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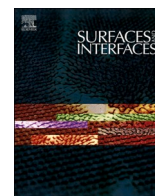
Adsorption induced bipolar excitation at semiconductor surface

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ABSTRACT

Adsorption on metal surfaces has been shown to lead to chemisorption induced electronic excitation but direct experimental evidence of chemisorption induced excitation on semiconductor surfaces is still missing. Here, we design and use high-quality Silicon (Si) p-n diodes to in-situ probe the charge transfer process taking place during vapor and liquid phase chemisorption of iodine molecules on H-Si (100) surface. We find that the diodes can generate electricity and feed an external circuit during the chemisorption process, demonstrating chemisorption-induced electron and hole generation and the means to electrically monitor the process. A bipolar semiconductor electrochemical model where a single semiconductor surface hosts the spontaneous oxidation (electron injection) and reduction (hole injection) reactions simultaneously on its conduction and valence bands without any electrolytes is proposed to explain the observations. Our work provides new insight on the energy relaxation processes of chemisorption and also calls for further studies on the observed chemovoltaic effect. Overall, the results indicate a possibility for developing electrolyte-free vapor phase chemical energy-to-electricity converters and detectors.

1. Introduction

Chemisorption plays a crucial role both in fundamental and in applied research. Over the past two decades significant discoveries have been made in the study of chemisorption of gas molecules on metal surfaces [1-3]. In particular, the chemisorption induced electronic excitation at metal surfaces has been demonstrated to lead to observable "chemicurrents" in Schottky diodes [4-6]. Furthermore, electron flow was also reported to be generated by gas phase exothermic catalytic reactions using Schottky nanodiodes [7-9]. The observations of the chemisorption induced electron-hole pair generation, however, have so far been limited to metal surfaces where the relaxation of "hot" electrons is extremely fast. In semiconductors on the other hand, such relaxation processes would be substantially slower due to the energy band gap. Despite the broad fundamental interest and recent discoveries [10,11], however, direct experimental evidence of chemisorption induced electron and hole generation at semiconductor surfaces is still missing.

The chemisorption of halogen molecules, e.g., iodine, on hydrogen-terminated silicon (H-Si) surface (usually obtained by HF etching) is of fundamental interest in both surface chemistry and Si-based

electronics. [12-15] Conventional surface characterization methods have already revealed that during the chemisorption of iodine on H-Si surface, the iodine molecules are dissociated and adsorbed to modify the Si-H bonds to Si-I bonds [16-20]. Despite the extensive studies of iodine chemisorption on H-Si surfaces, however, less attention has been paid to the in-situ dynamics of the reaction. We still lack the most fundamental chemical understanding of the adsorption process, as the lack of effective means to in-situ monitor the charge transfer processes taking place during the chemisorption process has prevented directly measuring if the chemisorption reactions can drive the semiconductor out of equilibrium.

Using the inherent capabilities of Si devices, forming the backbone of photovoltaics and photodetectors [21-23], to monitor the nature of the chemisorption processes, can therefore establish new measurement methodologies for such surface reactions. In our recent studies, we used both Si p-n diodes and photoconductors to explore their response to the metal-assisted chemical etching (MACE) process and demonstrated that both electron and hole injection into conduction and valence band occur during the chemical etching process [24,25]. In the same way, if the reactions taking place during the chemisorption of iodine on Si surface

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involve energy states from both conduction and valence bands, it would be interesting to consider using a charge carrier collecting p-n junction as a part of the chemisorption system. This could allow the direct collection of non-equilibrium free charges in both bands by a p-n junction during the chemisorption, thus providing insight on the dynamics of the chemisorption reaction in-situ.

In this work, we design and use a high-quality p-n diode to in-situ probe the charge transfer processes taking place during the chemisorption of iodine on H-Si (100) surface. Our results reveal that electricity is generated by the diode in the dark during the chemisorption process, for the first time providing direct evidence for chemisorption induced electron and hole generation at semiconductor surfaces. The finding further enables us to in-situ electrically monitor the chemisorption processes on semiconductor surfaces. Due to the chemically induced electron and hole generation at semiconductor surface leading to electricity generation, our work also represents a radically new approach to electrolyte-free vapor phase chemical energy-to-electricity conversion.

2. Materials and methods

2.1. Fabrication of the p-n junction diodes

High-quality p-n diodes were fabricated by following the previously reported process flow used for fabricating Si solar cells. [26] 280 nm-thick 4-inch phosphorous-doped n-type float-zone Si wafers with a resistivity of 1–5 Ω cm and $\langle 100 \rangle$ orientation were used as substrates. Firstly, the wafers were cleaned by standard RCA cleaning followed by a wet oxidation process at 1000 °C under O_2 ambient for 130 min resulting in ~550 nm thick SiO_2 layer on the surfaces. The purpose of this thick oxide was to serve as an ion implantation mask later in the process. The high oxidation temperature ensured the elimination of the possible bulk defects simultaneously. After oxidation, a lithography process and buffered hydrofluoric acid (BHF) were used to pattern the SiO_2 to create front active areas with 5 mm in diameter. Then, the wafers were cleaned by standard RCA cleaning and dry oxidized at 1000 °C under O_2 ambient for 20 min to form approximately 35 nm SiO_2 on the surfaces to avoid contamination during the following ion implantation process. After that, the front active areas were doped by ion implantation with a boron dose of 3×10^{15} cm^{-2}, a tilt angle of 7° and an energy of 10 keV, while the rear surfaces were implanted with a phosphorus dose of 2×10^{15} cm^{-2}, a tilt angle of 7° and an energy of 50 keV in order to form a back surface field. Afterwards, the screen oxide was removed in BHF and the dopants were activated by annealing in N_2 ambient at 1050 °C for 20 min followed by a dry oxidation in O_2 at 1050 °C for 20 min. After that BHF was used again to remove the grown SiO_2. As a result, a front emitter with a

sheet resistance of 45 Ω/sq was achieved. Then, 1 μm of Al was sputtered on both the front and rear surfaces respectively. The front Al was patterned by lithography and chemical etching. Thereafter, the wafers were annealed at 425 °C for 20 min in forming gas to sinter the Al contacts. Finally, the wafers were diced into actual samples with a size of 1.1×1.1 cm^2. The structure of the diode is schematically shown in Fig. 1a.

2.2. J-V and J-t measurements

Two insulated copper wires were attached to the front and back Al contacts of the diodes using conductive silver paste. The two copper wires were passed through two glass tubes which were attached to the diode using hot glue. After that the diodes were encapsulated with Apiezon Wax W leaving an active area of around 0.05 cm^2 exposed on the front surface. To remove the native oxide on Si surface and to prepare a H-Si surface, the encapsulated diodes were immersed in 5 % HF for 90 s and then rinsed by DI water and dried with nitrogen. The setup used for J-V and J-t measurements in vapor phase is schematically shown in Fig. 1b. After HF etching, the diodes were immediately placed directly above (~ 1 cm apart) a beaker with an aqueous solution of 0.1 M I_2 and 0.25 M KI. Due to the high volatility of molecular iodine, the iodine vapor easily reaches the diodes surfaces exposing the active area of the diodes to the molecular iodine vapor. In addition to the vapor phase tests, the chemisorption process of iodine on H-Si surface in aqueous and methanol solution was also studied. In these tests the devices were directly immersed in the aqueous (0.1 M I_2 and 0.25 M KI) and methanol (0.1 M I_2) solutions of iodine as schematically shown in Figure S1. The front and back side Al contacts of the diodes were connected to a potentiostat (Zahner ZENNIUM PRO). The J-V measurements were performed with different scan rates (0.5, 5 and 50 mV/s) and scan ranges (from −0.1 to 0.2 V and from −0.01 to 0.2 V). The J-t measurements were performed with the diodes at short-circuit conditions exposed to iodine vapor in the dark. The V_{oc}-time curve was measured with the freshly etched diode exposed to iodine vapor in the dark. The J-V measurements were also performed when the diodes were illuminated by 0.75 μW/cm^2 white light emitted from a commercial fluorescent lamp without any iodine exposure. The light intensity was determined by a Si photodiode power sensor (S130VC, Thermolab). All the measurements were performed in ambient pressure.

2.3. XPS characterization

For XPS measurements, three samples were prepared: a Si p-n diode after HF etching (denoted as Si-H), a Si p-n diode after HF etching and a
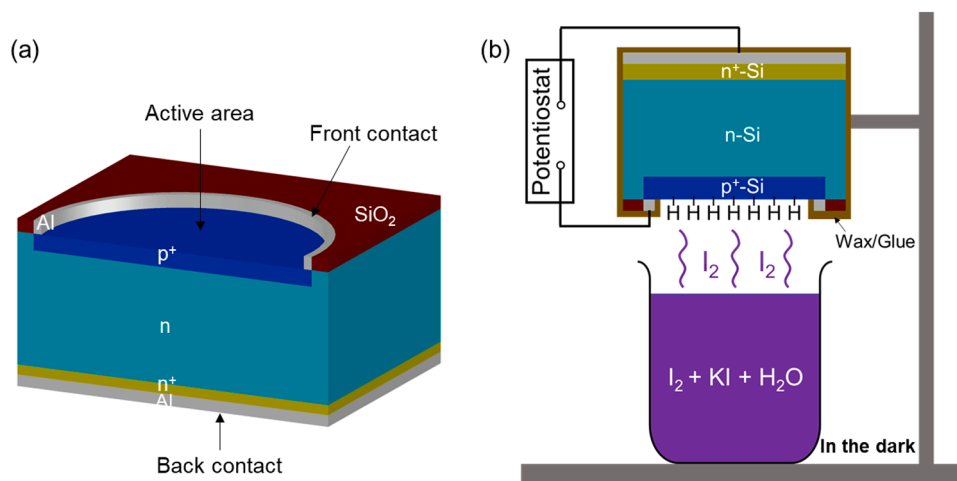

Fig. 1. Schematical illustration of the structure of the high-quality p-n diode (a) and the set up used for vapor phase measurements (b).

20-minute iodine vapor exposure in ambient pressure (denoted as Si-I) and a Si p-n diode with native oxide after a 20-minute iodine vapor exposure in ambient pressure as the control sample (denoted as Si/SiO$_x$-I). All these as-prepared samples were sealed in a plastic bag filled with N$_2$ gas and delivered to our collaborator for XPS measurements. XPS measurements were done with monochromatized (Al-Kα) Thermo Scientific Nexsa equipped with dual mode charge compensation. X-ray spot diameter was 200 μm and pass energy 50 eV. Binding energies are relative to Fermi level determined by a metallic reference.

3. Results and discussion

The *J-V* results of the freshly HF etched diode under vapor phase exposure are shown in Fig. 2a. In the dark without exposure to iodine vapor, the diode showed a standard rectifying curve (black line) with an open circuit voltage (V$_{oc}$) of zero and a very low leakage current of around 3 nA/cm^2. Quite remarkably, when the diode was exposed to iodine vapor, the *J-V* characteristics (red line) change dramatically, showing an electrical response with a V$_{oc}$ of 66 mV and a short circuit current density (I$_{sc}$) of 57 nA/cm^2. Conversely, no obvious change of the *J-V* curve was observed when the diode was placed above the aqueous solution of only 0.25 M KI (Figure S2). For comparison, the figure also shows the electrical response to white light illumination at a 0.75 μW/cm^2 power density produced by a commercial fluorescent lamp providing the same V$_{oc}$ of 95 mV as generated by the exposure to the iodine vapor in the dark at the very beginning of the *J-V* measurement.

Similarly, Fig. 2b shows the *J-V* results when the diode was immersed in the aqueous solution. Like in the vapor phase, the *J-V* characteristics also change dramatically when immersed in the 0.1 M I$_2$ and 0.25 M KI aqueous solution, generating a similar amount of electricity with a V$_{oc}$ of 73 mV and an I$_{sc}$ of 69 nA/cm^2. In the same way, no obvious change of the *J-V* curve was observed when the diode was immersed in the aqueous control solution of 0.25 M KI without iodine. For comparison, *J-V* measurements were also performed on the diode with the native Si oxide in place (i.e., without the preparatory HF etching), and the results are shown in Fig. 2c. With native oxide in place, no electricity was generated by the diode when exposed to either the aqueous solution of 0.1 M I$_2$ and 0.25 M KI or its vapours.

The *J-V* results were also performed with different scan rates (0.5 and 50 mV/s), with the results shown in Figure S3. For the freshly etched sample exposed to iodine vapor (Figure S3a) and iodine solution (Figure S3b), the measured value of V$_{oc}$ changes with the scan rate, as one might expect since the chemisorption process itself is a transient process. A lower scan rate corresponds to a smaller V$_{oc}$, which can be attributed to the decrease of V$_{oc}$ with increasing exposure to iodine vapor as shown in the V$_{oc}$-time curve of Figure S4. For the sample with native oxide exposed to iodine vapor (Figure S3c), there is no chemisorption and V$_{oc}$ is always zero, independent of the scan rate. This shows that the measured currents and voltages cannot be caused by capacitive charging effects in the measurement setup. Because only the front semiconductor surface is exposed to iodine vapor and iodine solution, any currents in the external circuit must originate from this single surface. Conventional charging process at this surface, however, cannot produce any observable electric current. Instead, the charge would simply transfer over the interface, charging a possible Helmholtz capacitance, forming space charge region in semiconductors without causing any currents observed in the external circuit.

The working principle of the p-n junction for light detection and solar cells is well known. When the diode is illuminated by light, excess electron-hole pairs are induced inside the Si. These photo-induced electron-hole pairs are separated by the p-n junction and transported to an external circuit, thus generating electricity. However, for the experiments exposing the freshly HF etched diode to iodine vapor or iodine aqueous solution in the dark, no light is present and obviously no photo-induced excess electron-hole pairs can be generated. This suggests that the excess electrons and holes were induced during the chemisorption of iodine on H-Si surface, resulting in the excitation of Si.

To explain the generation of excess electrons and holes in Si, we note that the process of iodine chemisorption on the H-Si surface is essentially a semiconductor electrochemical process, which can be broken into two half reactions, with some unconventional features. The first half reaction is the oxidation of the H-Si surface, and the second one is the reduction of the molecular iodine. In semiconductor electrochemistry the reactions proceed by electron or/and hole transfer between the energy bands of the semiconductor and the redox couples in the system e.g., the previously reported charge injection-caused electrochemiluminescence, photocurrent doubling effect and electrochemical etching of semiconductor electrodes [27-30]. It is worth noting that in these conventional semiconductor electrochemical studies, the semiconductor electrode usually only hosts one type of reaction, i.e., either oxidation or reduction reaction, and the other half reaction occurs on the counter electrode. In the system of iodine adsorption on H-Si surface studied in this work, however, there is no counter electrode, and it is the single Si electrode that hosts both the oxidation and reduction reactions. Moreover, in the case where the Si diode was exposed to iodine vapor, there are no liquids or any electrolytes which are considered essential in conventional electrochemical studies. These results necessitate establishing a bipolar semiconductor electrochemical model where one single semiconductor electrode hosts the spontaneous oxidation and reduction reactions simultaneously on its conduction and valence bands without any electrolytes. The presence of a single semiconductor surface supporting both the oxidation and reduction reactions bears similarities e.g. with some experiments in photocatalytic water splitting where hydrogen and oxygen evolution reactions take place on a single semiconductor surface in pure water or water vapor [31,32]. In our case, however, the reaction directions are reversed as we are dealing with an exoergic chemisorption process. The bipolar semiconductor electrochemical model was introduced in more detail in [Ref. 33].
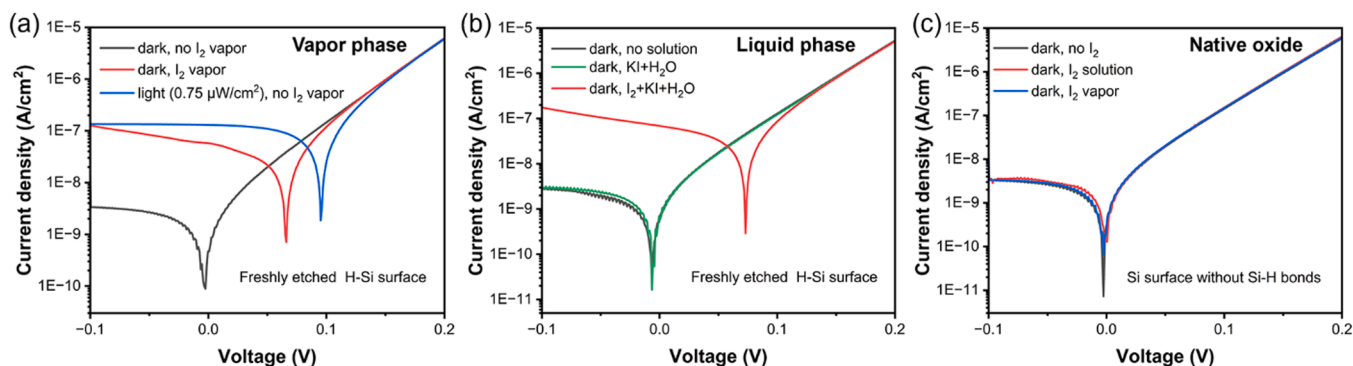

Fig. 2. Electricity generation by the p-n diode in the dark. J-V curves of the p-n diode with freshly etched H-Si surface exposed to (a) vapor phase and (b) liquid phase iodine and the p-n diode with native oxide (c) measured in both liquid and vapor phases.

Although exact values for the energy levels and especially for the redox potentials present in the system are not available, estimating their relative positions allows more insight on the pertinent thermodynamics. The energy level diagram of the elements in the system is schematically shown in Fig. 3 to illustrate the expected relative positions of the energy levels. The position of the conduction band minimum and the valence band maximum of Si are 4.05 and 5.17 eV relative to the vacuum energy level, respectively. [34] The two redox couples in this system are Si-H/Si-I and $I_2/2I^-$, respectively. H-Si has a strong reduction property, [35,36] but the precise value of the electrode potential of the oxidation of H-Si is not known. Recently, Lewis et al. showed that the oxidation potential of H-Si surface is more negative than the electrode potential of Si/SiO$_2$ which is -0.91 V vs. SHE. [37,38] Since the exact value of the potential does not affect our conclusions, we approximate the electrode potential of Si-H/Si-I to be equal to the electrode potential of Si/SiO$_2$ for illustration purposes. Iodine as a strong oxidant has been widely used in redox flow batteries and dye-sensitized solar cells owing to fast kinetics [39-41]. In the aqueous solution of I_2 and KI, the iodine molecule bonds to iodine ion forming triiodide (I_3^-). The reduction potential of iodine molecule to triiodide ion is considered to be 0.79 vs SHE [39]. In the vapor phase case, only the oxidized form i.e., molecular iodine exists but the exact value of the reduction potential of iodine in gas phase is not available. The energy position of the SHE relative to the vacuum energy level is around 4.45 eV. Thus, the energy position of the conduction band minimum and the valence band maximum of Si relative to the SHE are determined to be -0.4 and 0.72 eV, respectively.

Typically, the contributions of the two bands to the charge carrier exchange with one certain redox couple are of rather unequal magnitude, and one of them dominates the current. According to the well-known Gerischer model, a major part of the current arises from the band that is closer to the Fermi level (electrode potential) of the relevant redox couple [42,43]. Considering the system of Fig. 3, the conduction band overlaps well with the redox couple Si-H/Si-I, and the valence band overlaps well with the $I_2/2I^-$. Therefore, for the oxidation of H-Si charge carrier exchange would be expected to occur with the conduction band, and for the reduction of iodine it would be expected to occur with valence band for the system shown in Fig. 3.

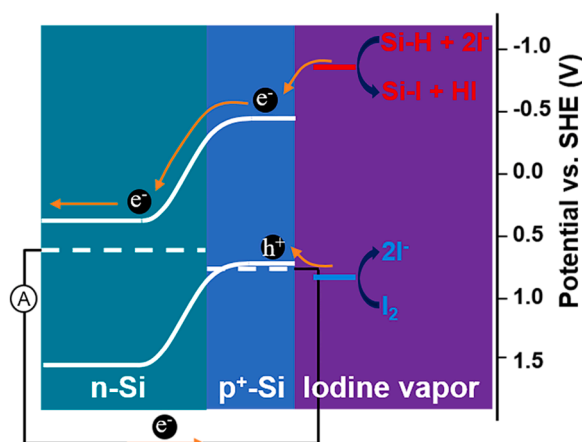The above experimental results and the reaction thermodynamics

Fig. 3. Thermodynamic model of the spontaneous bipolar charge transfer taking place during iodine vapor chemisorption on H-Si surface illustrating the origin of electricity generation by the diode. The energy band diagram of the p-n diode and the relative positions of the Si conduction-band (CB) minimum and valence-band (VB) maximum with the electrode potentials vs SHE of redox couples Si-H/Si-I and $I_2/2I^-$ are shown. The dominant charge carrier transfer between Si energy bands and redox couples are schematically shown by the orange arrows. In this system, the Si CB serves as a virtual anode, and the VB as a virtual cathode. The bulk Si (p-n junction) and the external circuit transfers the chemically induced electrons to recombine with the chemically induced holes, thus generating electricity in the circuit.

suggest the following mechanism for the electron and hole generation at Si surface and electricity generation of the Si p-n junction during the chemisorption of iodine. As the diode is exposed to iodine, the chemisorption of iodine molecules on H-Si surface occurs. Specifically, the iodine molecules gain electrons from the valence band of Si (injecting holes into the valence band) and are reduced to iodine ions (I-I bonds breaking) as shown in Eq. (1) below [16]. Concurrently, due to the low oxidation potential of H-Si, the electrons in Si-H bonds are injected into the conduction band (Si-H bonds breaking) [44,45], forming positively charged Si$^+$ species and proton (H$^+$) on the surface as shown in Eq. (2) [37]. The formed Si$^+$ species and protons then combine with the iodine ions generated by the hole injection reaction forming new Si-I bonds on the surface and releasing hydrogen iodide molecules as shown in Eq. (3). The electron injection into the conduction band of semiconductors was also proposed to explain the photocurrent doubling effect observed in semiconductor photoanodes [46]. In the process, electrons and holes are generated in Si with the overall reaction shown in Eq. (4). The chemically induced excess electrons and holes (e_{CB}^- and h_{VB}^+) increase the carrier densities on the surface with respect to their equilibrium densities, which causes the carriers to spread out from the surface through diffusion. When the carriers reach the p-n junction, they are separated by the built-in electrical field and can be efficiently transported even through the external circuit as shown in Eq. (5). The relevant reactions and transport processes are described as:

Cathodic reaction: $I_2 \rightarrow 2I^- + 2h_{VB}^+$ (hole injection into the valence band) (1)

Anodic reaction: Si-H$\rightarrow$Si$^+$ + H$^+$ + 2e$_{CB}^-$ (electron injection into the conduction band) (2)

and Si$^+$ + H$^+$ + 2I$^-$ $\rightarrow$Si-I + HI (3)

Overall reaction: Si-H + $I_2\rightarrow$Si-I + HI + 2e$_{CB}^-$ + 2h$_{VB}^+$ (4)

Bulk semiconductor/external circuit: e_{CB}^- + $h_{VB}^+\rightarrow$bulk recombination and/or an external electric current (transmitting the e$_{CB}^-$ to recombine with the h$_{VB}^+$) (5)

In addition to the bipolar charge transfer process for chemical bond formation proposed above, charge transfer due to changes in the space charge region and band bending at the surface can also occur when exposing a Si surface to iodine molecules. Such processes can produce displacement currents that can be detected as small external currents using suitable experimental setups. For example, Hagemann et al. reported external currents due to the charge displacement currents when exposing a Schottky junction and a semiconductor surface to an atomic metal beam [47]. Such displacement currents changing the surface band bending or charge, however, are not expected to be able to produce any observable electric currents in our measurement setup. Instead, we expect any unipolar displacement currents to be bound in the depletion layer unless the charge they produce is compensated by an opposite charge. Such balancing charge, however, only becomes available if the charge generation process is bipolar, and provides both electrons and holes over the surface. As such displacement currents are excluded as a viable explanation for our observations. Another possible mechanism for the generation of electricity by the Si p-n diode during the chemisorption of iodine on its surface could result from direct surface chemical reactions promoting electrons from the valence band to the conduction band, either directly or indirectly through electron-phonon coupling. For example, Amirav and Cardillo reported the electron-hole pair creation via electron-phonon coupling during Xe atom scattering at InP surfaces [48]. Recently Bünermann et al. reported that collisions with hyperthermal H atoms can excite electrons from valence band to conduction band at Ge surface [10].

Electricity generation by the diode when exposed to molecular iodine vapor suggests that we can use the diode for in-situ monitoring of the chemisorption reaction by detecting the electrical response of the

diode. To test this in practice, a separate *J-t* measurement was performed on the freshly HF etched diode when exposed to iodine vapor under short-circuit conditions in the dark. The result is shown in Fig. 4a. Before exposure to iodine vapor, the current was essentially zero. When the diode was exposed to the iodine vapor a sharp increase of the current density was observed, corresponding to the onset of the excitation of the diode by the chemisorption of iodine. The observed current decreased exponentially with time, essentially decreasing back to zero 20 min after being exposed to iodine. After the *J-t* test, the *J-V* curve of the diode was also measured under the exposure to iodine vapor in the dark with the result shown in Fig. 4b. Obviously, no electricity was generated anymore, suggesting that essentially all the Si-H bonds were changed to Si-I bonds during the 20-minutes exposure to iodine vapor.

Separate XPS measurements were performed on the HF etched diode (Si-H), HF etched diode after 20-minute exposure to iodine vapor (Si-I) and the diode with native oxide after 20-minute exposure to iodine vapor (Si/SiO$_x$-I). The I3d spectra of the samples are shown in Fig. 4c. The I3d spectrum of the Si-I sample clearly shows the well-separated I3d$_{5/2}$ and I3d$_{3/2}$ spin-orbit doublet peaks. Each of the peaks was resolved into two peaks which can be ascribed to the dominant I-Si bonds and I-O bonds, respectively [18,49]. The I3d signal intensity collected from the Si/SiO$_x$-I sample is much lower than that collected from the Si-I sample, and the peaks can be ascribed to I-O bonds [49]. The I3d spectra strongly suggest that after exposure to iodine vapor, iodine was adsorbed on the H-Si surface and Si-I bonds were formed, in accordance with the literature [16-20,49]. The C1s and O1s spectra (Figure S5 in supporting information) show that 1) all the samples were also exposed to carbon and 2) the Si-H and Si-I samples were also partially oxidized by air. Since the samples were exposed to the ambient atmosphere during the experiments and during placing the samples to the XPS chamber, oxidation by air and carbon exposure are considered unavoidable.

The working principle of using a p-n diode to in-situ monitor the chemisorption reaction is based on the cross-disciplinary combination of Si electronics with surface chemistry, as schematically shown in Fig. 4d. Before being exposed to molecular iodine vapor the surface of the p-n diode is hydrogen-terminated. When the iodine vapor reacts with the H-Si surface changing Si-H bonds to Si-I bonds, both electron and hole
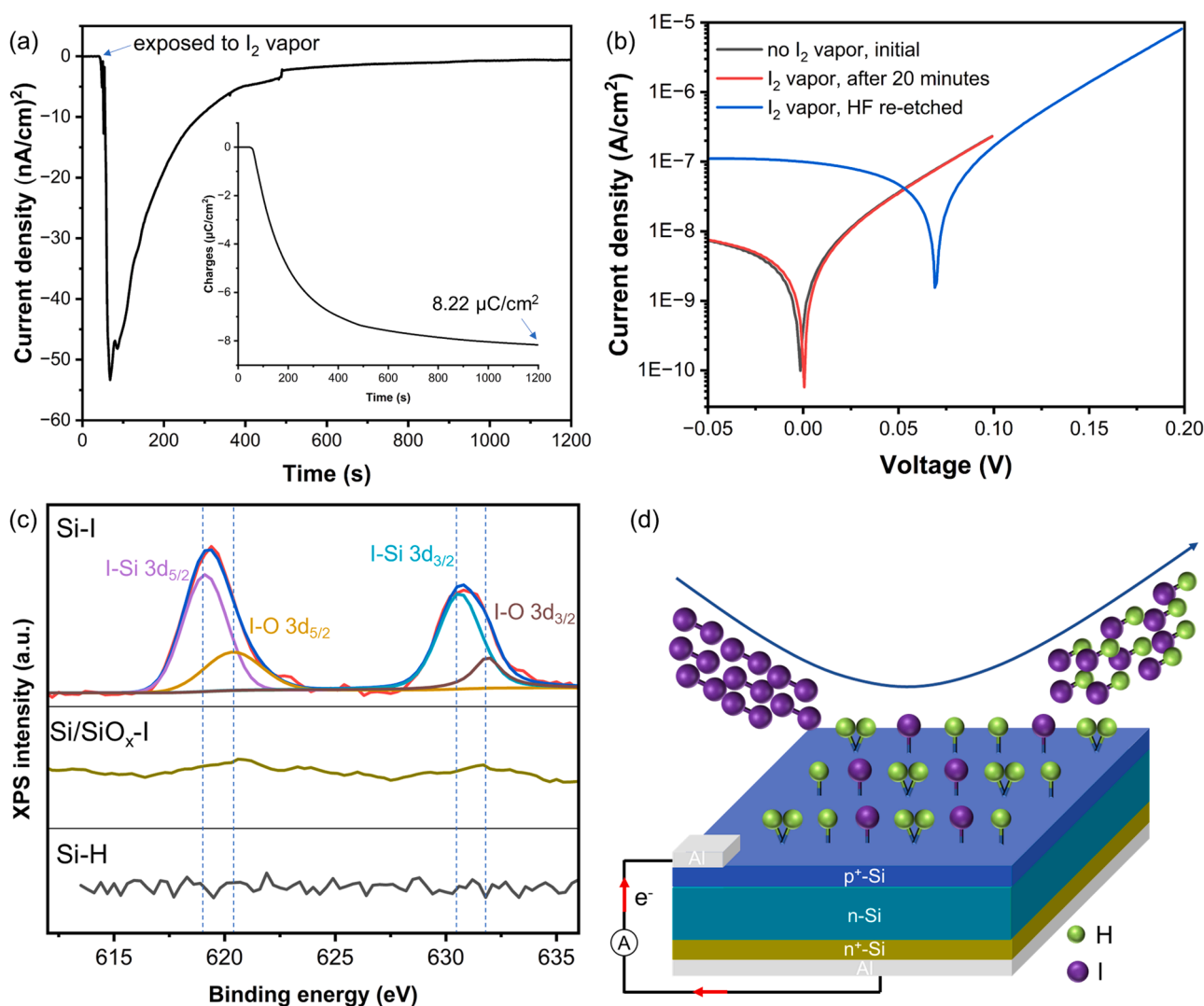

Fig. 4. In-situ monitoring of iodine vapor chemisorption on H-Si surface. (a) J-t curve of the diode under short-circuit condition when exposed to iodine vapor in the dark. Inset is the charge density-time curve obtained as an integral of the J-t curve. (b) J-V curves of the diode in the dark without I$_2$ exposure before J-t measurement, with I$_2$ exposure after J-t measurement, and with I$_2$ exposure after being re-etched by HF solution. (c) I3d XPS spectra of the HF etched Si p-n diode surface without (Si-H) and with (Si-I) a 20-minute iodine vapor exposure and the Si p-n diode with a native oxide after a 20-minute iodine vapor exposure (Si/SiO$_x$-I). (d) Schematic illustration of using a p-n diode for in-situ monitoring of iodine vapor chemisorption on H-Si surface by detecting the electrical response of the diode. For simplicity, we draw the surface as atomically flat even though surface reconstruction reported for HF etched Si (100) surface likely affects the surface morphology of the real samples [50,51].

injection into the conduction and the valence bands of Si occurs, resulting in an excitation at the surface of Si. The excited carriers spread further inside the semiconductor by diffusion, resulting in the chemically induced electrons and holes to be separated and collected by the p-n junction, which leads to an observable electrical signal (Fig. 4a), providing in-situ information about the dynamics of the reaction. Since the diode current is proportional to the charge carrier injection rate i.e., the rate of the reaction, one can also estimate the time-evolution of the reaction rate based on the *J-t* curve. Assuming that the full exposure to iodine starts at the time when the current reaches the maximum, the reaction rate is determined by the coverage of Si-H bonds on Si surface after that. The exponential decay of the current with time then indicates a first-order kinetic dependence of the reaction on the surface coverage of hydrogen. The iodine dissociation rate may depend on various H-terminated surface properties, but studying these in any detail is out of scope of this manuscript.

By integrating the *J-t* curve we could also estimate how much charge carriers the diode collected during the *J-t* measurement and compare the result with the number of electrons involved with the surface reaction. The integration of the *J-t* curve results in a total charge of 8.22 $\mu C/cm^2$ being extracted by the diode during the experiment. On the other hand, if all the surface Si atoms (the atomic density on Si (100) plane is 6.78×10^{14} atoms/cm^2) were hydrogen terminated and each of them could inject two electrons into the conduction band while forming one monolayer of Si-I bonds, one could expect (assuming a quantum efficiency of η) to extract a charge of $\eta \times 12.6$ $\mu C/cm^2$ which matches with the measured value when η is 65 %. This strongly suggests that reactions (Eq. (1) and Eq. (2)) indeed have a dominating role in the charge transfer dynamics, in line with the Gerischer model quantifying the strength of the interactions using the overlap between the redox-levels and respective semiconductor energy bands [42,43].

To show that after the *J-t* measurement the diode could also be reused to detect the adsorption of iodine once the surface is hydrogen-terminated again, one week after the *J-t* measurement (during which the diode was stored at room temperature and exposed to lab air) the diode was freshly etched by HF solution to form a new Si-H monolayer on the Si surface, and another *J-V* measurement was performed on the diode when exposed to iodine vapor in the dark. The result is shown in Fig. 4b. When exposed to iodine vapor, the diode generated electricity with a V_{oc} of 69 mV, i.e., essentially the same values as in the original measurements. To minimize the influence of water, oxygen and KI, *J-V* curves were also measured in a 0.1 M methanol solution of iodine. The results are shown in Figure S6. The diode generated electricity with a V_{oc} of 74 mV and an I_{sc} of 51 nA/cm^2, indicating that water, oxygen and KI do not seem to play an important role in electricity generation by the diode during iodine chemisorption.

The possibility of electricity generation by a p-n diode in the dark when exposed to iodine vapor and the established spontaneous bipolar charge transfer model indicate the possibility of a semiconductor-based electrolyte-free vapor phase chemical energy-to-electricity conversion approach. In particular, if both redox reactions in the system were realized using a vapor phase reactants and reaction products instead of the current Si-H –> Si-I self-limiting surface reactions, the reaction and electricity generation could additionally become continuous. This was demonstrated by our recent work showing that electricity was generated by a GaAs p-n diode exposed to methanol vapor [33]. The conventional chemical energy-to-electricity converters e.g., batteries and fuel cells contain two spatially separated electrodes (i.e., anode and cathode) and electrolytes for ion transport between the two electrodes [52]. While we previously reported the electricity generation by a Si p-n diode during MACE, the earlier systems also included electrolytes (HF+H_2O_2 aqueous solution) [24]. One of the biggest possible advantages of the direct chemical energy to electricity conversion by a semiconductor p-n diode (e.g., a solar cell) is therefore demonstrated by this work: the approach does not need an electrolyte (i.e., it can be fully electrolyte-free) to support ion transportation because both the electrochemical oxidation and reduction reactions occur on a single semiconductor surface, meaning that they are not spatially separated. In essence, our approach replaces the electrodes conventionally used in batteries and fuel cells with virtual electrodes formed by the semiconductor's energy bands. Specifically, as shown in Fig. 3, the conduction band serves as a virtual anode where the oxidation of H-Si surface occurs injecting electrons into the conduction band, and the valence band serves as a virtual cathode where the reduction of iodine molecules occurs injecting holes into the valence band. The injection of both electrons and holes leads to excitation of the semiconductors. The band gap of the semiconductor prevents the immediate recombination of the electrons and holes, directing them to diffuse to the p-n junction and to the external circuit generating electricity.

4. Conclusion

In summary, we have demonstrated that chemisorption induces bipolar electron and hole generation at the semiconductor surface by showing electricity generation by a Si p-n diode with hydrogen-terminated surface when exposed to iodine vapors and aqueous and methanol solution of iodine. A bipolar semiconductor electrochemical model where one single semiconductor electrode hosts the spontaneous oxidation and the reduction reactions simultaneously on its conduction and valence bands without any electrolytes was suggested to explain the observations. Additional theoretical and experimental work is nevertheless still needed to fully elucidate the mechanism. Independent of the mechanism, our work provides a means for in-situ monitoring chemisorption processes on semiconductor surfaces. The work also presents an electrolyte-free vapor phase chemical energy conversion approach which may introduce electrolyte-free fuel cells with important benefits in future.

CRediT authorship contribution statement

Shengyang Li: Conceptualization, Methodology, Writing – original draft, Writing – review & editing, Validation, Investigation. **Kexun Chen:** Methodology, Investigation. **Mahdi Alizadeh:** Methodology, Writing – review & editing. **Ville Vähänissi:** Methodology, Writing – review & editing. **Hele Savin:** Methodology, Writing – review & editing, Funding acquisition. **Jani Oksanen:** Conceptualization, Methodology, Writing – review & editing, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.surfin.2024.104499.

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