The advance and successful commercialization of crystalline silicon (c-Si) solar cells demonstrates the practicality of large scale photovoltaic energy production. The high efficiencies that can be reached with wafer-based technologies, however, come along with the energy and cost intensive wafer production process. In contrast, thin film solar cells made from hydrogenated amorphous (a-Si:H) and microcrystalline silicon (μc-Si:H) can be deposited directly on inexpensive substrates like glass and are superior with regard to material consumption and cost effectiveness. 1–7 Despite these apparent benefits, thin-film silicon solar cells exhibit inferior electronic properties and mobilities, further understanding of the microscopic nature of these shallow states is necessary, which requires tailor made characterization tools capable of characterizing device limiting defects.

In μc-Si:H, the relevant defects are paramagnetic. 10–13 This renders electron paramagnetic resonance (EPR) the method of choice to unravel the microscopic defect structure and shed light on the influence of defect centers on charge-carrier transport mechanisms. In particular, hyperfine interactions (HFI) between the unpaired electron spin and nuclear spins in its vicinity constitute ultra sensitive probes of the defect wave function and the material composition in the vicinity of the defect. μc-Si:H is a mixed phase material with crystalline grains embedded in a hydrogenated amorphous matrix. 14 n-type μc-Si:H or intrinsic μc-Si:H under white light illumination show a prominent EPR signal with a g-value of g = 1.9970–1.9985 [denoted as conduction electron (CE) center]. 10,11 Several possibilities for the microscopic origin of the CE center have been discussed in literature: (a) free electrons in the conduction band (CE resonance), 10 (b) interface defects at the boundary of amorphous and crystalline phases, 15 (c) electrons confined to an inversion layer at the boundary of amorphous and crystalline phases of the material (Ref. 16) and (d) localized states due to internal twin grain boundaries inside of crystalline columns (Refs. 7 and 13). One way to distinguish between these models is to identify the microscopic structure of the CE center by determining how the unpaired electron spin is distributed over atoms in its vicinity. This requires knowledge about HFIs with nuclei in the first and second coordination shell accessible by EPR. However, the wave function of defects and impurities decays exponentially, and the vast majority of HFIs is small (< 10 MHz) and usually not resolved in field-swept EPR spectra. Zhou et al. 17 investigated CE centers in μc-Si:H samples by electron-spin-echo envelope modulation (ESEEM) spectroscopy to detect small HFIs of the CE center with magnetic nuclei in their vicinity. They found that ESEEM spectra of CE centers lack contributions from hydrogen HFIs and therefore concluded that the vicinity of these centers is depleted from H atoms. This important finding implies that CE centers cannot be located at the interface between amorphous and crystalline phases of μc-Si:H due to the fact that the amorphous phase is H rich. 12 However, it remains unclear whether this assignment also holds true for CE centers in fully processed μc-Si:H solar cells, since Zhou et al. 17 studied highly crystalline and fairly conductive (dark conductivity @300 K: σRT = 10−5 S/cm) powder samples with material properties being far from state-of-the-art thin-film solar cell materials (for a definition of state-of-the-art silicon materials see Ref. 2, Table 3.2, p. 55, Ref. 7, Chap. 3, and Ref. 18). However, ESEEM relies on conventional EPR and is therefore not applicable to fully-processed thin-film solar cells due to the low sensitivity of EPR. Very recently it was shown that this limit may be lifted by combining the sensitivity of electrical detection with advanced pulsed EPR detection schemes in an electrically detected (ED)-ESEEM experiment. 19 This progress essentially relies on the introduction of pulsed electrically detected magnetic resonance (pEDMR) techniques 20 approaching sensitivities down to single spin detection. 21 In the present work, we applied this method to study spin-dependent transport processes in a fully processed multilayer thin-film μc-Si:H solar cell with
TABLE I. PECVD deposition conditions for different layers of the investigated μc-Si:H solar cells. SC denotes the silane concentration in H2; the dopant gas concentration is given as a percentage of the silane gas flow, P denotes the reactor power density, \( p_{\text{deg}} \) the chamber pressure during deposition, and \( T_s \) the substrate temperature. Sample laboratory reference: FZ-Jülich 05L-309.

<table>
<thead>
<tr>
<th>Layer</th>
<th>SC [%]</th>
<th>Dopant gas [%]</th>
<th>( P ) [W/cm²]</th>
<th>( p_{\text{deg}} ) [Torr]</th>
<th>( T_s ) [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>( p )</td>
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<td>0.5 (TMB)</td>
<td>0.28</td>
<td>10</td>
<td>200</td>
</tr>
<tr>
<td>( i )</td>
<td>0.8</td>
<td>-</td>
<td>0.25</td>
<td>10</td>
<td>150</td>
</tr>
<tr>
<td>( n )</td>
<td>9.1</td>
<td>1.0 (PH₃)</td>
<td>0.02</td>
<td>3</td>
<td>200</td>
</tr>
</tbody>
</table>

few electron spins (number of spins \( \approx 10^4 \)). We show that this approach allows us to selectively investigate transport determining paramagnetic sites in the multilayer device.

Thin-film silicon \( p-i-n \) solar cells were deposited using 13.56 MHz plasma-enhanced chemical vapor deposition (PECVD) in the high radio-frequency power and high deposition pressure regime (for an overview of the PECVD deposition conditions see Table I). The cells are deposited on Corning glass and consist of a layer stack with 150 nm ZnO:Al ITO, boron-doped \( p \)-μc-Si:H, 1-μm intrinsic μc-Si:H absorber, phosphorous-doped \( n \)-a-Si:H emitter, ZnO, and silver as a back contact. The total phosphorus and boron solid-phase concentration is estimated to be 1.5 at.% and 0.2 at.%, respectively. The hydrogen concentration and boron in the thin \( n \)-a-Si:H layer is estimated to be 12(2) at.%. The crystallinity of the intrinsic μc-Si:H layer in the fully processed solar cell is 65% as determined by Raman spectroscopy. The hydrogen concentration in the intrinsic μc-Si:H layer is estimated to be 8(2) at.%. Assuming that the crystalline phase contains negligible amounts of hydrogen, we can estimate the hydrogen content of the amorphous phase of the intrinsic μc-Si:H layer to be 22 at.%. All measurements were carried out on a commercially available BRUKER E580 spectrometer at 9.7 GHz in a dielectric ring resonator (ER 4118X-MD5) and using a laboratory-built current detection extension. The current response of the sample was recorded by a current amplifier and integrated from 3 μs to 8 μs for spin echo measurements to obtain a charge \( \Delta Q \). A detailed description of the experimental setup can be found in Ref. 29.

Figure 1 shows a field-swept pEDMR spectrum of the μc-Si:H solar cell recorded as a transient current change 3 μs after a 100 ns π pulse. The pEDMR spectrum shows narrow resonances attributed to \( e \) and CE centers in addition to a broad resonance of \( P^0 \) donor states split by a large isotropic HFI. Deconvoluted pEDMR spectra are shown by dotted lines. ESEEM measurements are carried out at magnetic-field positions indicated by \( g_e \) and \( g_{\text{CE}} \). The excitation profile of a 32 ns π-pulse is shown by the dashed line (red).

and therefore separates \( e \) center from \( P^0 \) donor transitions spectrally. The remaining signal has been assigned to hopping transport among CE centers \( [g_{\text{CE}} = 1.9975(5)] \) in the μc-Si:H absorber layer. Since hopping transport can only occur between localized states in the mobility gap, CE centers observed here by EMDR cannot be attributed to free electrons in the conduction band (see above: model a).

In the following, we apply ED-ESEEM to investigate paramagnetic states in thin-film silicon solar cells, \( e \) centers in the \( n \)-type \( a \)-Si:H emitter and CE centers in the μc-Si:H absorber layer. From ED-ESEEM spectra, we estimate HFIs and discuss the microscopic origin of the investigated paramagnetic centers. ESEEM is based on a two-pulse sequence \( \pi/2 - \tau_1 - \pi - \tau_2 \) where coherences are refocused at \( \tau_2 = \tau_1 \) to generate a spin echo, whose amplitude is measured as a function of \( \tau = \tau_1 \). For electrical detection of the spin echo, the standard two-pulse ESEEM sequence is augmented with a \( \pi/2 \) readout pulse at the time of echo formation to transfer electron coherence to polarization [see Fig. 2(a)]. The observed EMDR hopping transport signals originate from two coupled \( S = 1/2 \) electron spins \( S_1 \) and \( S_2 \) and can be described within the coupled radical pair model. As an example, we consider \( e \) center \((S_1)\) and \( P^0 \) donor \((S_2)\) electron-spin pairs. Transitions between CE states are described in a similar way and we assume that spin pairs are weakly coupled. Let us further assume that \( S_1 \) is coupled to a nuclear spin \( I_1 = 1/2 \) of, for now, arbitrary origin and that \( S_2 \) is solely coupled to its \( 31P \) nuclear spin \( I_2 = 1/2 \). If the HFI between the excited electron spin \((S_1)\) and \( I_1 \) is anisotropic, ESEEM is induced by the formation of coherence-transfer echoes. Quantitatively, the two-pulse ED-ESEEM echo intensity for weakly coupled spin pairs as a function of \( \tau \) under
selective excitation of $S_1$ can be adapted from a calculation of spin-correlated radical pairs\textsuperscript{36} and is given by

$$V_{2p}(\tau) = 1 - \frac{k}{4}(2 - 2 \cos \omega_e \tau - 2 \cos \omega_\beta \tau + \cos \omega_e \tau + \cos \omega_\beta \tau)$$

with nuclear frequencies of $I_1$: $\omega_{I_1} = \sqrt{(\omega I_1 \pm \frac{3}{2})^2 + \frac{B_f^2}{4}}$, $\omega_e = \omega_{I_1} \pm \omega_\beta$ and the modulation depth parameter $k = (\frac{B_f}{\omega_{I_1}})^2$. For an axially symmetric HFI between $S_1$ and $I_1$ the secular and the pseudo-secular part can be expressed as $A = A_{\text{iso}} + A_{\text{dip}}(3 \cos^2 \theta - 1)$ and $B = 3A_{\text{dip}}(\sin \theta \cos \theta)$, where $A_{\text{iso}}$ and $A_{\text{dip}}$ denote the isotropic and anisotropic HFI, respectively and $\theta$ indicates the angle between the external magnetic field vector and the axis connecting electron and nuclear spins.\textsuperscript{37}

To record ESEEM, we incremented the delay times simultaneously $\tau_1 = \tau_2 = \tau$ and eliminated the unmodulated part of the echo envelope (approximate exponential decay time constant $T_D = 1.6 \mu s$) through division by a polynomial fit. The remaining modulated part of the echo envelope is shown in Fig. 2(b). Before fast-Fourier transformation (FFT), the time traces were apodized by a Kaiser $2\pi$ window to obtain a high side-band suppression and zero filled up to 4096 points.

The upper curve in Fig. 2(c) shows the FFT of the $e$ center echo envelope. Several pronounced resonance peaks are observed at frequencies matching computed $\omega_I$ or $2\omega_I$ of $^{29}$Si, $^{31}$P, and $^1$H nuclei, indicated by vertical lines in Fig. 2(c). According to Eq. (1), this means that each nuclear spin with nuclear frequencies $\omega_{I_1} \approx \omega I$ exhibits weak anisotropic and negligible isotropic HFI. Hence, the observed ESEEM pattern originates from a large number of distant matrix nuclei. Eq. (1) shows that in addition to modulations at the nuclear frequencies $\omega_{I_1}/\beta$, the present ESEEM pulse sequence also gives rise to modulations at $\omega_{e} \approx 2\omega_I$. Echo modulations at $\omega_{e} \approx 0$ are usually not observed since they overlap with the intense zero-frequency component of the time trace. The spectrum of $e$ centers shows strong $^{31}$P ESEEM since these centers are located in the a-Si:H emitter layer of the solar cell doped with a large concentration of phosphorous. Doping studies of a-Si:H showed that phosphorous atoms occur in threefold-coordinated ($P_3$) and fourfold-coordinated ($P_4$) atomic configurations, where only the latter acts as a dopant.\textsuperscript{38}

Although the experiment shows that the electron spins are coupled to $^{31}$P nuclei, it is not immediately clear whether the $^{31}$P nuclei are part of the diamagnetic ($P_3^0$) or paramagnetic ($P_3^+$) atomic configuration of P impurities. In both cases, the $^{31}$P nuclear spin will interact with the electron spin of the $e$ center ($S_1$) via HFI, also in case the paramagnetic $P_3^+$ is the actual spin-pair partner of the $e$ center (special case $I_1 = I_2$). In the latter case, however, forbidden transitions involving a simultaneous flip of the electron and nuclear spin are shifted in energy relative to allowed $S_1$ transitions due to the large HFI between $I_1$ and $S_2$ ($\approx 800 \text{ MHz}$). In this case, the condition for a simultaneous excitation of allowed and forbidden transitions, a prerequisite for the observation of ESEEM,\textsuperscript{39} is not met due to a limited experimental excitation bandwidth ($\approx 100 \text{ MHz}$).

We therefore attribute the $^{31}$P nuclei observed by ESEEM to a-Si:H absorber. In a-Si:H emitter layer of the solar cell, $^{31}$P centers are located in the a-Si:H emitter layer of the solar cell doped with a large concentration of phosphorous. Doping studies of a-Si:H showed that phosphorous atoms occur in threefold-coordinated ($P_3$) and fourfold-coordinated ($P_4$) atomic configurations, where only the latter acts as a dopant.\textsuperscript{38}

CE centers were investigated under otherwise identical conditions by slightly tuning the magnetic field to excite centers with $g_{\text{CE}} = 1.9983$. The resulting ESEEM spectra are similar to those of $e$ centers, but show a strong reduction of the $\omega_{e}^{(31)P}/\omega_{e}^{(29)Si}$ intensity ratio [see lower curve in Fig. 2(c)] since CE centers are located in the undoped $\mu$-c-Si:H absorber. The residual contribution of $^{31}$P ESEEM is attributed to an...
off-resonant excitation of $e$ centers by the broad excitation profile of the microwave pulses and does not arise due to HFI between CE centers and $^{31}$P nuclear spins. This is verified by a numerical simulation of the microwave pulse sequence excitation profile (see Fig. 1), which shows that the employed microwave pulses still excite a rather large fraction of the $e$ center resonance. A quantitative simulation shows that the off-resonant $e$ center contribution is only reduced by a factor of two when tuning the magnetic field to $g_{CE}$ (see Fig. 2(c)).

We therefore conclude that the residual $^{31}$P ESEEM does not originate from CE centers.

The same argumentation holds for $^1$H ESEEM observed in the case of CE centers. The signal contributions at $\omega_I(^1H)$ or $2\omega_I(^1H)$ are reduced by about a factor of two as compared to $e$ centers and can again be assigned to an off-resonant excitation of $e$ centers. To recover the true ESEEM spectrum of CE centers free of contributions from off-resonant excitation of $e$ centers, we first scale the $e$ center ESEEM spectrum to the CE center spectrum using the $2\nu(^{31}P)$ peak as a normalization point and, second, subtract the scaled spectrum from the CE center spectrum. The true CE center ESEEM spectrum after subtraction is shown by the blue trace (lowest spectrum) in Fig. 2(c). We see that within the signal-to-noise ratio, the CE centers do not exhibit ESEEM signal contributions at $\omega_I(^1H)$ or $2\omega_I(^1H)$. Hence, the density of distant hydrogen atoms around CE centers is significantly smaller than in the case of $e$ centers. This observation now allows us to distinguish between microscopic models for the CE center introduced above (models b–d). Due to the lack of H coupling, the states must be located within H-free regions of the material. The crystalline columns present in $\mu$-c-Si:H consist of grains of perfect crystal quality separated by grain boundaries.40 In contrast to the columns present in a-Si:H, dislocations or point defects are absent in crystalline columns and grains.40 The only important lattice distortions or crystal defects in crystalline grains are coherent twin boundaries with a high density (twin fault probability $\lambda = 0.1$).40 Theoretical studies of the atomic and electronic structure of silicon twin grain boundaries revealed that they induce shallow localized electronic states.41,42

The latter can be rationalized qualitatively by considering that coherent twin grain boundaries conserve the tetrahedral coordination of the lattice while the bond lengths and angles of Si atoms at the grain boundary are disturbed. This shifts the bonding and antibonding orbitals of Si-Si bonds, inducing the formation of electronic states at the band edges. A similar effect has been observed in the case of tilt boundaries in silicon bicrystals giving rise to conduction band tail states.43

We therefore assign the microscopic origin of CE centers to localized conduction band tail states induced by twin grain boundaries. These centers are restricted to the crystalline phase of $\mu$-c-Si:H.

In conclusion, we investigated $e$ and CE centers in $\mu$-c-Si:H thin-film solar cells by ED-ESEEM. Echo modulations arise due to highly-abundant matrix nuclei ($^{29}$Si, $^{31}$P, and $^1$H), which exhibit small HFIs and are therefore weakly coupled to paramagnetic sites. ESEEM of $e$ centers in the a-Si:H emitter layer show a pronounced contribution of $^{31}$P nuclei since the emitter layer is doped with a large amount of phosphorous. This contribution is strongly reduced in the case of CE centers since they are located in the undoped $\mu$-c-Si:H absorber. In contrast to $e$ centers, CE centers are not coupled to H atoms, and their vicinity is depleted from H. CE centers are assigned to localized states of twin grain boundaries in crystalline columns or grains of $\mu$-c-Si:H.

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18 Please note that in contrast to Schropp et al. (Ref. 2), device-quality $\mu$-c-Si:H material giving the highest solar cell performance is usually found to be a mixture of a-Si:H and $\mu$-c-Si:H (Raman crystallinity about 60%) and is generally not highly crystalline (Raman crystallinity about 90%) (see Ref. 28 and Sec. 3.3 in Ref. 7).


