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Multi-frequency EDMR applied to microcrystalline thin-film silicon solar cells

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ABSTRACT

Pulsed multi-frequency electrically detected magnetic resonance (EDMR) at X-, Q- and W-Band (9.7, 34, and 94 GHz) was applied to investigate paramagnetic centers in microcrystalline silicon thin-film solar cells under illumination. The EDMR spectra are decomposed into resonances of conduction band tail states (e states) and phosphorus donor states (P states) from the amorphous layer and localized states near the conduction band (CE states) in the microcrystalline layer. The e resonance has a symmetric profile at all three frequencies, whereas the CE resonance reveals an asymmetry especially at W-band. This is suggested to be due to a size distribution of Si crystallites in the microcrystalline material. A gain in spectral resolution for the e and CE resonances at high fields and frequencies demonstrates the advantages of high-field EDMR for investigating devices of disordered Si. The microwave frequency independence of the EDMR spectra indicates that a spin-dependent process independent of thermal spin-polarization is responsible for the EDMR signals observed at X-, Q- and W-band.

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1. Introduction

Thin-film solar cells bear the potential of converting solar energy at much lower costs than the well established wafer-based technology. Among the various materials used in thin-film solar cells, hydrogenated amorphous silicon (a-Si:H) and hydrogenated microcrystalline silicon (μc-Si:H) play a key role. Both materials can directly be deposited from the gas phase using low-temperature processes on inexpensive substrates and require only a fraction of the material that is necessary for crystalline silicon (c-Si) solar cells [1–4]. By choice of the deposition parameters a-Si:H and μc-Si:H can be produced with the same deposition equipment and can thus easily be combined in one device. This allows for the fabrication of tandem solar cells utilizing the different band gaps of a-Si:H and μc-Si:H and, consequently, a more efficient use of the solar spectrum.

Since the fabrication of the first a-Si:H solar cell in 1976 [5], the maximum conversion efficiencies increased steadily to more than 12% for a-Si:H/μc-Si:H tandems [6,7]. However, this value is well below the maximum efficiencies achieved with c-Si-based cells [8]. This gap is due to the inferior electrical properties of amorphous thin-film silicon as compared to its crystalline counterpart. Deep defects due to dangling bonds (db) and localized tail states in the band gap induced by strained bonds act as recombination centers and traps, respectively, and thereby influence the charge transport of photogenerated charge carriers. They thus diminish the performance of the cell. Understanding these loss mechanisms on a microscopic level is a necessary prerequisite for the development of advanced cell concepts minimizing the detrimental influence of defect states on the cell performance.

Whenever a localized defect state is occupied by an odd number of electrons, it is paramagnetic and can be detected by electron paramagnetic resonance (EPR) spectroscopy. EPR can determine defect concentrations and thus allows for an optimization of a-Si:H and μc-Si:H deposition parameters [9]. Since the electron spin trapped in a defect state constitutes a sensitive probe for electron and nuclear spins in its vicinity, EPR and related multi-resonance techniques can deliver helpful information on defect structures in solar cell materials [10–12]. In particular a multi-frequency approach has recently proven successful for the investigation of the EPR parameters of dbs in a-Si:H [13].

Whether these paramagnetic defects are indeed involved in trapping and recombination processes can conveniently be analyzed when combining EPR with a photocurrent measurement. The resulting technique, electrically detected magnetic resonance (EDMR) [14], interferes with spin-dependent recombination or

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hopping rates and probes the resulting change in conductivity. EDMR employing continuous wave (cw) microwave (mw) excitation has been applied to film silicon films and devices for a couple of years [15]. More recently the combination of electrical detection with pulsed mw excitation schemes was shown to provide new insight into charge carrier recombination and hopping transport in thin-film silicon devices [16–18]. On the one hand, exploiting the time regime enabled the discrimination between spectrally overlapping EDMR signals associated with different spin-dependent processes in a-Si:H and μc-Si:H-based solar cells [19,20]. On the other hand, pulsed EDMR (pEDMR) has paved the way for the application of sophisticated detection schemes known from mw-detected EPR [21–24].

The present study is an extension of previous pEDMR work performed on μc-Si:H p-i-n thin-film solar cells [19,20]. Based on X-band pEDMR at cryogenic temperatures three resonances in the pEDMR spectrum could be identified (Fig. 1). First, a signal at $g_{CE} = 1.9975(5)$ (CE signal) from shallow localized states in energetic proximity to the μc-Si:H conduction band. This signal could be further attributed to states within μc-Si:H grains by electrically detected ESEEM [24]. Second, a resonance at $g_e = 2.0049(5)$ (e signal) originating from n-a-Si:H conduction band tail states. Third, doublet signals of P donor states in n-a-Si:H. These signals are centered around $g_P \approx 2.003(1)$ (P signal) and exhibit a ^{31}P hyperfine splitting ($I = 1/2$, natural abundance 100%) of ≈25 mT.

All three signals were assigned to spin-dependent hopping processes in the μc-Si:H and n-a-Si:H layers. Since the energetic position of the quasi Fermi levels under the experimental conditions used here is supposed to be in the range of the band tail states, electrical transport is strongly influenced by hopping of charge carriers along localized states. No indications for spin-dependent recombination via db states could be found in the EDMR spectra. Possibly, the strong hopping signals superimpose a weaker db recombination signal. This hypothesis is consistent with the results of a previous study, where an EDMR recombination signal could only be found in purely microcrystalline p-i-n solar cells, but not in cells with amorphous p- and/or n-doped layers exhibiting strong EDMR signals from hopping transport via tail states [20].

Despite the fact that detailed insight about spin-dependent transport processes could be obtained from the above mentioned studies, several important questions remained unsolved. The limited spectral resolution at X-band frequencies did not allow for extracting field-dependent EDMR line shapes. These parameters reveal important information about the electronic structure of paramagnetic states contained in the distribution and canonical values of the electronic g-matrix. In order to obtain these pieces of information, high field/high frequency EDMR experiments are required. Furthermore, recent X-band pEDMR works on μc-Si:H solar cells assumed spin pair processes to be responsible for the observed spin-dependent transport processes. These processes do not depend on the equilibrium Boltzmann spin polarization. However, studies limited to one polarization regime may miss other important spin polarization dependent transport processes like, e.g. recombination of electrons and holes in the conduction and valence bands with thermalized spin polarization [25], trapping of conduction electrons at ionized donors [26], spin-dependent scattering [27] or polarization transfer from donors to delocalized electrons [28]. In order to investigate the impact of these processes, EDMR experiments at different resonance fields and/or temperatures are required. Finally, an unambiguous assignment of paramagnetic states in μc-Si:H solar cells by X-band EDMR is limited by the fact that field-dependent (Zeeman interaction) and field-independent (spin–spin interactions) line shape contributions cannot be discriminated.

In order to lift these restrictions we extend X-band EDMR in the present work to a multi-frequency EDMR approach. Thereby, we benefit from the enhanced spectral resolution at Q- and W-band frequencies and discriminate between field-dependent and field-independent line shape parameters, advantages which are routinely used in conventional EPR spectroscopy [13,29]. With this approach it is possible to assign magnetic field-dependent line broadening contributions to the different spectral components. Furthermore, we will investigate whether significant thermal spin polarization, which exists for low temperature W-band EDMR, influences the nature of the spin-dependent processes and thereby the EDMR spectrum.

After briefly describing the X-, Q- and W-band setups, we present the results of the multi-frequency study. First, the experimental spectra are described followed by the explanation of the methods for the spectral deconvolution. Afterwards we determine precise g-values of the e and P signals and corroborate hyperfine (hf) interaction as the reason for the splitting of the P resonance and consider the line profile of the CE line making use of the decomposed spectra. We analyze the influence of field-dependent line broadening effects of the deconvoluted CE and e signals on the spectral resolution in the EDMR spectra. Finally, we discuss the effect of thermal spin polarization on the EDMR spectrum.

2. Materials and methods

2.1. Principle of EDMR

The concept of pulsed EDMR [16,17] is explained by discussing the most prominent spin-dependent charge transport processes in the investigated device at low temperature. Illumination of the

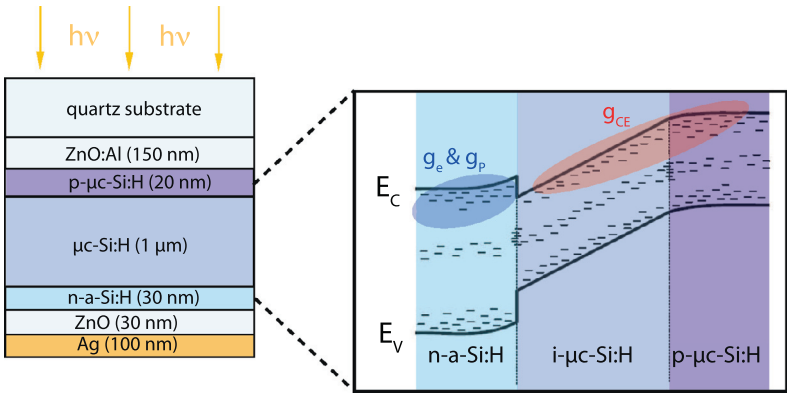

Fig. 1. Left: layer structure of the μc-Si:H p-i-n thin-film solar cells. Right: schematic representation of the energy-band diagram at room temperature without illumination. The amorphous layer can be identified by the larger band gap. The detected signals are assigned to hopping transport via shallow conduction band tail states at a g-value of g_{CE} in the μc-Si:H regions and conduction band tail states at g_e as well as phosphorus donor states at g_P in the amorphous layer.

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