

Chapter 1

Introduction

Solar cells provide a nearly inexhaustible, environmentally neutral way to produce electricity. After the first discovery of the photoelectric effect in 1839 by Becquerel [1], the technological breakthrough came in 1954 when D.M. Chapin, C.S. Fuller, and G.L. Pearson first reported of a crystalline silicon based solar cell with a conversion efficiency of $\eta = 6\%$ [2]. Since then a lot of progress, in both the scientific and the technological sense, has been made, and nowadays conversion efficiencies for silicon solar cells of up to 20% for commercial manufacture and above 24% on the laboratory scale have been achieved [3]. However, the costs of photovoltaics are still too high to be competitive with classical electricity production, e.g. coal/oil/gas-fired or nuclear fission powerplants. Thin film solar cells offer a great potential for a reduction of costs as they combine the advantage of low temperature procession, low material consumption, large area producibility as well as the prospect of monolithic series connection to modules [4, 5]. The most promising materials for thin film solar cells are copper-indium-gallium-diselenite (CIGS), cadmium-tellurite (CdTe), and thin film silicon in various modifications. Photovoltaic modules based on amorphous silicon were the first thin film solar cells commercially available and are presently the only thin film devices that have an impact on the photovoltaic world market [5]. However, the conversion efficiencies of solar cell modules based on amorphous silicon are low ($\eta=4-7\%$ [6]), caused by the presence of defects, tail states, and light induced degradation, known as Staebler-Wronski effect (SWE) [7].

Recently, microcrystalline silicon ($\mu\text{c-Si:H}$) has attracted interest due to its higher stability against light induced degradation, with the absorption extending into the near infrared, similar to crystalline silicon. First produced as a thin film by Vepřek and Mareček in 1968 [8] using a hydrogen plasma chemical transport technique, it has been shown about 10 years later by Usui and Kikuchi [9] that $\mu\text{c-Si:H}$ can also be prepared using plasma enhanced chemical vapor deposition

(PECVD), providing compatibility with already well established amorphous thin film technology. In the last few years much progress regarding the preparation, the solar cell performance as well as the understanding of the structural and electronic properties of $\mu\text{c-Si:H}$ has been made. However, there are still tremendous technological and scientific challenges, e.g. the understanding of the interrelation between the solar cell performance and the material properties of $\mu\text{c-Si:H}$ are of great interest. Microcrystalline silicon as referred to in the literature describes a wide range of silicon material rather than a well defined system. In fact, $\mu\text{c-Si:H}$ is a structure modification consisting of varying amounts of microcrystallites, hydrogenated amorphous silicon and voids [10, 11]. Interestingly, it has been shown that not, as one might expect, material with the highest crystalline volume fractions and the largest crystallite size but material prepared close to the transition to amorphous growth yields the highest conversion efficiencies [12, 13]. Obviously, the transition between microcrystalline and amorphous growth is of great importance. Approaching this transition, e.g. by increasing the silane concentration, the structural as well as the optoelectronic properties, e.g. the electronic conductivity, the photosensitivity as well as the spin density, of the $\mu\text{c-Si:H}$ material change significantly [14, 15, 16, 17, 18, 13]. The variation of the amorphous volume content is often accompanied by changes of the compactness of the material. In particular it is generally observed that deposition conditions which lead to the technologically needed high deposition rates, tend to result in a porous structure. Also attempts to grow material with large grain size in order to improve the carrier mobility, frequently result in porous material. Although it has been reported that $\mu\text{c-Si:H}$ is more resistant [13] and highly crystalline material even does not suffer from SWE [19], the presence of crack-like voids makes this material susceptible to in-diffusion of impurities and atmospheric gases which might lead to various metastable and irreversible effects. Earlier investigations on highly crystalline material prepared with chemical transport deposition show that atmospheric gas adsorption and/or oxidation affects the density of surface states, electrical transport and the electron spin density [20]. So far only a few investigations on in- and meta-stable effects on recently prepared material exists [21, 22, 23], and the detailed nature of these effects is presently still not understood. The rather complicated structure has major consequences on the electronic structure, e.g. the density of states (DOS) within the band gap. In particular, since there is no well defined structure, the microscopic identification of states observed is complicated as they can be located in the various phases, at boundaries or at interfaces. It is therefore not surprising that there exists no conclusive DOS map and the understanding does in many cases not go beyond a phenomenological description. Thus a study of the density and properties of defect states as a function of the structural composition is of great importance.

Electron spin resonance (ESR) is a powerful tool to investigate and identify

defect states provided that they are paramagnetic and it has been successfully applied to amorphous silicon and its alloys (see e.g. [24, 25, 26]). First applied to $\mu\text{c-Si:H}$ in the 80s [20, 27, 28], systematic studies have only been performed in the last recent years, and various ESR signals have been identified [29, 30, 31, 32]. Intrinsic $\mu\text{c-Si:H}$ shows an asymmetric signal with contributions at $g=2.0043$ (db_1) and $g=2.0052$ (db_2). The origins of these lines are still under discussion. While it has been suggested that the asymmetry results from an axial symmetric g -tensor of defects on grain surfaces [31], there are a number of indications that these lines originate from two independent states located in different microscopic environments [21, 33, 34, 35, 36, 32]. For n-type material and also for illuminated material a third resonance at $g=1.996$ - 1.998 can be observed. According to a similar resonance found in polycrystalline silicon this resonance has been called CE-Line and has been attributed to electrons in the conduction band [27, 29] and later also to shallow localized states in the conduction band-tail [35, 36, 37, 38]. A number of reports on ESR properties of highly crystalline n-type $\mu\text{c-Si:H}$ have been published and show that highly crystalline n-type material shows a nearly linear dependence of the dark conductivity σ_d on phosphorous doping concentrations for $PC = [\text{PH}_3]/([\text{PH}_3]+[\text{SiH}_4])$ higher than 10 ppm [30, 39, 40]. For lower doping concentrations the conductivity deviates from this linear dependence. It is likely that within this doping regime the Fermi level shift is governed by the compensation of gap states. However, this has not been proven yet and will be a key task of this work.

Moreover, the presence of localized states within the bandgap has a major influence on the transport properties and has to be considered in order to explain transport features. In contrast to c-Si, the occurrence of band-tail states and deep defects open additional transport paths, they might act as traps for charge carriers, or form barriers. There is, of course, a wide range of possible structures in microcrystalline silicon materials. This explains the large spread in reported drift mobilities and transport properties. In the past, various models have been proposed to describe the transport in $\mu\text{c-Si:H}$. These models adopt and combine former approaches successfully applied for either polycrystalline or pure amorphous material, e.g. for n-type $\mu\text{c-Si:H}$ the so called "grain boundary trapping model" [41], successfully applied to poly-crystalline silicon, has been used to describe the transport behavior [42, 43] and also percolation models were applied to interpret conductivity and Hall effect data [44, 45]. On the other hand, similarities between a-Si:H and $\mu\text{c-Si:H}$ suggest that structural disorder are from constitutional importance and transport might take place by direct tunneling between localized states (hopping) or by trap-limited band motion (multiple trapping) [46, 47, 48, 49].

This work provides a comprehensive study of paramagnetic centers in $\mu\text{c-Si:H}$. Material with different structure compositions and doping levels have been inves-

tigated by ESR and electrical conductivity. It will be shown that structural changes influence the nature as well as the density of the defects. Accompanied by structural changes the material tends to be susceptible of instabilities due to adsorption and chemical reactions of atmospheric gases. The present work investigates and identifies instability effects caused by adsorption and oxidation in state of the art material, with a wide range of structure compositions. The application of additional n-doping will be used as a probe for the density of gap states. Additionally, the transport properties of highly crystalline $\mu\text{c-Si:H}$ will be studied using transient time-of-flight experiments.

This thesis is organized as follows:

Chapter 2: A short summary of the structural properties as well as their impact on the electronic structure of microcrystalline silicon is given. In the second part, the influences of the electronic properties on electrical transport will be treated. Different transport models proposed for $\mu\text{c-Si:H}$ material are shown and compared.

Chapter 3: A short presentation of the experimental techniques, used in this work, is followed by a brief description of the deposition process and the particular preparation of the samples.

Chapter 4: In Chapters 4-8, the results of the material characterization are presented and discussed. Chapter 4 addresses the properties of paramagnetic states in intrinsic $\mu\text{c-Si:H}$ with varying structure compositions ranging from highly crystalline to fully amorphous.

Chapter 5: In this Chapter films with different structure compositions and doping levels are studied by ESR and electrical conductivity. n-Doping densities in the range of the intrinsic defect density are used as a probe for the density of gap states.

Chapter 6: Electron spin resonance and conductivity measurements are used to study adsorption and oxidation effects on $\mu\text{c-Si:H}$ with different structure compositions. The magnitude of observed meta-stable and irreversible effects will be discussed with respect to changes of the active surface area.

Chapter 7: The hole transport properties of highly crystalline material are studied in this Chapter. Transient photocurrent measurements are presented and consistently analyzed using the model of multiple trapping in an exponential band-tail.

Chapter 8: In this chapter, the information derived from the studies in Chapters 4-7 will be combined and summarized in a schematic picture of the density of states in both, a spatial and energetic sense.

Chapter 9: In this last chapters, the most important results will be summarized and the conclusions are drawn.

