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Light Enhanced Electron Transduction and Amplified Sensing at a Nanostructure Modified Semiconductor Interface

*William I. Laminack and James L. Gole**

Visible and UV light are demonstrated to significantly enhance the sensing properties of an n-type porous silicon (PS) extrinsic semiconductor interface to which TiO_2 and titanium oxynitride ($TiO_{2-x}N_x$) photocatalytic nanostructures are fractionally deposited. The acid/base chemistry of NH_3, a moderately strong base, and NO_2, a moderately strong acid, couples to the majority charge carriers of the doped semiconductor as the strong acid (TiO_2) enhances the extraction of electrons from NH_3, and the more basic $TiO_{2-x}N_x$ decreases the efficiency of electron extraction relative to the untreated interface. In contrast, NO_2 and a TiO_2 or $TiO_{2-x}N_x$ nanostructure-decorated PS interface compete for the available electrons leading to a distinct time dependent electron transduction dynamics as a function of TiO_2 and $TiO_{2-x}N_x$ concentration. Only small concentrations of TiO_2 and its oxynitride and no self-assembly are required to enhance the response of the decorated interface. With light intensities of less than a few lumens/cm^2-sterad-nm, responses are enhanced by up to 150% through interaction with visible (and UV) radiation. These light intensities should be compared to the sun's radiation level, ≈500 lumens/cm^2-sterad-nm suggesting the possibility of solar pumped sensors. The observed behavior in these systems is largely explained by the recently developed Inverse Hard/Soft Acid/Base (IHSAB) concept.

1. Introduction

Where electrical power is at a premium, the ability to create a sensor response at room temperature using only white light (or minimal UV light) excitation can provide a valuable asset. Since white light represents the major component of the solar spectrum, a light absorption process that subsequently leads to directed electron transduction corresponds to "solar pumped" sensing. Sensors which operate in the absence of or with minimal battery power and can be based on solar energy offer a significant development in our ability to detect analytes and, if properly configured, sequester and destroy analytes.

W. Laminack, Prof. J. L. Gole
School of Physics
Georgia Institute of Technology
Atlanta, GA 30332-0430, USA
E-mail: James.Gole@physics.gatech.edu
Prof. J. L. Gole
School of Mechanical Engineering
Georgia Institute of Technology
Atlanta, GA 30332-0405, USA

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The cost and accessibility of UV photons has made it desirable to develop highly stable and inexpensive pollutant mediating photocatalysts which have significant activity under visible light excitation utilizing the solar spectrum or interior room lighting.[1] These photocatalysts can also offer the potential for the significant improvement of sensor devices.[2] Here, we have used the strong acid, TiO_2, and its visible light absorbing and more basic counterpart, $TiO_{2-x}N_x$, as the agents to mediate electron transduction at a treated extrinsic semiconductor interface. This study demonstrates that solar and/or interior room lighting absorbed by a photocatalyst at room temperature can enhance electron transfer that can be used to improve a sensing process by modifying the conductivity due to the concentration of available electrons in an n-type extrinsic semiconductor interface.

To demonstrate white light enhanced sensing we combine a metal oxide nanophotocatalyst with a porous n-type extrinsic silicon semiconductor interface. We form a light accessable nanostructure decorated nanopore coated microporous array[2,3] (**Figure 1**) to which the active nanostructures are deposited. We describe results obtained as nanostructured acidic TiO_2 and its visible light absorbing counterpart, $TiO_{2-x}N_x$, to which we introduce considerable basic character, are deposited, in fractional deposition, to an n-type porous silicon (PS) interface and optically pumped. The observations made for the doped systems are compared to and gauged by the electron transduction observed in the absence of light as well as that observed for the untreated PS interface. The nanostructure deposition[2,3] must be maintained at a sufficiently low level so as to avoid cross-talk between the nanostructures, which can lead to a noisy device and the loss of functionality.

Figure 1d represents a schematic diagram of the donor level population and the level structure as a function of temperature for an n-type extrinsic semiconductor. At 300 K, the donor level population has been depleted sufficiently so that there are a significant number of levels available for population when a basic analyte interacts with the decorated semiconductor interface, contributes electrons to the donor levels, enhances the majority charge carrier concentration, and increases conductance. This process can eventually "top out" the level population.[4] Similarly,

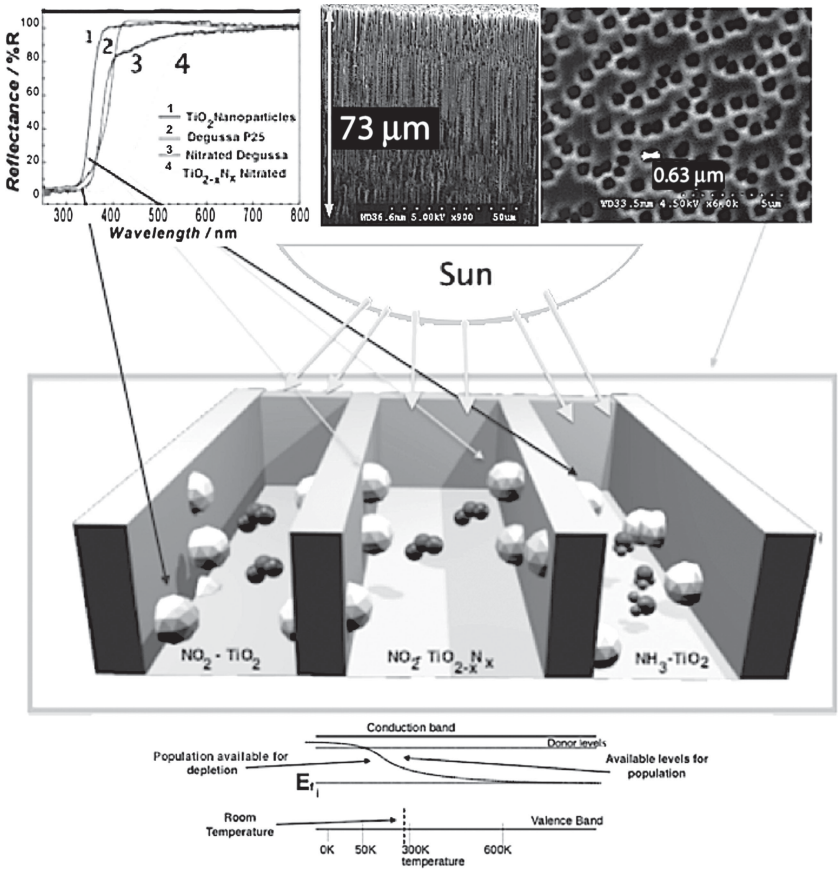

Figure 1. a) UV-visible reflectance spectra of 1) TiO_2 nanocolloid particles, 2) Degussa P25 TiO_2 powder, 3) Degussa P25 TiO_2 powder nitridated with triethyl-amine, and 4) nitridated $TiO_{2-x}N_x$ nanocolloid particles. b) Pore structure of etched n-type PS. c) Schematic representation of portion of porous silicon (PS) nanopore coated microstructure (large grey structure) treated with active TiO_2 and $TiO_{2-x}N_x$ nanostructures (grey/white spheres) acting to enhance solar pumped reversible sensing. d) Schematic of n-type extrinsic semi-conductor level structure and populations.

an acidic analyte, as it withdraws electrons, decreases conductance, depletes, and can eventually "bottom out" the donor level population. If we deposit nanostructures of TiO_2 and $TiO_{2-x}N_x$ to the PS interface, these processes can be influenced, directed, and enhanced both by the nanostructure deposition and through optical excitation of the nanostructures. The energy level and density of states structure for TiO_2 and its oxynitride have been discussed previously[1,4] as have the onsets for optical pumping.[5–7] The energy levels shift notably on conversion to $TiO_{2-x}N_x$, however, the change in electronic level structure as a function of temperature range in these experiments varies by a very small energy increment[1] as kT is only of the order 208 cm^{-1} (0.025 eV) at 298 K and $k\Delta T$ is a small fraction of this amount.

2. Results

Figure 2a,b show scanning electron microscopy (SEM) images which compare the pore structure for the undecorated porous silicon surface and that for the TiO_2 decorated pores. The corresponding X-ray photoelectron spectroscopy (XPS) spectra associated with the TiO_2 decorated pores are depicted in Figures 2c,d.

The responses in **Figures 3**,4 demonstrate results obtained when NH_3 interacts with both an untreated and a nano-photocatalyst (TiO_2, $TiO_{2-x}N_x$) deposited n-type PS interface, 2 × 5 mm in total dimension (see Figure 1). NH_3, as a Brönsted base, donates electrons to the n-type PS interface, increasing the donor electron (Figure 1d) majority charge carrier concentration and the conductance as measured by a decreasing resistance. Figure 3 demonstrates the expected decreasing resistance and, as well, indicates that both white light and UV light have no effect on the response of an "untreated" PS interface to NH_3. This PS response can be viewed as a backdrop for comparison to the data in Figure 4.

The response to 1–5 and 10 ppm of NH_3 for an interface treated with a deposition of "acidic" TiO_2 nanostructures, and[3–6] this same interface where the deposited nanostructures are converted in situ from TiO_2 to the more basic $TiO_{2-x}N_x$ is compared to that for an untreated PS interface in Figure 4a. TiO_2, a strong (hard) acid, enhances the capture of electrons, and increases conductance (decreases resistance) relative to the undecorated interface. $TiO_{2-x}N_x$, once formed, through in situ treatment of the TiO_2 deposited surface, has gained considerable basic character[8] and does not capture electrons as efficiently as does the untreated PS interface. Therefore, the interface conductance decreases. The observed trends are explained within the framework of the Inverse Hard/Soft Acid/Base concept[3,4] which we will briefly outline.

Figure 4b indicates the response of a TiO_2 nanostructure treated PS interface before and during exposure to both "white light" and UV radiation. Visible radiation has a negligible effect on both the TiO_2 treated and the untreated PS interface. When illuminated by UV light, the signal from the TiO_2 decorated sensor interface is improved by well over 100%. The UV light source emits radiation whose energy (3.4 eV, 365 nm, mercury) exceeds the 3.2 eV bandgap of anatase TiO_2. This process facilitates the transfer of electrons to the decorated PS interface leading to an increase in conductance as TiO_2 becomes more acidic on optical excitation and thus attracts electrons more effectively. The exposure of this interface to a 25 W "white light" source provides no increase in conductance over that of the TiO_2 treated interface. The slight increase in resistance for white light excitation indicates the effect of a slight interface heating (carefully avoided in all additional experiments). The signal observed in the absence of surface heating is identical to that of the untreated PS interface. Optical pumping of the TiO_2 decorated interface and the enhancement of interface sensitivity occurs at energies exceeding the TiO_2 bandgap.

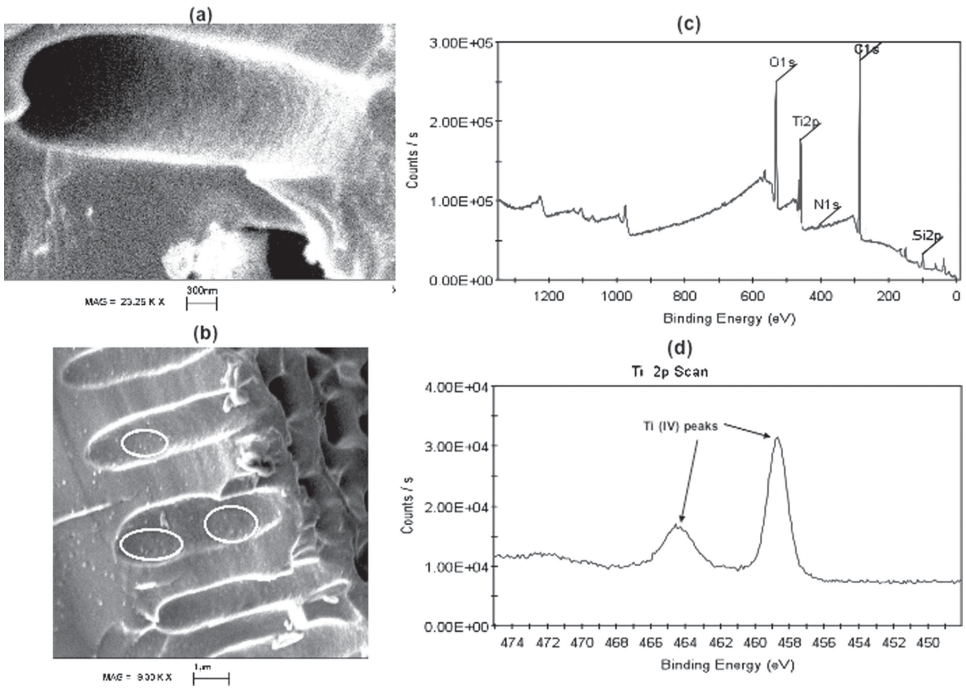

Figure 2. a) SEM image of undecorated porous silicon pore structure. The pore is approximately one micrometer in diameter and four micrometers in length. b) SEM image of porous silicon structure deposited with TiO_2. Some of the TiO_2 nanostructures (10–20 nm) are encircled in white. c) XPS spectrum for the decorated porous structure showing the overall XPS spectrum including background peaks and d) close-up of Ti 2p XPS region.

Figure 4c depicts the response of a $TiO_{2-x}N_x$ treated interface to UV and white light. Here, the response of the sensor, as manifest by an increase in conductance, is seen to increase by 100% or more, as a result of UV and "white light" excitation, as the electron withdrawing power of the $TiO_{2-x}N_x$, which becomes more acidic on excitation, increases. However, this increase occurs for a strong base, NH_3, whose contribution of electrons to the n-type semiconductor may be sufficient to "top out" the donor level population.[3,4,9] It is apparent that we have observed the optical pumping of the $TiO_{2-x}N_x$ decorated PS interface at energies well into the visible spectral region. The ability to electronically excite $TiO_{2-x}N_x$ with visible radiation is consistent with its "effective bandgap", which is of order 2 eV.[1,5–7]

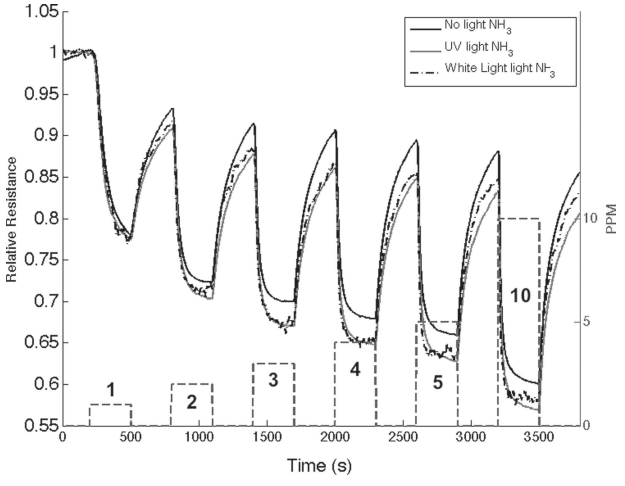

Figure 3. Comparison of responses for a PS interface exposed to white light (black dash), to UV light (grey), and in the absence of light (black). The magnitude of the response changes upon UV and white light exposure are identical to those in the absence of light. The gray dashed sawtooth boxes indicate the analyte concentration and the range over which this concentration is exposed to the sensor interface. The numbers in the figure denote the ppm concentration of these exposures.

The temperature dependence for an n-type semiconductor (Figure 1d), with donor levels just below the conduction band, provides a basis for electron transfer to and from the extrinsic semiconductor. At 0 K, the Fermi level lies at an energy E_d (≈0.025 eV)/2 below the conduction band. E_d corresponds to the donor level ionization energy. At moderate temperatures, a major portion of the donor level population has been depleted into the conduction band and the semiconductor reverts to that of an intrinsic material at temperatures above 600 K.[10] The Fermi level has shifted to the energy $E_{Fi} \approx E_g/2$, where E_g is the intrinsic semiconductor bandgap energy. If an analyte donates electrons to the decorated n-type PS interface and these electrons are not impeded by chemical bond formation, the majority charge carriers will increase within the donor levels and, consequently, the conductance will increase. The addition of electrons to an n-type system can contribute to the eventual saturation of the donor level population. The data in Figure 4a,b demonstrate a saturating effect as the change in resistance decrease[4] as a function of increasing concentration begins to decrease between 3 and 4 ppm.

The responses in **Figures 5**,**6** demonstrate results obtained when the moderate Lewis acid, NO_2, interacts with and attempts

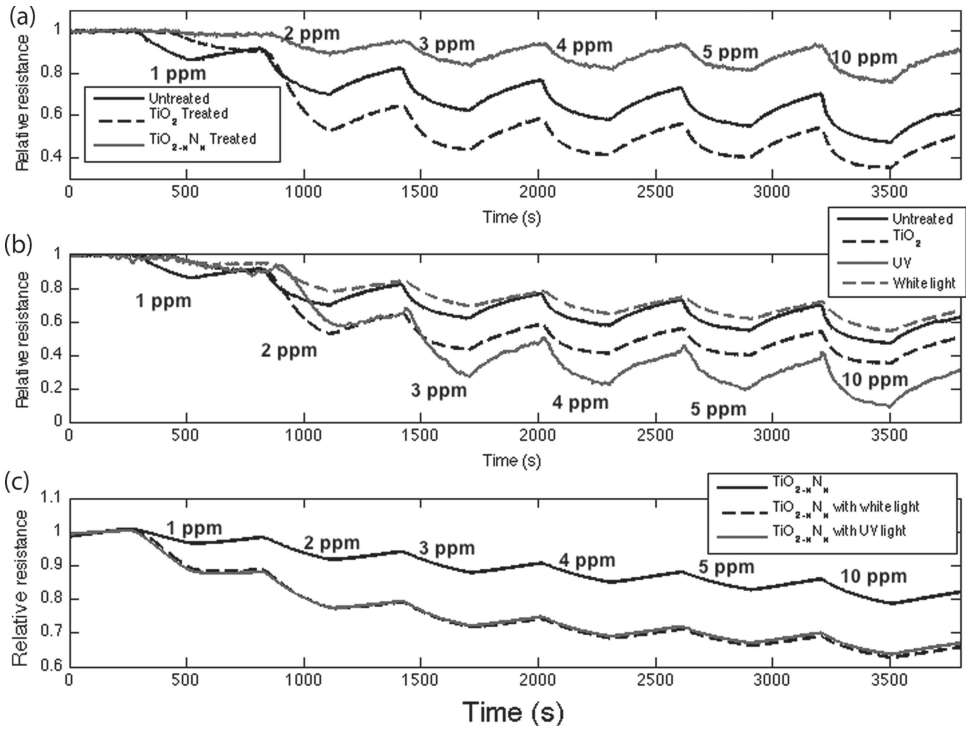

Figure 4. a) Response corresponding to decreasing resistance as NH_3 contributes electrons to TiO_2 (black dashed) and $TiO_{2-x}N_x$ (grey) treated PS interfaces and to an untreated (black) PS interface. The $TiO_{2-x}N_x$ treated interface is notably more basic (less acidic) than the untreated PS interface. The TiO_2 treated PS corresponds to a more acidic interface. b) Response to NH_3 of a TiO_2 treated PS interface without light exposure (black dashed) and exposed to "white light" (grey dashed) and UV radiation (grey). The untreated PS response is inserted for comparison. c) Response of a $TiO_{2-x}N_x$ treated PS interface with no light exposure (black) and exposed to UV (grey) and white light (black dashed). Light exposure produces a moderately higher response at higher analyte concentrations.

to extract electrons from a TiO_2 and $TiO_{2-x}N_x$ nanostructure decorated n-type interface. Here, the balance between the electron withdrawing power of NO_2 and that of the metal oxide and oxynitride decorated semiconductor interface must be considered. If the electron withdrawing power of NO_2 dominates, this analyte depletes electrons from the majority charge carrier concentration, decreases conductance, and increases sensor resistance.[4] However, at a sufficient concentration, the strong acid TiO_2 can reverse this process. The mode of interaction and the ultimate sensitivity (ppb) of the interface depends on the relative acid strength of the analyte and that of the fractionally deposited nanostructures.[3,4]

Figures 5 demonstrates the effect of TiO_2 fractional nanostructured depositions on the response of the PS interface to NO_2. The untreated PS interface (Figure 5a) displays a significant increase in resistance as NO_2 attracts electrons and depletes majority carriers. Figures 5b corresponds to the response at low TiO_2 deposition times (≤10 s), conditions that do not produce sufficient concentrations of nanostructured TiO_2 to facilitate its ability to compete with NO_2, attracting electrons to the PS interface. The response to NO_2, as it extracts electrons, corresponds to a resistance increase (conductance decrease). Figures 5c demonstrates the effect that an intermediate TiO_2 fractional nanostructured deposition (20 s) has on the response of an n-type PS interface to NO_2.The fractionally deposited strong acid, TiO_2 now competes effectively with the moderately strong acid, NO_2, for the available electrons. At NO_2 analyte concentrations in excess of 2 ppm, as the response begins to rapidly increase with the introduction of NO_2 (resistance increase), it is suddenly and rapidly quenched. This behavior, associated with the dynamics of electron transduction, is more pronounced at higher analyte concentrations.

As NO_2 is introduced to the decorated PS interface and attempts to extract electrons, the resistance rises rapidly to a point where the electron depletion reaches a limiting value. Here, the nanostructured TiO_2 islands, coupled to the PS interface, compete with and counteract the extraction of electrons by NO_2, preventing further electron withdrawal, and reversing the flow of electrons so as to increase the donor and conduction level electron concentrations. This is manifest by a sharp decrease in the resistance. The effect increases in direct proportion to concentration.[9] The dynamic nature of this interplay is further evident as the resistance drops to a minimum value and then begins to again increase as NO_2 is removed. As NO_2 is introduced in a new cycle the spike-like increase in resistance is again observed followed once more by a sharp drop in resistance. The process of interaction is a dynamic one, as TiO_2 and NO_2 compete for the available electrons.

At higher fractional depositions (Figure 5d, 30 s deposition time) the TiO_2 coupled to the PS interface overcomes the electron withdrawing power of NO_2 and the response is that of a system which attracts electrons to the decorated

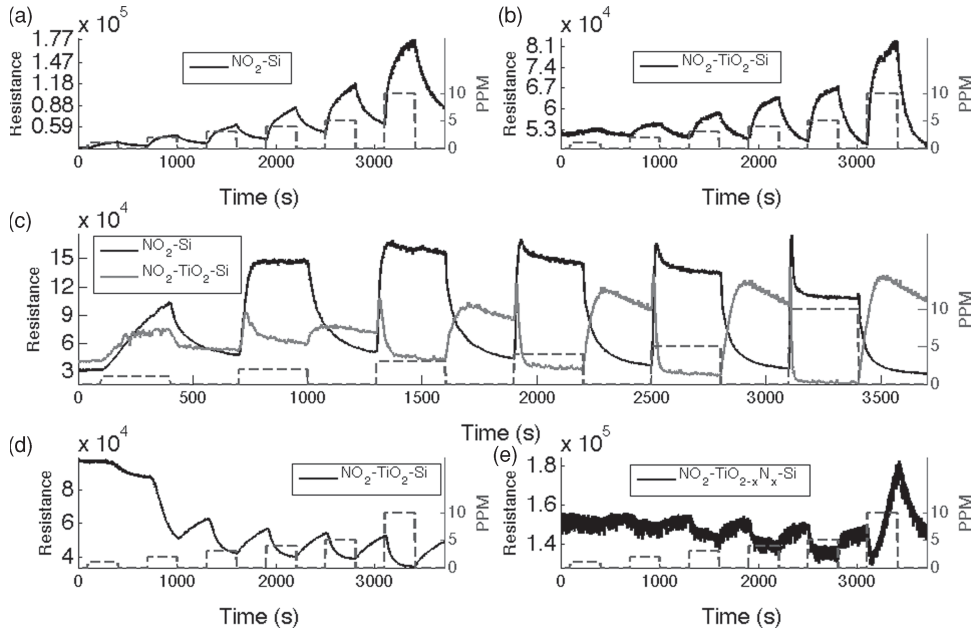

Figure 5. Comparison of responses to 1,2,3,4,5, and 10 ppm NO_2 for a) a PS interface consisting of an untreated n-type surface with b) a TiO_2 nanostructure deposited PS interfaces for low TiO_2 deposition, with c) the overlap of the response observed for the untreated PS interface (black) to an interface modified with an intermediate concentration of TiO_2 (grey), with d) a TiO_2 nanostructure deposited PS interface for TiO_2 depositions notably higher than those associated with (b) and (c). Whereas the response curve for the untreated n-type interface corresponds to an increase in resistance with NO_2 concentration, the TiO_2 decorated surface displays a decrease in resistance (increase in conductance) as TiO_2 now facilitates electron extraction from NO_2. The signal begins to saturate between 3 and 4 ppm. e) A $TiO_{2-x}N_x$ treated PS interface obtained by treating the TiO_2 surface (d) which has now been made more basic. The grey dashed saw-tooth boxes indicate the analyte concentration and the range over which this concentration is exposed to the sensor interface.

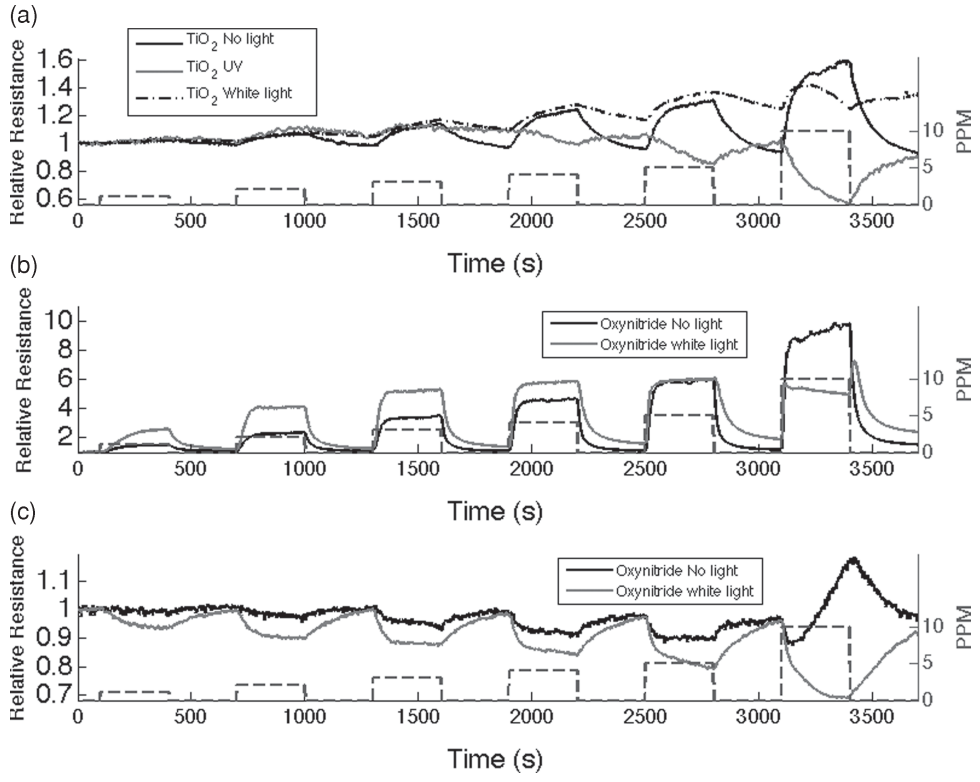

Figure 6. a) Response corresponding to increasing resistance as NO_2 extracts electrons from a TiO_2 treated PS interface compared to the same interface exposed to UV and white light. The response corresponds to a decrease in resistance for the UV pumped interface. b,c) Responses to NO_2 of two $TiO_{2-x}N_x$ treated PS interfaces without light exposure and exposed to white light. b) Lower fractional deposition such that NO_2 dominates TiO_2. c) Significantly higher fractional deposition. The grey dashed saw-tooth boxes indicate the analyte concentration and the range over which this concentration is exposed to the sensor interface. The white light exposure greatly enhances response. See text for discussion.

PS interface, leading to a decrease in resistance (increase in conductance).

To obtain the data in Figure 5e, we have converted the TiO_2 nanostructure deposit of Figure 5d in situ to the corresponding oxynitride, $TiO_{2-x}N_x$, diminishing the ability of the deposited nanostructures to attract electrons. At NO_2 concentrations ≤5 ppm, the system again responds to the analyte by removing electrons from NO_2. This corresponds to a decrease in resistance, although the decrease is notably less than that for the TiO_2 decorated system (Figure 5d). However, an NO_2 concentration of 10 ppm is now sufficient to reverse this response, leading to a positive resistance change which results from a dominant electron extraction by NO_2. It is against the dynamic changes outlined in Figure 5 that we consider the response upon exposure to visible and ultraviolet light.

The data in Figure 6a compares the response of a TiO_2 treated n-type PS interface to the responses for this same interface, subsequently exposed to UV and "white light" excitation for NO_2 concentrations of 1–5 and 10 ppm. This experiment was carried out at a sufficiently low TiO_2 concentration, so that NO_2 dominates TiO_2 depleting the majority charge carriers from the extrinsic semiconductor interface[3,4] (Figure 5b). The depletion saturates at a concentration of 10 ppm as the resistance increase does not double that at 5 ppm. However, as indicated previously (Figure 5c), nanostructured "acidic" TiO_2 islands, as hard acids, act to prevent electron withdrawal, increasing the donor and conduction level electron concentrations. Therefore, at sufficiently high TiO_2 depositions, the conductance will increase (decreasing resistance). Figure 6a demonstrates that at the lower TiO_2 depositions, the introduction of "white light" somewhat diminishes the ability of TiO_2 to compete with NO_2 as indicated by a slight increase in resistance. By contrast, the exposure to UV light creates an interface which competes so effectively for the available electrons that the resistance response decreases and subsequently reverses. This corresponds to a conductance increase (resistance decrease) with analyte concentration as the treated interface extracts electrons from NO_2. The effect, apparent with increasing NO_2 concentration, is quite pronounced at 10 ppm, where one observes a significant signal reversal relative to the TiO_2 treated interface that is not exposed to UV radiation. Optical pumping has created a strongly acidic electronically excited TiO_2^* modified interface which is much more efficient at attracting and transferring electrons to the PS interface.

Figure 6b depicts the response of a $TiO_{2-x}N_x$ treated PS interface. The conversion to $TiO_{2-x}N_x$ creates a more basic site that does not compete nearly as effectively with the acidic NO_2 for electrons. In addition, the more basic $TiO_{2-x}N_x$ fractional deposition contributes electrons more effectively than can TiO_2.[4,8,11] When the decorated sensor is exposed to a low level of "white light", its enhanced basicity, which also translates to visible light absorption, results in an enhanced electron transfer from $TiO_{2-x}N_x$ to NO_2. The interface resistance response is seen to increase to levels which are well over 100% for the lowest concentrations (1–3 ppm) used in this study. While the response increases linearly with exposure for the lowest concentrations it begins to saturate at concentrations in excess of 3 ppm. At 5 ppm the signal observed with and without white light excitation is virtually identical as the oxynitride surface, at this NO_2 analyte concentration, begins to counter electron extraction by NO_2. The increased NO_2 concentration now induces a more rapid response from the oxynitride decorated interface and a back extraction as the $TiO_{2-x}N_x$ interface no longer allows the extraction of additional electrons even in the presence of "white light" excitation. At a 10 ppm NO_2 exposure, the response of the $TiO_{2-x}N_x$ interface at first increases with NO_2 electron extraction. However, it then begins to decrease with time in comparison to the lower NO_2 concentrations, as the enhanced ability of NO_2 to extract electrons from the decorated oxynitride surface is countered more rapidly by the far more acidic "white light"-excited decorated surface. The more expanded view in **Figure 7** demonstrates that the observed dynamic behavior is analogous to the back transfer process depicted in Figure 5c. Here, as the NO_2 is introduced to the sensor interface and the electron extraction process increases rapidly, the response again rises to a resistance response comparable to the peak of the 5 ppm response. The resistance is then seen to decrease as a function of time, indicating the back transfer of electrons to the interface and an increase in conductance as the considerably more acidic $TiO_{2-x}N_x^*$ interface is now more efficiently extracting electrons. As the NO_2 concentration is rapidly removed, there is a corresponding spiked increase in resistance. This is a dynamic electron transduction process analogous to those observed in Figure 5c, but now resulting from the interaction of a strongly acidic $TiO_{2-x}N_x^*$ excited state on the PS interface.

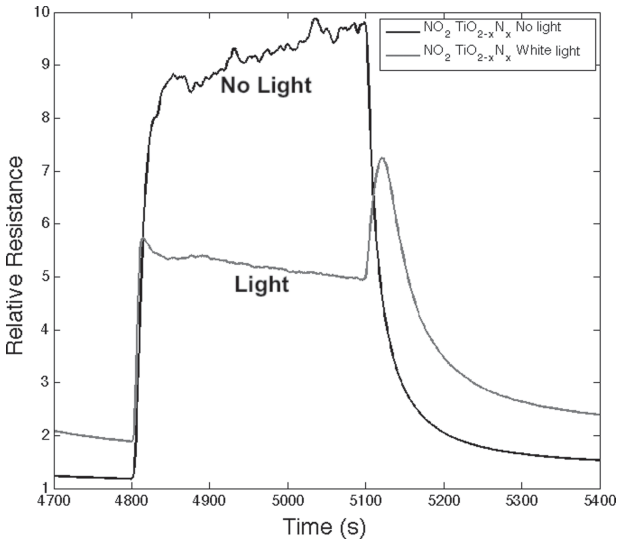

Figure 7. Close up view of response of $TiO_{2-x}N_x$ decorated PS interface at an NO_2 concentration of 10 ppm. The response at first begins to rise during the initial exposure to NO_2 and subsequently decreases rising again sharply as the NO_2 flow ceases.

Figure 6c depicts the response of an oxynitride treated interface where the $TiO_{2-x}N_x$ is optimized at a considerably higher fractional deposition level analogous to that in Figure 5d,e. At concentration levels of 1–5 ppm NO_2, this leads to a dominance of the oxynitride. Electrons, extracted from NO_2, contribute to the majority charge carrier concentration and a decrease in resistance. However, in an opposite sense to the dynamic

behavior observed in Figure 6b, an NO_2 concentration of 10 ppm is sufficient to overcome $TiO_{2-x}N_x$ decorated interface and the response now corresponds to a resistance increase as NO_2 now dominates and majority charge carriers are removed. The introduction of "white light" clearly enhances the electron capturing power of the oxynitride, as all of the responses now show a significant decrease in resistance (over 100%) versus the unexposed oxynitride treated surface. Even more striking is the complete reversal of the response for the 10 ppm NO_2 exposure. The responses in Figure 6b,c clearly demonstrate that "white light" excitation greatly amplifies the sensitivity of the decorated interface. The data demonstrates the manifestation of the optical pumping of the $TiO_{2-x}N_x$ decorated PS interface at energies well into the visible as might be expected from the light response curves indicated in Figure 1. However, the more concentrated oxynitride, while more basic than TiO_2, still possesses a sufficient acidic character to overcome the electron withdrawing power of NO_2.

We find that, "white light" excitation enhances the response both when NO_2 dominates the oxynitride decorated interface and when the decorated interface dominates NO_2. In one case, Figure 6b, the increased signal is manifest by a resistance increase whereas, in the second example, Figure 6c, by a conductance increase. The effect of optical pumping is to amplify the signal obtained at both regimes of nanostructure modification.

The results presented in Figures 6a,b must be considered with respect to the response of NO_2 to light as it interacts with the PS interface. **Figure 8** demonstrates that the response to NO_2, which corresponds to an increased resistance, decreases for both white light and UV excitation as NO_2 is extracting electrons at a decreased rate. This decrease is counter to the increase in resistance observed in Figure 6b suggesting that the observed increase in resistance in the presence of $TiO_{2-x}N_x$ represents a lower bound. The data in Figure 8 would suggest a decrease in electron extraction by NO_2 with optical pumping. However, NO_2 in the presence of PS alone still extracts electrons, counter to the data in Figure 6a that demonstrates the interface extracts electrons under UV excitation. The optically pumped conversion of TiO_2 and $TiO_{2-x}N_x$ to their acidic excited states produces a dominating interface upon UV and visible excitation.

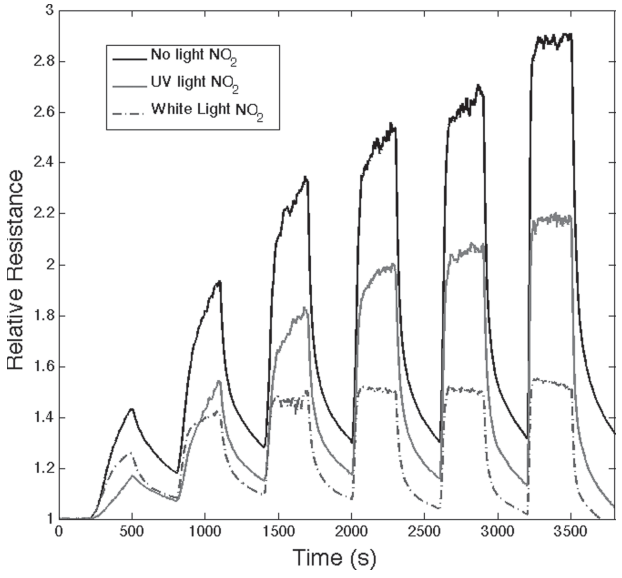

Figure 8. Response of untreated porous silicon sensor to NO_2 (black line), to NO_2 in the presence of ultraviolet light excitation (grey line), and to NO_2 in the presence of white light excitation (dot-dashed line).

3. Discussion

The IHSAB concept[3,4] allows the minimization of chemical bonding to maximize electron transfer at an extrinsic semiconductor interface. The coupling of analyte/interface acid-base chemistry, provides a balance between surface electron transduction and chemisorption, and outlines a framework for active metal oxide or metal oxynitride nanostructures to utilize these differences. The semiconductor interface is modified by introducing additional metal oxide "island" sites in fractional deposition, these nanostructures form a superstructure on the semiconductor. The nanostructures focus electron transduction to couple with the majority charge carrier concentration of an extrinsic p- or n-type[3,4] semiconductor and the transfer of electrons to (basic) or from (acidic) analytes. If an analyte donates electrons to an n-type semiconductor, the majority charge carriers, electrons, and the population of the donor levels increase. The dynamics of this process is strongly influenced by the fractional nanostructure coverage of the semiconductor interface. While the increase or decrease in conductance associated with the response to a given analyte is determined predominantly by the p or n-type character of the extrinsic semiconductor interface, the dynamics of conduction[3,4,9] can be modified as a result of the acid/base strength of the fractionally deposited nanostructures. This can be exploited to enhance sensor sensitivity and selectivity. The prepared interfaces are superior to traditional metal oxide systems as they not only operate at room temperature but also can function over a broad range of environments and stable, readily accessible, elevated temperatures.[12] The nanostructure deposition[2–4] requires no self-assembly but must be maintained at a sufficiently low level in order to avoid cross-talk between the nanostructures that can lead to a noisy device and the eventual loss of functionality.

The results obtained in this study indicate that the electron transduction-dominated interaction of an analyte is strongly influenced by light absorption. The semiconductor interface can be modified through treatment with nanostructured metal oxides, many of which are photocatalysts of varying degrees and levels of acidity. These oxides can also be converted to more basic oxynitrides. This provides a range of materials which, when properly engaged, provide a variable enhancement of the response from a given extrinsic semiconductor interface to ensure sensitive and selective directed physisorption that can be enhanced through solar pumping.

The results shown above outline a means for the significant improvement of nanostructure treated environments where electrical or battery power is at a premium. Here, solar radiation can be used to significantly enhance the sensor response. The average spectral brightness of the sun is its luminance divided by the bandwidth of the sun's visible output, which is 300 nm

for the visible wavelength region (400–700 nm). The average spectral brightness of the sun is $L_{v\lambda} \approx 1.5 \times 10^5$ lumens/cm^2-steradian/300 nm = 500 lumens/cm^2-sterad-nm. The light impingent on the sensors leading to the observed responses, obtained from an incandescent light bulb, positioned 10 cm from the sensor interface in the current experiments, corresponds, at most, to a few lumen/cm^2-sterad-nm. This light level can easily be obtained with solar radiation. The insertion of a chopper, allowing one to lock onto the impinging radiation, will further improve the signal to noise. While these sensor suites are readily assembled, we again caution that a fractional deposition of the TiO_2 and $TiO_{2-x}N_x$ is required.[3,4,9] The deposition process should be carefully monitored to avoid over depositing and/or the creation of a surface coating.[3,4] Further, the optical pumping of the surfaces must also be done in a manner which does not lead to significant thermal excitation of the TiO_2 and $TiO_{2-x}N_x$ nanostructure treated surface. Both coating, as opposed to fractional deposition, and thermal excitation are found to greatly diminish sensitivity.

4. Conclusions

TiO_2 nanostructure island sites deposited to a sensor interface can greatly enhance the surface acidity, however, the deposition process must be limited to avoid crosstalk between the nanostructures. The sensitivity to NH_3 is greatly enhanced by the TiO_2 deposition and increases as UV light impingent on the sensor increases the acidic character of TiO_2. NO_2, as a moderate acid, extracts electrons from a PS interface and treatment with limited concentrations of TiO_2 enhances this process. UV light reverses this process, increasing the acidity of the optically pumped TiO_2 treated interface which extracts electrons from the moderately acidic NO_2. In situ nitridation of the deposited TiO_2 to form the oxynitride, $TiO_{2-x}N_x$, enhances the visible light response, basicity, and sensitivity of the decorated interface. At low fractional oxynitride depositions, NO_2 dominates $TiO_{2-x}N_x$, and white light excitation increases sensor response. With higher deposition, white light increases the sensor response in the form of an increased conductance as the $TiO_{2-x}N_x$ decorated interface extracts electrons. With average light intensities less than a few lumens/cm^2-sterad-nm, it is possible to enhance responses by up to 150% through interaction with visible (and UV) radiation. These light intensities should be compared to the sun's radiation level, ≈500 lumens/cm^2–sterad-nm, suggesting the possibility of solar pumped sensing.

5. Experimental Section

TiO_2 nanoparticle colloidal solutions (anatase phase) were prepared through the controlled hydrolysis of titanium(IV) tetraisopropoxide in water. Transmission electron microscopy (TEM) demonstrates that the nanoparticles ranged in size from approximately 3 to 11 nm. They were stable for extended periods under refrigeration.[5,6] Active $TiO_{2-x}N_x$ photocatalysts tuned to absorb across the visible spectral region (Figure 1) could be formed, in seconds, from the direct nitridation of the anatase TiO_2 nanocolloid solutions with alkyl ammonium compounds.[5] The absorption onset of the catalytically active[5,6] anatase $TiO_{2-x}N_x$ extended well into the visible region at ≈550 nm (Figure 1). By comparison, Degussa P25 TiO_2 was nitridated over a period of several days at a much lower efficiency.[6] While the TiO_2 nanocolloid reflectance spectrum was, as expected, blue-shifted relative to the larger (≈30 nm) Degussa P25 structures, it was striking that the nitridated $TiO_{2-x}N_x$ nanocolloids displayed a reflectance spectrum considerably red-shifted from that of a Degussa sample. This red-shift formed the basis for a "visible light" absorbing[5,6] photocatalyst that could be deposited to an appropriate semiconductor to form effective electron transducing sites for the passage of electrons from analyte to interface with minimal chemical bond formation.

To create the framework to develop highly efficient light trapping[13] nanostructure modified interfaces on n-type PS, a nanopore coated microporous interface must be generated[2] (Figure 1). The PS interface was generated by electrochemical anodization of 1–20 Ω cm, n-type (phosphorous doped) (100) silicon wafers (Wafer World). The anodization of the n-type wafers was carried out under topside illumination using a Blak-Ray mercury lamp. After the wafer was etched in a 1:1 solution of hydrogen fluoride (HF) and ethanol, the prepared n-type anodized sample was placed in methanol for a short period and then transferred to a dilute HF solution for a 30 min period. This process created a porous structure with pore diameters of order 0.5–0.7 μm and pore depths varying from 50 to 75 μm[14] (Figure 1). These "light harvesting" interfaces, in combination with TiO_2 and $TiO_{2-x}N_x$, provided the means for enhancing the visible and UV response of the interface.

Before anodization, an insulation layer of SiC (≈1000 Å) was coated onto the c-Si substrate by PEVCD methods and windows of 2 × 5 mm were opened in this layer by reactive ion etching (RIE). SiC makes it possible to form the hybrid micro/nanoporous PS structure in the specified windows during electrochemical anodization because of its resistance to HF, and aids the placement of gold contacts exclusively on the porous layer for resistance measurements, acting as an electrical insulator on the doped silicon. The formation of low resistance gold contacts has been discussed in detail previously.[2,3] The PS hybrid arrays of nanopore covered micropores were tested at room temperature for their individual sensor response. The selection of the nanostructures and the variable surface sensitivities that are produced as they form in situ metal oxide deposits, introduced a distinct systematics of design, which can be predictably formatted. The approach is unique in that the nanostructures are deposited fractionally to the PS micropores, and this fractional deposition does not require any time consuming self-assembly within the pores. This is not a coating technique or one that requires an exacting structural film arrangement but is, in fact, a much simpler process. The untreated PS hybrid structures were exposed to dilute (DI) solutions containing TiO_2 for 10 to 30 s and placed in DI H_2O and MeOH for consecutive 120 s periods. The metal oxide was treated in situ to form the oxynitride. The metal oxide depositions, when characterized before deposition, had partially transformed to amorphous structures displaying weak diffraction patterns. Therefore, it was difficult to envision their crystallization during the short deposition and subsequent surface cleaning process. After deposition the decorated surfaces were cleaned for 120 s in DI and 120 s in methanol.

In all cases, the analyte gas being sensed was brought to the hybrid surface after entrainment at room temperature in UHP (ultra high purity) nitrogen (Matheson 99.999+%). The system was purged with UHP nitrogen for a minimum of 30 min before use. The typical resistances for the base PS structures ranged between 300 and 5000 Ω at room temperature. The gas flow for the analyte and the entraining UHP nitrogen was controlled by MKS 1179A mass flow controllers. The mass flow controllers used to control the anaylte gas and the entraining nitrogen flow responded in less than two seconds. The diffusion time of the analyte gas to the sensors, which provides the longest system time constant, varied from four to five seconds for the lowest analyte concentrations to of order 1 to 2 s for concentrations greater than 2 ppm. These are the delay times for the observation of a signal due to the analyte in the supply line. The sensors responded to the analyte gas on a time scale much less than two seconds. The change in resistance was measured in one-second intervals using a DC current. This voltage

bias used in these experiments was 3 V to obtain an optimum signal to noise ratio. A NI DAQPad-6015 was used for gathering data and supplying the DC current. Labview software was used to control the experiment and record the results. MATLAB was used in the analysis of the data.

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