# Influence of physisorbed water on the conductivity of hydrogen terminated silicon-on-insulator surfaces

G. Dubey and G. P. Lopinski[a)]
*Steacie Institute for Molecular Sciences, National Research Council, 100 Sussex Drive, Ottawa, Ontario K1A 0R6, Canada*

F. Rosei
*INRS-EMT, University of Quebec, 1650 Lionel-Boulet, Varennes, Quebec J3X 1S2, Canada*

The sheet resistance of hydrogen terminated silicon-on-insulator substrates increases significantly with time in air due to depletion of free carriers, attributed to the growth of electrically active defects as the surface oxidizes. Surprisingly, physisorbed water (via adsorption from ambient or controlled exposure in vacuum) causes an increase in the conductivity. This effect is largely reversible when the water layer is displaced by inert gas purging, heating, or pumping. The observed conductivity changes are correlated with Hall voltage changes, indicating that the adsorbed water layer induces accumulation of majority carriers on *n*-doped substrates. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2822417]

On semiconductor surfaces adsorption or reaction events which result in charge redistribution give rise to changes in electrical conductivity through long range field effects. However, excepting few special cases,[1–4] surface conductivity measurements on conventional wafers are relatively insensitive to surface processes due to conducting paths through the bulk. Silicon-on-insulator (SOI) substrates exhibit increased sensitivity to field effects as the top layer thickness is generally less than or equal to the depletion length. The increased sensitivity of SOI to surface effects was initially exploited to measure surface state conduction on clean silicon surfaces.[5–7] More recently, it has been used to sense *p*H changes and the adsorption of charged biomolecules.[8,9] These measurements demonstrate that two-dimensional SOI structures are highly sensitive platforms for chemical and biomolecular sensing applications, offering an interesting alternative to one-dimensional silicon nanowires.[10–15] Since planar two-dimensional (2D) systems are easier to fabricate and characterize, they serve as a useful starting point for understanding the behavior of nanowire systems, particularly with regard to investigating the effects of surface chemical modification.

Hydrogen passivated silicon surfaces present interesting model systems for surface conductivity studies. Obtained by etching in HF or ammonium fluoride,[16,17] these surfaces exhibit a low density of electrically active defects[16,18,19] and have recently been used to form high mobility 2*d* electron gases.[20,21] In this letter, we report surface conductivity measurements on lightly *n*-doped H-terminated SOI(111) substrates. The sheet resistance is observed to increase significantly with time in ambient air due to depletion of free carriers attributed to the growth of electrically active defects as the surface oxidizes. In addition, water adsorption (either from the ambient humidity in air or controlled dosing in vacuum) is seen to cause additional reversible changes in the conductivity due to accumulation of majority carriers. The observation that adsorbed water can induce significant band bending and surface conductivity modulation has implications for the interpretation of electrical measurements on Si surfaces and nanowires in ambient or aqueous solutions.

SOI(111) samples made via wafer bonding (Tracit, 1 $\mu$m buried oxide layer, 3 $\mu$m top layer) were thinned down by successive thermal oxidation and etching cycles to obtain a top layer thickness of 1 $\mu$m. Hydrogen terminated samples were prepared by cleaning in piranha solution followed by etching in degassed ammonium fluoride for 15 min and a brief water rinse.[22] Conductivity measurements were performed both in ambient and in a turbo-pumped high vacuum system (base pressure of $1 \times 10^{-7}$ torr). Sheet resistance was measured using four probe measurements in the van der Pauw (ambient) or in-line (vacuum) geometry using Keithley 2400 source meters. Contact to the top silicon layer was made via tungsten probes touching small InGa eutectic drops. A rare earth permanent magnet was used for Hall effect measurements.[23]

Figure 1(a) shows the sheet resistance ($R_s$) of a *n*-doped H-SOI(111) surface as a function of time in ambient conditions. The initial measured resistance corresponds to a resistivity of $\sim$10 $\Omega$ cm, close to that expected based on the doping level of $\sim 10^{15}$ cm$^{-3}$, consistent with the low density of electrically active defects expected on H-passivated silicon surfaces.[16,18,19] However, this resistance increases immediately upon commencing measurements, increasing by $\sim$20 times after 12–18 h.[24] The increase in resistance is attributed to the growth of electrically active defects which trap majority carriers (electrons) resulting in an upward band bending and depletion of free carriers. Hall voltage measurements (Fig. 2) confirm that the increased resistance is correlated with a decrease in carrier density. The growth of electrically active defect states on H-terminated surfaces in ambient environments is presumably due to oxidation as the initial resistance value is recovered by reetching the oxidized surface in HF.

To reduce the rate of oxidation (and hence the resistance increase), the sample was purged with dry inert gases (Ar or N$_2$). Although the slope of $R_s(t)$ decreases under gas purging as expected, the surprising observation is that initiating the flow of purge gas over the sample causes a sharp increase in the sheet resistance, as shown in Fig. 1(b). The effect is

---

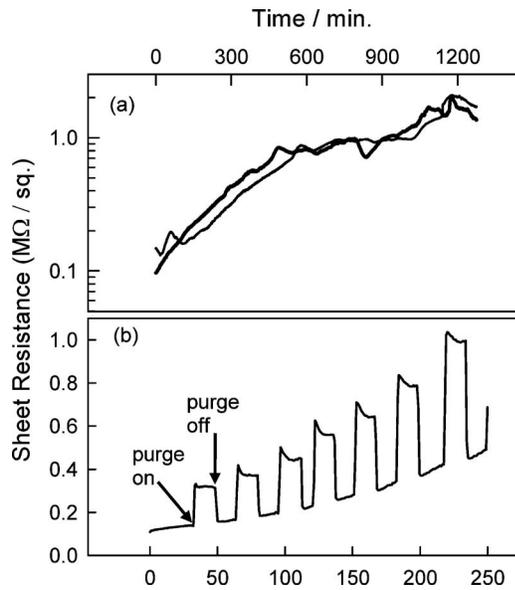[a)]Electronic mail: gregory.lopinski@nrc-cnrc.gc.ca.

**91**, 232111-1

FIG. 1. (a) Air-oxidation of *n*-type 1 $\mu$m thick H-SOI(111) observed by increasing sheet resistance. (b) Purging with dry Ar results in reversible changes in the sheet resistance.



FIG. 2. The sheet resistance along with free carrier densities extracted from the Hall voltage ($B_Z$=540 G) as a *n*-type H-SOI(111) is cycled between bare (purge on) and "H₂O-covered" (purge off) states. The table demonstrates that the ratio of sheet resistances ($R$) and carrier densities ($n$) in the two states scale together with time as the surface oxidizes and goes into depletion.



FIG. 3. Effect of water on the resistance of *n*-type H-SOI(111) in vacuum. Pumping down a sample from ambient increases the resistance while exposure to 15 torr of water vapor causes a decrease similar to that observed upon venting to laboratory air. Venting a sample with water already present on the surface causes only a small change in the resistance.

largely reversible with the resistance decreasing upon stopping the gas flow. At elevated substrate temperatures ($\sim$80 °C), the sensitivity of the resistance to gas purging decreases twofold, suggesting that the reversible resistance changes upon inert gas purging are due to the displacement of physisorbed water molecules likely present on the H-terminated silicon surface in ambient.

The presence of a water layer can alter the observed conductivity either directly by introducing an additional conducting path through the water layer itself or indirectly by modifying the substrate conductivity via field effects. To account for the observed conductivity changes in Fig. 1(b) via direct conduction through the water layer, this layer would need to exhibit a surface conductance of $\sim$10⁻⁵ S, approximately ten orders of magnitude higher than previously reported for ambient water layers on Teflon and quartz surfaces.[25] To definitively attribute the observed conductivity
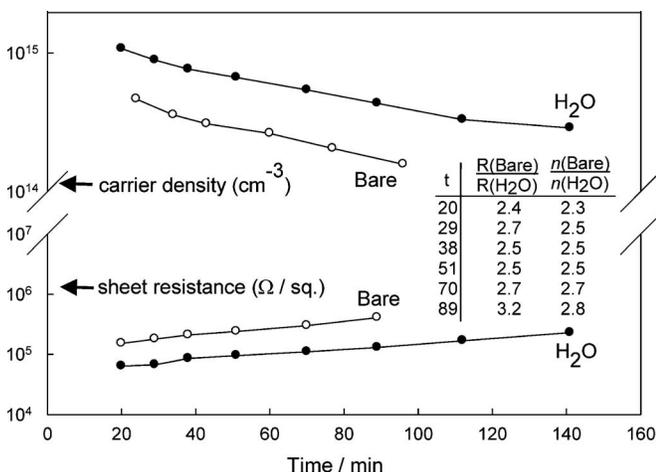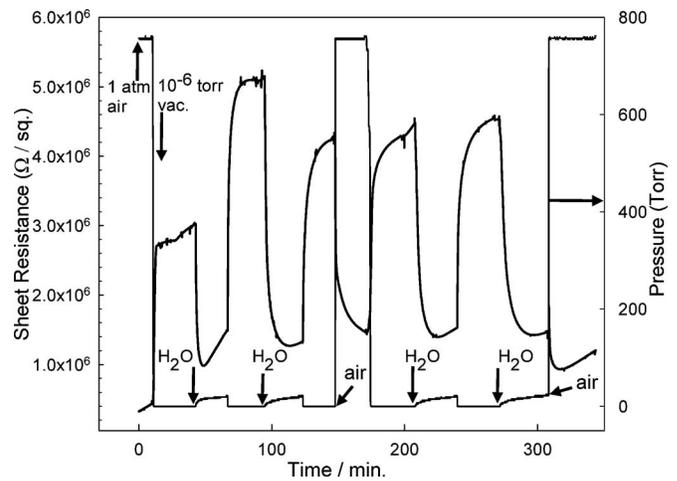
changes to a field effect, the observed resistance changes were correlated with Hall voltage measurements, which represent the sign and density of free carriers. Figure 2 shows that the increase in resistance associated with inert gas purging and desorption of the water layer is accompanied by a decrease in the carrier density. Although the carrier density decreases with time due to the oxidation of the H-terminated surface, at any given time the carrier density is always lower on a sample under dry gas purge than when adsorbed water is present. As seen in the table in Fig. 2, the ratios of resistances for "bare" and water covered surfaces correlate with the ratio of the carrier densities, indicating that the mobility remains constant. The effect of the adsorbed water layers can therefore be attributed to downward band-bending effects, leading to accumulation of majority carriers.

The combined Hall effect and resistance measurements also facilitate estimation of the degree of band bending induced by the adsorbed water layer. The initial measurements in Fig. 2 (obtained 20 min after preparation of the H-terminated surface) indicate that the sheet resistance and carrier density are 64 k$\Omega$ and $1.1 \times 10^{15}$ cm⁻³ with the adsorbed water layer and change to 152 k$\Omega$ and $4.7 \times 10^{14}$ cm⁻³ upon purging to at least partially displace the layer. This indicates that the adsorbed water layer has increased the surface conductance by +9 $\mu$S (relative to the purged sample), which requires 86 mV of band bending into accumulation.

To conclusively attribute the effects observed in the ambient purge experiments to the displacement of adsorbed water layers, conductivity measurements were repeated in the more controlled environment of a high vacuum system. As seen in Fig. 3, pumping on a H/SOI surface exposed to ambient air causes a large increase in the resistance. This is similar to the effect of inert gas purging although the magnitude of the change induced by pumping is larger.[26] Exposure of the surface to water vapor (at pressures of 10–15 torr) reversibly lowers the resistance, analogous to the effect of stopping the gas flow in Fig. 1(b).

The ability of adsorbed water to cause significant downward band bending on the Si–H surface could arise either from a charge transfer interaction of the water molecules

with the substrate or as a result of the field of a partially oriented layer of molecular dipoles. On the basis of the electrical data presented here, these mechanisms are indistinguishable; only the effective charge at the surface can be inferred. From the amount of band bending required to account for the observed conductivity changes, the field at the surface is ~50 kV/cm and the positive surface charge is $6.3 \times 10^{10}$ cm$^{-2}$. In terms of the charge transfer picture, this requires a low coverage ~0.0001 ML of integrally charged water molecules or a complete monolayer with a fractional charge of ~$0.0001e$/H$_2$O molecule. An electrochemical charge transfer process involving transfer of electrons to a weakly acidic (H$_3$O$^+$ containing) water layer has been proposed previously to account for the observation of water induced $p$-type surface conductivity on hydrogen terminated diamond surfaces.[4,27] However, this type of mechanism cannot account for the current observation as the surface conductivity observed on H/Si(111) is of the opposite character ($n$ type), requiring the water layer to act as an electron donor. Within the dipole picture, the field strength from an array of point dipoles can be calculated by summing over the fields of individual dipoles.[28] Using this approach, the required field (50 kV/cm) can be obtained for submonolayer coverages of water molecules with a dipole moment of 1.85 D.

Our observations indicate that SOI substrates are sensitive platforms for monitoring physical processes at silicon surfaces. The resistance of H-terminated SOI(111) substrates was found to increase significantly with time, due to depletion of majority carriers caused by oxidation. Physisorbed water was found to further modulate the conductivity, inducing downward band bending and accumulation of majority carriers. This ability of adsorbed water to induce band bending must be accounted for in the interpretation of electrical transport measurements on silicon surfaces in ambient or aqueous solutions.

[1] C. Jiang, S. Hasegawa, and S. Ino, Phys. Rev. B **54**, 10389 (1996).
[2] M. I. Landstrass and K. V. Ravi, Appl. Phys. Lett. **44**, 975 (1989).
[3] F. Maier, M. Riedel, B. Mantel, J. Ristein, and L. Ley, Phys. Rev. Lett. **85**, 3472 (2000).
[4] G. P. Lopinski, B. J. Eves, O. Hul'ko, C. Mark, S. N. Patitsas, R. Boukherroub, and T. R. Ward, Phys. Rev. B **71**, 125308 (2005).
[5] K. Yoo and H. H. Weitering, Surf. Sci. **482**, 482 (2001).
[6] K. Yoo and H. H. Weitering, Phys. Rev. Lett. **87**, 026802 (2001).
[7] K. Yoo and H. H. Weitering, Phys. Rev. B **65**, 115424 (2002).
[8] M. G. Nikolaides, S. Rauschenbach, S. Luber, K. Buchholz, M. Tornow, G. Abstreiter, and R. Bausch, ChemPhysChem **4**, 1104 (2003).
[9] M. G. Nikolaides, S. Rausenbach, and A. R. Bausch, J. Appl. Phys. **95**, 3811 (2004).
[10] Y. Cui, Q. Wei, H. Park, and C. M. Lieber, Science **293**, 1289 (2001).
[11] X. T. Zhou, J. Q. Hu, C. P. Li, D. D. D. Ma, C. S. Lee, and S. T. Lee, Chem. Phys. Lett. **369**, 220 (2003).
[12] J. Hahm and C. M. Lieber, Nano Lett. **4**, 51 (2004).
[13] Z. Li, Y. Chen, X. Li, T. I. Kamins, K. Nauka, and R. S. Williams, Nano Lett. **4**, 245 (2004).
[14] Y. L. Bunimovitch, Y. S. Shin, W. S. Yeo, M. Amori, G. Kwong, and J. R. Heath, J. Am. Chem. Soc. **128**, 16323 (2006).
[15] E. Stern, J. F. Klemic, D. A. Routenberg, P. N. Wyrembak, D. B. Turner-Evans, A. D. Hamilton, D. A. LaVan, T. M. Fahmy, and M. A. Reed, Nature (London) **445**, 519 (2007).
[16] E. Yablonovitch, D. L. Allara, C. C. Chang, T. Gmitter, and T. B. Bright, Phys. Rev. Lett. **57**, 249 (1986).
[17] G. S. Higashi, Y. J. Chabal, G. W. Trucks, and K. Ragavachari, Appl. Phys. Lett. **56**, 656 (1990).
[18] G. Oskam, P. M. Hoffmann, and P. C. Searson, Phys. Rev. Lett. **76**, 1521 (1996).
[19] W. Henrion, M. Rebien, H. Angermann, and A. Roseler, Appl. Surf. Sci. **202**, 199 (2002).
[20] K. Eng, R. N. McFarland, and B. E. Kane, Appl. Phys. Lett. **87**, 052106 (2005).
[21] K. Eng, R. N. McFarland, and B. E. Kane, Phys. Rev. Lett. **99**, 016801 (2007).
[22] High resolution electron energy loss spectroscopy confirmed the resulting surfaces were monohydride terminated with minimal oxidation or hydrocarbon contamination and imaging by scanning tunneling microscopy revealed the surfaces were atomically flat and of similar quality to that achieved on conventional Si(111) wafers.
[23] The field strength at the sample (for ambient measurements) was determined to be 540 G via calibration measurements using silicon wafers with known doping concentrations.
[24] As demonstrated by the two traces in Fig. 1, while small deviations in the behavior are observed from run to run the overall rate of increase is highly reproducible.
[25] Y. Awakuni and J. H. Calderwood, J. Phys. D **5**, 1038 (1972).
[26] This is presumably due to the greater efficacy of pumping as compared with purging in removing the adsorbed water layer.
[27] K. Larsson and J. Ristein, J. Phys. Chem. B **109**, 10304 (2005).
[28] M. Yu. Volokobinskii and A. S. Yastrebov, Tech. Phys. **44**, 807 (1999).