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Molecular Modulation of Conductivity on H-Terminated Silicon-On-Insulator Substrates

Girjesh Dubey, Federico Rosei, and Gregory P. Lopinski*

The adsorption of a range of molecular species (water, pyridine, and ammonia) is found to reversibly modulate the conductivity of hydrogen-terminated silicon-on-insulator (H-SOI) substrates. Simultaneous sheet-resistance and Hall-effect measurements on moderately doped (10^{15} cm^{-3}) n- and p-type H-SOI samples mounted in a vacuum system are used to monitor the effect of gas exposure in the Torr range on the electrical-transport properties of these substrates. Reversible physisorption of “hole-trapping” species, such as pyridine ($\text{C}_5\text{H}_5\text{N}$) and ammonia (NH_3) produces highly conductive minority-carrier channels (inversion) on p-type substrates, mimicking the action of a metallic gate in a field-effect transistor. The adsorption of these same molecules on n-type SOI induces strong electron-accumulation layers. Minority/majority channels are also formed upon controlled exposure to water vapor. These observations can be explained by a classical band-bending model, which considers the adsorbates as the source of a uniform surface charge ranging from $+10^{11}$ to $+10^{12} q \text{ cm}^{-2}$. These results demonstrate the utility of DC transport measurements of SOI platforms for studies of molecular adsorption and charge-transfer effects at semiconductor surfaces.

1. Introduction

The adsorption of charged or polar species on a semiconductor surface can modulate the electrical properties of the substrate through long-range field effects. Adsorbate-induced changes in conductivity were first noted in pioneering experiments in the 1950s, leading to considerable debate as to the

precise origin of these effects.^[1–4] These early experiments, carried out on germanium surfaces covered by thin native oxide layers, indicated that relative humidity can have a strong influence on the surface potential. The effect of water vapor was seen to be large enough to drive p-type substrates into inversion, creating a minority (n-type) channel at the surface.^[4] Recently the development of nanostructured semiconductor materials has led to renewed interest in these effects. In particular, the conductivity of silicon nanowires (Si-NWs) has been shown to exhibit a sensitive response to a range of molecular-adsorption events, from small molecules in the gas phase^[5,6] to biomolecules (oligonucleotides, proteins) in solution.^[7–12] A key property of these nanostructured materials is that one or more of the physical dimensions are less than or comparable to the depletion length ($\approx 1 \mu\text{m}$ at doping levels of $\approx 10^{15} \text{ cm}^{-3}$). Hence, the conductivity of these structures is expected to be extremely sensitive to adsorption events that result in charge redistribution at the surface.

Silicon-on-insulator (SOI) substrates consist of a thin silicon layer (30–3000 nm) separated from a bulk wafer by a buried oxide (BOX) layer. The presence of the BOX serves to isolate conducting paths to the bulk substrate, rendering the conductivity highly sensitive to surface processes. Compared to Si-NWs, use of the planar SOI geometry facilitates a more direct interpretation of the effects

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of adsorption events, as well as enabling the application of standard surface-science techniques for characterization of the active interface. Thin-film resistors based on oxidized SOI substrates operating in electrolyte solutions have been explored for biosensing applications.^[13–16] Oxide-free, hydrogen-terminated SOI (H-SOI) substrates are model systems for investigating the ability of adsorbed or covalently attached molecules to modulate the conductivity.^[17] Each surface atom is fully coordinated and the low density of defect states ($D_{it} \approx 10^{10} \text{ cm}^{-2} \text{ eV}^{-1}$) results in nearly flat bands.^[18–20] These substrates are stable enough to be handled in ambient atmosphere for several minutes without oxidizing and have extended lifetimes once in high vacuum ($<10^{-5}$ Torr).

Previously we have reported that ambient humidity or adsorption of water vapor under vacuum conditions enhances the conductivity of n-type 1- μm -thick H-SOI substrates,^[21] an effect recently confirmed by others.^[22] Here, we show that controlled exposure of H-SOI substrates to a range of molecular species is found to significantly modulate the conductivity in a reversible manner. Combining four-probe-resistance and Hall-voltage measurements allows the observed conductivity changes to be correlated with changes in carrier density and effects due to majority and minority carriers to be distinguished. While water adsorption on n-type H-SOI is confirmed to induce accumulation of majority carriers, adsorption of this molecule on p-type H-SOI is seen to lead to minority-carrier-dominated conduction (inversion), as observed in the early studies on germanium.^[1–4] Pyridine is found to give rise to similar but larger effects than water, inducing strong accumulation and inversion layers on n- and p-type H-SOIs, respectively. Similar electron donors (ammonia, triethylamine) are found to behave like pyridine, while certain aromatic molecules, such as toluene and thiophene, have minimal effects on the conductivity. These observations demonstrate the utility of transport measurements on H-SOI substrates for studies of adsorption events at silicon surfaces and suggest potential applications in chemical sensing.

2. Results and Discussion

2.1. Water Vapor on n-Type H-SOI Surfaces

Figure 1 illustrates the response of the sheet resistance $R_s(t)$ of an n-type (148 nm) H-terminated SOI (SIMOX) substrate to pure water vapor under vacuum conditions. Under a pressure of 11 Torr of water, the sheet resistance is found to be constant at 40 k Ω . Upon pumping away the water vapor, the sheet resistance increases nearly twenty-fold to 762 k Ω . This is consistent with our previous observations,^[21] although the magnitude of the resistance change is much greater due to the fact that the SOI is considerably thinner than the 1- μm samples employed previously. In addition, here, we have also monitored the Hall voltage associated with changes in the sheet resistance. The measured Hall coefficient increases from -400 to

$-8840 \text{ cm}^3 \text{ C}^{-1}$, proportional to the increase in sheet resistance. The Hall coefficient (R_H) and sheet-resistance measurements can be used to extract the free-carrier density and mobility from the standard expressions:

$$n = \frac{1}{d} \int_0^d n(z) dz = \frac{I_x B_z}{V_H q d} = \frac{1}{R_H q} \quad (1)$$

$$\mu_n = \frac{V_H}{I_x R_s B_z} \quad (2)$$

The scaling of the Hall coefficient with resistance indicates that the conductivity changes are associated primarily with changes in carrier density induced by a field effect rather than changes in mobility. The increase in resistivity and Hall voltage as water desorbs from the surface indicates that the presence of water on the surface acts to increase the carrier density (i.e., induce accumulation of majority carriers).

Upon pumping away the water, the sheet resistance follows an exponential rise back to its initial value with a time constant of 1.7 min (significantly longer than the 20 s required for the pressure to be reduced to below $\approx 10^{-4}$ Torr). Assuming that the relaxation of the conductivity reflects desorption of water, the observed time constant corresponds to a binding energy of 0.86 eV (assuming a prefactor of 10^{13} s^{-1}), considerably higher than expected for physisorbed water molecules. To account for the formation of the accumulation layer indicated by the observations in Figure 1 requires an induced surface-charge density of $Q_s = +2.2 \times 10^{11} q \text{ cm}^{-2}$ (see Supporting Information S2 for details of this calculation).

Figure 1. Monitoring the rise in sheet resistance of an n-type 150-nm H-SOI(100) film as 11 Torr of H_2O is pumped from the vacuum system. Pressure is shown in red. Both the Hall coefficient (calculated from the measured Hall voltage at $I_x = 100 \text{ nA}$, $B_z = 280 \text{ G}$) and resistance increase 20-fold in vacuum, indicating that conductivity enhancement in water occurs via a field effect that increases carrier density rather than mobility. The dashed curve represents a fit to an exponential rise to maximum with a time constant of 1.7 min.

One possibility is that this surface charge originates from a small amount of strongly bound water, which undergoes charge transfer and adsorbs as a positive species. This requires a spectroscopically undetectable coverage of $\approx 0.03\%$ or one integrally charged H_2O molecule for every 3000 Si atoms. This ionosorbed component will have a higher activation to desorption than the surrounding physisorbed water, which is expected to desorb rapidly ($\approx 10\text{ }\mu\text{s}$ for an activation energy of 0.4 eV). Another possibility is that the timescale for the changes in sheet resistance is not determined by desorption but by electronic processes (i.e., detrapping from charged donor states at the surface).

2.2. Water Vapor on p-Type 3- μm H-SOI Surfaces

Hall-effect measurements on thin ($<200\text{ nm}$) boron-doped nominally p-type SIMOX samples indicated n-type conduction in the top silicon layer, even though the substrate (below the BOX) remained p-type. This a well established effect for SIMOX samples and has been attributed to the introduction of unintentional donors (leading to dopant overcompensation) during the implantation and annealing steps.^[23–28] The change in carrier type renders the influence of physisorbed water on the conductivity of either n-type or overcompensated p-type H-SIMOX the same, causing electrons to accumulate on both surfaces. To investigate the effects of water adsorption on p-type SOI, we used 3- μm -thick boron-doped samples formed by the Unibond method. In these samples, the Hall voltages from the top silicon layer are consistent with lightly doped p-type conduction; however, since the thickness of the top silicon layer is larger than the depletion length, reduced sensitivity to field effects is expected. Attempts to thin these samples to $1\text{ }\mu\text{m}$ by repeated thermal oxidation and etching cycles resulted in increased sensitivity to adsorption events but also resulted in Hall-effect measurements, indicating n-type conduction, likely due to the oxygen-donor mechanism discussed above.^[29]

The sheet resistance response to water exposure cycles for 3 μm p-type H-SOI is shown in **Figure 2**. On exposure to 11 Torr of H_2O , the resistance is seen to decrease from an initial value $R_s^{[\text{vac}]} = 88\text{ k}\Omega$ down to $R_s^{[\text{gas}]} = 64.8\text{ k}\Omega$. As on n-type substrates, this effect is observed to be reversible upon pumping the water vapor from the chamber. However, in contrast with the resistance decrease seen in Figure 1, in this case, the Hall voltage is observed to change sign. This change in sign of the Hall voltage implies that the increase in surface conductivity on the p-type substrates is due to the formation of a minority-carrier channel at the surface (i.e., inversion). Another difference from the behavior of n-type substrates is the fact that the resistance change with water exposure

Figure 2. Sheet-resistance changes to water adsorption and desorption cycles on p-type 3- μm -thick H-SOI(111). The surface becomes inverted in 11 Torr H_2O , indicated by a change in sign of the Hall voltage from its value in vacuum (measured at $I_x = 1\text{ }\mu\text{A}$, $B_z = 560\text{ G}$). The transition from depletion to inversion is weakly visible for this thickness and adsorption rate, as shown in the inset. The Hall coefficient in vacuum ($+10\text{ }580\text{ cm}^3\text{ C}^{-1}$) remains the same before dosing and after pumping away the water.

is not monotonic. On p-type H-SOI, the resistance is found to increase slightly before decreasing. This initial change is expanded in the inset of Figure 2.

We attribute this behavior in $R_s(t)$ to the initial depletion of majority carriers (holes), which increases the resistance before additional adsorption leads to inversion (decreased resistance, negative Hall voltage). Due to the large thickness of the top silicon layer, the initial increase in resistance is small (in contrast to films where the thickness is smaller than the depletion length). The rate of adsorption and time resolution of the measurements also will also affect the shape of this transition. A positive surface charge of $\approx 1 \times 10^{11} q\text{ cm}^{-2}$ is sufficient to account for the observations in Figure 2. A band-bending diagram consistent with the measured sheet resistance and discussion of the Hall voltage measurements is given in Section S3 and S4 of the SI, respectively.

2.3. Water-Induced Band Bending

The data presented above clearly demonstrates that water induces accumulation on n-type and inversion on p-type H-terminated substrates. This is consistent with downward band bending in both cases. This is not particularly surprising since charge transfer and orientation of H_2O molecules on the H-Si surface is expected to be independent of doping type. A surface charge of the order of $\approx 10^{11} q\text{ cm}^{-2}$ is required to account for the observations on both substrates. This example illustrates the importance of measuring changes in both R_s and V_H to distinguish between accumulation or inversion, since both scenarios result in an increased surface conductance.

It is interesting to note that, although two different surface orientations and etching procedures have been used here (the n-type samples are HF etched (100) and the p-type samples are ammonium fluoride etched (111)), the effective surface charges induced by water adsorption are similar. In our previous report, similar positive charge densities were reported for water on n-type ammonium-fluoride-etched SOI(111) substrates.^[21] Taken together, these observations indicate that, despite the differences in morphology and structure of these two types of H-terminated SOI surfaces, the field effects induced by water adsorption are quite similar.

As mentioned in the introduction, observation of water-induced field effects on p-doped surfaces dates back to the 1950s. In early studies on germanium n-p-n bipolar junction transistors, humid nitrogen gas was shown to lead to the formation of an inversion layer in the base.^[1,4] The appearance of donor-like states induced by water adsorption was used to explain the origin of this inversion layer. For instance, Brown^[2] suggested that neutral donor impurities are ionized by water adsorption. Given the low density of surface charge ($\approx 1 \times 10^{11} q \text{ cm}^{-2}$) required to induce the effects observed here, it is difficult to rule out the presence of ionizable impurities at this level originating from the etching procedures. However, the observation that surfaces etched in both HF and ammonium fluoride exhibit similar effective charge densities in the presence of water perhaps argues against this explanation as different residual impurities are expected on these surfaces. Future studies on SOI surfaces hydrogenated in ultrahigh vacuum should provide further insight into the possible role of impurities. The other possibility, already discussed above, is that water itself acts as a donor, undergoing a charge-transfer interaction with the substrate. Theoretical calculations of the

interaction of water on H-terminated silicon are required to further substantiate this possibility.

2.4. Pyridine Vapor on n-Type H-SOI Surfaces

The strong influence of physisorbed water on the conductivity of H-SOI suggests exploration of the effects of other molecular species. Pyridine ($\text{C}_5\text{H}_5\text{N}$) is an interesting candidate as a polar molecule (with a dipole moment of 2.2 D) with an active electron lone pair. It is a well known base, making it susceptible to hole capture (electron donation). Its electronic interaction with hydrogen-passivated silicon has not yet been investigated.

Figure 3a shows the result of pyridine exposure on an n-type SIMOX substrate with film thickness $d = 148.7 \text{ nm}$. Within minutes of leaking pyridine into the chamber, the conductivity of the sample increases by almost two orders of magnitude as the pressure is allowed to increase continuously to 13 Torr. Hall-voltage measurements prior to and after adsorption are found to scale with sheet-resistance changes. As with water adsorption on n-type Si, this observation shows that pyridine gives rise to strong accumulation of the majority carriers (electrons). Simulations (as discussed in S2 of the SI) indicate that $\approx 172 \text{ mV}$ of downward band bending is required to account for the observed changes in sheet resistance, requiring an external charge of order $\approx 10^{12} q \text{ cm}^{-2}$, nearly six times greater than that induced by water at a similar pressure. A summary of electrical parameters presented here is given in Table S1 of the SI for additional reference and comparison.

Evacuation of the pyridine confirms the reversibility of most of this effect upon desorption, as illustrated in

Figure 3. a) Adsorption of pyridine vapor on an n-type 150-nm H-SOI(100) film from vacuum. The conductivity, as well as the Hall coefficient (taken at $I_x = 100 \text{ nA}$, $B_z = 560 \text{ G}$), increases by almost two orders in magnitude on exposure. b) Evacuation of pyridine eliminates the accumulation layer and the resistance and Hall coefficients return to values comparable to that measured initially.

Figure 3b. A double asymptotic exponential rise in Figure 3b can be fitted with a fast time constant ($\tau_1 \approx 0.9$ min) with an overall slow tail ($\tau_2 \approx 9.9$ min). The slower time constant suggests that at least some pyridine binds more strongly to the hydrogen-terminated surface than water. The final sheet resistance in vacuum was approximately 30% higher than its initial value, suggesting that some degradation of the H-terminated surface may have occurred. The combined effect of pyridine with another impurity in the chamber or gas line is the most probable cause. For instance, water combined with pyridine is known to accelerate oxidation of H-terminated porous silicon.^[30]

2.5. Pyridine Vapor on p-Type H-SOI Surfaces

Pyridine exposure to Unibond p-type 3- μ m SOI is shown in **Figure 4a**. As with water, the same peak features (shown in the inset) show that R_s evolves from an initially depleted state to a stable inverted state, supported by a change in sign of the Hall voltage. The reverse process is illustrated in Figure 4b. The resistance quickly increases to a maximum as the n channel vanishes but, as residual pyridine continues to desorb, the surface slowly comes out of depletion and the resistance decays back to its initial value shown on the dotted line. The Hall voltage is also restored to its original positive value in vacuum.

The surface charge required to account for the changes observed in Figure 4 is $\approx 3.7 \times 10^{11} q \text{ cm}^{-2}$, more than a factor of three times greater than that induced by the presence of

water. This can be attributed to the donor-like nature of the nitrogen lone pair, which can trap holes from the surface, resulting in $(\text{C}_6\text{H}_5\text{N})^+$. This mechanism is consistent with previous studies of pyridine adsorption in highly doped p-type porous silicon layers.^[31] Using infrared spectroscopy^[31] and electron-spin resonance, Osminika et al. demonstrated hole capture into surface states of adsorbed pyridine at low pressures (100 mTorr).

2.6. Other Gases on p-Type H-SOI

The ability of a few other gases to modulate the conductivity of H-SOI surfaces has also been investigated on p-type H-SOI substrates. Dry oxygen or nitrogen gas did not significantly affect R_s over a pressure range of 1–1000 Torr. Not surprisingly, amines, such as ammonia (NH_3) and triethylamine ($\text{N}(\text{C}_2\text{H}_5)_3$), induced similar effects to pyridine, causing the resistance of 3- μ m p-type H-SOI to decrease from $\approx 56 \text{ k}\Omega$ to $\approx 6 \text{ k}\Omega$, accompanied by inversion of the Hall voltage. As for pyridine and water, this effect is reversible with the conductivity and bulk carrier type restored upon pumping away the gases. Similar to pyridine, both species are polar and have a basic lone pair that can abstract holes from the surface. Ammonia and triethylamine inverted the surface at much lower pressures ($\approx \text{mTorr}$ range) than pyridine or water and so rapidly that the depletion–inversion peak feature was not observed. Pressure–resistance measurements over a wide pressure range may provide useful contrast between these species.

Figure 4. a) Sheet-resistance changes to adsorption of pyridine vapor on p-type 3- μ m-thick H-SOI(111). A change in sign of the Hall voltage on exposure indicates that the surface becomes inverted by pyridine adsorption. b) The corresponding desorption isotherm shows that this effect is reversible.

Figure 5. Monitoring the effect on the sheet resistance when toluene, thiophene, and pyridine are sequentially exposed to p-type 3- μ m H-SOI(111), respectively. The conductivity is unaltered upon exposure to toluene or thiophene. Exposure to pyridine induces the large resistance change observed previously.

We note that ammonia has been reported to induce significant changes in the response of Si-NW transistors.^[5]

The specificity of the gating effect to certain classes of molecules is demonstrated in **Figure 5**, in which a p-type H-SOI substrate is exposed sequentially to three different types of molecules. To minimize cross contamination between doses, the common gas line is gently baked for several minutes when changing to a new molecule. The vacuum resistance of this sample is 65.7 k Ω while the Hall voltage is measured to be +224 μ V (at 1 μ A and 560 G). There is a negligible change when 15 Torr of toluene ($C_6H_5CH_3$) is leaked into the chamber/pumped away. Like pyridine, toluene is a hexacyclic aromatic molecule, except it is non-polar and does not have lone pairs that can participate in charge donation. The lack of an observed response for this molecule supports the hole-trapping mechanism suggested for the pyridine observations. Again, there is a negligible change (<1%) when 20 Torr of thiophene (C_5H_4S) is introduced or evacuated. Although thiophene has a dipole moment, its lone pair is heavily incorporated into its aromaticity, rendering its activity similar to toluene. When $\approx$ 10 Torr pyridine is introduced, the familiar depletion–inversion peak feature is observed; there is a brief rise in resistance to 65.9 k Ω , followed by a significant decrease to 24.4 k Ω along with an inversion of the Hall reading to -58μ V. After pumping away the pyridine, the resistance returned back to 65.7 k Ω and Hall voltage was restored to its previous value.

3. Conclusion

We have shown that H-SOI substrates are interesting model platforms that enable the use of conductivity measurements to probe molecular adsorption/desorption events. In addition to monitoring the sheet resistance,

complementary information can be obtained from Hall-voltage measurements. This facilitates distinguishing between accumulated, depleted and inverted states. Using this approach, adsorption of water is found to strongly and reversibly increase the conductivity of both n- and p-type H-SOI substrates. These conductivity changes can be attributed to water-induced field effects that lead to accumulation of majority carriers on n-type substrates and formation of a minority-carrier channel (inversion) on p-type substrates. The surface charge densities required to account for these effects are $\approx 10^{11} q \text{ cm}^{-2}$. Pyridine adsorption gives rise to similar, yet even stronger, reversible conductivity-modulation effects as compared with water on both n- and p-type substrates. Adsorption of pyridine in the Torr range gives rise to positive surface charges of $4 \times 10^{11} q \text{ cm}^{-2}$ (p-type) and $1 \times 10^{12} q \text{ cm}^{-2}$ (n-type), resulting in a surface electric field 3–6 times higher than that caused by water adsorbed on the same surface. The ability of nitrogen-containing molecules, such as pyridine, ammonia, and triethylamine, to reversibly bias p-type surfaces into inversion demonstrates a new type of molecular-triggered electronic switch where adsorption is used to reversibly gate transport through the silicon substrate.

4. Experimental Section

Separation by implantation of oxygen, SIMOX (IBIS, 380-nm BOX, 150–200-nm top Si film) SOI(100) samples, boron or phosphorus doped, and boron-doped Unibonded p-type (Tracit, 1- μ m BOX, 3- μ m top Si layer) SOI(111) samples cut to $\approx 20 \text{ mm} \times 7 \text{ mm}$ have been used. Hydrogen termination on (111) samples was achieved by cleaning in piranha solution followed by etching in degassed ammonium fluoride for 15 min and a brief water rinse.^[32] SIMOX SOI(100) samples were immersed in 2% hydrofluoric acid for 2 min. Hazards: Piranha solution should be handled with care

Figure 6. Schematic illustration of the setup and measurement geometry. An in-line/Hall-bar configuration is made with six contacts to the H-terminated samples before pumping to high vacuum and dosing with the test gas.

and isolated from organic substances. Protective measures should be taken with fluoride etchants.

High-resolution electron-energy-loss spectroscopy (HREELS) on H-SOI samples confirmed the expected Si–H stretch and bend modes with minimal Si–O–Si and hydrocarbon peaks. On the H-SOI(100) substrates, a strong Si–H₂ scissor mode was observed, as expected for these surfaces, which are known to exhibit a mixture of mono and dihydride species. Vibrational spectra are presented in S5 of the SI. The low-energy, low-current-density incident beam (6 eV) effectively probes surface vibrational modes without causing observable desorption or defect formation. Scanning tunneling microscopy (STM) revealed that the H-SOI(111) samples were atomically flat and of comparable structural quality to surfaces prepared using conventional wafer substrates.

Samples were mounted in a turbo-pumped high-vacuum system (base pressure of 1×10^{-7} Torr). Solutions were freeze-pump-thawed with liquid N₂ before exposure of the vapor into the chamber. Contact to the top silicon film was made via 2.5-μm-diameter tungsten probes (six in total) touching small eutectic gallium indium drops (EGaIn) of work function 4.1 eV applied directly onto the H-terminated samples. The eutectic made an Ohmic contact on n-type samples and slightly rectified on p-type. The sheet resistance (R_s) was measured using a Keithley 2400 source meter and a four-probe in-line configuration (shown schematically in **Figure 6**) with 5-mm spacing between contacts. A constant current was sourced between the two outer probes and the voltage drop between two inner probes was sensed with high impedance to give the four-probe resistance, eliminating the contact resistance. In this geometry, the measured four-probe resistance was multiplied by a geometric factor of $f \approx 1.6$ – 1.9 to obtain the correct sheet resistance. Sheet resistances remained largely unchanged whether the substrate was grounded or allowed to float.

Complementary Hall voltages were measured in the four-probe Hall-bar geometry using two additional probes perpendicular to the current density along the sample width. Rare earth permanent magnets were used to source the magnetic field. The direction of the magnetic field was always reversed by rotating the permanent magnets 180° around the sample, so that the resulting difference between both readings ($2V_H$) effectively eliminated parasitic offset voltages. Hall-voltage and sheet-resistance measurements on several Si wafers with a range of doping densities were used to obtain an estimate of the apparent field strength at the sample.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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- [1] W. H. Brattain, J. Bardeen, *Bell Syst. Tech. J.* **1953**, 32, 1.
- [2] W. L. Brown, *Phys. Rev.* **1953**, 91, 518.
- [3] R. H. Kingston, *Phys. Rev.* **1954**, 93, 346.
- [4] R. H. Kingston, *Phys. Rev.* **1955**, 98, 1766.

- [5] A. A. Talin, L. L. Hunter, F. Leonard, B. Rokad, *Appl. Phys. Lett.* **2006**, *89*, 153102.
- [6] X. T. Zhou, J. Q. Hu, C. P. Li, D. D. D. Ma, C. S. Lee, S. T. Lee, *Chem. Phys. Lett.* **2003**, *369*, 220.
- [7] Y. L. Bunimovich, Y. S. Shin, W. S. Yeo, M. Amori, G. Kwong, J. R. Heath, *J. Am. Chem. Soc.* **2006**, *128*, 16323.
- [8] Y. Cui, Q. Wei, H. Park, C. M. Lieber, *Science* **2001**, *293*, 1289.
- [9] J. Hahn, C. M. Lieber, *Nano Lett.* **2004**, *4*, 51.
- [10] I. Park, Z. Li, X. Li, A. P. Pisano, R. S. Williams, *Biosens. Bioelectron.* **2007**, *22*, 2065.
- [11] E. Stern, J. F. Klemic, D. A. Routenberg, P. N. Wyrembak, D. B. Turner-Evans, A. D. Hamilton, D. A. LaVan, T. M. Fahmy, M. A. Reed, *Nature* **2007**, *445*, 519.
- [12] G. Zheng, F. Patolsky, Y. Cui, W. U. Wang, C. M. Lieber, *Nat. Biotechnol.* **2005**, *23*, 1294.
- [13] S. Q. Lud, M. G. Nikolaides, I. Haase, M. Fischer, A. R. Bausch, *ChemPhysChem* **2006**, *7*, 379.
- [14] P. A. Neff, A. Serr, B. K. Wunderlich, A. R. Bausch, *ChemPhysChem* **2007**, *8*, 2133.
- [15] P. A. Neff, B. K. Wunderlich, S. Q. Lud, A. R. Bausch, *Phys. Stat. Sol. A* **2006**, *203*, 3417.
- [16] M. G. Nikolaides, S. Rauschenbach, A. R. Bausch, *J. Appl. Phys.* **2004**, *95*, 3811.
- [17] T. He, J. He, M. Lu, B. Chen, H. Pang, W. F. Reus, W. M. Nolte, D. P. Nackashi, P. D. Franzon, J. M. Tour, *J. Am. Chem. Soc.* **2006**, *128*, 14537.
- [18] W. Henrion, M. Rebien, H. Angermann, A. Röseler, *Appl. Surf. Sci.* **2002**, *202*, 199.
- [19] G. Oskam, P. M. Hoffmann, P. C. Searson, *Phys. Rev. Lett.* **1996**, *76*, 1521.
- [20] E. Yablonovitch, D. L. Allara, C. C. Chang, T. Gmitter, T. B. Bright, *Phys. Rev. Lett.* **1986**, *57*, 249.
- [21] G. Dubey, G. P. Lopinski, F. Rosei, *Appl. Phys. Lett.* **2007**, *91*, 232111.
- [22] S. A. Scott, W. Peng, A. M. Kiefer, H. Jiang, I. Knezevic, D. E. Savage, M. A. Eriksson, M. G. Lagally, *ACS Nano* **2009**, *3*, 1683.
- [23] S. Cristoloveanu, *J. Electrochem. Soc.* **1991**, *138*, 3131.
- [24] S. Cristoloveanu, *Vacuum* **1991**, *42*, 371.
- [25] S. Cristoloveanu, S. S. Li, *Electrical Characterization of Silicon-on-Insulator Materials and Devices*, Kluwer, Boston, MA, USA **1995**.
- [26] S. Cristoloveanu, D. Munteanu, M. S. T. Liu, *IEEE Trans. Electron Devices* **2000**, *47*, 1018.
- [27] A. M. Ionescu, S. Cristoloveanu, D. Munteanu, T. Elewa, M. Gri, *Solid-State Electron.* **1996**, *39*, 1753.
- [28] Y. Shibata, M. Ichimura, E. Arai, *Solid-State Electron.* **2004**, *48*, 1249.
- [29] M. Ichimura, S. Ito, E. Arai, *Solid-State Electron.* **2002**, *46*, 545.
- [30] G. Mattei, V. Valentini, V. A. Yakovlev, *Surf. Sci.* **2002**, *502*, 58.
- [31] L. Osminkina, A. Vorontsov, E. Konstantinova, V. Timoshenko, P. Kashkarov, *Semiconductors* **2005**, *39*, 458.
- [32] G. S. Higashi, Y. J. Chabal, G. W. Trucks, K. Raghavachari, *Appl. Phys. Lett.* **1990**, *56*, 656.

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