APPLIED PHYSICS LETTERS **89**, 153102 (2006)

Large area, dense silicon nanowire array chemical sensors

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(Received 1 June 2006; accepted 21 August 2006; published online 9 October 2006)

The authors present a simple top-down approach based on nanoimprint lithography to create dense arrays of silicon nanowires over large areas. Metallic contacts to the nanowires and a bottom gate allow the operation of the array as a field-effect transistor with very large on/off ratios. When exposed to ammonia gas or cyclohexane solutions containing nitrobenzene or phenol, the threshold voltage of the field-effect transistor is shifted, a signature of charge transfer between the analytes and the nanowires. The threshold voltage shift is proportional to the Hammett parameter and the concentration of the nitrobenzene and phenol analytes. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2358214]

Nanowires have emerged as promising elements for chemical and biological sensing, with proof-of-principle devices demonstrated for detection of various gases,[1–3] *p*H in aqueous media,[4] antibody binding,[4] and DNA hybridization.[5] The high surface-to-volume ratio of nanowires results in a strong dependence of carrier concentration on charge transfer from the surface and changes in nanowire conductance. Silicon nanowires (SiNWs) are particularly appealing for sensing applications, since the Si oxide can effectively passivate surface dangling bonds, and at the same time can be chemically modified through the well known silanol chemistry to provide surface functionalization and, therefore, selectivity for particular analytes.

To date, most nanowire sensors were fabricated by a labor intensive sequence of steps that included NW synthesis and dispersion followed by direct-write lithography and metallization, resulting in one or a few selected specimens.[6] Top-down techniques based on electron beam lithography to define individual SiNWs on silicon-on-insulator (SOI) substrates have also been demonstrated.[7] Alternative approaches such as electric field directed deposition[8,9] or fluidic assembly[10] are promising, but still present challenges. Furthermore, synthesized NWs often exhibit a variation in diameter, which can introduce a spread in the electrical response of nanowires to analyte gases.[6,11]

Here, we demonstrate a simple, top-down technique based on nanoimprint lithography[12,13] (NIL) to define SiNWs over a large area and with high density and uniformity. We measure the transport and transistor characteristics of these NWs and demonstrate their application to chemical sensing using ammonia gas and liquid solutions of nitrobenzene and phenol in cyclohexane. The results indicate that the sensing mechanism is charge transfer between the analytes and the NWs and scales with the value of the Hammett parameter and the concentration of the organic solutions. Furthermore, we show that while the hole mobility for the SiNWs is essentially the same as for a thin film device, the sensing of the SiNWs is enhanced as a result of an increased surface- to-volume ratio and decreased capacitance.

Boron doped (10–20 Ω cm) SOI wafers with a 100 nm thick device layer and a 155 nm buried oxide layer were purchased from Silicon Quest Inc. One wafer was thermally imprinted using a Nanonex 2000 NIL tool[14] using a 200 nm dense pitch (100 nm line/space) Si grating mold, which iself was fabricated using laser interference lithography. The resulting pattern was transferred into the underlying SOI device layer using reactive ion etching with Cl_2/HBr plasma. Scanning electron Microscopy (SEM) images of the individually addressable Al electrodes over the SiNWs are shown in Figs. 1(a) and 1(b), while cross sections at 60° and 90° with respect to the plane of the figure are shown in Figs. 1(c) and 1(d). The SEM images clearly demonstrate the uniformity of the SiNWs, which have an average diameter of 76±5 nm with a LER of 5 nm.

To form source and drain contacts, arrays of interdigitated Al electrodes, 180 μm long and 4 μm apart, were defined over the SiNWs using optical lithography followed by electron beam evaporation and lift-off. Each Al electrode array consisted of 32 individually addressable, parallel contacts, with 900 SiNWs spanning the gap between any pair of electrodes. The metallized wafer was then annealed in vacuum at 450 °C for 20 min to render the Al contacts Ohmic and exposed to O_2 plasma to remove residual organics and ensure that the nanowire surface was clean and oxidized. Al contacts were similarly patterned and annealed on an additional SOI wafer from the same batch, but which was

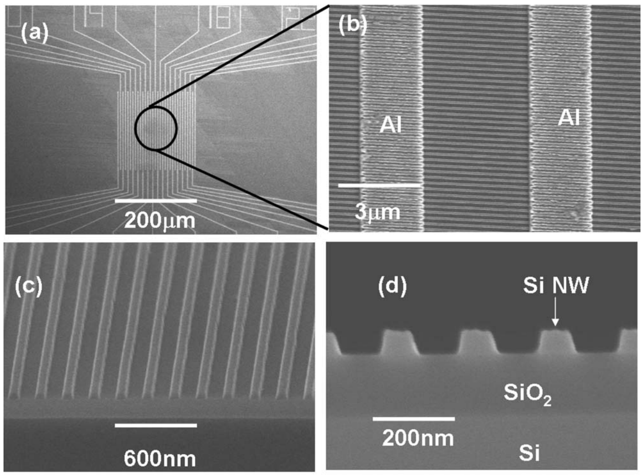

FIG. 1. Top-down image of one SiNW device showing the interdigitated Al source-drain electrodes. (b) Close-up image of SiNWs between two Al electrodes. [(c) and (d)] Cross section SEM images at 60° and 90° tilt.

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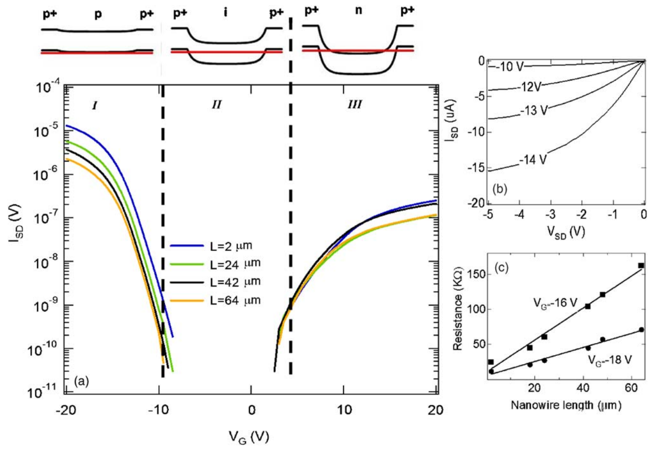

FIG. 2. (Color online) (a) I_{SD} vs V_g for one SiNW device collected for different Al electrode pairs with V_{SD} set at 0.1 V. (b) I_{SD} vs V_{SD} for the same SiNW device collected at different gate voltages. (c) Resistance of the nanowire array of (a) as a function of nanowire length.

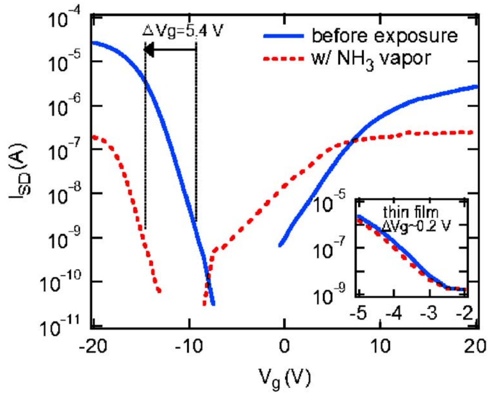

FIG. 3. (Color online) Variation in I_{SD} vs V_G for a SiNW array exposed to ammonia vapor. Inset shows response of SOI thin film device to similar exposure.

not patterned using NIL. For both the NW and thin film devices, the *p*-doped Si substrate of the SOI wafer was used as the gate, with an In Ohmic bottom contact.

A family of gate voltage sweeps, I_{SD}-V_g, collected at $V_{SD}=1.0$ V for different Al electrode pairs for a selected interdigitated array is shown in Fig. 2. The I_{SD}-V_g curves correspond to three regimes: hole accumulation (I), intrinsic or "off" (II), and electron accumulation (III), as indicated by the three band diagrams in the figure. (We believe that the contacts are heavily *p* doped as a result of Al diffusion during the contact formation process.) The I_{SD}-V_{SD} behavior of the device in the hole accumulation regime shows behavior similar to *p*-channel metal-oxide-semiconductors field-effect transistors, as indicated in Fig. 2(b).

Figure 2(c) plots the resistance of the device of Fig. 2(a) as a function of nanowire length (i.e., for different pairs of electrodes) in the hole accumulation regime, indicating that the resistance scales linearly with nanowire length, and thus that the transport is diffusive. Analysis of the I_{SD}-V_g characteristics using a standard transistor diffusion model gives a mobility of 81 $\text{cm}^2/\text{V s}$, where an expression for the capacitance which accounts for the NW array geometry was used.[15] Similar analysis for the thin film device yields a mobility of 78 $\text{cm}^2/\text{V s}$. While these mobilities are lower than those typically reported for *p*-channel SOI transistors, there is no significant degradation for the nanowire cross sections used here.

To explore the chemical sensing characteristics of the NIL-based SiNWs we first tested the device sensitivity to ammonia vapor.[16] Ammonia is a strong reducing agent and its effect on carbon nanotube transistors is to make the threshold voltage more negative.[17] Figure 3 indicates that similar behavior is observed for our SiNW sensors, where the I_{SD}-V_g curves are shifted to the left by 5.4 V. Also shown in Fig. 3, as an inset, is the response for the thin film device, which shows a much smaller shift.

The enhanced response of the SiNWs can be understood by considering the charge in the channel with and without analytes, $env=AC(V_t-V_g)$ and $env+e\alpha a^{-1}\theta s=AC(V_t'-V_g)$, where n is the number of carriers per unit volume, a is the area that a molecule occupies on the surface, $e\alpha$ is the charge transferred per molecule, θ is the surface coverage, C is the capacitance per unit area, V_t is the threshold voltage, A is the device footprint area, and s is the area exposed to analytes [equal to $(2t+w)ML$ for M nanowires of length L and equal to A for the thin film]. Subtracting these two equations we get an expression for the shift in threshold voltage

$$\Delta V_t = e\alpha a^{-1}\theta C^{-1}(s/A). \tag{1}$$

From a simple space filling argument, one may expect that the capacitance will be proportional to $(l+\kappa w)/(l+w)$, where l is the separation between nanowires and κ is the gate oxide relative dielectric constant. The shift in threshold voltage then becomes

$$\Delta V_t \propto (2t+w)/(l+\kappa w), \tag{2}$$

where the thin film limit is given by $w\to\infty$. Equation (2) shows that larger sensitivity can be reached with small l or w, highlighting the need for dense arrays of small diameter nanowires. We note that the benefit of using small diameter nanowires is only realized when $2t/l > 1/\kappa$. For our SiNW device the s/A ratio is essentially unchanged from the thin film device, indicating that it is the lower capacitance (×0.5) for the SiNW array which is responsible for the increased sensitivity by a factor of ~2. Another factor that may contribute to further increase in the sensitivity of the NW device, as observed experimentally, is the LER, which gives a larger s/A ratio and additional binding sites for the analytes created by the reactive ion etch.

To explore the sensing characteristics of the SiNWs in a more quantitative manner, we measured the effect of different concentrations of nitrobenzene and phenol in cyclohexane solutions on the device electrical characteristics. Nitrobenzene and phenol are electron withdrawing and electron donating molecules, respectively, and their solution in cyclohexane has previously been used to change the I_{SD}-V_g characteristics of carbon nanotube transistors.[18] Solutions of nitrobenzene and phenol in cyclohexane with concentrations ranging from 0.001*M* to 0.25*M* were applied using a micropipette directly over one of the SiNW devices, while I_{SD}-V_g curves were measured just before and just after the solution application. The resulting curves for one of the concentrations of each chemical are shown in Fig. 4, where it can be seen that the increase (decrease) in I_{SD} is consistent with the electron withdrawing (donating) character of nitrobenzene (phenol), as it effectively dopes the SiNWs *p* type (*n* type). This is further highlighted in Fig. 4(b)(inset), where the change in gate bias corresponding to I_{SD} of 1 nA is

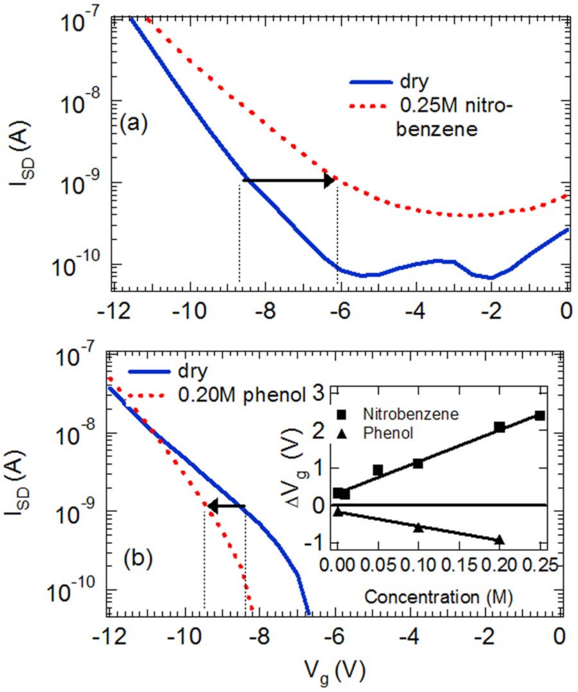

FIG. 4. (Color online) Variation in I_{SD} vs V_G for (a) $0.25M$ of nitrobenzene and (b) $0.2M$ of phenol, dissolved in cyclohexane and applied directly over the SiNW array sensor. Inset shows shift in V_G necessary to maintain $I_{SD} = 1$ nA in accumulation mode as a function of the solute concentration.

plotted as a function of the concentration, indicating a linear behavior. Note that no measurable shift for the thin film device was observed when exposed to similar concentrations of nitrobenzene.

We now consider the adsorption of the molecules on the nanowire surface with the goal of extracting the binding energy. To relate θ to the analyte concentration in the liquid, we consider equilibrium between the liquid and the surface, with the partition function[19]

$$Z = 1 + z_{\mathrm{vib}} e^{(\mu - E_b)/kT}, \tag{3}$$

where μ is the chemical potential of the analyte in the liquid, E_b is the binding energy of the molecule to the surface, and z_{vib} is the contribution to the partition function due to vibrations. The chemical potential is $\mu = \mu_0 + kT \ln x$, where μ_0 is the chemical potential of the pure substance and x is the mole fraction. For a pure substance $\mu_0 = \Delta H_f - TS$, where ΔH_f is the enthalpy of formation and S is the entropy.

Assuming that the mole fraction of the solute is much less than the solvent, we obtain the equilibrium surface coverage as a function of the solute concentration

$$\theta = c/(c + c_0), \tag{4}$$

where

$$c_0 = \bar{c} z_{\mathrm{vib}}^{-1} e^{-\mu_0/kT} e^{E_b/kT}, \tag{5}$$

with $\bar{c}$ the solvent concentration. For $c \ll c_0$, Eqs. (1) and (4) give

$$\Delta V_g = (2t + w) L e \alpha a^{-1} C^{-1} (c/c_0). \tag{6}$$

A least-squares fit to the data of Fig. 4(inset) for nitrobenzene gives a value for the prefactor of 8.47 ± 0.53 V/M. Using Eqs. (5) and (6), a value of μ_0 of -0.56 eV, and assuming $\alpha = 1$ and $z_{\mathrm{vib}} = 1$ we obtain a value for the binding energy of 440 meV. This value indicates strong physisorption of the nitrobenzene on the NW surface. The fact that $E_b \gg kT$ explains why our devices are very stable once exposed to the analytes. But just as important, the binding energy is much less than chemisorption binding energies, and thus provides the opportunity to refresh the device, as our simple pure cyclohexane rinse has demonstrated. From these calculations, we estimate the density of molecules on the NW surface at $0.25M$ to be 0.3 molecules/nm/NW. This small density is consistent with the linear behavior of Fig. 4.

Previous work on the sensing properties of carbon nanotubes[18] has shown that the voltage shift is proportional to the Hammett parameter σ_p. For nitrobenzene, $\sigma_p = 0.78$ while for phenol $\sigma_p = -0.4$; the ratio ~ -2 is in reasonable agreement with the ratio of the slopes from Fig. 4 equal to -2.4.

In summary, a top-down approach based on nanoimprint lithography is demonstrated to deliver high fidelity, dense arrays of silicon nanowires over large areas. When used as a transistor channel, the nanowire array is sensitive to solutions of analytes, with the response proportional to the Hammett parameter and the concentration of the analytes.

The authors thank Blake Simmons for technical help and Paul Dentinger for useful discussions. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract No. DE-AC04-94-AL85000.

[1] Y. Xia, P. Yang, Y. Sun, Y. Wu, B. Mayers, B. Gates, Y. Yin, F. Kim, and H. Yan, Adv. Mater. (Weinheim, Ger.) **15**, 353 (2003).
[2] Z. Fan and J. G. Lu, Appl. Phys. Lett. **86**, 123510 (2005).
[3] E. Comini, G. Faglia, G. Sberveglier, Z. Pan, and Z. L. Wang, Appl. Phys. Lett. **81**, 1869 (2003).
[4] Y. Cui, Z. Wei, H. Park, and C. M. Lieber, Science **293**, 1289 (2001).
[5] Z. Li, Y. Chen, X. Li, T. I. Kamins, K. Nauka, and R. S. Williams, Nano Lett. **4**, 245 (2004).
[6] Y. Cui, X. Duan, Y. Huang, and C. M. Lieber, in *Nanowires and Nanobelts Materials, Properties, and Devices*, Metal and Semiconductor Nanowires, Vol. 1, edited by Z. L. Wang (Kluwer, Boston, 2003), p. 26.
[7] S.-M. Koo, M. D. Edelstein, Q. Li, C. A. Richter, and E. M. Vogel, Nanotechnology **16**, 1482 (2005).
[8] F. Léonard, F. E. Jones, A. A. Talin, and P. M. Dentinger, Appl. Phys. Lett. **86**, 093112 (2005).
[9] C. S. Lao, J. Liu, P. Gao, L. Zhang, D. Davidovic, R. Tummala, and Z. L. Wang, Nano Lett. **6**, 263 (2006).
[10] F. Patolsky and C. M. Lieber, Mater. Today **8**, 20 (2005).
[11] Y. Cui, L. J. Lauhon, M. S. Gudiksen, J. Wang, and C. M. Lieber, Appl. Phys. Lett. **78**, 2214 (2001).
[12] S. Y. Chou, P. R. Krauss, W. Zhang, L. J. Guo, and L. Zhuang, J. Vac. Sci. Technol. B **15**, 2897 (1997).
[13] S. Y. Chou, in *Alternative Lithography*, edited by T. S. Sotomayor (Kluwer, Boston, 2003), pp. 15–23.
[14] G. Y. Jung, W. Wu, N. Ganapathiappan, D. A. A. Ohlberg, M. S. Islam, X. Li, D. L. Olynick, H. Lee, Y. Chen, S. Y. Wang, W. M. Tong, and R. S. Williams, Appl. Phys. A: Mater. Sci. Process. **81**, 1331 (2005).
[15] We used the expression for the total capacitance per NW $C = 2\pi\varepsilon_0 \kappa L / \lfloor 2\Sigma_{n=1}^{M/2} \ln(\sqrt{h^2 + n^2 l^2}/nl) + \ln(4h/w) \rfloor$, derived from the electrostatic potential of an array of cylindrical nanowires of diameter w embedded in the dielectric, and at a distance h from a conducting plate.
[16] A small cotton applicator stick was soaked in $8M$ ammonium hydroxide solution and placed several inches from a SiNW array under test.
[17] K. Bradley, J.-C. Gabriel, M. Briman, A. Star, and G. Gruner, Phys. Rev. Lett. **91**, 218301 (2003).
[18] A. Star, T.-R. Han, J.-C. P. Gabriel, K. Bradley, and G. Gruner, Nano Lett. **3**, 1421 (2003).
[19] J. M. Blakeley and J. C. Shelton, in *Surface Physics of Materials*, edited by J. M. Blakeley (Academic, New York, 1975). Vol. 9, p. 208.