Journal of Magnetic Resonance 251 (2015) 26–35

Contents lists available at ScienceDirect

Journal of Magnetic Resonance

journal homepage: www.elsevier.com/locate/jmr

# High resolution *in-operando* microimaging of solar cells with pulsed electrically-detected magnetic resonance

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ARTICLE INFO

*Article history:*
Received 1 September 2014
Revised 13 November 2014
Available online 9 December 2014

*Keywords:*
ESR
EPR
Electrically-detected magnetic resonance
Semiconductor defects

ABSTRACT

The *in-operando* detection and high resolution spatial imaging of paramagnetic defects, impurities, and states becomes increasingly important for understanding loss mechanisms in solid-state electronic devices. Electron spin resonance (ESR), commonly employed for observing these species, cannot meet this challenge since it suffers from limited sensitivity and spatial resolution. An alternative and much more sensitive method, called electrically-detected magnetic resonance (EDMR), detects the species through their magnetic fingerprint, which can be traced in the device's electrical current. However, until now it could not obtain high resolution images in operating electronic devices. In this work, the first spatially-resolved electrically-detected magnetic resonance images (EDMRI) of paramagnetic states in an operating real-world electronic device are provided. The presented method is based on a novel microwave pulse sequence allowing for the coherent electrical detection of spin echoes in combination with powerful pulsed magnetic-field gradients. The applicability of the method is demonstrated on a device-grade 1-μm-thick amorphous silicon (a-Si:H) solar cell and an identical device that was degraded locally by an electron beam. The degraded areas with increased concentrations of paramagnetic defects lead to a local increase in recombination that is mapped by EDMRI with ~20-μm-scale pixel resolution. The novel approach presented here can be widely used in the nondestructive *in-operando* three-dimensional characterization of solid-state electronic devices with a resolution potential of less than 100 nm.


## 1. Introduction

Paramagnetic species are an inseparable and essential part of any solid-state device, from the simplest diode through solar cells, complex three-dimensional silicon-based chips, and up to futuristic quantum computing devices. Many paramagnetic species are intentionally inserted into the material (e.g., neutral phosphorus in silicon) while others represent unwanted by-products, such as point defects and crystal impurities. Thus, both desirable and undesirable paramagnetic species constitute an inevitable part of the electronic devices' functionality [1–3]. Traditionally, the identification, study, and manipulation of such paramagnetic entities are carried out using electron spin resonance (ESR). For example, in the case of point defects, impurities, or states induced by local disorder in inorganic and organic semiconductors, ESR makes it possible to characterize the defects' atomic structure [4–8], learn about impurity concentrations and distributions [9,10], and bridge the gap between paramagnetic and electronic properties [11,12]. However, the limited sensitivity of ESR often allows neither *in-operando* studies of real-world devices nor mapping the paramagnetic manifold on a nanoscale level.

One approach recently adopted in order to resolve these problems involves the development of an ultra-high-sensitivity ESR imaging setup that makes use of miniature microwave resonators [13,14] coupled with high-performance gradient coils [15]. For an isotopic-enriched phosphorous-doped $^{28}$Si sample ($^{28}$Si:P) it was shown that a sensitivity of less than 1000 electron spins of the neutral P atom and a spatial resolution of less than 1 μm can be achieved [16]. While this represents a significant milestone in the field of ESR spectroscopy, it should be mentioned that this performance can only be achieved on samples with long spin lattice ($T_1$) and spin–spin ($T_2$) relaxation times. While some important devices may be based on such materials [17,18], most real-world samples are much more challenging.

A different approach to the ultra-sensitive detection of paramagnetic species in solid-state samples is based on electrical

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http://dx.doi.org/10.1016/j.jmr.2014.11.008
1090-7807/

detection, which was introduced in the 1970s and is known today as electrically-detected magnetic resonance (EDMR) [19]. EDMR monitors spin-dependent current changes and is selective to electronic transitions between paramagnetic states that contribute to charge carrier transport. By combining the spectroscopic information contents of ESR with the sensitivity of a charge current measurement, EDMR provides a perfect *in-operando* tool to study the impact of paramagnetic states on the electric device's performance with an almost single spin detection limit [20–22]. There are several possible mechanisms that can result in spin-dependence of the charge carrier current, e.g., hopping, trapping, recombination, and tunneling through paramagnetic states. If these electronic processes involve localized states, the spin-dependent mechanism is usually associated with the formation of spin pairs [23]. Under steady state conditions, a certain occupation of the possible spin-pair configuration (four in case of two spin 1/2 particles) will emerge, which may then be disturbed by a resonant microwave irradiation. This will lead to changes in the occupation and hence to transitions between the different spin-pair configurations that can be detected as a net change in the charge carrier current. The charge transport routes gated in this manner by magnetic resonance spin manipulations may be those associated with device efficiency, such as leakage currents, recombination through defect states, or hopping through localized states in photovoltaic devices [24], or they may exist as part of the desired device attributes, e.g., in organic electronic and spintronic devices [25], depending on the type of the device and experimental conditions (applied voltage, temperature, etc.) [26–28]. In the EDMR detection scheme, the energy quanta to be detected per spin is in the order of eV, depending on the device's operating voltage, which is ~4–5 orders of magnitude larger than the energy quanta per spin in a typical ESR induction detection scheme. This leads to a much improved spin sensitivity of about 100 spins or better in a broad range of materials and devices [21,29], thus dramatically surpassing the conventional spin sensitivity attainable via the conventional method known as induction detection.

The EDMR method can be employed either with continuous microwave irradiation (CW-EDMR) or with pulsed microwave excitation (pulsed EDMR – pEDMR). The former is simpler [19], while the latter is more complicated [30] but offers considerably more information about the relaxation properties of the paramagnetic species involved and the mechanism and dynamics of the spin-dependent process. With EDMR, the magnetic fingerprint of the spin species involved in charge carrier transport can be easily collected to allow a full *in-operando* analysis of the material or the device [8].

In recent years, pEDMR has developed into a mature technique and has incorporated the most common pulsed ESR detection sequences, e.g., rotary echoes [31,32], Hahn-echo sequences [33,34], electron spin echo envelope modulation (ESEEM) [35,36], electron–electron double resonance (ELDOR) [37], and electron nuclear double resonance (ENDOR) detection [38,39]. However, a major drawback of the EDMR technique is that it spatially integrates over the conductive area of the sample under study, and therefore provides no spatial resolution unless multiple contacts are used and little current spreading exists.

A recent method that potentially provides both spectral and spatial high resolution images is the EDMR microscope based on a combined ESR-AFM setup with a conductive tip [40]. This method succeeded in providing measurable EDMR signals with sufficient *g*-factor resolution and a spatial resolution determined by the size of the $\sim 3 \times 3\ \mu m^2$ electrode. However, this EDMR microscope suffers from significant current noise due to the instability of the AFM contact. Furthermore, it requires the performance of sequential scanning of the surface, and its current sensing mechanism is not necessarily local due to current spreading and also cannot be generalized to three-dimensional (3D) imaging requirements. A major difference between the CW-EDMR microscope and the method presented here is that the latter relies on coherent spin manipulation.

Another alternative to enhance the spatial resolution of EDMR, suggested more than a decade ago, involves the use of fixed magnetic field gradients which spatially encode the sample in conjunction with CW-EDMR data acquisition [41]. This approach is relatively simple technically-wise but very ineffective when the sample has a broad spectral line width, leading to a very crude spatial separation. The first experimental proof was accomplished on a crystalline silicon wafer, on which an image resolution of ~1.9 mm was obtained using gradients of ~0.2 T/m [41]. Clearly, such limited resolution is of no practical use to the vast majority of materials and electronic devices of relevance; consequently, this approach was not developed further.

In this paper we present a novel approach that makes use of a new pEDMR detection protocol combined with powerful pulsed magnetic-field gradients to provide EDMR images of the paramagnetic states in operating thin-film silicon solar cells with an experimental spatial resolution of ~20 μm. Furthermore, since the resolution in our experiment is limited mostly by the current noise, with an optimized sample layout a resolution of ~100 nm could be within reach. The new EDMR imaging scheme retains the complete ESR information regarding the paramagnetic spectrum of the measured species, thereby enabling their spatially-resolved assignment and *in-operando* characterization. Therefore, our line of work is very promising and can lead to a new type of ESR analysis tool for solid-state electronic devices with both high spatial and spectroscopic resolution.

## 2. Materials and methods

EDMR measurements were carried out on thin-film silicon solar cells (see Fig. 1) with 1-μm-thick hydrogenated amorphous silicon (a-Si:H) absorber layers sandwiched between microcrystalline silicon (μc-Si) p and n layers, and transparent top and bottom contacts made from Al-doped ZnO. Solar cell samples were deposited on quartz substrates by plasma-enhanced chemical vapor deposition in superstrate configuration [42], which allows illumination through the substrate.

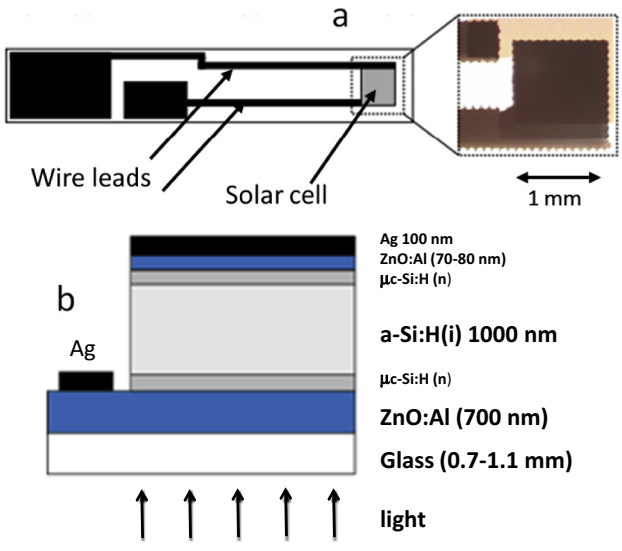


**Fig. 1.** (a) General layout of the a-Si:H thin-film silicon solar cell used in this study. A close-up of the solar cell is shown on the right. (b) Lateral structure of the cell; light enters through the glass substrate.