

Hybrid Silicon-Polymer Photodetector Engineered Using Oxidative Chemical Vapor Deposition for High-Performance and Bias-Switchable Multi-Functionality

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Abstract

Black silicon (b-Si) featured by anti-reflective surfaces has been extensively studied to realize highly sensitive photodetectors. The key to augmenting the light-detection capability of b-Si is to facilitate charge extraction while limiting undesired recombination events at surface defects. To this end, oxidative chemical vapor deposition (oCVD) was leveraged to form a highly conformal and conductive ($3,000 \text{ S cm}^{-1}$) organic transport layer, poly(3,4-ethylenedioxythiophene) (PEDOT), on b-Si nanostructures. The oCVD PEDOT instrumentally extracts photo-induced charges, through which b-Si photodetectors implementing oCVD PEDOT achieve a superior photo-detectivity of 1.37×10^{13} Jones. Furthermore, by engineering the pore dimension of b-Si, we contrive a mode-tunable Si photodetector, where the functions of broad-band and visible-blinded modes are switched facile by a bias polarity. The unprecedented device paves the way for extending the applications of Si detectors toward novel sensory platforms such as night-vision, motion tracking, and bio-sensing.

1. Introduction

For decades, Silicon (Si) has been a primary element for the semiconductor industry. The material application is now being expanded to photodetectors owing to its bandgap (1.12 eV) suitable for broadband detection.^[1,2] An early version of Si-based photodetectors has been fabricated in the form of p-n or p-i-n diodes vertically stacked on a flat wafer. Due to the insufficient light collection capability of these early photodetectors, an anti-reflective coated glass, consisting of multiple dielectrics, needed to be used as a substrate which causes process complexities and a surge in unit price.^[3,4] To address such limitation, chemical and physical etching processes that induce nanostructured surfaces have been proposed as the most promising alternatives to boost the light-collection efficiency without an aid of the supplementary glass.^[2,5–7] The nanostructure surface of Si, refined from a flat shape to a vertically aligned nanostructure, instrumentally enhances light collection as a “self” anti-reflector. Such a nanostructure uniquely forms a continuous decrease in the refractive index from the bulk Si to air^[8] and, consequently, the wafer achieves a dramatically depressed reflectance (< 10%).^[5,7] This approach has been extensively utilized with the term 'black silicon (b-Si)' as an essential building block for a wide range of optoelectronic devices such as solar cells and photodetectors.

The increment of the surface area during the etching process inevitably causes unexpected issues known as “surface recombination”.^[9–11] Photo-induced electron-hole pairs are readily recombined at surface defects, critically limiting efficient charge extraction. In this respect, to advance the b-Si photodetectors, it is essential to secure a passivation layer or charge transport layer to stabilize the surface defects or reinforce a charge separation capability through a built-in potential, while maintaining process simplicity.^[9–14] A well-known passivation layer, atomic layer deposited (ALD) Al₂O₃, has already contributed to the fabrication of high-performance solar cells with an efficiency of above 22%.^[9–11] However, the strategy based on the highly resistive insulating layer limited the device configuration to the form of a back-

contact-back-junction which is not favorable for the fabrication of multi-pixel sensors (e.g., image sensors).^[10] Alternatively, inorganic charge transport layers (e.g., Si_xN_y or a-Si:H) have been employed to construct a vertical-type device while depressing the surface recombination.^[6,12–14] However, they require a sophisticated and time-consuming process accompanied by a high thermal budget to form a uniform layer on the b-Si wafer. Moreover, the high refractive index of the inorganic layers (e.g., 3.5–4.5 for a-Si:H), suppressing the anti-reflective effect, provokes an additional issue due to an undesirable increment of the reflectance.^[15,16] Conductive polymers, such as poly(3,4-ethylene dioxythiophene) (PEDOT) and its derivatives, are promising alternatives for the transport layers due to their low refractive index (1.2–1.6) close to air.^[17–21] Furthermore, their relatively affordable and straightforward process is another key benefit for making the materials attractive compared to other inorganic counterparts. However, the relatively low charge mobility, inefficient charge extraction capability from the Si, and poor step-coverage of conventional solution-processed polymers remain unresolved.

There is a demand for new functionality along with the enhancement of optoelectronic properties of the Si-based photodetector. Conventional Si detectors are designed to be broadband spectral and need to be equipped with an auxiliary bandpass filter to aim for a specific purpose (e.g., daily light imaging or night vision imaging requiring a NIR-blocking or passing filter, respectively).^[22–25] However, as complementary filters are added, the scope of application of the vision system can become progressively narrower. For example, even if a bare Si device has the potential to be used for night-vision, its functionality is limited to visible-light imaging as soon as the NIR-blocking filter is permanently mounted (i.e., single mode operation for the visible). Therefore, a breakthrough approach to a more functional and broadly applicable vision system must be presented to maximize the value of Si-photodetectors.

Oxidative chemical vapor deposition (oCVD) is a recently emerged technique for gas-phase synthesis of a polymer film.^[26–29] As well as the superior electrical property of oCVD-

based polymers, distinctly notable step coverage of the gas-phase deposition, compared to conventional solution-based coating methods, have been highlighted in a wide range of research fields such as a lithium-ion battery^[26] and light-emitting diodes.^[27] Herein, for the first time, we hybridize the oCVD technology and the b-Si wafer approach to realize a high-performance Si photodetector that demonstrates the responsivity of 1.14 A W^{-1} and detectivity of 1.37×10^{13} Jones. The oCVD process enables conformal coating of highly conductive PEDOT ($3,000 \text{ S cm}^{-1}$) on the rough and porous surface of b-Si so that the surface recombination is effectively inhibited while facilitating the charge transport. As a result, the synergistic effect realizes the superior peak detectivity, which is three and seven times higher than that of a conventional PEDOT:PSS-covered b-Si and planar-Si detectors, respectively. Furthermore, we suggest a novel photodetector that operates in unique dual-function modes. By tuning the applied bias, the device functionality is reversibly switched from a broad-band detection mode to a visible-blinded near-infrared (NIR) detecting mode. To the best of our knowledge, this is the first demonstration representing a multi-functional Si photodetector, paving the way for developing an unprecedented and practical vision system for night vision, motion tracking, and bio-sensing.

2. Result and Discussion

2.1. Characterization of oCVD PEDOT deposited on a silicon wafer

The key distinction of the oCVD technique from conventional polymer processing is gas-phase polymerization (**Figure 1a**) through a single step process of synthesis, deposition, and doping. The monomer (3,4-Ethylenedioxythiophene, EDOT), vaporized at a separate jar, is injected into the vacuum chamber with a controlled flow rate through a throttling valve and is directly polymerized on a substrate, where the oxidative polymerization is initiated by sublimated FeCl_3 gas, the oxidizing agent. The conductivity of oCVD PEDOT was investigated using the transmission line method (TLM) as shown in Figure 1b (the experimental setup is described in Supporting Information with Figure S1).^[30] Spin-casted PEDOT:PSS film was prepared as a control sample, representative of a solution-based polymer. It is well known that the insulating domain (PSS-dominant) of PEDOT:PSS serves as a charge scattering center so that a post-treatment is necessary to amplify the conductivity of the film (see in experimental section).^[31] In this regard, two PEDOT:PSS samples before and after the post-treatment were prepared and denoted as LC (low conductive)- and HC (high conductive)-PEDOT:PSS, respectively. The film thicknesses of the oCVD PEDOT, LC-PEDOT:PSS, and HC-PEDOT:PSS were adjusted to 30-40 nm of which the condition was selected to compare these PEDOT films with similar optical transmittance of 80-85%. The conductivity of the oCVD PEDOT, estimated from the TLM analysis, was $3,000 \text{ S cm}^{-1}$ which is superior to the LC- ($\sim 1 \text{ S cm}^{-1}$) and HC-PEDOT:PSS ($1,000 \text{ S cm}^{-1}$) (Figure 1c). The results were revalidated using a four-point probe measurement. The superior conductivity of the oCVD PEDOT is associated with more ordered structure, proved by XRD analysis shown in Figure S2 (Supporting Information).^[32,33]

The Raman spectrum of the samples was analyzed using a 633 nm laser source to characterize and compare the charge transport behavior between the PEDOT layers and Si substrates. All stretching modes of oCVD PEDOT, assigned in the Raman spectrum, are summarized in Figure S3 (Supporting Information).^[27,34] It should be noted that although the

peak shape and positions were mostly similar, a significant difference in the peak intensity between the PEDOT films was clearly identified (Figure 1d). For example, the symmetric $C_{\alpha}=C_{\beta}$ stretching peak (1420 cm^{-1}) of the oCVD PEDOT was 30 times higher than that of the PEDOT:PSS films. In addition, the two deposition methods had opposite effects on the Si-Si stretching peak, designated at 520 cm^{-1} , despite the similar thickness of all PEDOT films. The stretching mode of the Si surface was dramatically suppressed when covered with the oCVD PEDOT, whereas a higher peak intensity was observed under the PEDOT:PSS layers.

Raman scattering enhancements of chemicals attached to Si substrates can be explicated based on a charge transport (CT) mechanism.^[35–40] Upon irradiating a short wavelength laser (633 nm) on the Si-PEDOT system, electron excitation takes place from the valence band (VB_{Si}) to the virtual excited state (VS_{Si}) of Si, which is the excited states under the laser injection.^[38] The excited electrons readily recombine through two different pathways (Figure S4, Supporting Information). One is the direct transition from the VS_{Si} to a vibrational state of Si, slightly above the VB_{Si} , which emits a Raman photon, representing a vibrational mode of the Si lattice.^[38] The second recombination path is initiated with a charge transfer (CT) from the virtual state of Si to that of PEDOT through resonant tunneling and terminated as the transferred electrons are promptly recombined with the holes of the VB_{Si} .^[38,39] During the process, the emitted photons leave vibrational quantum energy in the PEDOT layer, implying that the CT-based recombination originates the Raman scattering peaks relevant to PEDOT.

The most significant prerequisite for prompting the CT mechanism is that the chemical should be covalently bonded to the semiconductor substrate to facilitate charge transports at the heterogeneous interface.^[29,35–40] For the transport process, it must be considered that a single photon triggers only one of the two potential recombination routes, which means that an intensity trade-off occurs between the Si and PEDOT Raman peaks (e.g., the Raman scattering intensity of PEDOT tends to increase with decreasing that of Si). In this regard, the amplified PEDOT peak of the oCVD PEDOT/Si interface, along with a significant decrement of Si

stretching, implies that the absorbed photons in Si dominantly activate the inter-layer charge transition rather than in intra-band recombination in Si. Therefore, the different Raman scattering responses, depending on the type of PEDOT, vindicates that the oCVD PEDOT was more strongly grafted to the Si substrate than the PEDOT:PSS, which concurs with the notion that covalent chemical bonds (i.e., linker-free grafting) form a bridge between the substrate and the oCVD film.^[29] The covalent bonds at the oCVD PEDOT/Si interface work favorably to promote an effective charge transfer between the oCVD PEDOT and Si layers.

We hypothesize that the EDOT monomer, injected during the oCVD process, is initially grafted on the Si surface and serves as a linker to hold the PEDOT film. To prove the hypothesis, we prepared a new Si wafer, exposed to EDOT vapors in the oCVD chamber without injection of oxidizing agents (Figure S5, Supporting Information). The EDOT-modification permanently convert the surface of Si to hydrophobic nature, substantiating that the hydrophilic native oxides were transformed into the form of hydrophobic Si-O-EDOT (Figure S5a). To gain theoretical insight into the binding chemistry, we conducted a density functional theory (DFT) calculation (Figure S5b-f). The binding energy of the EDOT with O and Si atoms of the Si were -2.21 and -0.002 eV, respectively (Figure S4b and c for O and Si sites, respectively), indicating that the surface oxygens plays an adsorbent to form a covalent bond with the EDOT molecule.

To investigate surface defects of the PEDOT-coated Si wafers, photoluminescence (PL) measurements, excited by a 325 nm light source (Figure S6, Supporting Information), were conducted. The significant difference of the samples between the oCVD and spin-coating is a broad emission of 400-500 nm, which was only observed in the LC-PEDOT:PSS/Si sample. It is well known that the blue-green emission is attributed to the recombination occurring at oxygen defects (O^{2-}),^[41] representing that the oxygen plasma treatments used for the solution-based coating created the surface defects. Therefore, it is expected that charge separation is much facilitated in the oCVD PEDOT/Si junction, compared to the PEDOT:PSS/Si, by avoiding the defect-assisted recombination.

The unique functionality of the oCVD PEDOT (high electrical conductivity and efficient charge extraction capability from Si) is eligible to be the key features in realizing a high-performance Si-polymer photodetector. To certain the benefits of oCVD PEDOT more directly, we fabricated a set of PEDOT/planar-Si photodetectors in the form of a Schottky diode where PEDOT was used as a hole transport layer placed between the planar-Si substrate and the ITO/MoO₃ top electrode (Figure S7, Supporting Information). The planar-Si wafer was exploited to solely (w/o b-Si manufacturing) test the role of oCVD PEDOT, excluding the potential anti-reflective effect of b-Si. Current-voltage (I - V) curves of the oCVD PEDOT, LC-PEDOT:PSS, and HC-PEDOT:PSS detectors are shown in **Figure 2a** and **2b**, respectively. The mathematical relation between the I and V in Schottky diodes is expressed as follows:^[42–45]

$$I = AA^*T^2 \exp\left(-\frac{q\phi_B}{k_B T}\right) \left[\exp\left(\frac{qV}{nk_B T}\right) - 1 \right] \quad (1)$$

where A is the active area of the diode (4 mm²), A^* is the Richardson's constant of the n-type Si (120 A cm⁻² K⁻²). q , k_B , and T are the unit charge, Boltzmann constant, and absolute temperature, respectively. ϕ_B and n are the Schottky barrier height and ideality factor of the diode, respectively, which can be extracted by empirically measured I - V curves in a mathematical formula

$$\phi_B = \frac{k_B T}{q} \ln\left(\frac{AA^*T^2}{I_0}\right) \quad (2)$$

$$n = \frac{q}{k_B T} \frac{dV}{d \ln I} \quad (3)$$

The ϕ_B of the oCVD PEDOT/planar-Si device (at 293 K) was found to be 0.75 eV, which is 200 and 300 meV higher than that of the LC-PEDOT:PSS- and HC-PEDOT:PSS/planar-Si, respectively. The larger Schottky barrier height of the diode integrating oCVD PEDOT results in the highest rectifying ratio of 70 at ± 1 V, which is 4-7 times higher than that of the PEDOT:PSS-based diodes (Figure 2c). The notable ratio of the oCVD PEDOT/planar Si diode

was maintained even raising the voltage to 2 V (Figure 2d) owing to the least dark current (leakage current) (35 nA at -2 V vs. 76 nA and 180 nA of LC-PEDOT:PSS/planar-Si and HC-PEDOT:PSS/planar-Si, respectively).

The ideality factors (n) of the PEDOT/planar-Si samples were estimated as 3.3, 5.0, and 4.5 for the oCVD PEDOT-, LC-PEDOT:PSS-, and HC-PEDOT:PSS/planar-Si diodes, respectively. The ideality factor higher than 2 indicates that the system possesses abundant trap sites in the heterogeneous interface or PEDOT layer itself.^[42,44] Those traps create multiple current paths which are activated at different electric fields, leading to high ideality factors. In this regard, the smallest ideality factor of the oCVD PEDOT/planar-Si diode represents that the oCVD process can significantly depress the undesired trap sites, compared to those with solution processed PEDOT:PSS; thus, trap-assisted surface recombination is expected to be reduced in the oCVD-based diode.

The photocurrent was measured under 625 nm light (irradiance of 1 mW cm⁻²) at different biases from -2 to 2 V (Figure 2a and 2b). The significance of the PEDOT layer was confirmed first by comparing the photocurrent of the oCVD PEDOT/planar-Si (25 μ A) with a PEDOT-free device (4 μ A, Figure S8, Supporting Information). The on-off current ratio of the oCVD PEDOT/planar-Si device at -1 V was 2000, which is 76 and 50 times higher than that of the LC-PEDOT and HC-PEDOT:PSS/planar-Si devices, respectively (Figure 2c). The dramatical enhancement in the switching ratio is attributed to the synergistic effect of the low trap density, high Schottky barrier, and efficient charge transport capability of oCVD PEDOT, compared to the solution counterparts. Moreover, in the oCVD PEDOT/planar-Si device, the suppressed dark current maintained a notable performance (the on-off ratio of 700) even at a higher voltage (-2 V, Figure 2d).

As discussed with the Raman spectra (Figure 1d), we proposed the potential for grafting of EDOT monomer, capable of enhancing charge transport characteristics between the Si and PEDOT layer. An additional diode, consisting of PEDOT:PSS and EDOT-modified Si wafer,

was fabricated to identify the role of grafted-EDOT on the device performance. As shown in Figure S9 (Supporting Information), the photo-detecting performance was dramatically enhanced by the EDOT-modification in both suppressed dark current and amplified photocurrent simultaneously (description is in Supporting Information with Figure S9 in more detail). Those results reveal that the grafted-EDOT not only served to suppress defects at the interface between the PEDOT:PSS and Si but also facilitated the collection of the photo-induced charges.

Besides, we additionally investigated the I - V curves of the two-terminal resistor consisting of PEDOT electrodes and a Si channel (high-doped p-type Si) to compare the contact properties according to the deposition methods (Figure S10). As a result, the contact resistance of the resistor based on the oCVD PEDOT electrode was 500 times lower than that of the device with the HC-PEDOT:PSS, substantiating the charge exchange between the layers is expected to be much facilitated in the oCVD PEDOT/Si interface.

2.2. Optoelectronic properties of oCVD PEDOT-covered black-Si detector

To further elevate the photodetection efficiency of the Si-polymer diodes, we utilized a porous Si, known as a “black-Si (b-Si)” substrate, instead of a planar-Si wafer. A b-Si specimen was prepared using a metal-assisted chemical etching (MACE) method described in the Experimental Section.^[46–48] As shown in Figure S11a and S11b (Supporting Information), SEM images of the b-Si substrate, the surface of the etched Si became a rough and porous architecture, consisting of mesopores and macropores with a size of 40-500 nm. The depth of the pores was adjusted to less than 500 nm. The porous surface, forming a refractive gradient, is well known to provide an anti-reflective effect,^[10,11,46–48] resulting in critically lowered optical reflectance under a broad range of wavelengths from UV to NIR light (e.g., <10% vs. 40% of the planar-Si under 625 nm, Figure S11c).

Si-polymer diodes based on the b-Si wafer were fabricated with the same device configuration as the planar-Si diodes (Figure S7, Supporting Information). The top-view (**Figure 3a**) and cross-sectional (Figure S12a, Supporting Information) SEM images of the oCVD PEDOT-coated b-Si (oCVD PEDOT/b-Si) demonstrate that the porous surface was maintained even after the oCVD PEDOT deposition. The vapor-phase reactants in the oCVD process successfully permeated into the inner pores and realized a uniform film, conformally covering both of the side walls and top of the nanostructures. The superior step coverage is clearly distinguished from the solution coating method, which made a dense film covering only the top of the nanostructures and undesirably lost the intended b-Si structure (Figure S12b, Supporting Information). Moreover, like the planar-Si case, a Raman spectrum of the oCVD PEDOT/b-Si diode (Figure S13, Supporting Information) demonstrated much stronger PEDOT information with a depressed Si peak than those of the PEDOT:PSS/b-Si; indicating oCVD PEDOT facilitates charge transport at the PEDOT and b-Si junction.

The I - V curves were investigated to compare the optoelectronic performances of the prepared Si-polymer diodes (Figure 3b and Figure S14 in Supporting Information). In this section, the HC-PEDOT:PSS-based device was selected as a control sample, representative of solution-based methods, to avoid redundant descriptions. The dark current of the oCVD PEDOT/b-Si diode at -2 V was 30 nA (Figure 3b), which is approximately 4-7 times lower than that of the PEDOT-free (120 nA) and HC-PEDOT:PSS/b-Si (200 nA) diodes (Figure S14, Supporting Information). The low dark current level was comparable to the planar-Si device, implying the surface defects were effectively passivated by oCVD PEDOT, which also effectively blocked a direct contact between the Si and top electrode (ITO/MoO₃).

The 625 nm and 980 nm LED sources (irradiance of 1 mW⁻²), the representatives for visible and NIR lights, respectively, were exploited to investigate a photo-detecting performance under the broadband spectral region. The highest photocurrent (55 μ A), as well as the highest on-off ratio (1800 at ± 2 V), were recorded in the oCVD PEDOT-implemented

detector under 625 nm light illumination, among all devices described in this research. In addition, the responsivity (R_λ), the amount of photocurrent per unit light intensity, was calculated as a significant figure of merit of the photodetectors (Figure 3c). The synergistic effect of the oCVD PEDOT/b-Si heterojunction resulted in the highest responsivity (1.14 A W^{-1}) under the 625 nm light, which is 2.20, 1.14, and 3.22 times higher than that of the oCVD PEDOT/planar-Si, HC-PEDOT:PSS/b-Si, and PEDOT:PSS/planar-Si diodes, respectively. The R_λ under NIR light was still maximal in the oCVD PEDOT/b-Si diode as well, implying a broadband enhancement was achieved using the oCVD PEDOT and b-Si.

The conformal PEDOT coating is of paramount importance for efficient collection of photo-induced charges by avoiding charge recombination. Besides, the density of undesirable recombination sites could be incremented during the plasma treatment that is the prerequisite process for the spin-coating method. Therefore, the conformal polymer/b-Si interface and the independence to the pre-treatment make the oCVD process much beneficial for realizing a high-performance photodetector.

The R_λ of the oCVD PEDOT/b-Si diode was investigated in more detail by varying the irradiance (Figure 3d). Under 625 and 980 nm, the R_λ became 4.5 and 1.09 A W^{-1} at the low irradiance $< 1 \mu\text{W cm}^{-2}$, respectively. The detectivity (D_λ), another figure of merit representing the detection limit of a photodetector, was calculated as follows with an assumption that shot noise is the dominant factor of the overall noise level:

$$D_\lambda = \frac{R_\lambda}{\sqrt{2qI_d A^{-1}}} \quad (4)$$

where q , I_d and A are the unit charge, dark current and active area of the device, respectively. The detectivity reached 1.37×10^{13} (Jones), which is 3 and 7 times higher than that of the PEDOT:PSS/b-Si and planar-Si detectors, respectively. Moreover, the achieved values of R_λ and D_λ are comparable to that of state-of-the-art heterojunction-based Si detectors (Table S1, Supporting Information).^[17,19,49–57]

The detection speed was tested under a 1,000 Hz light pulse. The rise time was estimated as a required time for the current to reach 90% of the stabilizing level under light injection; the decay time was defined as the time required to fall to 10% of the saturation level after turning off the light source. As a result, 110 and 90 μ s of the rise and decay times (Figure 3e) were recorded, respectively, comparable to high-performance Si detectors with heterojunctions (Table S1 in Supporting Information). Additionally, the repeatability of the device was tested under a periodic light pulse (5 s on / 5 s off), demonstrating a consistent and stable photocurrent generation for more than 300 cycles (for 3,000 s) as shown in Figure 3f. This set of PEDOT/b-Si detectors validate that the combination of oCVD PEDOT and b-Si enabled the construction of the high-performance detector with a superior figure of merits in terms of sensitivity (responsivity and detectivity), sensing speed, and stability by mitigating the surface recombination and poor light-collection issues simultaneously.

2.3. Bias-modulated switching from broadband to NIR-selective detection

The previous section mainly investigated the photo-detection capability of the diodes in the reverse bias regime. We, in this section, emphasize significant information of the forward-bias current and suggest a novel dual-mode detection strategy. Notice should be taken that the diode generated an observable photocurrent (1.98 μ A) at +2 V only when 980 nm (NIR) light was illuminated, but no measurable current change was detected with the 625 nm light (Figure 3b). This selective NIR detection appearing only at forward biases can be leveraged for switching the device functionality *via* facile modulation of bias polarity. To optimize the selective NIR detection in the forward bias, a new b-Si structure was contrived of which the pore depth was around 2 μ m (Figure S15a, Supporting Information), and the reflectance was less than 8% at 400-1,000 nm (Figure S15b, Supporting Information), hereafter denoted as 'b-Si-L'. The rationale for the optimized pore depth is provided in more detail later in this section.

Contrary to solution-processed PEDOT:PSS (Figure S16, Supporting Information), the oCVD approach is able to form a conformal PEDOT layer on the Si nanostructures with a high aspect ratio (**Figure 4a**). It was additionally substantiated by a Raman mapping image of the oCVD PEDOT/b-Si bilayer specimen (Figure S17, Supporting Information), which reveals conformally covered nanostructures with the oCVD PEDOT layer. The difference between the oCVD and spin-coating was further identified using SEM-EDX analysis shown in Figure S18-S19 (Supporting Information), revealing that the vapor phase reactants in the oCVD chamber can pass through the pores and formulate the PEDOT layer on the side of the Si nanostructures, while the spin-coating method is restricted to creating the film on only top (Figure S20).

The I - V characteristics of the oCVD PEDOT/b-Si-L device (Figure 4b) were investigated under dark and light illumination conditions (980 nm or 625 nm with irradiance of 1 mW cm^{-2}). The responsivity and detectivity (Figure S21, Supporting Information) of b-Si-L devices, measured at -2 V, became less than half of those of the oCVD PEDOT/b-Si diode. It was predictable given that the deeper hole depth has more trap sites triggering more surface recombination events.^[7,11] On the contrary, the responsivity of b-Si-L devices, recorded at +2 V and under NIR light, was 8 times higher than that of the b-Si-based device while keeping the visible-blinded characteristic. In other words, the switching ability from the broad-band (-2 V) to the narrow-band (+2 V) could be strategically maximized by controlling the pore dimension of the b-Si.

The photodetection mechanism of the PEDOT/b-Si diodes can occur through two different pathways; one is attributed to the excitation from the valance-to-conduction band (VTC), and the other is the excitation from the localized state-to-conduction band (LTC) transition.^[58-60] The latter excitation proceeds in a consecutive route of i) electron trapping under an external electric field and ii) photo-triggered excitation from the localized states to the conduction band, resulting in a photocurrent^[60]. The origin of the mechanism is described in Supporting Information with Figure S22 (Supporting Information) in more detail. The MACE-

derived b-Si has a broader bandgap (1.6-1.7 eV) than that of the standard Si wafer (1.12 eV) due to the quantum confinement effect.^[60–62] The energy gap of the MACE-derived b-Si corresponds to a photon energy of light with a 730-780 nm wavelength, which is a boundary classifying between visible and NIR light. Therefore, the visible light only has sufficient energy to trigger the VTC transition in the b-Si, whereas the NIR light with weaker photon energy can be detected in the circumventing way (LTC).

The VTC-assisted photo-detection mainly occurs at a reverse bias, and a small negative photocurrent is generated at a forward bias; thus, the positive photocurrent generation of the oCVD PEDOT/b-Si-L at the forward bias is dominantly associated with LTC transition. Besides, the LTC-based mechanism is based on localized energy states in the etched Si layer so that the mechanism may further influence the b-Si-L device with deeper hole depth. Therefore, a higher photocurrent may be generated in the forward bias regime by increasing the thickness of the porous layer.

The effect of the pore-depth on the photo-detecting performance was investigated in Figure S23 and S24 (Supporting Information). We fabricated three diodes with pore depths adjusted as 0.3, 1.4, and 2.3 μm , respectively. Their I - V curves were investigated with and without the 980 nm light illumination, as shown in Figure S24. The dark and photocurrent at the reverse bias were identical regardless of the pore depth (Figure S24a-c), but significant variations were observed at the forward bias (the linear scaled plot is in Figure S24d and e). As shown in Figure S24d, the dark current gradually increased as the pore depth increased. The tendency is because the surface defects, non-passivated by the PEDOT, typically form a relatively high-doped area, causing a high leakage current. Contrary, the maximal photocurrent was recorded at the medium depth (1.4 μm , Figure S24e). As discussed in Figure S22, the uncovered-Si region plays a key role in the NIR detection at the forward bias *via* LTC transition. Unfortunately, the defects, largely distributed in the uncovered zone, tend to serve a charge recombination center that hinders an effective charge collection. In other words, the diode with

narrow pore depth is lack of region to cause enough LTC transition, while the abundant defects in the deeper pore depths trigger the undesired recombination; thus, it is essential to make the b-Si with a trade-off depth to give rise to high-photocurrent at the forward bias.

We contrived a novel photo-detecting system using a pulsed voltage (-2 V to 2 V, Figure 4c) based on the optimized device. Under the red-light illumination (625 nm), the photocurrent was generated only at the negative voltage, whereas the NIR light (980 nm) triggers the photocurrent at both bias polarities. In other words, the platform was able to selectively extract NIR information from a broad-band spectral illumination composed of both visible and NIR lights. Additionally, a spatial current mapping image based on a single-pixel imaging system was obtained under an artificial light environment, consisting of a uniformly spread visible light (6,000 K cool white light) and centralized NIR light (980 nm) (Figure 4d and e). The photocurrent was continuously measured while moving the position of the stage, on which the device was placed. At -2 V, although the photocurrent was more strongly generated at the central region, the signal is not clearly discriminated from the surrounding. Thus, the device served as a broadband detector in the mode, sensitive but non-selective, detecting both visible and NIR light. In contrast, the photocurrent was selectively measured only at the center region as the bias was switched to +2 V. It should be noted that the results reveal two unprecedented functionalities distinct from traditional Si-diodes. One is the potential for selective NIR detection from a visible light noise without any band-pass filter, and the other is that the bias polarity readily and reversibly controls the operation mode (broad-band mode to NIR-detection mode). Therefore, the suggested structure integrating oCVD PEDOT and b-Si-L is expected to be a key for creating novel visionary systems such as night-vision sensors and motion sensors, which are beyond the limited applications of existing Si detectors.

3. Conclusion

Herein, we suggest a novel strategy to resolve two fundamental issues (the facilitated charge extraction and the multi-functionality) in b-Si photodetectors by using an oxidative chemical vapor deposition technique. Exceptionally conductive ($3,000 \text{ S cm}^{-1}$) oCVD PEDOT polymer was uniformly deposited on the wafer using the vapor-phase deposition tool which enabled a conformal film coating without undesired surface treatment. Furthermore, Raman scattering analysis demonstrated that oCVD PEDOT extracted photo-induced charges from planar or b-Si wafers more effectively than PEDOT:PSS. Therefore, these benefits of oCVD synergistically resulted in the high-performance PEDOT-Si photodetector with a detectivity of 1.37×10^{13} Jones, which is 3 and 7 times higher than that of a conventional PEDOT:PSS-covered b-Si and planar-Si detectors, respectively.

Furthermore, we contrived a novel photodetector that uniquely operates in dual-function modes: i) broad-band detecting mode at a reverse bias and ii) visible-blinded NIR detecting mode at a forward bias. The switchable functionality should be noticed, separately extracting both NIR and visible light information, particularly from a single device without any supplementary filters. This unprecedented achievement of a single photodetector with dual functionalities will be a game-changer in the existing versatile visionary systems such as night vision, motion tracking, and bio-sensing.

4. Experimental Section

Black Silicon (b-Si) fabrication: The b-Si wafer was fabricated using a conventional metal-assisted chemical etching (MACE) process. First, a Si wafer with the 100 nm of SiO_2 layer (<100>, n-type, 1-10 $\Omega \text{ cm}$, University Wafer) was pre-cleaned by acetone (VWR) and isopropyl alcohol (IPA, VWR) in sequence. Next, silver (Ag) catalysts were deposited by dipping the wafer in 0.01 M of silver nitrate (AgNO_3 , Sigma Aldrich) dissolved in 4.8 M of hydrofluoric acid (HF, VWR) solution for 3 min. Excess reactants after the reaction were washed with distilled water (DI). After drying the sample, the Ag-coated wafer was etched in

an HF, H₂O₂, and DI mixed solution with a volumetric ratio of 3:1:5, respectively for 2 min. The lingering Ag catalysts were removed using nitric acid (HNO₃, Sigma Aldrich) as soon as completing the above etching. The acidic environment can create a thin oxide layer on the etched Si surface. Thus, the wafer was dipped in a buffered oxide etchant (BOE, VWR) for 3 min to eliminate the potential oxide layer. After cleaning with DI, the wafer was dried using blowing and stored in a vacuum box to prevent the formation of native oxide.

Another b-Si wafer, named b-Si-L, having a deeper pore depth, was fabricated using the MACE process likewise but with the revised Ag catalyst deposition process. The pre-cleaned SiO₂/Si wafer was first immersed in BOE solution to remove the SiO₂ layer. Then, the bare Si surface was exposed to AgNO₃ solution (same concentration above) for 5 s. The short Ag deposition time is the key to making small and dispersed Ag nanoparticles which serve as catalysts for enabling anisotropic etching and realizing a deep hole depth (> 2 μm). Other processes were exactly the same as for the b-Si sample.

Oxidative Chemical vapor (oCVD) Deposition: The oCVD PEDOT thin film was deposited on silicon (Si) using a custom chamber capable of simultaneous injection of gas-phase monomers and oxidizing agents. 3,4-Ethylenedioxythiophene (EDOT, 97%, Sigma Aldrich) monomers, vaporized at 130°C in a separate jar, were injected into the chamber using a needle valve. Iron chloride oxidizing agent (FeCl₃, reagent grade, Sigma Aldrich), placed in a crucible, was sublimated by heating to 190°C. The flow rate of the EDOT was adjusted to reach a stable working pressure of 3-5×10⁻³ torr, and the inner wall temperature was maintained at 120°C. After stabilizing all chamber conditions, the deposition was initiated by opening the main shutter hiding the loaded sample. The substrate was maintained at 120°C, and the thickness was controlled by varying the deposition time. The PEDOT-coated samples were rinsed sequentially with saturated hydrobromic acid (HBr, J. T. Baker) and methanol (VWR) to remove un-reacted FeCl₃ and EDOT reactants. Once completely dry, the thickness of PEDOT was analyzed using an Ellipsometer (FilmSense FS-1).

PEDOT:PSS film deposition: The wafers were first pre-treated using oxygen plasma (PDC-001) to induce a hydrophilic surface. After, a PEDOT:PSS solution (PH 1000, Ossila) was spin-cased on the wafer at a rate of 3,500 rpm for 30 s. Then, the film was stabilized by annealing at 150°C for 10 min on a hot plate (the finalized sample was denoted as LC-PEDOT:PSS). To improve the film's conductivity, we added acid treatment where the LC-PEDOT:PSS coated wafer was immersed in a saturated HBr solution for 10 min, followed by a methanol cleaning. After drying it, it was stabilized again on a hot plate (150°C) for 10 min (the sample was denoted as HC-PEDOT:PSS).

Materials and device characterization: Functional groups on PEDOTs were analyzed utilizing Raman spectroscopy (WiTec Alpha 300) using a 633 nm expiation laser. PEDOT films on b-Si were observed using a scanning electron microscope (SEM, Thermo Fischer Scientific Teneo). The optical absorbance was measured using a UV-visible spectrometer (Lambda 950), equipped with an attenuated total reflectance accessory. The photocurrent was measured using an Agilent 4155B under the illumination of LEDs (625, and 980 nm, Mightex). Rise and decay times were measured using an oscilloscope (Hantek, DSO4254B).

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

S.L., B.-C. M., and H.K. conceived the study. H.K., Y.Z. and R.M. prepared the materials and devices. H.K. performed the measurements. Y.Z. conducted DFT calculation. H.K., K.R., Y.K., and H.S.J. conducted material characterizations. S.L., B.-C. M., and H. K. analyzed the data and wrote the manuscript. This work was partially supported by the U.S. National Science Foundation (NSF) Award No. ECCS-1931088.

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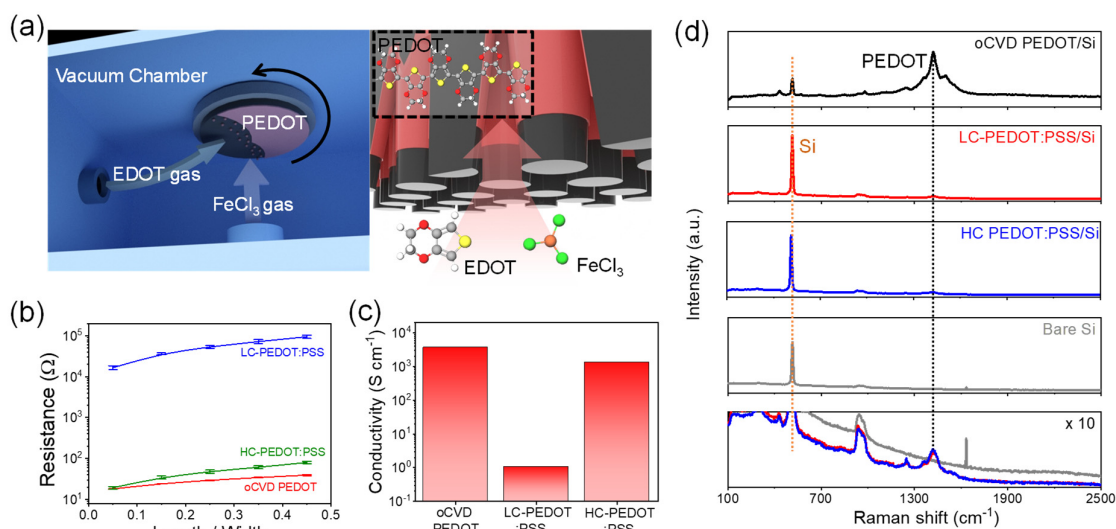


Figure 1. Characterization of oCVD PEDOT. a) A Schematic of the oCVD process. b,c) TLM analysis for estimating electrical properties of the PEDOTs. Plots of resistance vs. length/width (b) and estimated conductivities (c) of the oCVD PEDOT, LC-PEDOT:PSS, and HC-PEDOT:PSS based on the TLM analysis. d) Raman spectra of oCVD PEDOT/Si, LC-PEDOT:PSS/Si, HC-PEDOT:PSS/Si, and bare Si. The fifth panel represents 10-fold magnified spectra of the LC-PEDOT:PSS/Si, HC-PEDOT:PSS/Si and bare Si. Device configuration and simulated optical properties of the DSJ device.

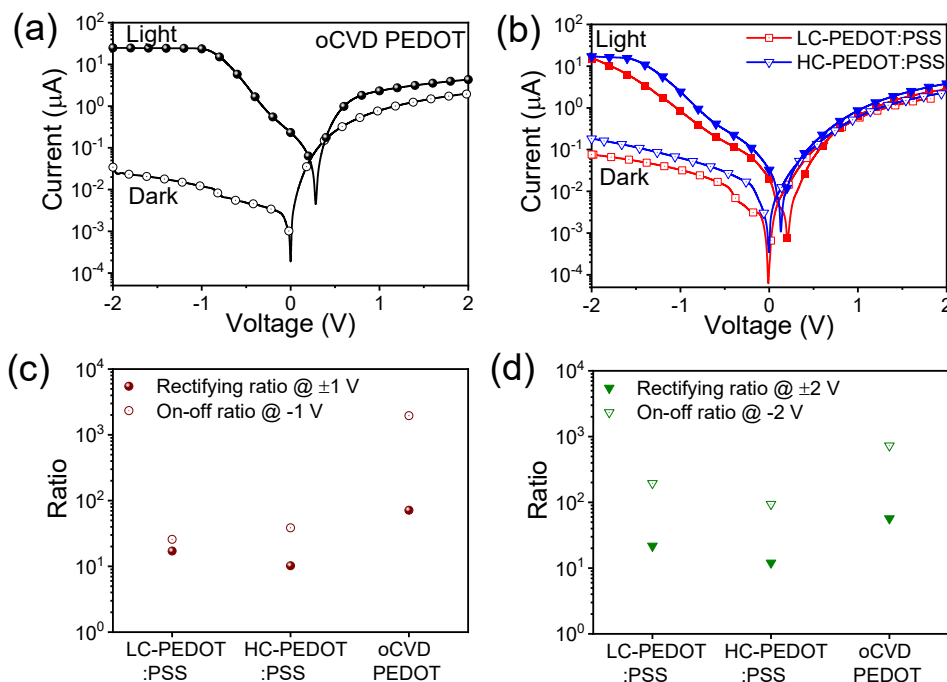


Figure 2. Photo-detecting performance of the PEDOT/planar-Si diodes. a,b) Optoelectronic properties of planar-Si diodes consisting of a PEDOT transport layer and ITO/MoO₃ electrode. (a) I - V curves of the oCVD PEDOT/planar-Si diode with and without the illumination of 625 nm light (1 mW cm⁻²). (b) I - V curves of the LC-PEDOT:PSS and HC-PEDOT:PSS-based diodes under the same condition. c,d) Rectifying ratio, measured under dark conditions, and photo-to-dark current ratio (on-off ratio) measured under the 625 nm light illumination with the irradiance of 1 mW cm⁻². Rectifying and the on-off ratio of the LC-PEDOT:PSS/planar-Si, HC-PEDOT:PSS/planar-Si, and oCVD PEDOT/planar-Si diodes, measured at 1 V (c) and 2 V (d).

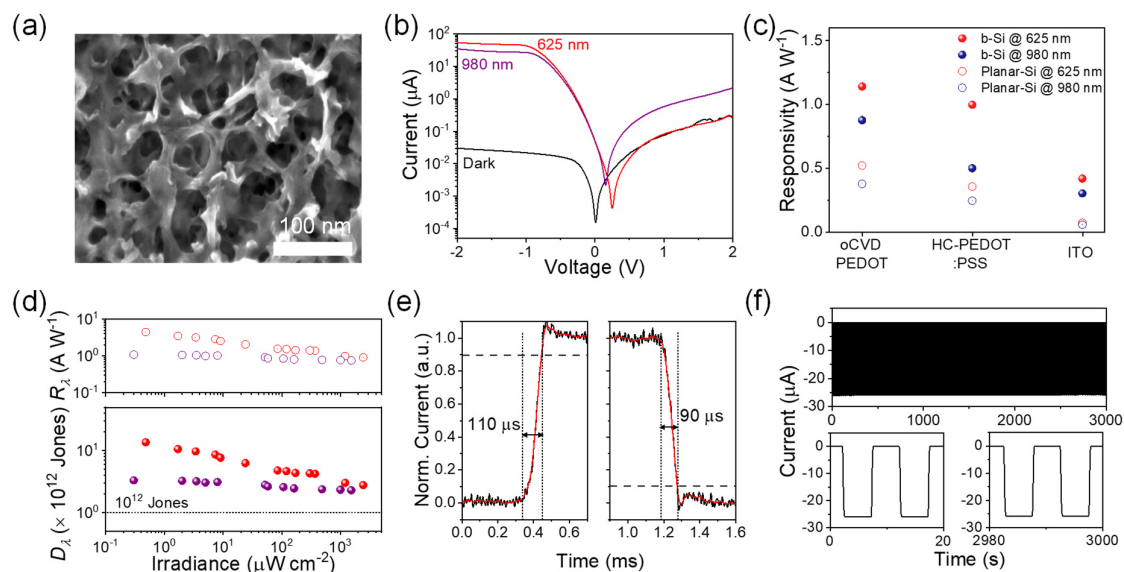


Figure 3. Photo-detecting performance of the PEDOT/b-Si diodes. a) An SEM image of the oCVD PEDOT/b-Si. b) I - V curves of the oCVD PEDOT/Si diode under dark and illumination of 625 nm light (1 mW cm^{-2}). Response to 980 nm light was additionally investigated under the same irradiance. c) Responsivities of the Si-polymer diodes. All combinations of three options for the transport layer (oCVD PEDOT, HC-PEDOT:PSS, and PEDOT-less) and two options for the Si wafer (b-Si and planar-Si) were investigated and compared. d) Responsivity and detectivity of the oCVD PEDOT/b-Si, investigated by varying the irradiance of light. e) Rise and decay times of the oCVD PEDOT under a 1,000 Hz light pulse. f) Repeatability test: time-resolved current measurement for 300 cycles of light pulses (5 s on / 5 s off). The lower panels represent the photocurrent at the initial (left) and after the repeatability test (right).

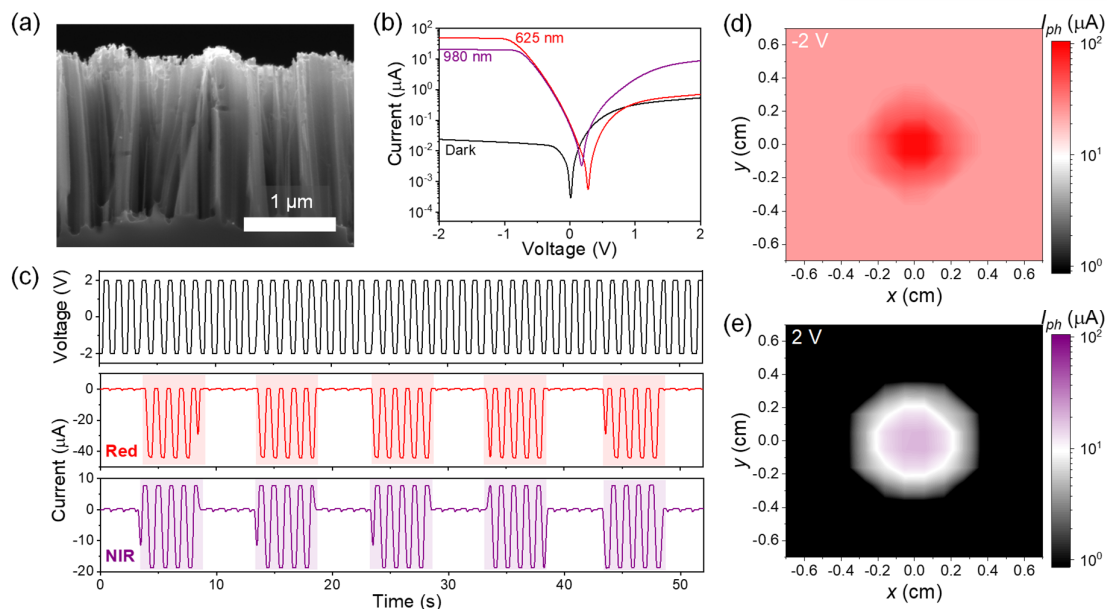


Figure 4. Bias-switchable functionality of the PEDOT/b-Si-L diode to visible-blinded NIR detection. a) A cross-sectional image of the oCVD PEDOT/b-Si-L. b) I - V curves of the oCVD PEDOT/b-Si-L diode under dark and light illumination (625 nm and 980 nm with an irradiance of 1 mW cm^{-2}). c) Time-resolved photocurrent measurement at a 1 Hz of pulse bias (-2 to 2 V). d,e) Spatial photocurrent mapping result. The photocurrent of the diode was measured under an artificial light illumination consisting of diffused white LED (6,000 K cool white) and centralized NIR light. The maps represent the photocurrent recorded at -2 V (d) and 2 V (e), respectively.

Table of contents

A dual-functional photodetector is realized utilizing conformal conductive polymers induced by oxidative CVD and black-silicon technology. The device functionality can be reversibly switched via bias polarity from the visible-NIR broadband to the visible-blinded NIR detection mode. This study identifies the role of Si pore-dimension on the dual-functionality and paves a way to augment the unique multimodal photodetection technology.

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Hybrid Silicon-Polymer Photodetector Engineered Using Oxidative Chemical Vapor Deposition for High-Performance and Bias-Switchable Multi-Functionality

