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Development of Amorphous Germanium Nanoabsorber Solar Cells

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Kurzfassung

Amorphes Germanium (a-Ge:H) wurde aufgrund seiner herausragenden Absorptionseigenschaften bereits vor etwa 25 Jahren als mögliches Absorbermaterial für Dünnschichtsolarzellen untersucht. Ziel war insbesondere die Verwendung als Infrarotabsorber in Mehrfachsolarzellen mit auf amorphem Silizium (a-Si:H) basierenden Topzellen. Aufgrund ungünstiger elektronischer Eigenschaften wurde a-Ge:H jedoch um die Jahrtausendwende weitgehend durch mikrokristallines Silizium (μ c-Si:H) ersetzt. Ein Nachteil besteht hierbei darin, dass für effiziente Infrarotabsorption mikrometerdicke μ c-Si:H-Schichten benötigt werden, während a-Si:H-Solarzellen typischerweise nur etwa 200-300 nm dick sind. Dies hat eine drastische Durchsatzreduktion, eine Erhöhung der Herstellungskosten, und einen höheren Modulpreis pro Wattpeak im Vergleich zu a-Si:H-Einzelzellen zur Folge.

In der vorliegenden Dissertation wird daher die Möglichkeit, a-Ge:H als Infrarotabsorber in Solarzellen zu nutzen, wieder aufgegriffen. Im Detail beschäftigt sie sich mit der Frage, ob eine derart drastische Reduktion der Absorberdicke möglich ist, dass eine deutliche Effizienzverbesserung bereits mit bestehender Materialqualität erreicht wird. Diese Idee beruht auf der Tatsache, dass geringere Absorberdicken in Solarzellen im Allgemeinen zu verbesserter Ladungsträgerextraktion führen. Um gleichzeitig effiziente Absorption zu ermöglichen, wurde die Ausnutzung von Fabry-Pérot-Resonanzen zur Verbesserung des Lichteinfangs untersucht. Hierzu wurden zwei Solarzellenkonzepte entwickelt, die sich im Wesentlichen in der verwendeten Resonanzordnung (und damit in der Resonatorlänge) unterscheiden.

Grundsätzlich konnte sowohl simulativ als auch im Experiment gezeigt werden, dass unter geeigneter Ausnutzung optischer Resonanzen nur etwa 10-25 nm dicke a-Ge:H-Schichten benötigt werden, um Infrarotabsorption zu erzielen, wie sie typischerweise in mikrometerdicken μ c-Si:H-Solarzellen erreicht wird. Dieses Prinzip konnte außerdem auf einfache Weise auf Mehrfachsolarzellen übertragen werden, indem langreichweitige Kohärenzeffekte über die Teilzell-Grenzen hinweg gezielt unterdrückt wurden, ohne dabei die erwünschten Resonanzen innerhalb der a-Ge:H-Solarzelle zu unterbinden.

Bei Verwendung von Resonanzen niedrigster Ordnung in Kombination mit einem Metall-Rückreflektor ergab sich dabei besonders breitbandige Absorption und entsprechend höhere Stromdichten, so dass sich dieses Konzept als besonders für den Einsatz in Einzelzellen geeignet erwies. Höhere Resonanzordnungen führen zu schmalbandigeren Absorptionsspektren, die nur in Mehrfachsolarzellen sinnvoll eingesetzt werden können. Aufgrund der höheren Resonatorlänge ergibt sich in diesem Fall jedoch mehr Spielraum für die elektrische Optimierung, so dass mit diesem Ansatz bessere elektrische Eigenschaften erzielt werden konnten. Insgesamt ermöglichten jedoch beide Ansätze aufgrund einer verbesserten Ladungsträgerextraktion eine Erhöhung der Einzelzell-Effizienz in a-Ge:H-Solarzellen gegenüber der Literatur.

Abstract

Due to its exceptional absorption properties, amorphous germanium (a-Ge:H) was investigated 25 years ago already as a potential infrared absorber material for application in thin-film solar cells. Here, a particular aim was to use the material in multijunction concepts together with amorphous silicon (a-Si:H) top cells. However, due to its unfavorable electronic properties, a-Ge:H was widely replaced by μ c-Si:H around the turn of the millennium. But one disadvantage of the latter material is that μ m-thick μ c-Si:H-layers are required to ensure efficient infrared absorption, while a-Si:H solar cells typically are only about 200-300 nm thick. This implies a drastic throughput reduction, an increase in fabrication costs, and higher module prices per Wattpeak compared to a-Si:H single junction solar cells.

Thus, this thesis revisits a-Ge:H as possible infrared absorber material for application in solar cells. In particular, it is explored whether a drastic absorber thickness reduction can be achieved, such that a considerable efficiency improvement is obtainable with state-of-the-art material quality already. This idea is based on the fact that, generally speaking, lower absorber thicknesses lead to improved charge carrier extraction in solar cells. To enable efficient absorption at the same time, the exploitation of Fabry-Pérot resonances as a light-trapping scheme was investigated. For this purpose, two different solar cell concepts were developed, which mainly differ in the resonance order (and hence resonator length) which is utilized.

It was shown using simulations as well as in experiments that, when taking advantage of optical resonances, only 10-25 nm thick a-Ge:H films are required to obtain infrared absorption comparable to μ m-thick μ c-Si:H solar cells. Moreover, this method can be easily applied to multijunction devices by suppressing long-range "inter-subcell" coherence while maintaining the desired resonances inside the a-Ge:H solar cell.

Lowest-order resonances in ultrathin cavities employing metal back reflectors enabled particularly broadband absorption and hence higher current densities, so that this concept was found to be especially suitable for application in single junction devices. Using higherorder resonances, spectrally much narrower absorption is obtained, which can be used in a reasonable manner only in multijunction devices. However, due to the higher cavity length used in this case, this approach yields more degrees of freedom for electrical optimization of the solar cells, leading to superior electrical properties. All in all, as a result of improved charge carrier extraction, both concepts enable a-Ge:H single cell efficiency improvements compared to the state-of-the-art.

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1 Introduction

Silicon thin-film solar cells aim to reduce the costs of photovoltaic (PV) energy production by replacing the mono- and polycrystalline forms of silicon, as used in conventional PV, with its more absorptive microcrystalline (μ c-Si:H) and amorphous (a-Si:H) counterparts. In a-Si:H single junction solar cells only about 200-300 nm thick absorbers are typically used. The downside of this technology are maximum efficiencies of only 10%, as compared to values well beyond 20% possible with conventional PV.^[1] Multijunction solar cells combining a-Si:H and μ c-Si:H were developed, improving efficiencies to more than 13%.^[1,2] However, several μ m thick μ c-Si:H layers are required to efficiently absorb infrared light, leading to a drastic throughput reduction, higher material consumption, and even increased module prices per Wp. While it was thought that the higher efficiency would reduce the system price in rooftop applications due to the high impact of balance of system (BOS) costs (e.g. inverters, mountings, installation), the achieved efficiencies are still too low to sustain high competitiveness in this area.

However, when used in *special applications*, silicon thin-film solar cells can take the most of their advantages. They contain no toxic or scarce materials and support largearea fabrication. A wide range of cost-effective substrate materials can be used, such as flexible and lightweight aluminium or plastic foils.^[3,4] By simply adjusting the deposited layer thicknesses or using laser-patterning steps, colored or semitransparent devices can be fabricated.^[5,6] This makes the technology highly suitable e.g. for *building-integrated photovoltaics (BIPV)*.^[6] This approach can lower the influence of BOS costs due to the multi-purpose use of the substrates and the omission of additional assembly systems, hence increasing the relative impact of coating costs on the final system price. In this field, full advantage should be taken of the large-area and high-throughput fabrication capabilities of silicon thin-film technology, rather than accepting drastic cost increases to attain moderate efficiency improvements.

This motivates the replacement of the thick and expensive μ c-Si:H layers by other materials that allow fast and cost-efficient fabrication. *Hydrogenated amorphous ger-manium (a-Ge:H)* is a particularly interesting material in this context. Its absorption coefficient is up to two orders of magnitude higher compared to μ c-Si:H, while the spectral range that can be absorbed is comparable.^[7] The downside of a-Ge:H is that even the best layers exhibit ten times higher defect densities compared to high-quality a-Si:H films.^[7–11] Hence, the material is generally considered as unsuitable for photovoltaics.

However, it was recently demonstrated that few nanometer thick germanium layers can yield broadband near-perfect absorption at visible wavelengths when placed inside a resonant *nanocavity* with a metal back reflector.^[12,13] Implementation of this concept in a-Ge:H solar cells could allow the use of drastically thinner absorber layers, resulting in much more efficient charge carrier extraction. However, it remained an open question whether and how this scheme can be implemented in solar cells.

1 Introduction

Aim & Outline

The aim of this thesis was to investigate the application of absorptive resonant cavities with ultrathin a-Ge:H nanoabsorbers to improve charge carrier extraction in a-Ge:H thin-film solar cells. In particular, the applicability of the *nanocavity* approach was studied. In accordance with the aim to replace μ c-Si:H, a strong focus was on the integration of the concepts in multijunction solar cells. To allow an experimental investigation of the concept, a-Ge:H thin-films and corresponding solar cells were developed and continuously improved during the course of this thesis. All experimental studies were supported by optical simulations of the investigated solar cell stacks.

The results of these studies have been compiled in the form of scientific publications, and are presented in Chapter 3. The following outline briefly summarizes the content of these papers and describes how each publication contributes to the overall aims pursued in this work.

Paper I presents the first investigation of *nanocavity*-enhanced solar cells. A simple theoretical description of this concept is given, allowing to gain a basic understanding of its underlying mechanisms. 1d optical simulations were performed to estimate the optimum required layer thicknesses as well as the potential short circuit current density (j_{SC}) reachable with the approach. A first experimental realization of this solar cell type yielded a j_{SC} of 20 mAcm⁻² using an only 13 nm thick a-Ge:H absorber.

Paper II investigates the applicability of this concept in a-Si:H/a-Ge:H tandem solar cells. Experimental quantum efficiency (QE) spectra of nanocavity-enhanced a-Ge:H bottom devices on moderately textured substrates were found to exhibit spectrally narrow interference patterns, which have a detrimental effect on the achievable j_{SC} . Optical simulations demonstrate that this is related to long-range coherent interaction of light traversing between both sub-cells of the tandem cell stack. This problem is solved by taking advantage of the effect that nanocavities keep their resonance properties even on highly textured surfaces. It is shown that using very rough substrates, long-range "inter-subcell" coherence effects are suppressed, while efficient absorption inside the nanocavity-enhanced a-Ge:H bottom cell is maintained. With an only 20 nm thick a-Ge:H layer, a j_{SC} comparable to a-Si:H/ μ c-Si:H solar cells can be reached.

The above results demonstrated an outstanding optical performance of *nanocavity*enhanced a-Ge:H solar cells. However, extremely thin doped layers are required for optimum resonance, hence making electrical optimization of such devices difficult. This problem is addressed in the following papers by specifically designing the a-Ge:H solar cell for application in tandem devices. In this case, only (infra)red light needs to be absorbed, so that the spectrally narrower second-order resonances of a thicker cavity can be employed. The higher cavity thickness allows using thicker doped layers, hence providing more degrees for electrical and optical optimization.

Paper III provides a description of this approach, presents first experimental results on single cells of this type, and investigates the applicability of the concept in a-Si:H/a-Ge:H

tandem solar cells. As expected, for the single junction device a lower short circuit current density is obtained due to the narrower resonance patterns. Nevertheless, the single cell efficiency could be increased to 4% due to an improved fill factor. Integration into tandem devices again requires suppression of coherence on inter-subcell scales, as already described in Paper II. However, the above-mentioned method of using strongly textured substrates is not compatible with long resonators. Instead, ZnO nanorods grown on top of the intermediate reflector were used as scattering elements. These were found to efficiently suppress inter-subcell coherence, while again maintaining the resonances inside the a-Ge:H bottom device. These results demonstrate that the exploitation of second-order resonances in a-Ge:H bottom cells is indeed feasible.

Paper IV thus investigates this concept in greater detail. In particular, the paper presents a study of the dependence of the optical properties of corresponding single junction devices on the exact absorber position inside the resonant cavity, on the resonator length, and on the absorber thickness. It is demonstrated that optimum resonance utilization is always obtained with a centered absorber position. A close relation of simulated and experimental quantum efficiency spectra to the optical field profile inside the cavity is found. By modeling the transmittance of an a-Si:H top cell, it is possible to predict the j_{SC} that these a-Ge:H single junction solar cells can achieve when being integrated in an a-Si:H/a-Ge:H tandem device. By combining this quantity with device characteristics extracted from current-voltage curves, it is estimated that an optimized a-Ge:H solar cell with an only 25 nm thick absorber layer can be used to replace a μ m-thick μ c-Si:H bottom device with a single cell efficiency of about 5%.

Thesis Structure

- Chapter 2 shortly summarizes the state of the art in the scientific fields relevant for this work, allowing a more detailed formulation of the fundamental problems that are addressed.
- Chapter 3 presents the main scientific findings of this thesis, which have been compiled in the form of journal articles.
- In Chapter 4 a conclusion is given, along with a discussion of potential applications for the presented devices and of questions that could be addressed in future works.

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2 State of the Art

2.1 Thin-Film Solar Cells

In *thin-film solar cells*, the goal of reducing PV costs is approached by replacing the crystalline silicon absorber used in conventional solar cells by more cost-effective and highly absorbing materials. Various technologies follow this approach and a short survey of the field is given in the following.

The highest lab-scale thin-film single cell efficiencies up to now are reached using III-V compound semiconductors, such as GaAs $(28.8\%^{[1]})$ and InP $(22.1\%^{[2]})$, followed by devices based on chalcogenides (CdTe, CIGS, both approximately $22\%^{[3]}$). However, these technologies either suffer from high fabrication costs resulting from high temperature fabrication and expensive raw materials (e.g. indium) or contain poisonous materials, such as cadmium. Much effort has been spent on the development of kesterite solar cells (CZTS, CZTSe,CZTSSe), which replace indium and gallium by zinc and tin.^[4] Up to now, efficiencies up to 12.6% have been reached with this technology.^[3,5] However, temperatures above 500 °C are typically required for their fabrication. Low-temperature fabrication is supported by many organic solar cells.^[6] They have the potential to enable very low-cost production, as many of them support solution processing. However, while initial efficiencies up to $13.2\%^{[7]}$ are reached, the technology suffers from various degradation effects.^[8] A similar situation applies to dye sensitized solar cells, in which a few nm thick dye is adsorbed on a mesoporous TiO₂ layer, so that strong absorption is achieved without requiring electrically thick absorber layers.^[9] Efficiencies up to 11.9% have been reached,^[3] but stability against UV light is a major challenge in this case as well.

Recently, a new material class, the so-called perovskites, has drawn great attention due to a rapid efficiency increase to over 20% in only a few years.^[3] Here the absorber is an organic-inorganic compound (typically $CH_3NH_3PbX_3$, where X is a halide) that supports solution-based fabrication. This suggests strong potential for the development of highly efficient low-cost PV devices. However, stability issues again are the main problem of this technology. Furthermore, the use of lead in these devices is considered problematic. Unfortunately, the high efficiency could not yet be maintained when replacing the lead with other materials.^[10,11]

As already stated in Chapter 1, silicon-based thin-film solar cells have the advantage that they contain no highly toxic or scarce materials. They are based on comparably inexpensive processes that are applicable on large scales, allowing low-cost and high-throughput fabrication. As this class of solar cells represented the starting point for the studies presented in this thesis, a more detailed overview of the field is provided in the following section.



Figure 2.1 Sketch of a simple a-Si:H solar cell stack with typical layer thicknesses.

2.2 Silicon Thin-Film Solar Cells

While monocrystalline or polycrystalline silicon is the base-material for conventional solar cells, silicon thin-film technology makes use of its microcrystalline and amorphous states. These materials are much more absorptive due to a reduced long-range structural order, which relaxes momentum conservation for optical transitions.^[12] They can be produced on large areas and at a comparably low temperature of about 200 °C using plasma-enhanced chemical vapour deposition (PECVD).^[13,14] For this reason, not only glass, but also more cost-efficient substrate materials can be used for solar cell deposition, such as flexible aluminium substrates or plastic foil.^[15,16]

A sketch of a typical a-Si:H solar cell is depicted in Figure 2.1. The device consist of an intrinsic a-Si:H layer surrounded by n-doped and p-doped films. A transparent conducting oxide (TCO) serves as the front electrode, through which light enters the device, while the metal serves as a back electrode and back reflector. The intrinsic layer is required because the doped films generally contain a high amount of defect states.^[17] These act as recombination centers, leading to *Shockley-Read-Hall recombination*.^[18] Hence, light absorbed inside these layers is generally considered as lost for current generation. One drawback of a-Si:H is that its electronic properties degrade upon strong illumination. Consequently, this so-called *Staebler-Wronski* effect (or light-induced degradation, *LID*) leads to a reduction of the solar cell efficiency until a certain equilibrium is reached.^[19,20] Hence, despite higher initial efficiencies, maximum stabilized lab-scale efficiencies of only 10.2% have been presented up to now,^[21] with module efficiencies being even lower. However, due to the high optical bandgap of a-Si:H (approximately 1.7 eV), only a small spectral part of incoming sunlight is absorbed, implying a potential efficiency increase when the remaining part is utilized by a second cell.

This has motivated the development of a-Si:H/ μ c-Si:H tandem solar cells and even triple junction devices based on these materials, where advantage is taken of the lower

bandgap of μ c-Si:H (about 1.1 eV) to allow absorption of infrared light.^[15,22–28] On one hand, this increases the amount of incoming light that contributes to the generation of electrical power. On the other hand, thinner a-Si:H top cells can be used in this case, which was found to reduce the impact of LID.^[29] Up to now, a record efficiency of 12.7% has been reached with a-Si:H/ μ c-Si:H tandem devices, and a-Si:H/ μ c-Si:H/ μ c-Si:H triple junction solar cells with 13.6% have been demonstrated.

However, while the absorber of a-Si:H solar cells is typically only about 300 nm thick, 1-3 μ m thick μ c-Si:H absorbers are required in tandem devices due to the lower absorption coefficient of this material. In the triple junction record device, nearly 4 μ m of μ c-Si:H were used.^[28] Of course, this implies a drastic increase in coating costs, while the efficiency is only moderately improved compared to a-Si:H single junction devices. As a result, the module price per Wp is significantly higher for the multijunction concepts.

This problem, which has also motivated the studies conducted in this thesis, was addressed by the research community in two different ways: First, alternative group IV based low-bandgap absorber materials with higher absorption coefficients have been studied. A survey of this field is given in Section 2.3. Second, various light management approaches have been investigated to enable a reduction of the absorber thickness while maintaining overall absorption of the devices. This approach is covered in Section 2.4.

2.3 Alternative Group IV Infrared Absorbers

To increase throughput in the fabrication of silicon thin-film multijunction solar cells, many research groups have focused on alloying the fabricated μ c-Si:H layers with germanium.^[30,31] This is easily achieved by adding a germanium precursor gas, such as germane (GeH₄), to the process chamber during the PECVD process. By changing the flow ratio between the germanium and silicon precursors, the germanium content in the resulting *microcrystalline silicon-germanium* (μ c-SiGe:H) films can be controlled. With increasing germanium content, the absorption coefficient is improved and the bandgap is lowered. Both effects lead to an increase in overall absorption efficiency. As a result, thinner absorber layers can be used to reach a specific short circuit current density (j_{SC}). In particular, solar cells using 1 μ m thick μ c-SiGe:H absorbers with 20% Ge content were demonstrated, which showed higher infrared response than corresponding 2 μ m thick μ c-Si:H cells.^[30]

However, the electronic material properties severely degrade with increasing germanium content, particularly for values higher than 20%. This is related to a faster incorporation of germanium into the film, leading to inhomogeneous film growth due to the formation of amorphous islands.^[31] At the same time, much higher germanium content would be required to reduce the absorber thickness to values comparable to a-Si:H top cells. This would lead to a large drop in open circuit voltage (V_{OC}) not only due to the deterioration of film properties but also as a result of the much lower bandgap. Hence, the potential for thickness reduction is strongly limited for this material class.



Figure 2.2 Absorption coefficient of a-Ge:H and μ c-Si:H. Data for a-Ge:H were taken from Drüsedau et. al.^[34]

The application of *amorphous silicon-germanium alloys (a-SiGe:H)* in tandem cells has also been investigated. ^[32,33] Again, starting with pristine a-Si:H, the incorporation of germanium improves the absorption coefficient and leads to a reduction of the bandgap. While in case of μ c-SiGe:H the increase of the absorption coefficient is the more important effect, the lower bandgap is desired in case of a-SiGe:H, so that the absorbed spectral range can be extended into the infrared part. However, similarly to μ c-SiGe:H, the electronic properties are strongly degraded with increasing germanium content. Hence, the amount of germanium that can be added without drastically deteriorating the device properties of corresponding solar cells is again limited. For this reason, a-SiGe:H is mainly investigated as absorber material for the middle cell in triple junction structures. To obtain material with an optical bandgap similar to μ c-Si:H, a germanium content near 100% is needed.

In fact, *pristine amorphous germanium* (*a*-*Ge*:*H*) has already early been proposed as potential low bandgap absorber for application in a-Si:H-based tandem solar cells.^[35–40] As depicted in Figure 2.2, the absorption coefficient of this material is higher by up to nearly two orders of magnitude compared to μ c-Si:H. At the same time, the optical bandgaps of both materials are similar, meaning that the same spectral range is absorbed.^[22,34] From this perspective, a-Ge:H is a highly promising alternative low-bandgap absorber material, capable to enable strong absorption in the near infrared with much thinner layers compared to μ c-Si:H. However, in view of the findings obtained for a-SiGe:H layers with high germanium content, it is not surprising that the best a-Ge:H layers demonstrated up to now still exhibit unfavorable electronic properties. Despite several studies trying to improve the material, the lowest defect densities reached so far are approximately ten times higher with respect to a-Si:H (i.e. > 10¹⁶ cm⁻³).^[34,41-43] Different deposition methods were investigated to improve the material quality, with sputtering and PECVD being the most widely studied ones.^[35,37,38,41,42,44-52] It turned out that techniques lead-

ing to a high ion bombardment of the growing films yielded the best material properties (e.g. remote ECR-PECVD, cathodic PECVD, sputtering), whereas lower ion bombardment, as typical for anodic PECVD, leads to inhomogeneous films with a high fraction of voids and high defect densities. In particular, a direct comparison of cathodic and anodic PECVD in the same reactor yielded an up to ten times higher photoconductivity in the cathodic case.^[53] Here the terms *anodic* and *cathodic* PECVD refer to a placement of the substrate on the grounded or powered electrode of the reactor, respectively. For the a-Ge:H films fabricated in the framework of this thesis, anodic PECVD has been used.

When comparing a-Ge:H with a-Si:H, the impact of defects on recombination is even worse in a-Ge:H, as its narrower bandgap results in a lower energetic distance of the defect states to the bands, implying higher transition probabilities. Indeed, poor solar cell performance is generally obtained, ^[36,54,55] the highest efficiency demonstrated for a-Ge:H solar cells until recently was about 3.5%, ^[54] which was achieved with an approximately 100 nm thick absorber layer. Hence, the material today is widely considered as unsuitable for PV application.

However, nearly all of the research studies dealing with a-Ge:H aimed to improve the electronic properties of this material, while only few studies directly investigated its behaviour in solar cells. During the course of this thesis, a different route was pursued. Instead of improving the material properties of a-Ge:H to enhance the extraction of photogenerated charge carriers, this work investigates the possibility to use drastically lower absorber thicknesses in the range of typically 10-25 nm to achieve this goal. Of course, this is only reasonable if strong absorption can be maintained in such thin layers. To achieve this, a highly efficient *light management* concept is required.

2.4 Light Management

In thin-film solar cells there is typically a trade-off between efficient absorption and efficient charge carrier extraction. This has motivated a vast number of research studies that deal with so-called *light-management* schemes, which aim to improve the absorption in thin films without the need to increase their thickness.^[56]

Many of these approaches aim to elongate the pathway that light traverses through the absorber by introducing rough interfaces. Here, feature sizes that are small compared to the relevant wavelengths of light have the additional advantage that they reduce reflection losses. This can be described by effective medium theory.^[57] In silicon thin-film solar cells, glass sheets coated with a transparent conducting oxide (TCO) film are widely used as substrates, so that a rough texture is typically imposed on this layer. In this case, wet-chemical edging is a widespread texturing method, ^[58,59] which can also be combined with plasma-assisted techniques to improve control over the surface morphology (e.g. to generate smoother edges).^[60] Furthermore, several TCO deposition techniques, such as low-pressure chemical vapor deposition (LPCVD), directly create a rough morphology already.^[61–65] Particularly interesting are the electrochemical and chemical bath deposition (ECD, CBD) of ZnO. These methods allow direct growth of nanostructures, such

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as nanorods.^[66–68] ECD-grown ZnO nanorods were utilized in this thesis to provide a scattering mechanism between the subcells of a-Si:H/a-Ge:H tandem devices (see Papers III and IV). More defined structures can be made with ECD in combination with a nanoparticle mask. For example, so-called honeycomb structures have been produced, allowing the fabrication of convoluted absorber layers.^[69] These provide a high absorber volume but are electrically thin, thus enabling efficient charge carrier extraction. Instead of texturing the TCO, it is also possible to generate a rough structure directly on glass, for example by using a laser.^[70] This has the advantage that parasitic absorption can be avoided by using very thin TCO layers on top of the textured glass.

While the above concepts mainly rely on a geometrical elongation of the distance that light covers inside the absorber layer, there are also various light management approaches that take advantage of optical resonances instead. Here, an increased electrical field strength inside the absorber is typically the underlying mechanism that enables improved absorption, but resonance-induced scattering can also be exploited. Recently, such concepts have been widely investigated due to great advances in the field of nanotechnology. For example, whispering gallery modes, ^[71–73] Mie resonances, ^[74,75] grating structures, ^[76–79] and photonic crystals ^[80,81] have been studied for this purpose. Many research groups have particularly focused on metallic nanoparticles and grating structures either as scattering elements or with the aim to exploit plasmonic resonances. ^[78,82–90] However, while many of these techniques enable significant absorption improvements, their implementation often requires elaborate multidimensional structuring steps, which hinders a cost-effective large-scale fabrication.

In contrast, planar optical resonators producing Fabry-Pérot resonances are well understood and can be fabricated using off-the-shelf deposition techniques, as they only rely on planar layers having different refractive indices.^[91] In solar cells, these resonators are mainly used in the form of anti-reflective coatings (ARC).^[92,93] Light waves impinging on the ARC are partially reflected at both of its interfaces due to a refractive index difference. The thickness of the coating is chosen so that destructive interference of the resulting partial waves suppresses the overall reflectivity of the layer stack. Generally, the refractive index n_{ARC} of the ARC is lower than that of the solar cell, and all layers can be treated as dielectrics. In this case, possible coating thicknesses leading to anti-reflective properties at wavelength λ are

$$d_{\rm ARC} = \lambda / (4n_{\rm ARC}) + N\lambda / (2n_{\rm ARC}), \qquad (2.1)$$

with $N \ge 0$ being an integer number that describes the resonance order.

Typically, only lowest-order Fabry-Pérot resonances are exploited in solar cells, as broadband absorption is required in these devices, while higher-order resonances lead to spectrally narrow interference patterns. For the case of ARCs, this means that so-called quarter wavelength coatings are widely used (N = 0 in equation 2.1).

Interestingly, the conditions for antireflective properties at the same time lead to a resonant field-enhancement inside the coating. Hence, instead of a transparent ARC, an absorbing material can also be used, together with a highly reflective layer on its back

side. In this case, the high optical fields generated as a result of the resonances lead to a strong absorption enhancement. Such absorptive resonant cavities are widely used in optoelectronic devices where a high degree of spectral selectivity is acceptable or even desired, as for example in photodetectors.^[94–97] However, as stated before, in solar cells only thin cavities supporting broadband resonances can be exploited in a meaningful way. Most semiconductors do not provide sufficient single-pass absorption when using the low film thicknesses required in this case. Hence, in photovoltaic devices, absorptive Fabry-Pérot resonators are only beneficial in combination with materials exhibiting very high absorption coefficients. Apart from the devices presented in this work, this approach has only been demonstrated in solar cells with organic absorber materials.^[98]

As the absorption coefficient of a-Ge:H is even higher compared to most organic absorbers, it is a very promising candidate for application of this scheme. Indeed it has been shown that this material even enables the use of a special form of Fabry-Pérot cavities, which allows using particularly low resonator lengths significantly below $\lambda/4n$. This approach, which will be referred to as the *nanocavity approach* throughout this work, is easily implemented by using a lossy metal as the back reflector of the resonator. This way, a particularly strong and broadband absorption enhancement with low sensitivity to angle of incidence variations is obtained. Strong absorption in only about 10 nm thick germanium films has been demonstrated.^[99–101] Tin monosulfide (SnS_x) layers have also been shown to support this concept.^[102] Additional control over the reflection phase shifts can be obtained using metamaterial mirrors instead of planar metal reflectors, ^[103,104] yielding a powerful method to further optimize the properties of such *nanocavities*. A detailed description of the underlying mechanisms of the *nanocavity* approach is provided in Paper I as well as in literature and shall not be reiterated here.

The above considerations indicate that planar resonant cavities could enable a tremendous absorber thickness reduction in a-Ge:H solar cells. From this, a strong improvement of the charge carrier extraction probability is expected. This route is pursued in the framework of this thesis. The *nanocavity approach* is particularly promising for this purpose due to the broadband absorption enhancement and the particularly low absorber thicknesses it enables. However, an alternative approach based on second-order resonances is investigated additionally. Particular attention is paid to the question whether and how the investigated concepts can be integrated in multijunction solar cells.

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3 Publications submitted in the Framework of this Thesis

Author Contributions

In the following, my personal contribution to each publication compiled in the framework of this thesis is stated:

Paper I

Title: Ultrathin Resonant-Cavity-Enhanced Solar Cells with Amorphous Germanium Absorbers Authors: Volker Steenhoff, Martin Theuring, Martin Vehse, Karsten von Maydell and Carsten Agert Published in: Advanced Optical Materials 3, 182 (2015) DOI: 10.1002/adom.201400386

Contribution: Idea, calculations/simulations, sample fabrication (except silver back contacts and laser scribing), QE- and jV-measurements, data analysis, main author of manuscript

Paper II

Title: Integration of a-Ge:H Nanocavity Solar Cells in Tandem Devices Authors: Volker Steenhoff, Alex Neumüller, Oleg Sergeev, Martin Vehse and Carsten Agert Published in: Solar Energy Materials And Solar Cells 145, 148 (2016) DOI: 10.1016/j.solmat.2015.07.032

Contribution: Idea, simulations, sample fabrication (except top cells, a-Si:H single cell, silver back contacts and laser scribing), QE-measurements, data analysis, main author of manuscript

Paper III

Title: Resonant Cavity Enhanced a-Ge:H Nanoabsorber Solar Cells for Application in Multijunction Devices

Authors: Volker Steenhoff, Maren Juilfs, Regina-Elisabeth Ravekes, Martin Vehse, Carsten Agert Published in: Nano Energy 27, 658 (2016)

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Paper IV

Title: Optimized Optical Field Profile in Resonant-Cavity-Enhanced a-Ge:H Nanoabsorber Solar Cells for Tandem Cell Application

Authors: Volker Steenhoff, Maren Juilfs, Regina-Elisabeth Ravekes, Maike Ahrlich, Martin Kellermann, Ortwin Siepmann, Martin Vehse, Carsten Agert

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Paper I: Ultrathin Resonant-Cavity-Enhanced Solar Cells with Amorphous Germanium Absorbers

Volker Steenhoff, Martin Theuring, Martin Vehse, Karsten von Maydell and Carsten Agert

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Abstract

Ultrathin 1D optical cavities enable strong and spectrally broad absorption in solar cells. This approach requires highly absorptive materials as well as tailoring of the phase shifts induced by the resonator interfaces. A current density of 20 mA cm⁻² is obtained using an amorphous germanium absorber with a thickness of only 13 nm.

Reduction of fabrication costs is one of the major challenges to promote the mass adoption of solar cells. In thin-film photovoltaics, materials with much higher absorption coefficients compared with crystalline silicon are employed to allow using thinner absorber layers. Apart from decreasing material consumption and deposition time, lower absorber thickness eases material quality constraints and hence allows using more cost-effective materials and fabrication methods. To improve absorption and enable further thickness reduction, numerous light-trapping schemes have been developed in the past. While the use of randomly textured interfaces represents a highly efficient and cost-effective approach that has proven useful on an industrial scale,^[1–3] the fundamental limits of this simple approach also motivated the investigation of more sophisticated concepts in the recent years.^[4–11] However, most of these techniques have not been proven experimentally or require complex multidimensional structuring steps hindering cost-efficient large-scale integration.

In this work, we show that 1D absorbing optical resonators can serve as an efficient light-trapping concept in solar cells based on highly absorbing materials. This approach allows large-scale fabrication using off-the-shelf processes, as it does not involve complex fabrication steps and is already used in various other types of photonic devices (e.g., photodetectors, LEDs, lasers).^[12]

The optical length of a resonant cavity determines the position and spectral width of the associated interference peaks, with higher thickness leading to narrower interference patterns. Absorbing resonant cavities are thus typically employed in cases where a high degree of spectral selectivity is acceptable or even desired. In contrast, broadband absorption is required in photovoltaic devices, meaning that the absorption minima produced by long resonators generally have a detrimental effect on the power conversion efficiency of such devices. However, broadband absorption enhancement can be obtained by taking advantage of the lowest-order absorption maximum of an ultrathin cavity. In this case, the phase shifts occurring for light reflected at the surfaces of the resonator strongly influence the spectral position and spectral width of the interference patterns. Kats et al.^[13] recently suggested that this effect might help improving the absorption in solar cells.

The authors obtained strong and spectrally broad absorption in ultrathin (<25 nm) germanium films on gold substrates due to the characteristic phase shifts induced by metals. Esfandyarpour et al.^[14] have recently used a similar mechanism based on a metamaterial mirror to optimize the position of standing waves inside an organic solar cell. However, resonators with deep subwavelength dimensions, as required to obtain the spectrally broad enhancement reported by Kats et al.,^[13] were not subject of their work. It is still unclear how all the additional films, required for electrical functionality of solar cells (e.g., doped layers, electrodes, absorber), can be integrated into a cavity having such dimensions.

We answer this question by demonstrating the first thin-film solar cell taking advantage of the described effect. Specifically, we apply the concept to the case of amorphous germanium (a-Ge:H) solar cells. A short summary is given on how the phase shifts influence the resonance conditions in our particular solar cell stack. 1D optical simulations are carried out for thickness optimization and potential evaluation. A device with an absorber thickness of only 13 nm was fabricated, showing a remarkable short-circuit current density of 20 mA cm⁻² and strong response in the infrared part of the spectrum.

As stated above, the phase shifts play an important role in our solar cell design. Absorption enhancement is achieved in cases where a total phase difference of π arises between two incident waves reflected at the first and second mirror of the cavity, respectively. Both partial waves may undergo different phase shifts upon reflection (ϕ_1 and ϕ_2 , respectively), and the difference $\Delta \phi = \phi_2 - \phi_1$ directly contributes to the total phase difference. Restricting our calculations to $-\pi \leq \Delta \phi < \pi$, this leads to a required resonator length $d_{\max} = (\pi - \Delta \phi) \lambda_{\max}/(4\pi n)$ to obtain a lowest order maximum near wavelength λ_{\max} , where *n* is the real part of the refractive index of the absorber material. Similar arguments lead to $d_{\min} = (2\pi - \Delta \phi) \lambda_{\min}/(4\pi n)$ for the lowest order minimum. As ϕ_1 and ϕ_2 are not necessarily equal to 0 or π for nonperfect materials, $\Delta \phi$ can take arbitrary values.

Thus, d_{max} can be reduced by adjusting $\Delta\phi$ to approach (but not reach) π . At the same time, the ratio $\lambda_{\min}/\lambda_{\max} = (\pi - \Delta\phi)/(2\pi - \Delta\phi)$ (calculated for fixed d and neglecting dispersion) indicates that a broadening of the interference patterns is obtained in this case. The above ratio also evidences a reduced sensitivity of the resonance conditions to angle of incidence variations and surface roughness, as a non-normal incidence can be described by a reduced wave vector in normal direction, translating to an increased wavelength in our formulas. This effect has also been observed experimentally by Kats et al.^[13].

Of course, the absorber needs to provide sufficient single pass absorption at the low thicknesses required here. For example, experimental results by Kempa et al.^[15] on hot electron extraction in ultrathin amorphous silicon (a-Si:H) solar cells seem to be strongly influenced by the resonance effects described here. However, the current density reached under resonance conditions in this cell stays far below the values that are achieved in standard a-Si:H devices, as the absorption coefficient of this material is not sufficient for

application of the ultrathin resonant cavity approach. Assuming a reflection coefficient of about 0.25 at the front mirror and nearly total reflection at the back reflector, results presented by Ünlü et al.^[12] can be used to estimate that the product $\alpha \cdot d$ is required to be greater than ≈ 0.25 to obtain a maximum quantum efficiency of at least 0.7, where α and d are the absorption coefficient and thickness of the absorber, respectively. Substituting d by d_{\max} and using $\Delta \phi = 0$, a rule of thumb estimating the minimum requirements on the absorption coefficient can be deduced, reading $\alpha > n/\lambda_{\max}$.

We choose a-Ge:H as absorber material, as it meets this rule for wavelengths below \approx 900 nm already, which corresponds to photon energies only slightly above its bandgap of \approx 1.1 eV.^[16] The low bandgap and high absorption coefficient of up to 10⁶ cm⁻¹ make a-Ge:H an ideal candidate for application as bottom cell absorber in multijunction solar cells. In particular, it could replace the micron-thick microcrystalline silicon (µc-Si:H) absorber layers that are commonly used in silicon thin-film solar cells. However, the high defect density in state-of-the-art a-Ge:H (> 10¹⁶ cm⁻³) leads to poor electrical properties, ^[16–20] up to now allowing for a maximum photovoltaic power conversion efficiency of \approx 3.5% only.^[21] Thus, solar cells based on this material may significantly benefit from the substantial absorber thickness reduction associated with the presented concept.

The cell design under simulative investigation is depicted in Figure 1a. Microcrystalline silicon, which has a lower absorption coefficient than germanium, was chosen for the pand n-doped layers. This was done to avoid parasitic absorption in these layers, as light absorbed in heavily doped films is generally considered as loss due to an increased defect density.^[22] A transparent conductive oxide (TCO) layer (80 nm) and a silver layer are employed as front contact and back contact, respectively (see Experimental Section). As silicon and germanium exhibit similar refractive indices in the relevant spectral range, ^[16,23] reflections at the interface between both materials can be neglected for our considerations. In contrast, the low refractive index of most TCOs compared with silicon leads to strong reflection of incident waves at the TCO/silicon interface.^[24,25] Hence, this interface forms the first (semitransparent) mirror of the resonator, while the highly reflecting surface of the silver back contact represents the second one.

Figure 1b shows calculation results for the corresponding phase shifts ϕ_1 and ϕ_2 . The TCO/silicon interface introduces a phase shift close to π for the most part of the relevant wavelength range, while pronounced deviation from the case of a perfect metal reflector occurs at the silver surface. This characteristic phase shift ultimately leads to values of $\Delta\phi$ between 0.3π and 0.9π . Depending on the desired resonant wavelength, this reduces the required cavity length by 30%-90% compared with the case of perfect metals and corresponds to a value of $\lambda_{\min}/\lambda_{\max}$ between 0.1 and 0.4. Hence, a strong broadening of the associated interference patterns can be obtained.

From the above results, the required absorber thickness as a function of λ_{max} can be deduced, which is depicted in Figure 1c. Results are shown with and without using doped layers. The graph reveals that an absorber thickness below \approx 45 nm is required to take advantage of the lowest order maximum, keeping in mind that only photons with energies above the bandgap of a-Ge:H (corresponding to \approx 1100 nm in wavelength) are absorbed. With doped layers that are 5 or 10 nm in thickness each, absorber thickness values well below \approx 35 or \approx 30 nm are required, respectively. For example, to achieve a λ_{max} of \approx 800 nm, an only 10-15 nm thick a-Ge:H layer is sufficient.

While the above calculations help understanding the idea of our work and provide a



Figure 1 Simulation results: **a)** Simulated solar cell stack. **b)** Phase shifts ϕ_1 and ϕ_2 and $\Delta \phi = \phi_2 - \phi_1$ for light reflected at front and back contact, respectively. **c)** Absorber thickness required to obtain resonance maximum at wavelength λ_{max} . **d)** EQE spectra for cases highlighted in (c); both coherent and incoherent simulation is shown for $d_{Ge} = 15$ nm. **e)** Short-circuit current density as function of absorber thickness.

rough estimate of the relevant absorber thickness range, no information on the total absorption can be deduced. To evaluate the potential of our cell design, we performed coherent 1D optical simulations of external quantum efficiency (EQE) spectra, which are presented in Figure 1d. Here, the doped layers were 5 nm in thickness each, which we consider as the minimum required for electrical functionality of the device. The results reveal that indeed an only 15 nm thick a-Ge:H absorber suffices to obtain an EQE of \approx 80% in the wavelength range between 500 and 800 nm. For comparison, an incoherent simulation is shown, emphasizing the strong and spectrally broad absorption enhancement occurring for the coherent case. As expected, a redshift of the EQE spectra is observed with increasing absorber thickness. The resonance positions, while not clearly visible due to their large spectral bandwidth, follow the same trend as predicted by the calculations presented in Figure 1c.

To find the optimum absorber thickness, EQE simulations were performed for a wide thickness range. Short-circuit current densities (j_{SC}) were deduced from the results and are depicted in Figure 1e, showing a maximum of 25 mA cm⁻² at 15 nm absorber thickness. Incoherent simulation results, which are more realistic for thick absorbers, reveal that j_{SC} saturates at thicknesses around 1 μ m showing a value of 32 mA cm⁻². This means that 80% of the maximum reachable current is attainable with an only 15 nm thick absorber already. At least 80 nm would be required to attain a higher value than in the resonant case.

Following these encouraging simulation results, we realized this type of a-Ge:H solar cells experimentally. Figure 2a shows a photograph of a typical sample, demonstrating the transparency of the active layers without the influence of the optical cavity (i.e.,



Figure 2 Experimental results: **a)** Photograph of a typical a-Ge:H solar cell sample (picture taken from the front glass/TCO side, illuminated from the same side; dark squares are due to the 1×1 cm² silver back reflectors). **b)** External quantum efficiency spectrum of a fabricated a-Ge:H solar cell with a 13 nm thick absorber layer (simulated and measured at -0.2 V reverse bias) and **c)** corresponding jV-curve and device characteristics.

without back reflector), while strong absorption is obtained at positions where a back reflector is present.

Compared with the optically optimized stack presented in Figure 1a, some modifications were made for electrical optimization of the device (see also Experimental Section): Undoped silicon buffer layers (5 nm) were required between the doped layers (5 nm) and the a-Ge:H absorber layer (13 nm), which is in line with the results presented by Zhu et al.^[21] The absorber thickness was slightly reduced to partly counter the influence of the thicker silicon layers on the resonance position. To reduce series resistance, a thick TCO layer was employed as front contact instead of using the optically optimized thickness.

These modifications have a slightly negative impact on the EQE of the cell (Figure 2b) due to the lower absorber thickness, additional parasitic absorption in the TCO, and a nonoptimal resonance position. However, a high response in the infrared spectrum is still achieved, similar to micron-thick μ c-Si:H solar cells employing sophisticated light-trapping concepts.^[26] A saturation current density of 20 mA cm⁻² is deduced from the experimental EQE. This is comparable to the highest j_{SC} reported for a-Ge:H solar cells to date (20.6 mA cm⁻²),^[27] while the absorber thickness in our device is thinner by a factor of five.

To validate our simulation model, the experimental curve is complemented by a revised simulation result accounting for the modifications used in the experimental stack. The interference fringes observed in the simulated curve are due to cavity resonances inside the TCO layer and are strongly flattened in the experimental case due to the nonvanishing roughness of the substrate. Apart from that, a good match between both curves can be found, indicating that the surface roughness indeed does not impede the effect of the ultrathin cavity.

The *jV* curve and device characteristics of the best sample are presented in Figure 2c. A power conversion efficiency of up to 3.6% was reached, which is in the same range as Zhu et al.^[21] reported for cells with more than 100 nm thick a-Ge:H absorbers. However, V_{OC} (373 mV) and fill factor (48%) are low compared with their results (470 mV, 55%), indicating a higher defect density in our a-Ge:H films.

In summary, we were able to demonstrate that 1D optical cavities can be employed as efficient light-trapping concept in thin-film solar cells. While the approach imposes strong limitations on the optical properties of the involved materials, its application to a-Ge:H

solar cells allowed us to reach a j_{SC} of 20 mA cm⁻² with an only 13 nm thick absorber layer. From the lower V_{OC} of the device compared with previous reports we conclude that the accomplished power conversion efficiency of 3.6% can be further improved by optimizing the material quality of the absorber. Furthermore, due to the compatibility of the presented concept with rough surfaces, j_{SC} could possibly be further improved by employing TCO substrates with higher surface roughness.

The high infrared response makes the proposed design an ideal solution for bottom cells in multijunction solar cells. Systematic tailoring of the phase shifts at the cavity surfaces as performed by Esfandyarpour et al.^[14] provides an interesting instrument to adjust the optical properties of the device to this use case. For example, the resonator could be tuned to achieve selective reflection of short wavelength light back into the corresponding top cell. Apart from the particular case of a-Ge:H, photovoltaic devices and photodetectors based on other materials might also benefit from the approach presented here. The substantial thickness reduction, possible due to the resonant cavity configuration, can significantly ease restrictions on the electrical properties of the absorber material. More precisely, materials with very low charge carrier mobility-lifetime products can be employed if the absorption coefficient meets the requirements deduced in this communication. Therefore, our results provide a way to extend the range of low-cost materials available for optoelectronic applications.

Experimental Section

Simulation

Complex refractive index data were taken from literature (a-Ge:H^[16] and silver^[28]) or were obtained by ellipsometric spectroscopy and subsequent modeling of the measured spectra (ZnO:Al, SnO₂:F, and μ c-Si:H), respectively. These data were used to calculate the complex phase of the Fresnel coefficients, yielding the phase shifts visualized in Figure 1b. Required absorber thickness d_{max} as function of the desired resonant wavelength (Figure 1c) was obtained as described in the main text but was reduced by $2d_{dop}n_{dop}/n_{Ge}$ to include contributions of the doped layers (n_{dop} and n_{Ge} are refractive indices of μ c-Si:H and a-Ge:H, respectively, d_{dop} is the thickness of the doped layers (see Figure 1a)). EQE spectra (Figure 1d) were calculated by simulating absorption spectra of the undoped layers using the software Scout/Code (by W. Theiss Hard- and Software) and assuming full charge carrier extraction. An 80 nm thick ZnO:Al front contact was used for the simulations, except for the result presented in Figure 2b, where the simulation was configured to match the experiment (see below). Short-circuit current density (Figure 1e) was calculated from the simulated EQE spectra by convolution with the standard AM1.5g spectrum.

Solar Cell Fabrication

In contrast to a flat 80 nm thick ZnO:Al layer used for the simulation study, a commercially available glass/SnO₂:F substrate ($10 \times 10 \text{ cm}^2$, $\approx 600 \text{ nm} \text{ SnO}_2$:F layer thickness, RMS surface roughness of 37 nm) from NSG (Nippon Sheet Glass Co., Ltd.) was used for our experiments. Silicon and germanium layers were deposited on this substrate
using the grounded electrode of a parallel-plate plasma-enhanced chemical vapor deposition (PECVD) reactor (FAP Forschungs- und Applikationslabor Plasmatechnik GmbH Dresden, 13.56 Mhz frequency, integrated in a cluster tool type CS400PS, Von Ardenne GmbH Dresden). H₂-diluted GeH₄ and SiH₄ were used as precursor gases for germanium and silicon deposition, respectively. B₂H₆ and PH₃ were added to achieve p- and n-doping of the silicon layers, respectively. In contrast to the cell stack presented in Figure 1a, amorphous silicon was used instead of μ c-Si:H for the doped layers to obtain higher V_{OC}. A silver back contact (\approx 150 nm) was deposited by electron beam evaporation. Laser scribing was used to separate 1 × 1 cm² cells. For the sample depicted in Figure 2a, a mask was used during silver deposition instead. Finally, the samples were annealed at 130 °C for 30 min.

Solar Cell Characterization

EQE spectra were determined from differential spectral response measurements using a reverse bias voltage of 0.2 V to ensure full charge carrier extraction. Illuminated jV-curves were measured under standard test conditions using a WACOM dual lamp solar simulator.

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Paper II: Integration of a-Ge:H Nanocavity Solar Cells in Tandem Devices

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Abstract

By taking advantage of spectrally broad resonances, nanocavity enhanced a-Ge:H solar cells with an absorber layer thickness below 20 nm can reach current densities similar to micron thick μ c-Si:H devices. However, as nanocavity enhanced devices are highly reliant on interference effects, further spectrally narrow resonance patterns are generated if an additional top cell is added to form a multijunction solar cell. This may complicate the integration of a-Ge:H nanocavity solar cells in tandem devices. We show that conventionally textured TCO substrates can be employed to suppress the top cell induced interferences, while the required broadband resonance of the a-Ge:H bottom cell nanocavity is maintained. This approach is realized in an a-Si:H/a-Ge:H tandem solar cell with an only 20 nm thick a-Ge:H bottom cell absorber. The spectrally broad quantum efficiency curve of the bottom cell corresponds to a photocurrent density of 12.3 mA cm⁻², which is comparable to values reached in micromorph devices.

Introduction

Silicon thin-film solar cells feature several advantages over other commercially available solar cell technologies. They are based on environment-friendly and abundant materials, and can be fabricated with comparably low energy consumption. Low film thicknesses and low deposition temperatures allow their fabrication on flexible and lightweight substrates^[1], suggesting high potential for cost reduction on the module level as well as for use in special applications such as lightweight construction roofs. To increase the efficiency of the silicon thin-film solar cell technology, tandem devices have been developed over the last twenty years which consist of an amorphous silicon (a-Si:H) top cell and a microcrystalline silicon (μ c-Si:H) bottom cell^[1,2]. This way, the lower thermalization losses of the a-Si:H top cell for short wavelength light can be combined with the ability of μ c-Si:H to absorb light having longer wavelengths. However, to match the current densities of both sub cells, more than 1 μ m thick μ c-Si:H bottom cells are typically required, while the top cell has a thickness of only about 300 nm. Hence, while the gain in cell efficiency is moderate compared to an a-Si:H single cell (12.7% vs. 10.2%^[3]), prolonged deposition time leads to significantly increased fabrication costs.

To address this issue, microcrystalline silicon germanium alloys (μ c-SiGe:H) have been investigated as alternative low bandgap absorbers^[4,5]. Alloying germanium to silicon increases the absorption coefficient and lowers the bandgap of the material. Unfortunately, the electronic properties strongly degrade with increasing germanium content, implying a rather limited potential for use in electro-optical devices. Although amorphous silicon germanium alloys (a-SiGe:H) have also been studied as replacement of the μ c-Si:H solar cells^[6,7], a germanium content close to 100% is required to take advantage of the same</sup>spectral range as in μ c-Si:H solar cells. In fact, pristine amorphous germanium (a-Ge:H) of highest electronic quality exhibits an optical bandgap of about 1.1 eV, which is very similar to the mobility bandgap of µc-Si:H. On the other hand, this material suffers from an approximately ten times higher defect density compared to a-Si:H^[8,9]. For this reason, solar cells using 100 nm thick high quality a-Ge:H absorber layers have reached efficiencies of only about 3.5%, up to now^[10]. Hence, it is helpful to reduce the absorber thickness to a few tens of nanometers to enable an efficient charge carrier collection. However, for such thin layers, efficient light absorption can only be achieved by applying a highly efficient light trapping concept.

As we have recently demonstrated, light-trapping can be addressed by using a Fabry-Pérot resonator to enhance the absorption of photons with energies slightly above the absorber bandgap^[11]. Such nanocavities have drawn attention due to their ability to produce strong and spectrally broad interference patterns^[12–14]. Depending on the phase jumps that light undergoes when it is reflected at the resonator surfaces, the required optical cavity length can be much lower than 1/4 of the wavelength for which resonant enhancement is desired. This leads to spectrally broad resonances rather than narrow interference patterns. Together with the exceptionally high absorption coefficient of a-Ge:H, this enables a current density of 20 mAcm⁻² in an a-Ge:H solar cell with an only 13 nm thick absorber layer^[11]. Although the cell efficiency has not been increased significantly compared to the best results reported by Zhu et al.^[10], a value of 3.6% has been reached with absorber material of lower quality. Apart from the particular case of a-Ge:H solar cells, this concept is also interesting for devices based on other highly absorbing materials which exhibit low charge carrier mobility lifetime products.

In view of the goal to replace the μ c-Si:H absorber in a-Si:H/ μ c-Si:H solar cells, the question arises of how such nanocavity-enhanced solar cells can be integrated into multijunction concepts. We use 1-dimensional optical simulations of an a-Si:H/a-Ge:H tandem device to show that additional top cell induced resonances strongly modify the infrared absorption of the bottom device compared to the single cell result. An approach to solve this problem is discussed and implemented in first a-Si:H/a-Ge:H tandem solar cells.

Methods

Simulation

One-dimensional optical simulations have been performed in order to calculate quantum efficiency (QE) spectra of single and tandem solar cells. Calculations were carried out using the software package Scout/Code (W. Theiss Hard- and Software). Complex refractive index data were taken from literature (a-Ge:H^[8] and silver^[15]) or were obtained by ellipsometric spectroscopy and subsequent modeling of the measured spectra (a-Si:H,

 μ c-Si:H), respectively. For ZnO, data were taken from the database provided with Scout/Code. Quantum efficiency (QE) spectra were calculated by simulating absorption spectra of the absorber layers (i.e. only for the a-Ge:H layer of the a-Ge:H cell) and assuming full charge carrier extraction. Short circuit current densities were afterwards calculated from these spectra by convolution with the AM1.5g spectrum.

Experimental

Glass/ZnO:Al substrates (size: 10×10 cm²) with an RMS surface roughness of 50 nm and 120 nm, respectively, have been used for our tandem cell experiments (high surface roughness has been achieved using wet chemical etching^[16]). Silicon and germanium layers were deposited onto these substrates using the grounded electrode of a parallelplate plasma-enhanced chemical vapor deposition (PECVD) reactor which was operated at a frequency of 13.56 Mhz. H_2 -diluted GeH₄ and SiH₄ were used as precursor gases for germanium and silicon deposition, respectively. B_2H_6 and PH_3 were added to achieve p- and n-doping of the silicon layers, respectively. All silicon layers were produced at a temperature of 200°C. For top cell depositions, a H_2/SiH_4 ratio of 20, a pressure of 3 Torr and an rf power density of 30 mW cm⁻² was used in all layers. The amorphous silicon layers of the bottom cell were fabricated at a H2/SiH4 ratio of 5, pressure of 0.75 Torr and an rf power density of 30 mW cm⁻². For μ c-Si:H deposition, we used a H2/SiH₄ ratio of 500, 150 mW cm⁻² rf power density and a pressure of 2.25 Torr. For a general overview on the properties and fabrication of a-Si:H and µc-Si:H layers, we refer the reader to $^{[17]}$. Germanium layers were fabricated at a substrate temperature of approximately 160°C at a pressure of 0.6 Torr, 16 mm electrode distance and an RF power density of 500 mW cm⁻². A H2/GeH₄ ratio of 40 was used. While deposition rates near 1 nm s⁻¹ are achieved in our standard process, we have reduced the rate to approximately 0.1 nm s⁻¹ by pulsing the plasma with a duty cycle of 10% at 3 kHz. This was done to decrease the impact of the plasma ignition phase on the absorber thickness. The PECVD deposition of all a-Ge:H bottom cells was carried out in a multi-chamber cluster tool (type CS400PS, Von Ardenne Anlagentechnik GmbH). The top cells were fabricated using a PECVD in-line tool from Leybold Optics.

After deposition of the a-Si:H top cells, ZnO:Al intermediate reflectors were fabricated in a DC magnetron sputtering system (Von Ardenne Anlagentechnik GmbH, Al concentration 2 wt%) at a chamber temperature of 200°C without preheating. This was followed by a 30 minutes annealing step under ambient conditions at 160°C and subsequent fabrication of the bottom cell stack using PECVD. Finally, silver back contacts (\approx 150 nm) were deposited by electron beam evaporation through a 1 × 1 cm² mask, followed by a second annealing step at 130°C for 15 hours. The front contacts were uncovered by using laser ablation. Quantum efficiency (QE) spectra were determined from differential spectral response measurements. For the tandem devices, blue or infrared bias light as well as a voltage bias was applied to measure the bottom cell and top cell, respectively. As the focus of our work is to align the optical effects in nanocavity enhanced solar cells with the concept of multijunction devices, the applied voltage bias was chosen separately for each sub cell (and also for the single junction device) to maximize the charge carrier extraction. Hence, all QE curves yield information on the charge carrier generation efficiency rather than the external quantum efficiency under



Figure 1 a) Simplified sketch of a nanocavity a-Ge:H solar cell. The given thickness values represent the cell stacks used for the absorption simulation presented in b).

short circuit conditions.

Results and Discussion

a-Ge:H Nanocavity Single Cells

While a detailed explanation of the general concept of a-Ge:H nanocavity solar cells has been given before [11,12], Figure 1 briefly illustrates the effect: Figure 1a displays a simplified version of the a-Ge:H solar cell stack used throughout this work. The a-Ge:H absorber layer as well as the silicon layers exhibit a high refractive index of around 4, while the TCO layers typically show a refractive index of about 2. This means that the interface between silicon and the TCO exhibits a comparably high reflectivity. Hence, Fabry Pérot resonances will be formed between this interface and the highly reflecting silver back contact. Figure 1b shows the simulated absorption inside the 7 nm thick a-Ge:H layer for two different total resonator lengths, which are realized using a varied silicon layer thickness. While a resonance maximum at a wavelength around 700 nm is observed in both cases, the higher order resonance of the longer cavity leads to a spectrally narrow resonance pattern. As broadband absorption is required in solar cells, such effects are generally undesired. However, as seen from the solid blue curve in Figure 1b, pronounced and spectrally broad absorption enhancement can be achieved by reducing the resonator thickness such that advantage is taken from the lowest order resonance of the cavity. To emphasize the impact of this resonance on the absorption efficiency, a simulation is shown which assumes incoherent behavior of light inside the semiconductor layers (dashed blue curve). Here, an only 27 nm thick cavity is sufficient to obtain a lowest order resonance maximum at wavelengths around 700 nm. This represents an optical pathway far below 1/4 of the resonant wavelength, leading to an additional broadening of the absorption curve. The characteristic phase shifts occurring at the silicon/silver interface play an important role for this effect^[11,12]. This also implies that a dielectric back reflector would be disadvantageous in this type of solar cells.

In our recent work on a-Ge:H nanocavity single solar cells we have obtained our best experimental single cell result using 5 nm thick doped and undoped silicon films on



Figure 2 a) Measured QE of the nanocavity a-Ge:H solar cell depicted in b)

both sides of a 13 nm thick a-Ge:H absorber layer, respectively^[11]. For our experiments on a-Si:H/a-Ge:H tandem devices presented here, we decided to slightly increase the thickness of the silicon films to improve the cell stability on textured TCO substrates. This leads to slightly non-optimal utilization of the ultrathin resonant cavity. However, this does not change the general conclusions drawn from our results, as the strong dependence of the device on resonance effects persists. Figure 2a shows a quantum efficiency curve of an a-Ge:H single cell with a 20 nm thick absorber layer. The cell stack is depicted in Figure 2b. Due to the resonance occurring inside the nanocavity, a strong and spectrally broad quantum efficiency curve corresponding to a short circuit current density of 22.3 mA cm⁻² is achieved. The smaller interference patterns can be attributed to interference effects inside the front TCO layer.

a-Si:H/a-Ge:H Tandem Devices

To investigate the feasibility of integrating such nanocavity enhanced solar cells in multijunction devices, we used the same a-Ge:H solar cell stack as described in the previous section for the fabrication of a-Si:H/a-Ge:H tandem solar cells. The thickness of the

Bottom absorber thickness [nm]	j_{SC} top cell [mA cm ⁻²]	j _{SC} bottom cell [mAcm ⁻²]
7	7.1	8.4
10	7.3	10.6
20	7.4	11.1
30	7.6	11.6

Table 1 Short circuit current densities of the individual sub cells corresponding to the QEs of the a-Si:H/a-Ge:H tandem devices presented in Figure 3.



Figure 3 a) *QE* and absorption (1-*R*) spectra of a-Si:H/a-Ge:H tandem cells with varying bottom cell absorber thickness, and QE spectrum of a-Si pin single cell as reference. **b)** Corresponding tandem cell stack.

a-Ge:H absorber was varied from 7 nm to 30 nm in a first sample set. Figure 3a displays the QE spectra and absorption (1-R) curves which we obtained from these cells. The corresponding cell stack is sketched in Figure 3b. As the a-Ge:H single cell stack was deposited in n-i-p superstrate configuration, we decided to keep this configuration for the tandem cells. Hence, the a-Si:H top cell needed to be fabricated in n-i-p configuration as well. This leads to high parasitic absorption inside the front n-layer, which was not optimized for low absorption. The ZnO:Al intermediate reflector at the front side of the a-Ge:H bottom cell is required to obtain the same reflectivity and phase shift as in case of the single cells, as this allows the same resonances to develop.

The QE spectra of the a-Ge:H bottom cells show clear interference patterns shifting to higher wavelengths with increasing bottom cell absorber thickness. The 1-R curves clearly reveal that these patterns are spectrally narrow. As demonstrated in the previous section, such narrow patterns are not produced by the nanocavity enhanced bottom cell. Instead, they can be attributed to additional resonances forming between the silver back reflector and the TCO front contact of the a-Si:H top cell. Although these top cell induced resonances lead to a local decrease of the bottom cell QE, the corresponding photocurrent densities reach values up to 11.6 mAcm⁻² for an a-Ge:H bottom cell absorber thickness of 30 nm (see Table 1). A value of 10.6 mA cm⁻² can be already achieved with a 10 nm thick bottom cell absorber. The QE curves of the top cells correspond to photocurrent densities of only 7.1 to 7.6 mA cm⁻², meaning that the short circuit current densities of the tandem devices are strongly top cell limited. However, a QE result obtained from a standard a-Si:H single cell is presented for comparison (dashed black curve), which yields 12 mAcm⁻². Compared to this device, most current is lost in the blue part of the spectrum. As stated before, this can be attributed to the high parasitic absorption inside the n-layer. Hence, we expect that the QE of the a-Ge:H



Figure 4 a) Simplified QE simulation of an a-Ge:H single cell (blue line) as well as of an a-Si:H/a-Ge:H tandem solar cell containing the same cell stack as bottom device; simulation of the tandem device has been performed fully coherent (orange line) as well as with incoherent treatment of light inside the top cell and intermediate reflector (black line) b) Sketch of the simulated solar cell stacks

bottom cell will be only slightly lower in a current matched tandem device.

However, since the shape and position of the narrow resonance patterns relies on the top cell thickness, the optimization of current matching will be rather difficult for such devices. This is particularly pronounced if thick top cells are required or if multiple sub cells are stacked on top of the a-Ge:H cell, as this leads to even narrower interference features. Figure 4a displays a comparison of QE spectra obtained by simulation of an a-Si:H/a-Ge:H tandem cell as well as of the corresponding a-Ge:H single cell (blue curve). The simulated cell stacks are depicted in Figure 4b. Compared to the experimental results presented in Figure 3, a thicker a-Si:H top layer was used in this simulation. For simplicity, the doped layers have not been modeled separately but were combined with the respective adjacent silicon layers. For the tandem device, two different curves are shown. A first result was obtained assuming fully coherent behavior of light (yellow curve), which is the same method which was applied for the single cell simulation. Similar to the experimental case, the a-Ge:H single cell shows a broadband QE spectrum which is almost free of interference features, while spectrally narrow resonance patterns are produced if the same cell stack is utilized as a bottom cell. As explained before, this behavior is related to coherent interaction of light propagating through both sub-cells, with light that is directly reflected at the front TCO contact of the cell. In our simulation, these top cell induced interference patterns can easily be suppressed: The black curve in Figure 4a represents a result which is obtained when coherent interaction of light propagating through the top cell or intermediate reflector is disabled, while coherence inside the bottom cell nanocavity is maintained. In this case, the QE spectrum of the a-Ge:H bottom cell is very similar to the a-Ge:H single cell curve, as expected. This raises the question of how such behavior can be achieved in a real device.

A common method to decrease the coherence of light in thin film solar cells is to introduce rough interfaces by using textured TCO substrates. However, by applying this



Figure 5 SEM image of an a-Si:H/a-Ge:H tandem cell cross section. The arrows roughly indicate the paths of light reflected at the top TCO/a-Si:H interface and at the bottom cell interfaces, respectively. The scale bar represents 200 nm.

approach to our a-Si:H/a-Ge:H tandem cell stack, the texture is also transferred to the a-Ge:H bottom cell. Hence, this might also suppress the required resonances inside the nanocavity of the bottom cell.

To investigate this, we repeated the a-Si:H/a-Ge:H tandem cell stack presented in Figure 3b but on a TCO substrate with an RMS surface roughness of 120 nm instead of 50 nm. In this experiment, only the 20 nm thick a-Ge:H bottom cell absorber was used. Figure 5 depicts an SEM image of the solar cell cross-section. It can be clearly seen that due to the highly conformal growth of the semiconductor layers, the a-Ge:H bottom cell has adapted the same surface texture as the a-Si:H top cell. As indicated by the arrows, light reflected at the front side of the top cell is likely to be scattered into different angles than light which reaches the back contact or the ZnO:Al intermediate reflector. This geometry strongly suppresses the coherence of the partial waves and hence inhibits the corresponding interference effects. On the other hand, light reflected at both interfaces of the a-Ge:H bottom cell nanocavity is most likely reflected into similar directions, as the curvature radius of the interface is large compared to the cavity thickness. In addition, the resonance patterns of ultrathin cavities are known to show lower sensitivity to angle of incidence variations as well as to small thickness variations^[11,12]. Hence, interference effects can persist in ultrathin nanocavities even on substrates showing high surface roughness, as recently demonstrated by Kats et al.^[18].

For this reason, the surface texture of the substrate can be chosen to suppress the top cell induced interference effects, while at the same time, the broadband resonances required inside the bottom cell are maintained. In Figure 6, the influence of the RMS surface roughness on the QE spectrum and on the 1-R curve is demonstrated. Corresponding photocurrent densities can be found in Table 2. The results clearly indicate that the top cell induced interference patterns are strongly suppressed when using higher



Figure 6 *QE* and 1-*R* curves of a-Si:H/a-Ge:H tandem cells with 20 nm bottom absorber thickness on substrates with different surface roughness. The corresponding a-Ge:H single cell spectrum is shown for comparison.

RMS roughness [nm]	j _{SC} top cell [mA cm ^{−2}]	<i>j</i> _{SC} bottom cell [mAcm ⁻²]
50	7.4	11.1
120	8.4	12.3

Table 2 Short circuit current densities of the individual sub cells corresponding to the QEs of the a-Si:H/a-Ge:H tandem devices presented in Figure 6

surface roughness. The a-Ge:H single cell result from Figure 2 is depicted for comparison, showing that the a-Ge:H bottom cell QE is very similar to the single cell curve in this case. This means that the resonances created inside the bottom cell nanocavity are not suppressed. A spectrally broad bottom cell QE with a maximum value of 60% at 800 nm is obtained, corresponding to a short circuit current density of 12.3 mA cm⁻².

Conclusion and Outlook

We have presented quantum efficiency measurements of a-Si:H/a-Ge:H tandem devices employing a nanocavity to increase the absorption inside the a-Ge:H bottom cell absorber. Our results demonstrate that textured substrates, which are commonly used in silicon based thin-film solar cells, can be employed to suppress the additional interference patterns induced by the top cell. At the same time, the nanocavity resonances required for efficient absorption inside the bottom cell are maintained. As suggested in the previous section, we believe that an ideal surface texture would be dominated by curvature radii that are large compared to the bottom cell thickness but similar to the top cell thickness. However, a systematic study is required to verify this assumption. The concept described in this work is not bound to the special case of a-Si:H/a-Ge:H tandem cells. Instead, we conclude that it can be applied, in principle, to integrate any nanocavity solar cell as a bottom cell in multijunction devices.

Furthermore, our results indicate that a short circuit current density of at least 12 mA cm⁻² is achievable in current matched a-Si:H/a-Ge:H solar cells with only 20 nm thick a-Ge:H absorbers. This is near to typical values reached in a-Si:H/ μ c-Si:H devices.

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Moreover, we expect that open circuit voltages similar to those achieved in μ c-Si:H devices should be possible with the a-Ge:H nanocavity single solar cells presented here. Using state of the art a-Ge:H material quality, voltages near 500 mV have been demonstrated in devices with much thicker a-Ge:H absorber layers already^[10]. Given that a good interface quality can be achieved, the lower thickness in our design should eventually enable even higher values. This would allow a reduction of the bottom cell deposition time by two orders of magnitude compared to micromorph devices, while keeping the cell efficiency nearly constant.

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Paper III: Resonant Cavity Enhanced a-Ge:H Nanoabsorber Solar Cells for Application in Multijunction Devices

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Abstract

A resonant-cavity-enhanced solar cell with a 25 nm thick amorphous germanium nanoabsorber is demonstrated. The device is specifically designed for use as bottom cell in multijunction devices. In this case, instead of relying on broadband absorption, only red light needs to be absorbed in the bottom cell. This allows exploiting the narrow resonance patterns of long Fabry-Pérot cavities to achieve efficient absorption inside the nanoabsorber. It is shown that this approach can only be integrated into multijunction devices when suppressing inter-subcell coherence. To achieve this, the intermediate reflector of the tandem device is textured using electrochemically grown zinc oxide nanorods.

Introduction

Hydrogenated amorphous germanium (a-Ge:H) is a group IV semiconductor featuring an exceptionally high absorption coefficient as well as a bandgap energy of about 1.1 eV.^[1] This value lies between the optimum bandgap energy for single junction solar cells (1.34 eV) and for bottom cell absorbers in tandem devices (0.94 eV),^[2] making a-Ge:H a good candidate for both use cases. In particular, the material would be very useful as a replacement of hydrogenated microcrystalline silicon (μ c-Si:H) in amorphous silicon/microcrystalline silicon thin-film solar cells,^[3] as the latter exhibits a similar bandgap but is by far less absorptive.^[1,4]

Hydrogenated amorphous silicon (a-Si:H), which is structurally similar to a-Ge:H, is widely utilized as high bandgap absorber material in thin film silicon PV.^[5,6] However, the absorber thickness should not exceed approximately 300 nm in these devices to ensure efficient charge carrier collection. As a-Ge:H layers of highest electronic quality exhibit even ten times higher defect densities compared to a-Si:H,^[1,7,8] it is not surprising that poor charge carrier extraction is obtained with a-Ge:H absorber layers of similar thickness. Hence, a-Ge:H is widely considered as unsuitable for optoelectronic applications. Indeed, the highest efficiency achieved in a-Ge:H solar cells with 100 nm thick absorber layers is only about 3.5%.^[9]

To address this issue, we recently demonstrated an approach that allows us to reach a short circuit current density $(j_{\rm SC})$ of 20 mAcm⁻² with an only 13 nm thick a-Ge:H absorber layer.^[10] To increase the absorption efficiency, advantage is taken of lowest-order Fabry-Pérot resonances produced between the reflecting electrodes of the solar cell. As the free spectral range of a resonator increases with decreasing resonator length (and hence with decreasing the resonance order),^[11] such nanocavities are known to enable strong and spectrally broad resonances rather than narrow interference patterns.^[12-14] In the devices described by our group, the resonator length comprises the thicknesses of the absorber layer as well as the doped and undoped silicon layers. It was shown that a total thickness of these layers in the range of 20 nm to 50 nm is required for optimum resonance. Recently, a-Ge:H nanocavity bottom cells with absorber thicknesses around 20 nm have been demonstrated to enable current densities around 12 mAcm⁻² in a-Si:H/a-Ge:H tandem devices.^[15]

The absorber thickness reduction achievable with this method is associated with a much shorter distance that photogenerated charge carriers need to move before they can be extracted from the absorber. As a result, this approach should clearly increase the charge carrier extraction efficiency at given material properties, hence significantly improving the prospects for the utilization of a-Ge:H in photovoltaics.

Nevertheless, no significant improvements in efficiency were achieved yet. One reason for this is the low required resonator length, which poses strong restrictions on the thickness of the doped layers and buffer layers. This complicates the electrical optimization of the devices, as it is not straight-forward to improve the quality of the germanium/silicon hetero-interfaces (e.g. by using bandgap grading layers as described by Zhu et. al.^[9]) or to include thicker doped layers for improved electrical stability.

Here we address this issue by specifically designing a resonant-cavity-enhanced (RCE) solar cell for use in multijunction configurations. While efficient broadband absorption is required in single junction solar cells, only infrared light needs to be trapped in the absorber layer of a bottom cell. This means that the narrower resonance patterns induced by higher order Fabry-Pérot resonances can be exploited instead of following the approach of using lowest-order resonances. This allows (and even requires) using a thicker solar cell stack between the reflecting electrodes, hence providing more degrees of freedom for optical and electrical optimization.

We present an RCE a-Ge:H single junction solar cell of this type yielding 4% efficiency. As it is our goal to enable the use of an only few nanometer thick a-Ge:H absorber, the resonator length is adjusted by mainly increasing the thickness of the doped and undoped silicon layers. Moreover, we demonstrate that when integrating such cells in multijunction configurations, light coherence on inter-subcell scales needs to be suppressed to avoid additional resonance effects. To achieve this, an intermediate reflector textured with electrochemically-grown zink oxide (ZnO) nanorods was employed.

Methods

Simulation

Fully coherent 1d optical simulations of the cell stack depicted in Figure 1 were performed using the commercially available software package Scout/Code (W. Theiss Hard- and Software). Quantum efficiency spectra were obtained by calculating the absorption inside

the germanium layer and assuming full charge carrier extraction. For simulation of the tandem cell configuration, a 350 nm thick a-Si:H layer as well as a 70 nm thick ITO front contact was added to the simulated solar cell stack. For the top cell, the absorption inside the a-Si:H layer has been calculated additionally. Refractive index data were taken from literature (a-Ge:H^[1] and silver^[16]), obtained by ellipsometric spectroscopy and subsequent modeling (a-Si:H, μ c-Si:H), or taken from the database provided with Scout/Code (ZnO and ITO).

a-Ge:H Single Cell Fabrication

Opaque and flexible aluminum substrates with a pre-deposited lacquer and silver layer (Alanod GmbH, Germany) were used and have been described elsewhere.^[17] The a-Ge:H solar cell stacks were fabricated in nip substrate configuration as depicted in Figure 1. All layers were fabricated using a cluster tool type CS400PS manufactured by Von Ardenne GmbH Dresden. Aluminum doped zinc oxide (AZO) was deposited in the DC magnetron sputtering tool integrated in this system (Al₂O₃ concentration 2 wt%) at a temperature of 200°C. Silicon and germanium layers were deposited on the grounded electrode of a parallel-plate plasma enhanced chemical vapor deposition (PECVD) reactor (13.56 Mhz frequency). As source gases, H2-diluted GeH₄ and SiH₄ were used for a-Ge:H and silicon, respectively. B₂H₆ and PH₃ were added to achieve p- and n-doping, respectively. For deposition of the ITO front contact a second DC magnetron sputtering system using a ceramic ITO target with 10 wt% SnO₂ and a heating temperature of 200°C was applied.

ZnO nanorod depositon

ZnO nanorods were grown by electrochemical deposition on the ITO front contact of the a-Ge:H solar cells, out of a $Zn(NO_3)_2$ solution (0.02 M), with a temperature of 70°C and a deposition time of 480 s at a constant potential of -915 mV vs. Ag/AgCl reference. The electrode configuration was a three electrode arrangement with a Pt counter electrode and an Ag/AgCl reference electrode using a VersaSTAT 4 potentiostat.

a-Si:H/a-Ge:H Tandem Cell Fabrication

For the device presented in Figure 5, a-Ge:H single cells with nanorod textured front contacts were fabricated as described above. Subsequently, a nip (30 nm/300 nm/25 nm) a-Si:H solar cell was deposited using the same PECVD system and precursor gases as described above, so that the ITO front electrode of the a-Ge:H device serves as intermediate reflector in the tandem configuration. Afterwards, an 80 nm thick ITO front contact was deposited using the same method as described above.

Solar Cell Characterization

QE spectra were determined from differential spectral response measurements. As this communication focusses on the optical aspects of the resonant-cavitiy as well as the nanorods, a voltage bias has been applied to maximize charge carrier extraction. Hence, all QE curves yield information on the charge carrier generation efficiency rather than the external quantum efficiency under short circuit conditions. jV-curves of $3 \times 3 \text{ mm}^2$



Figure 1 *RCE a*-*Ge*:*H* solar cell stack: **a)** Complete stack including layer thicknesses and approximate refractive indices. **b)** Simplified representation of the same cell stack

solar cells were measured under illumination using a WACOM dual lamp solar simulator (AM1.5g spectrum, class AAA, 1000 W m⁻²). As the contact pins produce significant shadowing during jV-measurement, j_{SC} was additionally determined from the QE and used to correct the curves.

Results and Discussion

RCE a-Ge:H Nanoabsorber Single Cells

Figure 1a depicts the cell stack under investigation. A simplified sketch of the same cell stack is presented in Figure 1b and is used throughout the rest of this communication. Due to the significantly higher refractive index of the silicon and germanium layers compared to the electrodes (indium tin oxide (ITO) front contact and AZO/silver back contact), a high fraction of incoming light is reflected at both electrode/silicon interfaces. This leads to the formation of Fabry-Pérot resonances. The spectral position of the corresponding resonant absorption maxima and minima can easily be tuned by adjusting the thickness of the silicon and germanium layers. The values given in Figure 1a have been designed to suit the application in a-Si:H/a-Ge:H solar cells, as we will show in the following.

Figure 2 displays experimental results of a sample with this thickness configuration. The quantum efficiency (QE) curve in Figure 2a exhibits a local absorption maximum in the infrared part of the spectrum, while a corresponding minimum is observed in the visible red. The QE curve of a typical a-Si:H solar cell is shown for comparison, demonstrating that the absorption minimum of the RCE a-Ge:H cell occurs in a wavelength range for which significant absorption can be obtained in a-Si:H devices. Hence, the lower absorption efficiency of the a-Ge:H layer in this spectral range should have only limited impact on j_{SC} in a-Si:H/a-Ge:H tandem cell configurations.

Figure 2b shows the *jV*-curve and device characteristics of the sample. As expected, in the single cell, the resonant absorption minimum leads to a lower short circuit current density of about 17 mA cm⁻², as compared to >20 mA cm⁻² for devices exploiting the



Figure 2 Experimental results for a-Ge:H solar cell stack as depicted in Figure 1: **a)** Quantum efficiency spectrum. A QE result of an a-Si:H single junction solar cell is depicted for comparison. **b)** jV-curve and device characteristics.

broadband resonances produced by nanocavities.^[10,15] Nevertheless, thicker doped layers and improved buffer layers allowed us to reach a high fill factor of 64%, leading to an efficiency of 4%. While this is still far from the 11.8% currently achieved with μ c-Si:H solar cells,^[18,19] single cell efficiencies should not be directly used as a figure of merit, as they do not reflect the fact that the RCE a-Ge:H solar cell presented here can show its full potential in multijunction configurations only.

Integration in Tandem Devices

As demonstrated recently,^[15] it is impossible to integrate an RCE a-Ge:H solar cell into a tandem device by merely stacking an a-Si:H solar cell on top of it. To illustrate this, Figure 3 depicts the simulated QE of an RCE a-Ge:H single solar cell as well as of a corresponding tandem cell stack. In case of the tandem configuration, the same RCE a-Ge:H solar cell stack is used as the bottom device, so that the ITO front contact serves as an intermediate reflector in this case. Compared to the single junction case, the addition of an a-Si:H top cell leads to the formation of additional inter-subcell interferences as well as to resonances inside the a-Si:H top cell. As the absorption inside the a-Ge:H layer strongly relies on resonances, this effect leads to a significant modification of the simulated bottom cell absorption spectrum.

This means that when incorporating RCE solar cells in multijunction devices, one of the two following solutions to this problem needs to be applied: An obvious approach would be to optimize the resonances of the complete solar cell stack. Due to the complex interaction of the different resonances, this would be a complicated task especially in devices using many junctions or thick top cells. Furthermore, the absorption inside the resulting device would likely be very sensitive to thickness fluctuations and hence inappropriate for industrial low-cost production.

In this communication we follow a different approach aiming to suppress the coherence of light on inter-subcell scales, while maintaining coherence inside the RCE a-Ge:H solar cell itself. This is achieved by texturing the surface of the ITO intermediate reflector using electrochemical deposition of ZnO nanorods.^[20–22] While ITO is not typically used



Figure 3 Simulated influence of inter-subcell resonances in a-Si:H/a-Ge:H tandem solar cells with a flat intermediate reflector: Schematic representation of the cell stack and simulated absorption spectra of an **a**) RCE a-Ge:H single cell and a **b**) tandem device with the same RCE a-Ge:H solar cell as bottom device.

as an intermediate reflector due to higher absorption losses compared to ZnO:Al or SiO_x ,^[23,24] the high lateral conductivity of this material is preferential in our case to enable homogeneous electrochemical deposition of the nanorods.

Figure 4a depicts a sketch of the resulting device along with an SEM image of the surface texture. As the ZnO nanorods were grown directly on top of the ITO layer without using an additional ZnO seed layer, no predominant growth direction can be identified. This configuration has been chosen to avoid additional parasitic absorption, as well as to obtain a randomized surface texture. To illustrate the influence of nanorods on the resonant cavity effect, Figure 4b presents a comparison of experimentally determined QE curves from a-Ge:H solar cells with and without the nanorods. The results demonstrate that the nanorods indeed lead to a significant modification of the QE curve. The resonance patterns are broadened, as incoming light is scattered at the air/ZnO interface and quasi-randomly scattered from normal incidence to higher angles. However, a local resonance minimum in the visible red spectral range is still observed. The local maximum in the infrared is only slightly reduced compared to the case without nanorods. These findings indicate that the desired resonances inside the a-Ge:H bottom cell stay in effect. As a result, the overall absorption of the device is strongly improved and j_{SC} calculated from the QE increases from 15.6 mA cm⁻² to 18.1 mA cm⁻².

When integrating this cell into an a-Si:H/a-Ge:H tandem device, the nanorod-textured ITO layer acts as an intermediate reflector that scatters light when it traverses between both sub-cells. Due to this scattering effect, inter-subcell coherence is suppressed, while resonances inside the bottom cell themselves persist. Figure 5 presents tandem cell



Figure 4 Influence of a nanorod-textured front contact on the quantum efficiency of RCE a-Ge:H solar cells: a) Schematic representation of the cell stack with nanorods along with an SEM image of the surface texture (white scale bar represents 1 μ m). b) Quantum efficiency spectra of a device with and without ZnO nanorods.



Figure 5 Tandem cell results: **a)** Schematic representation of the cell stack with arrows indicating the coherent (solid) and incoherent (dashed) behavior of light **b)** Comparison of the quantum efficiency spectrum of the tandem solar cell with the result of the corresponding RCE a-Ge:H single junction device.

results, showing that the negative impact of additional resonances on the bottom cell absorption is avoided this way. In the infrared part, the QE spectrum of the a-Ge:H bottom cell nearly resembles the corresponding single cell result. While a slight overall reduction of the QE curve is observed for the tandem device, this is most probably related to additional parasitic absorption inside the ITO front contact.

Our results show that a complex process of tuning the resonances of the complete cell stack is not required when using a textured intermediate reflector. This strongly simplifies tandem cell optimization, as both subcells can be optimized separately before integrating them into a multijunction concept.

Conclusion and Outlook

We have presented an RCE a-Ge:H nanoabsorber solar cell specifically designed for use as a bottom device in multijunction concepts. Instead of taking advantage of the lowestorder resonances of the cavity, as required for broadband absorption, this approach allows utilizing higher order resonances and hence thicker resonators. While the a-Ge:H absorber was kept ultrathin (25 nm), the cavity length was adjusted by changing the thickness of the doped silicon layers and buffer layers. Compared to the original nanocavity approach, this concept provides more degrees of freedom for electrical and optical optimization. This allowed us to increase the fill factor to 64%, thereby improving the overall efficiency to 4%. Furthermore, we demonstrated that such devices can be directly integrated into multijunction configurations when employing textured intermediate reflectors. These results not only improve the prospects for application of a-Ge:H in solar cells: While the original nanocavity approach can only be used for materials with absorption coefficients comparable to a-Ge:H, the concept presented here is by far less restrictive with respect to the required optical properties. This means that it can be applied to a wide range of potential bottom cell absorber materials.

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Paper IV: Optimized Optical Field Profile in Resonant-Cavity-Enhanced a-Ge:H Nanoabsorber Solar Cells for Tandem Cell Application

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Abstract

Amorphous germanium based solar cells exploiting second-order Fabry-Pérot resonances can reach strong infrared absorption with an absorber thickness of 25 nm or less. Hence they are a promising candidate for replacement of the μ m-thick μ c-Si:H bottom cells in a-Si:H/ μ c-Si:H tandem configurations. Here we present a detailed experimental and simulationaided analysis of the optical properties of such devices, with a particular focus on their potential application in tandem cells. A clear relation of the results to the field profile inside the cavity was found, and guiding rules for optimization are deduced. By modeling the transmission behavior of an a-Si:H top cell, we evaluate the potential of the fabricated devices for tandem cell application, allowing a benchmark against μ c-Si:H solar cells. The best sample was found to enable a tandem cell performance equivalent to a μ c-Si:H bottom device reaching 5% single cell efficiency.

Introduction

In the future energy mix, a high market share of photovoltaic energy sources can only be reached if low-cost technologies are developed that enable high-throughput fabrication and that do not suffer from resource limitations^[1]. Silicon thin-film solar cell technology does not rely on scarce materials and can be processed on large scales. A widespread representative of this class of solar cells is the so-called micromorph configuration, in which an approximately 200-300 nm thick amorphous silicon (a-Si:H) top cell is combined with a 1-3 μ m thick microcrystalline silicon (μ c-Si:H) bottom cell.^[2-6] These devices show improved efficiencies compared to a-Si:H single junction solar cells. However, the high required bottom cell thickness implies a strong throughput reduction, higher material consumption and a significant cost increase per watt peak. This has motivated the investigation of alternative bottom cell absorber materials with higher absorption coefficients, such as silicon-germanium alloys.^[7-10] Pristine amorphous germanium (a-Ge:H) is particularly interesting as a replacement of μ c-Si:H, as it exhibits a similar bandgap



Figure 1 Layer stack of an RCE a-Ge:H nanoabsorber solar cell: **a)** Cell stack including approximate refractive indices. **b)** Simplified representation of the same cell stack

energy, meaning that light from the same spectral range can be absorbed.^[11-13] At the same time, the absorption coefficient of a-Ge:H is higher by more than one order of magnitude, allowing the use of drastically thinner absorber layers.^[14-16] So far, high defect densities limited the maximum efficiency of a-Ge:H solar cells to about 3.5%, which was achieved with approximately 100 nm thick absorber layers.^[15] To improve charge carrier extraction, we recently demonstrated the exploitation of Fabry-Pérot resonances to enable efficient absorption in solar cells with only 10-25 nm thick a-Ge:H absorbers.^[17-19] Figure 1 depicts an example of such resonant-cavity-enhanced (RCE) a-Ge:H nanoabsorber solar cells. High reflectivity is obtained at the electrode/silicon interfaces due to a high difference of the refractive index. Reflections at the silicon/germanium interfaces can be neglected, as both materials exhibit comparable refractive indices. Hence, the device can be regarded as an absorptive optical cavity for which the electrodes constitute the mirrors. By tuning the cavity length, the resulting resonant field enhancement can be exploited to improve the absorption inside the a-Ge:H nanoabsorber.

Using the lowest-order resonances of such optical cavities, broadband absorption and a short circuit current density (j_{SC}) of more than 20 mA cm⁻² were obtained using only 10-20 nm thick absorber layers.^[17,18] While efficiencies up to 3.6% were reached this way, the low cavity length required for utilization of lowest-order resonances poses strong constraints on the thickness of the silicon layers. In particular, very thin doped layers need to be utilized, leading to imperfect charge carrier extraction.^[20] As a result, it is difficult to further improve the electrical characteristics of these devices. However, broadband absorption over the entire visible range, as supported by lowest-order resonances, is only required in single junction solar cells. When specifically designing the devices for application in a-Si:H/a-Ge:H tandem devices, it is sufficient if only red and infrared light is absorbed. In this case, it is acceptable if the resonant field enhancement occurs in a narrower spectral range. This allows the utilization of second-order resonances and hence of a longer resonator and thicker doped layers. We recently presented an a-Ge:H solar cell of this type, yielding a high fill factor of 64% and an improved single cell efficiency of 4%.^[19] Moreover, we demonstrated that application of the concept in a-Si:H/a-Ge:H tandem solar cells is feasible when integrating a scattering mechanism at the intermediate reflector. In this article we present a detailed analysis and optimization of this concept. The dependence of simulated and experimental single cell quantum efficiency spectra on the absorber position, resonator length, and absorber thickness is investigated. The results are related to the optical field profile generated inside the resonator, which is calculated using 1d optical simulations. This allows inferring guiding rules for device optimization. By modeling the transmission behavior of an a-Si:H top cell, the j_{SC} achievable in corresponding a-Si:H/a-Ge:H tandem solar cells is estimated from the single cell results. By combining this quantity with the results from jV-measurements, the potential of the devices for tandem cells is evaluated, allowing a benchmark against μ c-Si:H solar cells.

Methods

Experimental

a-Ge:H solar cells were fabricated in n-i-p substrate configuration as depicted in Figure 1. Flexible aluminum substrates with a pre-deposited lacquer and silver layer were utilized (Alanod GmbH, Germany)^[21] and coated with an 80 nm thick DC magnetron sputtered aluminum zinc oxide (AZO) film. Subsequently, an 80 nm thick DC magnetron sputtered ITO front electrode was deposited. All layers were fabricated using a cluster tool type CS400PS manufactured by Von Ardenne GmbH Dresden. Additional details on the fabrication processes can be found elsewhere.^[17,18] As recently shown, a straight-forward integration of resonant-cavity-enhanced solar cells in tandem cell configurations is only feasible if a scattering mechanism is used to optically decouple the subcells. [18,19] In the substrate configuration, this can be achieved for example with ZnO nanorods grown on top of the ITO front contact of the device. This has been performed for all devices in this work, except stated otherwise. For this purpose, electrochemical growth from a $0.02 \text{ M Zn}(\text{NO}_3)_2$ solution was carried out using a three electrode arrangement with a Pt counter electrode and an Ag/AgCl reference electrode, controlled with a VersaSTAT 4 potentiostat. Deposition time was 480 s at a constant potential of -915 mV vs. Ag/AgCl reference and at a temperature of 70 °C. Figure 2 shows a sketch of the resulting solar cell stack, along with an SEM image of the nanorods. Separation of individual solar cells was conducted using laser-scribing. Quantum efficiency (QE) spectra were determined from differential spectral response measurements at short circuit conditions. A WACOM dual lamp solar simulator (AM1.5g spectrum, class AAA, 1000 W m⁻²) was used to measure *jV*-curves of $4.5 \times 4.5 \text{ mm}^2$ solar cells under illumination.

Simulation

1d optical simulations of the cell stack depicted in Figure 1 were performed using the commercially available software package Scout/Code (W. Theiss Hard- and Software). In order to take into account that the resonances inside the front ITO layer are suppressed due to the ZnO nanorods, incoherent behavior of light was simulated for this film. QE spectra were simulated by calculating the absorption inside the germanium layer and assuming full charge carrier extraction. While this neglects the generation and extraction of additional charge carriers inside the undoped parts of the silicon layers, a clearer view of the resonance patterns is achieved. Refractive index data were either



Figure 2 Sketch of the a-Ge:H solar cell stack

with ZnO nanorods grown on top of the ITO

front contact, along with an SEM image of the



Figure 3 Weight function for bottom cell QE calculation, along with a calculated QE obtained by applying the function to the single cell QE of an a-Ge:H nanocavity solar cell. The experimental single cell and bottom cell QE curve are shown for comparison. Experimental results were taken from literature.^[18]

nanorods. The scale bar represents 1µm. literature.^[18] taken from literature (a-Ge:H^[13] and silver^[22]), obtained by ellipsometric spectroscopy

taken from literature (a-Ge:H^[13] and silver^[22]), obtained by ellipsometric spectroscopy and subsequent modeling (a-Si:H, μ c-Si:H), or were taken from the database provided with Scout/Code (ZnO and ITO).

Estimation of Bottom Cell **j**_{SC}

A weight function $w(\lambda)$, which models the transmittance of an a-Si:H top cell, is applied to the measured single cell QE spectra to estimate the short circuit current density (j_{SC}) of these devices in the tandem cell configuration ($j_{SC,bottom}$). For this, we used a sigmoid function of the form

$$w(\lambda) = rac{1}{1+{
m e}^{-(\lambda-\lambda_{
m CO})/\lambda_{
m w}}},$$

where λ is the wavelength, λ_{CO} is the cutoff wavelength (spectral position at which w=0.5) and λ_w is the cutoff width. At a distance λ_w left and right from λ_{CO} , the weight is w=1/(1+e) and w=1-1/(1+e), respectively. The parameters used throughout this work are $\lambda_{CO}=650$ nm and $\lambda_w=50$ nm. These values have been chosen to imitate the light transmission of an a-Si:H top cell yielding 12.5 mAcm^{-2}. We validated this method on QE results of a-Si:H/µc-Si:H tandem cells presented by Söderström et. al.^[6]

Figure 3 demonstrates the applicability of these parameters to estimate the potential of the a-Ge:H bottom solar cell in a-Si:H/a-Ge:H devices. The experimental QE spectrum of an a-Ge:H nanocavity single solar cell is depicted, together with a spectrum measured when utilizing the same cell stack as bottom cell in an a-Si:H/a-Ge:H tandem device. Additionally, the graph depicts a bottom cell QE spectrum obtained by weighting the single cell result, along with the weight function used throughout this work. Except for a small difference resulting from a shift of the interference fringes, the calculated result shows a good match with the experimental curve.



Figure 4 Simulated electric field distribution inside a silicon-only resonator with a length of **a**) 120 nm, **b**) 180 nm, and **c**) 220 nm. Upper axis displays the absolute distance from the back reflector; lower axis is the position relative to the front contact, normalized to the cavity length. Dashed lines are guides to the eyes highlighting field minima. Dotted lines represent the centers of the respective cavities. The "X" indicates the relevant second order resonance maxima.

Benchmarking Tandem Cell Performance

As the solar cells in this work are designed with the aim to replace μ c-Si:H in a-Si:H/ μ c-Si:H tandem configurations, a meaningful figure of merit is required to compare both device types. For this purpose, we assume that two single junction devices can perform equally in a tandem configuration if they yield the same product of open circuit voltage (V_{OC}) and fill factor (FF) and enable the same total tandem cell current density $j_{SC,total}$ (i.e. sum of all sub-cell j_{SC} values). Accordingly, we define the benchmark efficiency $\eta_{\text{Benchmark}} = j_{SC,total} \times V_{OC} \times FF/P_{in}$, where P_{in} is 1000 W cm⁻². For a-Si:H/ μ c-Si:H solar cells, $j_{SC,total}$ is close to the single cell j_{SC} of the corresponding μ c-Si:H device, as a thick μ c-Si:H layer can absorb all light that an a-Si:H top cell absorbs as well (see e.g. Söderström et. al.^[6]). Therefore, for a given a-Ge:H device, $\eta_{\text{Benchmark}}$ can be considered as the efficiency that a μ c-Si:H solar cells in this work, we estimate $j_{SC,total} = 12.5 \text{ mA cm}^{-2} + j_{SC,bottom}$, in accordance with the choice of the weight function described before.

Results and Discussion

Due to the standing waves formed inside RCE a-Ge:H nanoabsorber solar cells, the exact position of the a-Ge:H layer inside the silicon-based resonator plays a crucial role for the absorption. In particular, as the refractive indices of germanium and silicon are comparable, strong absorption is obtained when placing the absorber at positions at which the absorber-free cavity would generate its field maxima. Accordingly, Figure 4 shows the dependence of the simulated optical field profile inside a cell stack as depicted in Figure 1a, but without the a-Ge:H absorber. The results reveal that the positions of field maxima and minima for a specific wavelength are independent of the resonator



Figure 5 Influence of the absorber position on the QE spectrum. Absorber position is provided relative to the front electrode, normalized to the resonator length, which is 180 nm. a) Simulation results; the inset shows a sketch of the simulated experiment. b) Experimental results.

length. In particular, one field maximum corresponding to the second order resonance is always situated in the center of the resonator. The reason for this is that light inside the silicon layer undergoes no significant phase shift upon reflection at the back reflector. As a result, a first field maximum develops directly at the AZO surface for all wavelengths. Further field maxima are thus fixed to positions that are $d_{max} = N\lambda/(2n)$ away from the back reflector surface, where n is the refractive index at wavelength λ and N is an integer number. At the same time, the cavity length required for second order resonance at wavelength λ is given by $d_{\text{cavity}} = \lambda/n$. With N = 1 it follows $d_{\text{max}} = d_{\text{cavity}}/2$, meaning that one field maximum of the second-order resonance is always situated inside the center of the cavity. As described above, the other second order resonance maxima are directly adjacent to the reflecting interfaces. At these positions, the doped layers of the solar cell are situated. Extremely thin doped layers would be required to exploit these field maxima. However, as described before, the motivation for utilizing second-order resonances is to allow the use of thicker doped and undoped silicon layers. For this reason, the a-Ge:H layer should always be placed inside the center of the cavity for optimum absorption at the resonant wavelength.

To demonstrate how a non-optimal configuration influences the cell performance, Figure 5 shows the dependence of simulated and experimental QE spectra on the absorber position. The total resonator length and absorber thickness were 180 nm and 25 nm, respectively. A sketch of the experiment is depicted in Figure 5a, along with the simulation results. As expected, the QE spectra show narrow interference patterns with a first peak between 500 nm and 600 nm (third-order resonance maximum) and a second peak at about 750 nm (second-order maximum), separated by a distinct minimum between 600 nm and 700 nm. A significant enhancement of the second order peak is obtained when shifting the absorber layer from the front side towards the center of the resonator. A further displacement towards the back side shifts the peak position to lower wavelengths and leads to a reduction of the QE maximum. These results are in good agreement with the field profile presented in Figure 4, as a centered position leads to an optimal overlap of the absorber with the centered field maximum produced by the

second-order resonance. Simultanously, a blue-shift of the absorption minima is observed for an increasing distance from the front contact. As a result, the absorption edge in the IR range becomes steeper in this case, while a smaller slope is obtained for wavelengths below the resonance maximum. At wavelengths below 500 nm, the absorption of the a-Ge:H layer is reduced due to parasitic absorption inside the thicker front silicon layer. The experimental results depicted in Figure 5b confirm these qualitative findings. However, the resonance patterns are less pronounced for two reasons: First, due to the non-vanishing roughness of the substrates used for the experiment, a higher fraction of light is coupled into the silver layer of the back reflector and is absorbed. As strong resonances imply multiple reflections at the resonator surfaces, this has a particularly strong effect on the resonance maxima. Second, for the simulation results, only light absorbed inside the a-Ge:H layer was considered to contribute to the QE. However, in the experimental case, additional charge carriers generated inside the undoped parts of the silicon layers are extracted. This leads to less pronounced absorption minima inside the short wavelength part.

The results provide clear guidance on how to maximize the peak absorption of the device. However, no information on the performance in tandem cell configurations is obtained. In order to estimate the potential $j_{SC,bottom}$, we apply the weight function described in the methods section to the experimental results shown in Figure 5b. The corresponding calculation results are depicted in Figure 6. As expected, $j_{\rm SC,bottom}$ is significantly improved when shifting the absorber layer from the front side towards the center of the device. Although a centered absorber position leads to maximum peak QE, $j_{SC,bottom}$ is maximized at a normalized position of 0.34 already, reaching a value close to



Figure 6 Influence of the absorber position on the potential $j_{SC,bottom}$ in a-Si:H/a-Ge:H tandem cells, calculated from the measured QEs depicted in Figure 5b.

10 mAcm⁻². For positions closer to the center, a slight decrease is observed. This can be attributed to the absorption reduction at wavelengths around 900 nm, which results from the steeper absorption edge and slightly overcompensates for the QE increase at the resonant peak. One reason for this is that the increased peak absorption only partly contributes to $j_{SC,bottom}$ due to the effect of the weight function. This suggests that a centered absorber position would be optimal if the absorption maximum would be shifted to higher wavelengths. When further displacing the absorber beyond the center, a rapid drop is observed, which can be attributed to the lower peak value as well as to the blue-shift of the resonance maximum.

Of course, the QE peak position has a strong influence on the bottom cell absorption: When it is located at short wavelengths, the low transmittance of the a-Si:H top cell in this spectral range leads to low bottom cell current densities. On the other hand, when shifting the maximum too far to the infrared, the absorption of the a-Ge:H layer becomes too weak. Figure 7 displays the dependence of measured QE spectra and of



Figure 7 Influence of resonator length on the **a**) measured QE curve of a-Ge:H single cells (weight function depicted additionally for reference) and **b**) on the potential $j_{SC,bottom}$ in a-Si:H/a-Ge:H tandem cells calculated from these curves. The inset shows a sketch of the experiment.

the corresponding $j_{SC,bottom}$ on the resonator length. According to the findings above, a centered absorber position was used for this sample set, while the thickness of the absorber layer was fixed to 25 nm. As demonstrated in Figure 7a, the position of the QE maximum can be easily tuned to higher or lower wavelengths by varying the cavity length. This provides a simple way to optimize the cells for application in multijunction solar cells. While the maximum QE value constantly stays near 80% up to a resonator length of 210 nm, the calculated $j_{SC,bottom}$ is significantly improved from 8.5 mAcm⁻² to a maximum of 10.7 mAcm⁻². At higher cavity lengths, the peak value of the QE declines. However, due to the shift of the peak to higher wavelengths, its contribution to $j_{SC,bottom}$ is improved, leading to a broad plateau of this quantity around 10.5 mAcm⁻². This leaves room for electrical optimization as well as for adaption of the device to the specific characteristics of the top cell.

As the weight function describes an a-Si:H top cell yielding a j_{SC} of about 12.5 mA cm⁻², the above results mean that the cumulated short circuit current density $j_{SC,total} = j_{SC,top} + j_{SC,bottom}$ in an a-Si:H/a-Ge:H tandem device of this type can reach up to about 23 mA cm⁻². To fabricate a current-matched device, a thinner top cell with a lower j_{SC} of about 11.5 mA cm⁻² would be necessary, assuming that the additional light transmitted could be fully gathered by the a-Ge:H bottom cell. While these are promising numbers, they also imply that corresponding a-Si:H/a-Ge:H tandem devices would yield a slightly lower j_{SC} than state of the art a-Si:H/ μ c-Si:H solar cells.

Accordingly, the next step is to investigate how a change of the absorber thickness impacts the device performance. Corresponding experimental QE and $j_{SC,bottom}$ results are presented in Figure 8. Although a constant cavity length of 210 nm has been used, the QE spectra reveal a shift of the resonance position towards higher wavelengths with increasing absorber thickness. This can be attributed to the slightly higher refractive index of a-Ge:H compared to the silicon layers. As a result, when increasing the absorber thickness to 50 nm, the resonance shift combined with a lower absorption coefficient at higher wavelengths leads to a decrease of the maximum QE value. Nevertheless, for wavelengths above 800 nm, a significant increase in QE is obtained. As demonstrated

in Figure 8b, this leads to a further increase of $j_{SC,bottom}$ to >12 mA cm⁻², while a rapid decline is obtained when reducing the absorber thickness to 13 nm.



Figure 8 Influence of absorber thickness on the **a**) QE curve of a-Ge:H single cells and **b**) on the potential $j_{SC,bottm}$ in a-Si:H/a-Ge:H tandem cells calculated from these curves. The inset shows a sketch of the experiment.

Of course, changing the absorber thickness has a strong impact on the electrical properties of the devices. Measured single cell jV-characteristics of the devices from Figure 8 are depicted in Figure 9, where each value is the average of 6 cells. In this case, results are presented for devices with and without nanorods grown on top of the ITO front contact, as these have a significant influence on the electrical properties. In both cases, the device parameters show the same trends with increasing absorber thickness. While j_{SC} is enhanced with increasing thickness, the open circuit voltage (V_{OC}) is reduced. This is the typical behavior of solar cells in which the charge carrier recombination is dominated by bulk defect states. While the fill factor is relatively constant for a thickness of 13 nm and 25 nm, its value is strongly reduced for a 50 nm thick a-Ge:H layer. This is a result of the high defect density inside the a-Ge:H layers. With the nanorods on top, a clear deterioration of the electrical properties (V_{OC} , FF) compared to the case without the nanorods is observed, while a clear improvement of j_{SC} is observed. This is accompanied by a lower shunt resistance $(1.1 \times 10^3 \ \Omega \ \text{cm}^2 \ \text{vs.} \ 2.7 \times 10^3 \ \Omega \ \text{cm}^2)$. We conclude that the deterioration of the electrical properties is mainly due to a corrupted laser separation of the cells, resulting from the high surface roughness. In both cases an optimum single cell efficiency of 3.5% is achieved with a 25 nm thick a-Ge:H absorber.

Although this is comparable to the performance of the best a-Ge:H nanocavity solar cells, the devices presented here enable a higher performance in tandem devices due to their high IR absorption. To demonstrate this effect, the benchmark parameters $j_{\rm SC,total}$ and $\eta_{\rm Benchmark}$ were calculated, as described in the methods section. For these calculations, we assumed that the negative effect of the nanorods on the electrical device properties can be mitigated by optimizing the corresponding process parameters or using a different scattering mechanism. Hence, the electrical parameters of the devices without nanorods were used together with the $j_{\rm SC,bottom}$ values of the samples with nanorods. The results, which are displayed in Figure 9, suggest that the tandem cell performance currently achievable with devices using a 25 nm thick a-Ge:H absorber is equivalent to



Figure 9 Influence of absorber thickness on measured device characteristics. Experimental results are presented for devices with and without nanorods on the ITO front contact. Additionally, the benchmark parameters $\eta_{Benchmark}$ and $j_{SC,total}$ are provided. The values of FF and V_{OC} used for calculation of these parameters are highlighted as well.

that of a μ c-Si:H device with 5% efficiency.

Conclusion

We presented a simulation-aided study of the optical properties of resonant-cavityenhanced a-Ge:H nanoabsorber solar cells exploiting second-order Fabry-Pérot resonances. We showed that the QE characteristics can be clearly related to the optical field distribution inside the resonator. In particular, it was shown that optimum utilization of the resonances is achieved by placing the absorber layer inside the center of the resonator. From the QE spectra, we estimated the short circuit current density that can be achieved in corresponding a-Si:H/a-Ge:H tandem solar cells ($j_{SC,bottom}$). Our results indicate that a cumulated j_{SC} of 23 mAcm⁻² is possible in such devices with an only 25 nm thick bottom cell absorber. This shows that the approach could indeed allow a low-cost high-throughput replacement of μ c-Si:H absorbers, provided that a further optimization of the electrical device characteristics is possible. While the absorber thickness which is required to achieve a certain $j_{SC,bottom}$ seems to be slightly higher compared to the nanocavity approach, the concept investigated here shows higher potential for electrical optimization due to the thicker silicon layers that can be utilized. The single cell efficiency of 3.5%, which was achieved in this work, is similar to the best nanocavity devices. However, due to the optimized infrared absorption, we estimate that the tandem cell performance of the device is equivalent to that of a μ c-Si:H solar cell yielding 5% single cell efficiency.
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4 Conclusions & Outlook

The objective of this work was to apply the concept of planar resonant cavities to enable a significant absorber thickness reduction in a-Ge:H solar cells, aiming to improve the charge carrier extraction. The work particularly focused on the applicability of this approach in multijunction solar cells, to pursue the overall goal of replacing μ c-Si:H in a-Si:H/ μ c-Si:H tandem devices. Two different kinds of resonant-cavity-enhanced (RCE) a-Ge:H solar cells, which mainly differ in the exploited resonance order, were investigated for this purpose.

While the *nanocavity* approach, studied in Paper I and II, exploits extremely broadband lowest-order resonances generated in ultrathin cavities using a metal back reflector, the second concept, investigated in Paper III and IV, utilizes the spectrally narrower *second-order* resonances in a longer cavity. In both cases, highly efficient absorption of the red/infrared spectrum, comparable to results achieved with typical μ c-Si:H solar cells, was obtained with a-Ge:H nanoabsorbers that were only 25 nm or less in thickness. Moreover, in accordance with the overall goal of replacing μ c-Si:H based bottom cells, it was demonstrated that both cell concepts are also compatible with tandem cell integration, which only required suppression of additional "inter-subcell" resonances. Due to the low absorber thickness, charge carrier extraction was significantly improved. Both nanocavity-enhanced a-Ge:H solar cells and RCE devices utilizing second-order resonance were capable of reaching efficiencies higher than the best literature results for a-Ge:H solar cells. Furthermore, while 4% single cell efficiency was reached using the second-order approach, its specific design for the tandem cell case was estimated to allow replacing a μ c-Si:H bottom cell with a higher single cell efficiency of about 5%.

Although this value is still too low for a reasonable replacement of μ c-Si:H, this result is particularly remarkable due to the fact that anodic PECVD has been used for the fabrication of the a-Ge:H layers. This deposition method is known to produce a-Ge:H films with less favorable electronic properties compared with cathodic PECVD, ECR-PECVD or sputtering. In fact, despite the improved overall efficiencies, the open circuit voltage of the devices presented here is lower compared to the best literature values. It is thus likely that the material quality of the utilized films is significantly below state of the art. Furthermore, as a result of the low absorber thickness, high impact of potential defect states at the hetero-interfaces between the a-Ge:H layer and the adjacent silicon layers is expected. Thus, having demonstrated the striking optical performance of RCE a-Ge:H solar cells, further work should clearly focus on improving the electronic properties of the absorber layers to reach state-of-the-art material quality, as well as on an optimization of the interfaces. In doing so, open circuit voltages equal to or in excess of the literature results should be possible. From this it can be estimated that μ c-Si:H devices with about 8% efficiency or more could be replaced in this case using the second-order approach.

4 Conclusions & Outlook

When comparing the two concepts described in this work with each other, both routes have their advantages and drawbacks, so that both should be investigated further.

In contrast to the second-order approach, nanocavity-enhanced a-Ge:H solar cells exhibit spectrally broadband absorption. This concept is thus particularly interesting for the single cell case, as it supports higher short circuit current densities. However, the concept also shows superior optical performance in the infrared spectral range, enabling higher current densities in tandem cells. Furthermore, nanocavities show much lower sensitivity to angle of incidence variations. This is a great advantage as it implies a low time-of-day variation of the absorption efficiency, which is particularly important in the tandem cell case, where the current densities generated by the top and bottom cell need to be matched. Moreover, while integration of the second-order approach in tandem devices most likely requires the fabrication of additional light scattering elements on the intermediate reflector, integration of nanocavity-enhanced devices was shown to be as simple as using a strongly textured TCO substrate. Such textured substrates are already widely used in silicon thin-film solar cells, meaning that this does not imply additional processing steps. It can be concluded that a-Si:H/a-Ge:H solar cells with nanocavityenhanced a-Ge:H bottom devices can easily be fabricated using existing silicon thin-film fabrication lines, and without using additional processing steps.

The downside of this approach is that the doped silicon layers need to be extremely thin to realize the low required cavity length. Hence, the electrical optimization of nanocavity-enhanced a-Ge:H solar cells is difficult. Here, the specific design of the second-order concept for the tandem cell case has the advantage that a longer cavity can be used, meaning that the doped layers can be thicker and, in principle, a bandgap grading can be used to improve the silicon-germanium hetero-interface. Despite a lower short circuit current density, the better electrical device properties resulting from thicker doped layers have led to a higher single cell efficiency in the experiment. Moreover, in the tandem cell case, the difference between both approaches with respect to short circuit current density is much lower than in the single cell case, so that the second-order concept currently has a significantly higher potential for this application.

A potential way to further improve the optical properties is to combine the resonantcavity approach with other light management concepts. For example, honeycomb structures could be used to implement geometric scattering to allow light to penetrate the resonator multiple times. Furthermore, for the nanocavity concept, it could be helpful to replace the doped silicon layer on the front side by a material having the same refractive index as the TCO (see Figure 1). In this case, the new doped layer were optically not part of the resonator anymore but instead would constitute a part of the semi-reflective mirror, meaning that it could be made thicker to improve electrical properties without changing the cavity length. Here, a wide-bandgap a-SiC:H(n) layer would be potentially suitable. Lastly, utilization of metamaterial mirrors to systematically tailor the phase shifts at the resonator interfaces could be an interesting option to achieve even more broadband absorption, perhaps also without the use of lossy metals.

Going beyond the specific case of a-Ge:H, other materials that are otherwise considered unsuitable for optoelectronic applications might also benefit from the drastic thickness



Figure 1 Nanocavity solar cell for which the n-doped layer on the front side is optically not part of the resonator.

reduction demonstrated here. Here, materials with high refractive indices are particularly suitable, as in this case, the semi-reflective interface required for resonances can easily be formed in combination with most TCOs. A rule of thumb to estimate whether or not a material is suitable for the nanocavity approach has been given in Paper I.

In summary, resonant-cavity-enhanced a-Ge:H nanoabsorber solar cells integrated in a-Si:H/a-Ge:H tandem devices would indeed allow a drastic throughput increase compared to the a-Si:H/ μ c-Si:H configuration, while yielding similar current densities. In particular, existing fabrication lines from the silicon thin-film industry could potentially be reused. Up to now, the efficiencies of the presented cells are too low for a reasonable implementation of the concept. However, the low absorber thickness strongly enhances charge carrier extraction, hence significantly improving the efficiency potential for a-Ge:H solar cells employing state-of-the-art absorber material quality. Currently, devices exploiting second-order resonances show higher potential for this application due to easier optimization of their electrical properties. However, a-Ge:H nanocavity solar cells should clearly be investigated further as well, as they yield vastly superior optical properties. In particular, provided that the efficiency can be increased further, this concept could be promising for low-cost high-throughput single junction solar cells for use in special applications, such as BIPV.

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Publications in Peer-Reviewed Journals

- V. Steenhoff, M. Juilfs, R.-E. Ravekes, M. Ahrlich, M. Kellermann, O. Siepmann, M. Vehse, and C. Agert. Optimized Optical Field Profile in Resonant-Cavity-Enhanced a-Ge:H Nanoabsorber Solar Cells for Tandem Cell Application. IEEE Journal of Photovoltaics, 2016. doi:10.1109/jphotov.2016.2617039.
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Other Scientific Contributions

- V. Steenhoff, M. Vehse, and C. Agert. Optimal utilization of the optical field distribution in RCE a-Ge:H nanoabsorber solar cells. 32nd European Solar Energy Conference, Munich, Germany, June 2016. Talk.
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Submitted Patents

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Erklärung gemäß §12 der Promotionsordnung

Hiermit erkläre ich, Volker Steenhoff, dass ich die Dissertation selbstständig verfasst habe und dass die benutzten Hilfsmittel vollständig angegeben sind. Die vorliegende Arbeit wurde in Teilen bereits veröffentlicht. Die entsprechenden Textabschnitte sind entsprechend gekennzeichnet und eine Publikationsliste ist beigefügt. Des Weiteren erkläre ich, dass die Dissertation weder in ihrer Gesamtheit noch in Teilen einer anderen Hochschule zur Begutachtung in einem Promotionsverfahren vorliegt oder vorgelegen hat. Die Leitlinien guter wissenschaftlicher Praxis der Carl von Ossietzky Universität Oldenburg wurden bei der Erstellung dieser Arbeit befolgt. Es wurden im Zusammenhang mit dem Promotionsvorhaben keine kommerziellen Vermittlungs- oder Beratungsdienste in Anspruch genommen.

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