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Chemical Excitation of Silicon Photoconductors by Metal-Assisted Chemical Etching

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ABSTRACT: The chemical transformations taking place during many of the reactions of the Si surface have been well documented, but the in situ dynamics of the reactions remain largely unexplored even for widely used electrochemical processes such as metal-assisted chemical etching (MACE). In this work, we design both n- and p-type Si photoconductors covered with silver nanoparticles to demonstrate photoconductors' sensitivity to the MACE process and their ability to provide in situ information about the dynamics of the reactions occurring during MACE. The experimental results show that both n- and p-type photoconductors exhibit a response to MACE that is much stronger than their response to light with an intensity of 2 mW/cm². The observations are further explained by a thermodynamic analysis of the relevant energy levels of the system, showing how both electron and hole injection into the conductors' response and excite Si. These results clearly demonstrate a new



chemical operating mode for photoconductors, showing that in addition to being sensitive to excitation by light, a photoconductor can also be excited by chemical reactions providing means to monitor the dynamics of the reactions in situ and thus also for chemical sensing.

INTRODUCTION

Metal-assisted chemical etching (MACE) as an effective method to fabricate semiconductor (especially Si) nanostructures has been widely studied over the past twenty years and is attracting more and more interest from both the scientific and technological communities.¹⁻⁸ The Si nanostructures produced by MACE have been widely used in energy harvesting and storage,⁹⁻¹² sensors,¹³ and biomedical technologies.¹⁴⁻¹⁶ In addition, inspired by the MACE reaction, plasmonenhanced nanomotors moving at the silicon/MACE etching solution interface have been developed based on the attractive plasmon resonance of noble metal, e.g., Ag and Au, nanocrystals.^{3,17–19} The MACE process is based on the highly site-selective oxidation of Si when it is brought into contact with metal nanoparticles (typically silver nanoparticles, AgNPs) and oxidants (typically hydrogen peroxide, H_2O_2) in a fluorine-containing solution.^{20,21} The oxidized products of Si can be easily etched away by a fluoride solution and thus highaspect-ratio silicon nanostructures are produced in the end. After twenty years of studies, the chemical transformations that take place during MACE have been well characterized,² but the dynamics of the detailed charge transfer process taking place during the process have not been reported so far.

The Si-metal-oxidant nanosystems formed during MACE have been usually considered as microscopic and shortcircuited galvanic cells where Si serves as an anode and the metal nanoparticles serve as cathodes.^{22,23} This description focuses on the overall charge flow proceeding from Si to oxidants instead of detailing the role of Si energy bands in the charge transfer process. Cui et al. proposed a Schottky barrier (formed between metal and silicon) mechanism for charge transfer during MACE,²⁴ which was challenged by a recent study where the oxide-assisted chemical etching was first reported.²⁵ Another more widely accepted proposal is Si oxidation by the injected hole from H_2O_2 in the valence band.^{26,27} Focusing only on the valence band reactions, these descriptions, however, do not consider the role of the conduction band and related electron injection process on the charge transfer during MACE.

In our recent study,²⁸ we found that electricity was generated by a p-n junction device during MACE. Consequently, we suggested that both conduction and valence bands are involved in MACE and lead to the excitation of Si. In contrast to p-n junction devices, however, the response of photoconductors is governed by majority carriers, suggesting that one can separately focus on the electron or hole generation process using n- and p-type photoconductors to the

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(a)



Figure 1. (a) Schematic illustration of the structure of the photoconductors. (b) Surface SEM image of the p-type photoconductor after AgNP deposition. (c) Schematic illustration of the setup used for electrochemical measurements, using an n-type photoconductor as an example.



Figure 2. Current–voltage curves of n-PC-planar (a), n-PC-AgNPs (b), p-PC-planar (c), and p-PC-AgNPs (d) in different conditions. The black lines in panels (a, c) are not clearly visible because they almost completely overlap with the blue lines.

light-induced excess carriers and their simple structure make them attractive candidates for studying the electrochemical injection of excess carriers (either electron or hole) by the semiconductor/liquid interface, also providing information about the dynamics of the surface reactions in situ.

In this work, we use both n- and p-type Si photoconductors covered with AgNPs to explore their response to the charge flow in the Si-metal-oxidant nanosystems formed during MACE. Current-voltage (I-V) and current-time (I-t)measurements are carried out on the photoconductors during MACE, showing a strong response with a significant increase in the slope of the I-V curves and the current in the I-tmeasurement. A theoretical analysis of the positions of the quasi-Fermi levels of the Si energy bands relative to the electrode potentials of the redox couples in the system is also carried out to describe the thermodynamics of MACE and to explain the experimental results. These results unambiguously show that both electrons and holes are injected into the conduction and valence band of Si during MACE, resulting in the chemical excitation of Si and also demonstrating a new mechanism for chemical sensing and the possibility to use photoconductors as chemical sensors.

METHODS

Fabrication of Photoconductors. n- and p-type Si photoconductors were fabricated on high-resistivity (>10 k Ω cm) Si wafers doped either with phosphorus (n-type) or boron (p-type). The detailed fabrication process of the samples is provided in the Supporting Information. A schematic representing the most important processing steps in the

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process flow for the fabricated n- and p-type Si photoconductors is presented in Figure S1. Briefly, the wafers were first cleaned and then subjected to a wet oxidation treatment to grow a thermal buffer oxide layer for doping masking. After that, the regions for metal contacts were opened and heavily doped to obtain a good ohmic contact in both n- and p-type photoconductors. For the n-type photoconductors, the n⁺ regions were created by diffusion doping, while for the ptype photoconductors, boron implantation was employed to create the p⁺ regions. Afterward, the thermal oxide was entirely removed from the front and back side of both n- and p-type wafers by BHF etching. This was followed by aluminum (Al) film deposition and patterning on the back side of the wafer. After that, the Al contacts were annealed at 425 °C for 20 min in a forming gas atmosphere. The structure of the photoconductors is schematically shown in Figure 1a.

AgNP Deposition. The prepared photoconductors were first encapsulated by hot glue and then subjected to an AgNO₃ and HF aqueous bath. Specifically, two insulated copper wires were attached to the two Al contacts of photoconductors using conductive silver paste. The two copper wires were passed through two glass tubes covered with hot glue, and the samples were insulated with hot glue apart from the around 1 cm² front side active area of the sample that was left exposed. Then, the sample was immersed in the aqueous solution of 5 mM AgNO₃ and 6 M HF for 8 min, during which the AgNPs were deposited on the active area of the sample by the displacement reaction of Si with Ag ions.²⁹ After that, the sample was thoroughly rinsed with DI water and dried with nitrogen. An SEM image of the p-type photoconductor surface after AgNP deposition is shown in Figure 1b. The diameter of deposited AgNPs is around 100 nm. Hereafter, the samples with the ntype photoconductor without AgNP coating, the n-type photoconductor with AgNP coating, the p-type photoconductor without AgNP coating, and the p-type photoconductor with AgNP coating are called n-PC-planar, n-PC-AgNPs, p-PC-planar, and p-PC-AgNPs, respectively.

Device Performance Characterization. The setup used for electrochemical measurements is schematically shown in Figure 1c. The two Al contact electrodes were connected to a two-channel source meter (Keithley 2612B) used as a potentiostat. The samples were placed in a beaker with a 0.4 M H₂O₂ and 6 M HF solution, which is usually used for MACE.³⁰ The *I*–*V* measurements were performed in the dark by scanning from -1 to 1 V with a scan rate of 50 mV/s. *I*–*t* curves were measured at a bias of 0.5 V in the same solution with *I*–*V* measurements for 30 min in the dark. For the *I*–*V* measurements of the samples under illumination without contacting any solutions, the samples were illuminated by a solar simulator (HAL-320 W, Asahi Spectra), and the light intensity on the sample was 2 mW cm⁻², as measured by a Si photodiode power sensor (S130VC, Thermolab).

RESULTS AND DISCUSSION

I-V measurements were performed on the above-mentioned four types of devices in the dark and under exposure to light or different solutions, and the results are shown in Figure 2. In darkness and without exposure to any solution (black lines close to zero), all of the devices exhibited an ohmic behavior but very small current (the I-V curves were straight lines with a very small slope implying a high resistance for the devices). When exposed to light with an intensity of 2 mW cm⁻² (red lines), all four devices worked as photoconductors and

exhibited a clear response to illumination, which was reflected by the increase of the slopes of the I-V curves. When exposed to the MACE solution (HF and H_2O_2 , blue line) in the dark, quite interestingly, both n-PC-AgNPs and p-PC-AgNPs showed a strong response, which was seen as a significant increase of the slopes of I-V curves that was much higher than their response when exposed to light with an intensity of 2 mW cm⁻². Correspondingly, no obvious response was observed when the devices were exposed only to the HF solution without H₂O₂ (green lines) or when n-PC-planar and p-PCplanar were exposed to the MACE solution (blue line). In addition, no obvious response was observed when the devices were exposed only to the H_2O_2 solution without HF (Figure S2). Current saturation at large bias voltages was confirmed by simulations (not shown) to arise from the decreased concentration of the majority carriers near the positively biased Al contact electrode in the case of p-type photoconductors (and vice versa for n-type photoconductors).

Current transport in photoconductors is primarily based on the flow of majority carriers, and under illumination, the generation of excess majority carriers then changes the device conductance.³¹ However, for the measurements performed on n-PC-AgNPs and p-PC-AgNPs under exposure to the MACE solution, the optical generation of carriers is obviously absent due to the absence of light. The strong response of n-PC-AgNPs and p-PC-AgNPs to the HF + H_2O_2 solution nevertheless implies the generation of a large number of excess majority carriers in Si by the electrochemical reactions taking place during MACE. An obvious question then arises: What drives the excess carrier generation?

To explain the dynamics of the reactions at the fundamental level, we note that MACE is essentially a semiconductor electrochemical process, which can be broken into two halfreactions. One is the oxidation of Si, and the other is the reduction of the oxidant (H_2O_2) in this work). In semiconductor electrochemistry, the reactions proceed by electron or/and hole transfer between the energy bands of the semiconductor and the redox couples in electrolytes, and these processes are ultimately governed by the thermodynamics of the reactions, depending on the energy differences between the quasi-Fermi levels of the energy bands and the Fermi levels (i.e., electrode potentials) of the redox couples. Therefore, to answer the above question, we now add to the previous treatments (ref 28) a quantitative analysis of the relative position between quasi-Fermi levels of Si energy bands and electrode potentials of relevant redox couples in the system as well as a discussion on how the positions reflect on the expected charge transport processes.

The conduction band minimum $(E_{\rm C})$ and valence band maximum $(E_{\rm V})$ of Si are 4.05 and 5.17 eV below the vacuum energy level, respectively.³² Without excitation, the quasi-Fermi level of conduction and valence bands are in the same position and can be determined from the resistivity of the wafer. The Fermi level of the n-type $(E_{\rm F,C})$ and p-type photoconductors $(E_{\rm F,V})$ used in this work is calculated to be 4.5 and 4.76 eV below the vacuum level, respectively (see the details in the Supporting Information). Two types of Si oxidation half-reactions could occur during MACE.²² One is the divalent oxidation of Si, which is accompanied by the generation of hydrogen, with a standard electrode potential of -1.2 V vs the standard hydrogen electrode (SHE), as shown in eq 1.³³ The other is the tetravalent oxidation with a standard electrode potential of -0.91 V vs SHE, as shown in eq 2.³⁴ The electrochemical reduction of H_2O_2 proceeds, as shown by eq 3, with a standard electrode potential of 1.77 V vs SHE.³⁵ The energy position of SHE relative to the vacuum energy level is around 4.45 eV.³⁶ Thus, the energy position of the divalent oxidation of Si, tetravalent oxidation of Si, and the reduction of H_2O_2 relative to the vacuum energy level are determined to be 3.25, 3.54, and 6.22 eV, respectively. The energy diagrams of the relevant items in the system are shown in Figure 3.

$$Si + 6F^{-} + 2H^{+} \rightarrow SiF_{6}^{2-} + H_{2} + 2e^{-} E^{0} = -1.2 V$$
(1)

Si + 6HF
$$\rightarrow$$
 SiF₆²⁻ + 6H⁺ + 4e⁻ $E^0 = -0.91$ V (2)

$$2H_2O_2 + 4H^+ + 4e^- \to 4H_2O \quad E^0 = 1.77 \text{ V}$$
(3)



Figure 3. Energy diagram showing the absolute positions of the Si conduction-band minimum $(E_{\rm C})$, the Si valence-band maximum $(E_{\rm V})$, and the calculated Fermi levels of n-type Si $(E_{\rm F,C})$ and p-type Si $(E_{\rm F,V})$ used in this work. The electrode potentials vs SHE of reaction 0: Si + $6{\rm F}^- + 2{\rm H}^+ \rightarrow {\rm SiF}_6^{-2-} + {\rm H}_2 + 2{\rm e}^-, \textcircled{0}$: Si + $6{\rm HF} \rightarrow {\rm SiF}_6^{-2-} + 6{\rm H}^+ + 4{\rm e}^-$, and 0: $2{\rm H}_2{\rm O}_2 + 4{\rm H}^+ + 4{\rm e}^- \rightarrow 4{\rm H}_2{\rm O}$ are also shown. The charge carrier transfer between Si energy bands and redox couples is schematically shown by the arrows.

The driving force for electron transfer in semiconductor electrochemistry is always the difference between the quasi-Fermi levels and/or electrode potentials, albeit in the literature, the Fermi level is often approximated to coincide with the closest band edge. Furthermore, the contributions of the two energy bands to the charge carrier exchange between redox couples in the system are of rather unequal magnitude, and one of them dominates the current.³⁷ The dominant contribution to the current typically comes from the band that is closer to the electrode potential of the redox couple. As shown in Figure 3, in the MACE system, the conduction band overlaps well with the oxidation reactions of Si, and the valence band overlaps well with the reduction reaction of H_2O_2 . Therefore, for the oxidation of Si, the charge carrier exchange would be mainly expected to occur with the conduction band, and for the reduction of H_2O_{24} it would mainly occur with the valence band. With the energy level of Si oxidation (both divalent and tetravalent oxidation) higher than the quasi-Fermi-levels of the conduction band of both the n- and p-type Si, and the energy level of the H₂O₂ reduction lower than the respective quasi-Fermi-levels of the valence band, as shown in Figure 3, the dominant charge carrier exchange between the energy bands and redox couples in the MACE system would be electron

injection from the oxidation of Si to the conduction band and hole injection from the reduction of H_2O_2 to the valence band for both n- and p-type photoconductors. In addition to thermodynamics, which determines the direction of the reaction, kinetics is also an important factor to be considered in the charge carrier transfer process. AgNPs as noble metal nanoparticles, which have been widely used as highly efficient catalysts for various (electro)chemical reactions, could decrease the activation energy of the reactions due to their high catalytic activity and thus significantly enhance the kinetics of the charge carrier injection processes.³⁸

The analysis of the charge flow based on the Fermi level positions in the MACE system, as shown in Figure 3, is fully consistent with the experimental results obtained for photoconductors. That is, both electron and hole injection into the conduction and valence bands, driven by the pertinent thermodynamics, are involved in MACE, and this increases the conductivities of both n- and p-type photoconductors when exposed to the MACE solution. For n-PC-planar and p-PC-planar, despite the thermodynamic feasibility, the high activation energy of the Si oxidation and H2O2 reduction kinetically prevented the charge injection from the redox couples to the energy bands due to the lack of AgNPs catalyzing the reactions and decreasing the activation energy. For the case where n-PC-AgNPs and p-PC-AgNPs were exposed only to the HF solution without H_2O_2 , the hole injection half-reaction in MACE was blocked due to the lack of a strong oxidant, and thus no response was observed. For the case where n-PC-AgNPs and p-PC-AgNPs were exposed only to the H_2O_2 solution without HF, the Si oxide layer on the Si surface prevented oxidation below the surface, and thus no response was observed.

To investigate the response of the device to the MACE process in the longer term, we measured the change of current at a bias of 0.5 V when p-PC-AgNPs (Figure 4a) and n-PC-AgNPs (Figure 4b) were exposed to the etching solution and etched in the solution for 30 min in the dark. When the devices were exposed to the MACE solution, a sharp increase in current was observed from both devices due to the strong chemical excitation of the devices during MACE. The current gradually decreased with time, mostly due to mass transport limitations for the etching and/or the increased recombination when more surface area was exposed when the etching proceeded inside of Si. The I-V curves of the photoconductors measured in the MACE solution in the dark after the 30-min etching are shown as insets in Figure 4a,b, showing that even after the long etching, the main features of the I-Vcharacteristics under exposure to MACE remain unchanged. The cross-sectional SEM images of p-PC-AgNPs after the 30min I-t measurements are shown in Figure 4c,d. Si nanowire arrays with a diameter of around 100 nm and a length of 28 μ m were produced during the etching. The high catalytic activity of AgNPs is clearly observed in Figure 4d as the Si only below the AgNPs was selectively etched, also highlighting why no obvious response was observed from the photoconductors without AgNP coating when exposed to the etching solution.

It is well known that the MACE etching rate is directly affected by the concentration of H_2O_2 .³⁹ To show that the photoconductor could also be used to study the kinetics of MACE, we additionally measured the *I*-*V* curves of p-PC-AgNPs in the MACE etching solution with 0.04 and 0.15 M H_2O_2 in the dark. The results are shown in Figure 5, repeating the *I*-*V* curve of 0.4 M H_2O_2 of Figure 2d and comparing it



Figure 4. Current-time curve of p-PC-AgNPs (a) and n-PC-AgNPs (b) when exposed to the MACE solution in the dark. Insets are the I-V curves of the devices measured in the MACE solution in the dark after 30 min of etching. (c, d) Cross-sectional SEM images of p-PC-AgNPs after 30 min of etching.



Figure 5. Current–voltage curves of p-PC-AgNPs measured in 6 M HF solutions with 0.04, 0.15, and 0.4 M H_2O_2 in the dark. The current of the devices at 0.5 V bias (*I*@0.5 V) is summarized in the inset table.

with the I-V curve of 0.15 M and 0.04 M H₂O₂. The chemical excitation intensity, which is reflected by the slope of the I-V curve and the current at 0.5 V bias, increased with the increase in H₂O₂ concentration, indicating the increase in hole injection rate from H₂O₂ into the valence band with the increase in H₂O₂ concentration.

Finally, based on the experimental results and the above theoretical analysis, we schematically compare the response mechanism of the photoconductors (using an n-type photoconductor as an example) to light and MACE in Figure 6a,b. Figure 6a shows a typical sketch used to illustrate how the extra electron—hole pairs are generated within the photoconductor when it is illuminated by light and electrons are collected from



Figure 6. Schematic comparison of the response mechanism of n-type photoconductors to optical illumination (a) and the MACE process (b).

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the conduction band through the n-type contacts. Similarly, Figure 6b illustrates how the difference in the charge transport is that the redox reactions which take place on the Si/ electrolyte interface induce electron-hole pairs when the device is in contact with the etching solution.

CONCLUSIONS

In summary, we have used both n- and p-type Si photoconductors coated with AgNPs to in situ probe the dynamics of the surface chemical reactions taking place during metalassisted chemical etching of silicon. The I-V and I-t results show that both types of photoconductors exhibit a strong response to the MACE process. A quantitative thermodynamic analysis was shown to be consistent with the observed dynamics of MACE. These results unambiguously confirm that both electron and hole injections into the conduction and valence bands by the Si/etching solution interface are involved during MACE and result in a chemical excitation of Si that can be monitored by the photoconductor. Our work, therefore, demonstrates that photoconductors as semiconductor devices can be chemically excited providing significant general insight into semiconductor electrochemistry. While photoconductors have been widely used for light detection, the chemical excitation of photoconductors reported here implies that they can also be used to probe the dynamics of the chemical reactions in situ and thus also for chemical sensing.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpcc.2c08627.

Experimental details of the fabrication of photoconductors; process flow containing the most important processing steps for the fabricated n- and p-type photoconductors; current-voltage curves of n-PC-AgNPs and p-PC-AgNPs measured in the 0.4 M H_2O_2 solution; and calculation of the Fermi level of n-and ptype Si used in this work (PDF)

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Notes

The authors declare no competing financial interest.

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