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Light-induced degradation has been identified to be a critical issue for most silicon-based solar cell technologies. This study presents an observation of an opposite light-induced enhancement (LIE) effect in photovoltaic performance in poly(3,4-ethylthiophene):polystyrenesulfonate/n-Si organic-inorganic hybrid solar cells. The reduced density of interface states under light soaking (LS) is found to be responsible for the LIE of the hybrid solar cells. An increased minor carrier lifetime under LS and a switchable photoluminescence intensity while applying a voltage bias are observed, providing evidence for the underlying physical mechanism. *Published by AIP Publishing.*
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The potential of achieving a high performance/cost ratio in organic-inorganic hybrid solar cells has attracted increasing attention from researchers.[1–6] In particular, heterojunction solar cells composed of a poly(3,4-ethylenedioxythiophene): polystyrenesulfonate (PEDOT:PSS) emitter and an n-type crystalline silicon (c-Si) absorber have achieved a high power conversion efficiency (*PCE*) greater than 16% (Ref. 7) with a series of advantages such as low-temperature fabrication processes, simple device geometries, and potential low-cost processing.[4–6,8]

Solar cells are devices meant to work under sun-light illumination. Thus, performance test under light soaking (LS) has been developed to be a standard test procedure for all solar cell technologies. However, most c-Si solar cells unfortunately suffer from light-induced degradation (LID). For example, the formation of recombination-active boron–oxygen complexes[9,10] and iron-boron pair dissociations in the bulk of p-type Si wafers after LS[11,12] deteriorate c-Si cell performance. LS leads to an increased defect density in hydrogenated amorphous silicon (a-Si) and also degrades a-Si thin-film solar cells and the interface quality between intrinsic a-Si and c-Si heterostructures.[13–15] However, when comes to silicon heterojunction (SHJ) solar cells, there is an exceptional light-induced enhancement (LIE) effect.[16,17] This LIE effect in SHJ cells has a practical significance. For instance, as reported in a previous work, a 20%-efficient module with 320 W could be rated at 324.5 W using LS, with an annual excessive production increase of 1.4%.[16]

In this work, we found that PEDOT:PSS/Si organic-inorganic hybrid solar cells, which were studied in full swing, also exhibit a clear LIE effect. We associated this LIE with a previously identified electrochemical passivation mechanism[18] that is initiated by injecting carriers into the interface through LS or an applied voltage bias.

n-type float zone (FZ)-grown (100)-oriented double-side-polished Si wafers, with a resistivity in the range of 1–5 Ω cm (280 μm thick, Topsoil), were selected as the substrates of the hybrid solar cells discussed in this work. The wafers were dipped in a hydrofluoric acid (HF) solution (10%, 3 min) to remove the naturally grown SiO_x layer. PEDOT:PSS (Clevios, PH-1000) was mixed with 3 wt. % dimethyl sulfoxide (DMSO) (D3, for short) as a front emitter layer and spin-coated on the surface of 2-in. Si wafers at 2500 rpm and annealed at 130 °C for 10 min at atmospheric pressure. A Mg/Ag stack thin film was introduced to act as a back surface field (BSF) and metallization. The basic principle for Mg BSF and subsequent fabricated details for the hybrid solar cells can be seen elsewhere.[19] Photovoltaic (PV) performances of the solar cells were characterized by current density-voltage (J-V) at the standard test conditions (AM1.5, 100 mW/cm², and 25 °C). The LS was carried out *in situ* in the J-V measurement stage, with a stable temperature by a semiconductor cooling system. The effective minority carrier lifetime (τ_{eff}) of the passivated wafer was measured to explore the electronic changes at the PEDOT:PSS/Si interface by using the transient photoconductance decay techniques on the WCT-120 facility. To assure the consistency of the lifetime measurement with the solar cell process (D3 was used as a front emitter layer), a geometry of the passivated symmetrically both-side polished Si wafer, i.e., D3/n-Si/D3, was adopted. The photoluminescence (PL) measurements under different poling voltages were performed using an indium tin oxide (ITO)/PSS/n-Si/PSS/ITO sample geometry.

Figure 1(a) shows the PV parameters [open circuit voltage (V_{oc}), short circuit current density (J_{sc}), fill factor (*FF*), and *PCE*] of the hybrid solar cell as a function of the LS time. With the increase in the LS time, V_{oc} shows a rapid increase by 72 mV (relatively ~15%) in the first 20 min and reaches a rather stable value thereafter. *FF* increases first by about 2% (relative) and then turns downward slowly. In addition, J_{sc} just slightly increases with the increase in the

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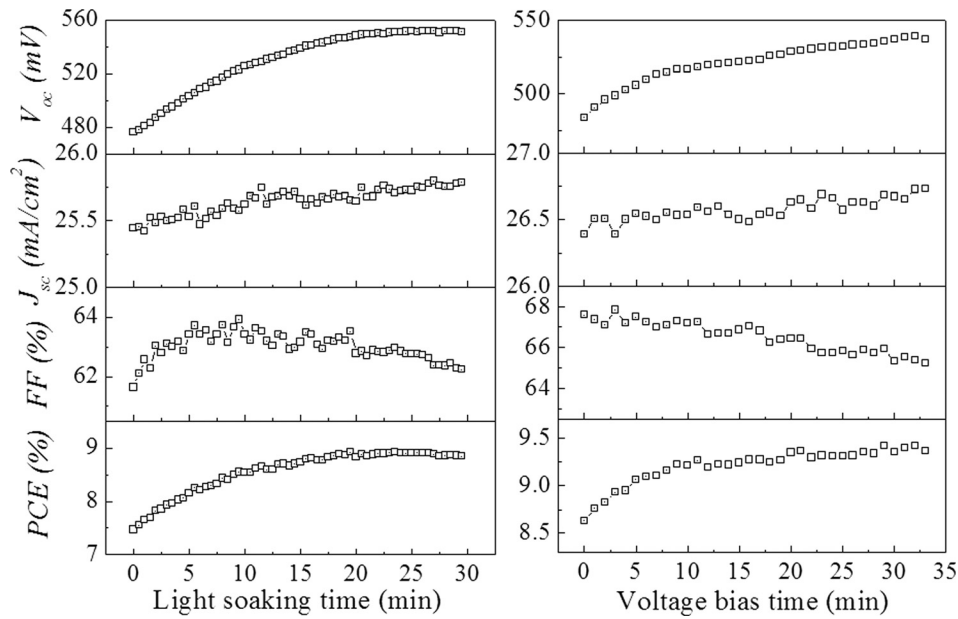b)Authors to whom correspondence should be addressed: xuying@hbu.edu.cn and yaohuamai@jnu.edu.cn

FIG. 1. The PV parameters such as open circuit voltage (V_{oc}), short circuit current density (J_{sc}), FF (fill factor), and PCE of the D3/Si organic-inorganic hybrid solar cell as a function of the LS time (a) and the forward-bias application time (b). The device was measured in an ambient environment, with a relative humidity (RH) of 66%.

LS time. Compared to the above mentioned LIE phenomenon in SHJ solar cells, the organic-inorganic hybrid solar cells exhibited a more pronounced increase in their PV performance, such as a relative V_{oc} gain of 15% and a relative PCE gain of 20%. For the longer illumination, the applicability of the LIE depends on the long-term stability of the device itself under LS conditions. However, the stability of the PEDOT:PSS/c-Si solar cell performance is a major problem because PEDOT:PSS films are hygroscopic and will uptake moisture when handled in ambient after baking [see Fig. S1(a) in the supplementary material or Ref. 20]. When the stability of the device was improved, for example, using a capping layer of ITO in this work, the LIE effect remained (see Fig. S2 in the supplementary material).

The LS injects carriers into the solar cell and may affect the charge transfer at the interface. In order to investigate the possible effect of carrier injection, a forward voltage bias of 0.5 V was applied to the solar cells in the dark to simulate the carrier injection in the above light soaking experiment. Figure 1(b) shows the PV parameters of the hybrid solar cell as a function of the forward-bias application time. A similar improvement of PCE was clearly observed under forward-bias conditions. This result suggests that the LIE of the hybrid solar cells is linked to charge injection. FF variations in both cells are likely a result of competition between the reduction of interface recombination and the increase of series resistivity (see Figs. S1 and S3 in the supplementary material).

Next, we worked to unveil the underlying physics of this LIE. In our simple device geometry, the factors that could cause stability issues were the PEDOT:PSS thin film material and/or the PEDOT:PSS/n-Si interface. The contribution of the light-induced change in PEDOT:PSS material properties on the observed LIE effect was excluded due to unchanged photoelectric properties and surface morphologies between before and after LS (Fig. S4 in the supplementary material). In our previous work, we found that PEDOT:PSS was able to passivate Si surfaces well, and the passivation effect mainly originated from the PSS species rather than the PEDOT ones.[21]

The passivation of the Si surface by PSS obeys an electrochemical oxidation mechanism at the PSS/Si interface, which can be controlled by electron transfer at the Si surface, following the redox reaction equation [Eq. (1)], which is given as[8]

$$\equiv \text{Si} \bullet + \text{PSS} \underset{e^{-}}{\overset{h^{+}}{\rightleftharpoons}} \text{Si–O–R,} \tag{1}$$
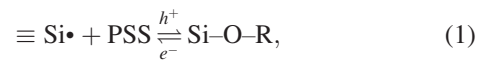
where holes and electrons are denoted by h^{+} and e^{-}, respectively, Si represents the dangling bonds at the Si surface, and R is the surplus O-containing constituent in the PSS molecule. The PEDOT:PSS/n-Si heterojunction solar cell is a p^{+}/n Schottky junction device with an internal electric field (E_{in}) along the direction from the n-Si to the PEDOT:PSS layer, as shown in the sketch in Fig. 2. Upon LS, photo-excited electron-hole pairs are created in the Si absorber and then separated by E_{in}. E_{in} (Si→PEDOT:PSS) ensures that the holes transfer from the Si bulk to the PEDOT:PSS/Si
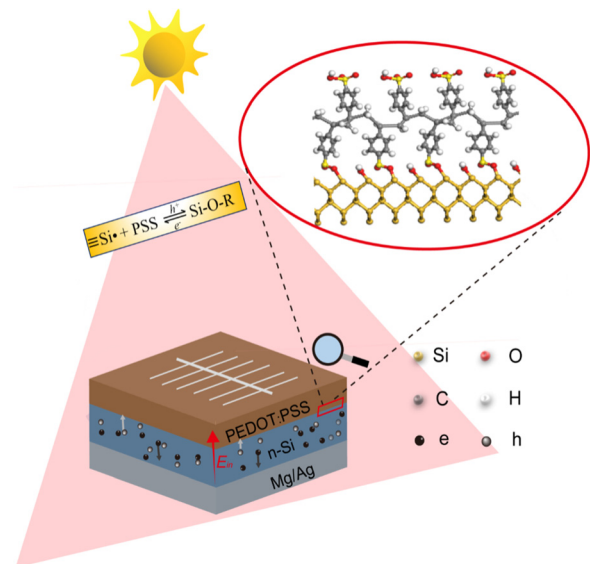

FIG. 2. The sketch of the underlying physics of the LIE in the hybrid solar cells.
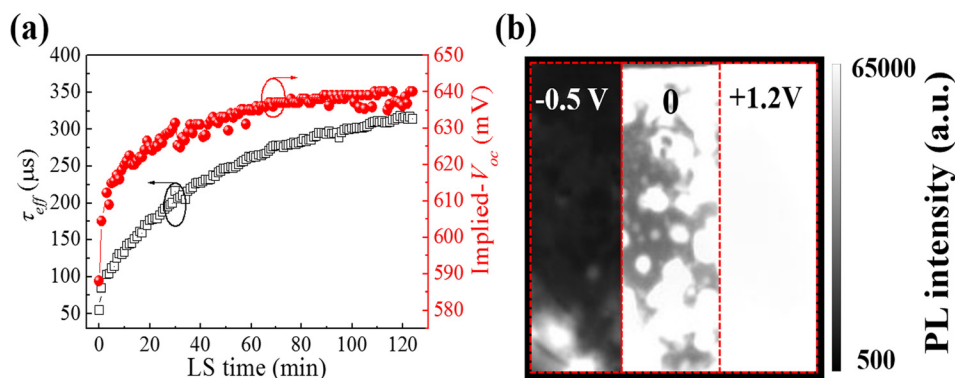
FIG. 3. (a) The τ_{eff} and implied V_{oc} of D3/n-Si/D3 as a function of the LS time. (b) PL intensity images of ITO/PSS/n-c-Si/PSS/ITO after applying different voltages.

interface, which favours the forward reaction in Eq. (1) and results in the oxidation of the Si surface.[18] This phenomenon reduces the interface defect states and suppresses minority carrier recombination and thus increases V_{oc} and *PCE* of the hybrid solar cells. For the forward voltage bias case, charge injection was performed by an external field, and a similar principle can be understood. Note that this electrochemical passivation is a reversible behaviour [Eq. (1)], so V_{oc} drops to its initial magnitude rather than remaining enhanced after LS is terminated for a period of time. However, when the device was exposed to LS again, the LIE can be obtained again (see Fig. S5 in the supplementary material). This temporary withdrawal is insignificant because solar cells have always worked in a LS environment.

The τ_{eff} and PL measurements in Fig. 3 support the above explanation of interface defect reduction. Figure 3(a) shows τ_{eff} and implied V_{oc} as a function of the LS time. The implied-V_{oc} is the energetic distance between the electron and hole quasi-Fermi levels,[22] which is described by the following equation:

$$\text{implied-}V_{oc} = \frac{kT}{q}\ln\left(\frac{\Delta n(\Delta n + N_D)}{n_i^2}\right), \quad (2)$$

where Δn is the excess carrier density, n_i is the intrinsic carrier concentration, and N_D is the effective bulk donor concentration. τ_{eff} and implied V_{oc} exhibit a rapid increase in the initial stage and then a closely stable value, which is consistent with the tendency of the V_{oc} variation in the device. The τ_{eff} evolution depended on the interface defects, such as the Si dangling bonds, which were passivated through the electrochemical grafting of the O groups in PSS onto the Si surface. This passivation was controlled by the injected carrier type. When holes were injected, an oxidised interface and thus better surface passivation were presented and vice versa. Thus, the origin of the LIE of the hybrid solar cells was clarified. Similarly, the interface defect states could also be tuned by the applied voltage bias. Figure 3(b) shows the PL mapping of the PSS passivated on both sides of the n-Si layer at a positive and a negative poling voltage. PL is the optical radiation emitted by the Si bulk that results from band-to-band radiative recombination in the near-surface region. The details of the PL mapping configuration can be found elsewhere.[23] The PL image exhibited a high intensity when a positive voltage was applied and a low intensity when a negative voltage was applied, indicating that the PSS/Si

interface state could be switched by charge transfer. These results are consistent with the LIE and potential-induced enhancement in the hybrid solar cells above. Based on this underlying mechanism, we briefly speculate that other X:PSS/c-Si(n) heterojunction solar cells (X represents a high work function material) may exhibit the LIE effect due to the existence of a PSS/Si interface.

In summary, we observed a pronounced LIE in organic-inorganic hybrid solar cells. However, unlike the LIE mechanism in SHJ cells, via the movement of the Fermi-level of doped a-Si:H/intrinsic a-Si:H exposed to LS, the LIE of the hybrid solar cells originates from an electrochemical-passivated interface state, which can be tuned by charge transfer. It is hence expected that, with the development of organic-inorganic hybrid solar cells, the observations in this work could lead to research with realistic importance that potentially increases the productivity similar to that of SHJ technology.

See supplementary material for the PEDOT:PSS material properties at different ambient RHs and temperatures and the performance variations of the PEDOT:PSS/Si organic-inorganic hybrid solar cell at the different RHs, with a capping layer and after LS is terminated.

[1]Y. Han, Y. Liu, J. Yuan, H. Dong, Y. Li, W. Ma, S. T. Lee, and B. Sun, "Naphthalene diimide-based n-type polymers: Efficient rear interlayers for high-performance silicon-organic heterojunction solar cells," ACS Nano **11**(7), 7215–7222 (2017).
[2]Q. Liu, R. Ishikawa, S. Funada, T. Ohki, K. Ueno, and H. Shirai, "Highly efficient solution-processed poly(3,4-ethylenedio-xythiophene):poly(styrenesulfonate)/crystalline-silicon heterojunction solar cells with improved light-induced stability," Adv. Energy Mater. **5**(17), 1500744 (2015).
[3]S. Jäckle, M. Liebhaber, C. Gersmann, M. Mews, K. Jäger, S. Christiansen, and K. Lips, "Potential of PEDOT:PSS as a hole selective front contact for silicon heterojunction solar cells," Sci. Rep. **7**, 2170 (2017).
[4]J. He, Z. Yang, P. Liu, S. Wu, P. Gao, M. Wang, S. Zhou, X. Li, H. Cao, and J. Ye, "Enhanced electro-optical properties of nanocone/nanopillar dual-structured arrays for ultrathin silicon/organic hybrid solar cell," Adv. Energy Mater. **6**(8), 1501793 (2016).

[5]Y. Zhang, W. Cui, Y. Zhu, F. Zu, L. Liao, S. Lee, and B. Sun, "High efficiency hybrid PEDOT-PSS nanostructured silicon Schottky junction solar cells by doping-free rear contact," Energy Environ. Sci. **8**, 297 (2015).

[6]J. P. Thomas and K. T. Leung, "Defect-minimized PEDOT:PSS/planar-Si solar cell with very high efficiency," Adv. Funct. Mater. **24**(31), 4978–4985 (2014).

[7]Z. Yang, P. Gao, J. He, W. Chen, W.-Y. Yin, Y. Zeng, W. Guo, J. Ye, and Y. Cui, "Tuning of the contact properties for high-efficiency Si/PEDOT:PSS heterojunction solar cells," ACS Energy Lett. **2**(3), 556–562 (2017).

[8]D. Zielke, A. Pazidis, F. Werner, and J. Schmidt, "Organic-silicon heterojunction solar cells on n-type silicon wafers: The back PEDOT concept," Sol. Energy Mater. Sol. Cells **131**, 110–116 (2014).

[9]V. V. Voronkov and R. Falster, "Latent complexes of interstitial boron and oxygen dimers as a reason for degradation of silicon-based solar cells," J. Appl. Phys. **107**(5), 053509 (2010).

[10]J. Schmidt and K. Bothe, "Structure and transformation of the metastable boron- and oxygen-related defect center in crystalline silicon," Phys. Rev. B **69**(2), 024107 (2004).

[11]D. H. Macdonald, L. J. Geerligs, and A. Azzizi, "Iron detection in crystalline silicon by carrier lifetime measurements for arbitrary injection and doping," J. Appl. Phys. **95**(3), 1021–1028 (2004).

[12]S. Rein and S. W. Glunz, "Electronic properties of interstitial iron and iron-boron pairs determined by means of advanced lifetime spectroscopy," J. Appl. Phys. **98**(11), 113711 (2005).

[13]M. Stuckelberger, M. Despeisse, G. Bugnon, J. W. Schüttauf, F. J. Haug, and C. Ballif, "Comparison of amorphous silicon absorber materials: Light-induced degradation and solar cell efficiency," J. Appl. Phys. **114**(15), 154509 (2013).

[14]S. De Wolf, B. Demaurex, A. Descoeudres, and C. Ballif, "Very fast light-induced degradation of a-Si:H/c-Si(100) interfaces," Phys. Rev. B **83**(23), 233301 (2011).

[15]E. M. El Mhamdi, J. Holovsky, B. Demaurex, C. Ballif, and S. De Wolf, "Is light-induced degradation of a-Si:H/c-Si interfaces reversible?," Appl. Phys. Lett. **104**(25), 252108 (2014).

[16]E. Kobayashi, S. De Wolf, J. Levrat, G. Christmann, A. Descoeudres, S. Nicolay, M. Despeisse, Y. Watabe, and C. Ballif, "Light-induced performance increase of silicon heterojunction solar cells," Appl. Phys. Lett. **109**(15), 153503 (2016).

[17]E. D. Kobayashi, S. De Wolf, J. Levrat, A. Descoeudres, M. Despeisse, F.-J. Haug, and C. Ballif, "Increasing the efficiency of silicon heterojunction solar cells and modules by light soaking," Sol. Energy Mater. Sol. Cells **173**, 43–49 (2017).

[18]J. Chen, Y. Shen, J. Guo, B. Chen, J. Fan, F. Li, H. Liu, Y. Xu, and Y. Mai, "Silicon surface passivation by polystyrenesulfonate thin films," Appl. Phys. Lett. **110**(8), 083904 (2017).

[19]B. Chen, J. Chen, Y. Shen, K. Ge, J. Guo, F. Li, H. Liu, Y. Xu, and Y. Mai, "Magnesium thin film as a doping-free back surface field layer for hybrid solar cells," Appl. Phys. Lett. **110**(13), 133504 (2017).

[20]J. Hossain, Q. Liu, T. Miura, K. Kasahara, D. Harada, R. Ishikawa, K. Ueno, and H. Shirai, "Nafion-modified PEDOT:PSS as a transparent hole-transporting layer for high-performance crystalline-Si/organic heterojunction solar cells with improved light soaking stability," ACS Appl. Mater. Interfaces **8**(46), 31926–31934 (2016).

[21]J. Chen, Y. Shen, J. Guo, B. Chen, J. Fan, F. Li, B. Liu, H. Liu, Y. Xu, and Y. Mai, "Electrochemical passivation of silicon via electron transfer at polymer/silicon hybrid interface," Electrochim. Acta **247**, 826 (2017).

[22]R. A. Sinton and A. Cuevas, "Contactless determination of current–voltage characteristics and minority-carrier lifetimes in semiconductors from quasi-steady-state photoconductance data," Appl. Phys. Lett. **69**(17), 2510–2512 (1996).

[23]K. Matsuda, T. Saiki, S. Nomura, and Y. Aoyagi, "Local density of states mapping of a field-induced quantum dot by near-field photoluminescence microscopy," Appl. Phys. Lett. **87**(4), 043112 (2005).