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Design of electron beam evaporated Si thin films for solid phase crystallized solar cells on glass

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Design of electron beam evaporated Si thin films for solid phase crystallized solar cells on glass

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Abstract

The solid phase crystallization of high-rate electron beam evaporated amorphous Si layers on glass is a promising low-cost approach to fabricate high-quality polycrystalline thin film solar cells. This thesis presents a comprehensive structural analysis of high-rate electron beam evaporated Si layers on various SiN- and ZnO-coated and nanostructured sol-gel coated glass substrates. Derived design parameters are used to develop e-beam evaporated Si thin film solar cells and explore novel cell concepts embedded in a transparent conductive ZnO front contact and light harvesting architectures.

A systematic analysis of the solid phase crystallization kinetics of evaporated Si on SiN and ZnO-coated glass substrates with different topographic features reveals an essential correlation between the surface roughness of the substrate, the deposition temperature of the Si and the crystal nucleation rate. The crystal growth velocity, however, is not influenced by the substrate topography. In addition, the time-lag decreases with increasing deposition temperature, being consistent with a declining structural disorder in the amorphous material. These results define design rules that allow for the systematic control of the microstructure of the resulting poly-Si film and give rise to the development of poly-Si solar cells on glass. A conversion efficiency of 6.8% is achieved for poly-Si mini-modules on planar SiN-coated glass deposited at a deposition rate of 600 nm/min by systematically varying the deposition parameters. This result is equivalent to the highest efficiencies in an established low-rate PECVD-based reference system. The implementation of a rear-side light trapping structure into the device leads to a record efficiency of 8%. A working device on a ZnO:Al front contact layer, however, requires implementing a diffusion barrier that separates the ZnO layer from the poly-Si film. Texture-etched ZnO and self-organizing spheres embedded in sol-gel are found to be e-beam compatible statistical light trapping approaches, providing a sufficiently flat template to grow compact poly-Si in accordance to the distinct growth characteristics of e-beam evaporated Si. Advanced photon management demands a controlled design of nanostructured Si. An easily scalable fabrication process for periodic arrays of equidistant free-standing Si crystals is developed on nano-imprinted sol-gel coated glass substrates by selectively etching e-beam evaporated Si. The design is extremely versatile and can simply be controlled by varying the feature size of the used imprint stamp. Crystalline Si arrays on a sol-gel template with a $2\mu\text{m}$ period exhibit a tremendous absorption, inspiring the development of periodic three-dimensional solar cell architectures.

Contents

1. Introduction	1
2. Background	7
2.1. Theory of crystallization kinetics in amorphous Si	7
2.1.1. Metastable states of Si	8
2.1.2. Thermodynamics of nucleus formation	9
2.1.3. Kinetics of nucleation	14
2.1.4. Crystal growth	18
2.1.5. Isothermal transformation curves - JMAK model	21
2.2. Photovoltaic characteristics	22
2.2.1. Current-voltage characteristic of a solar cell	22
2.2.2. Recombination mechanisms and diffusion length	24
3. Experimental	27
3.1. Functional transparent coatings and nanostructures	27
3.2. Electron beam evaporation of Si	31
3.2.1. PVD a-Si growth characteristics	31
3.2.2. Electron beam evaporator	32
3.3. Poly-Si solar cell device fabrication	34
3.3.1. Mini-module fabrication on SiN-coated glass	34
3.3.2. Poly-Si solar cell concept on ZnO-coated glass	37
3.4. Characterization techniques	38
3.4.1. Electron microscopy	38
3.4.2. Atomic force microscopy	40
3.4.3. Raman spectroscopy	42
3.4.4. Photothermal deflection spectroscopy	42

3.4.5. Photovoltaic characterization	44
3.5. Conclusion	45
4. Characterization and control of the crystallization kinetics in Si	47
4.1. Introduction	47
4.2. Sample preparation	48
4.3. Scientific method of investigation	49
4.3.1. Experimental procedure	49
4.3.2. Analysis of the crystal growth velocity	50
4.3.3. Determination of the nucleation rate $I(t)$	52
4.4. Influence of the substrate topography on the crystallization process	54
4.5. Influence of the structural disorder in a-Si on the nucleation process . . .	60
4.6. Discussion	63
4.6.1. Characteristics of the nucleation process in a-Si and a-Si:H	63
4.6.2. Steady state nucleation rate and $E_{I_{ss}}$	64
4.6.3. Correlation between time-lag and structural disorder in a-Si	66
4.6.4. Design rules	66
4.7. Conclusion	69
5. Development of poly-Si thin film solar cells on planar glass	71
5.1. Introduction	71
5.2. Optimization of poly-Si thin film mini-modules on SiN-coated glass . . .	72
5.3. 8% efficient thin film mini-module with implemented backside texture . .	77
5.4. Poly-Si solar cells with an implemented ZnO:Al front contact layer . . .	78
5.5. Discussion	80
5.5.1. Deposition parameters	80
5.5.2. Comparison to PECVD poly-Si on planar glass	83
5.5.3. Design components for an optimized front contact layer	84
5.6. Conclusion	85
6. Statistical light trapping approaches	87
6.1. Introduction	87
6.2. Self-organizing silica spheres and wet-chemical etched ZnO	88
6.3. Analysis and discussion	89
6.3.1. Structural properties	89

6.3.2. Light trapping characteristics	92
6.4. Conclusion and outlook	95
7. Periodic arrays of Si crystals on nano-imprinted structures	97
7.1. Nanostructured photon management	97
7.2. Fabrication process	98
7.3. Microscopic analysis	101
7.4. Design versatility and applicability	104
7.5. Conclusion	106
7.6. Outlook	107
8. Conclusion	109
A. Appendix	113
A.1. Surface topography of SiN and ZnO-coated glass substrates	113
A.2. Determination of the activation energies of I_{ss} and τ	116
A.3. Diffusion profiles of Zn and Al in Si on ZnO:Al	120
A.4. Poly-Si on nano-imprinted sol-gel coated glass prepared by direct growth	121
Bibliography	123
List of Figures	143
List of Tables	145
Acknowledgement	147
List of publications	149

1. Introduction

With its annual energy demand of 16 TWyr and a projected increase of 50% by 2035, the world is entering an era of 'extreme energy'. New energy sources such as deepwater oil reservoirs, petroleum deposits in oil sands, biomass and off-shore wind farms, which were considered beyond reach just a decade ago, are becoming viable options [1]. However, only renewable energy resources can cover this surging demand for energy at a stabilized carbon dioxide concentration in the atmosphere, while also offering a sustainable solution to reduce our 'carbon footprint' and ultimately end our dependence on crude oil [2, 3]. With 125,000 TW of global incident sunlight, photovoltaics (PV) is a prominent form of renewable energy that can tackle this 'terrawatt challenge' by commercializing effective methods to tap this abundant source of energy [4].

Although extensive research in photovoltaics has facilitated the progress in device engineering and performance, resulting in crystalline Si solar cells exhibiting conversion efficiencies above 20% and optimized III-V compound semiconductors in multi-junction concepts yielding a record efficiency of over 41% in highly concentrated sunlight, the costs for photovoltaics still exceed those of other renewable energy sources [5, 6, 7, 8]. Consequently, the key goal is the fabrication of highly effective solar cell devices by utilizing inexpensive production processes at minimized material costs.

The abundance of the non-toxic material Si and the technological achievements of the Si semiconductor industry in the last 50 years have spurred the commercialization of monocrystalline and multicrystalline Si wafer-based solar cells, which cover over 80% percent of today's solar cell production. However, the high material consumption and a complex series connection of the individual cells still inhibit their cost reduction potential [9].

Si thin film technologies utilize a large area deposition process of a 300 nm to 2 μm

thick Si layer on a foreign substrate, decreasing the cell thickness by a factor of 300. Amorphous hydrogenated Si thin film solar cells are deposited by chemical vapor deposition (CVD) on glass substrates or flexible plastic substrates in a roll-to-roll process, and modules are subsequently produced in a monolithic cell interconnection [9, 10, 11]. A transparent conductive oxide (TCO) serves as a contact layer and allows for an effective current collection from the a-Si:H layer [12, 13]. However, a-Si:H is prone to light-induced degradation. This process is commonly known as the Staebler-Wronski effect [14, 15]. Single-junction a-Si cells yield an efficiency of 10% and are only able to reach a stabilized efficiency of 6-8% in commercial applications [6].

The development of advanced multi-junction systems consisting of an a-Si and a nanocrystalline Si (nc-Si) cell, which comprises nano-crystallites embedded in an amorphous matrix, has led to an improvement of the performance due to the deviating absorption properties of amorphous and crystalline Si [16]. These optimized tandem-devices currently have an efficiency of 12% [6]. However, the microstructure of the constituents in the deposited a-Si and nc-Si limits the electronic quality and thus the prospects of dramatic performance improvements.

Polycrystalline Si thin film solar cells

Polycrystalline Si thin film (poly-Si) solar cell concepts strive to fabricate crystalline Si thin films of excellent electronic quality on foreign substrates by using the advantages of thin film technology. Various approaches are being pursued to economically produce high-quality poly-Si layers and explore the potential of the poly-Si thin film technology. For example, seed layer approaches are based on the preparation of thin crystalline layers that impose the crystalline structure onto a subsequently epitaxially grown Si layer in a second deposition process. Aluminium induced crystallization (AIC) and laser crystallization processes attempt to produce a seed layer, consisting of large grains with a preferential structural orientation [17, 18]. While the AIC process allows the preparation of grains of $\sim 10\ \mu\text{m}$ size, even larger crystals (up to $\sim 100\ \mu\text{m}$) have been obtained by laser crystallization [19]. Recently, researchers utilized the AIC process to create a poly-Si cell with an efficiency of 8% [20].

The crystallization of deposited a-Si layers in a solid phase crystallization process (SPC) by thermal annealing at 600°C is a noncomplex and appealing option to prepare poly-Si layers with crystal grains in the micrometer size range. In the 1990s, Sanyo applied the solid phase crystallization method to produce poly-Si cells on steel substrates, yield-

ing a conversion efficiency of 9.2% [21, 22, 23]. CSG Solar optimized the preparation conditions and device fabrication for cells prepared on commercial float glass (SCHOTT Borofloat 33) and began to produce these commercially in 2004 [24]. The company set a new benchmark for poly-Si solar cells by presenting a 10.4% efficient module in 2007 [25].

This conventional poly-Si thin-film technology relies on the low-rate plasma enhanced chemical vapor deposition (PECVD) technique with deposition rates of 30 nm/min and necessitates a sophisticated contacting structure that ensures a sufficient charge carrier collection. However, in order to improve the competitiveness of the SPC concept in a rapidly growing solar cell market, it is necessary to enhance the cell efficiency while simultaneously reducing the associated module production costs. A prerequisite is the design of a poly-Si thin film solar cell concept that is embedded in an excellent light harvesting architecture and simple contacting scheme, utilizing an inexpensive high-rate deposition technique.

The high-rate deposition technique electron beam (e-beam) evaporation presents a potential alternative to the PECVD technique with deposition rates of 1 $\mu\text{m}/\text{min}$ and allows for the production of Si layers in a drastically reduced time span. In addition, the technique is simple and applicable to continuous in-line processes and does not involve toxic gases. High-throughput evaporators are industrially used for optical coatings, but the technology's feasibility for the fabrication of PV-grade Si has yet to be fully explored. In 2007, the highest reported efficiencies of evaporated poly-Si thin film solar cells were between 2-3% [26].

Further, the additional implementation of a transparent and conductive aluminum-doped zinc oxide (ZnO:Al) film facilitates an excellent electric front contact and permits the incorporation of a simple contacting scheme based on a monolithic series connection, which has already been established in other thin film technologies. Recent studies confirmed that the electric properties of ZnO:Al layers implemented in a cell structure improve during a thermal treatment, showing a charge carrier mobility of 67 cm^2/Vs [27]. These characteristics underscore the compatibility of ZnO:Al with the thermal treatments required for the poly-Si production and suggest the development of an evaporated poly-Si cell with an embedded ZnO:Al front contact layer. However, this task demands an accurate assessment of the influence of the ZnO:Al layer on the growth process of evaporated Si and its associated electronic properties.

The optimization of the optical design of poly-Si thin-film solar cells by employing efficient and easily scalable techniques is of crucial importance for the enhancement of the absorption of the incident light and hence the current collection at significantly reduced cell thicknesses. Wet-chemical etched ZnO:Al is known to serve as effective light trapping layers, while the controlled preparation of nanostructures, whose absorption properties can exceed the limit of randomly textured Si layers, open design possibilities for advanced photon management [28]. However, the design of an efficient poly-Si solar cell embedded in such novel structures requires the investigation of the microstructure of evaporated poly-Si and its correlation to the underlying substrate texture.

This thesis will present a comprehensive structural analysis of e-beam evaporated Si layers on ZnO-coated and sol-gel based nanostructured glass substrates, by elucidating the influence of the surface roughness on the solid phase crystallization kinetics of Si and linking the characteristics of the substrate texture to the microstructure of the crystallized Si. The derived design parameters will be used to explore the potential of the application of e-beam evaporated poly-Si in thin film solar cells.

Thesis outline

In chapter 2, the framework for an accurate analysis of evaporated poly-Si thin film solar cells is established. A concise review of the basics of the phase transformation in amorphous Si serves as a foundation for the analysis of the crystallization kinetics. An introduction to the photovoltaic characteristics of poly-Si solar cells completes this chapter.

Chapter 3 provides a precise overview of the employed fabrication processes, experimental methods and analytical techniques. The developed transparent functional coatings and sol-gel based nanostructures are described, which serve as bases for studying the growth characteristics of amorphous Si prepared in a customized electron beam evaporator system. The poly-Si thin film mini-module fabrication process on SiN-coated glass and the simplified cell preparation on ZnO-coated glass are then outlined, before concluding with the presentation of the employed microscopy and spectroscopy techniques.

Chapter 4 presents a comprehensive study of the growth and nucleation processes of Si on SiN and selected ZnO:Al with various nano-roughnesses. It elucidates on the influence of

the surface topography of the substrate and the structural disorder of the e-beam evaporated a-Si on the solid phase crystallization kinetics. This investigation is the basis for the identification of the design rules that allow for a controlled fabrication of large-grained poly-Si on a wide range of substrate topographies.

Chapter 5 discusses the applicability of high-rate e-beam evaporated poly-Si thin film solar cells on planar glass and addresses the potential of novel device concepts. Based on the design requirements established in the previous chapter, the electronic quality of e-beam evaporated poly-Si on planar SiN-coated glass is critically assessed through the optimization of the deposition process and by subsequently comparing it to the PECVD reference system. The opportunities and challenges of the fabrication of an efficient poly-Si cell embedded in a ZnO-based front contact layer are highlighted.

Chapter 6 explores the applicability of statistical light trapping approaches to e-beam evaporated Si. The investigation of the growth process of evaporated Si on wet-chemical etched ZnO and self-organizing silica spheres embedded in sol-gel leads to the definition of certain design restrictions for the growth of high-quality poly-Si. An optical and photovoltaic analysis of the textured layers complements the structural investigation and leads to the development of a novel poly-Si solar cell design.

Chapter 7 is devoted to a novel technique for the large-area fabrication of free-standing equidistant Si crystals on nano-imprinted sol-gel coated glass templates prepared in a solid phase crystallization process (SPC) and subsequent selective etching. A microscopic analysis of the structures examines the distinct growth mechanism of e-beam evaporated Si, which ultimately enables the realization of these periodic structures in a selective etch process. The versatility of the preparation process and the beneficial light trapping properties of the presented structures open design possibilities for three-dimensional solar cell architectures with integrated photonic structures.

Chapter 8 concludes by summarizing the achieved results and highlighting the quintessential design considerations for e-beam evaporated thin film solar cells.

2. Background

This chapter provides an introduction to the fundamental concepts, which serve as a foundation for the kinetic, structural and photovoltaic characterization of evaporated poly-Si films and solar cell devices.

Section 2.1 presents a concise summary of the essential aspects of the solid phase crystallization kinetics in Si, addressing the different metastable states of Si before elaborating upon the kinetics of the nucleation and crystal growth processes.

Section 2.2 briefly summarizes the essential photovoltaic parameters of a solar cell device and reviews the specific recombination processes in poly-Si, which impose restrictions on the design of poly-Si solar cell devices.

2.1. Theory of crystallization kinetics in amorphous Si

A precise description of the crystallization kinetics in amorphous Si necessitates a review of the basic concepts of the involved phase transformation. First, section 2.1.1 summarizes the basic definitions and terminologies of metastable Si. Section 2.1.2 reviews the thermodynamic foundation for an accurate description of a phase transformation. In section 2.1.3, the kinetic models for nucleation in amorphous films are presented, while section 2.1.4 is dedicated to the concept of crystal growth. Finally, section 2.1.5 addresses the phenomenological model for phase transformations which allows for the analysis of the crystallization process.

2.1.1. Metastable states of Si

Crystallization entails a phase transformation from a disordered to an ordered state. A disordered state does not exhibit a long-range translational and long-range orientational order. Such characteristics are found in (undercooled) liquids and amorphous materials. Materials in amorphous states can be prepared by direct deposition or by quenching from their liquid phase. The transformed and therefore ordered state, in contrast, has a well established long-range order.

Upon cooling a liquid rapidly below its melting temperature, an immediate crystallization process can be inhibited, since the formation of crystal nuclei requires the creation of an energetically unfavorable solid-liquid interface (section 2.1.2). Therefore, the liquid state can be retained below T_{melt} in a process called undercooling [29]. If the liquid is quenched rapidly without starting to crystallize, the material will reach a configurationally frozen state due to the increasing viscosity of the material and the lower atomic mobility. The states are called amorphous while the material itself is a glass¹. The configurational freezing takes place upon cooling below the glass transition temperature T_g , referring to the temperature at which the viscosity approaches a value of the order of 10^{12} Pas [30, 31]. The frozen nature of amorphous states gives rise to the existence of various metastable states with dissimilar local energetic minima. Since amorphous materials tend to approach equilibrium conditions, structural relaxation processes can initiate a transition between one amorphous configuration to an energetically favourable disordered state. A disordered material between the melting temperature T_{melt} and the glass transition temperature T_g , however, exhibits a sufficiently high atomic mobility to reach the state of an undercooled liquid in an internal metastable equilibrium. The transition between the amorphous state and undercooled liquid is called glass transition [32].

In 1959, Cohen and Turnbull stated the universality of the glass transition and predicted that all liquids undergo a glass transition if the cooling process is carried out fast enough to avoid crystallization [33].

Silicon exhibits a complex phase transition between its metallic liquid state and its semi-conducting amorphous state, consisting of consecutive transformation events occurring in a narrow temperature range among undercooled metallic liquid and semiconducting

¹It should be noted that the term glass is only reserved for amorphous materials prepared by quenching from the liquid phase and does not include directly deposited amorphous films.

liquid states and multiple metastable semiconducting amorphous states [34, 35, 36]. In 2004, the existence of the theoretically predicated glass transition in a-Si between the semiconducting amorphous Si and undercooled liquid semiconducting Si was finally experimentally proven [34].

The unique phase transition of Si is the cause for its reluctance to form a glass by thermal cooling from the liquid phase. In irradiation experiments with picosecond laser pulses, cooling rates of 10^9 K/s had to be exceeded to suppress crystallization and re-solidify liquid Si in its disordered amorphous state [37, 38].

Since these high cooling rates make the fabrication of a-Si by quenching liquid Si not favorable, technologically important amorphous Si is directly prepared by employing chemical and physical vapor deposition techniques or by amorphizing c-Si by ion-bombarding to displace atoms directly from their lattice sites [15, 39]. The structural parameters of those prepared amorphous Si depend on the deposition condition of the chosen method, allowing for the preparation of a-Si films in various amorphous states with deviating enthalpy, dangling bond concentration, atomic structure and optical and vibrational properties [40, 41, 42, 43, 44, 45].

Figure 2.1 shows the free energy diagram for two amorphous states (relaxed and unrelaxed) and the metallic liquid state with respect to its crystalline phase. The free energy of a-Si is always higher than the one of c-Si, being manifested in the frozen metastable nature of the amorphous states. Assuming that the heating rate provided by a ultra-short laser pulse is high enough to inhibit solid phase crystallization, the amorphous-liquid phase transformation depends on the initial state of the silicon film and shows a decreasing melting temperature T_{melt} with increasing structural disorder. If the heating rate is too low, crystallization cannot be suppressed, resulting in the initiation of a solid phase crystallization process at temperatures above $\sim 500^\circ\text{C}$ [39, 46].

2.1.2. Thermodynamics of nucleus formation

The nucleation process in amorphous materials can either be driven by their intrinsic parameters in a homogeneous nucleation process or a foreign substrate can be involved in a heterogeneous nucleation process. The presentation of the thermodynamics of nucleus

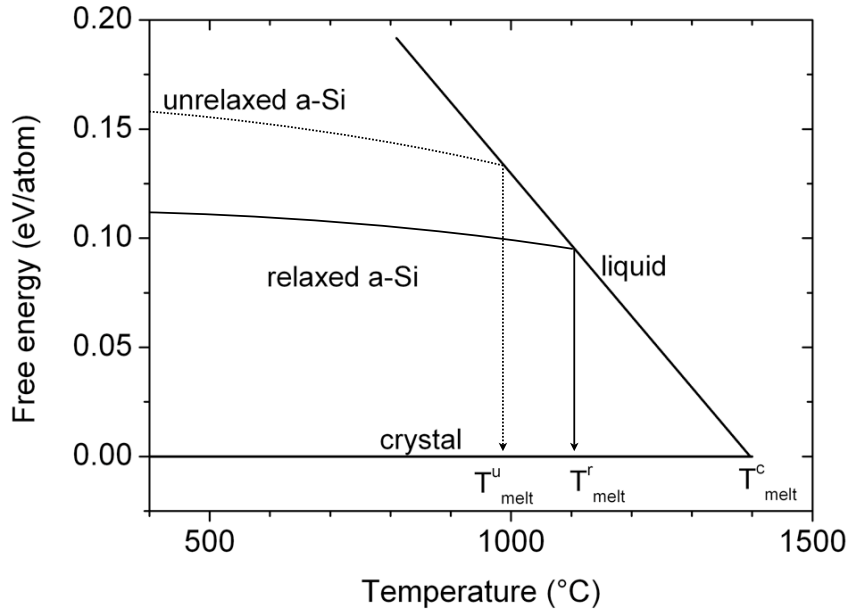


Figure 2.1: Free energy diagram of amorphous and liquid Si with respect to crystalline Si as a function of the temperature. Unrelaxed amorphous Si exhibits a lower melting point T_{melt}^u than relaxed Si (T_{melt}^r). Note that the free energy difference between the relaxed amorphous state and the crystalline state ΔG_{ac} is 0.11 eV at 600°C [46].

formation for either of these processes is inevitable for an accurate description of the kinetic process of nucleation.

Homogeneous nucleation

Nucleation theory is based on the assumption that clusters develop by acquiring atoms in a series of bimolecular reactions [29, 32, 47]. Starting from a single atom α , a sequence for cluster formation can be evolved:



β_i denotes a cluster containing i atoms. The second law of thermodynamics is the thermodynamic foundation of a phase transition. At a constant temperature and externally imposed pressure, the stability of each cluster containing i atoms in the crystal phase is

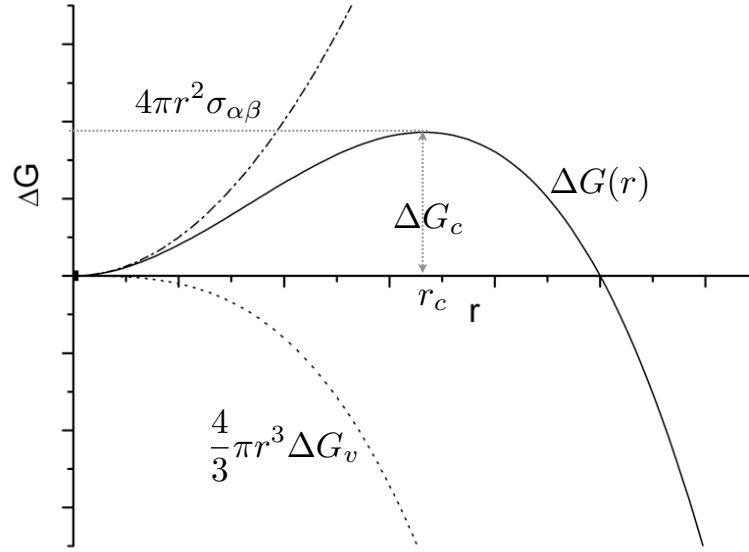


Figure 2.2: The Gibbs free energy of a growing cluster is depicted, which is determined by a superposition of a volume and surface-related term. The cluster has to exceed a critical size in order to initiate nucleation, according to Equation 2.5.

determined by its free energy ΔG_i . Crystallization occurs when it is accompanied by a decrease of ΔG_i , making ΔG_i the driving force for a phase transition [48]. The bulk formation in a cluster leads to a decrease of the Gibbs free energy and is represented by a negative volume term proportional to i , whereas the formation of the α - β interface requires addition of work due to surface tension, which is proportional to the number of atoms at the cluster surface s_i :

$$\Delta G_i = \Delta G_v \cdot i + \sigma_{\alpha\beta} \cdot s_i \quad (2.2)$$

ΔG_v denotes the free energy change associated with the adhesion of one atom to the cluster and $\sigma_{\alpha\beta}$ is the interface free energy of each atom at the α - β interface. The volume term ΔG_v is equal to the free energy difference ΔG_{ac} existing between the amorphous and the crystalline phases subtracted by a negligible, size dependent, free energy increase Δg_{el} , due to elastic expansion with respect to the bulk lattice of ordered clusters [46].

For spherical clusters, the number of atoms in the volume i and surface s_i of a cluster can

be correlated to the cluster's radius r , leading to the expression of $\Delta G(r)$:

$$\Delta G(r) = \frac{4\pi r^3}{3} \Delta G_v + 4\pi r^2 \sigma_{\alpha\beta} \quad (2.3)$$

According to Equation 2.3, ΔG increases with increasing r for small cluster sizes and reaches a maximum ΔG_c at a critical cluster size r_c . Upon expanding the cluster with increasing r , ΔG declines steadily. Therefore, clusters with $r < r_c$ tend to decay, whereas clusters with $r > r_c$ can grow to macroscopic sizes. Figure 2.2 shows ΔG as a function of r and illustrates the influence of the bulk and surface related terms on the characteristics of ΔG [29, 32, 48, 49]. The work to form a critical nucleus ΔG_c and critical cluster size r_c are derived from Equation 2.3 by solving $\frac{d\Delta G}{dr} = 0$:

$$\Delta G_c = \frac{16}{3} \pi \frac{\sigma_{\alpha\beta}^3}{\Delta G_v^2} \quad (2.4)$$

$$r_c = -\frac{2\sigma_{\alpha\beta}}{\Delta G_v} \quad (2.5)$$

Studies on a-Si reported a critical radius r_c of 0.58 nm and ΔG_c of 2 eV [46]. Calorimetric measurements demonstrated that the free energy difference ΔG_{ac} between the relaxed a-Si and the crystalline phase is 0.11 eV/atom (Figure 2.1) [39, 40]. In addition, Δg_{el} is $\approx 5.3 \cdot 10^{-3}$ eV/atom [46, 50].

Heterogeneous nucleation

Homogeneous nucleation is regarded as an intrinsic process which depends exclusively on intrinsic parameters. However, foreign phases can influence the nucleation process. The deliberate implementation of metals, such as Al or Ni, in amorphous Si is conducted to alter the crystal formation in a metal induced crystallization process [18, 51]. However, in contrast to these actively implemented impurities, incorporated defects in the deposited material and existing interfaces can represent preferential nucleation sites [29, 49, 52]. Volmer developed a model for an interface-assisted nucleation process between a flat foreign substrate and the investigated material, which is illustrated in Figure 2.3 [53]. Clusters grow to spherical caps with radius r , comprising the same curvature at any point due to the isotropy of the disordered and ordered phase. A geometrical analysis provides the expression for the work of the exposed volume fraction $f(\theta)$ and exposed surface

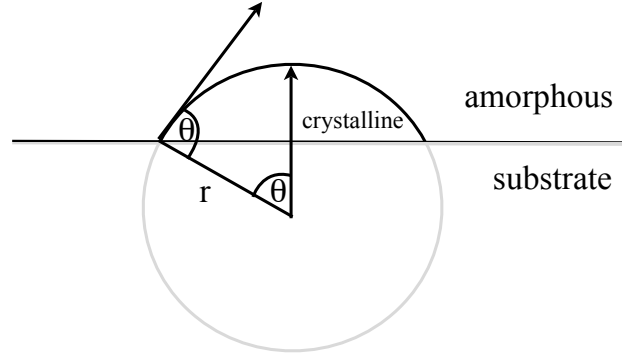


Figure 2.3: Volmer's model for an interface-assisted nucleation process is illustrated. Due to the isotropy of the parent phase, the crystal grows like a spherical cap. The exposed volume fraction $f(\theta)$ can be derived from the contact angle θ .

fraction as function of the contact angle θ .

$$\begin{aligned} f(\theta) &= \frac{(2 + \cos \theta)(1 - \cos \theta)^2}{4} \\ s(\theta) &= \frac{1 - \cos \theta}{2} \end{aligned} \quad (2.6)$$

The exposed volume fraction $f(\theta)$ ranges between 1 at $\theta = 0^\circ$ and 0 at $\theta = 90^\circ$. The work for heterogeneous cluster formation ΔG^{het} , is obtained in analogy to the homogeneous case (Equation 2.3), by considering $f(\theta)$ and $s(\theta)$ in the respective volume and surface related terms and a third term arising from the replacement of the amorphous-substrate interface by the crystal-substrate interface [52, 32].

$$\Delta G^{het}(r) = \Delta G_v \cdot f(\theta) \cdot \frac{4}{3} \pi r^3 + \sigma_{\alpha\beta} \cdot s(\theta) \cdot 4\pi r^2 + \pi(r \sin \theta)^2 (\sigma_{\beta s} - \sigma_{\alpha s}), \quad (2.7)$$

α and β respectively denote the amorphous and crystalline phase and s being the substrate. The Young equation correlates the contact angle θ with the free interfacial energies [52]:

$$\sigma_{\beta s} - \sigma_{\alpha s} = -\sigma_{\alpha\beta} \cos \theta \quad (2.8)$$

Plugging Equation 2.8 into Equation 2.7 gives:

$$\Delta G^{het}(r) = \left(\Delta G_v \cdot \frac{4}{3} \pi r^3 + \sigma_{\alpha\beta} \cdot 4\pi r^2 \right) f(\theta) \quad (2.9)$$

Comparing Equation 2.9 to Equation 2.3 yields:

$$\Delta G_c^{het} := \Delta G^{het}(r_c) = \Delta G_c^{hom} \cdot f(\theta) \quad (2.10)$$

Consequently, the heterogeneous nucleation process is driven by a lower work to form a critical nucleus, with $f(\theta)$ determining the phase transition [32, 52, 53]. While the condition $\theta = 0^\circ$ resembles the case of homogeneous nucleation and clusters grow to spheres without the assistance of the interface, $0 < \theta < 90^\circ$ leads to a decreasing ΔG_c^{het} in an interface-assisted nucleation process, with the critical number of atoms i_c^{het} in a cluster and hence the volume of a critical cluster being reduced by the factor $f(\theta)$.

2.1.3. Kinetics of nucleation

Classical nucleation theory originated in the 1920s and is mainly attributed to the work of Volmer and Weber, and Becker and Döring [49, 54, 55].

Model based on an equilibrium distribution of clusters

Based on the thermodynamic results, Volmer and Weber developed the first kinetic model for nucleation, employing the equilibrium cluster distribution n_i^{equ} (Maxwell-Boltzmann statistics) [56]:

$$n_i^{equ} = n_0 \cdot \exp\left(-\frac{\Delta G_i}{k_B T}\right) \quad (2.11)$$

n_0 represents the total number of clusters in a mixture of $n_1 \dots n_i$ clusters, and T and k_B denote the temperature and the Boltzmann constant.

Volmer and Weber ignored n_i^{equ} for clusters exceeding the critical number of atoms i_c since n_i^{equ} diverges for large i , and assumed that nucleation occurs when a critical cluster acquires one more atom. [29, 32, 49, 54]. The occurrence of nucleation is therefore determined by

$$\beta_{i_c} + \alpha \xrightarrow{k_{i_c}^+} \beta_{i_c+1}, \quad (2.12)$$

where $k_{i_c}^+$ represents the jump frequency from the disordered state to a critical cluster to initiate nucleation.

The nucleation rate I_{equ} defined by the number of nuclei per unit volume and time is then

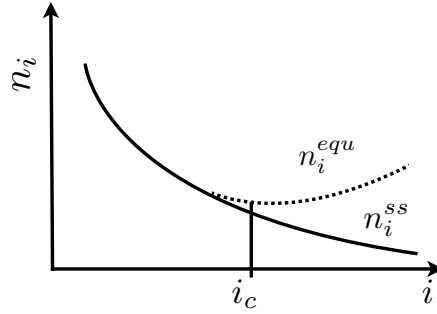


Figure 2.4: The equilibrium cluster distribution n_i^{equ} introduced by Volmer and Weber and the steady state cluster distribution n_i^{ss} developed by Becker and Döring as a function of the cluster size i . The distribution functions converge for small clusters but differ drastically after exceeding the critical cluster size containing i_c atoms.

given by

$$I_{equ} = s_{i_c} \cdot k_{i_c}^+ \cdot n_{i_c}^{equ} = s_{i_c} \cdot k_{i_c}^+ \cdot n_0 \cdot \exp\left(\frac{-\Delta G_c}{k_B T}\right), \quad (2.13)$$

where s_{i_c} denotes the number of surface atoms in the critical cluster.

Steady state model

The equilibrium distribution model is based on the assumption that every crystal grows to a macroscopic size as soon as it reaches its critical cluster size. However, post-critical clusters can decay with a certain probability and the equilibrium distribution cannot be reached. This represents a fundamental drawback of this model. Therefore, Becker and Döring developed a nucleation model based on a steady state cluster distribution n_i^{ss} , which is formed by clusters acquiring and losing individual atoms [29, 32, 49, 55]. Since particle conservation demands the integral over the steady state distribution to converge, n^{ss} essentially becomes zero for large i . At subcritical sizes, however, a cluster population close to the equilibrium value is reached since the natural tendency to form the crystalline phase is balanced by high values of atom jump rates k_i^- producing cluster dissolution. Both distributions are displayed in Figure 2.4.

The resulting steady state nucleation rate I_{ss} consists of a k_i^+ -dependent term that is ascribed to cluster generation, and a second term which takes the back-flux (i.e. cluster decay) into consideration [29, 32, 55]:

$$I_{ss} = s_i \cdot k_i^+ \cdot n_i^{ss} - s_{i+1} \cdot k_{i+1}^- \cdot n_{i+1}^{ss} \quad (2.14)$$

I_{ss} can be determined by using the analytical approach of Kelton, Greer and Thompson, considering the boundary conditions $n_i^{ss} \rightarrow n_i^{equ}$ for $i \rightarrow 0$ and $n_i^{ss} \rightarrow 0$ for $i \rightarrow \infty$ [57, 46].

$$I_{ss} = s_{i_c} \cdot k_{i_c}^+ \cdot n_0 \cdot \left(\frac{\Delta G_c}{3\pi k_B T} \right)^{\frac{1}{2}} \cdot \exp \left(\frac{-\Delta G_c}{k_B T} \right) \quad (2.15)$$

The steady state nucleation I_{ss} differs from the Volmer-Weber equation (Equation 2.13) by the so-called Zeldovich factor

$$\Gamma_z = \left(\frac{\Delta G_c}{3\pi k_B T} \right)^{\frac{1}{2}}, \quad (2.16)$$

which exhibits a weak temperature dependence and takes into account the changes of the nucleation rate accompanied by choosing a steady state cluster distribution [29, 32, 55]:

$$I_{ss} = \Gamma_z \cdot I_{equ} \quad (2.17)$$

The influence of a heterogeneous nucleation process on the steady state nucleation rate becomes evident, when Equation 2.10 is revisited in the light of the just derived kinetic concept. Lowering ΔG_c immediately leads to an increase of the steady state nucleation rate I_{ss} . The difference between I_{ss}^{hom} and I_{ss}^{het} for the same system is ultimately determined by $f(\theta)$ and can exceed several orders of magnitude.

In general, the steady state model applies to experimental settings of a certain duration which allows for establishing a steady state distribution n_i^{ss} . If the time frame is too short, n_i^{ss} cannot be reached and transient effects may have to be taken into account.

Transient nucleation - Time dependence of $I(t)$

Since clusters evolve in a series of bimolecular reactions, the temperature-dependent steady state cluster distribution n^{ss} cannot change immediately upon changing the temperature, but has to be established. Due to the inability of these configurational fluctuations to occur instantaneously, a sudden increase of the annealing temperature from T_{low} to T_{high} results in a transition from a $n^{ss}(T_{low})$ to $n^{ss}(T_{high})$ within a certain time [47]. The regime in which the cluster distribution $n_{i,t}$ exhibits a time dependence and still has to acquire its steady state is referred to as the transient regime of the nucleation process. Figure 2.5 illustrates the nucleation rate as a function of the isothermal annealing time t . First, the time-lag τ defines the time between the start of the isothermal annealing and the first ob-

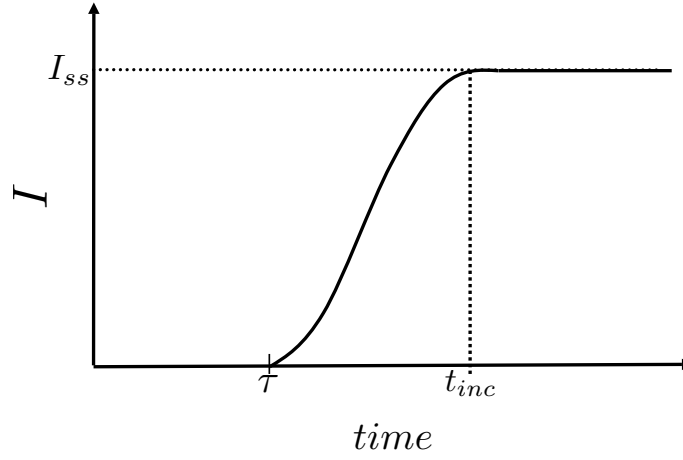


Figure 2.5: The nucleation rate $I(t)$ is displayed as a function of time t . The steady state nucleation rate I_{ss} is reached after the incubation time t_{inc} has passed. τ denotes the time lag, the time before the first nucleation event happens.

served nucleation event [29, 52, 58]. Within the time regime $\tau < t < t_{inc}$, the nucleation rate increases until it reaches its steady state level at the incubation time t_{inc} [47, 46]. For $t > t_{inc}$, the nucleation rate does not exhibit a time dependence.

The kinetic factor in amorphous-crystal transformations

Turnbull and Fisher determined the corresponding prefactor k_{ic}^+ for amorphous-crystalline phase transitions [59, 49, 29]. Since the cluster formation in Si is achieved by the diffusive motions of neighboring atoms, the diffusivity D in the amorphous state limits these diffusive jumps per atom k_{ic}^+

$$k_{ic}^+ = \frac{6D}{\lambda_d^2}, \quad (2.18)$$

with λ_d denoting the inter-atomic distance [32]. Substituting Equation 2.18 in Equation 2.15 leads to the nucleation rate for diffusion-limited crystallization:

$$I_{ss} = s_{ic} \cdot \frac{6D}{\lambda_d^2} \cdot n_0 \cdot \Gamma_z \cdot \exp\left(\frac{-\Delta G_c}{k_B T}\right) \quad (2.19)$$

The intrinsic parameter D can be correlated to the macroscopic viscosity η via the Einstein-Stokes relation [60]:

$$\eta D = \frac{k_B T}{3\pi\lambda_d} \quad (2.20)$$

Replacing D in Equation 2.19 by η of Equation 2.20 leads to:

$$I_{ss} = s_{ic} \cdot \frac{2k_B T}{\eta \pi \lambda_d^3} \cdot n_0 \cdot \Gamma_z \cdot \exp\left(\frac{-\Delta G_c}{k_B T}\right) \quad (2.21)$$

Equation 2.21 demonstrates that the temperature dependence of the nucleation rate I_{ss} is essentially determined by the exponential term and the temperature dependent viscosity η . The linear temperature-dependence as well as the weak temperature dependence of Γ_z can be disregarded [29, 49].

2.1.4. Crystal growth

The crystal growth process in amorphous Si is based on a bond-breaking mechanism at the amorphous/crystalline interface which enables the positioning of atoms from irregular positions to lattice-site positions [46]. Therefore, the crystal growth velocity v is controlled by the time-independent rearrangement frequency k , the fraction of sites f , in which new atoms can be incorporated, and the interatomic distance λ_d [29, 32]:

$$v = f \cdot k \cdot \lambda_d \quad (2.22)$$

k denotes the difference between the atomic jump rate from the amorphous to the crystalline phase k^+ and its corresponding reverse jump rate from the crystalline to the amorphous phase k^- :

$$k = k^+ - k^- \quad (2.23)$$

The initiation of a growth process requires k^+ to be larger than k^- . This condition is fulfilled in a state of a non-equilibrium at a temperature T below the equilibrium temperature T_{equ} , in which the Gibbs free energy of the amorphous state G_a exceeds the Gibbs free energy of the crystalline phase G_c . Figure 2.6 illustrates the Gibbs free energies of the amorphous state and crystalline state for $T < T_{equ}$ [32]. With ΔG_{ac} being the difference in free energy between the crystalline and an amorphous state per atom, the forward and

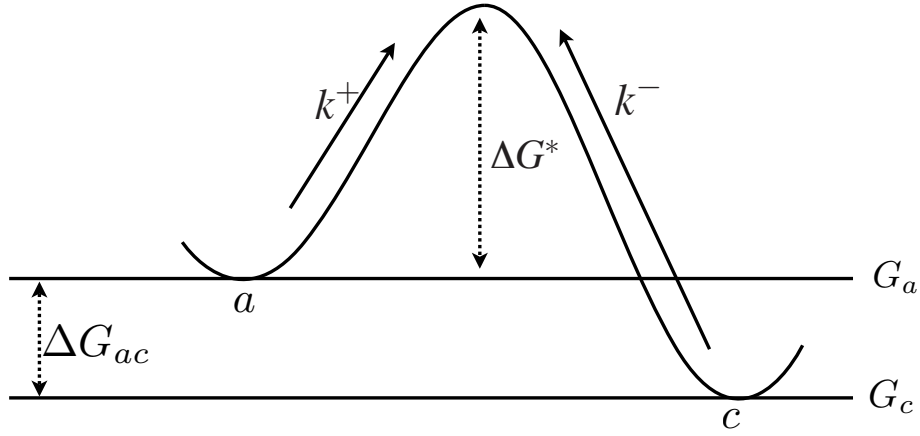


Figure 2.6: The free energy diagram describes the crystal growth process. Below the equilibrium temperature, G_a is higher than G_c , causing k^+ to exceed k^- and finally initiating the growth process. a and c denote the amorphous and the crystalline phase, respectively.

reverse rates are:

$$k^+ = k_0 \cdot \exp\left(-\frac{\Delta G^*}{k_B T}\right) \quad (2.24)$$

$$k^- = k_0 \cdot \exp\left(-\frac{\Delta G^* + |\Delta G_{ac}|}{k_B T}\right) \quad (2.25)$$

The jump frequency k can then be written as (Figure 2.6):

$$k = k^+ \cdot \left[1 - \exp\left(-\frac{|\Delta G_{ac}|}{k_B T}\right)\right] \quad (2.26)$$

Finally, the crystal growth velocity can be obtained, combining Equation 2.26 and Equation 2.22.

$$v = f \cdot \lambda_d \cdot k^+ \cdot \left[1 - \exp\left(-\frac{|\Delta G_{ac}|}{k_B T}\right)\right] \quad (2.27)$$

The growth process itself is driven by the greater probability to acquire rather than to remove an atom from the cluster [32].

Studies on the regrowth mechanism of amorphous Si on defect-free Si surfaces in a so-called solid phase epitaxial (SPE) process revealed a strong dependence of the interface velocity v on the growth direction. The growth velocity v on $\langle 110 \rangle$ and $\langle 111 \rangle$ oriented Si substrates are respectively 2.5 and 25 smaller than on $\langle 100 \rangle$ oriented substrates [61]. A

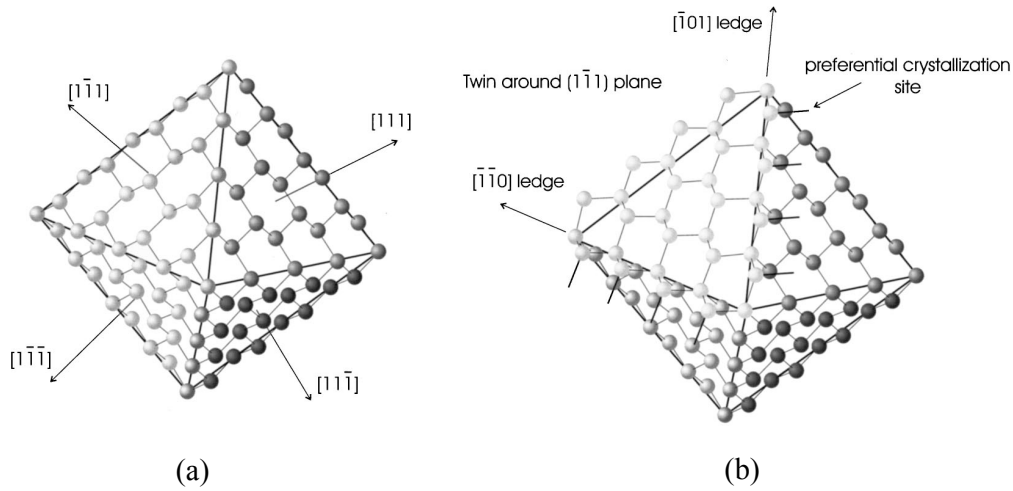


Figure 2.7: (a) illustrates the atomic structure of a defect-free crystal grain consisting of perfectly matched $\{111\}$ oriented planes. (b) shows the atomic structure of a Si grain with a twin defect on the $(1\bar{1}1)$ facet. On this plane, the atomic bonds of the crystal atoms are rotated by 180° around the $[1\bar{1}1]$ direction, forming bonds along the $\langle 110 \rangle$ ledges that dangle toward the adjacent $\{111\}$ facet. These bonds are preferential nucleation sites. (taken from [46])

structural model explains the orientation dependent growth, in which the c-a interface establishes a free-energy minimum by forming $\langle 111 \rangle$ oriented terraces connected by $\langle 110 \rangle$ ledges [46, 32]. The growth process proceeds via a bond breaking process and subsequent rearrangement along the $\langle 110 \rangle$ ledges which form in this terraced interface structure. Experimentally observed growth processes along the $\langle 111 \rangle$ direction could be explained by twinning phenomena on the terraces. On the basis of these results, Spinella postulated a ledge assisted crystal growth mechanism for solid phase crystallized clusters [46]. A defect-free grain is established by a single crystal domain, with surfaces formed by the most energetically favored $\{111\}$ planes in a perfectly matched double pyramid structure. Figure 2.7(a) displays a double pyramid structure of a Si crystal. However, due to the absence of ledges on the terraces at the grain surface, the growth process is very inefficient, leading to very small jump rates k^+ and k^- [61]. As soon as the cluster exceeds the size of several nm, it is favorable for the $\{111\}$ interfaces to break up, with twins forming at the grain surface, subsequently leading to terraced structure and a growth process along the $\langle 110 \rangle$ ledges in analogy to the SPE process (Figure 2.7(b)). This twin assisted ledge formation enhances the crystallization process and results in preferential crystal growth along the $\langle 121 \rangle$ orientations. In thin films, the location of the $\{111\}$ twin plane with

respect to the film surface is crucial for the resulting shape of the growing crystals. A $\langle 111 \rangle$ oriented crystal, having a $\{111\}$ twin plane parallel to the film surface, exhibits a circular shape as a result of isotropic growth in the film plane. If the $\{111\}$ twin plane is perpendicular to the film surface, the growing crystal has an elongated shape due to the $\langle 211 \rangle$ preferential growth orientation, with branches forming in other coplanar $\langle 211 \rangle$ directions [62].

2.1.5. Isothermal transformation curves - Johnson-Mehl-Avrami-Kolmogorov model

The Johnson-Mehl-Avrami-Kolmogorov description of the crystallization process of a-Si has been widely used to extract steady state nucleation rates and growth velocities by modelling measured crystalline material fraction curves $\chi(t)$ [63, 46]. This phenomenological model correlates the three dependent parameters nucleation rate $I(t)$, crystal growth velocity v and crystalline material fraction $\chi(t)$ [64, 65, 66, 67]. However, the JMAK-model is not only restricted to crystal nucleation, but applies to all kinds of phase transformation involving nucleation and growth in any arbitrary spatial dimension, thereby making it a universal technique. It is based on the consideration of impinging processes of adjacent clusters which nucleate and grow with a finite distance to each other, assuming that growth processes stop as soon as their cluster surfaces are in contact with each other.

The crystal growth in thin films with lateral dimensions significantly exceeding the film thickness can be approximated with a 2 dimensional analysis, thereby neglecting the period needed for each crystal to reach a size equal to the film thickness [29, 46]. Further, in conformity with classical nucleation theory, the nucleation rate is assumed to be in a steady state and therefore time-independent. Based on these two premises, the time dependence of the crystalline fraction $\chi(t)$ can be expressed as a function of the time-independent I_{ss} and v

$$\chi(t) = 1 - \exp \left[- \left(\frac{t}{\tau_c} \right)^3 \right]. \quad (2.28)$$

τ_c denotes the characteristic crystallization time and is given by:

$$\tau_c = \left(\frac{3}{\pi I_{ss} v^2} \right)^{1/3} \quad (2.29)$$

Equation 2.28 describes 2D crystallization processes based on a steady state nucleation rate and time-independent crystal growth velocity, starting at $t = 0$. However, transient effects induced by the characteristic time dependence of the nucleation rate are not considered in the JMAK model. A detailed description of the model and its application to crystallization processes in various dimensions is given by Christian [29].

2.2. Photovoltaic characteristics

2.2.1. Current-voltage characteristic of a solar cell

The current-voltage characteristic of a solar cell under illumination is the fingerprint of its photovoltaic performance. Various simulation models, ranging from simple one-dimensional models to sophisticated multi-dimensional models have been developed in order to describe current density- voltage (J-V) characteristics and quantify parasitic losses in solar cells [68].

A commonly used model to describe the J-V curve of a solar cell is the two-diode model which represents the J-V characteristics of a one-sided abrupt p-n junction uniform solar cell without considering multi-dimensional effects [69, 70, 71]. Figure 2.8 shows the circuit layout of the two-diode model, consisting of a photogenerated current density J_{ph} , two diodes D_1 and D_2 and the parasitic shunt and series resistances R_{sh} and R_s . When an external current flow is present, the voltage drop across $V_D = V + J \cdot R_s$ has to be taken into account, leading to:

$$J = J_{ph} - J_{D_1} \left[\exp \left(\frac{V_D}{n_1 V_t} - 1 \right) \right] - J_{D_2} \left[\exp \left(\frac{V_D}{n_2 V_t} - 1 \right) \right] - \frac{V_D}{R_{sh}} \quad (2.30)$$

J_{D_1} and J_{D_2} denote the saturation current densities for the first diode D_1 and the second diode D_2 . V_t is the thermal voltage ($k_B T / q$). The standard two-diode model assumes

the ideality factors for D_1 and D_2 to have the constant values $n_1 = 1$ and $n_2 = 2$ which describe individual recombination processes. Recombination processes in the bulk are usually related to $n_1 = 1$, whereas n_2 refers to recombination in the space charge region at the p-n junction [70, 72, 73, 74]. It should be noted that the ideality factor $n_2 = 2$ for D_2 represents an ideal case, with recombination being confined to a space-charge region at a defined p-n junction. However, in real devices, n_2 is usually smaller than 2 due to recombination processes occurring at extended space charge regions with n and p dopants present, and at trap states at different energetic levels [75, 76].

According to Equation 2.30, the parasitic losses R_s and R_{sh} influence the characteristic shape of the J-V curve and subsequently drastically change the maximum available power of the cell. Figure 2.9 illustrates the J-V characteristics of solar cell under illumination. The essential parameters are the open-circuit voltage V_{oc} and the short circuit current density J_{sc} , the efficiency η and the fill factor FF . The actual maximum obtainable power ($V_{MP} \cdot J_{MP}$) (MP) compared to the theoretically maximum obtainable power ($V_{oc} \cdot J_{sc}$) defines the fill factor FF and is essentially a measure for the quality of the solar cell:

$$FF = \frac{V_{MP} \cdot J_{MP}}{V_{oc} \cdot J_{sc}} \quad (2.31)$$

The efficiency η is determined by the ratio of the power at MP and the power of the incident light P_i .

$$\eta = \frac{FF \cdot V_{oc} \cdot J_{sc}}{P_i} \quad (2.32)$$

In order to ensure the comparability of individual measurements, light J-V measurements are carried out at defined standard test conditions (STC), utilizing an AM 1.5G solar

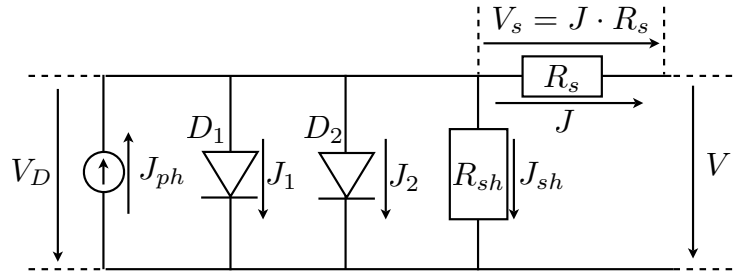


Figure 2.8: The two-diode model equivalent-circuit diagram of solar cells consists of the photo-generated current J_{ph} , two diodes D_1 and D_2 and the parasitic resistive elements R_s and R_{sh} .

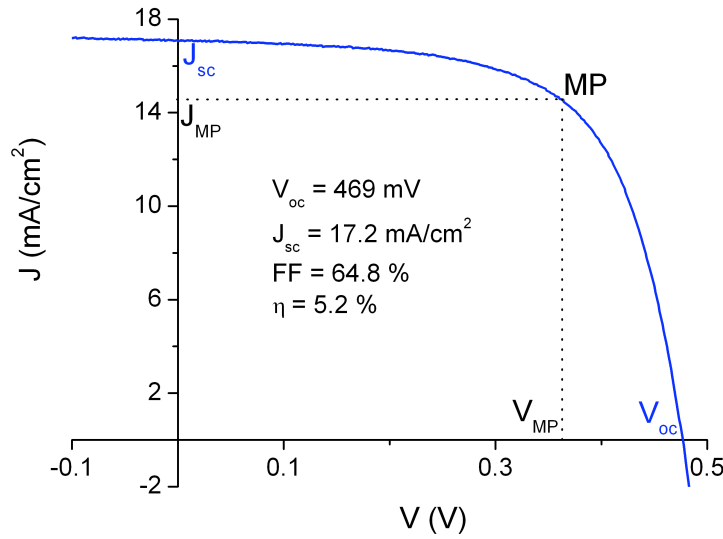


Figure 2.9: Illustration of a measured J - V curve of a solar cell under illumination. The open-circuit voltage V_{oc} , the short-circuit current J_{sc} and the fill factor FF determine the conversion efficiency η of the solar cell. MP denotes the maximum power point, with V_{MP} and J_{MP} being the respective voltage and current density at MP .

spectrum for illuminating the sample at an intensity P_i of $100 \text{ mW}/\text{cm}^2$ at a constant substrate temperature of 25°C .

2.2.2. Recombination mechanisms and diffusion length

The charge carrier transport in semiconductors is limited by three fundamental recombination mechanisms - the radiative recombination, the Auger recombination and the Shockley-Read-Hall recombination [77, 78].

Radiative (rad) recombination is predominantly found in direct semiconductors and is the reversal process of charge carrier generation. A electron and hole from the conduction and valence band recombine directly, emitting a photon with an energy similar to the bandgap. The indirect nature of band diagram of Si makes this mechanism quite unlikely to occur since large energies have to be supplied for a direct band-to-band recombination and an indirect band-to-band recombination process requires an additional momentum provided by a phonon.

Auger recombination presents a band-to-band recombination process which is the reversal process of the impact ionization. The recombining electron and hole pass their energy along to a third carrier, which is excited to a higher energy level without being emitted. Since Auger recombination increases with the square of the present charge carrier concentration, it is dominant in highly doped semiconductors as well as at high injection levels. The Shockley-Read-Hall (SRH) recombination is by far the most influential recombination mechanism in Si. Defects in the material caused by interstitials, stacking faults, vacancies, contaminations and dopants as well as grain boundaries, lead to the formation of additional energy levels within the band gap. These energetic levels or bands act as traps and recombination centers for charge carriers. In Si, dangling bonds are very effective recombination centers, which are commonly saturated by H atoms [15]. In contrast to trap states in the bulk, recombination at not sufficiently passivated surfaces and interfaces results in a continuous distribution of defects states over the entire band gap [77]. Thin film poly-Si is completely dominated by the SRH-recombination, for the existence of grain boundaries and intra-grain defects exhibit a source for many possible recombination centers.

Recombination processes limit the lifetime of charge carriers and hence inhibit the charge carrier transport, reducing the voltage and current of a solar cell. In particular, it is the lifetime of the minority charge carriers, that affects the performance of a device. In p-type Si, the electron lifetime τ_e and the effective lifetime τ_{eff} are governed by:

$$\frac{1}{\tau_e} = \frac{1}{\tau_{rad}} + \frac{1}{\tau_{Auger}} + \frac{1}{\tau_{SRH}} \quad (2.33)$$

$$\frac{1}{\tau_{eff}} = \frac{1}{\tau_e} + \frac{1}{\tau_s} \quad (2.34)$$

τ_{rad} , τ_{Auger} and τ_{SRH} denote the lifetimes of the three respective recombination mechanisms, while τ_s is ascribed to surface recombination.

The lifetime τ_e correlates with the respective bulk diffusion length L_e , the distance a electron can move before it recombines.

$$L_e = \sqrt{D_e \cdot \tau_e} \quad (2.35)$$

D_e represents the diffusion coefficient for electrons [77]. In Si wafers D_e is $\leq 34.9 \text{ cm}^2/\text{s}$, while the diffusion coefficient for holes is $\leq 12.4 \text{ cm}^2/\text{s}$. In poly-Si, however, the diffusion coefficients are considerably smaller due to a reduced carrier mobility [79].

The diffusion length for the minority carriers presents a crucial design restriction for Si solar cells. The diffusion length must exceed the film thickness of the absorber layer to grant effective charge carrier collection at high voltages. Therefore, the thickness of the absorber layer as well as the doping level of the absorber have to be well balanced to maximize the performance.

3. Experimental

This chapter is dedicated to a precise description of the used thin film coatings and nanostructures, and employed experimental methods and analytical techniques. Section 3.1 addresses the characteristics of the provided functional transparent SiN and ZnO coatings and describes the preparation process of sol-gel based self-organizing and imprinted nanostructures. Section 3.2 focuses on the electron beam evaporation of amorphous Si. The growth characteristics of the directional deposition process at oblique incidence are discussed, followed by the presentation of the layout of the employed electron beam evaporator. In section 3.3, the fabrication process of evaporated poly-Si mini-modules on SiN-coated glass in a state-of-the-art contacting structure will be presented. In addition, the significantly simplified process on the transparent conductive oxide ZnO will be addressed. Section 3.4 provides an overview of the spectroscopic and microscopic techniques, which are used for the structural analysis of a-Si and poly-Si thin films. The presentation of the techniques to determine the photovoltaic characteristics of fabricated solar cells completes this chapter.

3.1. Functional transparent coatings and nanostructures

Various transparent thin films and nanostructures on glass substrates were prepared in different deposition processes and serve as a basis for the structural investigation of the evaporated Si and the design of thin film solar cell devices. This section provides an overview of the used coatings and nanostructures in this study which are summarized in Table 3.1. SiN is used as a diffusion barrier and wide bandgap anti-reflection coating to

protect the electrically active Si layer from diffusing contaminants and plays a pivotal role in the preparation of high-quality poly-Si layers and solar cells (chapters 4 & 5). Al-doped zinc oxide layers (hereafter referred to as ZnO:Al or ZnO) facilitate an excellent front contact in solar cells in superstrate configuration and provide superior light trapping after wet-chemical etching. The influence of the roughness of the ZnO on the crystallization kinetics of evaporated Si (chapter 4) and its associated electronic quality will be elucidated (chapter 5), while its applicability for light trapping in poly-Si cells will be assessed in chapter 6. Two sol-gel based processing techniques allow for the controlled fabrication of nanostructures for light management in poly-Si cells. The self-organization process is a low-cost approach for the design of tailor-made silica nanospheres. The benefits of these light scattering objects embedded in a sol-gel matrix in e-beam compatible solar energy harvesting structures will be investigated (chapter 6). Sol-gel based nano-imprint lithography presents an excellent technique for fabricating periodic nanostructures on large areas, which will provide a template for the design of advanced 3 dimensional light harvesting architectures (chapter 7).

Table 3.1: *Functional thin films and nanostructures used for the investigation of the evaporated Si and the design of poly-Si solar cells.*

Coating	Deposition	Function	Chapter	Provided by
SiN	PECVD	diffusion barrier anti-reflection	4 & 5	CSG Solar
ZnO:Al	Sputter dep.	front-contact layer light trapping	4 & 5 6	FZ Jülich/HZB
Nanospheres	Dip-coating	light trapping	6	SCHOTT AG
Periodic nano-imprints	Dip-coating	advanced photon management	7	SCHOTT AG

Hydrogenated silicon nitride prepared by PECVD

Amorphous thin films of hydrogenated silicon nitride are commonly prepared by chemical vapor deposition and serve as high-quality transparent barrier coatings. The optical and the structural properties of the deposited window layers can be adjusted by varying the

deposition parameters [80]. With a bandgap energy of ~ 3 eV, a refractive index n of ~ 2 and a high mass density of up to 3 g/cm^3 , transparent thin layers of SiN can serve as diffusion barriers and anti-reflection layers between glass and silicon [81, 82].

CSG Solar provided hydrogenated SiN layers which were deposited on Schott Borofloat 33 glass panels (thickness 3.3 mm) in a commercial large-area plasma enhanced chemical vapor deposition system. The optical and structural properties of the SiN layers had been optimized for their application in poly-Si thin film solar cells on glass and provide optical transparency in the visible range and prevent contaminants from diffusing from the glass into the electrically active Si layer.

Al-doped zinc oxide prepared by sputter deposition

Highly Al-doped sputtered ZnO is a prominent type of a transparent conductive oxide (TCO) and is embedded in manifold optoelectronic applications, which require conductive layers with a high optical transmittance in the visible and near infrared regime. The magnetron radio frequency sputter deposition of Al-doped ZnO layers on a glass substrate from a ceramic ZnO target is an established process for fabricating high-quality transparent front contact layers for nanocrystalline Si thin film solar cells, featuring a carrier concentration above $\sim 10^{20} \text{ cm}^{-3}$ and charge carrier mobility of $45 \text{ cm}^2/\text{Vs}$ [13]. Sputter-deposited ZnO comprises a polycrystalline structure, with (0001)-oriented $\sim 100 \text{ nm}$ wide columnar grains growing in a wurtzite crystal structure in normal direction to the substrate [83]. The electrical and optical properties as well as the structural morphology of the deposited ZnO depend on the preparation conditions of the sputter process and constituents of the used target. The surface of the deposited layers can be modified in an additional wet-chemical etching process in diluted HCl, forming crater-like structures in the μm size range [84]. These textures are already employed as efficient light trapping features in a-Si/nc-Si solar cell designs [85]. Recent studies demonstrated that the charge carrier mobility of Al-doped ZnO implemented in a cell structure improves to $67 \text{ cm}^2/\text{Vs}$ during thermal annealing. These characteristics highlight the supreme compatibility of the front contact layer ZnO with the poly-Si thin film solar cell preparation processes at elevated temperatures [27, 86, 87]. Various Al-doped ZnO layers with different surface morphologies were supplied by Forschungszentrum Jülich and prepared at Helmholtz Zentrum Berlin for this study. The preparation conditions of the used ZnO layers will be addressed in the individual chapters.

Self-organizing silica spheres embedded in a sol-gel matrix

The self-organization process presents a low-cost bottom-up approach for the controlled fabrication of so-called structure-bearing particles in the nm to micron size range. Synthesized particles are bonded in the matrix of an inorganic sol-gel solution and applied to the substrate by dip-coating. The final structure evolves upon removing the immersed substrate from the sol-gel solution at a defined velocity, with these structure-bearing particles starting the self-organization process. In contrast to the commonly used implementation of defined SiO₂ beads in a top-down approach, this process is based on the synthesis of particles from nano-particles in the Stöber-process [88]. The size and the shape of these synthesized particles can be adjusted from 50 nm to the μm size range by varying the concentration of the precursors. The particle-to-matrix ratio defines the density of the particles in the sol-gel film, while the film thickness is determined by the dip-coating parameters [89, 90]. A subsequent thermal annealing step enhances the thermal and mechanical stability of the applied layer.

Thin films of self-organizing silica spheres with a diameter of 200 nm embedded in a sol-gel matrix on (10x10) cm² Schott AF 45 glass substrates were developed and prepared by SCHOTT AG. A 70 nm thick zircon oxide (ZrO) anti-reflection coating was applied to selected samples by dip-coating and tempering in a second thermal annealing process.

Periodic structures prepared by nano-imprint lithography

Nano-imprint lithography presents a versatile low-cost approach for a large-area fabrication of well-defined nanostructures. SCHOTT AG developed and produced sol-gel based two dimensional structures with a period of 300 nm and 2 μm .

Fabricated master stamps with a 2 dimensional periodic structure provide the desired pattern for the nano-imprint process and define the structure geometry. After a (10x10) cm² reusable polysiloxan replica stamp has been fabricated from the master structure, the replica stamp is pressed into a wet sol-gel film on glass (Schott AF 45, thickness 0.7 mm). The sol-gel solution consists of nanoparticles synthesized with functionalized hybrid polymers and is applied to the glass by dip-coating. A short UV curing step of a few seconds prior to the stamp removal ensures that the imprint of the replicated structure is preserved. A post-imprint thermal annealing step enhances the mechanical and thermal stability of the sol-gel layer [89]. A conformal film of a 70 nm thick ZrO anti-reflection coating was prepared by dip-coating and subsequently tempering in a second thermal annealing process.

3.2. Electron beam evaporation of Si

Electron beam (e-beam) evaporation is a type of physical vapor deposition in which the target material is evaporated by electron bombardment. The beam of electrons is generated in a charged tungsten filament and subsequently directed onto the target in the magnetic field of deflection coils or a set of permanent magnets, providing sufficient energy input to produce a directional flux of evaporated material from a molten target. It is instructive to review the essential aspects of the growth mechanism of vapor-deposited amorphous layers (section 3.2.1), before the layout of the employed e-beam evaporator is presented in section 3.2.2.

3.2.1. PVD a-Si growth characteristics

The growth of amorphous Si films requires a preparation process at low deposition temperatures, at which the atomic mobility is sufficiently small to enable the formation of a disordered structure. Due to the reduced atomic mobility of Si atoms deposited on the growing film, the atoms are unable to acquire a compact homogeneous structure, but form a columnar microstructure perpendicular to the substrate surface. While denser amorphous films can be prepared at higher deposition temperatures between 150°C and 300°C, depositing amorphous films at low deposition temperatures below 100°C might lead to the formation of porous material which ultimately is unable to adhere to the substrate [91].

The microstructure of the deposited a-Si is also strongly correlated to the angle at which the incident Si atoms hit the surface. Films deposited at oblique incidence comprise a lower density, growing in arrays of compact parallel uniform rods which are surrounded by a void network. With increasing angle of incidence, the growth direction deviates from the normal of the substrate towards the direction of the incident Si flux, resulting in a non-conformal coating of textured surface features. The column orientation is described by the empirical law,

$$2 \cdot \tan \beta = \tan \alpha, \quad (3.1)$$

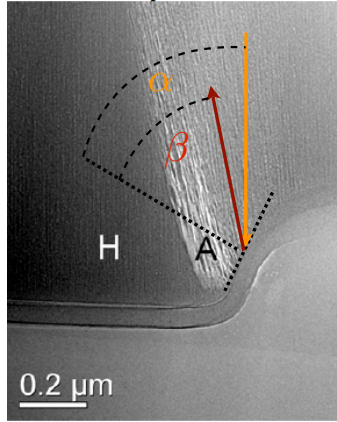


Figure 3.1: Cross-sectional TEM image of e-beam evaporated a-Si on horizontal (H) and inclined (A) surfaces: The direction of growth in horizontal regions is parallel to the incident Si atoms. According to Equation 3.1, the growth direction on inclined surfaces is tilted towards the direction of the incident flux (A) (Modified version of Ref. [96]).

with α being the angle between the normal and the vapor beam and β representing the column orientation relative to the substrate normal [91, 92, 93, 94]. The column separation expands with increasing angle of incidence, leading to an almost linear increase of the porosity of the anisotropic a-Si with $\tan \alpha$. Simulations confirmed that geometric shadowing of the vapor beam by the growing film is responsible for the observed development of these columns [95]. Figure 3.1 shows a cross-sectional image of an e-beam evaporated a-Si layer on a structured surface [96]. While the columnar growth direction on a horizontal surface is parallel to normal of the interface (H), the direction of growth at inclined surfaces is tilted towards the direction of the incident flux (A). In addition, the material at these steep edges exhibits a reduced density, visualized by the image contrast of the respective areas (A) and (H).

Concluding, the growth characteristics of the directional deposition process e-beam evaporation gives rise to a non-conformal coating of rough surfaces, in contrast to chemical vapor deposition processes which provide an omni-directional flux of Si [97].

3.2.2. Electron beam evaporator

Figure 3.2 shows a schematic illustration of the main components of the evaporation system used for all Si depositions throughout this study. A cryopumped chamber is equipped

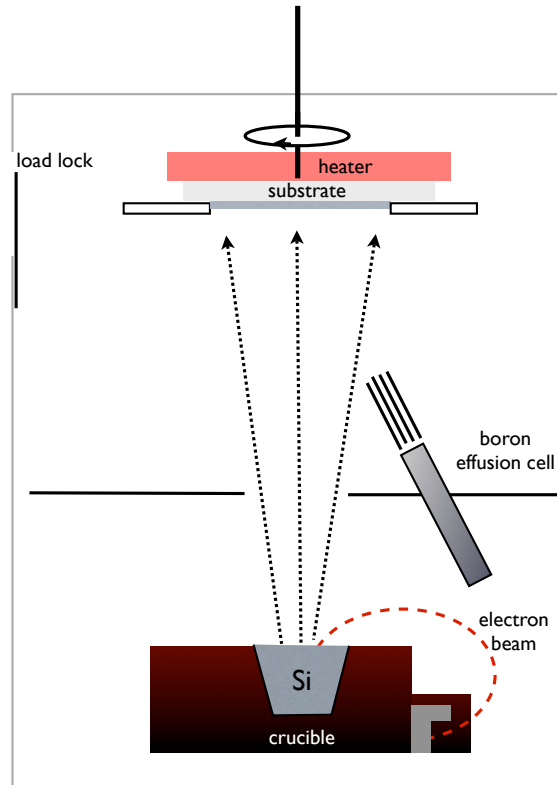


Figure 3.2: Schematic of the electron beam evaporator: An electron beam directed at a Si target provides a direct flux of evaporated Si, which is deposited on a rotating substrate, whose temperature can be controlled by a graphite heater. A boron effusion cell controls the release of elemental boron for the deposition of p-type Si.

with a (270°) electron gun, a crucible, a substrate heater and a boron effusion cell. The target material consists of a custom-made high-purity Si ingot which is accurately placed in the truncated cone shaped 100 cm³ large copper crucible. A control unit provides the power for the e-gun and allows for a variation of the beam intensity and hence the deposition rate of the evaporated Si. At a constant voltage of 10 kV, currents of 200 mA and 400 mA are used to achieve deposition rates of 300 nm/min and 600 nm/min, respectively. The base pressure in the chamber is $1 \cdot 10^{-8}$ mbar, while the pressure increases during deposition by one order of magnitude. An effusion cell filled with high-purity elemental boron provides the controlled release of boron in a thermally activated evaporation process at temperature ranging from 1600 to 2050 °C and enables preparing boron doped Si layer with doping concentrations of $5 \cdot 10^{15} \text{ cm}^{-3}$ to $1 \cdot 10^{20} \text{ cm}^{-3}$. A graphite heating element placed on top the substrate holder determines the substrate temperature during

the deposition process, which can be continuously varied between room temperature and 750 °C. The substrate temperature defines the structural characteristics of the deposited Si. While Si deposited at $T < 350^\circ\text{C}$ is still amorphous, partially nanocrystalline Si is evaporated at a T_{dep} between 350 °C and 600 °C. At $T_{dep} \geq 600^\circ\text{C}$, the deposited Si consists of columnar several hundred nm wide crystalline Si, being referred to as directly deposited poly-Si [98]. The substrate holder is rotated during the deposition process at 5 rpm, ensuring a uniform heat distribution and doping concentration over the sample. Custom-designed sample holders permit the simultaneous deposition of either up to five (2.5 x 2.5) cm² substrates or of one (10 x 10) cm² substrate.

3.3. Poly-Si solar cell device fabrication

Two different poly-Si thin film solar cell device concepts are employed in this study. The potential of e-beam evaporated poly-Si as a base material is investigated, by fabricating 12-cell mini-modules in an established device structure on SiN-coated glass developed by CSG Solar.

The implementation of a transparent front contact ZnO gives rise to simplifying the contacting scheme in the cell structure. The preparation of poly-Si solar cells embedded in a simple ZnO-based contact structure is presented.

3.3.1. Mini-module fabrication on SiN-coated glass

Structure

The investigated cell structure on SiN-coated glass is assembled in a superstrate configuration and comprises a plasma enhanced chemical vapor deposited n^+ -type Si emitter layer, and a p^- -type base and a p^+ -type layer deposited by e-beam evaporation. The 100 nm thick SiN layer and the 35 nm thin n^+ -type emitter layer with a doping concentration N of $1 \cdot 10^{20} \text{ cm}^{-3}$ are deposited in an industrial plasma enhanced chemical deposition reactor on Schott Borofloat 33 (size (10 x 10) cm²) glass substrates. To remove the oxide layer on the amorphous Si that formed while being exposed to air, the sample surfaces are treated with hydrofluoric acid (HF) with a concentration of 1% vol. directly prior to loading for

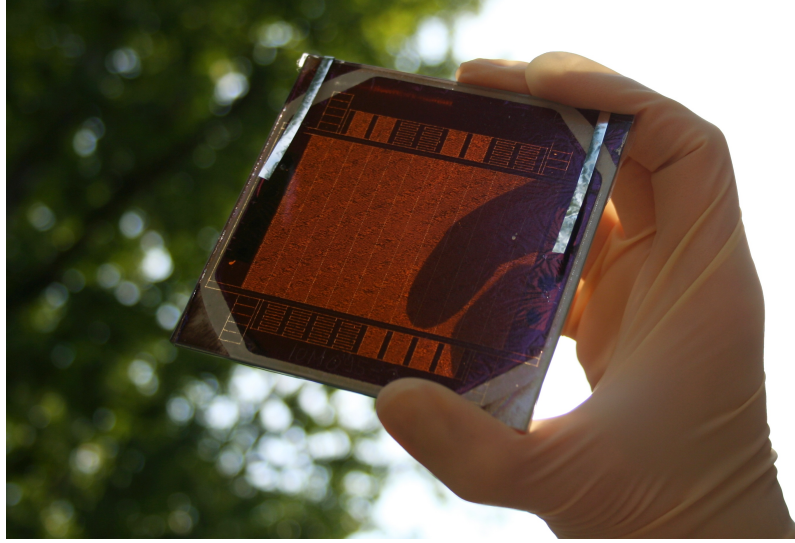


Figure 3.3: Photograph of a fabricated 12-cell mini-module: In addition to the 12 cell connected in series, individual test structures are located at the top and the bottom of the module.

Si deposition. $1.5 - 2.3 \mu\text{m}$ thick p^- -type base layers and the 60 nm thick p^+ -type layers - the latter of which with a doping concentration of $1 \cdot 10^{19} \text{ cm}^{-3}$ - are deposited consecutively without breaking vacuum. The doping levels are controlled by adjusting the temperature of the calibrated boron effusion cell to the desired level.

The following post-deposition treatments and module fabrication steps presented in subsection 3.3.1 were carried out at CSG Solar, Sydney, Australia.

SPC and post deposition treatments

The deposited samples are subsequently annealed at 600°C for 20 h to take the material from the amorphous to the crystalline phase. After crystallization, two essential post-deposition treatments contribute to an improvement of the material quality. Rapid thermal annealing (RTA) at 950°C is applied for several minutes to activate dopants and enhance point defect healing [99, 100]. A subsequent hydrogen passivation (HP) process then saturates remaining dangling bonds [101, 102]. Prior to the HP process the oxygen layer on the sample surface is removed in a 3 min long 2% -concentrated HF drop. The impact of the post-deposition treatments on the cell performance has already been optimized in extensive studies. The parameters of the rapid thermal annealing process have to be adjusted to the specific glass type in order to maximize the heat transfer into the material while minimizing the induced stress in the Si film [100, 103]. Experiments confirmed

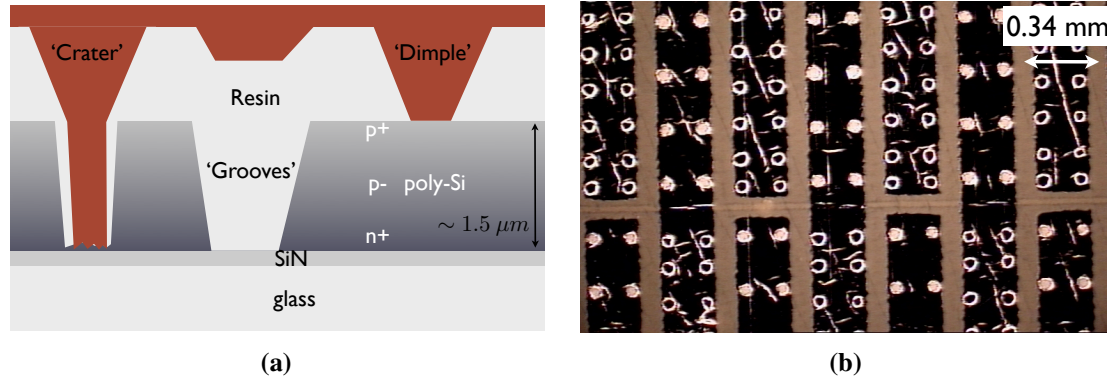


Figure 3.4: (a): Schematic showing the key features of the state-of-the-art poly-Si on glass module technology. 'Craters' and 'dimples' provide the contact holes for the n^+ -type and p^+ -type Si, while the cells are separated by 'grooves'. (b): Top-view of the finalized module, with arrays of defined 'crater' (brighter) and 'dimple' (darker) contact holes: The 'grooves' separating the individual cells are located in the middle of the image perpendicular to the rows of 'dimples' and 'craters'.

that annealing temperatures of 950°C to 1000°C and durations of 1 to 3 min are the optimal process parameters for poly-Si films on Schott Borofloat 33 glass. The hydrogen passivation was found to be most effective for PECVD-based poly-Si at a plateau temperature of 550°C to 600°C for a duration of 10 min. While poly-Si cells prior to HP have a V_{oc} of $\sim 250\text{ mV}$, passivated poly-Si cells exhibit a V_{oc} of $\sim 460\text{ mV}$. Poly-Si cells that are hydrogen passivated but not treated in RTA commonly show a V_{oc} of $\sim 300\text{ mV}$ [101, 104].

Module fabrication

Mini-modules consisting of 12 cells, each of which having a size of 2.886 cm^2 , are fabricated by laser scribing grooves in the Si layer to define individual cells, spin-coating a white resin layer, ink-jet printing to form the contact vias, etching the vias to expose the front and rear contact layers and sputtering Al. The device is finalized by scribing Al to create the cell interconnection pattern [105, 106, 107]. Figure 3.3 displays a photograph of a processed mini-module, while Figure 3.4 illustrates a sketch of the fabricated solar cell structure and a top-view image of the metallization pattern.

3.3.2. Poly-Si solar cell concept on ZnO-coated glass

The device fabrication is simplified in a poly-Si solar cell concept on ZnO:Al-coated glass. A ($n^+/p^-/p^+$)-type Si stack is embedded in a ZnO:Al front contact layer and Al back contact layer. 30 nm thick amorphous highly phosphorous doped layers are deposited with a conventional parallel plate 13.53 MHz RF-PECVD reactor at 210 °C on ZnO:Al coated glass substrates ((2.5 x 2.5) cm²). The used pre-cursor gases are silane, SiH_4 at 10 sccm, and phosphine, PH_3 (1% in H_2) at 1 sccm. Prior to e-beam deposition of a $\sim 1.1 - 1.4 \mu m$ thick p^- -type layer, oxygen is removed from the sample surface in a 15 s long drop in 0.5%-concentrated HF solution. The duration and HF concentration is reduced due to observed undercutting of the n^+ -type doped layer at higher concentrations. After crystallization at 600 °C for 20 h, samples undergo a RTA step at 950 °C for 60 s, followed by a hydrogen passivation treatment at 600 °C for 10 min.

Highly p-doped a-Si:H layers of 60 nm thickness are deposited by electron cyclotron resonance chemical vapor deposition (ECR-CVD) at a substrate temperature of 130 °C. The used precursor gases are silane, SiH_4 , at 5 sccm, and diboran, B_2H_6 (0.5% in H_2), at 5 sccm.

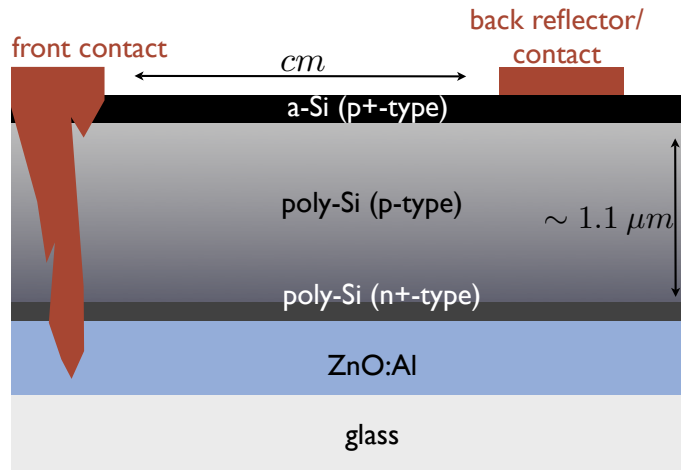


Figure 3.5: The structure of one of the prepared poly-Si cell on ZnO in superstrate configuration is illustrated, consisting of a ZnO front contact, a 30 nm thick PECVD n^+ -type poly-Si emitter layer, a $\sim 1.1 \mu m$ poly-Si layer and a 60 nm thick p^+ -type a-Si:H layer. Al contacts define the cell area and serve as a back reflector, while Al filled grooves provide the contact to the front-side at the edge of a (2.5 x 2.5) cm² large sample.

A 1 μm thick aluminum layer finalizes the solar cell structure. 9.0 mm² and 1.6 mm² large deposited Al dots provide the back contact and define the area of individual solar cells, while Al deposited on grooves exposing ZnO:Al at the borders of the sample provides the contact to the front-side. ZnO:Al is exposed by removing the Si cover with a gentle scratch with a diamond. Figure 3.5 shows an illustration of an investigated solar cell structure on ZnO. Since the individual cells are not defined by laser scribes, Si from areas adjacent to the Al cell spot can contribute to the current generation and therefore leads to an overestimation of the measured current density in J-V measurements. The high resistivity of a-Si:H minimizes shunting between the Al of the front contact overlapping onto the p^+ -type layer and the back-contact, and is therefore a necessity for the realization of the chosen cell structure. Nevertheless, the used concept prototype presents an easy method to assess the potential of the poly-Si films based on the implemented ZnO. The development of a contacting scheme for poly-Si in a monolithic series connection is beyond the scope of this study.

3.4. Characterization techniques

3.4.1. Electron microscopy

Electron microscopy is a high-resolution imaging technique based on the interaction of an incident beam of coherent electrons with the irradiated specimen. In addition, electron microscopy can provide local information of the structure of the sample due to Bragg diffraction of the incident electrons at crystal lattice planes [108].

Scanning electron microscopy (SEM) utilizes a coherent beam of electrons to scan the sample surface. The detection of the secondary electrons of an energy of several eV which are emitted in inelastic scatter interactions within a few nanometers from the sample surface permit an analysis of the surface topography of a specimen.

The method electron backscatter diffraction (EBSD) allows for an analysis of the crystallographic orientation of the sample. Backscattered electrons which are diffracted at the periodic lattice planes of the crystalline structure at Bragg-condition, generate characteristic lines in the detection pattern, the so-called Kikuchi diffraction pattern. The local

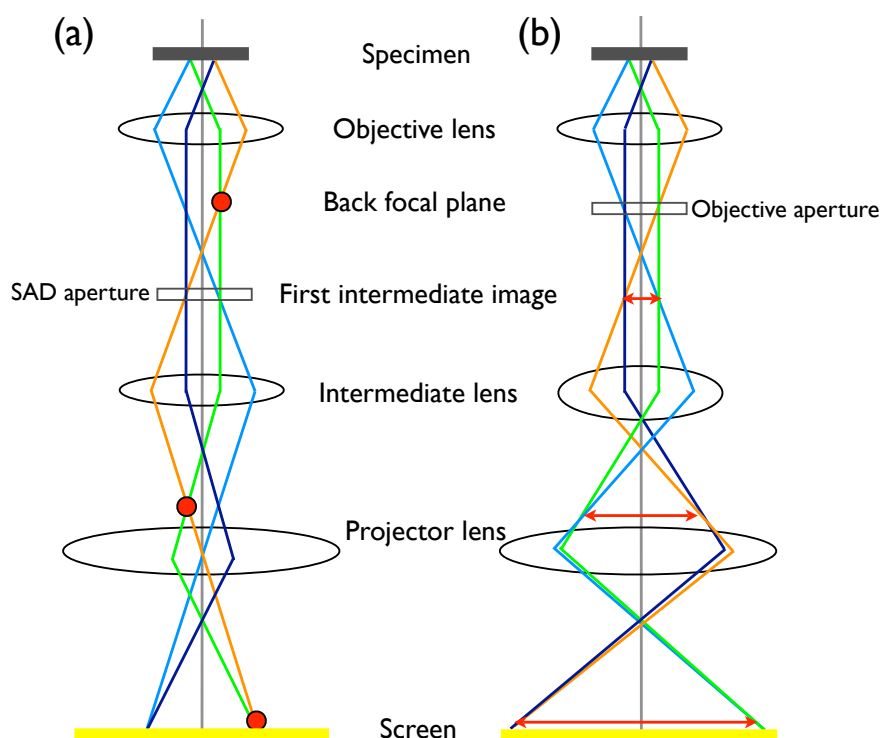


Figure 3.6: The two basic operation modes involve the projection of the diffraction pattern (a) on the viewing screen and the projection of the image (b) on the viewing screen. In diffraction mode (a), the intermediate lens selects the back focal plane as its object, whereas the image plane is selected as the object in image mode (b).

structural orientation of crystals can be deduced from the pattern and the width of these Kikuchi-lines.

Transmission electron microscopy (TEM) operates in transmission mode and requires the specimen to be electron transparent (< 100 nm). The transmitted part of focused electron beam that interfered with the specimen is guided through a complex imaging system, consisting of multiple magnetic lenses. Different operation modes can be selected by adjusting lenses in the system. The two main operation modes are the diffraction mode and the image mode, whose basic concepts are illustrated in Figure 3.6. The specimen is located in the object plane of the objective lens, which creates a diffraction pattern of the specimen on its back focal plane.

In diffraction mode, the object plane of the intermediate lens is chosen to coincide with the back focal plane of the objective lens and reproduces the diffraction pattern in its

image plane (indicated by the red diffraction dot in Figure 3.6(a)). A screen visualizes the final diffraction pattern after being magnified by the projector lens. A circular selected area diffraction (SAD) aperture can be inserted in the image plane of the objective lens to define a circular region on the specimen.

In image mode, the object plane of the intermediate lens is equal to the image plane of the objective lens (indicated by the red arrow in Figure 3.6(b)). This alignment produces an image of the specimen on the screen. A circular objective aperture is inserted in the back focal plane of the objective lens to select either the direct beam (bright field) or the diffracted beam (dark field) [108].

The surface topography and its crystal grain orientation (EBSD) were analyzed with a Hitachi S4100 scanning electron microscope equipped with a cold field emitter and acceleration voltage of 30 kV. Cross-sectional TEM analyses in image mode and diffraction mode on selected samples were conducted with a Philips CM12/STEM (with supertwin lens modification and a LaB6 cathode and an acceleration voltage of 120 kV).

Cross-sectional TEM sample preparation requires a precise execution of the numerous preparation steps involving manual cutting, polishing and ion-milling. First, the sample is broken manually into smaller pieces, two of which are subsequently used for a face-to-face preparation with epoxy resin. A wire saw slices off 0.5 mm plates, which are afterwards polished down to a thickness of 5 μm . The sample thickness is controlled with a simultaneously prepared Si reference sample. After this mechanical thinning step, the specimen is supported by an O-ring and thinned to the desired thickness of 30 nm to 50 nm by ion-milling with a Ar^+ -ion beam directed at the sample at grazing incidence.

3.4.2. Atomic force microscopy

An atomic force microscope (AFM) is a high-resolution scanning probe microscope which is capable of analyzing three-dimensional surface topographies with a lateral resolution of nanometers and a vertical resolution in the sub-nanometer regime [109, 110].

The surface of a specimen is scanned with a super fine tip mounted on a cantilever, whose movement in lateral direction is controlled by two piezoelectric scanners. A laser beam is reflected at the upper side of the cantilever and detected by a position-sensitive split photo-

diode detector. After bringing the tip into proximity of the surface of the specimen, forces between the sample and the tip cause the cantilever to deflect. This deflection results in a change of the position of the laser beam, providing information about the topography of the surface of the sample. The detection mechanism is connected to a feedback loop system which subsequently readjusts the height of the scanner.

In tapping mode, the cantilever is oscillated at or close to its resonance frequency with a constant amplitude between 20 nm and 100 nm. At every single oscillation minimum at the sample surface, the oscillation amplitude is damped, giving rise to a readjustment of the cantilever height to maintain the setpoint amplitude of the oscillation. Hillocks on the surface lead to an increase of the cantilever to prevent the amplitude from decreasing, while the scanner is lowered at depressions¹.

In this study, an Anfattec Instruments standard level AFM equipped with a 10 nm large tip was employed for a quantitative determination of the surface roughness of the prepared substrates. The AFM was operating in tapping-mode at a resonance frequency of 330 kHz. The extracted data of the investigated $(2 \times 2) \mu\text{m}^2$ surface area were subsequently processed with the software WSxM [111].

The root mean square roughness (δ_{rms}) and the power spectral density (PSD) provide essential information of the lateral and vertical feature sizes of the surface morphology [112, 113]. δ_{rms} represents the standard deviation of the distribution of surface heights and describes the vertical characteristics of the surface deviations:

$$\delta_{rms} = \sqrt{\frac{1}{nm} \sum_{k=0}^{n-1} \sum_{l=0}^{m-1} [z(x_k, y_l) - \mu]^2} \quad (3.2)$$

μ represents the mean value of the height, z , across all in-plane coordinates (x, y) . Equation 3.2 illustrates the limitations of this simple statistical description. The δ_{rms} does not account for the lateral distribution of the surface features and is computed indiscriminately towards the height value relative to the average height, i.e. it does not distinguish between positive peaks and negative valleys. Power spectral density (PSD) of the surface topography provides a more accurate description of the surface features by decomposing the

¹An AFM can also be operated in contact mode: In contact mode, the deflection setpoint is maintained at a constant value while scanning the surface of the specimen.

surface profile into its spatial wavelengths. The characteristic topographic lengths given by their respective spatial frequencies can be derived from surface roughness PSDs.

3.4.3. Raman spectroscopy

Raman phonon scattering comprises inelastic scattering processes of photons in molecules. In contrast to Rayleigh scattering which describes the elastic scattering of photons, Stokes- and anti-Stokes scattering refers to the inelastic scattering of photons via a virtual energetic level. The energetic difference of the incident photon and emitted photon is compensated by the generation (Stokes) or the elimination (Anti-Stokes) of a phonon.

Raman spectroscopy employs the Raman effect for materials analysis and allows for the specific structural investigation of the material based on the states of its molecular constituents [114]. It has become an established characterization technique in Si research. The field of application ranges from the detection of stress in c-Si and the evaluation of the crystalline quality of nanocrystalline Si to the detection of the structural distortion in a-Si [115, 116, 117, 118].

To analyze the structural disorder in e-beam evaporated amorphous Si thin films, a micro-Raman spectrometer DILOR/ ISA LabRAM 010 in backscatter configuration was used, with an unpolarized HeNe laser (wavelength 632.82 nm, spectral resolution 1 cm^{-1}) providing the excitation signal. The power of the incident radiation was set to $(300 \pm 5)\text{ }\mu\text{W}$ distributed over a circle of $\sim 1\text{ }\mu\text{m}$ in diameter to avoid sample crystallization or structural relaxation due to heating.

3.4.4. Photothermal deflection spectroscopy

Photothermal deflection spectroscopy (PDS) is a powerful and sensitive technique to measure the absorption in materials, based on the change of the thermal state of the sample resulting from the absorption of radiation [119]. The basic concept of the technique in

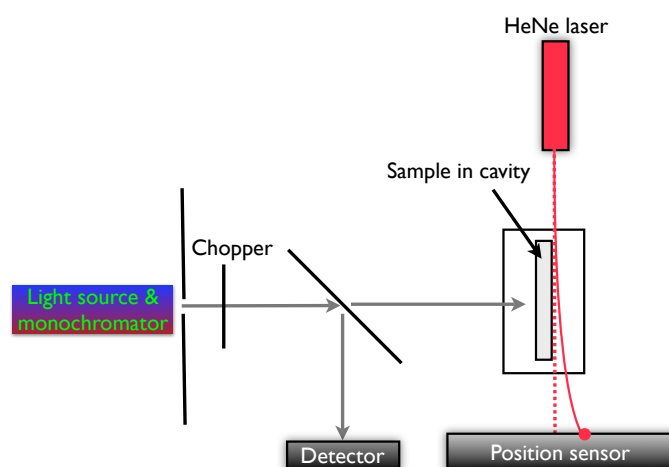


Figure 3.7: A sample which is positioned in a cavity filled with a perfluorohexane solution absorbs monochromatic light provided by a light source, leading to heating of the sample. A thermal gradient in the surrounding liquid results in the change of its refractive index and hence a deflection of the grazing laser beam. The absorption of the sample correlates with the deflection signal and can be extracted from the detection of the pump beam and the position of the deflected laser beam, using conventional lock-in technique.

transverse mode² is illustrated in Figure 3.7. A halogen light source and monochromator provide the pump beam for a wavelength selective irradiation in normal direction to the sample surface, which is situated in a glass cavity filled with a perfluorohexane solution (index of refraction $n \sim 1.3$). A HeNe laser ($\lambda = 632 \text{ nm}$) grazes the sample surface perpendicular to the direction of light irradiation. The absorption of monochromatic light in the sample leads to heating of the sample and a thermal gradient in the surrounding liquid due to non-radiative recombination processes of excited carriers in the sample. The temperature gradient in the liquid then results in a change of its refractive index and a deflection of the passing HeNe laser beam. The deflection signal which is detected with a position sensor (quadrature detector) correlates with the absorptance in the sample.

PDS exceeds the sensitivity of conventional UV-VIS spectroscopy by 3-4 orders of magnitude and is insensitive to scattering, which becomes a prominent source distortion in conventional optical measurements in the near band-gap region in Si [120, 121]. There-

²In addition to transverse PDS, collinear PDS is an alternative form of PDS, in which the gradient of the index of refraction n is both created and probed within the sample.

fore, PDS is commonly the method of choice to measure the sub- and near-band gap absorption in Si [122, 123, 124]. In this study, PDS was employed for an accurate evaluation of the light trapping properties by measuring the true absorption properties without scattering and reflection phenomena in the wavelength region of 600 nm to 1100 nm.

3.4.5. Photovoltaic characterization

Current density-voltage measurements and quantum efficiency measurements are carried out to determine the photovoltaic performance of the prepared poly-Si thin film solar cells and mini-modules. A conventional sun-simulator was employed for J-V measurements. A xenon light source and a filter system was used to replicate the solar spectrum. The light intensity was calibrated with a certified poly-Si thin film and Si-wafer solar cell positioned on a thermo-chuck at a constant temperature of 25 °C. Prepared mini-modules were measured at CSG Solar, Sydney, Australia, while measurements on solar cells on ZnO:Al and front-side textures were carried out at HZB.

The wavelength sensitive determination of the quantum efficiency (QE) provides a measure for the current collection at a specific wavelength λ . The QE is defined as the ratio of the number of generated electron-hole pairs to the number of the irradiating photons with the energy $\hbar\omega$. q denotes the elementary charge, while J_{ph} represents the photogenerated current density.

$$QE = \frac{J_{ph}/q}{P_i/\hbar\omega} \quad (3.3)$$

While the external quantum efficiency (EQE) considers P_i , the internal quantum efficiency (IQE) takes into account the reflectance R of the incident light at the interfaces and considers only the part P_i that irradiates the solar cell.

$$IQE = \frac{1}{1 - R(\lambda)} \cdot EQE \quad (3.4)$$

In the ideal case, the QE of a solar cell should maintain a value close to 1 over the entire wavelength region. However, due to the weak absorption properties of Si, thin film devices require the implementation efficient light harvesting structures to increase QE in the long wavelength region. The QE measurement presents the ideal tool for an λ -selective evaluation of the effectiveness of light trapping structures.

The short-circuit current can be calculated by integrating the product of the EQE spectrum and the incident solar photon flux $\Phi(\lambda)$ which is derived from the AM 1.5G solar spectrum:

$$J_{sc}^{EQE} = \int q \Phi(\lambda) \cdot EQE(\lambda) d\lambda \quad (3.5)$$

In this study, a 1000 W xenon light bulb and a 500 W tungsten halogen light bulb provided the light sources for a wavelength-sensitive analysis of the EQE from $\lambda = 300$ nm to 1100 nm. The samples were measured under short circuit condition while being irradiated with white bias light. The EQE could be calculated by determining the signal with respect to a reference cell with known spectral response.

3.5. Conclusion

In this chapter, we have established the framework required for an accurate analysis of evaporated poly-Si thin film solar cells.

The first section addressed the preparation of functional transparent coatings and nanostructures. SiN layers deposited in a PECVD process serve as transparent diffusion barriers and anti-reflection coatings. Al-doped ZnO prepared by sputter deposition provides both, a transparent conductive front contact for a poly-Si cell and the desired surface texture for the implementation of efficient light trapping features. A sol-gel based dip-coating technique was employed to fabricate light scattering spheres in a self-organization process. Nano-imprint lithography was used to fabricate 2-dimensional sol-gel based gratings for the development of advanced light trapping architectures.

Second, the growth characteristics of e-beam evaporated a-Si were presented. As a directional deposition process, e-beam evaporation does not provide a conformal coating on textured substrates, but leads to the growth of compact Si on planar surfaces and porous material at steeper edges. This dependence of the material quality on the angle of incidence becomes of significant importance for the development of a textured solar cell front side.

Third, the fabrication process of 12-cell mini-modules on SiN-coated planar glass was presented, thereby addressing the n^+ (PECVD)/ p^- (e-beam)/ p^+ (e-beam) cell structure,

the essential process steps and the contacting scheme, in which the cells are embedded. A simplified contact structure was realized by implementing ZnO as a front contact layer. Finally, a review of spectroscopic and microscopic techniques provides vital information about the analytical methods used for the investigation of the structural properties of a-Si (Raman spectroscopy), partially crystalline Si and poly-Si (TEM & SEM). In addition, AFM allows for the determination of the substrate topography and PDS can be used to characterize the absorption properties of poly-Si films. The basic photovoltaic characterization techniques were introduced. J-V curves represent the fingerprint of the solar cell's photovoltaic characteristics, while EQE measurements allow for a wavelength sensitive detection of the charge carrier collection.

4. Characterization and control of the crystallization kinetics in Si

4.1. Introduction

The photovoltaic performance of a poly-Si thin film solar cell is significantly influenced by the material quality of the crystalline Si. Defects at grain boundaries and intra-grain defects present effective recombination centers which affect the diffusion length of the minority charge carriers and compromise the cell performance. Consequently, it is desirable to optimize the production process of poly-Si, by preparing tailor-made layers with large grains which exhibit a very limited concentration of defects. This chapter is dedicated to the characterization and control of the solid phase crystallization kinetics of e-beam evaporated Si deposited on various SiN and ZnO:Al-coated glass substrates and elucidates the influence of the topographic features (in the nm regime) of the substrate and the structural disorder of the e-beam evaporated a-Si on the solid phase crystallization kinetics. The fundamental analysis serves as a basis for the identification of design rules that enable controlling the fabrication of large-grained poly-Si on various substrate topographies and creating vertically aligned grain structures. Section 4.2 presents the fabrication of the investigated samples, while section 4.3 outlines the scientific method to extract the characteristic parameters which individually control the growth and nucleation processes. Section 4.4 and section 4.5 are dedicated to the detailed analysis of the influence of the substrate topography and structural disorder of the a-Si on the nucleation process. A critical discussion of the achieved results in section 4.6 leads to the definition of design parameters for a controlled fabrication of poly-Si thin films.

4.2. Sample preparation

100 nm thick SiN layers were fabricated on Schott Borofloat 33 glass (thickness 3.3 mm) in an industrial plasma enhanced chemical deposition reactor and serve as an anti-reflection coating and diffusion barrier. The 30 cm x 40 cm large SiN-coated glass panels were manually cut into individual pieces of $(10 \times 10) \text{ cm}^2$ and subsequently cleaned in 10 % vol. isopropyl alcohol solution. Atomic force microscopy analyses confirmed that SiN has a very smooth surface topography with a δ_{rms} of merely 0.3 nm. Based on the smooth SiN substrate, 4 additional substrate types with rougher surface topographies were generated in additional deposition processes. A surface topography with δ_{rms} of 5 nm could be prepared by depositing a 850 nm thick ZnO:Al film on the SiN-coated glass at a substrate temperature of 300 °C by non-reactive radio frequency sputtering from a ceramic ZnO target containing 1 % wt. Al_2O_3 [13, 125]. Even rougher ZnO:Al surfaces of $\delta_{rms} = 10 \text{ nm}$ were fabricated in a sputter deposition process from a ceramic ZnO target containing 2 % wt. Al_2O_3 at 200 °C. The characteristic surface features arise from the crystalline structure of the columnar $\sim 100 \text{ nm}$ wide ZnO grains. In addition, two ZnO:Al substrates were flattened by depositing a 35 and 50 nm thick SiN diffusion barrier, leading to a respective roughness δ_{rms} of 4.4 and 2.3 nm. Table 4.1 summarizes the properties of the five prepared substrates, while a complete overview of the characterization involving an analysis of their power spectral densities is given in appendix A.1.

Table 4.1: The characteristic roughnesses of the five prepared substrates are listed. The complete analysis is presented in appendix A.1.

substrate	$\delta_{rms} \text{ (nm)}$
glass/SiN	0.3
glass/SiN/ZnO:Al/SiN(50 nm)	2.3
glass/SiN/ZnO:Al/SiN(35 nm)	4.4
glass/SiN/ZnO:Al	5
glass/SiN/ZnO:Al	10

Subsequently, $1 \mu\text{m}$ thick $2 \cdot 10^{16} \text{ cm}^{-3}$ boron doped a-Si films were deposited by e-beam evaporation on $(2.5 \times 2.5) \text{ cm}^2$ substrates at a deposition rate of 300 nm/min at four different substrate temperatures, ranging from 150 °C to 300 °C. The temperature range was restricted to 300 °C, since a deposition at temperatures exceeding 350 °C would lead to

partially crystalline material [98]. Finally, the deposited samples were again manually cut, providing enough specimens (size $(10 \times 5) \text{ mm}^2$) for an extensive analysis of the crystallization process. To relocate the same spot on the samples at different time steps, a region of interest was marked with gentle scratch.

4.3. Scientific method of investigation

4.3.1. Experimental procedure

A temperature-dependent analysis of the nucleation and growth process requires an accurate heating device and a detection technique that is sensitive enough to discriminate crystalline parts from amorphous parts. A tube furnace meets the requirements for an accurate isothermal annealing procedure. The samples were placed on a textured Si wafer supported by a quartz carrier and inserted in the furnace in N_2 atmosphere at 500°C , a temperature being sufficiently below the temperature regime that is relevant for crystallization to occur. A 10 min long isothermal phase at 500°C ensured that a stabilized temperature on the specimen was reached. Subsequently, a control unit ramped up the temperature to the isothermal annealing temperature ranging between 560°C and 610°C at a defined heating rate of 5 K/min . After the isothermal anneal at the desired temperature, the specimen was cooled down to 500°C at an inverse rate. After annealing the samples for a certain period of time, a visualization of the sample's surface provides essential information about the impact of the thermal treatment on the progress of the crystallization process. Optical microscopy operating in transmission mode is an appropriate technique to detect crystalline features. Due to the dissimilar absorption coefficients of a-Si and crystalline Si, the crystals can clearly be distinguished as bright spots from the dark background of the amorphous matrix. Figure 4.1 illustrates a series of optical microscopy images of Si on SiN annealed at 600°C taken of the same area at different stages of the crystallization process. The series enables us to track the nucleation and growth process of the Si crystals and calculate the individual characteristic parameters.

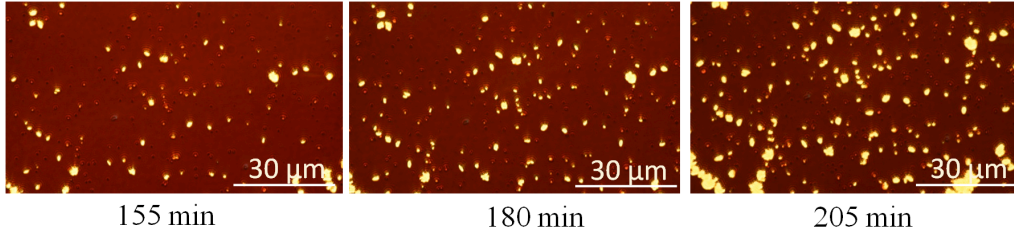


Figure 4.1: Illustration of 3 transmission optical microscopy images of Si on SiN of the same location annealed at 600°C for 155 min, (155+25) min and (155+25+25) min, respectively. Crystals can be identified as bright areas and clearly distinguished from the dark, still amorphous background.

4.3.2. Analysis of the crystal growth velocity

A standard image processing software was used to calculate the area A_j of an individual crystal j at different annealing steps t and $t + \Delta t$ [126]. The growth velocity v_j was subsequently determined by calculating the change of the radius r_j of a sphere with size A_j within the annealing step Δt .

$$v_j = \frac{\Delta r_j}{\Delta t} \quad (4.1)$$

Repeating this analysis for approximately 50 crystals enables the calculation of the average time-independent crystal growth velocity v for a specific annealing temperature [127, 128, 129]. The sufficiently high number of crystals is required for the calculation of v to guarantee enough statistics for the averaging process, due to the orientation-dependence of the growth velocity in Si (section 2.1.4).

The crystal growth velocity for different temperatures exhibits Arrhenius behavior and can be fitted with

$$v = v_0 \cdot \exp\left(\frac{E_v}{k_B T}\right) \quad (4.2)$$

where v_0 indicates a constant pre-factor and E_v can be specified by revisiting Equation 2.27.

The growth velocity v can be rewritten by substituting k^+ of Equation 2.27 with Equation 2.24:

$$v = f \cdot \lambda_d \cdot k_0 \cdot \exp\left(-\frac{\Delta G^*}{k_B T}\right) \cdot \left[1 - \exp\left(-\frac{|\Delta G_{ac}|}{k_B T}\right)\right] \quad (4.3)$$

ΔG^* can be split into its activation enthalpy ΔH^* and its activation entropy ΔS^* . Following the rules of basic thermodynamics, ΔH^* consists of the activation energy ΔE^* and an activation volume ΔV , resulting in [56]:

$$\Delta G^* = \Delta E^* + p\Delta V^* - T\Delta S^* \quad (4.4)$$

Since ΔV^* is marginal in comparison to ΔE^* at normal pressure, Equation 4.3 becomes:

$$v = v_0 \cdot \exp\left(-\frac{\Delta E^*}{k_B T}\right) \cdot \left[1 - \exp\left(-\frac{|\Delta G_{ac}|}{k_B T}\right)\right] \quad (4.5)$$

v_0 summarizes all temperature independent parts. For temperatures of $\sim 600^\circ\text{C}$, ΔG_{ac} is ~ 0.11 eV, resulting in a negligible contribution of the term $\left[1 - \exp\left(-\frac{|\Delta G_{ac}|}{k_B T}\right)\right]$ to v [130, 39]. Hence, it can be concluded:

$$E_v = \Delta E^*. \quad (4.6)$$

Finally, the activation energy for crystal growth can simply be calculated with the fit function shown in Equation 4.2.

The annealing procedure outlined in section 4.3.1 not only consists of actual isothermal tempering, but also involves heating and cooling processes during which growth and nucleation processes naturally occur. The kinetic effects during these transient heating periods have to be taken into account and lead to a correction of the crystal growth velocity and isothermal annealing time.

The growth process is simulated based on E_v (Equation 4.2) and on a set of N time steps t_i and their corresponding temperature T_i during one annealing process:

$$\Delta D = 2 \cdot \sum_{i=1}^N v(T_i) \cdot (t_i - t_{i-1}) = 2 \cdot \sum_{i=1}^N v_0^{sim} \exp\left(-\frac{E_v}{k_B T_i}\right) \cdot (t_i - t_{i-1}) \quad (4.7)$$

The fit parameter v_0^{sim} has to be adjusted, so that Equation 4.7 is satisfied. Afterwards, v is determined with Equation 4.2 using E_v and the simulated factor v_0^{sim} [128, 129]. Performing this simulation for each annealing temperature results in a new set of values v that determine the new activation barrier E_v in the Arrhenius plot. This iteration process has to be carried out several times, each time with the newly gained E_v , until E_v converges.

Finally, the new crystal growth velocity determines the actual annealing time, according to Equation 4.1.

4.3.3. Determination of the nucleation rate $I(t)$

The analysis of the nucleation process is based on one microscopic image taken at a stage of the crystallization process at which approximately 600 crystals have not yet impinged each other, referring to a crystalline fraction of 1-5 %. The moment of nucleation of each crystal is calculated by employing the time-independent crystal growth velocity v after determining its radius [131]. The largest crystal determines the starting point of the crystallization and defines the time-lag τ . The derivative of the number of crystals N at a specific time t_i normalized by the still amorphous fraction $(1 - \chi(t_i))$ represents the nucleation rate I at t_i .

$$I(t_i) = \frac{\dot{N}(t_i)}{1 - \chi(t_i)} \quad (4.8)$$

$\dot{N}(t_i)$ is determined in a linear regression of a set of three data points N at $[t_{i-1}, t_{i+1}]$, while the Johnson-Mehl-Avrami model (Equation 2.28) is used for $t \geq \tau$ to interpolate the crystalline fraction $\chi(t_i)$ measured after each annealing step [131]. This normalization process is crucial since the growth process of already nucleated crystals successively reduces the amorphous surface area that provides room for new nucleations to occur. Figure 4.2 displays the number of crystals N , the crystalline fraction χ and the nucleation rate I as a function of the annealing time for Si on SiN treated at 580 °C. In conformity with classical nucleation theory, the nucleation rate $I(t)$ reaches a steady state I_{ss} after passing a transient regime.

The time-lag τ represents a characteristic parameter for the transient regime of the nucleation rate, whereas I_{ss} represents the essential parameter for the nucleation process in steady state condition [47].

I_{ss} (Equation 2.15) can be rewritten by replacing k_{ic}^+ with Equation 2.24:

$$I_{ss} = \varepsilon \cdot s_{ic} \cdot k_0 \cdot \exp\left(-\frac{\Delta G^*}{k_B T}\right) \cdot n_0 \cdot \Gamma_z \cdot \exp\left(\frac{-\Delta G_c}{k_B T}\right) \quad (4.9)$$

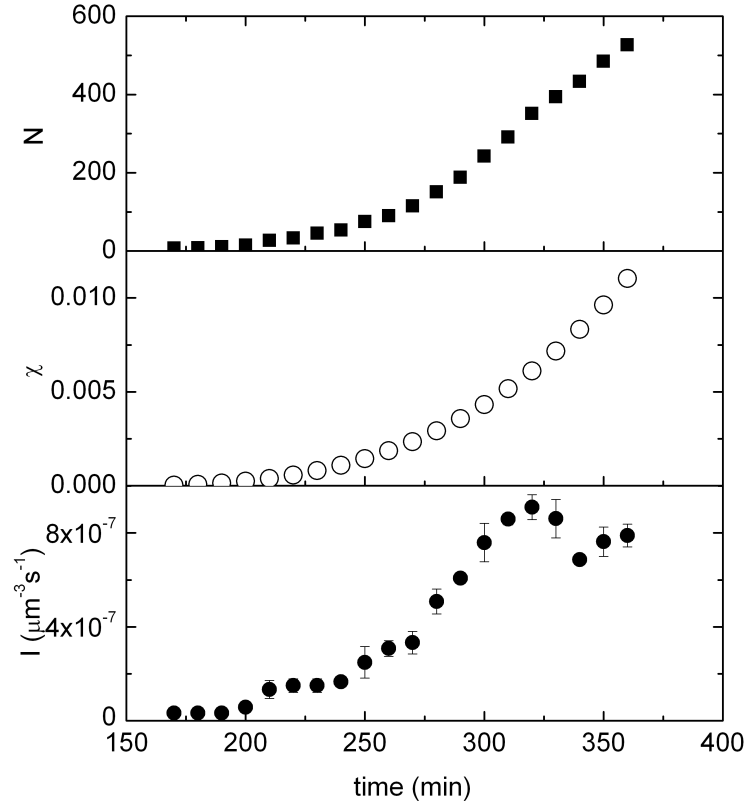


Figure 4.2: The number of crystals N and the crystalline fraction $\chi(t)$ are illustrated as a function of annealing time at 580°C for $\alpha\text{-Si}$ deposited on SiN . The time dependence of the nucleation rate $I(t)$ is calculated from Equation 4.8. In accordance with classical nucleation theory, $I(t)$ reaches a steady state nucleation rate I_{ss} after passing a transient regime.

With Equation 4.4 and assuming the same factors as in section 4.3.2, we obtain:

$$I_{ss} = \varepsilon \cdot s_{ic} \cdot k_0 \cdot n_0 \cdot \Gamma_z \cdot \exp\left(-\frac{\Delta E^*}{k_B T}\right) \cdot \exp\left(\frac{-\Delta G_c}{k_B T}\right) \quad (4.10)$$

If the slight temperature dependence of Γ_z is disregarded, I_{ss} can be summarized as follows

$$I_{ss} = I_{ss0} \cdot \exp\left(-\frac{E_{I_{ss}}}{k_B T}\right), \quad (4.11)$$

with

$$\Delta G_c = E_{I_{ss}} - E_v. \quad (4.12)$$

Finally, Equation 4.12 presents a simple correlation between the activation energy for growth E_v , the activation energy for a steady state nucleation $E_{I_{ss}}$ and the work to form a critical nucleus ΔG_c . Equation 4.11 grants a temperature-dependent analysis based on the Arrhenius law and leads to an identification of the activation barrier $E_{I_{ss}}$.

4.4. Influence of the substrate topography on the crystallization process

Figure 4.3 shows the averaged time-independent crystal growth velocity as function of $1/k_B T$ for Si deposited at 300 °C on SiN ($\delta_{rms} = 0.3$ nm) and ZnO:Al ($\delta_{rms} = 5$ nm) in the investigated temperature regime of 560 °C to 610 °C. With activation energies E_v of (2.6 ± 0.2) eV for Si on SiN and (2.5 ± 0.2) eV for Si on ZnO:Al, both systems exhibit identical crystal growth velocities within the accuracy of the measurement. Hence, the crystal growth velocity of the deposited Si is independent of the surface topography of the underlying substrate. Within the error margins, the activation energies are in accordance with previously gained results on various kinds of amorphous Si, such as evaporated Si, ion-implanted a-Si as well as hydrogenated amorphous Si [63, 132, 133, 134, 135].

In contrast to the crystal growth process, the investigation of the nucleation behavior reveals that the substrate roughness has a crucial impact on the steady state nucleation rate. The comprehensive analysis is based on the determination of the nucleation parameters of each individual sample in the investigated temperature regime of 560 °C to 610 °C. Table 4.2 summarizes the activation energies for the steady state nucleation $E_{I_{ss}}$ and time-lag E_τ for Si films prepared at deposition temperatures T_{dep} of 150 °C, 200 °C, 250 °C and 300 °C on substrates with deviating topographies. A complete overview of the derived nucleation parameters is presented in appendix A.2, including the respective Arrhenius plots as well as fit parameters for I_{ss} and τ .

The nucleation process exhibits a complex correlation with the substrate topography and the deposition temperature of the amorphous Si, necessitating a systematic presentation and interpretation of the obtained results.

Table 4.2: The essential parameters that characterize the nucleation behavior on the specific substrates are listed. δ_{rms} and T_{dep} respectively denote the root mean square roughness of the substrate and the deposition temperature of the α -Si, while $E_{I_{ss}}$ and E_{τ} represent the activation energy for the steady state nucleation rate I_{ss} and the time-lag τ .

substrate	δ_{rms} (nm)	T_{dep} (°C)	$E_{I_{ss}}$ (eV)	I_{ss} at 600 °C ($\mu\text{m}^{-3}\text{s}^{-1}$)	E_{τ} (eV)	τ at 600 °C (min)
ZnO:Al	10	300	1.8 ± 0.2	$(2.4 \pm 0.2) \cdot 10^{-4}$	4.0 ± 0.7	13 ± 2
ZnO:Al	5	300	2.9 ± 0.4	$(7.9 \pm 1.9) \cdot 10^{-5}$	3.8 ± 0.3	14 ± 3
ZnO:Al	5	250	3.6 ± 0.2	$(3.7 \pm 0.7) \cdot 10^{-5}$	3.2 ± 0.3	49 ± 2
ZnO:Al	5	200	5.1 ± 0.4	$(2.3 \pm 0.1) \cdot 10^{-6}$	3.2 ± 0.5	90 ± 18
ZnO:Al	5	150	4.5 ± 0.4	$(3.4 \pm 0.3) \cdot 10^{-6}$	3.5 ± 0.7	61 ± 4
ZnO:Al/SiN (35 nm)	4.4	300	3.5 ± 0.2	$(1.2 \pm 0.1) \cdot 10^{-4}$	3.2 ± 0.2	34 ± 16
ZnO:Al/SiN (50 nm)	2.3	300	4.2 ± 0.6	$(4 \pm 1) \cdot 10^{-6}$	2.9 ± 0.3	48 ± 12
SiN	0.3	300	5.0 ± 0.6	$(5 \pm 2) \cdot 10^{-6}$	2.3 ± 0.7	49 ± 13
SiN	0.3	250	4.4 ± 0.5	$(4 \pm 1) \cdot 10^{-6}$	3.4 ± 0.2	181 ± 8
SiN	0.3	200	4.2 ± 1.1	$(3.7 \pm 0.3) \cdot 10^{-6}$	3.2 ± 0.3	216 ± 12
SiN	0.3	150	5.1 ± 0.7	$(6 \pm 1) \cdot 10^{-6}$	3.2 ± 0.1	279 ± 6

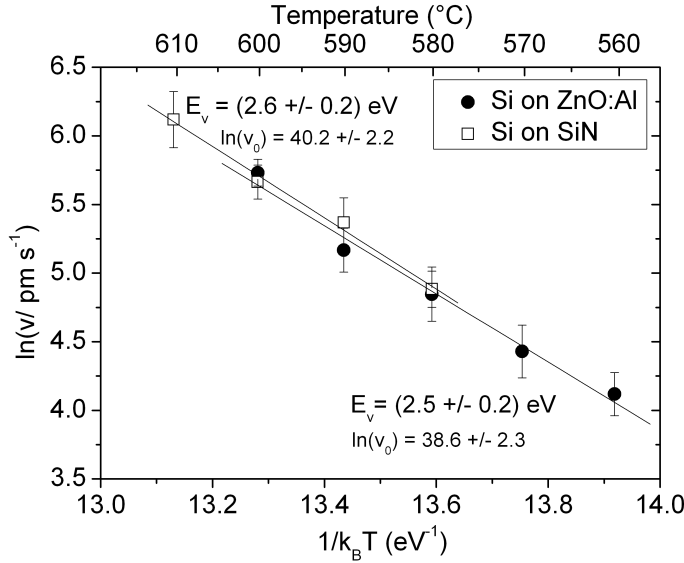


Figure 4.3: The crystal growth velocity v for Si deposited on SiN and ZnO at 300 °C as a function of $1/k_B T$ is illustrated. In accordance to the Arrhenius law the slope of the fitted data represents the activation energy for growth E_v .

Figure 4.4 illustrates $E_{I_{ss}}$ as a function of the roughness for the prepared samples listed in Table 4.2. At a deposition temperature of 300 °C, $E_{I_{ss}}$ decreases steadily with increasing substrate roughness. At $\delta_{rms} = 0.3$ nm, $E_{I_{ss}}$ is 5 eV, and decreases gradually to 4.2 eV at $\delta_{rms} = 2.3$ nm, 3.5 eV at $\delta_{rms} = 4.4$ nm, 2.9 eV at $\delta_{rms} = 5$ nm and finally 1.8 eV at $\delta_{rms} = 10$ nm. The decrease in $E_{I_{ss}}$ is accompanied by an increase in I_{ss} and translates directly into the formation of smaller grains. This correlation is visualized by the insets in Figure 4.4, showing SEM images of defect etched fully crystalline samples prepared on SiN ($\delta_{rms} = 0.3$ nm), ZnO ($\delta_{rms} = 5$ nm) and ZnO ($\delta_{rms} = 10$ nm). The defect etch removed the disordered material such as point defects, dislocations and grain boundaries, highlighting the contours of individual crystalline features [136]. While crystals on SiN exceed several μm in size, crystals on ZnO get considerably smaller with increasing substrate roughness.

However, for a specific substrate type with high surface roughness, the deposition temperature of the a-Si has an essential impact on the nucleation behavior and was exemplarily investigated on the substrates SiN ($\delta_{rms} = 0.3$ nm) and ZnO:Al ($\delta_{rms} = 5$ nm). The high nucleation rate and low $E_{I_{ss}}$ of 2.9 eV of Si on ZnO:Al ($\delta_{rms} = 5$ nm) obtained for $T_{dep} = 300$ °C is sensitive to changes in the deposition temperature. At a reduced deposition temperature of $T_{dep} = 250$ °C, we observe a decline in the nucleation rate of Si on

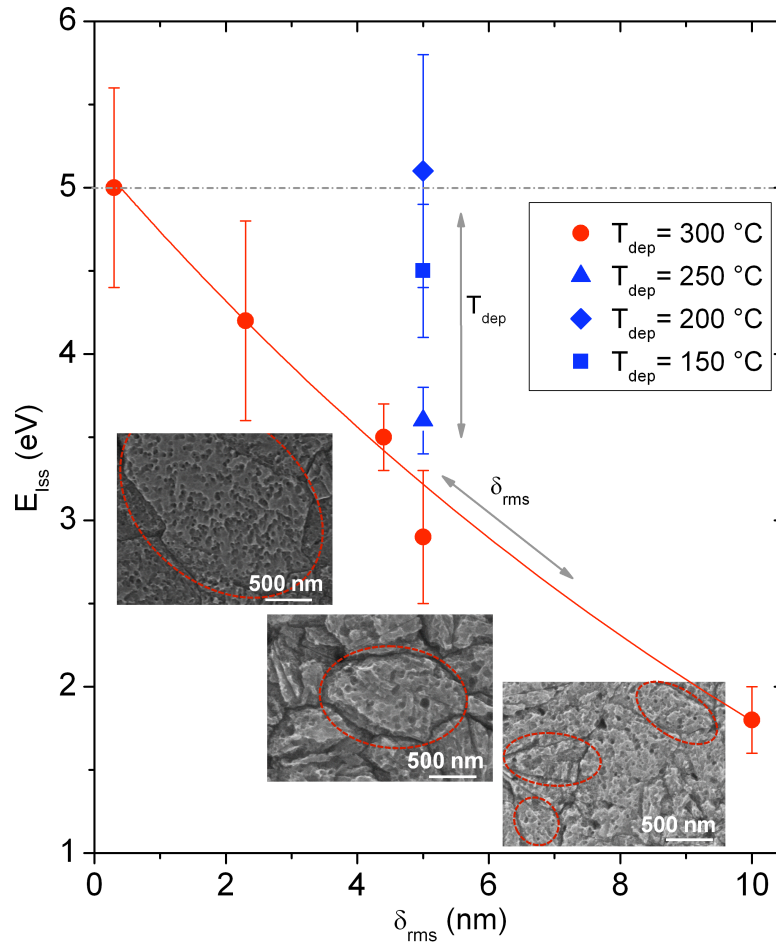


Figure 4.4: The activation energy for the steady state nucleation rate $E_{I_{ss}}$ is shown as a function of the root mean square roughness δ_{rms} of the substrate for deposition temperatures T_{dep} ranging from 150 °C to 300 °C. The solid red line is added as a guide for the eye. The insets illustrate SEM images of defect-etched samples, with the red circles indicating the size of the crystalline features.

ZnO:Al, while its activation energy increased to (3.6 ± 0.2) eV. The nucleation rate can be decreased even further by lowering the deposition temperature to 200 °C. With an activation energy of (5.1 ± 0.7) eV and a lower nucleation rate, the material at $T_{dep} = 200$ °C exhibits a nucleation behavior similar to Si on SiN. While Si on ZnO:Al clearly shows a T_{dep} -dependent steady state nucleation rate and activation energy in the temperature regime between 200 °C and 300 °C, I_{ss} of Si on a smooth SiN surface is found to be temperature-independent in the entire investigated temperature regime (Table 4.2). Concluding, the nucleation rate and $E_{I_{ss}}$ are determined by the interplay between the sur-

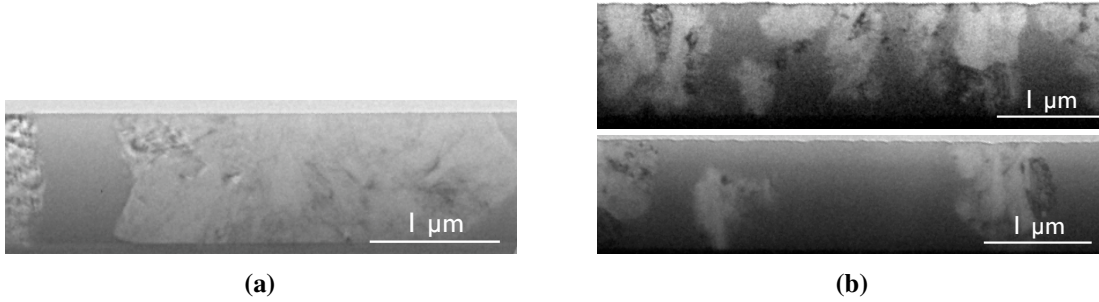


Figure 4.5: Cross-sectional TEM micrographs of partially crystallized Si on SiN ((a)) and ZnO:Al ((b)) deposited at $T_{dep} = 300^\circ\text{C}$. The SiN/Si interface on (a) and ZnO:Al/Si interface on (b) are located at the bottom of the image and Si surface is on top. Before TEM specimen preparation the samples were annealed at 600°C for 3.5 h ((a)) and for 45 min ((b)). The bright areas on the images correspond to the crystalline phase of Si, whereas the darker regions correspond to the amorphous matrix.

face roughness and the deposition temperature. While $E_{I_{ss}}$ drops with increasing substrate roughness at elevated deposition temperatures, an $E_{I_{ss}}$ of 5 eV can be restored for Si on rough textures by lowering T_{dep} .

Cross-sectional TEM was employed to locate the position of the nucleation centers and visualize the vertical size of the growing crystals. Figure 4.5(a) displays an a-Si layer on SiN-coated glass deposited at $T_{dep} = 300^\circ\text{C}$ and subsequently annealed at 600°C for 3.5 h, leading to 20% crystallinity, and clearly shows that crystals grow up to several micrometers in diameter before they impinge each other. After the crystals penetrate the $1\ \mu\text{m}$ thick Si layer, they continue growing laterally in two dimensions. Figure 4.5(b) depicts Si layers on ZnO:Al ($\delta_{rms} = 5\ \text{nm}$) with a crystalline fraction of 25% after annealing at 600°C for 45 min. The numerous crystals nucleated in the considerably shorter annealing time are significantly smaller than the crystals on SiN and do not nucleate at a preferential interface.

The influence of the surface roughness and T_{dep} on the transient regime is only restricted to the time-lag itself and not linked to E_τ (Table 4.2). Although the lowest E_τ of (2.3 ± 0.7) eV is found for the smoothest substrate and the highest E_τ of (3.9 ± 0.7) eV belongs to ZnO ($\delta_{rms} = 10\ \text{nm}$), E_τ does not deviate significantly from its average E_τ of 3.2 eV within the error margins upon changing T_{dep} and δ_{rms} .

Figure 4.6 illustrates the time-lag τ at 600°C as a function of the substrate roughness

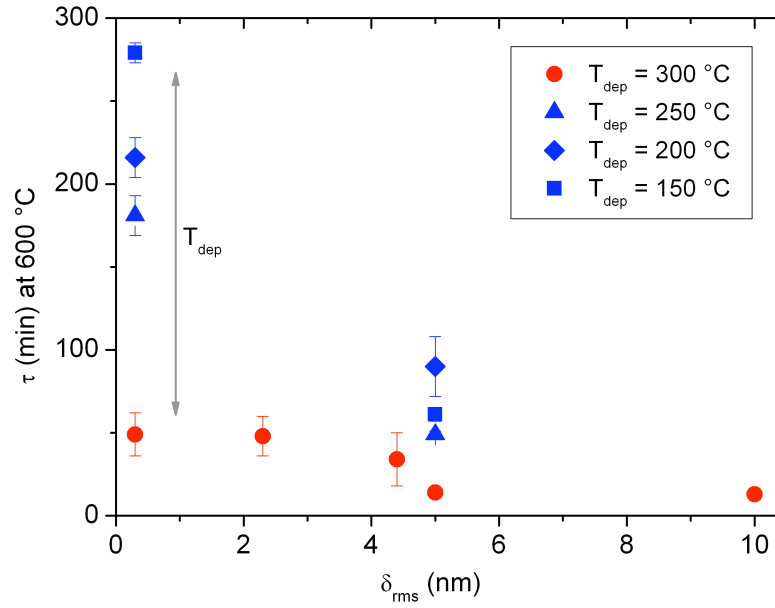


Figure 4.6: The time-lag τ at 600 °C is plotted vs. the root mean square roughness δ_{rms} of the substrate for deposition temperatures T_{dep} ranging from 150 °C to 300 °C.

δ_{rms} for the samples listed in Table 4.2. The surface topography influences the time-lag τ moderately for $T_{dep} = 300$ °C, with the time-lag τ decreasing from 49 min to 13 min upon increasing δ_{rms} from 0.3 nm to 10 nm at an isothermal annealing temperature of 600 °C. However, the deposition temperature represents a key parameter in altering the time-lag. A decrease in T_{dep} results in a significant increase of the time-lag on smooth and rough substrate surfaces alike. On SiN ($\delta_{rms} = 0.3$ nm), the nucleation starts after 49 min at $T_{dep} = 300$ °C, while τ at $T_{dep} = 250$ °C is 3 h, and increases further to 3.5 h at 200 °C and 4.5 h at 150 °C. We also observe a similar T_{dep} -dependent trend for Si on ZnO ($\delta_{rms} = 5$ nm). For an annealing temperature of 600 °C, the crystallization process already starts after 14 min at $T_{dep} = 300$ °C and increases to 49 min at 250 °C before reaching 90 min at 200 °C. With a time lag of 60 min at a deposition temperature of 150 °C, τ is surprisingly smaller than at 200 °C, interrupting the ascending trend of the time-lag. The nature of the correlation between T_{dep} and τ will be elucidated in a structural analysis of the amorphous silicon.

4.5. Influence of the structural disorder in a-Si on the nucleation process

In order to determine the influence of the structural properties of amorphous Si on the nucleation process, the as-deposited films on ZnO:Al ($\delta_{\text{rms}} = 5 \text{ nm}$) and SiN ($\delta_{\text{rms}} = 0.3 \text{ nm}$) were analyzed with Raman spectroscopy. Raman spectroscopy is a well-established technique to determine the structural disorder in amorphous Si [137, 138, 139, 140].

The Raman spectra were fitted by using the superposition of four Gaussian functions, respectively corresponding to transverse-optic-like (TO) at $(475 \pm 5) \text{ cm}^{-1}$, transverse-acoustical-like (TA) at $(147 \pm 3) \text{ cm}^{-1}$, longitudinal-optical-like (LO) at $(380 \pm 10) \text{ cm}^{-1}$ and longitudinal-acoustical-like (LA) at $(285 \pm 5) \text{ cm}^{-1}$ phonon bands. In addition, a linear background was subtracted. The Marquardt-Levenberg algorithm was used to find the minimum of the squared deviation of the fit function to the experimental data. Although the TA-like band is partly suppressed by the tail of the Rayleigh line at low wavenumbers, the chosen fitting procedure represents an adequate method to highlight the characteristic differences of the deposited layers within the given error margins. Figure 4.7 illustrates Raman spectra for a-Si deposited at T_{dep} of 150°C , 200°C , 250°C and 300°C on SiN-coated glass substrates. The intensity of the TA-phonon band and the TO-phonon band position clearly show a correlation with T_{dep} , which can be linked to modifications in the structural order of the amorphous material. Firstly, the short-range disorder in the material correlates with the position and linewidth of the TO-like phonon band. With increasing short-range disorder, the TO-like “phonon peak” shifts to smaller wavenumbers while the linewidth of this signal increases [137, 138, 140]. Secondly, an increasing intermediate-range disorder is manifested in an increase in the ratio of the intensity of the TA-like band to the intensity of the TO-like band, $I_{\text{TA}}/I_{\text{TO}}$ [139].

Figure 4.8 shows the crucial parameters that determine the short-range and intermediate-range disorder in a-Si on SiN and ZnO:Al as a function of the deposition temperature. In general, the structural disorder of Si on ZnO:Al and Si on SiN exhibits the same trends upon changing the temperature, demonstrating the minor effect of the roughness on the structural disorder in the material. The transverse-optic-like (TO) band position of Si on SiN shifts to higher wavenumbers with increasing deposition tempera-

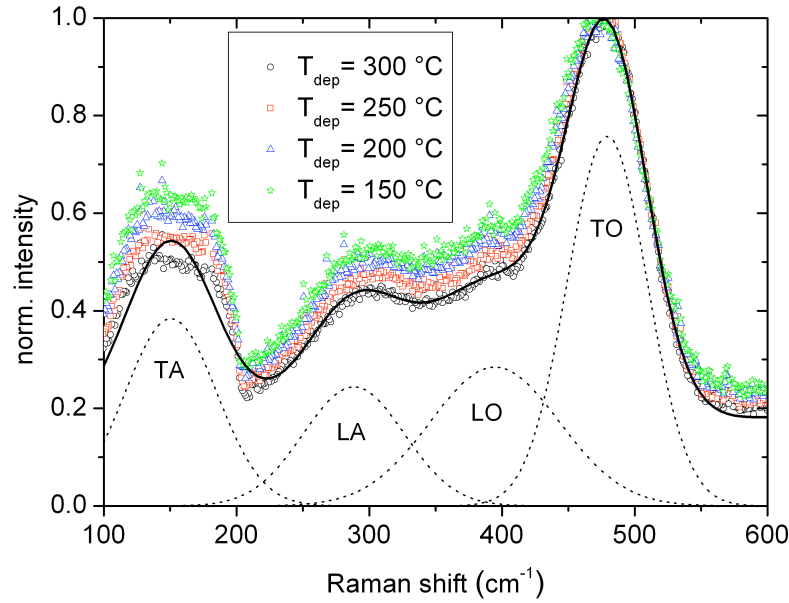


Figure 4.7: Raman spectra normalized to the TO-like band are displayed for *a*-Si layers deposited at T_{dep} ranging from 150 °C to 300 °C on SiN. The fit function consisting of 4 Gaussian function being respectively correlated to the TA-like, LA-like, LO-like and TO-like phonon bands is presented for *a*-Si on SiN at $T_{dep} = 300$ °C. Although the TA-like band is partially suppressed by the contributing tail of the Rayleigh line, the chosen fitting procedure is an adequate method to extract the characteristic differences between the individual spectra within the given error margins.

ture, indicating a lowering of the disorder at elevated deposition temperatures, a process being associated with a reducing linewidth Γ_{TO} of the TO-like band. On ZnO, the TO band position shifts from $(474.7 \pm 1.2) \text{ cm}^{-1}$ at 150 °C to $(480.4 \pm 0.5) \text{ cm}^{-1}$ at 300 °C, while the TO band position on SiN increases from $(475.9 \pm 0.9) \text{ cm}^{-1}$ to $(479.5 \pm 0.3) \text{ cm}^{-1}$ upon raising the temperature. The respective linewidth Γ_{TO} of the TO signal on SiN and ZnO:Al drops from $(74.2 \pm 2.2) \text{ cm}^{-1}$ to $(67.8 \pm 1.2) \text{ cm}^{-1}$ and $(76.2 \pm 2.2) \text{ cm}^{-1}$ to $(67.6 \pm 1.6) \text{ cm}^{-1}$. The I_{TA}/I_{TO} ratio of Si on ZnO:Al decreases from (0.68 ± 0.06) at 150 °C to (0.44 ± 0.03) at 300 °C, whereas I_{TA}/I_{TO} of Si on SiN ranges from (0.64 ± 0.06) at 150 °C to (0.49 ± 0.02) at 300 °C. Both systems show a decreasing intermediate disorder with increasing deposition temperature. In order to determine the influence of thermal annealing on the structural disorder, the heavily disordered material deposited at low T_{dep} was exposed to a 70 min long isothermal annealing step at 600 °C.

The disordered structure could be relaxed in the temperature treatment, resulting in a-

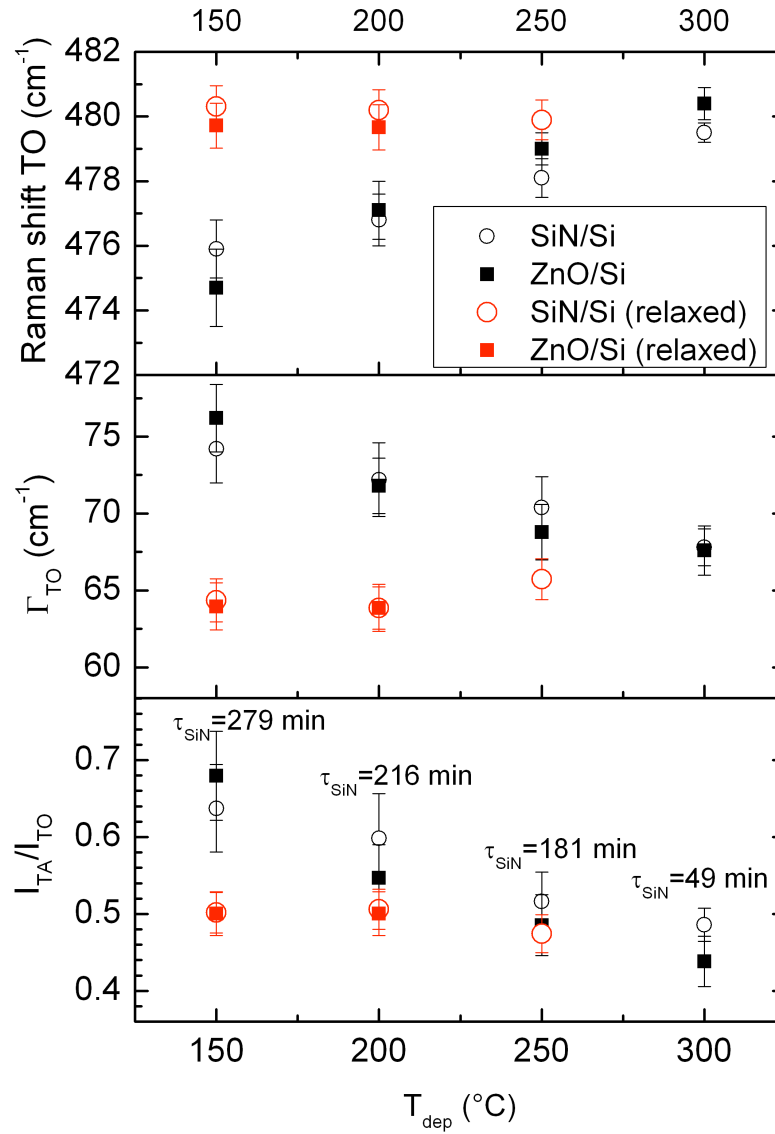


Figure 4.8: The position of the TO-like phonon band, its linewidth Γ_{TO} and the ratio of the intensity of TA- and TO-like signal $I_{\text{TA}}/I_{\text{TO}}$ are shown for a-Si deposited at various temperatures T_{dep} on SiN ($\delta_{\text{rms}} = 0.3 \text{ nm}$) and ZnO:Al ($\delta_{\text{rms}} = 5 \text{ nm}$) before and after relaxation of the samples at 600°C for 70 min.

Si with structural characteristics that are similar to those of untreated a-Si deposited at higher temperatures. Consequently, these structural relaxation processes were initiated before the first nucleation event took place and correlated to the transient regime of the nucleation process. The labels in Figure 4.8 denote the time-lag of a-Si layers deposited

on SiN at a specific T_{dep} and illustrate that the increasing bulk disorder is consistent with an increasing time-lag. Further, the disorder does not show a significant dependence on the substrate topography, linking the structural properties of the bulk material primarily to its corresponding deposition temperature.

4.6. Discussion

4.6.1. Characteristics of the nucleation process in a-Si and a-Si:H

In the last decades, many researchers investigated the nucleation behavior of a-Si prepared with various deposition parameters and dissimilar deposition techniques. The employed preparation techniques ranged from the deposition of a-Si by evaporation and ion-implantation to the deposition of hydrogenated a-Si:H in CVD processes [46, 133, 132, 141, 142, 143, 134, 144, 63]. It has been well established that the structural parameters of unhydrogenated a-Si depend strongly on the preparation parameters, such as the deposition temperature and energy and dose of the used ion-beam [40, 42, 43]. Upon thermal annealing, a reduction of the bond angle distortion in a-Si and an accompanying heat release prior to crystallization are initiated and have been attributed to structural relaxation in ion-implanted and evaporated a-Si [43, 44, 145, 146]. Calorimetric studies on a-Si conducted by Roorda et al. and Donovan et al. provide quantitative evidence for a heat release of 3.7 kJ/mole and (5.1 ± 1.2) kJ/mole in a-Si [40, 42]. In a-Si:H, the presence of hydrogen not only modifies the structural and electronic characteristics of the deposited film, but also influences the kinetics of the nucleation process. The time-lag of a-Si:H in hot-wire (HW) CVD material increases with increasing H concentration, while the nucleation rate decreases [142, 147]. Recently, nucleation centers were proposed to be attributed to regions comprising ordered material, with their size determining the incubation time, while changes in the microstructure upon H evolution play a diminishing role in the nucleation process [143].

Iverson et al. and Spinella et al. investigated the nucleation in self-implanted a-Si and published an $E_{I_{ss}}$ of (5.1 ± 0.2) eV and 5.3 eV, respectively [133, 46]. An $E_{I_{ss}}$ of 4.9 eV was reported for evaporated a-Si [132, 63]. Hydrogenated a-Si was studied by Masaki

et al. who reported an $E_{I_{ss}}$ of (5.1 ± 2.2) eV for a-Si:H by PECVD [134]. A rather low activation energy of 3.8 eV for PECVD a-Si:H on SiO₂ was revealed and attributed to a heterogeneous nucleation process at the Si/SiO₂ interface [141]. Further, various studies were conducted on a-Si and a-Si:H to determine the energy to form a critical nucleus, all of which independently confirmed a ΔG_c of ~ 2 eV [148, 134]. It is striking that, despite the fundamental differences in the preparation technique and deposition parameters, the overall values for $E_{I_{ss}}$ and ΔG_c are very similar amongst the different kinds of a-Si(:H). These results led to the postulation of the existence of a common intermediate a-Si state between the initial a-Si and c-Si which is reached after a structural relaxation process [134]. Hedler et. al. finally provided experimental evidence for the existence of such a state of an undercooled liquid in Si [34].

4.6.2. Steady state nucleation rate and $E_{I_{ss}}$

With (5.0 ± 0.6) eV, the activation barrier for nucleation of Si on SiN determined in this study resembles a value which has been reported for nucleation in a-Si. The energy to form a critical nucleus $\Delta G_c = (2.4 \pm 0.6)$ eV is also in accordance to previously published studies on a-Si and a-Si:H [63, 132, 133, 134, 148]. We do not observe an influence of the deposition temperature on either $E_{I_{ss}}$ or I_{ss} . In previous studies on a-Si:H, $E_{I_{ss}}$ was also found to be independent of the deposition temperature. However, it was also reported that I_{ss} in a-Si:H increased with increasing temperature, a discovery which researchers consequently correlated to a declining disorder in the material [141, 144].

In the light of these results, the crucial influence of the surface topography on the deposition temperature dependent $E_{I_{ss}}$ is surprising. An unique interplay between surface roughness and deposition temperature determines the nucleation behavior of Si. $E_{I_{ss}}$ increases at a specific deposition temperature with ascending roughness, whereas the deposition temperature determines the nucleation process for a-Si deposited on a particular surface topography. The decreased $E_{I_{ss}}$ consequently translates into a lowered ΔG_c . According to classical nucleation theory, a reduction of ΔG_c can be caused by a heterogeneous nucleation process at a preferential interface or nucleation sites in the bulk material (section 2.1.2). However, the nucleation sites in a-Si on ZnO:Al are not confined to the

Si/ZnO:Al interface, ruling out interface induced crystallization as an explanation for the low activation energies (Figure 4.5(b)).

Further, Al and Zn represent potential candidates for nucleation sites in the bulk of the Si film after penetrating the Si by diffusion in a thermally activated process. In-situ spectroscopic analyses confirmed that the ZnO/Si interface is modified by the SPC process, showing a higher concentration of Zn in Si in proximity to the interface [149, 150, 151]. Secondary ion mass spectroscopy measurements (SIMS) revealed the diffusion of Zn during the SPC process into the deposited Si (appendix A.3). In addition, an accumulation of diffused Al was found within 400 nm of the Si/ZnO:Al interface after SPC. Despite these findings, the dependence of $E_{I_{ss}}$ on the deposition temperature indicates the unlikelihood of a nucleation process that is induced by diffusing contaminants during SPC:

First, if the diffusion of Al and Zn were to influence the nucleation during annealing at 600 °C, we would expect an equivalent reduction of $E_{I_{ss}}$ for a-Si deposited at 200 °C and 300 °C. However, we found a strong dependence of $E_{I_{ss}}$ on the deposition temperature between 200 °C and 300 °C, with $E_{I_{ss}}$ of 5 eV resembling a value for homogeneous nucleation and a reduced $E_{I_{ss}}$ of 2.9 eV at 300 °C. Concluding, the heterogeneous nucleation process only occurs at elevated deposition temperatures, giving rise to a fundamental difference of the deposited a-Si layer.

Second, two substrates, which consist both of the diffusion barrier SiN on ZnO:Al, exhibit deviating surface roughnesses. Hence, the influence of diffusion processes could be suppressed, while creating new surface topographies. The nucleation on a SiN/ZnO:Al substrate with $\delta_{rms} = 4.4$ nm was substantially different from the nucleation in Si on a SiN-capped ZnO:Al substrate with $\delta = 2.3$ nm (Table 4.2), indicating a nucleation process that is primarily influenced by the substrate topography.

Third, a potential Al induced nucleation process can be excluded. An Al induced nucleation would lead to a preferential nucleation in proximity to the ZnO:Al/Si interface due to the aforementioned Al accumulation at the ZnO:Al/Si interface measured with SIMS. This, however, contradicts the observation in Figure 4.5(b), where crystal nucleation events are not confined to that particular interface.

These results indicate that the nucleation process is governed rather by T_{dep} -sensitive intrinsic structural properties of the deposited a-Si than by an impurity-induced nucleation.

4.6.3. Correlation between time-lag and structural disorder in a-Si

The activation energies obtained for the time lag of ~ 3.2 eV are in proximity to values reported in literature ranging from 2.7 to 3.4 eV [46, 133]. In particular, τ for a-Si on SiN deposited at 300 °C is in accordance with a value determined for a-Si evaporated at an identical temperature [63]. Raman spectroscopy on as-deposited a-Si on SiN revealed that the structural disorder of the amorphous material decreases with an ascending deposition temperature. In previous Raman spectroscopy studies, the structural properties of a-Si were found to exhibit a dependence on the deposition parameters, with structural relaxation processes and accompanying heat releases being initiated upon thermal annealing [43, 44]. The increasing disorder in Si on SiN correlates well with an increase of the time-lag, as disordered material naturally requires more time to undergo structural rearrangements to finally enable nucleation. Since the ΔG_c of ~ 2 eV is similar for all a-Si layers on SiN and I_{ss} is insensitive to alterations of the deposition temperature, the changes in the detected disorder can exclusively be ascribed to relaxation processes in the transient regime of the nucleation process. Although Si on rough ZnO:Al shows a more complex nucleation behavior with $E_{I_{ss}}$ depending on the deposition temperature and τ not falling consistently with T_{dep} , the overall trend of the transient nucleation regime is similar to a-Si on SiN. In fact, the intermediate range disorder and the short range disorder of a-Si on SiN and ZnO:Al deposited at identical temperatures coincide within the error margins. Subsequently, the disorder in the material on ZnO:Al correlates with the transient regime, but cannot explain the unique properties of the steady state nucleation regime of Si on ZnO.

4.6.4. Design rules

The design of the microstructure of poly-Si is governed by the temperature dependence of the nucleation process on a substrate with a specific roughness. Based on the presented analysis, we can determine the mandatory requirements for a preparation of large-grained poly-Si in a minimized production time. In order to ensure the growth of large-grained Si, T_{dep} has to be low for $E_{I_{ss}}$ to reach 5 eV. However, for τ to be as short as possible, T_{dep} should be chosen sufficiently high. To meet these opposing requirements, the tem-

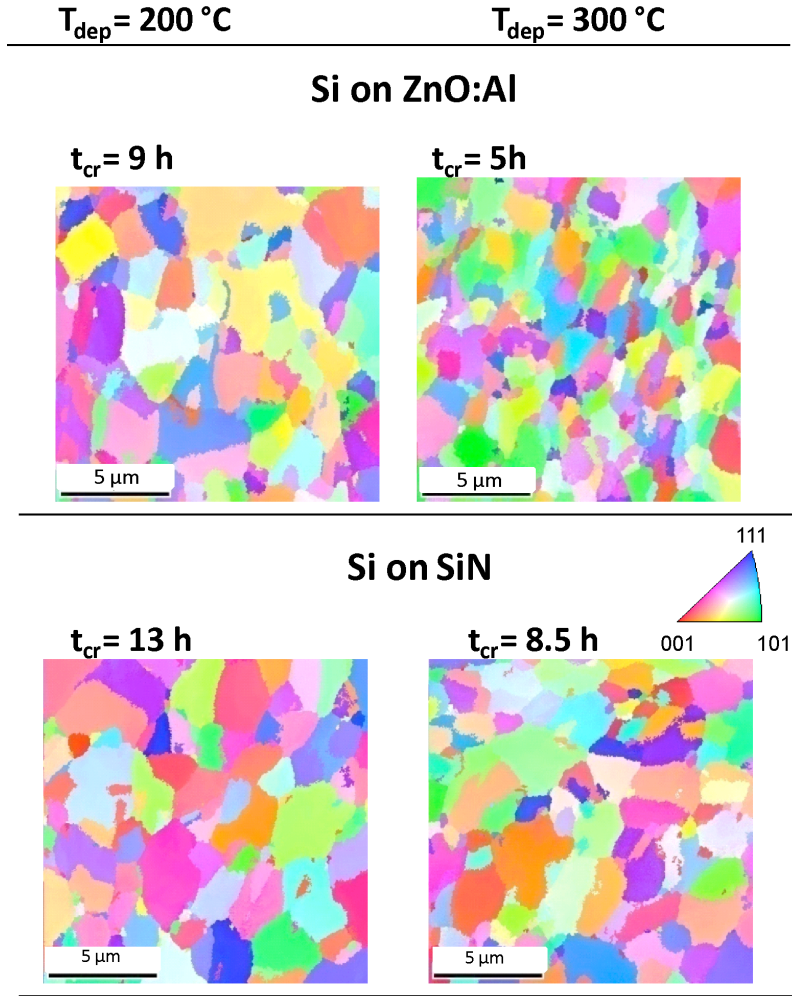


Figure 4.9: Electron backscatter diffraction (EBSD) inverse pole figure maps of poly-Si on ZnO:Al ($\delta_{\text{rms}} = 5 \text{ nm}$) and on SiN ($\delta_{\text{rms}} = 0.3 \text{ nm}$) deposited at 200°C and 300°C . t_{cr} denotes the time required to complete the crystallization process.

perature has to be individually adjusted for each specific type of substrate. Figure 4.9 shows EBSD pole figure maps for poly-Si layers on the two substrates ZnO:Al and SiN deposited at $T_{\text{dep}} = 200^\circ\text{C}$ and 300°C . The microstructure of Si on ZnO:Al prepared at $T_{\text{dep}} = 300^\circ\text{C}$ comprises grains with small features after completing the crystallization process in 5 h, while the microstructure of poly-Si on ZnO:Al at $T_{\text{dep}} = 200^\circ\text{C}$ consists of grains with several micrometers in diameter after a crystallization time of 9 h. The deposition temperature of 200°C is clearly favorable for this configuration due to the influence of T_{dep} on $E_{\text{I}_{\text{ss}}}$. On SiN, however, increasing the deposition temperature does not

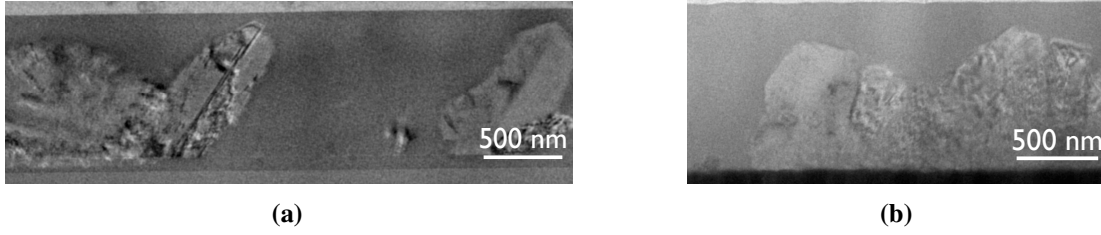


Figure 4.10: TEM cross-sectional images of partially crystalline Si on SiN ($\delta_{\text{rms}} = 0.3 \text{ nm}$) ((a)) and ZnO ($\delta_{\text{rms}} = 5 \text{ nm}$) ((b)) are shown. The Si layers consist of a 100 nm thick nucleation layer deposited at 300 °C followed by a 900 nm thick Si film deposited at 200 °C. The ZnO:Al/Si and SiN/Si interfaces are located on the bottom of the images.

affect the resulting microstructure but merely leads to a variation of the crystallization time from 13 h to 8.5 h, suggesting an ideal temperature of 300 °C.

Homogeneously deposited layers do not comprise preferential nucleation sites at particular interfaces (Figure 4.5(b)). However, the direction of growth can be controlled by implementing nucleation layers. Due to a decreasing time-lag with rising temperature, a thin a-Si layer deposited at higher temperatures can serve as a nucleation layer in a multi-layer system. Figures 4.10(a) and 4.10(b) show TEM micrographs of partially crystalline films on SiN and ZnO:Al, consisting of a 100 nm thick a-Si bottom layer deposited at 300 °C and a 900 nm thick a-Si layer deposited at 200 °C. The chosen annealing times of 120 min for SiN and 100 min for ZnO:Al at 600 °C correspond to a segment in the crystallization process, at which the crystallization process is already initiated for $T_{\text{dep}} = 300 \text{ °C}$ but still suppressed for $T_{\text{dep}} = 200 \text{ °C}$. The crystallization process in both multi-layer systems starts in the bottom layer and proceeds towards the Si surface, with nucleation centers being confined to the nucleation layer deposited at 300 °C, resulting in a microstructure with vertical grain boundaries. The grain size in the crystallized films is controlled by the a-Si properties of the nucleation layer and hence is governed by the temperature-dependence of its I_{ss} on the specific substrate.

4.7. Conclusion

In conclusion, we presented a comprehensive study of the crystallization kinetics in e-beam evaporated amorphous Si with deviating structural disorder on SiN and ZnO-coated substrates with dissimilar nanoroughnesses arising from the crystalline features of the deposited ZnO. It was demonstrated that the microstructure of the resulting poly-Si films can be systematically controlled by individually adjusting T_{dep} for a specific surface roughness δ_{rms} .

While the crystal growth velocity was found to be independent of the underlying substrate texture, an analysis of the influence of the surface topography on the nucleation process revealed a unique correlation between the steady state nucleation rate and substrate topography at an elevated deposition temperature of 300 °C. While the $E_{I_{ss}}$ of Si on smooth SiN ($\delta_{rms} = 0.3$ nm) at $T_{dep} = 300$ °C was in conformity with literature, $E_{I_{ss}}$ of Si declined gradually with increasing roughness, exhibiting an $E_{I_{ss}}$ of merely 1.8 eV on a ZnO film with $\delta_{rms} = 10$ nm. The reduction of $E_{I_{ss}}$ was accompanied by a significant increase of I_{ss} which led to a decline in grain size with increasing roughness. While the crystallized Si on smooth surfaces comprised grains with a feature size of several μm , Si on rough substrates could barely grow up to two μm . However, the characteristic value of 5 eV could be restored for Si on a specific substrate by successively reducing the deposition temperature. The steady state nucleation rate was determined by an interplay between the deposition temperature of the a-Si and the surface topography of the used substrate.

While E_{τ} was not affected by the substrate and an alteration of T_{dep} , τ itself decreased with increasing surface roughness. The deposition temperature was found to be the key parameter that determines τ , with τ becoming significantly longer at low T_{dep} . Films prepared at lower temperatures showed an initially higher disorder on any substrate type, but their structure could be relaxed by thermal annealing. We attributed the deviating structural relaxation processes prior to the initiation of the crystallization process to the dissimilar time-lags in a-Si.

The dependence of nucleation process on the substrate roughness and structural disorder allowed for the determination of a substrate-specific optimal deposition temperature to design large-grained poly-Si in minimal crystallization time. By implementing nucleation

layers, it is possible to control the direction of growth and design poly-Si layers with predominantly columnar grain structures and vertical grain boundaries.

5. Development of poly-Si thin film solar cells on planar glass

5.1. Introduction

The solid phase crystallization (SPC) of deposited amorphous Si thin films is an appealing option to manufacture crystalline Si solar cells on foreign substrates. In the 1990s, Sanyo applied the SPC process to fabricate thin film solar cells on quartz and steel substrates. [21, 22, 23]. After years of extensive research, CSG Solar revealed an improved concept for the fabrication of thin film poly-Si solar cells on float glass and went into commercial production. In 2007, the company presented a poly-Si thin film record module of 10.4% [24, 25, 152]. However, the research focus was continuously put on the optimization of cell designs based on the low-rate deposition technique PECVD, utilizing deposition rates of 30 nm/min, and a sophisticated contact structure, which limit the effectiveness of the poly-Si concept's production process.

This chapter explores the applicability of high-rate e-beam evaporated poly-Si for thin film solar cells, prepared at deposition rates of up to 600 nm/min. Further, the study sheds light onto the design components of a ZnO-based transparent front contact layer embedded in a poly-Si cell concept, which allows for the implementation of a simplified contacting structure and monolithic series connection. The design requirements established for the controlled fabrication of poly-Si with a defined microstructure (chapter 4) are the basis for the evaluation of the electronic quality of e-beam evaporated Si in a poly-Si solar cell device. Section 5.2 is devoted to optimizing the deposition parameters of e-beam evaporated Si, such as the base doping level, deposition rate and deposition temperature, using an established state-of-the-art device structure on planar SiN-coated

glass. In section 5.3, the benefits of an implemented rear-side texture will be presented. Section 5.4 addresses the requirements and challenges of an optimized ZnO-based front contact. Section 5.5 discusses the potential of e-beam evaporation in a critical comparison to PECVD-based poly-Si and examines its application in novel solar cell devices.

5.2. Optimization of poly-Si thin film mini-modules on SiN-coated glass

A systematic variation of essential deposition parameters was carried out to optimize the performance of poly-Si mini-modules embedded in a state-of-the-art device structure on SiN-coated glass with $\delta_{rms} = 0.3$ nm (chapter 4). Stacks of n^+ (PECVD)/ p^- (e-beam)/ p^+ (e-beam) type Si were deposited on SiN-coated glass substrates and subsequently processed to 12-cell mini-modules as outlined in section 3.3.1. First, the doping level of the p^- -type Si base was adjusted at a deposition rate of 300 nm/min and 600 nm/min. In addition, the influence of the base thickness and deposition temperature on the photovoltaic parameters was examined. Finally, by determining the photovoltaic performance at significantly increased background pressures, a fundamental aspect of the process scalability could be addressed. J-V measurements on the prepared mini-modules provided the essential characteristics of their photovoltaic performance. Each individual mini-module was measured twice - once directly after device fabrication (initial) and a second time 24 h after completing the module fabrication (delayed). Table 5.1 summarizes the crucial deposition parameters and the obtained photovoltaic parameters.

Base doping and deposition rate

With a constant absorber thickness of $(1.6 \pm 0.1)\mu\text{m}$ and $T_{dep} = 300^\circ\text{C}$ and background pressure $1 \cdot 10^{-7}$ mbar, various solar cells were prepared with four different base doping levels¹, ranging from not intentionally doped (nid) to a nominal doping concentration of $4 \cdot 10^{16}\text{cm}^{-3}$. A variation of the base doping clearly led to a remarkable change in the

¹The doping concentration was adjusted by controlling the temperature of the calibrated boron effusion cell and is the nominal doping concentration. It can be slightly higher than the concentration of the activated dopants, since a 100% activation rate might not be reached and n -type contaminants or elements such as oxygen must be compensated.

Table 5.1: A complete overview of the characteristic parameters of the prepared mini-modules is given. In various experimental series, the deposition temperature T_{dep} , the deposition rate, the background pressure P_{bg} , the absorber thickness D_{base} and base doping concentration N were individually varied. Light J-V measurements allowed for the determination of the photovoltaic parameters, the average open circuit voltage per cell $V_{oc}/cell$, the short-circuit current density J_{sc} , the fill factor FF and the conversion efficiency η . The J-V characteristics of a mini-module was determined in two separate J-V measurements performed on two consecutive days (initial and delayed). For four of the presented samples, only delayed J-V data is available.

T_{dep} (°C)	Dep. rate (nm/min)	P_{bg} (10^{-7} mbar)	D_{base} (μm)	N (10^{16} cm^{-3})	$V_{oc}/cell$ (mV)	J_{sc} (mA/cm^2)	FF (%)	η (%)
300	300	1	1.6	0	453	19.1	66.2	5.7
300	300	1	1.5	0.5	480 ± 6	19.1 ± 0.1	71.0 ± 0.2	6.5 ± 0.1
300	300	1	1.7	1.5	484 ± 3	19.5 ± 0.1	71.4 ± 0.1	6.7 ± 0.1
300	300	1	1.6	4	485 ± 4	17.4 ± 0.1	70.2 ± 0.1	5.9 ± 0.1
300	600	1	1.8	0.7	477 ± 3	20.3 ± 0.1	69.8 ± 0.1	6.8 ± 0.1
300	600	1	1.6	1.5	482 ± 6	19.3 ± 0.1	67.9 ± 0.2	6.3 ± 0.1
300	600	1	1.7	4	472 ± 5	17.1 ± 0.1	64.1 ± 0.2	5.3 ± 0.1
300	300	1	1.6	1.5	473 ± 1	18.9 ± 0.1	68.1 ± 0.1	6.1 ± 0.1
300	300	1	1.9	1.5	474 ± 1	19.7 ± 0.1	68.6 ± 0.6	6.4 ± 0.1
300	300	1	2.1	1.5	459 ± 1	20.5 ± 0.1	68.8 ± 0.1	6.5 ± 0.1
300	300	1	2.3	1.5	462 ± 1	20.8 ± 0.1	63.9 ± 1.3	6.1 ± 0.2
150	300	1	1.6	1.5	481 ± 1	19.3 ± 0.1	62.2 ± 2.7	5.8 ± 0.2
200	300	1	1.6	1.5	482 ± 1	19.5 ± 0.1	59.9 ± 4.5	5.6 ± 0.4
250	300	1	1.4	1.5	486 ± 1	19.3 ± 0.1	68.3 ± 0.2	6.4 ± 0.1
300	300	1	1.6	1.5	467 ± 9	19.6 ± 0.1	66.5 ± 1.6	6.1 ± 0.3
150	300	1	1.7	1.5	485	20.0	67.9	6.6
200	300	1	1.7	1.5	471	20.1	64.3	6.1
300	300	1	1.7	1.5	476	20.3	69.4	6.7
300	300	1	1.8	1.5	468 ± 5	20.5 ± 0.2	63.0 ± 0.7	6.1 ± 0.1
300	600	5	1.7	1.5	462 ± 1	21.0 ± 0.1	57.3 ± 0.4	5.5 ± 0.1
300	600	10	1.7	1.5	457 ± 1	20.1 ± 0.1	57.1 ± 0.6	5.2 ± 0.1
300	600	50	1.8	1.5	454 ± 1	20.6 ± 0.1	62.5 ± 0.3	5.8 ± 0.1
300	600	100 (N_2)	1.7	1.5	463 ± 1	20.5 ± 0.1	59.1 ± 0.1	5.6 ± 0.1

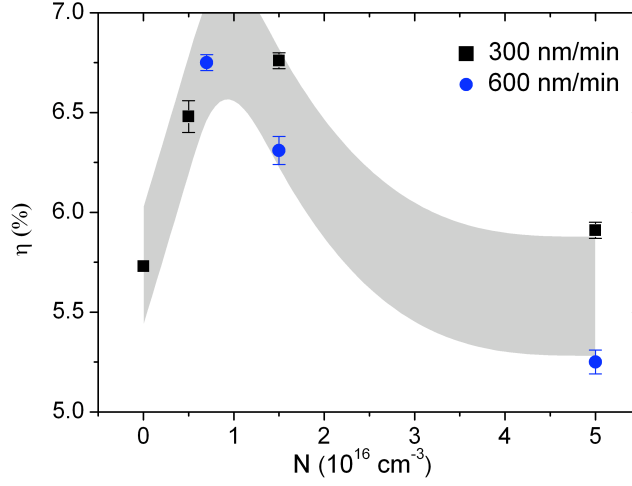


Figure 5.1: The dependence of the mini-module efficiency η on the nominal base doping level is illustrated. The absorber dopant concentration was adjusted by varying the temperature of the calibrated boron effusion cell. The shaded gray area serves as a guide for the eye, depicting the dependence of the efficiency on the doping concentration.

mini-module performance. Figure 5.1 depicts the efficiency as a function of the base doping level and illustrates that a base doping level of $5 \cdot 10^{15} \text{ cm}^{-3}$ to $1.5 \cdot 10^{16} \text{ cm}^{-3}$ is found to be optimal. Increasing the base doping level to $4 \cdot 10^{16} \text{ cm}^{-3}$ results in a decline of the performance due to a decrease of short circuit current. Modules with a not intentionally doped base exhibit a lower V_{oc} , giving rise to a lower efficiency, as well.

With a conversion efficiency of $(6.8 \pm 0.1)\%$, the best mini-module fabricated at a deposition rate of 600 nm/min has a base doping concentration N of $7 \cdot 10^{15} \text{ cm}^{-3}$ and is characterized by a short circuit current density J_{sc} of $(20.3 \pm 0.1) \text{ mA/cm}^2$, a fill factor of $(69.8 \pm 0.1)\%$ and an average open circuit voltage of $(477 \pm 3) \text{ mV}$ per cell. Modules which were prepared at a deposition rate of 300 nm/min and a base doping level of $1.5 \cdot 10^{16} \text{ cm}^{-3}$ show similar results, with a slightly higher V_{oc} of $(484 \pm 3) \text{ mV}$ per cell, a FF of $(71.4 \pm 0.1)\%$ and a lower J_{sc} of $(19.5 \pm 0.1) \text{ mA/cm}^2$.

Base thickness

As outlined in section 2.2.2, the total amount of recombination centers in the grain structure and at grain boundaries controls the diffusion length of the minority charge carriers and determines the electronic quality of the base layer. Consequently, the base layer has to be thinner than the diffusion length of the minority charge carriers for V_{oc} to maintain

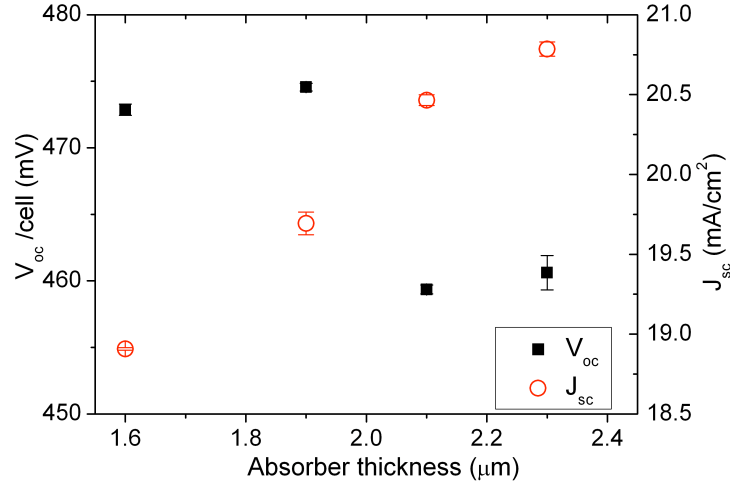


Figure 5.2: The average open circuit voltage per cell V_{oc}/cell and the short circuit current density J_{sc} are shown for 4 mini-modules with different absorber thicknesses.

on a high level. However, it should still be sufficiently thick for a high charge carrier collection. In order to evaluate the potential of the poly-Si quality, 4 mini-modules with absorber thicknesses of 1.6, 1.9, 2.1 and 2.3 μm were prepared, while keeping the deposition rate of 300 nm/min, the base doping level of $1.5 \cdot 10^{16} \text{ cm}^{-3}$ and the background pressure of $1 \cdot 10^{-7}$ mbar constant for all depositions.

Figure 5.2 illustrates that the short circuit current density increases with increasing base thickness, peaking at $(20.8 \pm 0.1) \text{ mA/cm}^2$ with a thickness of 2.3 μm . The open circuit voltage, however, declines with a cell thickness exceeding 2 μm . Starting with $(473 \pm 1) \text{ mV}$ at 1.6 μm , V_{oc} maintains at $(474 \pm 1) \text{ mV}$ for 1.9 μm but starts to drop by 14 mV at a thickness of 2.1 μm . Nonetheless, the efficiency increases from $(6.1 \pm 0.1)\%$ at a base thickness of 1.6 μm to $(6.5 \pm 0.2)\%$ at a thickness of 2.1 μm , since the current increase still compensates for the loss of voltage. The mini-module with a thickness of 2.3 μm exhibits a rather low efficiency of $(6.1 \pm 0.2)\%$ due to a poorer FF of $(63.9 \pm 1.3)\%$.

Deposition temperature

In order to analyze the influence of the deposition temperature of the base layer on the photovoltaic performance of the solar cells, seven mini-modules were processed, whose base layers were individually deposited at 150, 200, 250 and 300 $^{\circ}\text{C}$. The other deposition

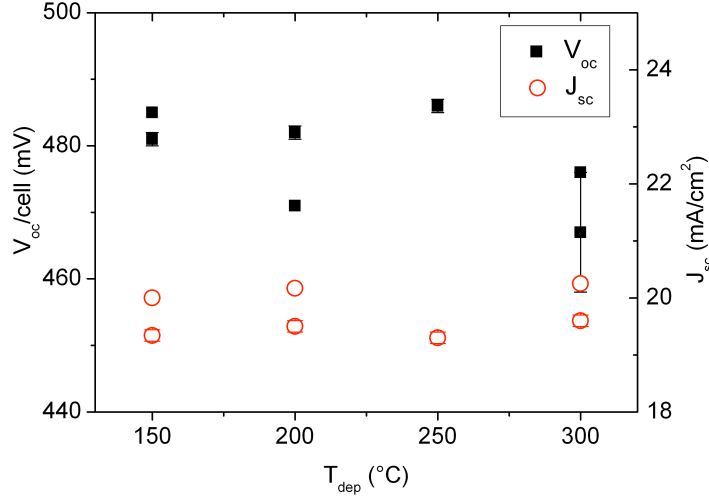


Figure 5.3: The dependence of the characteristic photovoltaic parameters V_{oc} and J_{sc} on the deposition temperature T_{dep} is illustrated for seven mini-modules.

parameters were kept constant. Figure 5.3 displays the V_{oc} and J_{sc} as a function of the deposition temperature, while Table 5.1 provides a complete overview of the parameters. J_{sc} is not affected by a change of the deposition temperature, being consistently above 19.2 mA/cm^2 . A correlation between V_{oc} and T_{dep} is not found either, with V_{oc} being above 470 mV.

Background pressure

The analysis of the influence of the background pressure during deposition on the photovoltaic performance of mini-modules enabled the assessment of a fundamental aspect of the deposition process scalability. The background pressure was accurately adjusted by controlling the air flow through a valve into the main chamber of the e-beam evaporator. The pressures at which the depositions were carried were chosen to be $1 \cdot 10^{-7}$ mbar, $5 \cdot 10^{-7}$ mbar, $1 \cdot 10^{-6}$ mbar and $5 \cdot 10^{-6}$ mbar. Figure 5.4 displays the average V_{oc} per cell and the J_{sc} as a function of the background pressure, while Table 5.1 summarizes the achieved results. A decline of the voltage from $(468 \pm 5) \text{ mV}$ at $1 \cdot 10^{-7}$ mbar to $(454 \pm 1) \text{ mV}$ at $5 \cdot 10^{-6}$ mbar is observed, while the J_{sc} does not change upon increasing the background pressure by a factor of 50. The decreasing voltage at increasing pressure causes the efficiency to drop. However, even at a drastically elevated background pressure of $5 \cdot 10^{-6}$ mbar the mini-module still exhibits an efficiency of $(5.8 \pm 0.1)\%$, declining by

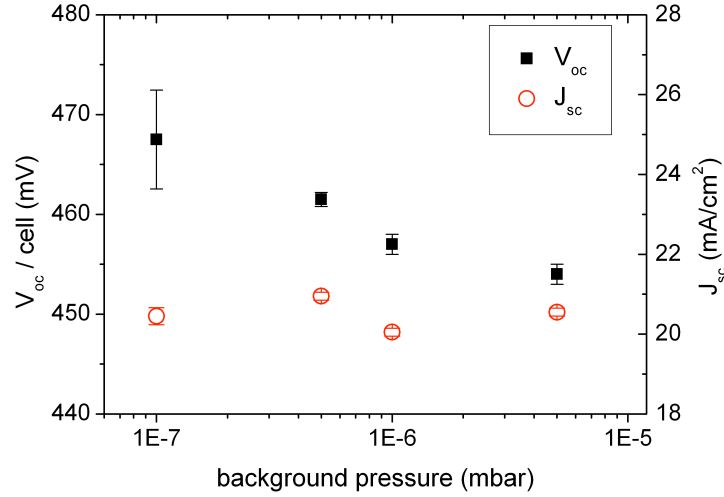


Figure 5.4: V_{oc} and J_{sc} are displayed for 4 mini-modules deposited at different background pressures.

0.3% abs. from $(6.1 \pm 0.1)\%$ at $1 \cdot 10^{-7}$ mbar. In an additional experiment, nitrogen was introduced into the chamber until a pressure of $1 \cdot 10^{-5}$ mbar could be established. With a V_{oc} of (463 ± 1) mV and a J_{sc} of (20.5 ± 0.1) mA/cm², the module deposited in N_2 ambient shows marginally worse characteristics than the sample deposited at $1 \cdot 10^{-7}$ mbar. Unfortunately, FF is low due to considerably high and fluctuating shunt and series resistances, affecting the efficiency of the individual mini-modules.

5.3. 8% efficient thin film mini-module with implemented backside texture

The efficiency of the mini-modules deposited on planar glass can be increased by implementing backside light trapping textures. A $1.6 \mu\text{m}$ thick p -type Si and a 500 nm thick p^+ -type Si stack were deposited on a planar glass/SiN/ n^+ (PECVD)-type Si structure and then subsequently processed as outlined in section 3.3.1. The thick p^+ -type layer was etched in a proprietary chemical etch process by CSG Solar after the crystallization process was carried out. The created random surface texture of the remaining p^+ -type-layer

contributes to enhancing the path length of the light reflected at the backside and finally results in an increase of the current. Figure 5.5 illustrates the rough surface texture of the poly-Si layer after applying the etch process. The produced mini-module shows a 12% higher short circuit current than the untextured device leading to a J_{sc} of 22.8 mA/cm². With a V_{oc} of 485 mV per cell and FF of 70.3%, the mini-module has an efficiency of 7.8%. Figure 5.6 shows the J-V characteristics of the textured module in comparison to the untextured reference mini-module². The potential of an optimized etch-back process was demonstrated in a slightly modified structure. By etching a 2.3 μm p^- -type base Si layer down to a thickness of 1.8 μm and subsequently applying a p^+ -type layer in a spin-on coating process by CSG Solar, we could fabricate a mini-module with an increased current density of 25.6 mA/cm², leading to a conversion efficiency of 8.0% at a V_{oc} of 472 mV per cell and a FF of 66.3%.

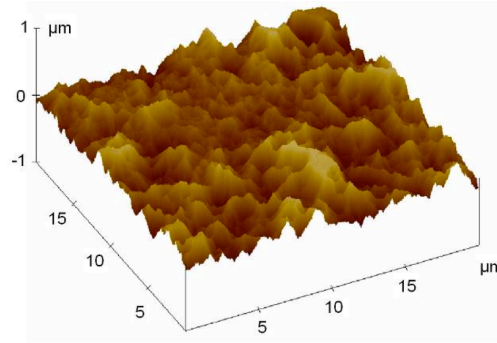


Figure 5.5: An atomic force microscopy (AFM) image depicts the surface texture of the etched rear-side of the poly-Si (modified version of [153]).

5.4. Poly-Si solar cells with an implemented ZnO:Al front contact layer

The feasibility of ZnO:Al as a front contact layer is systematically analyzed in two solar cell structures, with a n^+ (PECVD)/ p^- (e-beam)/ p^+ (ECR-CVD)-type Si stack either directly prepared on ZnO:Al or assembled on ZnO:Al coated with a 50 nm thick diffusion

²measured 24 h after completing the device fabrication

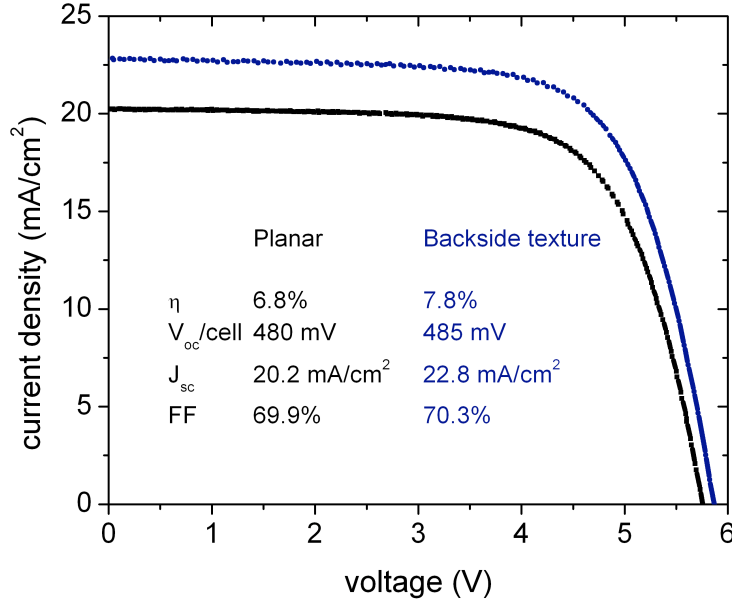


Figure 5.6: *J-V characteristics of mini-modules consisting of 12 cells with a planar structure (black) and with an implemented rear side texture (blue).*

barrier SiN. The preparation process and characterization of the ZnO:Al and ZnO:Al/SiN coated glass substrates with surface roughnesses δ_{rms} of 5 nm and 2.3 nm have already been presented in chapter 4. Amorphous films of $2 \cdot 10^{16} \text{ cm}^{-3}$ boron doped Si were deposited by e-beam evaporation of silicon at a deposition rate of 300 nm/min and substrate temperature of 200 °C to ensure the growth of large Si grains, according to the design rules established in chapter 4, and subsequently embedded in the device structure outlined in section 3.3.2. The characteristic parameters of the prepared cells are summarized in Table 5.2. Figure 5.7 shows the J-V characteristics of fully processed poly-Si solar cells on

Table 5.2: *The characteristic parameters such as the used substrate type, the base thickness D_{base} , the RTA process parameters and the V_{oc} of solar cells on a ZnO-based front contact are listed.*

substrate	D_{base} (μm)	RTA	V_{oc} (mV)
planar ZnO:Al/SiN(50 nm)	1.1	950 °C for 60 s	408
planar ZnO:Al	1.2	950 °C for 60 s	225
planar ZnO:Al	1.2	-	270

ZnO:Al and ZnO:Al/SiN coated glass substrates, having been exposed to rapid thermal annealing (RTA) and hydrogen passivation (HP). In addition, the J-V curve of a poly-Si sample on ZnO:Al which did not undergo RTA is illustrated. Since the current density is overestimated in J-V measurements due to the lack of a well-defined cell area, J_{sc} was determined in EQE measurements and used to scale the current density of the J-V data. The poly-Si sample on ZnO:Al without RTA exhibits a V_{oc} of 270 mV which is in the proximity to characteristic values for non-RTA-treated poly-Si samples. However, by comparing this poly-Si sample to the identical RTA-treated cell structure, it becomes obvious that the V_{oc} enhancement of typically 150 mV initiated by the short thermal annealing failed to occur, but led to a V_{oc} reduction from 270 to 225 mV instead. Hence, the high temperature treatment can be identified as the process step limiting the efficiency potential of poly-Si samples on bare ZnO:Al. However, this obstacle is overcome by implementing a diffusion barrier between ZnO:Al and poly-Si. The influence of the additional SiN between the ZnO and Si in a fully processed sample is compelling, giving rise to a voltage boost. The poly-Si sample on ZnO/SiN exhibits a V_{oc} and J_{sc} of 408 mV and 8.8 mA/cm², whereas the same structure deposited on ZnO has a V_{oc} and J_{sc} of 225 mV and 4.5 mA/cm². The rather low fill factor of 50% is not surprising, considering that the contacting scheme is a prototype and the SiN layer itself is not a specially designed conductive diffusion barrier for this proof-of-concept study.

5.5. Discussion

5.5.1. Deposition parameters

A variation of the deposition temperature between 150 °C and 300 °C for solar cells on SiN does not affect the performance, which is accordance to the design rules established in chapter 4. On SiN ($\delta_{rms} = 0.3$ nm), a variation of T_{dep} merely affects the time-lag, but does not result in an alteration of the nucleation rate and consequently the grain size. Hence the resulting microstructure of the base layer is identical for all deposition temperatures which is reflected in the independence of the photovoltaic performance of T_{dep} .

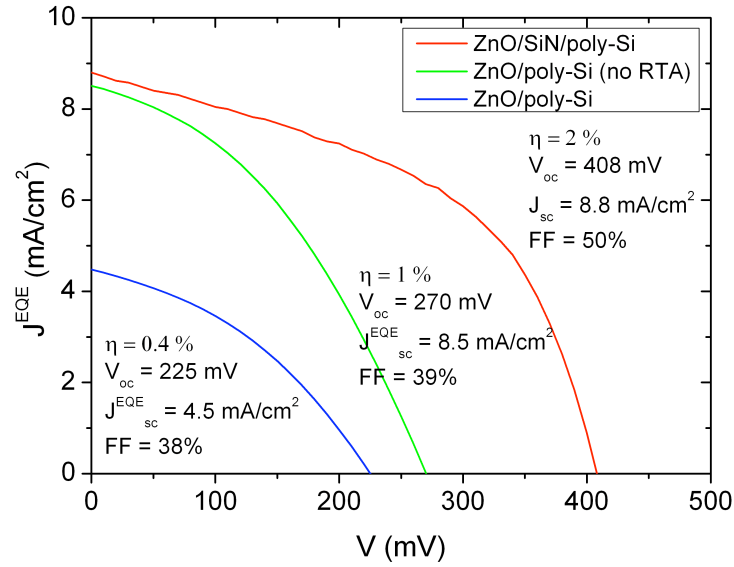


Figure 5.7: J - V characteristics of three poly-Si solar cells on ZnO and ZnO/SiN are shown. The photovoltaic characteristics of the individual cells are included as insets. J_{sc} was determined in EQE measurements and used to scale the current density, since the measured current density is overestimated due to not well-defined cell areas.

A deposition at 300 °C leads to the fastest crystallization process due to the minimized time-lag and is consequently the optimal deposition temperature for this configuration. The highest efficiency of 6.8% on planar glass without a backside texture was found for mini-modules with very lightly doped absorbers in the mid 10^{15} to the low 10^{16} cm⁻³ regime. For a not intentionally doped absorber, the performance is limited by the voltage, whereas the gradually decreasing J_{sc} with rising doping level curtails the efficiency for higher doping levels.

These findings are in perfect accordance to just recently published results for evaporated poly-Si cells with a p -type doped absorber [154]. The researchers reported a highest V_{oc} in the 10^{17} cm⁻³ region, while J_{sc} is maximized at the lowest doping concentration possible. Since J_{sc} dominated the dependence of the efficiency, the most efficient cells were reported to have lightly doped absorber layer.

These observed trends in poly-Si coincide with results reported on mono-crystalline and multi-crystalline Si wafer cells [78, 155] and can be explained within the scope of the presented recombination mechanisms and diode model (section 2.2.1). Since dopants represent potential defects in the absorber material, an increasing doping concentration

increases the amount of foreign atoms i.e. defects, causing a gradual decline of the life time τ_e (Equation 2.33) and hence triggers a decrease of J_{sc} . It can be concluded from this consideration that the highest J_{sc} can be found for the lowest absorber doping concentration.

For an exemplary study of the influence of the doping concentration on V_{oc} , it is assumed that V_{oc} is dominated by bulk recombination ($n = 1$), which holds for thick Si wafer cells with well passivated surfaces [78]. In addition, R_{sh} is neglected. Under open circuit conditions with $J = 0$ and $V_t \ll V_{oc}$, Equation 2.30 can be simplified to:

$$V_{oc} \approx V_t \cdot \ln \left(\frac{J_{ph}}{J_{D1}} \right) \quad (5.1)$$

with

$$J_{D1} = \frac{qD_e n_i^2}{N_A L_e} + \frac{qD_h n_i^2}{N_D L_h} \quad (5.2)$$

N_A and N_D denote the acceptor and donor concentrations, while n_i is the intrinsic carrier concentration. According to Equation 5.1 and Equation 5.2, the absorber doping concentration should be chosen as high as possible to maximize V_{oc} . However, the diffusion length of the minority carriers decreases with increasing doping level, limiting the V_{oc} again at high doping concentrations. Hence, the highest open-circuit voltages are achieved for single crystalline wafer solar cells at $N_A \sim 1 \cdot 10^{17} \text{cm}^{-3}$ [78, 156]. For a more accurate determination of the recombination processes in poly-Si, it is inevitable to consider recombination in the space charge region (SCR) [157]. Based on these assumptions, Wong et al. identified a superposition of shallow levels and deep levels as an adequate description for the recombination processes at dislocations and extended defects and grain boundaries in poly-Si, which explains the experimentally observed dependence of V_{oc} and J_{sc} on the base doping level [158, 159, 160].

An increase of the base thickness beyond $1.9 \mu\text{m}$ has a negative impact on the voltage, while J_{sc} increases with a thicker base due to the higher absorption (Figure 5.2).

O. Kunz simulated the effective diffusion length of e-beam evaporated poly-Si solar cells in an $(n^+/p^-/p^+)$ -type structure without considering grain boundaries and reported a diffusion length of 1.8 to $1.2 \mu\text{m}$ in a base doping range of mid 10^{15} to low 10^{16}cm^{-3} [156]. Results for the diffusion length of evaporated poly-Si cells extracted from EQE data were similar to the simulated outcomes [160]. Based on these reported findings,

Table 5.3: Photovoltaic parameters obtained from light J-V measurements (performed 24 h after the completion of the module fabrication) for textured and planar record mini-modules based on e-beam and PECVD-Si. The characteristics of the PECVD-Si mini-module are taken from [153].

Sample	D_{base}	$V_{oc}/cell$	J_{sc}	FF	η
	(μm)	(mV)	(mA/cm ²)	(%)	(%)
E-beam (planar)	1.7	480	20.2	69.9	6.8
E-beam (textured p^+)	1.6	485	22.8	70.3	7.8
E-beam (textured base/ spin-on p^+)	1.8	472	25.6	66.3	8.0
PECVD (planar)	1.6	485	18.2	72.8	6.5

the experimentally determined decline of V_{oc} for thicknesses larger than $1.9 \mu m$ can be correlated to a diffusion length limited solar cell performance.

However, the ascending trend of the J_{sc} as a function of the base thickness and the high V_{oc} maintaining with increasing thickness up to $1.9 \mu m$ reflect the good quality of the e-beam evaporated poly-Si, with a crystalline structure comprising grains with a feature size similar to the film thickness (Figure 4.9). The optimal cell design is based on a $1.9 \mu m$ thick absorber layer, whose current collection has to be optimized by implementing light trapping structures without losing in V_{oc} .

5.5.2. Comparison to PECVD poly-Si on planar glass

With an efficiency of 6.8%, a fill factor of 69.9%, the mini-module characteristics on planar glass deposited at 600 nm/min are equivalent to results achieved on standard PECVD poly-Si modules of the same structure and on planar substrates but at much lower deposition rates. Table 5.3 summarizes the key parameters of the fabricated e-beam based and PECVD-based record mini-modules. Moreover, the short circuit current density of 20 mA/cm² on planar glass is remarkable, considering that the white resin back reflector provides only modest light-trapping. The implementation of a rear-side texture in the p^+ -type and p^- -type Si layer leads to a further increase of the current and to a respec-

tive efficiency of 7.8% and 8.0%. These results set a new record for e-beam evaporated poly-Si solar cells, exceeding previously reported efficiencies by 50% [161]. A further improvement of the efficiency is expected for modules with a textured front-side.

These results demonstrate that e-beam evaporation is an excellent method to produce poly-Si solar cells even in non ultra-high vacuum conditions at rates that exceed commonly used deposition rates by a factor of 20. Concluding, e-beam evaporation presents a potential replacement for the established PECVD technique.

5.5.3. Design components for an optimized front contact layer

The J-V characteristics of solar cells with an implemented ZnO front contact reveal that the design of the interface between ZnO and Si is critical for the solar cell performance. Recent studies verified that the ZnO/Si interface is already modified by the SPC process, forming a SiO₂ layer and areas with higher concentration of Zn in proximity to the interface [149, 150]. While in-situ spectroscopic investigations on the effect of RTA on the interface are still ongoing, this study identified RTA as a crucial step because of its detrimental effect on the electronic quality of the solar cell with a ZnO/Si interface. Diffusion of Al and Zn at 950 °C does certainly occur during RTA and can provide a source for contamination and a reduction of the diffusion length (appendix A.3). Al can act as an acceptor close to the valence band, but its vicinity to the band makes it a rather ineffective recombination center. In contrast, Zn atoms can cause two thermally activated defect states in Si, with energetic levels positioned 0.55 eV below the conduction band and 0.31 eV above the valence band. Zn atoms can easily diffuse in Si, which is manifested in their high diffusion constant in crystalline Si of $\sim 10^{-6} \text{ cm}^2/\text{s}$ at 1000 °C [162]. In addition, the levels can be electrically activated by thermal quenching [163]. The position of the electrically active acceptor levels close to midgap of Si and its high diffusion constant are two main components for effective recombination centers in Si. Concluding, the diffusion of Zn and its activation is a plausible explanation for the observed decrease of the photovoltaic performance during RTA.

Therefore, a conductive diffusion barrier between ZnO:Al and Si is the prerequisite for a working poly-Si device on ZnO. The electronic properties of the implemented SiN were not optimized but rather served as a prototype in a proof-of-concept study. C. Becker et

al. investigated the contact resistances between ZnO and poly-Si without and with SiN of various thicknesses. While J-V measurements confirm that the contact between poly-Si and ZnO is ohmic, the implementation of a 50 nm thick SiN layer results in a non-ohmic contact between ZnO:Al/SiN and poly-Si [164]. Nevertheless, the electrical properties are still adequate to shed light on the necessary design components in the presented analysis. However, the requirements for an ideal diffusion barrier are manifold. The layer has to be optically transparent, dense enough to suppress diffusion, and conductive to provide an electrical contact between Si and ZnO. Ideally, the layer should also serve as a wide bandgap n-type emitter layer due to its potential to enhance the efficiency. Firstly, a doped wide bandgap material allows light in the UV region to transmit and hence leads to an improved current collection in the space charge region (SCR) in comparison to a conventional n-type poly-Si emitter. Secondly, the implementation of a hetero-junction could effectively prevent recombination of photogenerated charge carriers at the contact and additionally lead to a V_{oc} enhancement [20, 165, 166, 167]. Phosphorous doped SiN or SiON as well as doped SiC could be amongst the candidates for the development of such a barrier.

5.6. Conclusion

Photovoltaic performance of poly-Si mini-modules

Electron-beam evaporation was found to be an excellent deposition technique for the fabrication of poly-Si solar cells on planar SiN-coated glass. Mini-modules prepared with a deposition rate of up to 600 nm/min as a hybrid device structure consisting of planar glass/SiN/ n^+ (PECVD)/ p (e-beam)/ p^+ (e-beam)-type structure yielded an efficiency of $(6.8 \pm 0.1)\%$, a V_{oc}/cell of (477 ± 3) mV and a J_{sc} of (20.3 ± 0.1) mA/cm². These characteristics were equivalent to results for the same device based on PECVD material. The optimized deposition parameters can be summarized as follows:

- The base doping level was found to be optimal in the mid 10^{15} to low 10^{16} cm⁻³ region.

- The deposition temperature did not influence the device performance on smooth SiN in accordance to design rules established in chapter 4.
- The optimal cell thickness was revealed to be in the range of the diffusion length of the investigated poly-Si material. A V_{oc} decline at thicknesses exceeding $2\text{ }\mu\text{m}$ indicated an optimal thickness of $1.9\text{ }\mu\text{m}$.
- An increase of the background pressure by a factor of 50 led to an efficiency reduction of merely 0.3% abs., suggesting a possible application in large-area deposition systems in non ultra-high vacuum conditions.

8.0% and 7.8% efficient mini-modules could be processed by implementing a rear-side texture, exceeding the efficiency of previously reported results by more than 50% [161]. The implementation of an effective front-side texture is expected to lead to an additional efficiency enhancement. The potential and challenges of the design of such e-beam compatible front-side textures will be addressed in chapter 6.

ZnO-based front contact layer

The investigation of photovoltaic characteristics of solar cells on ZnO-coated glass identified the implementation of a diffusion barrier between ZnO and Si as a prerequisite for a working poly-Si solar cell device on ZnO. A V_{oc} over 400 mV was demonstrated in such device structures.

6. Statistical light trapping approaches

6.1. Introduction

As an indirect bandgap semiconductor, Si exhibits relatively weak absorption properties near its bandgap energy of 1.12 eV¹. Hence, a critical element in the preparation process of efficient thin film solar cells is the improvement of their optical absorption. While a sufficient absorption of incident photons demands an optically thick Si layer to grant superior current collection, a solar cell with high electronic quality has to consist of a Si layer which is thinner than the minority carrier diffusion length. In order to meet those opposing requirements, the implementation of highly effective light trapping features into 1 – 2 μm thin Si cells has to be achieved, thereby folding the incident light waves into the thin layer and significantly enhancing their path length [168]. Surface texturing is amongst the commonly chosen statistical approaches to diffract the incident light at the front-side, and to reflect the light at the metal-coated back-side, enhancing both, the path length of waves in comparison to the normal direction and the reflection back into the Si at angles larger than the critical angle of total internal reflection.

For an optimization of the coupling of the incident light into the Si layer, anti-reflection coatings (ARC) with a high refractive index (above 1.5) as well as nano-rough surfaces provide a refractive index gradient between the glass and Si, minimizing the reflection losses of the incident light at the substrate/Si interface [85, 168, 169, 170].

Aluminum induced texturing (AIT) and abrasion-etch texturing of glass substrates have been widely explored as possible candidates for light trapping structures in poly-Si thin film solar cells [25, 121, 171]. Dip-coating techniques for glass in a SiO₂ bead solu-

¹The bandgap energy of 1.12 eV corresponds to a wavelength of $\sim 1100\text{ nm}$.

tion were established for the low-cost fabrication of light trapping features and ARCs [25, 172, 173]. Many researchers also investigate the optimization of the topography of implemented transparent conductive oxides (TCO) such as tin oxide (SnO_2), indium-tin oxide (ITO), as well as ZnO prepared by low pressure (LP) CVD and sputter deposition. These TCOs provide light trapping and serve as an electrical front contact in thin film solar cells [85, 12, 174].

However, these investigated structures have been optimized for the omni-directional chemical vapor deposition of Si. The distinct directional growth characteristics of physical vapor deposited Si (section 3.2.1) prohibit the direct transfer of the already designed textures to the e-beam based poly-Si solar cell design, but necessitate a critical evaluation of the applicability of the light trapping structures. In addition, the exploration of novel concepts is required for a controlled incorporation of e-beam compatible light harvesting structures.

In this chapter, design parameters for the fabrication of e-beam compatible light trapping architectures will be established by evaluating the compatibility of two statistical approaches with e-beam evaporation. Section 6.2 addresses the preparation of poly-Si on self-organizing silica spheres embedded in sol-gel and on already developed wet-chemical etched sputtered ZnO:Al. Section 6.3 discusses the structural and optical properties of the prepared samples and evaluates the applicability of the two techniques to e-beam evaporated poly-Si solar cells. Finally, section 6.4 summarizes the characteristics of the investigated techniques, which serve as a basis for the design of an improved solar cell device structure.

6.2. Self-organizing silica spheres and wet-chemical etched ZnO

The self-organization process is a low-cost bottom-up approach for the controlled fabrication of light scattering particles, and was employed to prepare silica spheres with a diameter of 200 nm on $(10 \times 10) \text{ cm}^2$ Schott AF 45 glass substrates (section 3.1). A 70 nm thick zircon oxide (ZrO) anti-reflection coating was deposited by dip-coating and

tempered in a thermal annealing process to flatten the rough surface. For comparison, samples without additional ZrO layer were prepared. The poly-Si preparation process involved the deposition of a 1 μm thick films of $2 \cdot 10^{16} \text{ cm}^{-3}$ by e-beam evaporation at a deposition temperature of 300 °C and subsequent crystallization step at 600 °C.

Planar ZnO:Al layers ($\delta_{\text{rms}} = 5 \text{ nm}$), prepared in a RF-sputtering process from a 1 % wt. Al_2O_3 ceramic ZnO target at 300 °C, were textured in a wet-chemical etching process in diluted HCl (0.5 % vol.) for 15 s, generating a surface topography with so-called craters in the μm size range [84, 175]. The etching process has been optimized for light harvesting properties in a-Si and nanocrystalline Si thin film solar cells and is an established method to create light trapping textures [176]. The surface texture depends on the specific deposition conditions and the duration of the etching process [125]. With a treatment duration of 15 s, the resulting film comprises a mildly textured surface. The subsequent poly-Si preparation consisted of the e-beam evaporation of 1 μm thick a-Si layer at 300 °C and a crystallization step at 600 °C.

6.3. Analysis and discussion

6.3.1. Structural properties

Figure 6.1 displays SEM images of poly-Si layers on the two substrate types based on self-organizing nanospheres. Si deposited on exposed silica spheres exhibits a surface-texture dependent structure which is in conformity with the PVD-growth characteristics outlined in section 3.2.1. The density of the growing Si and its growth direction depend on the angle of incidence according to Equation 3.1, leading to the formation of porous "ice-cream cone" like features on top of the spherically shaped objects (Figure 6.1(a))² and the formation of compact poly-Si on flat regions. However, Figure 6.1(b) illustrates that SiO_2 spheres, which are covered with ZrO, provide a flat template to grow a homogeneous compact Si film. Hence, the fabrication of compact e-beam evaporated Si on textures based on the self organization of particles is possible if an implemented intermediate

²A detailed analysis of the microstructure of Si deposited at oblique incidence will be presented in section 7.3 of chapter 7.

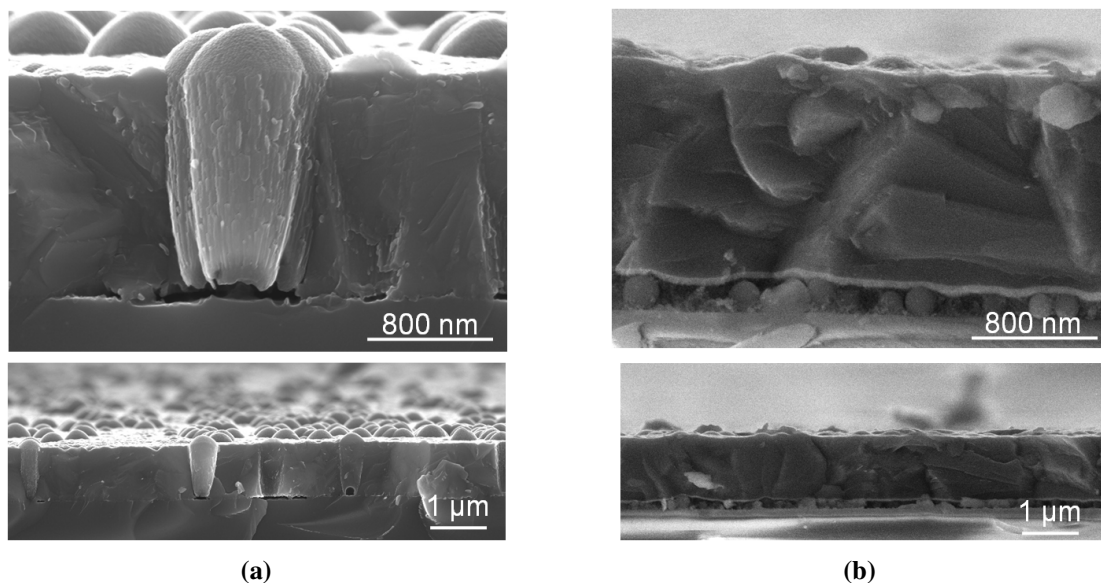


Figure 6.1: (a) illustrates cross-sectional SEM images of 1 μm thick poly-Si on self-organizing SiO_2 spheres, while (b) shows cross-sections of a poly-Si layer on silica nanospheres which are covered with a ZrO layer. While the flat template provided by the additional ZrO allows for the growth of homogeneous compact poly-Si, the deposition on uncovered spheres results in Si with porous and compact regions.

layer provides a smooth interface between Si and the light scattering SiO_2 spheres.

Figure 6.2 shows cross-sectional SEM and TEM micrographs and an EBSD pole figure map of a Si layer on ZnO and demonstrates that the Si adapts the smooth texture of the ZnO:Al, leading to a conformally grown compact Si layer, with crystal grains in the micron size range being present even at steeper edges of the ZnO texture.

To investigate the influence of the structural characteristics of the prepared poly-Si on its electronic quality, the open circuit voltages V_{oc} of n^+ (PECVD)/ p^- (e-beam)/ p^+ (e-beam)-type Si stacks were measured on sol-gel embedded nanospheres without a ZrO layer (Figure 6.1(a)) and with an additional ZrO (Figure 6.1(b)). A poly-Si structure which is directly deposited on exposed spheres exhibits a V_{oc} of merely $(129 \pm 25) \text{ mV}^3$, demonstrating the poor electronic quality of the Si. However, a poly-Si layer fabricated on nanospheres that are flattened with an additional ZrO layer (Figure 6.1(b)) exhibits a V_{oc} of $(413 \pm 2) \text{ mV}$, which is identical to the $V_{oc} = (413 \pm 6) \text{ mV}$ of a simultaneously

³ V_{oc} was measured with a sun-simulator after completing the post-deposition steps RTA and HP by contacting the n^+ -type and p^+ -type Si layers. The samples were not processed to separate cells.

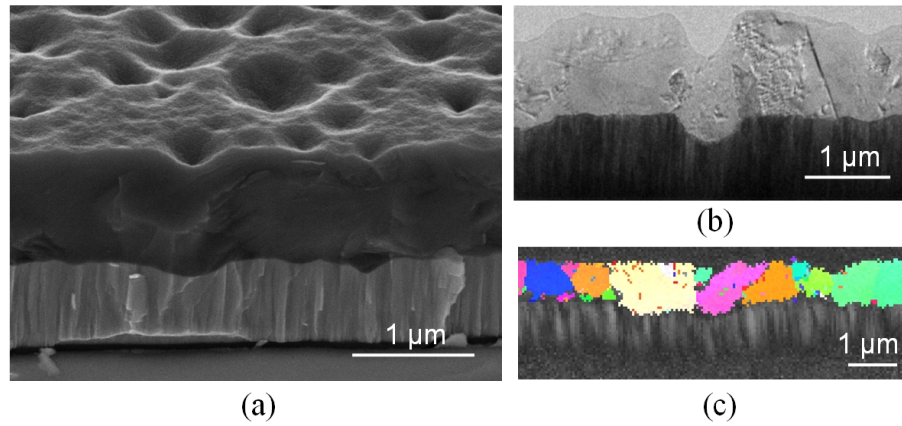


Figure 6.2: Cross-sectional SEM (a) and TEM (b) micrographs illustrate the compact nature of poly-Si layer on textured ZnO. (c) illustrates an EBSD pole figure map of the cross-section, showing the polycrystalline Si with grain sizes in the micron size range.

processed poly-Si reference sample on planar Schott AF 45 glass⁴.

Consequently, porous Si causes a decline of the photovoltaic performance of the entire cell. In fact, in section 7.3, a microscopic analysis will reveal that the inferior quality of the porous silicon is manifested in its microstructure. The porous Si structure resists the crystallization process and therefore the formation of crystal grains in the μm size range. Previously conducted analyses also revealed a high concentration of oxygen in such areas, giving rise to the assumption that diffusing oxygen inhibits the crystallization process [153, 96]. Hence, these defect-rich areas present sources for recombination centers and do not contribute to the current collection.

Moreover, due to their positioning on top of spheres and clear separation from the surrounding poly-Si material, these brittle features do not adhere to the substrate very well and can be removed or destroyed by applying mechanical force. In addition, the porous oxygen-rich phase can dissolve in HF containing etching solutions, which are used during the cell fabrication process, as shown in section 7.3. Hence, holes caused by etched or destroyed arbitrarily distributed porous features are sources for electrical shunts and responsible for a decline of the open circuit voltage of the entire poly-Si cell. Lock-in thermography performed on fabricated mini-modules on bead-coated substrates also confirmed that severe shunting at back-contacts positioned over such holes leads to an overall

⁴The voltages of poly-Si cells on Schott AF 45 glass do not reach the values achieved on Schott Borofloat 33 glass, since the post-deposition process RTA was not adapted to the thermal expansion characteristics of the Schott AF 45 glass/silicon stack.

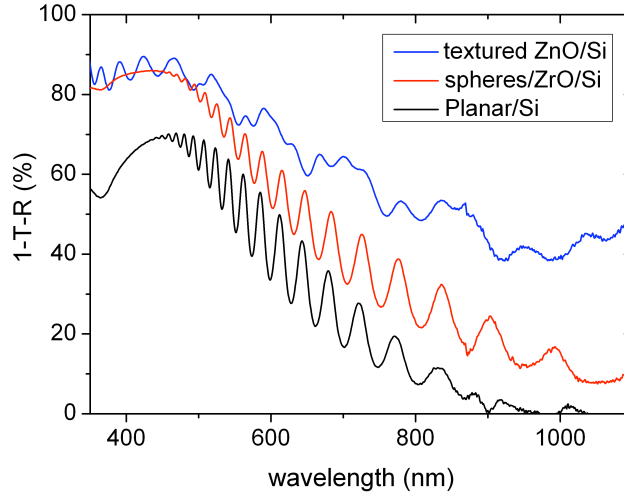


Figure 6.3: The optical absorption spectra of 1 μm thick poly-Si on planar glass (black), self-organized nanospheres/ZrO (red) and textured ZnO are illustrated (blue).

poor photovoltaic performance [153].

Concluding, a poly-Si layer with a compact structure is identified as a prerequisite for the realization of a poly-Si thin film solar cell with high electronic quality.

6.3.2. Light trapping characteristics

After having determined the basic requirements for the fabrication of material with high electronic quality, the potential of the sol-gel based and ZnO based e-beam compatible light trapping textures is explored. The wavelength sensitive measurement of the optical reflectance R and transmittance T reveal the AR characteristics in the near UV and the light trapping properties in the near IR regime of the two e-beam compatible structures. Figure 6.3 displays the absorption spectra $A = (1 - T - R)$ of 1 μm poly-Si on the nanospheres/ZrO and textured ZnO as a function of the wavelength⁵. For comparison, the spectrum of 1 μm poly-Si layer on planar glass is included. The anti-reflection properties of both substrates are manifested in a significant reduction of the reflection between 350 to 500 nm, consequently leading to an increase of the absorption. Both structures also

⁵A conventional optical spectrometer "Perkin Ellmer Lambda 19" was used for this analysis.

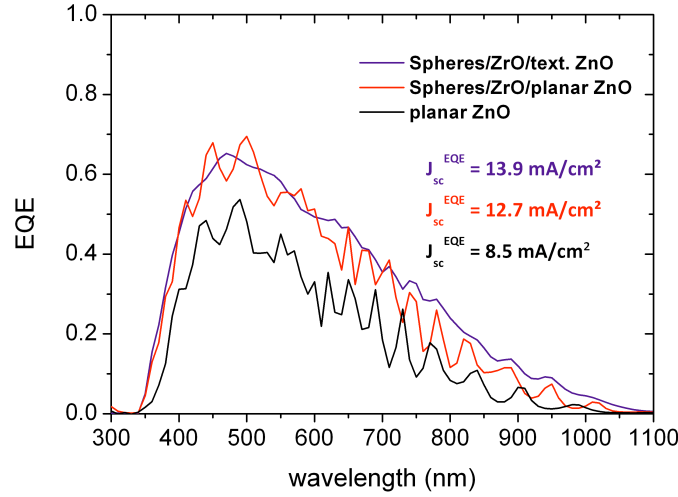


Figure 6.4: EQE spectra of poly-Si cells prepared on 3 different light trapping structures are shown: planar ZnO (black), self-organizing spheres/ZrO/planar ZnO (red) and self-organizing spheres/ZrO/textured ZnO (purple).

provide light trapping in the wavelength range between 500 to 1000 nm. The spectrum of Si on a nanosphere/ZrO texture exhibits characteristic fringes which are typically related to interference effects between the incident waves and the reflected waves at the normal of planar Si/air and Si/ZrO interfaces, indicating a not yet optimized design for light harvesting in the near-IR region. The detected absorption at $\lambda > 1100$ nm below the bandgap energy of Si is ascribed to total internal reflection in the glass [121]. Textured ZnO exhibits enhanced absorption properties for longer wavelengths. However, an accurate determination of A is limited to $\lambda < 750$ nm, since the absorption in the ZnO layer is superimposed on the absorption in Si in the near-IR region [13].

A wavelength selective analysis of the charge carrier collection provides essential information on the effectiveness of the light trapping structure in a complete solar cell device structure. To investigate the impact of the light scattering nanospheres on the photovoltaic characteristics of the solar cell, we prepared glass substrates that are coated with nanospheres/ZrO films and finished with planar ZnO:Al layers. Since the optical analysis revealed that textured ZnO and nanospheres comprise dissimilar light diffraction characteristics, the benefit of combining both layers is analyzed in a system consisting of nanospheres/ZrO and textured ZnO:Al. Planar ZnO:Al on glass serves as a reference

system. $1.2 - 1.4 \mu\text{m}$ thick e-beam evaporated p^- -type layers deposited at 200°C were embedded in a $n^+/p^-/p^+$ -type Si stack on three substrate types and subsequently processed to solar cells as outlined in section 3.3.2. Due to the detrimental effect of RTA to the layer stacks with a direct contact between ZnO and poly-Si (Figure 5.7), the samples were only HP treated and RTA was omitted, resulting in rather weak photovoltaic performance. Nevertheless, the chosen cells serve as a model system to analyze the potential of the presented statistical light trapping approaches. Figure 6.4 shows the EQE spectra of poly-Si solar cells on the three respective front-side textures.

The anti-reflection and light trapping properties of the sol-gel embedded spheres lead to an overall increase of the EQE between 350 nm and 1100 nm. The EQE increase related to anti-reflection is substantial between 350 nm and 450 nm and the light scattering properties of the 200 nm small spheres give rise to an increase of the carrier collection between 700 nm and 1100 nm. The additional implementation of textured ZnO:Al leads to an EQE increase between 600 nm and 1100 nm.

Starting with a J_{sc}^{EQE} of $8.5 \text{ mA}/\text{cm}^2$ for poly-Si on a planar ZnO substrate, J_{sc}^{EQE} could be successively increased by 56% to $13.9 \text{ mA}/\text{cm}^2$ by implementing a combination of silica spheres, ZrO and textured ZnO.

This result demonstrates the feasibility of the proposed light trapping structures for evaporated Si and opens design possibilities for light management in poly-Si solar cells on ZnO. The full potential of the presented light trapping structures has to be explored by optimizing their design parameters. The ZnO texture can be improved further by accurately adjusting the etching duration, creating a texture that is sufficiently rough to provide excellent light trapping, but still mild enough to grow compact Si. With only 200 nm in diameter, the chosen silica spheres are efficient for scattering light in the UV-VIS region, but are not the optimal scatter objects for light in the near IR-region. However, the self-organization approach features potential for tuning the light trapping properties by adjusting the size and shape of the silica spheres and their occupancy-rate in the film. Since the ZrO covering the SiO_2 particles provides a smooth template for the poly-Si film, the design possibilities are in no way limited by the growth characteristics of the evaporated Si layer.

6.4. Conclusion and outlook

The analysis of the structural and photovoltaic properties of poly-Si on differently textured substrates demonstrated that the growth of compact polycrystalline Si is a prerequisite for realizing poly-Si solar cells with high electronic quality. Existing porous regions were found to contribute to a decline of the open circuit voltage. Consequently, according to the PVD growth characteristics, the implementation of statistical light harvesting structures into an e-beam evaporated poly-Si solar cell was revealed to be feasible if the substrate for Si deposition is sufficiently flat. The texture of wet-chemical etched ZnO was mild enough to grow poly-Si material with grains in the micron size range whilst providing efficient light trapping. The design of the texture could be adjusted by varying the etching process and the preparation conditions of the ZnO. The fabrication of self-organizing SiO₂ spheres embedded in sol-gel presented an elegant approach to implement tailor-made light-scattering objects in thin film devices. The deposition of an additional ZrO coating was revealed to even the rough surface of the exposed spheres, providing a planar template on integrated objects for the growth of compact poly-Si material. An analysis of the optical properties of the chosen structures verified the beneficial absorption properties of both structures. While the 200 nm large SiO₂ particles predominantly scattered in the UV-VIS region, the nano-roughness and crater-like structure of textured ZnO provided both, anti-reflection, and light harvesting in the near IR-region. The beneficial optical and structural properties of the investigated light trapping structures were reflected in the electric properties of manufactured solar cell devices. The implementation of nanospheres led to an overall improvement of the charge carrier collection. However, the combination of light scattering nanospheres and ZnO textures resulted in a remarkable increase of 56% in the short circuit current compared to the device on planar ZnO.

The derived considerations for the front-side texture (section 6.3) and the identified prerequisites for a working device on ZnO (chapter 4 & 5) define the design components for the development of poly-Si with high electronic quality embedded in an efficient solar cell device structure. Figure 6.5 illustrates a sketch of a proposed structure. The front-side texture consists of self-organizing SiO₂ spheres and a wet-chemical etched ZnO layer, which are separated from the poly-Si layer by a thin diffusion barrier (DB). The rear-side of the

solar cell is textured in a wet-chemical etching process and finalized with a p^+ -type a-Si:H layer and Al back contacts. The implementation of a rear-side texture alone already led to a short circuit current density of 25 mA/cm^2 (section 5.3). Hence, combining an effective front-side texture with an optimized rear-side texture can contribute to an increase of the current density above 30 mA/cm^2 . In addition, a n^+ -type wide bandgap diffusion barrier and a poly-Si/a-Si heterojunction at the rear-side have the potential to raise the open circuit voltage above 500 mV [23]. Exciting challenges are the optimization of the front-side textures according to the PVD-based design restrictions, the development of a thin conductive diffusion barrier and the optimization of the heterojunction at the rear-side. However, with all these components successfully implemented, the poly-Si thin film technology is on the path to a conversion efficiency of 11-12%.

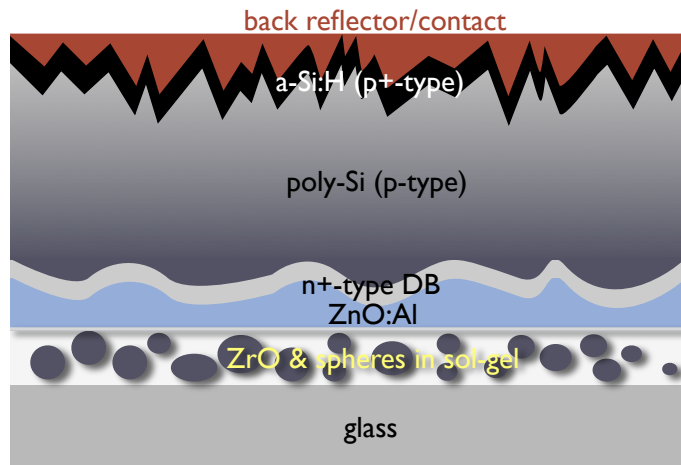


Figure 6.5: Illustration of a solar cell design in which the individually obtained design components are assembled: The front-side light trapping texture consists of self-organizing SiO_2 spheres embedded in sol-gel and flattened by an additional ZrO layer, and a wet-chemical etched ZnO:Al layer. A n^+ -type wide band gap emitter and diffusion barrier (DB) protects the poly-Si base from the detrimental diffusion of Zn. A rear-side texture is implemented in the poly-Si in an etch-back process and the deposition of an a-Si:H layer establishes a hetero-junction at the rear-side. A metal back reflector is used as a back-contact.

7. Periodic arrays of Si crystals on nano-imprinted sol-gel coated glass

7.1. Nanostructured photon management

Significant progress in nanotechnology stimulated extensive research on novel Si-based photonic structures and promising new technologies for photon management in electronic and photovoltaic applications [177, 178, 179, 180, 181, 182, 183].

In contrast to statistical light harvesting approaches (chapter 6) which are limited to a path length enhancement factor of $4n^2$ for fully randomized light, with n denoting the refractive index, designed patterns allow for a controlled coupling of incident free space radiation into propagating guided wave modes and for surpassing the so-called Yablonovitch limit [28, 178, 184].

However, the design of effective solar energy harvesting architectures in silicon-based photovoltaic devices demands the controlled manufacturing of micro- and nano-patterned Si. Extensive research on the growth of Si nano-wires and nano-rods already led to significant absorption enhancement in Si [178, 185, 186]. The potential of photonic crystals as back-reflectors was explored which could enhance the path length of light by several orders of magnitude [187, 188, 189, 190]. Many researchers already investigated the potential of nanostructured plasmonic layers and nanoparticles for optical absorption enhancement in amorphous Si thin films [177, 191, 192, 193, 194, 195]. Recently, the growth of periodic a-Si nano-dome arrays on textured substrates led to efficient light harvesting in a-Si solar cells [196, 197, 198].

The substantial challenge is the development of inexpensive and easily scalable fabrication methods for the controlled implementation of nanostructures into large-area solar

modules.

Nano-imprint lithography based on sol-gel technologies provides an elegant and scalable technique to economically fabricate well-defined textures on large areas with abundant design possibilities [199, 200, 201, 202, 203, 204, 205, 206, 89].

This chapter presents a novel technique for the large-area fabrication of periodic arrays of crystalline Si features on nano-imprinted sol-gel coated glass templates prepared in a solid phase crystallization (SPC) process of amorphous and partially nanocrystalline Si by thermal annealing. Section 7.2 is devoted to the development of an easily scalable fabrication process for equidistant free-standing Si crystals based on a nano-imprinted sol-gel coated glass substrate by selectively etching e-beam evaporated Si. Section 7.3 addresses the analysis of the microstructure and the distinct growth characteristics of high-rate e-beam evaporated Si on 100 cm^2 sol-gel templates with a nano-imprinted 2D grating, employing transmission electron microscopy and scanning electron microscopy. In section 7.4, the design versatility and applicability is discussed. The light trapping properties of crystalline Si arrays on a sol-gel template with a $2\text{ }\mu\text{m}$ grating are evaluated by measuring the optical absorption. An analysis of the scalability of this large-area and low-cost fabrication process gives rise to various design possibilities for tailor-made photonic crystals and novel 3 dimensional solar cell architectures.

7.2. Fabrication process

Figure 7.1 outlines the three steps of the fabrication process of periodic arrays of crystalline Si.

Nano-imprint lithography

A two-dimensional periodic pattern with a $2\text{ }\mu\text{m}$ pitch was imprinted in a sol-gel coated glass template (Schott AF 45, thickness 0.7 mm) by replicating the structure of a reusable $(10 \times 10)\text{ cm}^2$ polysiloxan stamp (Figure 7.1(a)). The sol-gel solution was applied by dip-coating. A short UV curing step prior to the stamp removal ensured that the imprint of the replicated structure was preserved, while a post-imprint thermal annealing step en-

hanced the mechanical and thermal stability of the sol-gel layer (section 3.1). Afterwards, a conformal film of a 70 nm thick ZrO anti-reflection coating was applied.

E-beam evaporation and SPC

Subsequently, $1.4\text{ }\mu\text{m}$ thick films of $2 \cdot 10^{16}\text{ cm}^{-3}$ boron doped Si were deposited at a background pressure of $1 \cdot 10^{-7}$ mbar and deposition rate of 300 nm/min. While fully amorphous Si films are deposited at a substrate temperature T_{dep} of 300°C , a deposition at an elevated T_{dep} of 450°C leads to the formation of partially nanocrystalline material [98]. Thereafter, the deposited amorphous Si films on glass were crystallized in an isothermal annealing process in a tube furnace in N_2 atmosphere at 600°C for 20 h. The prepared samples demonstrated excellent thermal and mechanical stability after selectively exposing them to a short rapid thermal anneal at 1000°C for 1 min.

The e-beam evaporated Si did not form a conformal coating on the overgrown sol-gel pattern, resulting in the growth of peculiar dome-shaped Si arrays for each individual deposition condition. While these features in amorphous and subsequently crystallized Si (SPC-Si) (Figure 7.1(c)) are considerably wide and exhibit a smooth surface texture, the nanocrystalline Si (nc-Si) features are thinner (Figure 7.1(b)) and are characterized by a rough surface topography.

Selective etching

Finally, the material covering the flanks of each individual sol-gel needle could be removed in a selective etching process step, leaving free-standing crystalline Si features on sol-gel tips that are embedded in a crystalline Si base layer. The used etch solution consists of 30 parts 65% conc. HNO_3 , 10 parts 85% conc. H_3PO_4 , 1 part 50% HF and 15 parts H_2O . The solution was dropped onto the sample surface and removed after treatment by rinsing the sample in DI water.

Figure 7.1(e) illustrates an array of crystalline Si cones after exposing a SPC-Si specimen to the etch solution for 1 min. Thin Si-pillars could be created after etching the nc-Si sample for 2.5 min (Figure 7.1(d)). In contrast to the Si pillars which reveal a rough surface texture after etching, the Si-cones were found to be well-defined.

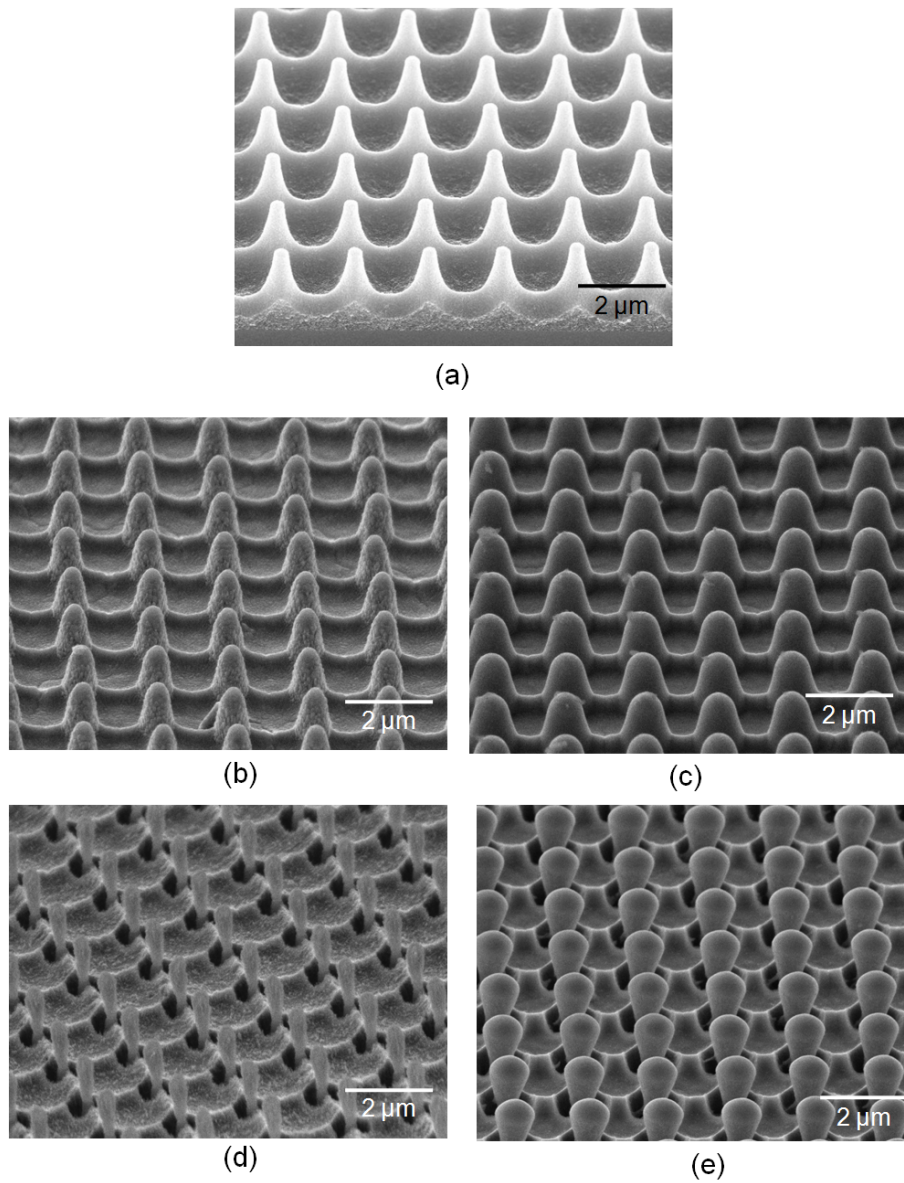


Figure 7.1: SEM images depicting the fabrication process of e-beam evaporated crystallized Si. The nano-imprinted sol-gel coated glass with a 2 μm period is shown in (a). (b) and (c) illustrate 1.4 μm thick crystallized layers of as-deposited nano-crystalline and amorphous Si, while (d) and (e) show the etched structures of the respective Si layers.

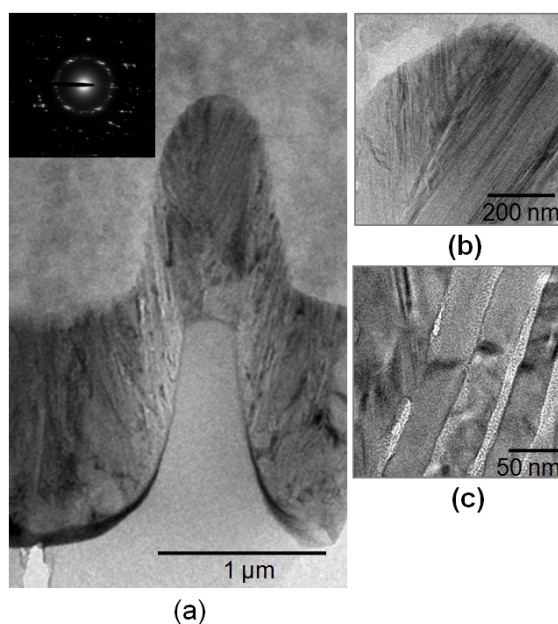


Figure 7.2: A cross-sectional TEM image (a) of 1.4 μm thick nc-Si and its corresponding diffraction pattern confirm the nanocrystalline nature of the sample. (b) and (c) illustrate the nanocrystalline regions at the tip and the side of a cone, respectively.

7.3. Microscopic analysis

In order to shed light onto the underlying growth processes and distinct microstructure of the crystallized Si, we performed a TEM analysis on the specimens. Figure 7.2(a) displays a cross-sectional TEM image through the tip of a dome of a nc-Si sample. The diffraction pattern in Figure 7.2(a) confirms the nanocrystalline nature of the specimen, with streaks indicating a significant number of stacking faults. However, the density of the material deposited at the flanks of the sol-gel needle varies from the material at the tip. While the nanocrystalline Si is more compact on the planar tip (Figure 7.2(b)), Si deposited at oblique incidence comprises nanocrystalline rods which are separated by voids (Figure 7.2(c)).

In contrast to the nanocrystalline specimen, the SPC-Si sample was found to have two apparent features in its microstructure (Figure 7.3(a)). While Si on the flat top of a sol-gel tip and the bottom was revealed to be crystalline, Si at steep edges grows in a columnar

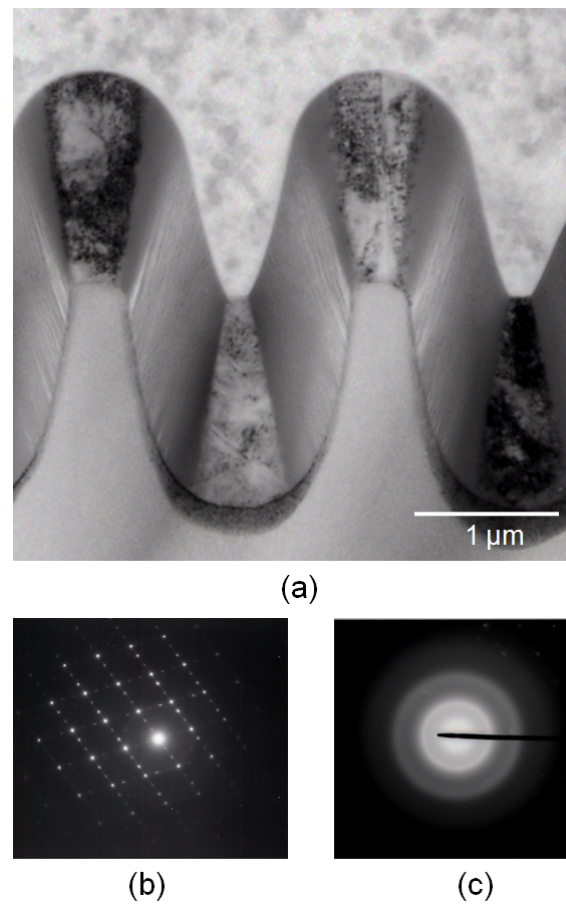


Figure 7.3: A cross-sectional TEM image of a 1.4 μm thick SPC-Si on nano-imprinted sol-gel (a) reveals the existence of well-defined crystalline Si on planar surfaces and columnar structures at steep edges. The diffraction pattern (c) confirms the amorphous nature of the material at the flanks, while the reflections in the diffraction (b) belong to a crystal at the tip with a $[110]$ orientation and a (111) twinning plane.

structure. Figure 7.3(b) displays the diffraction pattern of the crystalline region. The net of strong reflections corresponds to a single Si crystal in $[110]$ orientation, with the weak reflections at $1/3(hkl)$ revealing twinning along the (111) plane [62, 46]. The additional weak streaks can be caused by the twin lamellae. The crystalline phase reaches down to the tip of the sol-gel, resulting in the formation of spherical cone-like shaped single crystals standing on the tip of the sol-gel pattern. The microstructure of the areas comprising a columnar texture differs drastically from the crystalline region. The diffraction pattern of these features reveals the amorphous nature of the regions, with diffuse diffraction rings being associated with typical halo-reflections in a-Si (Figure 7.3(c)). While the spherical

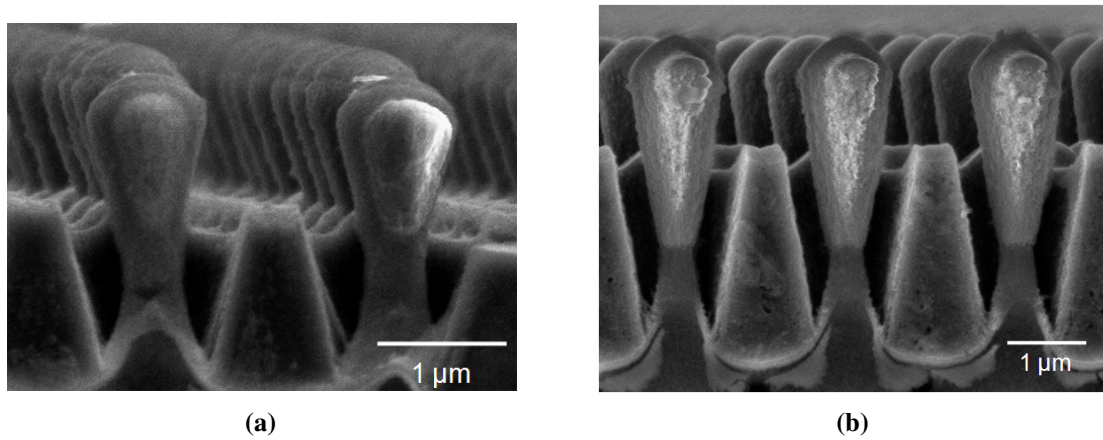


Figure 7.4: Cross-sectional SEM images of etched 1.4 and 2.4 μm high SPC-Si structures are shown in (a) and (b), respectively.

cone-shaped crystals are completely surrounded by a funnel-shaped amorphous matrix, the polycrystalline regions located in the bottom of each individual periodic sol-gel feature are interconnected, forming an underlying polycrystalline bottom layer.

It is this unique surface-dependent microstructure of the prepared samples that enables us to perform further surface modifications. By using an etch solution which predominantly reacts with porous disordered Si, the void-rich nanocrystalline flanks of the nc-Si sample could be removed, forming periodic arrays of compact nanocrystalline Si pillars on a sol-gel template. Even more striking is the result after the etching process on the SPC-Si. With its discretely separated phases, the porous amorphous regions could be removed entirely, leaving barely etched well-defined, free-standing single crystals on sol-gel needles. Figure 7.4(a) and Figure 7.4(b) show cross-sectional SEM images of realized periodic arrays consisting of 1.4 and 2.4 μm high crystalline cone-shaped features.

The outlined preparation process is based on the distinct growth process of physical vapor deposited (PVD) amorphous layers (section 3.2.1), with shadowing effects at a reduced adatom mobility determining the microstructure of the deposited a-Si at a specific angle of incidence [91, 15]. While Si that is deposited on a surface at normal incidence grows in a columnar structure perpendicular to the substrate in a compact way, films deposited at oblique incidence comprise a lower density, growing in column-like uniform rods which are surrounded by a void network. With increasing angle of incidence, the porosity of the anisotropic a-Si increases, which is accompanied by a deviation of the growth direction

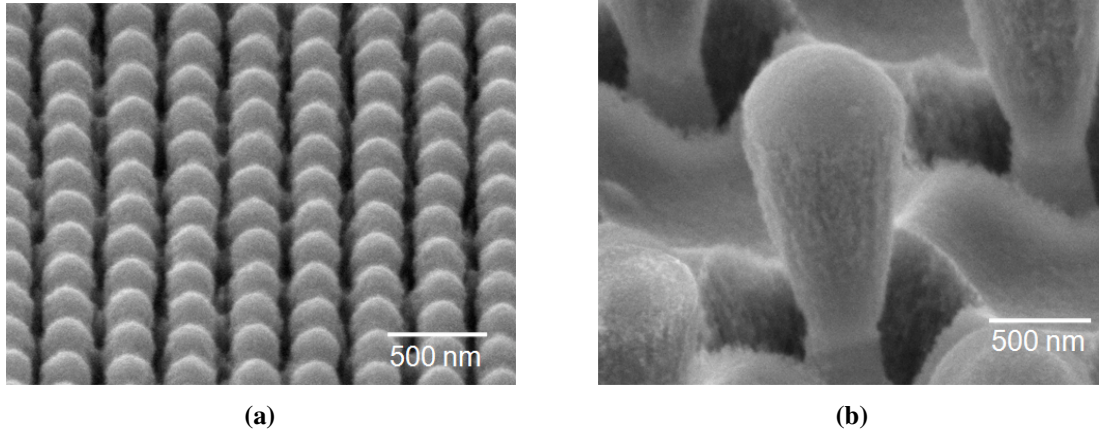


Figure 7.5: (a) shows a selectively etched Si structures with a 300 nm period. For comparison a 1.4 μm high structure on a 2 μm period grating is presented (a) .

from the normal of the substrate towards the direction of the incident Si flux. Porous amorphous Si evaporated at oblique incidence contains a significantly higher content of oxygen than compact Si after thermal annealing, giving rise to the assumption that oxygen diffusion via voids at elevated temperatures inhibits the crystallization process [96]. The influence of the adatom mobility and the angle of incidence on the microstructure can be deduced from Figure 7.2(a) and Figure 7.3(a). Firstly, the porosity of the deposited Si increases with increasing angle of incidence and secondly decreasing the deposition temperature leads to a lowering of the adatom mobility and hence decreases the material density. The latter mechanism subsequently results in a transition from a void-rich nanocrystalline Si to porous a-Si at oblique incidence.

7.4. Design versatility and applicability

The scalability of the feature size of the crystals was investigated by selecting a sol-gel coated glass with a nano-imprinted sol-gel template with a significantly smaller period of 300 nm and following the outlined fabrication process on a 400 nm thick Si layer. Figure 7.5(a) depicts 400 nm tall free-standing crystals on a sol-gel template. For comparison, a 1.4 μm high crystal on a sol-gel template with a 2 μm period is shown in Figure 7.5(b). This result illustrates that the design of free-standing crystals can be tailored

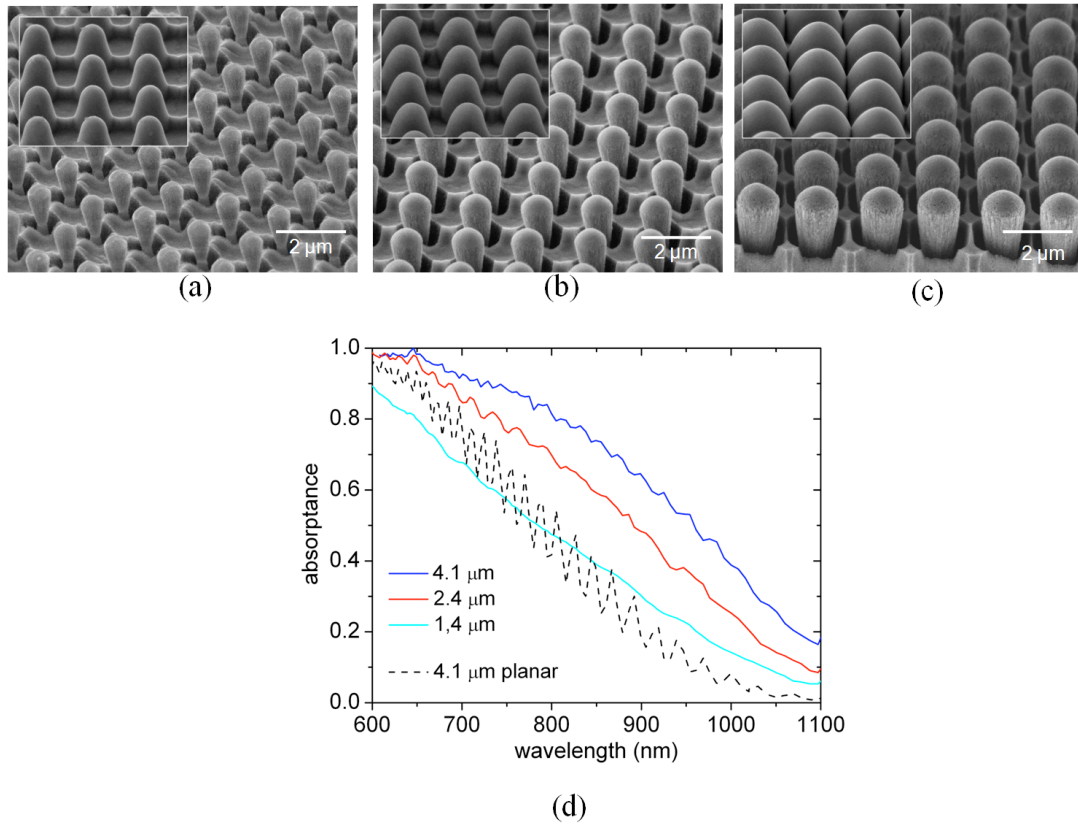


Figure 7.6: (a-c) present selectively etched crystalline 1.4, 2.4 and 4.1 μm thick Si structures with a 2 μm period. The insets illustrate the crystallized features before etching. The wavelength dependent absorbance of the structures ((a)-(c)) is depicted in (d).

by basically selecting a sol-gel template with the desired period.

The potential of these fabricated periodic arrays of Si crystals on a 2 μm period as advanced architectures for solar energy harvesting applications in photovoltaic devices was evaluated by analyzing their absorption properties. Photothermal deflection spectroscopy (PDS) was employed for the analysis as a powerful and sensitive tool to measure the absorption, since it is insensitive to scattering effects. Additionally to the 1.4 μm thick SPC-Si, 2.4 μm and 4.1 μm thick SPC-Si layers were prepared. Figure 7.6((a)-(c)) illustrate the produced Si structures, while the crystallized layers before etching are presented as figure insets. With increasing layer thickness, the deposited Si cones become wider. While the specimen with 1.4 μm Si layer appears to be optically dark brown, the samples

with the thicker Si layer are black. Figure 7.6(d) depicts the wavelength dependent absorptance of the 1.4, 2.4 and 4.1 μm high Si crystal features, showing a strong correlation between Si thickness and absorption properties. For comparison, the absorptance of a 4.1 μm Si layer on planar glass is included. Upon increasing the Si crystal feature size the absorption in the long wavelength region increases significantly. The 4.1 μm Si crystal array structure exhibits an absorbance of 0.63 at 900 nm and 0.4 at 1000 nm, translating into respective absorption enhancement factors of 3 and 5.5.

7.5. Conclusion

In conclusion, we presented a large-area and low-cost fabrication process for arrays of equidistant free-standing crystalline Si features on a 100 cm^2 large sol-gel nano-imprinted glass, prepared by solid phase crystallization of high-rate e-beam evaporated Si and subsequent selective etching. While nanocrystalline Si pillars could be fabricated from as-deposited nanocrystalline Si, periodic arrays of well-defined Si single crystals on a polycrystalline base layer were designed by selectively etching SPC-Si. The analysis of the microstructure and growth process revealed the peculiar growth mechanism of e-beam deposited amorphous Si, with a porous amorphous phase remaining at oblique incidence and compact crystalline features at areas of normal incidence. The final structure was realized by selectively etching the porous amorphous regions. Crystalline Si arrays on a sol-gel template with a 2 μm period exhibited a tremendous absorption enhancement in the long wavelength region compared to the respective Si layer on planar glass, inspiring the development of a highly efficient light trapping architectures for poly-Si thin film solar cell devices. Varying the period of the nano-imprinted sol-gel grating and the thickness of the deposited Si allows us to control the pitch of the created crystal arrays and feature sizes of the individual crystals. This extreme versatility and simplicity of the low-cost preparation process open design possibilities for large-area Si-based photonic structures in various opto-electronic devices.

7.6. Outlook

The successful fabrication of periodic arrays of Si crystals and the high electronic quality of e-beam Si on planar glass (section 5.2) inspire the innovation of e-beam based 3 dimensional solar cell architectures.

Figure 7.7 illustrates a possible design of a 3D solar cell architecture. A 2D periodic sol-gel pattern conformally coated with a thin layer of ZnO and a diffusion barrier (DB) serves as a texture and front contact, followed by a n^+ -type Si layer. This thin Si layer has to form a compact conformal bottom layer to resist the selective etching process, necessitating a deposition by PECVD. The crystalline cones on top of the sol-gel needles as well as the poly-Si base layer consist of a thick p^- -type and thin p^+ -type layer and a metal back contact layer. Since metal deposited by PVD exhibits the same growth characteristics as e-beam evaporated Si, metal deposited at an oblique incidence has a porous structure, giving rise to an elegant realization of the proposed structure by undercutting and lifting off the Al at the flanks in the selective etching process. The voids can subsequently be filled with a white resin. The promising optical and structural properties of the versatile architecture foster the expeditious realization of a working solar cell device with periodic features. Exciting challenges are the implementation of the unconventional contacting

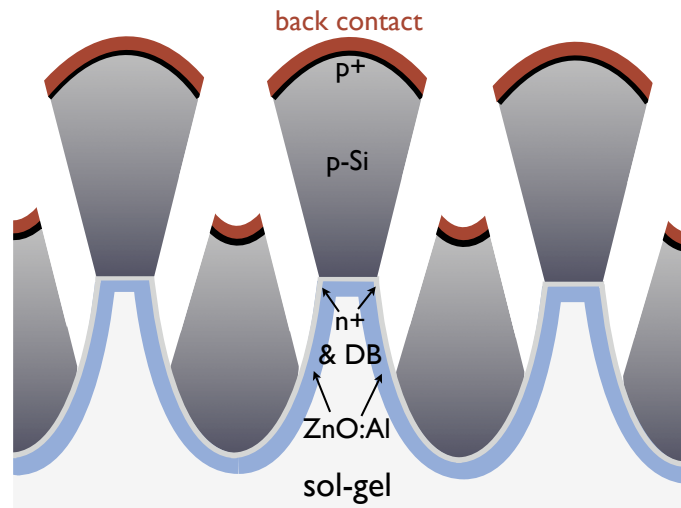


Figure 7.7: Illustration of a 3-dimensional periodic solar cell architecture on patterned sol-gel coated glass. A conformal coating of ZnO:Al, a conductive diffusion barrier (DB) and a n^+ -type Si layer serve as front contact and emitter layers. The poly-Si (p^- - and p^+ -type) cone-structure is fabricated in a selective etching process.

scheme, the improvement of the surface passivation due to an immensely increased surface area to volume ratio in comparison to a conventional design, and an optimization of the emitter area to grant the sufficient charge carrier collection. The analysis of the solar energy harvesting properties of the structures can be complemented by Finite Element Method simulations, enabling a simulation-aided design of an optimized structure.

8. Conclusion

Solid phase crystallized Si thin film solar cells on glass have the potential to reach high conversion efficiencies at considerably low production costs. A prerequisite for a low-cost production of high-quality solar cells is the creation of a novel cell concept, based on tailored Si material embedded in an optimally customized solar energy harvesting structure by utilizing a high-rate deposition technique. Within the scope of this study, a novel design concept that can fulfill these aforementioned requirements was presented. The systematic structural analysis of high-rate electron beam evaporated Si layers revealed design parameters, which enabled the controlled fabrication of efficient solid phase crystallized Si thin film solar cells that could be embedded in advanced light trapping architectures and Al-doped zinc oxide front contact layers.

The characterization of the crystallization kinetics of evaporated amorphous Si on SiN-coated and ZnO-coated substrates with different nano-roughnesses allowed us to derive the necessary parameters for a controlled fabrication of poly-Si layers. An analysis of the nucleation process of Si on substrates with different roughnesses δ_{rms} revealed a unique correlation between the steady state nucleation rate, the substrate topography and the deposition temperature T_{dep} . The growth velocity of nucleated Si crystals, however, was not affected by the surface morphology of the underlying substrate.

The nucleation rate and, consequently, the resulting crystal size were found to be determined by an interplay between the substrate roughness and the deposition temperature of the amorphous Si. The presented investigation showed that the nucleation rate and its associated activation energy $E_{I_{ss}}$ of Si deposited at a deposition temperature T_{dep} of 300 °C on a smooth SiN-coated surface ($\delta_{rms} = 0.3$ nm) were in conformity with the literature (5 eV). Upon increasing the roughness, $E_{I_{ss}}$ was found to decrease gradually, reaching only 1.8 eV on ZnO with $\delta_{rms} = 10$ nm. The decreasing $E_{I_{ss}}$ translated into the formation of

smaller crystals. While the Si crystals easily exceeded several μm on smooth SiN, the crystalline features were not significantly larger than 1 μm on ZnO. The characteristic value of 5 eV for $E_{I_{ss}}$ could be reached on substrates with a specific surface topography by successively lowering the deposition temperature of the a-Si.

An investigation of the transient regime of the nucleation process showed that the deposition temperature was the key parameter that controlled the start of the nucleation process. Amorphous Si films which were prepared at a lower deposition temperature on smooth and rough substrates alike showed a higher structural disorder than layers deposited at higher T_{dep} . The highly disordered structure could be relaxed by thermal annealing. Since disordered material naturally needed more time to relax, the deviating structural relaxation processes prior to the initiation of the crystallization process could be attributed to the dissimilar time-lags in a-Si.

The dependence of the nucleation process on the substrate roughness and structural disorder in the Si led to the determination of a substrate-specific optimal deposition temperature to manufacture large-grained poly-Si in minimal crystallization time. In addition, the dependence of τ on T_{dep} gave rise to the implementation of nucleation layers to control the direction of growth and thereby the creation of columnar grains with predominantly vertical grain boundaries.

Poly-Si thin film mini-modules consisting of a planar glass/SiN/ n^+ -(PECVD)/ p -(e-beam)/ p^+ -(e-beam) structure prepared at a deposition rate of 600 nm/min yielded a conversion efficiency of 6.8%. The device performance was optimized by systematically varying the deposition parameters. These achieved results were equivalent to the results for the same device based on PECVD material and demonstrated that high-rate e-beam evaporation can be an attractive low-cost alternative to the established low-rate PECVD technique. The additional implementation of a silicon surface texture on the rear-side led to a record efficiency of 8%, exceeding previous cell efficiencies reported in literature by more than 50 %.

The investigation of solar cells on ZnO-based front contact layers demonstrated that the implementation of a diffusion barrier between ZnO and Si was an utmost necessity for manufacturing a working device to suppress the diffusion of Zn during the high temperature fabrication process RTA. A prototype solar cell with an insulating SiN layer separating the ZnO and Si films showed a V_{oc} above 400 mV.

Surface textures with light trapping features in the 200 nm to 2 μ m size range were found to influence the resulting microstructure of the deposited Si layers. While Si formed a compact structure on planar surfaces, a deposition of a-Si at oblique incidence resulted in a porous structure, which resisted the crystallization process. Consequently, the implementation of statistical light harvesting structures into evaporated poly-Si thin-film solar cells necessitated a sufficiently flat substrate to ensure the growth of compact poly-Si. Mildly etched ZnO:Al layers met this requirement while also simultaneously providing light trapping. In addition, self-organizing silica spheres embedded in sol-gel presented an attractive low-cost approach for the fabrication of tailor-made light scattering objects. Covered by an additional ZrO layer, the sol-gel embedded spheres were revealed to provide a smooth template for a subsequent Si deposition, giving rise to design possibilities that are independent of the growth characteristics of the evaporated Si. These presented feasible front-side light trapping structures led to an improvement of 56% in the short circuit current of a solar cell device.

Based on these design considerations and results, we have been able to produce tailored poly-Si layers on ZnO-based front contact layers embedded in efficient front-side and rear-side light trapping structures. Some upcoming exciting challenges are the optimization of the light trapping structures in conformity with distinct growth characteristics of evaporated Si and the development of an adequate diffusion barrier between ZnO and poly-Si, which not only fulfills all structural, electrical and optical requirements but also serves as a wide bandgap emitter. A better light management and improved interface design will lead to an enhancement of the current and the voltage. With the presented design components successfully implemented, the proposed solar cell concept is on the path of reaching an efficiency of 11-12%.

An investigation of Si on nanostructured glass templates led to the development of a fabrication process of advanced Si architectures. Free-standing equidistant Si crystals on nano-imprinted sol-gel coated glass could be fabricated by solid phase crystallization of evaporated amorphous Si and subsequent selective etching. The distinct growth characteristics of the evaporated Si, with a porous amorphous phase remaining at oblique incidence and compact crystalline features at areas of normal incidence, enabled us to realize the final structure by selectively etching the porous amorphous regions. The new process was versatile, with feature sizes solely determined by the period of the nano-imprinted sol-

gel and the thickness of the deposited Si. Periodic arrays of crystalline Si on a template with $2\text{ }\mu\text{m}$ pitch exhibited a tremendous absorption enhancement in the long wavelength region compared to a Si layer on planar glass. The simplicity and versatility of this fabrication process inspired the design of novel three-dimensional solar cell architectures with large-area photonic structures.

The presented study highlighted that electron beam evaporated poly-Si solar cells on glass can hold the key to significant advances in Si thin film technology by providing cost-effective and highly efficient photovoltaic concepts.

A. Appendix

A.1. Surface topography of SiN and ZnO-coated glass substrates

This section is a supplement to the investigation of the crystallization kinetics presented in chapter 4 and covers the characterization of the surface topography of the prepared ZnO- and SiN-coated glass substrates, by employing AFM microscopy. Figure A.1 illustrates AFM scans of the prepared layers prior to the Si deposition. While the surface of the SiN-coated glass (Figure A.1(a)) has a very smooth morphology, ZnO-coated glass substrates shown in Figure A.1(d) and Figure A.1(e) exhibit a pronounced surface texture. The AFM images visualize the grain structure of the deposited ZnO layer, comprising ~ 100 nm wide ZnO crystal, which are individually grown in a columnar structure along their c-axis at normal direction to the substrate. The deposition of an additional SiN layer on top of the ZnO results in the suppression of the characteristic crystalline features of the underlying ZnO layer. While the ZnO grains can still be seen beneath a 35 nm thick SiN layer (Figure A.1(c)), a 50 nm thick layer covers the ZnO sufficiently for the crystalline features of the ZnO layer to be evened out (Figure A.1(b)). Consequently, these data provide the necessary information for the calculation of the roughness and the PSD spectra. Figure A.2 shows the PSD spectra of the prepared films and its corresponding δ_{rms} . The roughness of the fabricated layers (Figure A.1) continuously increases from 0.3 nm for SiN to 5 nm and 10 nm for ZnO. Layers with a higher δ_{rms} also show an increased PSD amplitude at spatial frequencies that correspond to larger topographic lengths. Consequently, the prepared samples shown in Figure A.1((a)-(e)) exhibit gradually increasing vertical and lateral surface features, leading to larger δ_{rms} and higher PSD amplitude at longer spatial wavelengths. SEM images of SiN and two ZnO layers on glass with their

respective roughness of δ_{rms} of 0.3 nm, 5 nm and 10 nm are displayed in Figure A.3 and provide a visual illustration of the range of the surface textures covered in this analysis.

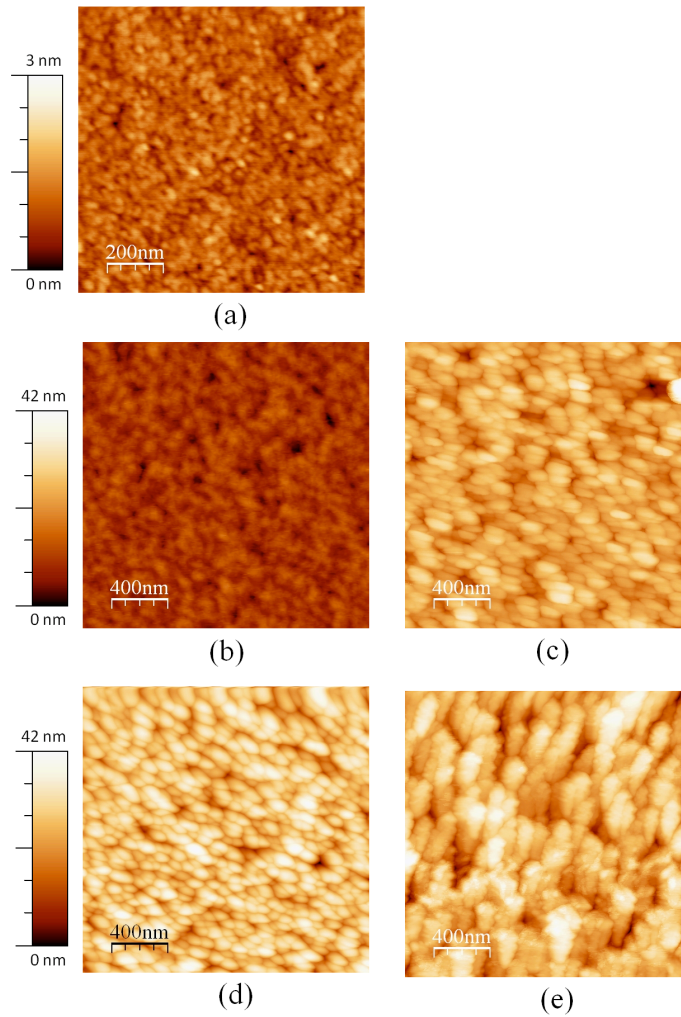


Figure A.1: AFM surface topography scans of SiN and ZnO-coated samples. (a) shows the topography of a smooth SiN surface exhibiting a roughness δ_{rms} of merely 0.3 nm. (b) and (c) show scans of ZnO surfaces that are respectively covered by a 50 nm thin SiN ($\delta_{rms}=2.3$ nm) and 35 nm ($\delta_{rms}=4.4$ nm) thin SiN layer. A ZnO surface with a δ_{rms} of 5 nm is illustrated in (d), while (e) shows an image of a different ZnO layer with $\delta_{rms}=10$ nm. Note the different height scale in (a).

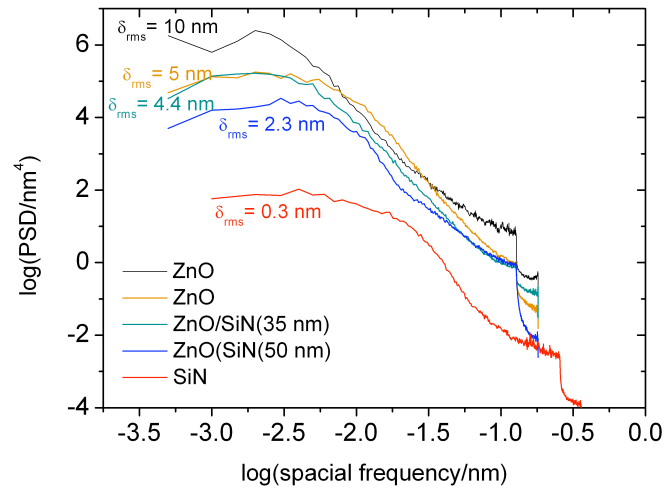


Figure A.2: The power spectral densities of 5 different surface topographies are illustrated. AFM scans of the respective topographies illustrated in Figure A.1 were the basis for the analysis.

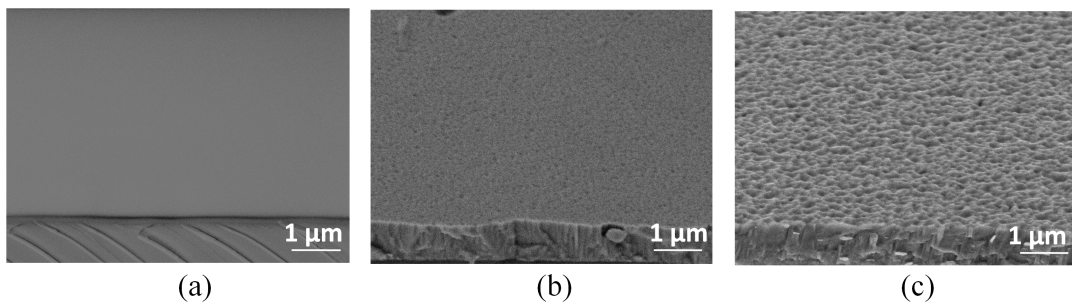


Figure A.3: SEM images of 3 prepared films with deviating topographies. (a) illustrates a smooth SiN-coated glass substrates with a δ_{rms} of 0.3 nm, while (b) and (c) show images of two different ZnO layers with a respective δ_{rms} of 5 nm and 10 nm.

A.2. Determination of the activation energies of I_{ss} and τ

The investigation of the dynamics of the nucleation process of Si deposited at different temperatures on deviating substrate textures (Section 4.4 and 4.5) is based on the analysis of the time- and temperature-dependent nucleation rate. The essential parameters derived from this analysis are presented in Table 4.2. This section, however, provides a complete description of the data and the characteristic parameters for the nucleation process of the investigated samples. Figure A.4 and Figure A.5 illustrate the steady state nucleation rates I_{ss} and time-lags τ for isothermal annealing temperatures ranging from 560 °C to 610 °C. Since the temperature-dependent nucleation process exhibits Arrhenius behavior (Equation 4.11), the respective activation energies for the steady state nucleation rate $E_{I_{ss}}$ and for the time-lag E_{τ} could be determined by a linear regression according to:

$$\ln(I_{ss}) = \ln(I_{ss0}) + \frac{E_{I_{ss}}}{k_B T} \quad (\text{A.1})$$

$$\ln(\tau) = \ln(\tau_0) + \frac{E_{\tau}}{k_B T} \quad (\text{A.2})$$

Table A.1 summarizes all fitting parameters extracted from the linear regressions in Figure A.4 and Figure A.5.

Table A.1: Fitting parameters for the Arrhenius plots of the steady state nucleation rate I_{ss} and time-lag τ are listed for all investigated samples. δ_{rms} and T_{dep} denote surface roughness of the substrate and the deposition temperature. A linear regressions according to Equation A.1 and Equation A.2 allowed the determination of the activation energies $E_{I_{ss}}$ and E_{τ} . $\ln(I_{ss0})$ and $\ln(\tau_0)$ denote the intercepts of the linear fits.

substrate	δ_{rms} (nm)	T_{dep} (°C)	$E_{I_{ss}}$ (eV)	$\ln(I_{ss0})$ I_{ss0} in ($\mu\text{m}^{-3}\text{s}^{-1}$)	E_{τ} (eV)	$\ln(\tau_0)$ τ_0 in (s)
ZnO:Al	10	300	1.8 ± 0.2	15.6 ± 2.6	4.0 ± 0.7	-46.0 ± 9.7
ZnO:Al	5	300	2.9 ± 0.4	28.7 ± 5.4	3.8 ± 0.3	-43.8 ± 3.5
ZnO:Al	5	250	3.6 ± 0.2	38.1 ± 2.1	3.2 ± 0.3	-34.3 ± 4.4
ZnO:Al	5	200	5.1 ± 0.4	54.0 ± 9.5	3.2 ± 0.5	-34.4 ± 6.1
ZnO:Al	5	150	4.5 ± 0.4	46.3 ± 4.5	3.5 ± 0.7	-37.9 ± 9.0
ZnO:Al/SiN (35 nm)	4.4	300	3.5 ± 0.2	36.9 ± 3.2	3.2 ± 0.2	-34.4 ± 2.4
ZnO:Al/SiN (50 nm)	2.3	300	4.2 ± 0.6	43.3 ± 8.7	2.9 ± 0.3	-31.2 ± 4.5
SiN	0.3	300	5.0 ± 0.6	53.6 ± 8.6	2.3 ± 0.7	-22.5 ± 9.1
SiN	0.3	250	4.4 ± 0.5	46.3 ± 6.1	3.4 ± 0.2	-36.2 ± 1.8
SiN	0.3	200	4.2 ± 1.1	42.1 ± 15.1	3.2 ± 0.3	-32.3 ± 3.4
SiN	0.3	150	5.1 ± 0.7	55.3 ± 10.3	3.2 ± 0.1	-32.5 ± 1.4

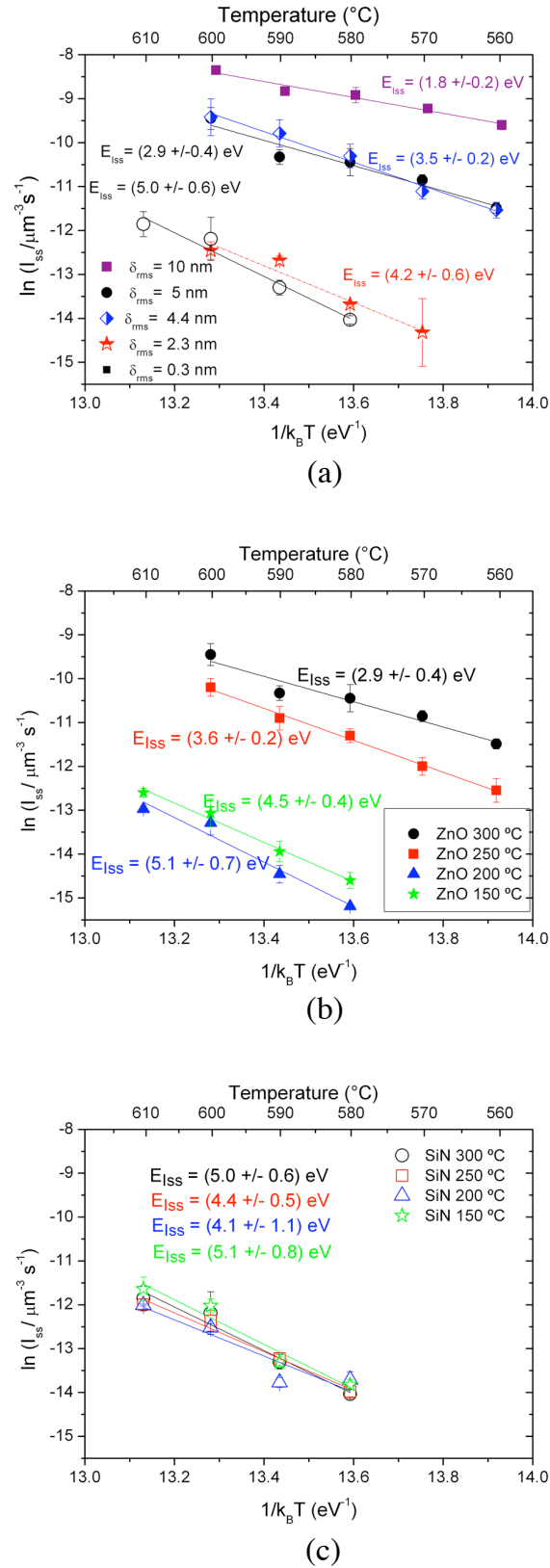


Figure A.4: The temperature dependence of the steady state nucleation rate I_{ss} of Si is depicted in an Arrhenius plot for Si deposited at 300 °C on substrates with deviating surface topographies ((a)). (b) and (c) show Arrhenius plots for Si on ZnO:Al ($\delta_{rms} = 5$ nm) and SiN ($\delta_{rms} = 0.3$ nm) prepared at deposition temperatures ranging from 150 °C to 300 °C.

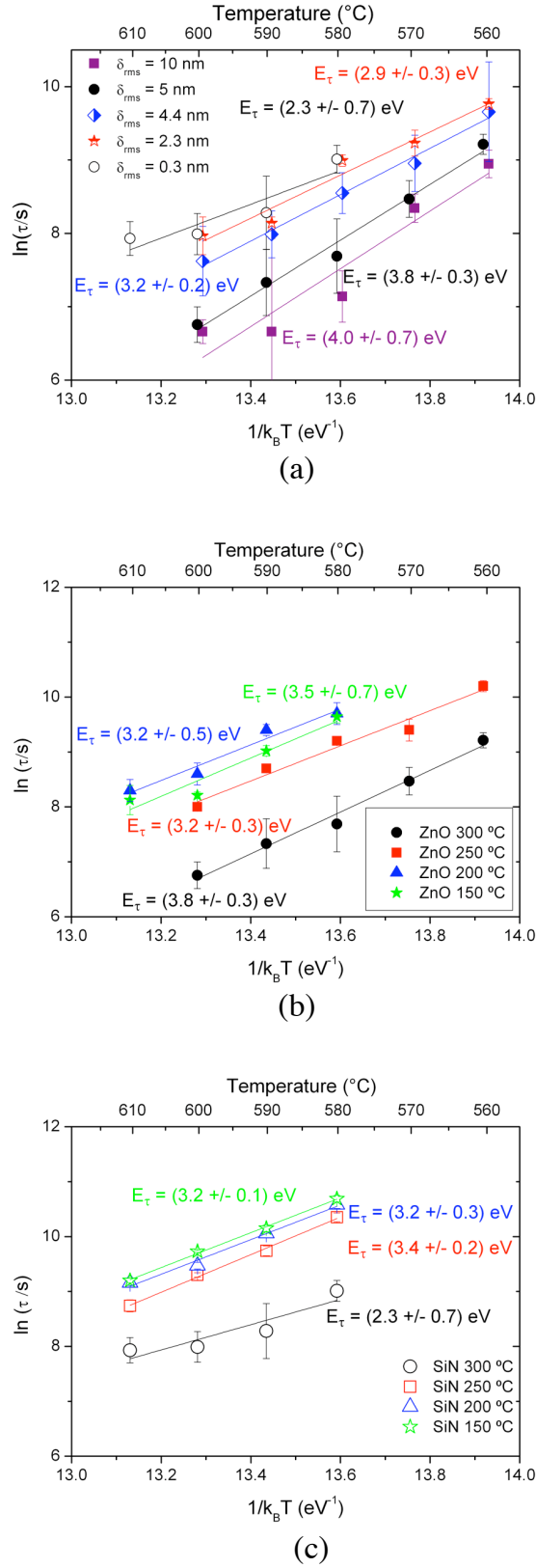


Figure A.5: (a) illustrates Arrhenius plots for the time-lag τ as a function of $1/k_B T$ for $a\text{-Si}$ deposited at 300°C on substrates with various roughnesses. The temperature dependence of the time-lag τ of Si is illustrated for Si on ZnO:Al ($\delta_{\text{rms}} = 5 \text{ nm}$) ((b)) and SiN ($\delta_{\text{rms}} = 0.3 \text{ nm}$) ((c)) prepared at deposition temperatures ranging from 150°C to 300°C .

A.3. Diffusion profiles of Zn and Al in Si on ZnO:Al

This section addresses an evaluation of the diffusion of Zn and Al from ZnO:Al into deposited Si during thermal processes. Secondary ion mass spectroscopy (SIMS) measurements were conducted in order to evaluate the influence of the SPC process at 600 °C for 12 h on the diffusion of Al and Zn [110]. A quantitative measurement of the Al concentration was carried out by calibrating the measurement with a reference sample with a known Al concentration in Si. However, the Zn concentration per volume in Si could not be determined quantitatively due to the lack of a reference standard for Zn in Si.

Figure A.6(a) illustrates the concentration of Al as a function of the film thickness for a-Si on ZnO:Al (black) and solid phase crystallized Si on ZnO:Al (red). The SPC process clearly leads to an increase of the Al concentration within 400 nm of the ZnO:Al/Si interface initiated by a thermally activated diffusion process. The characteristic diffusion profile exhibits a drastically increased Al concentration in Si from $3 \cdot 10^{15} \text{ cm}^{-3}$ to 10^{17} cm^{-3} within 100 nm to the ZnO:Al/Si interface. Figure A.6(b) shows the detected counts per seconds for Zn in a-Si and solid phase crystallized Si on ZnO:Al. An accumulation of Zn is already detected in the amorphous Si in proximity to the ZnO:Al/Si interface. However, the SPC process triggers a diffusion process, leading to an increase of the Zn concentration of 1 order of magnitude in the entire Si film.

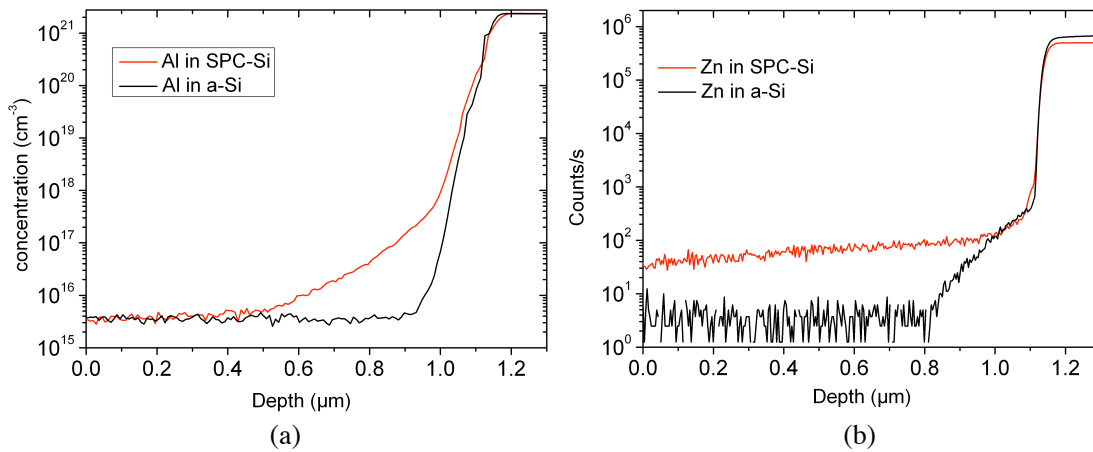


Figure A.6: (a) illustrates the concentration of Al per cm^3 as a function of the film depth in Si on ZnO:Al before and after crystallization, while (b) shows the counts per second for detected Zn in a Si/ZnO:Al layer stack. The Si/ZnO:Al interface is located at 1.1 μm .

A.4. Poly-Si on nano-imprinted sol-gel coated glass prepared by direct growth

Chapter 7 addressed the large-area fabrication of equidistant crystalline feature on nano-imprinted sol-gel coated glass by selective etching. A prerequisite for the realization of the etched structures was the presence of two areas that comprise a dissimilar microstructure. Porous nc-Si and a-Si could be removed by etching, while compact Si was not affected by the etch solution.

A deposition of Si at a temperature of 600°C led to the growth of columnar hundred nm wide crystalline Si grains. Figure A.7 illustrates a cross-sectional TEM image of a 1.4 μm thick poly-Si layer on a nano-imprinted sol-gel template. The growth process is in conformity with the presented PVD growth characteristics. At normal incidence, the material grows in $\sim 100\text{nm}$ wide poly-Si dense columns in a compact way, while the Si columns are separated by voids at steep edges. However, an application of the selective etch process to directly grown poly-Si failed, since the compact poly-Si columns at the flanks resisted the etch solution.

Concluding, due to the lack of two structural Si phases on the textured surface, the directly grown poly-Si cannot be modified in a selective etching process.

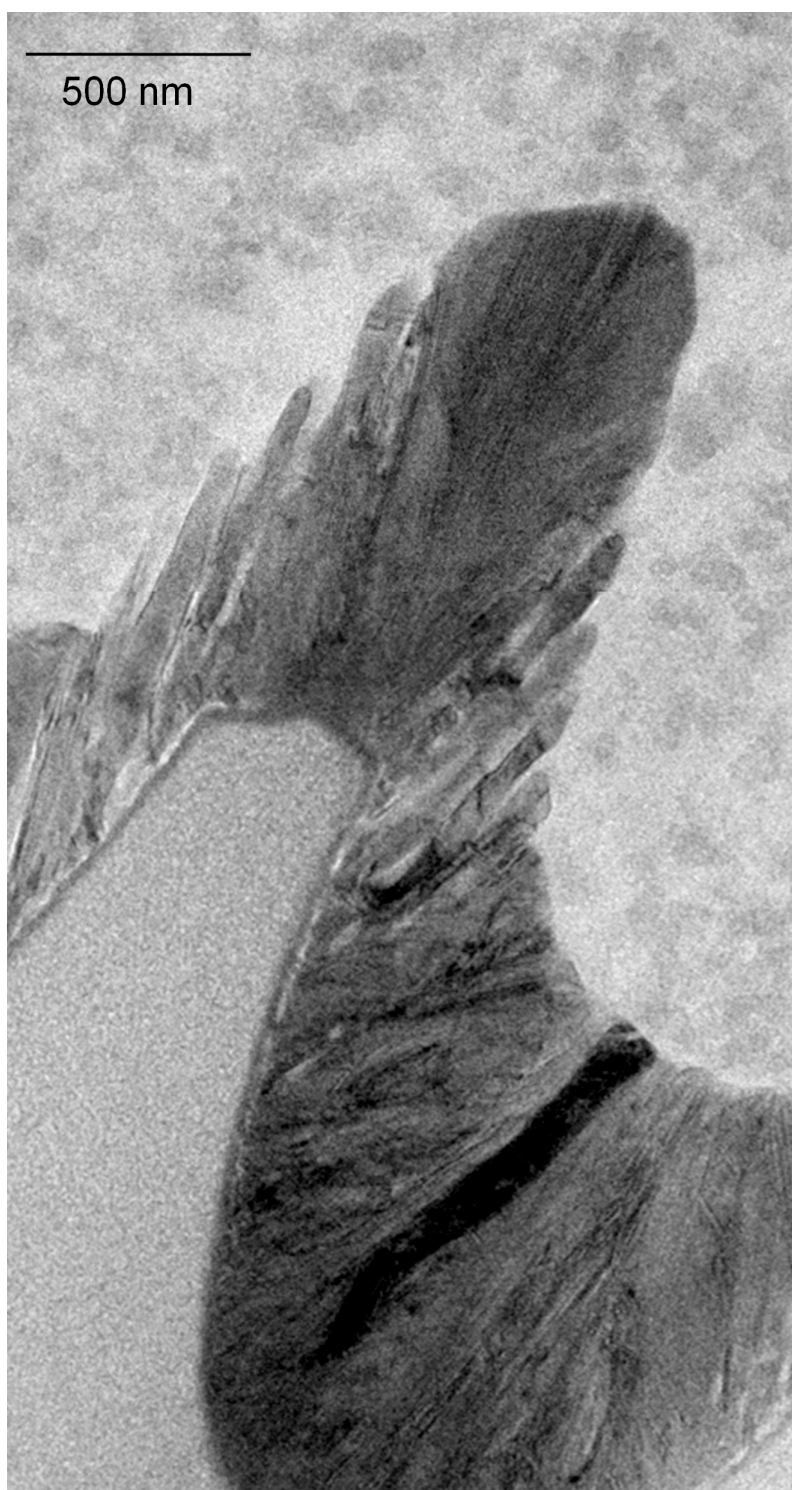


Figure A.7: A cross-sectional TEM image of a directly grown poly-Si layer at 600°C on nano-imprinted sol-gel coated glass is illustrated. While the material is compact on flat surfaces, ~ 100 nm wide crystalline Si columns form at the flanks of the sol-gel needles.

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List of Figures

2.1.	Free energy diagram of amorphous and liquid Si with respect to crystalline Si	10
2.2.	Gibbs free energy of a growing cluster	11
2.3.	Volmer's Cap model	13
2.4.	Volmer Weber and Becker Döring cluster distribution functions	15
2.5.	Steady state nucleation	17
2.6.	Free activation energy below the equilibrium temperature	19
2.7.	SPC growth model for Si grains	20
2.8.	Layout of the two-diode model	23
2.9.	J-V characteristics of a solar cell	24
3.1.	Directional a-Si growth on inclined surfaces	32
3.2.	Schematic illustration of the used e-beam setup	33
3.3.	Photograph of a fabricated mini-module consisting of 12 cells	35
3.4.	CSG mini-module contacting scheme	36
3.5.	Illustration of a solar cell structure on ZnO	37
3.6.	Ray path diagram of a TEM operating in diffraction mode and image mode	39
3.7.	Schematic illustration of a the photothermal defection spectroscopy setup	43
4.1.	Optical micrographs of partially crystalline Si on SiN	50
4.2.	Determination of the nucleation rate $I(t)$	53
4.3.	Crystal growth velocity as function of the annealing temperature	56
4.4.	The activation energy for the nucleation rate as a function of the roughness δ_{rms}	57
4.5.	Cross-sectional TEM images of partially crystalline Si on SiN and ZnO:Al	58
4.6.	The time-lag τ of Si deposited at different T_{dep} on various substrate topographies	59
4.7.	Raman spectra of a-Si deposited at T_{dep} ranging from 150 °C to 300 °C on SiN	61
4.8.	Characteristic parameters for the disorder in a-Si	62
4.9.	EBSD pole figure maps of poly-Si on ZnO:Al and SiN	67

4.10. Cross-sectional TEM micrographs of partially crystalline Si on SiN and ZnO:Al with implemented nucleation layer	68
5.1. Mini-module efficiency vs. base doping concentration	74
5.2. V_{oc}/cell and J_{sc} as a function of the absorber thickness	75
5.3. Influence of T_{dep} on V_{oc}/cell and J_{sc} of prepared mini-modules	76
5.4. Influence of the background pressure on V_{oc}/cell and J_{sc} of prepared mini-modules	77
5.5. AFM of rear-side texture	78
5.6. J-V characteristics of textured and planar mini-modules	79
5.7. J-V curves of solar cells with implemented ZnO	81
6.1. SEM cross-sections of poly-Si on spheres with and without ZrO	90
6.2. Cross-sectional SEM and TEM micrographs and EBSD image of poly-Si on textured ZnO	91
6.3. Optical absorption of 1 μm poly-Si on planar glass, self-organized nanospheres and textured ZnO	92
6.4. EQE of ZnO-based front side light trapping textures	93
6.5. Illustration of a proposed solar cell device structure	96
7.1. Fabrication process of periodic arrays of free-standing crystals	100
7.2. TEM analysis of the microstructure of nc-Si on a periodic imprint structure	101
7.3. TEM analysis of the microstructure of SPC-Si on a periodic imprint structure	102
7.4. SEM cross-section of selectively etched periodic arrays of crystalline Si	103
7.5. Versatility of the fabrication process of the periodic structure	104
7.6. Light trapping properties of the periodic structure	105
7.7. Illustration of a 3-dimensional solar cell architecture	107
A.1. AFM surface topography scans of SiN-coated and ZnO-coated glass substrates	114
A.2. Power spectral density of substrates with various surface topographies	115
A.3. SEM images of a SiN-coated and two ZnO-coated glass substrates	115
A.4. Temperature dependence of the steady state nucleation rate	118
A.5. Temperature dependence of the time-lag	119
A.6. Diffusion profiles of Al and Zn in a-Si and SPC-Si	120
A.7. Cross-sectional TEM image of directly grown poly-Si on nano-imprinted sol-gel coated glass	122

List of Tables

3.1. Functional thin film coatings and nanostructures	28
4.1. Roughness parameters of prepared SiN and ZnO layers on glass	48
4.2. Essential parameters for nucleation	55
5.1. Mini-modules prepared at various deposition conditions	73
5.2. Solar cells prepared on ZnO-coated glass substrates	79
5.3. Comparison of record e-beam mini-modules to state-of-the-art PECVD-based modules	83
A.1. Fit parameters for Arrhenius plots of the nucleation rate and time-lag . . .	117

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List of publications

Publications

1. **T. Sontheimer**, C. Becker, U. Bloeck, S. Gall, and B. Rech. Crystallization kinetics in electron-beam evaporated amorphous silicon on ZnO:Al-coated glass for thin film solar cells, *Applied Physics Letters*, 95:101902, 2009.
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