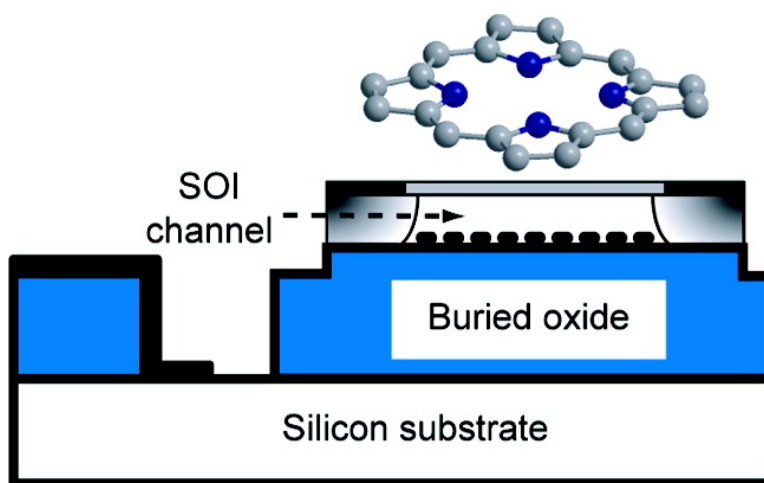Article

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Electrical Detection of Amine Ligation to a Metalloporphyrin via a Hybrid SOI-MOSFET

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Abstract: A close-packed monolayer of zinc 5,10,15,20-tetrakis(3-carboxyphenyl)porphyrin has been prepared and deposited on the thin native oxide covering the surface of an SOI-MOSFET (silicon-on-insulator metal-oxide-semiconductor field effect transistor) using Langmuir−Blodgett techniques. When the device is exposed to amine vapors in a nitrogen atmosphere, the amine coordinates to the zinc atom. The resulting change in electron distribution within the porphyrin leads to a large change in the drain current of the transistor, biased via a back gate. This change is sensitive to both the amount of amine present and the base strength of the amine. Only very small changes in drain current were observed with a monolayer of free base porphyrin or palmitic acid. After exposure to high pyridine concentrations, the device response saturates, but partially recovers after overnight exposure to flowing nitrogen gas. Interestingly, the device response is instantaneously reset by exposure to visible light, suggesting that photode-ligation occurs. An electrical model for the hybrid device that describes its response to ligand binding in terms of a change in the work function of the porphyrin monolayer has been developed. A transistor response to a few hundred attomoles of bound pyridine can be readily detected. This extreme sensitivity, coupled with the ability to reset the device using light, suggests that such systems might be useful as sensors.

Introduction

Many recent developments in nanotechnology, analytical chemistry, biomedical sensing and treatment, and similar areas involve interfacing "soft" organic or biological molecules to "hard" metal, semiconductor, and oxide materials. Understanding this interface—how molecules affect the properties of materials and vice versa—is vital to such developments, but in spite of much elegant work in the area, the study of the materials−molecule interface is still in its infancy. With the goal of contributing knowledge in this area, we report the preparation and study of properties of the interface between a single zinc porphyrin monolayer and a thin silicon dioxide layer residing on the surface of a silicon-on-insulator (SOI) wafer. As detailed below, changes in the electronic structure of the monolayer caused by the binding of amines from the vapor phase to the metal in the porphyrin lead to changes in the electron distribution within the silicon dioxide, and ultimately within the silicon layer below. The silicon layer is configured as a metal-oxide-semiconductor field-effect transistor (MOSFET). The drain current flowing in the MOSFET is affected by changes in the electron distribution due to the binding of amines to the metal porphyrin monolayer. In turn, the presence of the oxide below the porphyrin affects porphyrin binding to the amines, as detected by the response of the system to light.

In other studies relevant to those reported here, Di Natale and other researchers have demonstrated the use of metalloporphyrin array sensors for use as an electronic nose or tongue, based on optical or mass detection.[1] Andersson et al. examined the use of metalloporphyrins in conjunction with a semiconductor transducer.[2] By using a field-effect transistor with a thin gold gate contact coated with various metalloporphyrin species, it was possible to obtain variations in the electrical characteristics of the device on exposure to various vapors. The sensitivity of the device was very dependent on the thickness of the gold layer onto which the porphyrin layer was attached. In order to obtain reasonable sensitivity, the gold layer needed to be thick enough so as not to leave isolated metal contacts on the surface. However, thicker layers of gold also resulted in a loss of sensitivity as the change in the porphyrin during exposure to vapors was screened out by the thick gold layers. Li et al. prepared a sensor for NO_2 based on detecting the change in the conductivity of a copper porphyrin layer.[3] The copper porphyrin species was deposited using Langmuir−Blodgett techniques. When the gas was passed over the sensing layer, the current increased in the presence of 10 ppm NO_2. The group did not obtain a continuous porphyrin monolayer across their conducting membranes, which lead to multilayers being required to obtain

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[†] Center for Solid State Electronics Research.
[‡] Department of Chemistry and Biochemistry.

(1) Di Natale, C.; Paolesse, R.; D'Amico, A. *Sens. Actuators B* **2007**, *121*, 238−246.
(2) Andersson, M.; Holmberg, M.; Lundstrom, I.; Lloyd-Spetz, A.; Martensson, P.; Paolesse, R.; Falconi, C.; Proietti, E.; Di Natale, C.; D'Amico, A. *Sens. Actuators B* **2001**, *77*, 567−571.
(3) Li, J. P.; Tredgold, R. H.; Jones, R. *Thin Solid Films* **1990**, *186*, 167−176.
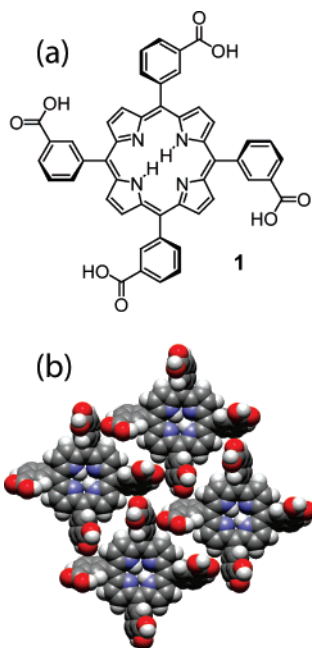
Figure 1. (a) Structure of porphyrin **1**. The zinc analog **1Zn**, in which the two central hydrogens are replaced by a zinc atom, was also employed. (b) CPK model of a packed array of four molecules of **1**. The area per molecule based on this structure is ~215 Å^2.

reliable and consistent changes in current when exposed to the incoming gas species. The thicker membranes reduce the sensitivity of the layers to the incoming gas due to the need for longer diffusion times through the multilayers.

The work reported below employs a back-gated SOI-MOSFET transistor having a thin native layer of oxide on the top, upon which a single monolayer of zinc tetraarylporphyrin is deposited using Langmuir−Blodgett (LB) techniques. In this arrangement, the organic film is only a single molecule thick, and the native oxide is very thin. Thus, the spatial relationship of the site of ligand binding to the underlying oxide is well defined, and the device has the possibility for very high sensitivity to changes in monolayer structure resulting from the binding of amines to the zinc atoms.

Results

In the paragraphs below, we will first describe the properties of the LB film, then the construction of the chemically modified MOSFET, and finally the electrical response of the hybrid system.

Film. The porphyrin employed in this work was 5,10,15,-20-tetrakis(3-carboxyphenyl)porphyrin[4] **1** (Figure 1) and its zinc analog **1Zn**. The aryl groups at the meso positions of the porphyrin reside at large angles relative to the plane of the porphyrin ring due to steric hindrance between them and the β-hydrogen atoms. The meta substitution pattern on the aryl rings was chosen so that the carboxyl groups could all be arranged more or less perpendicular to the plane of the porphyrin, thus facilitating interactions with a planar, hydrophilic surface such that the porphyrin and surface are approximately coplanar.

Monolayers of **1** and **1Zn** were prepared at the air−water interface by the Langmuir−Blodgett technique. The subphase

(4) Dattagupta, N.; Jones, E.; Thomas, L. K.; Malakar, D. *J. Ind. Chem. Soc.* **1981**, *58*, 1171−1172.
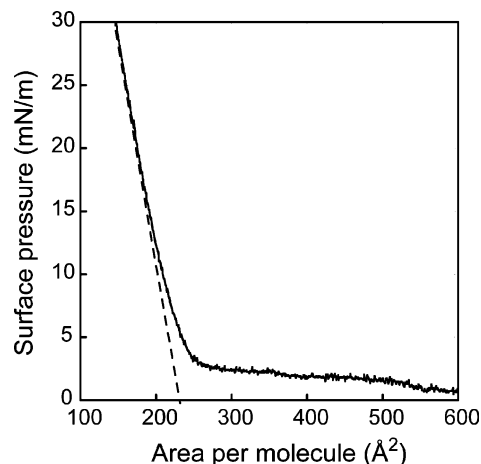

Figure 2. Isotherm for compression of a monolayer of zinc porphyrin **1Zn** on a water substrate at pH 4.5. The area per molecule estimated from the extrapolation shown is ~230 Å^2.

was highly purified water whose pH was adjusted to 4.5 with hydrochloric acid. At this pH, the porphyrin had little tendency to dissolve into the subphase (unlike at higher pH values where the carboxyl groups were deprotonated), yet the zinc atom was not removed from **1Zn**. The porphyrin was slowly applied to the top of the subphase as a 20 μM solution in a 2:1 mixture of dichloromethane and methanol. The organic solvent was allowed to evaporate/dissipate into the aqueous layer, and the barrier of the LB trough was slowly compressed. Typical results for **1Zn** are shown in Figure 2. From this isotherm, it is clear that the porphyrin forms a reasonably well behaved monolayer. The film is stable up to at least 30 mN/m. The area per molecule, from extrapolation of the isotherm as shown in the Figure, is ~230 Å^2. Figure 1b shows a possible packing arrangement for molecules of **1** on a planar surface. The area per molecule in this arrangement is ~215 Å^2. The agreement between this area and that found for the monolayer film suggests that in the film, the molecules of porphyrin lie flat on the surface, with all four carboxyl groups pointing toward the aqueous interface. It is interesting to note that compression of 5,10,15,20-tetrakis[4-(1-heptyloxy)phenyl]porphyrin at the air−water interface gives an unstable film that exhibits a practically continuous liquid-expanded phase, and does not form a single monolayer.[5]

The monolayer film was transferred to clean borosilicate glass microscope slides by immersing the slide vertically into the subphase, forming the monolayer and compressing it to 20 mN/m, holding the film at this surface pressure for 1 h to promote complete removal of any voids in the film, and finally withdrawing the slide at a rate of 2.3 mm/min. The area transfer ratio was 1:1 within experimental error, suggesting that a complete monolayer was deposited on each side of the slide, and that the molecular packing on the slide was similar to that in the film at the air−water interface. As an additional check, the deposited porphyrin was dissolved from the slide surface with a 2:1 mixture of dichloromethane and methanol, and the absorbance of the resulting solution was determined. Using a published extinction coefficient for zinc 5,10,15,20-tetraphe-nylporphyrin,[6] these data yielded a value of 7.0×10^{-11} moles

(5) Paolesse, R.; Valli, L.; Goletti, C.; Di Natale, C.; Froiio, A.; Macagnano, A.; Bussetti, G.; Chiaradia, P.; D'Amico, A. *Mater. Sci. Eng. C* **2002**, *22*, 219−225.

(6) Barnett, G. H.; Hudson, M. F.; Smith, K. M. *J. Chem. Soc. Perkin Trans. l* **1975**, 1401−1403.
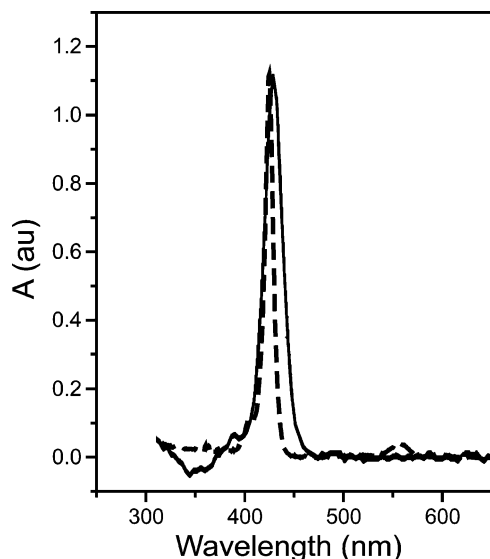
Figure 3. Absorption spectra of zinc porphyrin **1Zn** in solution in a 1:1 mixture of dichloromethane and methanol (- - -) and as an LB film on borosilicate glass (—). The absorbance values have been normalized at the Soret maximum for ease in comparison.

of porphyrin per cm². The area per molecule from the LB experiment, 230 Å², gives a coverage of 7.4×10^{-11} moles per cm². The close agreement between these experiments provides strong evidence that the surface of the slide is coated with a single monolayer of porphyrin, in which the porphyrin lies flat on the surface.

The absorption spectrum in the Soret band region of a typical slide coated with zinc porphyrin **1Zn**, taken in air, is shown in Figure 3, along with the spectrum of the same porphyrin in 1:1 dichloromethane:methanol solution. The spectrum from the film features the Soret band at 429 nm. The absorption maximum is very similar to that of the porphyrin in solution (where $\lambda_{max} = 425$ nm). The bandwidth is somewhat larger for the film. These results are consistent with a monolayer with the porphyrin molecules lying flat on the glass surface. A multilayer film or monolayer film with the porphyrin planes tilted with respect to the surface and stacked with one another would be expected to show larger spectral changes due to interaction of the chromophores. Similar results were obtained for monolayers of free base porphyrin **1** on borosilicate glass. The Soret maximum was observed at 422 nm. Porphyrins also have Q-band absorptions to the red of the spectral region shown in Figure 3, but the signal-to-noise ratio obtainable from a single monolayer was not high enough to yield clear spectra of this region.

Zinc porphyrins are known to bind a fifth ligand at the metal, and the binding constants for amines are reasonably large. For zinc 5,10,15,20-tetraphenylporphyrin in benzene, the binding constant for pyridine is 6030 M⁻¹ and that for piperidine is 112 000 M⁻¹.[7] Amine binding is known to result in shifts of the absorption band maxima of zinc porphyrins. The binding of pyridine to monolayers of **1** and **1Zn** on borosilicate glass was investigated using UV–vis spectroscopy. Monolayer-coated glass plates were housed in a sealed cuvette with a volume of ~3 mL. Figure 4a shows the normalized Soret band absorption of **1** in a dry nitrogen atmosphere, and after addition of 100 µL of dry nitrogen saturated with pyridine vapor to the cuvette.

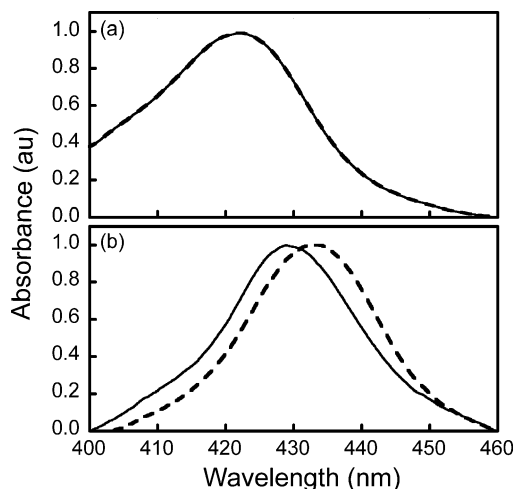(7) Kirksey, C. H.; Hambright, P.; Storm, C. B. *Inorg. Chem.* **1969**, *8*, 2141–2144.

Figure 4. Normalized absorption spectra (arbitrary units) of porphyrin monolayers deposited by the LB technique onto borosilicate glass slides. (a) Spectrum of a monolayer of free base porphyrin **1** in dry nitrogen (—) and in dry nitrogen saturated with pyridine vapor (- - -). The two spectra are virtually superimposable. (b) Spectrum of a monolayer of zinc porphyrin **1Zn** in dry nitrogen (—) and in dry nitrogen saturated with pyridine vapor (- - -). The 5-nm shift to longer wavelength indicates binding of pyridine to the zinc.

The maximum is found at 422 nm both before and after exposure to pyridine, indicating that pyridine does not bind to the free base porphyrin. Figure 4b shows the results of a similar experiment with a monolayer of zinc porphyrin **1Zn**. The Soret maximum is at 429 nm in the absence of pyridine, and 434 when exposed to the pyridine vapor. These experiments confirm that the zinc porphyrin in the deposited monolayer is still capable of pyridine binding.

MOSFET. The SOI-MOSFET transistor is shown schematically in Figure 5. It is fabricated from a p-type SOI wafer ($\rho = 2$–10 Ω·cm), with an initial SOI layer thickness of 200 nm and an underlying buried oxide (BOX) layer of 400 nm. The SOI channel thickness is thinned to 100 nm by wet oxidation at 1000 °C and source/drain contact regions are then formed via phosphorus doping. Reactive ion etching based on CF_4 chemistry is used to isolate the device and also to expose the underlying Si layer for contacting the substrate. Metal contacts consisting of 10 nm of chromium followed by 100 nm of gold were then deposited using standard lift-off techniques. The fully depleted SOI layer can be inverted by means of a back-gate voltage applied to the substrate, leaving the surface free from a gate contact. The native oxide coated active surface of the transistor is 50 µm × 600 µm. Details of the fabrication of this device have been reported.[8-10]

An advantage of this transistor architecture is the ability to form an electron inversion layer in the SOI-MOSFET by the means of a back-gate voltage applied to the substrate. This leaves the thin native oxide on top of the SOI channel available for interaction with the environment. In this work, the porphyrin monolayer was deposited directly on this native oxide surface of the active silicon by LB techniques. In this configuration, the threshold current of the device will be very sensitive to

(8) Yang, J.; de la Garza, L.; Thornton, T. J.; Kozicki, M.; Gust, D. *J. Vac. Sci. Technol. B: Microelectron. Nanometer Struct.* **2002**, *20*, 1706–1709.
(9) Laws, G. M.; Thornton, T. J.; Yang, J.; de la Garza, L.; Kozicki, M.; Gust, D. *Phys. Status Solidi B* **2002**, *233*, 83–89.
(10) Laws, G. M.; Thornton, T. J.; Yang, J.; de la Garza, L.; Kozicki, M.; Gust, D.; Gu, J.; Sorid, D. *Phys. E (Amsterdam, Neth.)* **2003**, *17*, 659–663.
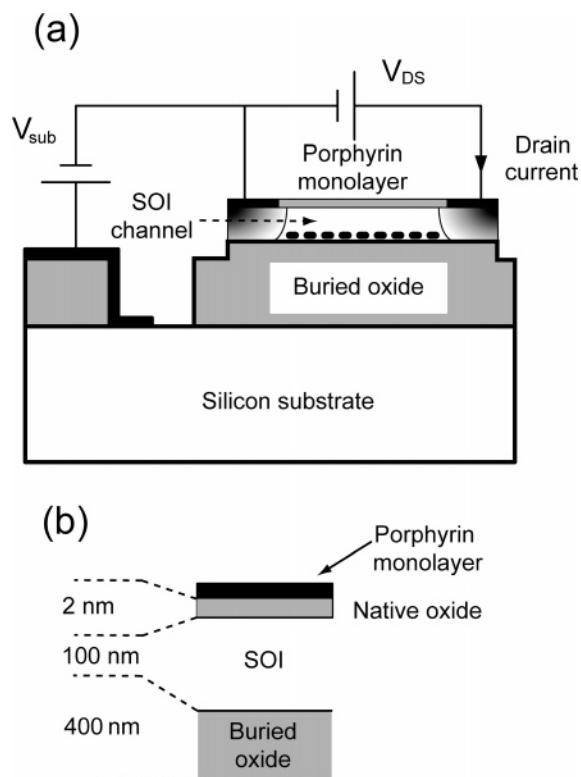
Figure 5. Schematic cross-section of the porphyrin-coated SOI-MOSFET; (a) overall transistor structure, (b) region of the SOI channel showing layer thicknesses.

changes in the surface charge. Thus, it was expected that ligand-binding between a suitable gas-phase molecule and a metalloporphyrin in a monolayer deposited on the SOI device could have a large effect upon the transistor properties.

Prior to deposition of the porphyrin monolayer onto the native oxide surface of the device, the initial oxide present after processing is removed in dilute hydrofluoric acid to enable oxide regrowth under clean room conditions. The HF treatment was followed by immersion of the device in hydrogen peroxide for 20 min. The preparation of a fresh oxide surface ensures that a porphyrin monolayer can be deposited onto a suitably hydrophilic surface free from process residuals. Water contact angle measurements on oxide surfaces prepared as described show contact angles of below 10°.

Monolayers formed by the LB technique were transferred to the native oxide surface of the transistor by a dipping technique identical to that described above for glass slides. Transfer ratios were again 1:1, within experimental error, although the error was larger in this case due to the smaller size of the devices. It is presumed that a monolayer was transferred to the entire device surface, but that only that portion of the monolayer deposited on the native oxide above the SOI channel has a significant effect upon device properties. Transfer ratios of 1:1 were also obtained for larger pieces of silicon wafer coated with native oxide. It was, of course, not possible to characterize the monolayers on the devices using UV−vis spectroscopy, but it is assumed that the structure of the monolayer deposited on the transistor is essentially identical to that deposited on glass.

Interaction with Pyridine Vapor. In order to investigate the response of the transistor to amine vapors, the device was wire bonded to a chip holder and placed in a sealable Teflon chamber of dimensions $2 \times 2.5 \times 10$ cm. The chamber featured

electrical feed throughs that allowed connection of the transistor to external circuits and valved ports for admission and exhaustion of gases. Typically, the chamber containing the transistor was flushed with dry nitrogen for several hours before use in order to remove water and other volatile materials from the surfaces. The chamber also contained a white-light-emitting LED for sample illumination. The light intensity at the transistor surface was $\sim$350 mW/cm^2. For most experiments, the transistor was illuminated with this light for 30 min, the light was then turned off, and the device was allowed to stabilize before any measurements were made. This procedure led to higher sensitivity and more reproducible results (vide infra).

For a transistor of this general type, the drain current at a given value of the drain voltage, V_{DS}, is a function of the substrate (bias) voltage V_{sub} (Figure 5). At low or negative values of V_{sub} (e.g., 0 to -5 V) the transistor is switched "off" and the drain current is very small (picoamps). When V_{sub} is increased in the positive direction beyond a threshold, the drain current increases exponentially, turning the transistor "on." Typical drain currents are in the range of hundreds of nA. For the transistors used in this work, the threshold voltage was in the region of 5 V. At high positive values of V_{sub} (e.g., 15 V), the drain current is no longer a strong function of V_{sub}. If the porphyrin monolayer and the SOI channel of the transistor can "communicate" electronically, then changes in the electron distribution within the porphyrin monolayer would be expected to alter the electron distribution in the SOI channel, and therefore the threshold characteristics of the transistor. Thus, the transistor would be expected to be most sensitive to such changes when biased close to the threshold voltage.

Before introduction of amines, the drain voltage was set to 0.1V and the substrate (bias) voltage was set to give an initial drain current of $\sim$50 nA. This current corresponds to the most sensitive portion of the drain current vs substrate voltage characteristic. There was a small downward drift in drain current with nitrogen flushing that continued for several hours before attaining a constant value. Presumably, this is due to gradual removal of traces of water and other impurities. For each device, a mixture of 4.5 mL of nitrogen and 500 μL of nitrogen saturated with pyridine vapor was introduced to the chamber at 10-min intervals. Figure 6 shows the change in drain current produced by introduction of pyridine vapor to various devices. The bare device shows a small increase in drain current in response to the pyridine. A similar response was observed with transistors bearing a monolayer of palmitic acid, deposited in the same way as the porphyrin monolayers. The small increase in drain current in both control devices is ascribed in part to nonspecific physisorption of pyridine to the surface. In the case of the palmitic acid coated devices, pyridine may be absorbed into the fatty acid chains of the monolayer. In the case of the bare oxide, pyridine may interact with surface silanol groups by hydrogen bonding or acid−base reactions. It is known that the native silicon oxide surface, with a high density of silanol groups, will interact with liquids on its surface in a pH-sensitive fashion.[11] The pyridine response is superimposed upon an upward drift in drain current with time. This response, seen in all devices, is ascribed to the fact that the nitrogen purge was

(11) Ashcroft, B.; Takulapalli, B.; Yang, J.; Laws, G. M.; Zhang, H. Q.; Tao, N. J.; Lindsay, S.; Gust, D.; Thornton, T. J. *Phys. Status Solidi B* **2004**, *241*, 2291−2296.
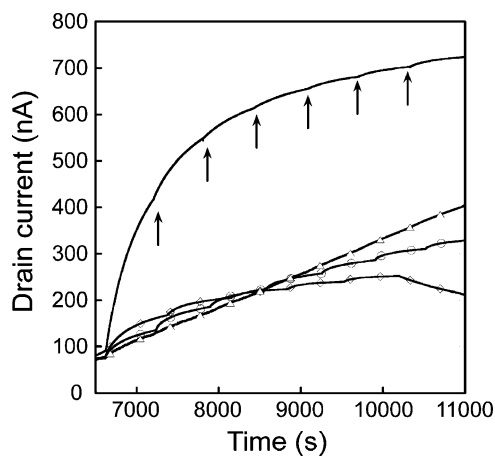
Figure 6. Response of the SOI-MOSFET drain current to exposure to pyridine vapor, as discussed in the text. The drain voltage was fixed at V_{DS} = 0.1 V and the substrate bias V_{sub} was adjusted to achieve an initial drain current of 50 nA. The MOSFET was enclosed in a Teflon chamber, and 5 mL aliquots of nitrogen gas to which had been added 0.5 mL of nitrogen saturated with pyridine vapor were introduced at 10-min intervals, as indicated by the arrows. The surface of the native oxide layer on the MOSFET was bare ($\diamond$), or bore a monolayer of zinc porphyrin **1Zn** (—), a monolayer of free base porphyrin **1** ($\triangle$), or a monolayer of palmitic acid (○).

Figure 7. Drain current response for a MOSFET bearing a monolayer of zinc porphyrin **1Zn** to pyridine (—) and to piperidine (- - -) vapor. The device in the chamber was initially prepared as described in the text and caption to Figure 6. At point (i) on the solid curve, 0.9 mL of nitrogen gas to which 0.10 mL of nitrogen saturated with pyridine vapor had been added was introduced. At point (ii), an additional 2.25 mL of nitrogen gas to which 0.25 mL of nitrogen saturated with pyridine vapor had been introduced. At point (iii), an additional 4.5 mL of nitrogen gas to which 0.50 mL of nitrogen saturated with pyridine vapor had been introduced. After resetting the device by overnight purging with dry nitrogen gas and light exposure as described in the text, an identical experiment was performed using piperidine vapor.

stopped when the vapor samples were introduced. This drift persisted until nitrogen flow was resumed. This may be due to small amounts of water vapor or other materials that outgas from the sample container.

When the transistor oxide bears a monolayer of free base porphyrin **1**, the response to pyridine is similar to that of the two control devices—very small responses to the amine superimposed on an upward-drifting base current. Thus, there is no specific interaction between the free base porphyrin and the pyridine.

The situation is quite different when the monolayer consists of zinc porphyrin **1Zn** (Figure 6). There is a significant stepwise increase in drain current with each addition of pyridine. The change is greatest for the initial addition, and gradually decreases with additional pyridine introduction. This is consistent with binding of the pyridine to the zinc atom, which gradually saturates as all of the zinc porphyrin binding sites become occupied. The large difference in response between the zinc porphyrin monolayer and the other three indicates a specific response of the zinc porphyrin—binding of pyridine—that is not present in the other cases. Thus, the electronic changes in the monolayer that occur upon binding are translated across the interface, leading to a change in device characteristics. Ligand binding to the porphyrin is reversible, and the MOSFET drain current slowly recovers after many hours exposure to a nitrogen purge.

Interaction with Piperidine Vapor. As mentioned above, the binding constant for the secondary aliphatic amine piperidine to a zinc porphyrin is approximately 19 times larger than that for pyridine. Figure 7 shows the results of an experiment designed to investigate the response of the transistor to these two different organic bases. After stabilizing the device, a mixture of 1 mL dry nitrogen and 0.1 mL nitrogen saturated with pyridine vapor was injected into the chamber housing at point (i) (solid line in Figure 7). Next, a mixture of 2.25 mL nitrogen and 0.25 mL of nitrogen saturated with pyridine vapor was injected (ii). Finally, a third injection of 4.5 mL of nitrogen
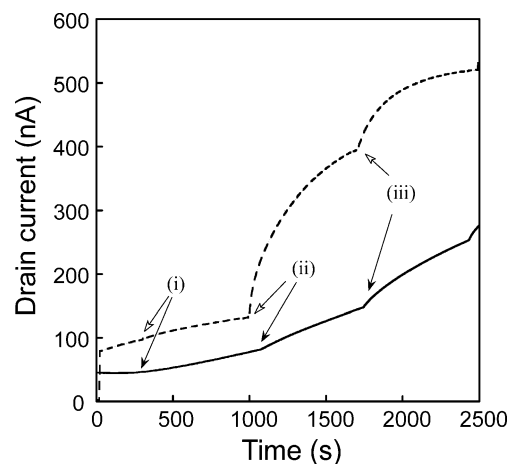
and 0.5 mL of nitrogen saturated with pyridine vapor was performed (iii). The pyridine was then removed by flushing with nitrogen gas overnight and light exposure (vide infra), and the sequence was repeated with piperidine (dashed line). It is clear from Figure 7 that the device response to a piperidine injection is 2−4 times larger than the response to a comparable pyridine injection, even though the boiling points of the two bases are similar (106 °C for piperidine and 115 °C for pyridine). This suggests that there is an equilibrium between free and bound amine, and that the larger binding constant for piperidine leads to more base bound to the transistor surface after comparable additions of vapor (vide infra).

Effect of Illumination. Illumination of the transistor with white light produced very interesting effects, as illustrated in Figure 8. A transistor bearing a monolayer of zinc porphyrin was biased to give an initial drain current of 50 nA. The transistor was prepared by purging overnight with nitrogen gas flowing through the Teflon container and then illuminating with the LED as mentioned above. The nitrogen flow was cut off, and the stabilized transistor was then exposed 8× to a mixture of 4.5 mL of nitrogen and 500 μL of dry nitrogen saturated with pyridine vapor over a period of 2 h, beginning at point (1) in the Figure. After this treatment, the drain current had increased to 600 nA, with diminishing response to each successive pyridine exposure as the monolayer approached saturation. At this time (point 2), the chamber was purged with dry nitrogen for 10 h, during which time the current fell slowly to 200 nA, as pyridine dissociated from the porphyrin and was flushed away. The rate of decay of the drain current suggests that although much of the pyridine has been removed from the surface, it would take a very long purge to return to the initial value of the drain current of ∼50 nA. After the purge, the cycle of 8 pyridine exposures was repeated (points 3 and 4), and the response was very similar to that observed initially. The maximum drain current, 550 nA, is nearly the same as that at
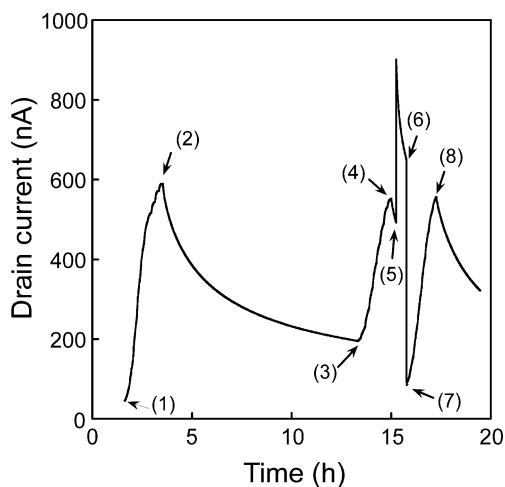
Figure 8. Drain current response to various stimuli of a MOSFET bearing a zinc porphyrin monolayer. Before the experiments shown, the device was preconditioned by purging with dry nitrogen and illumination with a white LED as described in the text. Beginning at (1) the device was exposed to 4.5 mL of nitrogen gas to which 0.50 mL of nitrogen saturated with pyridine vapor had been added. Additional identical portions of pyridine vapor were introduced for a total of eight additions at ∼10-min intervals. After this exposure to pyridine, the device was purged with dry nitrogen gas (2) overnight. After purging, the exposure sequence (3) followed by a nitrogen purge (4) was repeated, except that after a short purge time, the white LED was turned on (5) for 30 min. The LED and nitrogen purge were then turned off (6), whereupon the drain current returned to near its initial value. Finally, the exposure sequence was repeated once again (7), followed by a nitrogen purge (8). This cycling was repeated several times with similar drain current response each time.

point (2). After a few minutes of purging with nitrogen, the LED was used to illuminate the MOSFET for 30 min (point 5). The increase in current during illumination is due to electron−hole pair generation by the light, and initially saturates the amplifier used to measure current. At point 6, the LED and nitrogen flow were switched off; the drain current drops immediately to a value close to the initial 50 nA. At this point 7, the pyridine exposure was repeated, again producing a maximum drain current of 550 nA, and nitrogen purging was again performed (point 8). This cycle could be repeated numerous times.

The results in Figure 8 demonstrate that after pyridine exposure, nitrogen purging returns the drain current to its initial value only very slowly. However, purging in conjunction with illumination "resets" the transistor very rapidly, returning its original sensitivity to pyridine binding. This effect is not due to heating, as the temperature at the device was measured using a thermocouple during the irradiation, and no significant change in temperature was noted.

Discussion

Amine Binding and Sensitivity. It is clear that porphyrins **1** and **1Zn** form reasonably well-behaved compressed monolayers at the air−water interface, and that these can be transferred to glass and silicon dioxide surfaces by the Langmuir−Blodgett technique. The porphyrin molecules lie flat on the oxide surface, presumably with the four carboxyl groups facing down toward the oxide and binding the porphyrin to it via attractive interactions. Carboxylates are well-known to bind to metal oxide surfaces. Thus, the top of the derivatized MOSFET will be covered with a closely packed monolayer of porphyrin molecules. The UV−vis studies show that zinc

porphyrin monolayers deposited on glass specifically bind pyridine or piperidine molecules from the vapor phase, whereas free base porphyrin monolayers do not. This is consistent with the behavior of these porphyrins in solution. The results illustrated in Figures 6 and 7 demonstrate that the bare MOSFET and those bearing monolayers of palmitic acid or free base porphyrin interact weakly with pyridine, most likely through physisorption or relatively weak acid−base interactions with the oxide surface. These interactions alter the electronic charge distribution within the monolayer, and this alteration in turn changes the distribution of charge within the thin native oxide. This leads to changes in the carrier concentration within the SOI channel of the MOSFET, and a corresponding change in the drain current at a given V_{sub}. In the case of the zinc porphyrin monolayer, the response is much larger. This is consistent with and attributed to specific binding of pyridine to the zinc atoms, as is observed in solution and on the glass slides. Overall, changes in electron distribution in the monolayer that result from pyridine binding are transmitted across the interface to the electronic material, and sensitively detected by the MOSFET.

A rough idea of the resolution of the MOSFET may be obtained from the response data. Figures 6 and 8 show that the pyridine response saturates at around 600 nA. From the active area of the native oxide (3.0×10^{-8} m^2), and the area per molecule of 230 Å^2, it can be calculated that the FET bears 2.2×10^{-14} moles of zinc porphyrin. If we assume that a saturated response of about 600 nA corresponds to a maximum of one pyridine bound for each porphyrin, then the saturated response signifies 2.2×10^{-14} moles of bound pyridine. It is clear from the Figures that the signal-to-noise of the MOSFET is such that a 10 nA change is readily observable. Such a change corresponds to a few hundred attomoles of bound pyridine.

The extraordinary sensitivity of the SOI-MOSFET is due to a combination of factors. The fact that the porphyrin component is limited to a monolayer ensures that any changes in electronic structure that result from amine binding are transmitted to the underlying silicon dioxide without diminution due to intervening monolayers or other materials that are commonly found in conventional CHEMFETs. In turn, the thin (20 Å) native oxide layer on top of the SOI ensures that changes in the charge distribution at the upper surface of the oxide that result from changes in the monolayer are effectively transmitted to the SOI itself. This leads to changes in the sheet density and mobility of the inversion electrons in the SOI layer with a corresponding change in the MOSFET drain current. Finally, the ability to bias the transistor via the back gate, provided by the SOI design, greatly increases the amplification by the transistor of the small electronic changes near the native oxide interface. Thus, this design might be quite useful for a variety of sensor applications.

The shape of the response curves following exposure to amines seen in Figures 6, 7, and 8 are difficult to interpret quantitatively. Obviously, the amount of amine added to the chamber in the initial addition is vastly larger than that necessary to completely ligate all zinc atoms in the device. Thus, the fact that subsequent additions lead to further response indicates that there is an equilibrium between bound and unbound amine, and/or establishment of a steady state is very slow. The shape of the response curves for each addition, which seem to approach an equilibrium value after about 10 min, suggests that the majority of the effect is due to the operation of an equilibrium

between bound and unbound amine, which is pushed toward the bound state when additional amine vapor is introduced. The equilibrium constant for the porphyrin—pyridine complex for the monolayer in contact with the vapor phase is unknown. However, if we make a simple equilibrium calculation using the pyridine binding constant for zinc 5,10,15,20-tetraphenylporphyrin in benzene solution (6030 M^{-1}), the amount of pyridine added to the chamber (based on its vapor pressure), and the number of porphyrin molecules on the entire exposed oxide surface, a rough calculation indicates that when the transistor response is saturated (Figure 6), about half of the porphyrin molecules would be bound to pyridine at equilibrium. This result is consistent with the assumption of an equilibrium between bound and vapor-phase pyridine, given the approximations involved.

In the case of piperidine, the binding constant is larger, and the number of piperidine—porphyrin complexes present at equilibrium at any concentration below saturation would be larger than for the pyridine case. This doubtless accounts at least in part for the significantly larger response per addition noted for piperidine than for pyridine (Figure 7). An additional factor may be the enhanced base strength of piperidine ($pK_a = 2.80$) relative to pyridine ($pK_a = 5.19$). The fact that piperidine is a stronger electron pair donor to the zinc atom suggests that the electronic changes in the monolayer upon piperidine binding, and thus the changes in the carrier mobility and sheet density in the SOI channel, might be larger than for pyridine, and this might affect the relative magnitude of the device response.

Although the results for pyridine and piperidine show that the MOSFET device is sensitive to changes in both the chemical nature of the ligand and its binding constant, a single transistor would not show high selectivity for detection of any one of a related series of compounds in the presence of the others. An array of such sensors, each employing a different porphyrin monolayer, could be configured as an electronic "nose" that uses pattern recognition techniques to provide both specificity and quantitation.

Clearly, the response to the introduction of amine vapor into the chamber is not instantaneous. This response, 10 min or longer, is longer than the time necessary for the vapor distribution within the chamber to become uniform. The time for regeneration of the device by flushing with nitrogen is also slow. These timescales are much longer than the response time of the SOI-MOSFET to changes in V_{DS} or V_{sub}, which are estimated to be in the μs range when the device is biased close to threshold. It is possible that the response time is limited by the establishment of the equilibrium between amine in the vapor phase and amine coordinated to the monolayer.

Effect of Illumination. As shown in Figure 8, the transistor is reset rapidly by exposure to visible light, and only slowly by purging with nitrogen gas. In principle this change in response with illumination could be due to loss of pyridine from the monolayer, or from some electronic change within the transistor materials resulting from light exposure. However, the fact that the response of the MOSFET to pyridine vapor was essentially identical for numerous repetitions of the irradiation sequence indicates that the illumination results in de-ligation of the pyridine from the zinc porphyrin, creating an un-ligated surface. It is known that illumination of a zinc porphyrin that has bound pyridine in solution does not lead to de-ligation in the first

Table 1. Parameter Values Used for the Atlas Simulation of the SOI-MOSFET

Atlas simulation parameter	value
SOI channel thickness	100 nm
buried oxide thickness	400 nm
SOI channel doping	p-type (boron), 5×10^{15} cm^{-3}
floating electrode work function	
before pyridine	4.9 eV
after pyridine	4.725 eV
fixed oxide charge density	
at SOI channel-native oxide interface	1×10^{10} cm^{-2}
at SOI channel-buried oxide interface	1×10^{10} cm^{-2}
at buried oxide-silicon substrate interface	2×10^{10} cm^{-2}
interface trap density, N_{it} (trap energy relative to bottom of conduction band, $E_c - E_{trap}$)	4×10^{10} cm^{-2} (0.4 eV)

excited singlet state of the porphyrin. The emission spectrum of the porphyrin, as well as the absorption spectrum, is shifted in wavelength after pyridine binding, indicating that the pyridine is still bound in the excited singlet state.[12] (The triplet state chemistry was not investigated.) Thus, it is likely that some property of the silicon oxide surface or the underlying device may make the porphyrin monolayer subject to photode-ligation. The nature of this effect is unknown. With the planar orientation of the porphyrin on the oxide surface, it is possible that surface oxygen atoms from the SiO_2 may coordinate with the zinc atoms in the absence of another fifth ligand. To the extent that this occurs, it would weaken the binding between the zinc and the pyridyl nitrogen. Excitation may accentuate this effect. Additionally, illumination of the transistor induces formation of transient electron—hole pairs in the SOI channel. Charges at or near the native oxide surface, including any induced by changes in the charge distribution in the underlying SOI channel, will affect the electron distribution within the porphyrin, and therefore the binding constant for amines. Changes in charge distribution at the oxide surface would also be expected to affect the binding of small molecules to the bare oxide, in the absence of a monolayer. Indeed, an effect related to the light-resetting noted with the zinc porphyrin monolayer is also seen with bare native oxide.

Whatever the underlying cause of photode-ligation, the ability to rapidly remove the amine from the monolayer surface and regenerate a "clean" surface is potentially useful in device applications. For example, an amine sensor based on such a transistor could be rapidly reset for reuse using light, obviating the need for long purging with an inert gas.

Numerical Device Model. To better understand the effect that ligand bonding to the porphyrin has on the underlying MOSFET we have developed a numerical model of the device using the Atlas simulator from Silvaco Corporation (http://www.silvaco.com). In the model, we define the known semiconductor device parameters such as the thickness of the SOI layer and the buried oxide, and the channel doping concentration. Other parameters such as the thickness of the native oxide are not known precisely but reasonable estimates can be used. To model the presence of the monolayer above the 2-nm native oxide on the surface of the SOI channel we defined an electrode with a work function of 4.9 eV, consistent with the value expected for the zinc porphyrin **1Zn** monolayer.[13] This electrode

(12) Gust, D.; Moore, T. A.; Moore, A. L.; Kang, H.-K.; DeGraziano, J. M.; Liddell, P. A.; Seely, G. R. *J. Phys. Chem.* **1993**, *97*, 13637—13642.
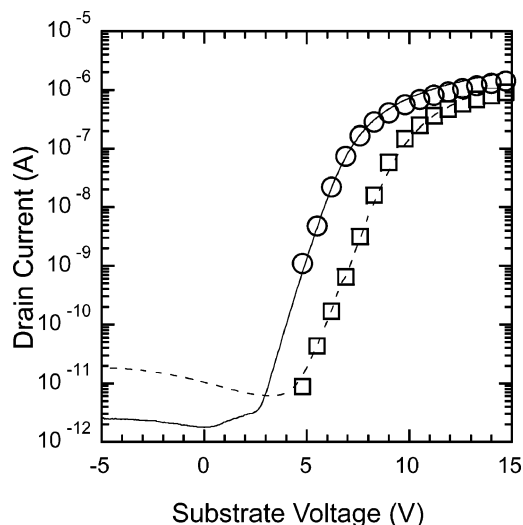
Figure 9. Measured (lines) and simulated (open symbols) drain current as a function of substrate voltage before (- - -, squares) and after (—, circles) exposure to 4.5 mL of nitrogen gas to which 0.50 mL of nitrogen saturated with pyridine vapor had been added. The drain voltage was fixed at $V_{DS} = 0.10$ V.

is floating, i.e., it is not connected to a voltage or current source, and therefore no current flows through this electrode from the source to the drain. The model parameters are given in Table 1.

The numerical model has been used to simulate the drain current flowing in the SOI channel before and after exposure to pyridine. In Figure 9, we plot the turn-on characteristics of the device, i.e., the drain current as a function of the substrate voltage for a fixed drain bias of $V_{DS} = 0.1$ V. The dashed line shows the measured data before exposure to pyridine, whereas the open symbols show the result of the simulation. The very reasonable fit between the measured and simulated responses has been achieved by using the fixed oxide charge concentration at the native oxide and the interface trap density as adjustable fitting parameters. The values used are given in Table 1. The values used for the fixed oxide charge concentration and interface trap density are very reasonable for these SOI materials.[14] The assignment of the trap level and density is somewhat arbitrary and other similar values give equally good fits to the data.

The solid line in Figure 9 shows the response of the device after exposure to pyridine vapor. We attribute the change in the drain current to a reduction in the work function of the zinc porphyrin **1Zn** as a result of donation of electron density from the pyridine into the monolayer. To reproduce the drain current response after pyridine exposure we simply modified the device model by reducing the work function of the floating electrode to 4.725 eV *keeping all of the other parameters the same*. Again, a reasonable fit to the data is achieved as shown by the open symbols, confirming that the device response can be described using one set of model parameters, and changing only the work function of the top layer to reproduce the drain current response

before and after exposure to pyridine. The 175 mV reduction in the work function of the **1Zn** monolayer is consistent with data from Kelvin probe contact potential difference measurements.[15] This earlier work showed that the work function of the zinc porphyrin monolayer on silicon oxide surfaces is reduced by 0.2 eV after exposure to pyridine vapors. Cyclic voltammetric experiments performed using a similar zinc porphyrin in solution show that the first oxidation potential is decreased by 110 mV after coordination with pyridine,[12] a result that is somewhat analogous to the reduction in work function that we observe in dry monolayers. Although the model we have developed for the porphyrin-coated MOSFET does not address the molecular details of the interaction of the monolayer with the oxide surface, the fact that it reproduces the device response using the measured change in the work function strongly suggests that this is the dominant mechanism by which the MOSFET senses the ligand binding event.

Conclusion

Langmuir–Blodgett techniques have been used to deposit porphyrin monolayers on the surface of a silicon-on-insulator MOSFET. The drain current flowing in a MOSFET coated with a zinc porphyrin shows an increase after exposure to pyridine or piperidine vapor that saturates after multiple exposures to the analyte. The response of the zinc porphyrin coated device is significantly larger than that demonstrated by the control samples, including a MOSFET coated with the free-base porphyrin. These results demonstrate that electronic changes in the monolayer resulting from amine binding are transmitted to the underlying oxide, and thence to the SOI channel of the transistor, where they are amplified to produce a large change in drain current. A numerical model of the MOSFET accurately reproduces the change in the drain current after exposure to pyridine using the work function of the porphyrin as the only variable parameter. This model provides a framework for understanding the effect that ligand binding to porphyrin molecules has on the underlying electronic materials. Interestingly, the electronic materials of the device also have significant effects on the chemistry of the zinc porphyrin. The binding of the pyridine is reversible, and de-ligation is accelerated by exposure to visible light. Such photode-ligation is not observed for zinc porphyrin molecules in solution, suggesting that the porphyrin–pyridine bond is significantly weakened, at least in the excited state, by effects of the underlying material.

The hybrid MOSFET is able to detect pyridine at the attomole level. This extreme sensitivity coupled with the ability to reset the device with light suggest that such systems might be excellent candidates for sensor applications.

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(13) Pfeiffer, M.; Leo, K.; Karl, N. *J. Appl. Phys.* **1996**, *80*, 6880−6883.
(14) Pavenello, M. A.; Martino, J. A. *Solid State Electronics* **1999**, *43*, 2039−2046.

(15) Grover, R.; Carthy, B. M.; Zhao, Y.; Jabbour, G. E.; Sarid, D.; Laws, G. M.; Takulapalli, B.; Thornton, T. J.; Gust, D. *Appl. Phys. Lett.* **2004**, *85*, 3926−3928.