Influence of Minority Carrier Gas Donors on Low-Frequency Noise in Silicon Nanowires

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***Abstract*—The interaction of gases such as NH_3 and NO_2 with the surface of core/shell Si/SiO_2 nanowires has been shown to influence their electrical conductivity because NH_3 and NO_2 are electron and hole donors, respectively. Using arrays of n- and p-type Si nanowires, we demonstrate that their influence on the low-frequency noise characteristics of the nanowires is largest when the donors are minority carriers. The impact of NO_2 and NH_3 on 1/*f* noise of p- and n-type nanowires, respectively, is limited. However, 1/*f* noise increases in n-Si nanowires under influence of NO_2 while it decreases in p-Si nanowires for NH_3. This effect is attributed to oxygen vacancies in the SiO_2 and the presence or absence of holes, h^+ in the humid gas environment. In addition, gas molecule adsorption in a humid atmosphere influences the pH and thus the surface charge density on the SiO_2 shell, causing changes in the low-frequency noise level via electrostatic interactions.**

***Index Terms*—Gas sensing, low-frequency noise, nanowire (NW), silicon.**

I. INTRODUCTION

SI NANOWIRES (NWs) are being used in a multitude of electronic applications covering field-effect transistors (FETs), photovoltaics, thermoelectrics, sensors, etc. Their desirability lies in the ubiquitous character of Si, its stable oxide, and their large surface to bulk ratio which translates small changes in the condition of the surface into variation of the carrier transport in the bulk. Conductance variations of bare and functionalized Si NWs in response to inorganic gases such as NO_2 and NH_3 have been reported in the literature. A recent overview of different approaches can be found in [1] and the references therein. The two main approaches in which Si NWs are used as sensors are in resistive mode or in a FET configuration. The sensing principle in both cases is based on the electron donating or withdrawing character of adsorbed NH_3 and NO_2 molecules, respectively, on the surface of the NWs. While FETs tend to increase the sensitivity of the sensors due to the voltage amplification offered by the gate, the resistive structures are often easier to fabricate. An example of a resistive sensor based on a Si nanowire array (NWA) can be found in [2]. In this case, an ordered array of vertically upstanding p-type Si NWs with a diameter of $\sim$200 nm and length of 4–6 μm is fabricated with a porous top contact to allow easy access of the molecules to the NWs. Highly sensitive resistive detection was achieved in a humid atmosphere on p-type NWAs for NH_3 and NO_2, confirming the electron and hole donor effect, respectively, of both gases. Recently, low-frequency noise (1/*f* noise) is being used as a tool to support the detection of specific molecules in the ambient [3], [4], [16]. Although noise is normally regarded as disrupting the measurement accuracy, 1/*f* noise is very sensitive to the surface states and can thus potentially be used as a detection parameter.

The SiO_2 layer around the Si NW core contains oxygen vacancies which, under normal circumstances, behave as neutral traps with a large electron capture cross section [5]. H_2O diffuses into the oxide and can change the trap density [6] and thus 1/*f* response. As a consequence, 1/*f* noise will respond to the interaction of the SiO_2 with the environment. The level of the 1/*f* noise is influenced not only by the traps, but also by the majority carrier type in the wires, as well as the ambient in which the measurement is carried out. In [7], it is shown that NH_3 has a passivating influence on the 1/*f* noise in p- and n-type Si NWAs. Another aspect of measurements carried out in a humid ambient is the interaction of the gas species with H_2O. NH_3 in a humid environment will produce the alkaline NH_4OH, while NO_2 and H_2O near a SiO_2 surface produce the acid HNO_3 [8]. Thus, the pH of the ambient surrounding the Si/SiO_2 core/shell NWs will be higher and lower than that of H_2O, respectively. The density of the positive surface charges on SiO_2 nanostructures is determined by the value of the pH and decreases with decreasing pH [9].

To summarize, three aspects play a role in the sensing of NH_3 and NO_2 molecules when using bare Si/SiO_2 core/shell NWs in a humid environment: the oxygen vacancies and their interaction with the molecules, the electron/hole donating character of the gases, and the pH of the surrounding which determines the density of surface charges.

In this study, we present the results of 1/*f* noise measurements on n- and p-type Si NWAs in the presence of NH_3 and NO_2 in a humid atmosphere. We find that the open-circuit voltage noise power spectral density (PSD), S_V is mostly influenced by the gas that donates the minority carrier type to the core/shell structure. This feature, together with the different reactions of the SiO_2 with H_2O in the presence or absence of holes, determines the direction of the variation of the noise amplitude.

II. SAMPLE PREPARATION AND SETUP

The Si NWAs are fabricated using metal-assisted electroless etching (MACE) [10], [17] on Si (100) substrates. Silicon

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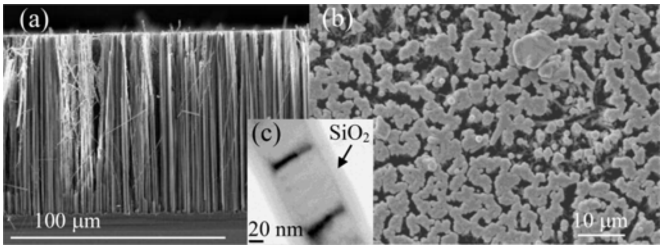

Fig. 1. (a) SEM image of the cross section of an array of Si NWs. (b) SEM image of the top of a metallized NWA. (c) TEM image of an 80 nm NW wrapped with SiO_2.

wafers with resistivity of 1–10 $\Omega \cdot$ cm were used in the experiments. Two wafers are attached to each other with polymethyl methacrylate (PMMA) to protect one surface of the samples from etching. The outer surface of each wafer is etched during the subsequent MACE process. After cleaning the sample in isopropanol and deionized water, it is immersed in a solution of 0.03 M $AgNO_3$ and 5.6 M HF. An oxidizing agent can be added. In this case, etching is accelerated using nitrate ions. This process creates vertically aligned Si NWAs of crystalline character that are wrapped by a thin SiO_2 layer. Following NW etching, residual Ag particles are removed using a concentrated (5 M) solution of HNO_3. Finally, the intermediate PMMA layer is removed in acetone, separating the two Si wafers. The NWAs are dipped briefly in buffered HF to remove the oxide on top of the wires and rinsed in DI water. Contacts are defined on the NWAs, using a sputtered ~50/500 nm Cr/Au layer on p-type Si-NWAs and an ~500–nm-thick Al layer on n-type Si-NWAs. Rapid thermal annealing in Ar ambient at 450 °C is used to improve the contact characteristics. SEM/TEM images of an NWA are given in Fig. 1.

The length of the NWs is determined by the etch time and temperature. In Fig. 1(a), the NW length is approximately 75 μm. A distribution of wire diameters exist, between 50 and 250 nm in our process. Fig. 1(c) shows one NW with a diameter of ~80 nm and a ~5 nm SiO_2 wrapping. High-resolution TEM has shown that these wires are crystalline. Due to the wet chemical etch and the elasticity of the wires, surface tension will cause the tops of the NWs to bundle together [11]. After metallization, this discontinuity remains in the metal contact [see Fig. 1(b)]. The NWs in the array cluster in approximately 5–10 μm bundles with gaps of the same order of magnitude. The disadvantage of a noncontinuous Ohmic contact is the sensitivity of the current amplitude on probe position. The advantage, however, is the easier path for the gases to reach the NW surfaces. Sputtering is done with the samples under a 45° angle. There is no shorting of the NWs via the deposited metal. This has been confirmed by EDS, SEM, and current–voltage measurements. Fig. 2 gives the SEM cross section at three positions along the NWA, from top to bottom, for both the Cr/Au as well as the Al contact. Some Al particles can be found along the length of the wires. None have been identified for the Cr/Au deposition.

Low-frequency noise is measured using a dedicated home-made closed cylindrical container with a volume of $V \approx 3$ cm^3 (see Fig. 3). Contacts to the NWA are made with a 3 mm diameter spring-loaded Au top probe and a Cu back plate. The NWAs are biased using a battery powered circuit. Noise data are obtained in a frequency range from 1 Hz to 100 kHz at 300 K for the NWA under a constant bias of 1 V. Background noise is measured using the zero-biased sample and subtracted from the total device noise. The voltage fluctuations S_V from the load resistor R_L connected in series with the NWA are analyzed using an SR770 fast Fourier transform spectrum analyzer. The voltage across the NWA and R_L is measured using a battery-powered Agilent U1242B digital multimeter which has a precision of $\pm 0.09\%$. The current is then calculated from the ratio of the voltage and R_L. The gases were supplied via a 40 cm long, 5 mm diameter plastic tube from an evaporating liquid pool, with a volume of ~1.6 cm^3, into the measurement chamber. The complete setup is placed in an electromagnetic shield.

Two different ambient environments are investigated, NH_3 and NO_2 in air with a relative humidity of ~70%. The humidity was measured using a pen type humidity and temperature meter from IDT. The temperature and humidity were not controlled during the measurements, but were recorded before each experiment, showing a fluctuation of less than 7%. The adsorption of NH_3 was investigated by filling ½ of the glass flask with 28% NH_4OH (ammonium hydroxide), generating ~16 μmol NH_3 based on the ideal gas law. When vapor pressure is reached in the glass flask, NH_3 (ammonia) evaporates readily from the NH_4OH pool [12] and then diffuses through the narrow tube to the probe chamber. In order to obtain NO_2 gas (nitrogen dioxide), 1 mg of Cu shaving is supplied to the glass flask. With all

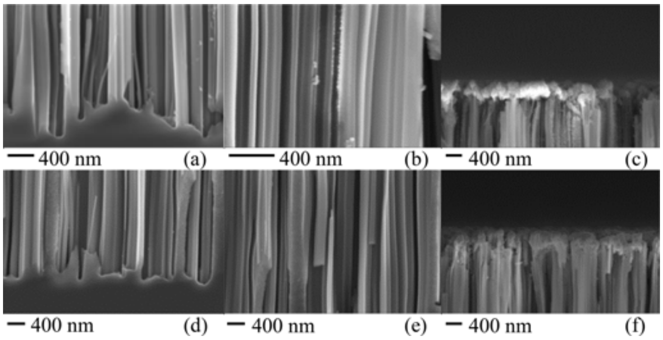

Fig. 2. SEM images of the cross section of metallized arrays of Si NWs. Left to right: bottom, middle, and top of the metallized NWA. (a)–(c) Al contact. (d)–(f) Cr/Au contact.

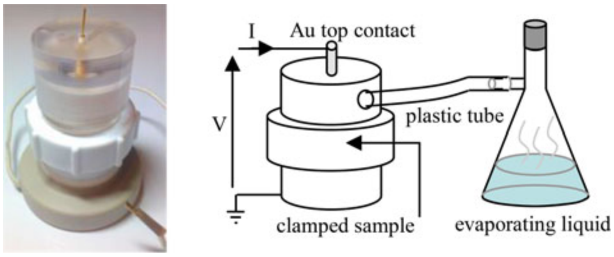

Fig. 3. Left: picture of the cylindrical container. Right: schematic of the closed NWA probing chamber and gas supply setup including the glass flask with evaporating liquid.

TABLE I
CHANGES IN CURRENT AS A FUNCTION OF GAS ADSORPTION FOR THE NWA SAMPLES UNDER 1 V BIAS

Sample	$I_{\mathrm{p-NWA}}$ (A)	$I_{\mathrm{n-NWA}}$ (A)
NH_3	$4.3\ 10^{-4} \rightarrow 3.9\ 10^{-4}$	$2.5\ 10^{-4} \rightarrow 5.2\ 10^{-4}$
NO_2	$5.7\ 10^{-3} \rightarrow 5.8\ 10^{-3}$	$4.4\ 10^{-4} \rightarrow 8.9\ 10^{-5}$

The arrow indicates the variation of the current after the introduction of the gas.

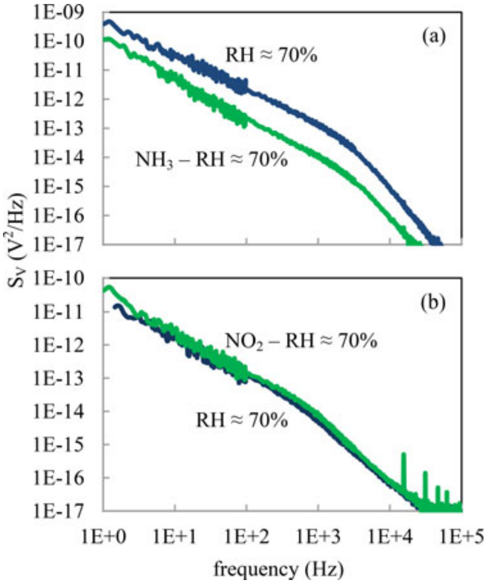

Fig. 4. Low-frequency noise spectral density of p-type Si NWA. Response to (a) NH_3 and (b) NO_2.

connections in place, 0.5 mL of nitric acid, HNO_3 is added to the flask onto the metal shavings. 0.5 mL HNO_3 gives ~0.25 mL NO_2 based on the reaction: Cu + 4 HNO_3 $\leftrightarrow$ $Cu(NO_3)_2$ + 2 NO_2 + 2 H_2O. Thus, ~11 μmol NO_2 is produced based on the ideal gas law. NO_2 then diffuses to the probe chamber. This results in a small supply of NO_2 into the sample casing, as can be observed from the color gradient of the diffusing gas through the plastic tube. The reactions were carried out at room temperature. The quantitative value of the volume of gases in the sample container was not recorded. However, the volumes of the reacting chemicals used were the same for both n- and p-type NWA measurements.

III. RESULTS AND DISCUSSION

Low-frequency noise and current measurements were taken on both n- and p-type Si NWAs in different ambient environments, at room temperature. The sample area is approximately 1 cm × 1 cm. The current of the p-type NWA decreases in NH_3 and increases in NO_2, while the opposite current changes occur for the n-type samples, consistent with [1] and [7]. The current variation under constant voltage of 1 V is given in Table I.

For the noise measurements, the samples were biased at a constant voltage of $V = 1$ V. The results for S_V as a function of frequency f on a log–log plot are given in Figs. 4 and 5.

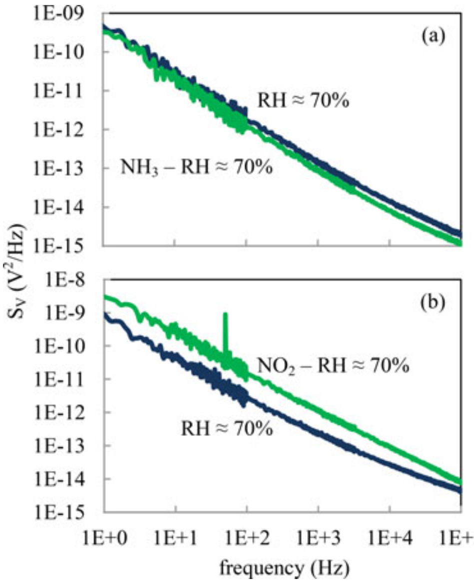

Fig. 5. Low-frequency noise spectral density of n-type Si NWA. Response to (a) NH_3 and (b) NO_2.

The p-type Si NWAs have a generation-recombination (GR) center [see Fig. 4(a) and (b)] around 10^3 Hz. The GR center is independent of the gases adsorbing on the surface of the NWs as there is no shift in the frequency of the trap center. Thus, the GR center is due to the core of the NW and the 1/*f* noise response to the gases is due to SiO_2 related interactions. Two different p-NWA samples are being used in these measurements, both fabricated from the same substrate.

The PSD of the n-type Si NWAs [see Fig. 5(a) and (b)] follows a $1/f^\gamma$ plot with $\gamma \approx 1$.

The measurements show a large reduction in noise for the p-NWA under influence of NH_3, while only a small increase is observed for NO_2. The opposite happens for the n-NWA. Limited S_V decrease is happening under influence of NH_3, while a large increase is observed for NO_2. All responses are reversible. When leaving the NWAs in air overnight, the noise characteristics measured in air are reestablished. In [5], the samples' conductance response time to NH_3 was measured to be of the order of ~2 min. However, recovering the 1/*f* noise characteristics in air can take up to 5 h due to the presence of slow traps.

In order to understand the 1/*f* noise spectra, we first consider diffusion of H_2O into the oxide and the influence of the availability of holes, h^+. Diffusion of H_2O into the oxide causes some of the $O_3{\equiv}Si–O–Si{\equiv}O_3$ bonds to break, making –OH sites: $O_3{\equiv}Si–OH$ [13]. These bonds are quite strong. However, when a hole h^+ is present, these can break the OH groups and reform the Si–O–Si bridges [5] or leave $O_3{\equiv}Si–O\cdot$ bonds [14]. This defect is neutral but has a large electron trap cross section. This process is associated with a release of H^+. H^+ can easily diffuse in the SiO_2 toward the Si/SiO_2 interface and increase the number of trapping centers. It is clear that the presence or absence of h^+ has an impact on the trap density both in the SiO_2 as well as at the Si/SiO_2 interface and thus will influence the 1/*f* PSD. We use this feature, together with the donating effect of

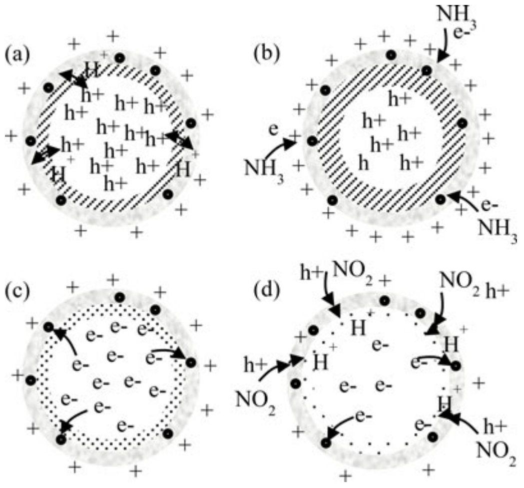

Fig. 6. Cross section of an NW. (a) p-NW in a humid environment. (b) p-NW in a NH_3 environment. (c) n-NW in a humid environment. (d) n-NW in a NO_2 environment. h+ holes, e– electrons, + positive surface charges, H+ ionized hydrogen atom, arrows indicate diffusion, black dots are oxygen vacancies, hatched areas: depletion region and dotted area: inversion region.

the gases and the pH of the environment to explain the differences in the response of the n- and p-type NWA. A schematic presentation of the processes is given in Fig. 6. It gives the cross section of an NW with surface charges, majority carrier type, molecule exchange around and in the SiO_2 and enhancement or depletion regions. A single arrow implies carrier donation, while a double arrow means carrier donation followed by H^+ generation and diffusion.

Fig. 6(a) and (c) gives the charge situation for p- and n-type NWs in a humid environment, respectively. The surface charge is positive with a concentration determined by the pH of the humid environment, assumed to be ~7. In the case of p-NWs, this will repel majority carriers from the Si/SiO_2 surface while e^- will be attracted to the surface in the n-type wires. This implies depletion and enhancement, respectively, of majority carriers in a humid environment unless the H_2O layer near the surface allows hopping conduction along the SiO_2 surface [4]. From a point of view of 1/*f* noise, the majority carrier holes h^+ from the core will react with the Si–OH bonds in the SiO_2 to release H^+, causing an increased trap density near the Si/SiO_2 surface and thus form a 1/*f* noise source in the p-type NWs. For the n-type NWs, the large number of electrons available in the core can be trapped by the oxygen vacancies and create 1/*f* noise. It is interesting to see how this picture changes when minority carrier donor molecules are adsorbed on the surface of the NWs. When NH_3 is released near a SiO_2 surface in a humid environment, the environment becomes more alkaline. As a result, the density of positive surface charges is increasing [see Fig. 6(b)]. This implies that the electrostatic repulsion decreases for the h^+ charges in the core, decreasing the current and keeping the free carriers further removed from the trap centers near the Si/SiO_2 surface. This then decreases the availability of h^+ to generate H^+ within the oxide, reducing the trap density at the Si/SiO_2 compared to Fig. 6(a). At the same time, the electron donor character of the NH_3 will decrease the number of available unpopulated oxide traps. This combination of processes leads to a decrease in overall density of trap centers and thus 1/*f* noise.

For the n-type NW, introducing NO_2 in the humid system will lead to a more acid environment, causing a decreased density of positive surface charges [see Fig. 6(d)]. The attractive force between surface charge and the majority carriers in the core decreases. This decreases the carrier enhancement near the Si/SiO_2 surface and thus lowers the current. Although the number of electrons available in the vicinity of the oxide traps decreases, NO_2 is a hole donor. This changes the picture of interactions happening in the SiO_2. The donation of h^+ to the oxide in a humid environment leads to the formation of H^+ which will diffuse to the Si/SiO_2 surface and increase the density of traps there. In addition, it also increases the oxygen vacancies density. This tends to cause an overall increase in trap density and an increase in the 1/*f* noise in the n-type NWs.

Introducing gases that donate majority carriers do not seem to change the picture as given in the H_2O environment. When a gas is introduced that donates majority carriers, two effects happen. Due to the change in surface charge, the majority carrier concentration increases in both cases, increasing the current. Thus in principle, based on McWorther's carrier number fluctuation model [15], more carriers would be available for trapping. However, for n-NWs, the e^- donation by NH_3 helps passivate the oxide vacancies, lowering the active trapping centers for the majority carriers in the core. For p-NWs, the reduction in surface charge allows the diffusion of H^+ toward the SiO_2/air interface rather than the SiO_2/Si interface thus limiting the trap creation at this surface which has an impact on the majority carriers in the core. We notice that the overall effect is only a slight increase in noise for NO_2 and reduction for NH_3.

IV. CONCLUSION

Noise is shown to be an additional parameter to investigate the adsorption of gases such as NO_2 and NH_3 on the surface of an array of Si NWs. Experiments confirm that NO_2 increases the current in n-type NWs and decreases it in p-type NWs. The opposite current change happens for NH_3. We associate the current change to the change in pH in the humid environment surrounding the Si/SiO_2 core/shell structures because pH changes the surface charge density. The measurements show that the change in the 1/*f* noise, given by the open-circuit voltage noise PSD, S_V, changes mostly in the case the gases are donating minority carriers. This is explained by a combination of different concurrent processes that include pH variations, depletion of majority carriers, and the availability or absence of h^+ which influences trap generation.

REFERENCES

[1] A. Cao, E. J. R. Sudhölter, and L. C. P. M. de Smet, "Silicon nanowire-based devices for gas-phase sensing," *Sensors*, vol. 14, pp. 245–271, 2014.
[2] H. J. In, C. R. Field, and P. E. Pehrsson, "Periodically porous top electrodes on vertical nanowire arrays for highly sensitive gas detection," *Nanotechnology*, vol. 22, pp. 355501–355506, 2011.
[3] Q. Guo, T. Kong, R. Su, Q. Zhang, and G. Cheng, "Noise spectroscopy as an equilibrium analysis tool for highly sensitive electrical biosensing," *Appl. Phys. Lett.*, vol. 101, no. 9, pp. 093704-1–093704-5, 2012.

[4] K. Fobelets, M. M. Ahmad, S. Rumyantsev, and M. S. Shur, "Influence of ambient on conductivity and 1/*f* noise in Si nanowire arrays" presented at the *International Conference on Noise and Fluctuations*, Montpellier, France, Jun. 23–28, 2013.

[5] I. G. Batyrev, M. P. Rodgers, D. M. Fleetwood, R. D. Schrimpf, and S. T. Pantelides, "Effects of water on the aging and radiation response of MOS device," *IEEE Trans. Nucl. Sci.*, vol. 53, no. 6, pp. 3629–3635, Dec. 2006.

[6] K. R. McIntosh and X. Dai, "Damp-heat degradation and repair of oxide-passivated silicon," *Phys. Status Solidi A*, vol. 208, no. 8, 1931–1936, 2011.

[7] C. Li, E. Krali, K. Fobelets, B. Cheng, and Q. Wang, "Conductance modulation of Si nanowire arrays," *Appl. Phys. Lett.*, vol. 101, no. 22, pp. 222101-1–222101-3, 2012.

[8] A. L. Goodman, G. M. Underwood, and V. H. Grassian, "Heterogeneous reaction of NO_2: Characterization of gas-phase and adsorbed products from the reaction, $2NO_2(g) + H_2O(a) \rightarrow HONO(g) + HNO_3(a)$ on hydrated silica particles," *J. Phys. Chem. A*, vol. 103, pp. 7217–7223, 1999.

[9] K. W. Goyne, A. R. Zimmerman, B. L. Newalkar, S. Komarneni, S. L. Brantley, and J. Chorover, "Surface charge of variable porosity $Al_2O_3(s)$ and $SiO_2(s)$ adsorbents," *J. Porous Mater.*, vol. 9, pp. 243–256, 2002.

[10] K. Peng, J. Hu, Y. Yan, Y. Wu, H. Fang, Y. Xu, S. Lee, and J. Zhu, "Fabrication of single-crystalline silicon nanowires by scratching a silicon surface with catalytic metal particles," *Adv. Funct. Mater.*, vol. 16, no. 3, pp. 387–394, 2006.

[11] C. B. Li, K. Fobelets, M. S. Tymieniecki, M. Hamayun, Z. A. K. Durrani, and M. Green, "Bunch-free electroless-etched Si nanowire array," *ECS Trans.*, vol. 33, pp. 9–13, 2010.

[12] J. Nordin, *The First Responder—Technically Speaking*, vol. 6, no. 10, 2006.

[13] K. L. Brower, "Electron paramagnetic resonance studies of Si-SiO_2 interface defects," *Semicond. Sci. Technol.*, vol. 4, pp. 970–979, 1989.

[14] G. Dubey, G. P. Lopinski, and F. Rosei, "Influence of physisorbed water on the conductivity of hydrogen terminated silicon-on-insulator surfaces," *Appl. Phys. Lett.*, vol. 91, pp. 232111-1–232111-3, 2007.

[15] A. L. McWhorter, "1/*f* noise and germanium surface properties," in *Semiconductor Surface Physics*. Philadelphia, PA, USA: Univ. Pennsylvania Press, 1957, pp. 207–228.

[16] K. Fobelets, M. Meghani, and M. M. Ahmad, "Conductance and low frequency noise in Si nanowire arrays for gas sensing," presented at the *39th International Conference on Micro and Nano Engineering*, London, U.K., Sep. 16–19, 2013.

[17] Y. Q. Qu, L. Liao, Y. J. Li, H. Zhang, Y. Huang, and X. F. Duan, "Electrically conductive and optically active porous silicon nanowires," *Nano Lett.*, vol. 9, no. 12, pp. 4539–4543, 2009.

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