>Average</td>
<td>1.95</td>
<td>0.962</td>
<td>483</td>
<td>26.2</td>
<td>65.8</td>
<td>8.37</td>
</tr>
</tbody>
</table>

Fig. 6.12  Current density versus voltage curves of the highest efficiency cell of  
the three batches under illumination.
In **Batch B**, the a-Si:H(i) layer covered the entire surface of the solar cells. As expected in the process sequence designs, and described in **Section 6.2.1**, **Batch B** had the highest average values in \( J_{sc} \), \( V_{oc} \), \( FF \) and cell efficiency among the three batches, which indicated that the a-Si:H(i) layers in **Batch B** have better cell performance than in **Batch A**. Moreover, the good reproducibility of the sequence of **Batch B** was observed, which has higher average cell efficiency. The slightly higher \( R_s \) could be due to the contact resistance of the interfaces of **metal grid–a-Si:H(i) layer** and **metal grid–emitter**.

**6.2.4 Quantum efficiency**

Subsequently, the finished cells were characterized by **J-V measurement** and using the Enlitech solar cell analysis system QE-R for the QE and reflectance measurements. To study the effect of surface passivation using a-Si:H(i) layers, the internal quantum efficiency (IQE) in a range of \( 350 \text{ nm} < \lambda < 600 \text{ nm} \) was measured. The average IQE and the error bars for **Batch A–C** are plotted in **Fig. 6.13**. It is evident that the samples with a-Si:H(i) layers (**Batch A–B**) have higher values than the samples without a-Si:H(i) layers (**Batch C**), which is predominately due to lower surface recombination.

![Fig. 6.13 Measured average internal quantum efficiencies with error bars of Batch A–C. The error bars as drawn as filled areas.](image-url)
6.2.5 Lock-in thermography

A preliminary study of the spatially resolved Lock-in Thermography (LIT) techniques was implemented for the cells on graphite substrates. The conditions are shown in Table 6.7.

It is important to note that ELLI was carried out using an InGaAs camera (spectral response: 0.8 µm to 1.8 µm), whereas the other LIT techniques using an InSb camera (spectral response: 1.5 µm and 5 µm) as mentioned in Section 3.2.6.

Cell Gra.C-5 has the best performance in its batch, to which both LSSC formation and hydrogen passivation were applied. Fig. 6.14 shows the crystalline Si boundaries in an ELLI image. The positions of breakdown sites are shown in Fig. 6.14 (d). Fig. 6.14 (c), (e), and (f) show the pattern of defects due to surface contaminants.

It is necessary to note that Fig. 6.15 (b)–(c) and (e)–(f) show the grain boundaries using LIT techniques. As shown in Fig. 6.16, these techniques can also show the non-recrystallized Si area, where there is a great deal of poly-Si, which induces high recombination at the boundaries.

Fig. 6.14 LIT technologies for cell Gra.C-5. (a) Top view (b) ELLI (c) High current–DLIT (d) Reverse bias DLIT (e) \( V_{oc}-\text{ILIT} \) subtracted by \( J_{sc}-\text{ILIT} \) for 10 min. a.u. (0.0 to 0.2). (f) An enlarged view of the defect area under the optical microscope.
Compared to the LIT techniques listed in Table 6.7, the ELLI technique has a large practical advantage in revealing more information regarding cell performance, e.g. location of defects and distribution of grain boundaries, in a short integration time. Therefore, to date the other LIT techniques are widely used as auxiliary characterization methods.

Table 6.7 Parameters of Lock-in Thermography imaging.

<table>
<thead>
<tr>
<th>Method</th>
<th>Bias</th>
<th>Integration time (min)</th>
<th>a.u.</th>
</tr>
</thead>
<tbody>
<tr>
<td>ELLI</td>
<td>+ 0.8 V</td>
<td>1.00</td>
<td>-1.10 to 8.50</td>
</tr>
<tr>
<td>Shunt imaging DLIT</td>
<td>± 0.5 V</td>
<td>7.00</td>
<td>-0.25 to 1.00</td>
</tr>
<tr>
<td>High current DLIT</td>
<td>+ 0.6 V</td>
<td>10.0</td>
<td>0.25 to 1.25</td>
</tr>
<tr>
<td>Reverse bias DLIT</td>
<td>- 5.2 V</td>
<td>3.70</td>
<td>0.00 to 17.0</td>
</tr>
<tr>
<td>V_{oc}–ILIT</td>
<td>open voltage</td>
<td>10.0</td>
<td>0.00 to 0.50</td>
</tr>
<tr>
<td>J_{sc}–ILIT</td>
<td>short circuit</td>
<td>10.0</td>
<td>0.00 to 0.50</td>
</tr>
</tbody>
</table>

Fig. 6.15 LIT technologies for cell Batch.C-5. (a) Top view (b) ELLI (c) High current–DLIT (d) Reverse bias DLIT (e) (V_{oc}–ILIT) subtracted by (J_{sc}–ILIT) for 10 min. a.u. (0.0 to 0.2). (f) An enlarged view of the grain boundaries under the optical microscope.
6 Solar cells on graphite substrates

Fig. 6.16 LIT technologies for cell Batch D-1. (a) Top view (b) ELLI (c) High current–DLIT (d) Reverse bias DLIT (e) (V_{oc}–ILIT) subtracted by (J_{sc}–ILIT) for 10 min. a.u. (0.0 to 0.2). (f) An enlarged view of the grain boundaries under the optical microscope.

6.3 Chapter summary

In order to develop cell concepts on graphite substrates, the investigation focused on hydrogen bulk passivation and surface passivation using a SiN_{x}/a-Si:H(i) stack.

As seen in the primary studies in Chapter 4 and 5, these three methods, i.e., LSSC formation and the best processing sequences for bulk and surface passivation, were developed for CSiTF solar cells on graphite substrates. Moreover, the optimized SiN_{x}/a-Si:H(i) stacks, i.e., process parameters and best thickness values for low optical losses, were used to fabricate crystalline silicon thin-film solar cells on graphite substrates. The precise thickness of the SiN_{x}/a-Si:H(i) stacks was then measured using the FIB-STEM technique, and the result correlated well with the optical properties calculated in the study. For our cell concepts, the photoconductive techniques are of limited use, as the SiC layer and the graphite substrate are conductive. Consequently, the quantum efficiency measurement was applied and this
demonstrated that the a-Si:H(i) layer reduced the surface recombination and improved the current collection at short wavelengths.

Furthermore, the cell fabrication process can be simplified by performing the metallization of all contacts at the same time. Those methods result in an increase of $V_{oc}$ and $FF$. The recombination losses in the bulk and the surface are the main limitations on the cell performance. Therefore, 7.8% cell efficiency was subsequently achieved on an aperture area of 4 cm$^2$ using LSSC, 10.2% cell efficiency using hydrogen passivation, and so far 10.8% using surface passivation.

It also to be expected that the LSSC strategy and the optimal bulk and surface passivation process sequences can be applied not only to CSiTF solar cells of graphite substrates but also to cells based on other high temperature foreign substrates.
6 Solar cells on graphite substrates
7 Summary and outlook

Abstract

This chapter summarizes the main achievements and important experimental and simulated results demonstrated in this thesis. The technical requirements for realizing the CSiTF solar cells on graphite substrates are discussed in detail. An approach based on the multi-junction architecture is presented as an outlook for boosting the record efficiencies of Si PV devices towards even higher values.
7 Summary and outlook

7.1 Summary

In this work, three new strategies are presented to improve CSiTF solar cells on graphite substrates at low temperatures (< 350°C). They are the laser single side contact formation (LSSC), hydrogen bulk passivation and a-Si:H(i) surface passivation. Therefore, this work is categorized into five main chapters, and the main contributions of this work for CSiTF solar cells on graphite substrates are:

1. Single side contact formation was applied in solar cells on graphite substrates using laser technologies. Cell performance is improved by decreasing series resistance and by increasing \( V_{oc}, J_{sc}, \) and \( FF \). This leads to an increase in cell efficiency of 1.0 percentage points for the cells on graphite substrates.

2. The optimal experimental conditions of the PECVD system for deposition and passivation were investigated. Hydrogen bulk passivation is optimized to work at 350°C for 50 min under pressure of 0.035 mbar. The best hydrogen passivation sequence was made directly after the phosphor diffusion process.

3. The optimized thickness of a SiN\(_x\)/a-Si:H(i) stack as double reflection coatings is proven to be approximately 80 nm/15 nm, when the refractive index is 1.7/2.2. Moreover, FIB-STEM method was applied to characterize the cross section of the SiN\(_x\)/a-Si:H(i) stack. Measured parameters using the FIB-STEM are in agreement with those measured using spectroscopic ellipsometer and in agreement with optical simulation.

4. Lock-in thermography techniques were applied to characterize the cells and to identify regions with a high density of crystal defects.

5. Both hydrogen bulk passivation and a-Si:H(i) layer passivation methods improved cell performance, such as the increases in the \( V_{oc}, J_{sc}, FF \), and efficiency. An increase in cell efficiency of 2.4 percentage points to 10.2% was achieved using hydrogen passivation, furthermore an increase in cell efficiency of 0.6 percentage points to 10.8% was achieved using a-Si:H(i) layer passivation. So far, 10.8% is the highest efficiency of a 40 \( \mu \)m thick, 4 cm\(^2\) aperture area CSiTF solar cell on graphite substrate.

7.2 Outlook

A number of aspects offer considerable potential for the further development and investigation of the CSiTF solar cells on foreign substrates. They are listed below:
(1) One advantage of the graphite substrate is its high purity, but it is limited by its cost. It is necessary to reduce the production costs of these materials.

(2) It would be better if any well-developed CVD system could be applied to produce a more homogenous plasma atmosphere on a large scale. It would then be possible to improve the quality of both bulk and surface passivation on graphite substrates. In other word, the quality of CVD is an essential factor in a progressive approach to high efficiency.

(3) The hydrogen passivation process at high temperature (~700°C) in few seconds can be investigated and compared with the process at low temperature (~350°C), especially for cells on foreign substrates. The fabrication process in a few seconds at high temperature is reported to be cost-effective with high passivation quality.

(4) The deposition accuracy of a-Si:H(i) layers is supposed to reach ±1 nm (now approximately ±5 nm), and hence it will be expected to achieve a higher light absorption and a lower surface recombination after surface passivation. In addition, a CVD system with an in-situ spectroscopic ellipsometer, would be very helpful.

(5) Spatially resolved characterization techniques will be more and more popular due to their simple setup, time-efficiency, and high resolution imaging processes. These characterization techniques must be further developed and investigated for the thin-film solar cells with complex structures on different foreign substrates.

(6) To date, our cell concepts have not included optimum designs of metal grids, light trapping, local diffusion or rear surface passivation. Thus, there are still many cell concepts which can be explored for further improvement.
7 Summary and outlook
Appendix A: Cell concepts

A.1 Graphite substrates

Catchpole and McCann et al. have classified the substrate materials for crystalline silicon thin-film (CSiTF) solar cells into two main categories: native substrates [38] and foreign substrates [281]. Native substrates include ribbon growth silicon [87, 282-285] and lift-off silicon [45, 59, 60], whereas foreign substrates include graphite [12, 18, 102, 286], metal [287], window glass [288], borosilicate glass [105], ceramics (such as alumina and mullite) [9, 108, 289, 290], etc. These foreign substrate materials are generally used for CSiTF cell fabrication with the high temperature approach. The properties of these substrate materials are compared by Brendel [93], p. 99, Poortmans [20], p. 102 and Carnel [43], p. 54.

The major ingredient of graphite is carbon. Graphite is neither an insulator nor transparent. Graphite has many advantages as a foreign substrate. It can be processed at high temperatures over 1300°C. It is available at high purity, with an impurity content of about 30 ppm [4], and with low thermal expansion characteristics of $2 \times 10^{-6} \text{K}^{-1} - 6 \times 10^{-6} \text{K}^{-1}$ similar to silicon at $3 \times 10^{-6} \text{K}^{-1}$ and SiC of $2.77 \times 10^{-6} \text{K}^{-1}$. While standard graphite types (approximately 450 €/m²), will not meet cost requirements (approximately lower than 30 €/m²), developments for low-cost types such as biogenic substrates are in progress [19].

In this work, three substrates were chosen for the production of poly-Si solar cells: borosilicate glass, multi-Si wafers, and graphite. Borosilicate glasses (Schott Borofloat® 33) with a size of 20 mm $\times$ 10 mm $\times$ 2.2 mm were used for Raman spectrometer measurements. Multi-Si wafers are used as a model for a reference sample. New cell concepts were developed for solar cells on high-purity graphite substrates (“FP479”, Schunk Kohlenstofftechnik GmbH) with a size of 100 mm $\times$ 100 mm $\times$ 2 mm.

A.2 Deposition of the epitaxial layers

Chemical vapor deposition (CVD) techniques were widely used in this work, i.e., convection-assisted CVD (CoCVD) [3] and plasma enhanced CVD (PECVD) [275]. A SiC encapsulation layer of 10–20 µm as an intermediate layer, i.e., barrier layer, is deposited on the surface of the graphite substrate, to avoid the out-diffusion of
Appendix A: Cell concepts

contaminants from the substrate into the devices. The SiC layer has a resistivity of $1.6 \times 10^8 \Omega \text{cm}$, and hence it is conductive to be available to a back side contact for solar cells. The SiC layer was deposited in a hot wall CVD system at atmospheric pressure. The precursor gas consisted of methyltrichlorosilane, argon, and hydrogen. The deposition temperature was 1200°C to 1300°C on graphite substrates [2]. Note that the other materials, e.g. SiNx and SiOx, can also be used as intermediate layers. So far, a SiOx intermediate layer has been demonstrated to provide a better quality of surface passivation than a SiC layer [143].

Subsequently, thin c-Si($p^+$) layers were fabricated on top of the intermediate layer. Those c-Si($p^+$) layers were deposited on top of the SiC layers using convection-assisted chemical vapor deposition (CoCVD) [3]. In order to cover small hillocks, a relatively thick c-Si($p^+$) layer of 20 µm was grown. Boron doping was applied aiming at an acceptor concentration of $4 \times 10^{18}$ cm$^{-3}$. As a consequence, the layers serve as a back surface field. The resulting layers had a grain size of less than 5 µm. The grain size has to be increased by a recrystallization process. Therefore, those c-Si($p^+$) layers are also called the seeding layers [4].

The CoCVD was also used to deposit the c-Si($p$) absorber layers with a thickness of approximately 20 mm and a boron doping concentration of approximately $2 \times 10^{16}$ cm$^{-3}$ [11]. Furthermore, the antireflection coatings, i.e., the SiNx and a-Si:H($i$) layers, were deposited using remote-PECVD. The PECVD system used including a RF glow discharge unit, which can weak the ionized plasmas productively.

McCann et al. [38] and Poortmans et al. [20] have introduced more details about the CVD techniques. They compared the cost, deposition rate, working temperature and pressure, and appropriate scopes of different CVDs. At the ZAE Bayern, CoCVD is applied actively using thermal convection to control the gas flow inside the reactor and to make full use of gaseous precursors. The reactor can be tilted by an angle against the horizontal orientation [20], p. 28.

Note that another successful method for producing c-Si($p$) absorber layers is based on the solid phase crystallization technique. Amorphous Si layers can be annealed in a furnace at typically 600°C for several hours until a completely crystallized poly-Si film is formed (grain size: 1–3 µm) [114], p. 10.

A.3 Layer recrystallization

A great amount of recombination centers exist at the grain boundaries, which negatively affects the silicon solar cell performance. In this work, increasing the
Appendix A: Cell concepts

average grain size of silicon is applied as an approach to improve the bulk quality. The material specification is given in Fig. A.1 by the grain size [291], p.454 and [292], p.7. Poly-Si has a smaller grain size than multi-Si, and hence poly-Si has more grain boundaries, corresponding to more recombination centers in poly-Si, e.g. defects and dislocations, than in multi-Si. Zone melting recrystallization (ZMR) was applied here to increase the grain size of the c-Si($p^+$) seed layers. ZMR is a high-temperature recrystallization technique, which can enlarge the size of the silicon grains in order to reduce the density of the electrically active defects and increase the cell efficiencies [293, 294]. There is one more step in the process, but a low cost and a low purity foreign substrate can be used [295].

Note that the low-temperature crystallization techniques include laser crystallization, solid-phase crystallization [112, 114, 136], rapid thermal processing, and vacuum and furnace annealing [295].

A.4 Plasma enhanced chemical vapor deposition

Plasma can break chemical bonds and achieve a given growth rate at low temperature. A PECVD system, the Roth & Rau AK1000, with microwave excitation frequency at 2.45 GHz is investigated in this work. This system has a heating stage in size of 40 × 40 cm², which is designed for large-scale solar cells. Kintzel et al. [275] measured the $S_{eff}$ of the Si wafers on the heating stage. His results show that these Si wafers have the $S_{eff}$ value of 32 ± 6 cm/s, and hence the experimental condition was not homogeneous.

As shown in Fig. A.2, the structure of the PECVD process is further investigated to improve the operation. There are two microwave generators (MW1 and MW2) on the chamber and four antennas guiding the microwave into the chamber. The NH₃ showers are over the antennas and the H₂ and SiH₄ showers are between the antennas and the heating stage. When the microwave generators are running, the two areas (Plasma area 1 and 2) will be covered by plasma. In these two areas, a homogeneous condition is expected.
The PECVD can work under pressure up to 0.001 mbar. The actual temperature on the sample stage is in the range of 0 to 350°C. The power of the microwave generators can work at 800 W to 1000 W. Low generator power (800 W) induces inhomogeneous plasma distribution in the chamber and further inhomogeneous deposition, whereas high generator power over 1000 W induces high energy reflection, i.e., energy loss, from the antennas to the generators, and hence the deposition will be also inhomogeneous and it will damage the microwave generators. In this work, 1000 W was set as default value in process.

The PECVD system has a remote plasma source and causes less surface damage during deposition. Furthermore, in PECVD the uniform and high quality layers can be produced at low temperatures. In addition, the plasma-induced damage can be reduced by depositing the layers at temperatures over 420°C or annealing at temperatures over 500°C [296]. Note that the PECVD system does have one drawback: Changing samples or releasing the pressure of PECVD is time-consuming, which can induce impurities into the chamber and the hydrogen effusion out of silicon solar cells, respectively.
A.5 Laser edge isolation

In our earlier works [8], edge isolation of thin-film cells was performed by plasma etching. In that process, a shadow mask is placed on the cell before the whole stack is exposed to the plasma. However, the process parameters for the plasma etching process were developed for monocrystalline silicon wafers, and obviously are not fully adequate for the thin-film crystalline cells. One frequently observed drawback was the partial under-etching of the full area. The reason for this is strongly varying surface properties of recrystallized layers on foreign substrates, as compared to a silicon wafer surface. The significantly higher surface roughness as well as the inhomogeneous orientation of the recrystallized grains are the dominant features causing the under etching.

Laser patterning and edge isolation is a very attractive alternative to plasma etch isolation. Specifically for amorphous Si thin-film solar cells, laser patterning and isolation have become standard production processes. Stimulated by the progress in laser patterning thin-film solar cells, a Nd:YVO₄ laser system (Rofin Power Line LP20, wavelength 1064 nm, 18W) was chosen for the edge isolation of thin-film recrystallized Si cells, so-called laser edge isolation (LEI). Typical laser pulses for Si ablation had a width of 30 ns and energy of about 2 mJ. The diameter of the laser beam in the focus was about 50 µm and allowed us to pattern trenches of approximately 75 µm width into the absorber and the p⁺ layer in a single step [11].

A.6 Spin on doping and rapid thermal process

Spin on doping (SOD) is a basic technique for phosphor diffusion. The doping concentration and the depth of p-n junction can be measured by sheet resistance, which is highly dependent on the SOD process temperature and duration.

The following rapid thermal process RTP decides the depth of p-n junction using UniTemp GmBH. Table A.1 gives the measured results of corresponding parameters. In this work, the best cell efficiency was achieved based on the same experimental condition as Sample 4 in Table A.1.
Appendix A: Cell concepts

Table A.1 Temperature–Sheet resistance for the volume of phosphor solution is 2 ml, the duration is 100 sec. $T_p$ denotes the peak temperature of SOD. The float-zone 0.5 $\Omega$ cm $2 \times 2$ cm$^2$ $p$-Si wafers were used as substrates. Corresponding donator concentrations ($N_D$) were simulated by PC1D.

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References


References


[16] IHS, "Global PV demand could reach 57 GW in 2015."


References


References


[88] V. Yelundur, A. Rohatgi, J. Ji-Weon, and J. I. Hanoka, "Improved string ribbon silicon solar cell performance by rapid thermal firing of screen-


References


References


References


S. Riessler, G. Micard, O. Breitenstein, A. Zuschlag, S. Seren, B. Terheiden, *et al.*, "Comparison of the recombination velocity at grain boundaries gained by lock-in thermography and light beam induced


References


# List of Acronyms

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<td>Al-BSF</td>
<td>Aluminum as Back Surface Field</td>
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<td>Al₂O₃</td>
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<td>a-Si:H(i)</td>
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<td>BDEW</td>
<td>Bundesverband der Energie- und Wasserwirtschaft</td>
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<td>Back Surface Field</td>
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