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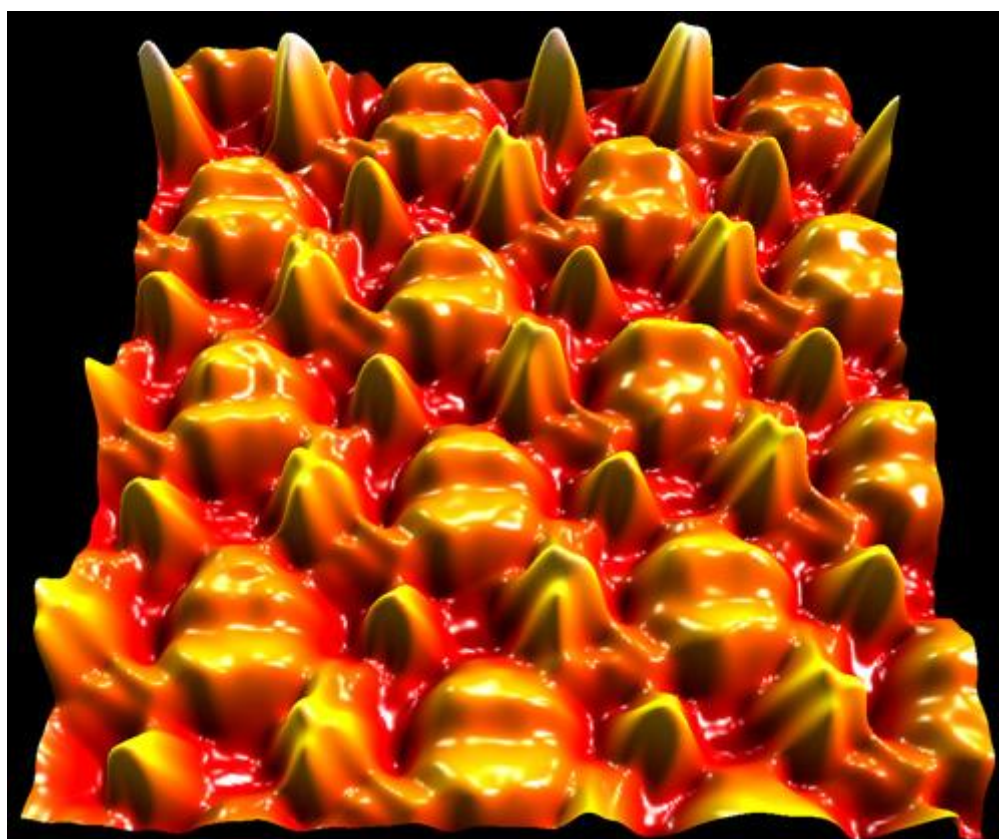
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Highly sensitive electrical detection of TCNE on chemically passivated silicon-on-insulator†‡

Girjesh Dubey,^{*ab} Federico Rosei^b and Gregory P. Lopinski^a

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Adsorption of tetracyanoethylene (TCNE) onto hydrogen terminated, *n*-type silicon-on-insulator is shown to cause significant depletion of majority carriers. Employing an ambient pseudo-MOSFET, ppm levels of TCNE vapour rapidly decrease the *n*-channel saturation current by at least two orders of magnitude. Covalent passivation with a decyl monolayer improves the reversibility of the response while only slightly decreasing the sensitivity.

Adsorption events leading to charge re-distribution on semiconductor surfaces can significantly alter the substrate conductivity through long-range electric field effects, suggesting a strategy for molecular sensing.¹ The electrical response of silicon-on-insulator (SOI) substrates has been used to monitor a range of surface processes including surface state conduction on clean surfaces in ultrahigh vacuum,^{2,3} biomolecule^{4,5} and gas adsorption⁶ on oxidized surfaces, and covalent modification of hydrogen terminated surfaces by polar molecules.^{7,8} Recently, lightly doped ($\sim 10^{15} \text{ cm}^{-3}$) hydrogen terminated silicon-on-insulator (SOI-H) has been shown to be a highly sensitive platform for electrical monitoring of molecular adsorption.^{9–12} In particular, adsorption of polar molecules of electron donating character such as pyridine and ammonia was found to strongly modulate the conductivity of SOI-H.¹¹

Tetracyanoethylene, C_6N_4 (TCNE), is a prominent electron acceptor with an electron affinity of 3.2 eV.¹³ TCNE forms classic charge-transfer complexes with many organic compounds,^{14,15} and exhibits molecular magnetism in special inorganic metal complexes.¹⁶ Single molecules of TCNE have been shown to exhibit charge transfer with metal surfaces.¹⁷ Similar charge transfer on a semiconductor such as silicon would be expected to induce a substantial field effect. In the current work, an *n*-channel pseudo-MOSFET^{12,18} formed on

chemically modified SOI surfaces is used to investigate the interaction of TCNE with oxide-free silicon. TCNE exposure is found to lead to large changes in the output characteristics of the device, reducing the drain current in saturation by at least two orders of magnitude, corresponding to flat-band shifts of $\sim 1 \text{ V}$ or higher. Surprisingly, this effect is observed readily in ambient atmosphere by simply exposing a source of solid TCNE in close proximity ($< 5 \text{ mm}$) to the Si device layer, allowing its room temperature sublimation vapour ($2 \times 10^{-3} \text{ Torr}$)¹⁹ to adsorb onto the surface. While a large response is observed on SOI-H, the current modulation is not completely reversible. Chemical modification of SOI-H to form a decyl monolayer (SOI-C10) improves the degree of reversibility in drain current while only reducing the current modulation approximately five-fold. These observations suggest that TCNE behaves as an electron acceptor on silicon, adsorbing with anionic character, inducing depletion of majority carriers on the *n*-type substrates used here.

Fig. 1 shows a schematic representation of the experiments. In the pseudo-MOSFET configuration, the source and drain contacts are formed at the top surface, which serves as the active sensing element. Application of a gate voltage (V_G) on the silicon substrate modulates the current between the source and the drain. Details of contact formation, H-termination and electrical measurements have been discussed previously.¹² The SOI used here is made by the SIMOX method starting from lightly *n*-doped ($\sim 1 \times 10^{15} \text{ cm}^{-2}$) Si(100). Application of a positive gate voltage (with respect to the source contact) is

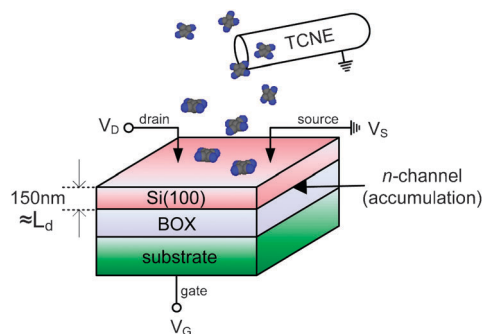


Fig. 1 Schematic illustration of the experiments (not to scale). Solid TCNE powders are brought in close proximity ($< 5 \text{ mm}$) to a surface for a controlled duration (3 s), and then retracted. The drain current is monitored and the exposure is repeated under the same conditions.

^a Steacie Institute for Molecular Sciences, NRC-SIMS, 100 Sussex Dr., ON K1A 0R6, Ottawa, Canada.

E-mail: Gregory.Lopinski@nrc-cnrc.gc.ca; Fax: +1-613 991-4278; Tel: +1-613-990-4155

^b Institut National de la Recherche Scientifique, INRS-EMT, Université du Québec, 1650 Boul. Lionel-Boulet, QC J3X 1S2, Varennes, Canada

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used to activate a conductive majority (electron) channel at the device layer/buried oxide (BOX) interface (accumulation mode). The voltage required to induce this channel is termed the flat-band voltage (V_{FB}), and is determined from the drain current (I_D) vs. drain voltage characteristics.¹² To monitor the effect of TCNE exposure, the saturation drain current ($I_{D,sat}$) at fixed V_D and V_G is measured as a function of time as the TCNE source is introduced and then retracted over the sensing area between the top contacts.

Current response $I_{D,sat}(t)$ of the SOI-H surface to four successive exposures of TCNE is shown in Fig. 2a. This exposure time was chosen based on the minimum duration required to induce a large signal that recovered in a reasonable amount of time.²⁰ The introduction of TCNE is seen to cause the current to drop abruptly by over two orders of magnitude.²¹ As seen in the figure, the measured On/Off ratio (I_{max}/I_{min}) is somewhat variable, ranging from 3.0×10^2 to 1.5×10^3 .²² The current response is seen to be largely reversible with the current rapidly recovering to close its initial value, presumably due to the TCNE desorbing from the surface.

Although the effect of TCNE is also observed at room temperature, heating the substrate to 60 °C was found to reduce recovery times and increase reversibility as well as yielding the highest sensitivity (the temperature dependence is discussed in more detail below). Close examination of the current response shows that the recovery of the current upon retracting the source is not complete. This is clearly seen in the inset to the right of Fig. 2a where the response is plotted on a linear scale and the current is seen to return to a lower value after each successive exposure. By the end of the 4th dose, I_{max} is reduced by ~17% with respect to the initial value. This is not too surprising as the H-terminated surface is known to oxidize in ambient, causing shifts in the flat-band voltage.¹² In addition, some TCNE could remain on the surface due to a

very strong physical interaction or even reaction with the H-terminated surface.

To improve the stability of the device layer, the SOI-H surface was modified by a gas-phase, photochemically-induced reaction with decene^{12,23} to form a decyl monolayer, Si-(CH₂)₉CH₃ (SOI-C10). The current response of this decyl modified surface to TCNE adsorption (under the same conditions as for SOI-H) is shown in Fig. 2b. The lower initial current level observed on SOI-C10 is attributed to interface state formation during the alkylation process.¹² Exposure of TCNE on the decyl modified surface still leads to large changes in current, although the On/Off ratios are somewhat reduced ($\sim 0.6 \times 10^2$ – 2.3×10^2). Decyl modification clearly improves the reversibility of the response with no overall decrease in current observed after the 4th dose as seen in the linear plot to the right of Fig. 2b. Interestingly, the presence of the dielectric monolayer (with thickness ≈ 1 nm) only moderately reduces the tendency of the adsorbed TCNE molecules to abstract electrons from the surface. A possible mechanism involves adsorption onto the monolayer followed by electron abstraction across the ultra-thin insulating barrier. Partial penetration of TCNE molecules into the monolayer is also conceivable, although less likely since the alkyl chains are densely packed.¹²

Surface vibrational spectroscopies were used to further probe the interaction of TCNE with hydrogen and decyl terminated Si(100) surfaces and account for the observations made in the electrical measurements. Attenuated total internal reflection Fourier transform infrared (ATR-FTIR) spectra for both surfaces upon exposure to TCNE are shown in Fig. 3. On the Si(100)-H surface (Fig. 3a), successive exposure of TCNE leads to a broad absorbance band from 2180–2260 cm⁻¹, with a distinct peak centered at 2220 cm⁻¹ and a weaker shoulder at 2195 cm⁻¹. These features overlap with the range of nitrile group stretch frequencies known for various TCNE complexes,²⁴ thereby suggestive of monolayer level coverage of TCNE that does not desorb effectively at room temperature. Additionally, the weak shoulder at 2195 cm⁻¹ is within the acceptable range for an anionic species TCNE⁻, although assignment of this peak is not definitive.

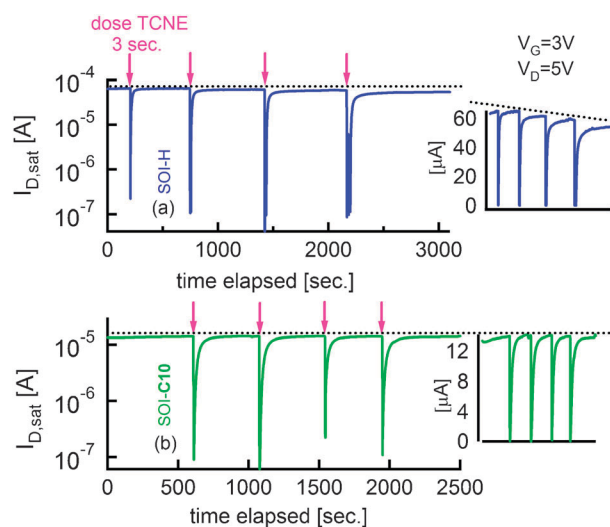


Fig. 2 Current response to successive TCNE exposures (marked by arrows) shown for (a) H-termination (SOI-H) and (b) decyl modification (SOI-C10). The drain current in saturation $I_{D,sat}(t)$ is sampled at 1 Hz at $V_G = 3$ V and $V_D = 5$ V at a substrate temperature of 60 °C. The current responses on a linear scale are shown in the insets at right to more clearly show changes in reversibility.

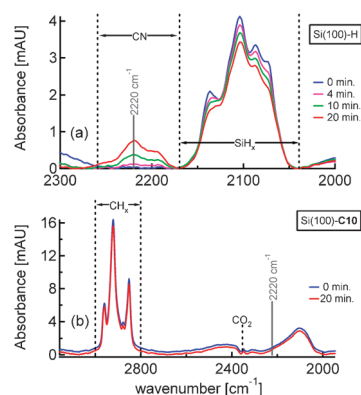


Fig. 3 ATR-FTIR spectroscopy shows (a) the appearance of the nitrile group stretch at $\nu_{CN} = 2220$ cm⁻¹ after 10 min exposure of TCNE on Si(100)-H and (b) the absence of the CN stretch on Si(100)-C10 under the same exposure conditions (spectra have been offset).

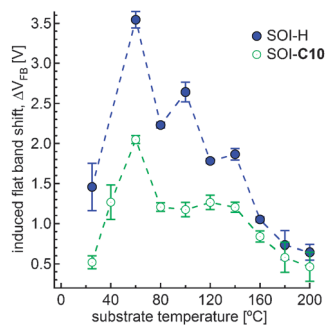


Fig. 4 TCNE induced flat-band voltage shifts (ΔV_{FB}) corresponding to the current responses observed on SOI-H and SOI-C10 surfaces as a function of substrate temperature.

Since modes in this region could also be due to oxidation of the hydrogen substrate, as the Si–H stretch shifts to higher frequency upon oxygen insertion into the backbone, high resolution electron energy loss spectroscopy (HREELS) was also carried out to examine this possibility. HREELS spectra of Si–H surfaces exposed to TCNE vapour confirm that this exposure does not result in appreciable oxidation of the surface (see ESI^\dagger) as indicated by the absence of Si–O–Si modes. Taken together, the HREELS and FTIR spectra strongly suggest that the irreversibility observed in the electrical response of the SOI-H surface is due to the accumulation of strongly bound TCNE species. Although TCNE adsorption on alumina hydrolyzes forming the tricyanoalcoholate ion,²⁵ we did not observe evidence for the expected C–O band around 1580 cm^{-1} associated with this species. In contrast to the behavior on Si–H, the same exposure conditions on Si–C10 did not produce peaks in the CN region as shown in Fig. 3b. The absence of persistent TCNE related modes on the decyl surface is consistent with the increased reversibility in the electrical signals observed in Fig. 2.

The temperature dependence of the TCNE charge transfer effect has also been investigated. The observed current responses over a range of temperatures, from $25\text{ }^\circ\text{C}$ up to $200\text{ }^\circ\text{C}$, are similar to those in Fig. 2. The large current modulation cycles $I_{\text{max}} \leftrightarrow I_{\text{min}}$ can be converted to shifts in the flat-band voltage (ΔV_{FB}). These shifts are computed based on the quadratic model for the saturation current using parameters from the initial $I_{\text{D}}-V_{\text{D}}$ output characteristics.¹² Fig. 4 shows the resulting temperature dependence of the TCNE induced flat-band shifts (ΔV_{FB}) on both SOI-H and SOI-C10.

At all temperatures considered, the adsorption of TCNE increases V_{FB} , in accordance with decrease in current observed in Fig. 2. This direction is consistent with negative charge density at the surface causing upward band-bending, thereby depleting the surface of free carriers and raising the (positive) threshold voltage on the substrate required to activate the accumulation channel. The shifts are clearly larger on SOI-H and reduced on SOI-C10. In addition, both surfaces exhibit the same trend in ΔV_{FB} , increasing to a maximum near $60\text{ }^\circ\text{C}$, suggesting that the charge transfer may be thermally activated. The decrease in ΔV_{FB} above this optimal temperature can be explained by faster desorption rates/shorter residence times at the surface.

The degree of charge transfer induced by TCNE adsorption can be estimated from the values of ΔV_{FB} in Fig. 4.^{12,26}

The changes in surface charge density required to account for the observed shifts at $25\text{ }^\circ\text{C}$ are $-8.50 \times 10^{10}\text{ cm}^{-2}$ and $-3.17 \times 10^{10}\text{ cm}^{-2}$ for the SOI-H and SOI-C10 surfaces, respectively. At $60\text{ }^\circ\text{C}$, the charge transfer increases to $-2.07 \times 10^{11}\text{ cm}^{-2}$ and $-1.25 \times 10^{11}\text{ cm}^{-2}$. Decyl modification therefore is seen to reduce the effective charge transfer by a factor of ~ 2 to 3 . If these charge densities ($\sim 10^{11}\text{ cm}^{-2}$) can be ascribed to singly occupied TCNE⁻ at the surface, then a lower bound on the coverage required to induce these effects is of the order $\sim 10^{-4}$ ML.

In conclusion, the pseudo-MOSFET technique has been used to demonstrate highly efficient electrical detection of TCNE vapour on oxide-free chemically modified SOI. This effect is attributed to significant charge transfer from the silicon substrate to adsorbed TCNE molecules. The use of a decyl monolayer to passivate the H-terminated surface was found to increase the reversibility of the TCNE induced current modulation, while only slightly decreasing the sensitivity, demonstrating the utility of alkyl monolayers as ultrathin dielectrics in molecular sensing applications. The large shifts in device characteristics observed in ambient atmosphere are promising for the rapid detection of other high electron affinity species such as explosive compounds.

Notes and references

- 1 D. Cahen, R. Naaman and Z. Vager, *Adv. Funct. Mater.*, 2005, **15**, 1571.
- 2 K. Yoo and H. H. Weitering, *Phys. Rev. Lett.*, 2001, **87**, 026802.
- 3 P. Zhang, E. Tevaarwerk, B. Park, D. E. Savage, G. K. Celler, I. Knezevic, P. G. Evans, M. A. Eriksson and M. G. Lagally, *Nature*, 2006, **439**, 703.
- 4 M. G. Nikolaides, S. Rauschenbach and A. R. Bausch, *J. Appl. Phys.*, 2004, **95**, 3811.
- 5 P. A. Neff, A. Serr, B. K. Wunderlich and A. R. Bausch, *ChemPhysChem*, 2007, **8**, 2133.
- 6 B. R. Takulapalli, *ACS Nano*, 2010, **4**, 999.
- 7 T. He, J. He, M. Lu, B. Chen, H. Pang, W. F. Reus, W. M. Nolte, D. P. Nackashi, P. D. Franzon and J. M. Tour, *J. Am. Chem. Soc.*, 2006, **128**, 14537–14541.
- 8 T. He, A. Corley, M. Lu, N. H. Di Spigna, J. He, D. P. Nackashi, P. D. Franzon and J. M. Tour, *J. Am. Chem. Soc.*, 2009, **131**, 10023.
- 9 G. Dubey, G. P. Lopinski and F. Rosei, *Appl. Phys. Lett.*, 2007, **91**, 232111.
- 10 S. A. Scott, W. Peng, A. M. Kiefer, H. Jiang, I. Knezevic, D. E. Savage, M. A. Eriksson and M. G. Lagally, *ACS Nano*, 2009, **3**, 1683.
- 11 G. Dubey, F. Rosei and G. P. Lopinski, *Small*, 2010, **6**, 2892.
- 12 G. Dubey, F. Rosei and G. P. Lopinski, *J. Appl. Phys.*, 2011, **109**, 104904.
- 13 S. Chowdhury and P. Kebarle, *J. Am. Chem. Soc.*, 1986, **108**, 5453.
- 14 R. E. Merrifield and W. D. Phillips, *J. Am. Chem. Soc.*, 1958, **80**, 2778.
- 15 M. F. Rettig and R. M. Wing, *Inorg. Chem.*, 1969, **8**, 2685.
- 16 J. S. Miller and A. J. Epstein, *Chem. Commun.*, 1998, 1319.
- 17 D. Wegner, R. Yamachika, Y. Wang, V. W. Brar, B. M. Bartlett, J. R. Long and M. F. Crommie, *Nano Lett.*, 2008, **8**, 131.
- 18 S. Cristoloveanu and S. Williams, *IEEE Electron Device Lett.*, 1992, **13**, 102.
- 19 R. H. Boyd, *J. Chem. Phys.*, 1963, **38**, 2529.
- 20 Although longer exposure times/shorter distances produced stronger effects on SOI-H, they were slower to recover and less reversible.
- 21 A control vial with no molecule did not change the drain current.
- 22 Control over the flux at the surface is likely the largest source of this variation as TCNE was manually manipulated.
- 23 B. J. Eves and G. P. Lopinski, *Langmuir*, 2006, **22**, 3180.
- 24 J. S. Miller, *Angew. Chem., Int. Ed.*, 2006, **45**, 2508.
- 25 K. W. Hipps and U. Mazur, *J. Phys. Chem.*, 1982, **86**, 5105.
- 26 H. J. Hovel, *Solid-State Electron.*, 2003, **47**, 1311.