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Disorder Dominated Microwave Conductance Spectra of Doped Silicon Nanowire Arrays

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ABSTRACT

Conductance spectra of doped silicon nanowire (SiNW) arrays were measured from 0.5 to 50 GHz at temperatures between 4 and 293 K. For arrays consisting of 11 to >10^4 SiNWs, the conductance was found to increase with frequency as f^s, with $0.25 < s < 0.45$, consistent with behavior found universally in disordered systems. A possible cause is disorder from Si/SiO_x interface states dominating the conductance due to the high surface-to-volume ratio of the nanowires.

Modern nanomaterials such as semiconductor nanowires are thought to have novel electrodynamic properties that are relevant to both fundamental nanomaterial physics and applications in high-speed electronics and sensors. For example, recent reports of dc ballistic transport characteristics in Ge/Si and InAs nanowires[1–3] suggest that such materials may have extremely fast, very low dissipation microwave response beyond the limit of conventional Drude transport. The sensitivity of the dc electrical properties of various nanowires to molecules adsorbed on their surfaces[4–7] also raises the question of whether similar ac conductance changes exist and can be exploited for chemical sensor purposes. Although there exists a large body of research on nanowire dc electrical properties, as well as attempts to prototype potential high-frequency nanowire devices,[2,8,9] relatively little is known about the fundamental microwave electrodynamic response of nanowires. One reason for this is that an individual nanowire presents a very small cross section to the microwave field, which often prevents sufficient electrical coupling to produce a signal above the instrumental background. Additionally, as in dc contacted measurements, separating the effects of the coupling from the intrinsic nanowire response is difficult.

To circumvent this limitation, we have measured the broadband microwave conductance spectra of arrays consisting of 11 to >10^4 silicon nanowires (SiNWs). By using a relatively large number of SiNWs, excellent signal levels were achieved and, because of the SiNW insulating oxide surface, the ac coupling was simply capacitive. These features allowed us to accurately measure the conductance spectra of the SiNW arrays across a broad frequency range of 0.5−50 GHz. The complex ac conductance of the SiNW arrays exhibited a sublinear power law increase with frequency that is consistent with behavior observed universally in disordered electronic systems.[10,11]

Doped crystalline SiNWs were synthesized by vapor−liquid−solid growth using phosphine[12] (n-type) and trimethylboron[13] (p-type) as the dopant gases. The P:Si and B:Si inlet gas flow ratios were 2×10^{-3} and 2×10^{-2}, respectively. The SiNWs were grown with an average length of 7 μm and average diameter of approximately 50 nm with variation of roughly 50% about the mean and possessed a native oxide surface layer. Two techniques were utilized to measure ac conductance: one for arrays consisting of ∼500 to >10^4 SiNWs and the other for arrays of 11 to ∼200 SiNWs. In the first technique, broadband microwave coplanar waveguides[14] (CPWs) were fabricated with 20 nm Ti and 200 nm Au evaporated on 0.5 mm thick fused quartz substrates with 3 μm gaps between the center signal and adjacent ground electrodes. Using SiNWs suspended in deionized water, arrays consisting of approximately 500 to over 10^4 SiNWs were then assembled by ac dielectrophoresis

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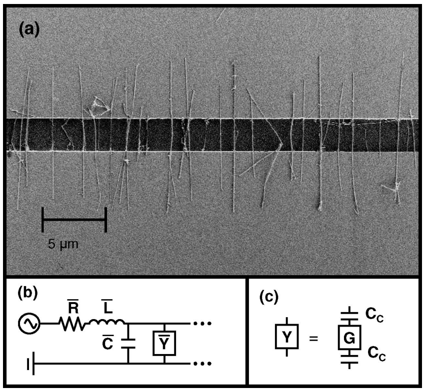

Figure 1. (a) Scanning electron microscope (SEM) image of a CPW segment with SiNWs assembled across an electrode gap between the center signal electrode and one adjacent ground electrode. The other electrode gap (not shown) was assembled similarly. (b) Circuit element transmission line model for a CPW with shunt admittance per unit length $\bar{Y}$ due to the addition of SiNWs. (c) Simple circuit model for the total array admittance Y with complex conductance G coupled capacitively C_C to the CPW.

(ACDEP)[15–17] across the electrode gaps of several CPWs (the "test" CPWs), as in Figure 1a, while others on the same substrate remained bare (the "control" CPWs). No additional metallization or annealing was done.

The substrates were mounted in a darkened cryogenic probe station where complex reflection and transmission coefficients (S parameters)[14] were measured with a vector network analyzer from 0.5 to 50 GHz at several temperatures between 4 and 293 K. A room temperature measurement was taken in the atmosphere and all other measurements were taken in 10^{-5} Torr vacuum after baking overnight at 395 K. Each substrate included CPWs made for impedance calibration designed with identical transverse dimensions and characteristic impedance to the test and control CPWs. The NIST developed multiline through-reflect-line method[18,19] and StatistiCAL software were used to accurately calibrate the measurements at each temperature.[21]

The SiNW array conductance is directly related to a change in the test CPW propagation constant k, calculated from S parameters[20,21] measured before and after ACDEP. In practice, it is more reliable to compare k from the test and control CPWs measured alongside each other at the same stage of the experiment (i.e., same sample mounting and calibration). The variation in k for the test and control CPWs measured prior to ACDEP and the control CPWs after ACDEP (measured alongside the assembled test CPWs) quantify the CPW uniformity and measurement reproducibility. This variation in k was found to be less than 1% at all frequencies and provides an estimate of the systematic error of the experiment. For an array of 500 SiNWs, the signal to systematic error ratio ranged from approximately 1 at lower frequencies to 10 at higher frequencies. For arrays of 10^4 SiNWs, it ranged from approximately 100 at low frequency to 1000 at higher frequencies.

The bare CPWs are treated as standard transmission lines with distributed series resistance $\bar{R}$, inductance $\bar{L}$, and shunt capacitance $\bar{C}$ per unit length.[14] The SiNW array conductance is modeled by the addition of a distributed admittance per unit length $\bar{Y}$ as in Figure 1b, calculated from the S parameters of the test and control CPWs.[21,22] The array is modeled as a continuous distribution because the spacing of the SiNWs (~1 μm) is very small relative to the wavelengths involved ($\lambda > 3$ mm). $\bar{Y}$ then represents a sum of individual nanowire contributions over a unit length scale on the order of a wavelength. The approximation is then made that this averaged $\bar{Y}$ does not vary over the length l of the CPW, i.e., that the SiNW array distribution is uniform over a length scale $\lambda < d < l$ (when $\lambda < l$). Within the context of this model, it is convenient for later comparisons to discuss the admittance of the entire array $Y \equiv \bar{Y}l$. The oxide layer of the SiNWs produces a dc contact resistance in excess of 10^9 Ω, so Y is modeled as a complex conductance G coupled capacitively to the CPW as in Figure 1c. The admittance data of the SiNW arrays confirmed the capacitive coupling[21] which, when subtracted, resulted in a complex conductance G that increased sublinearly with frequency as f^s,where $s \approx 0.3$ and satisfied the necessary Kramers–Kronig relation for a sublinear ac conductance,[10]

$$\frac{\mathrm{Im}\ G}{\mathrm{Re}\ G} = -\tan\left(\frac{s\pi}{2}\right)$$

To more accurately fit the data, while accounting for known dc conductance in the SiNWs, the data were then fit with the SiNW array conductance given by

$$G(f) = G_{\mathrm{dc}} + A\left[\cos\left(\frac{s\pi}{2}\right) - i\ \sin\left(\frac{s\pi}{2}\right)\right]f^s \qquad (1)$$

Admittance data for all SiNW arrays measured, n-type and p-type, clearly showed sublinear frequency dependent conductance, with s in the range 0.25–0.45. The accuracy of fit parameters is affected not only by signal strength relative to systematic errors but also by spectral fluctuations at higher frequencies due to variations in array uniformity. These factors contributed to an estimated uncertainty in s of 20% or less. Estimation of the dc conductance from the microwave spectrum is particularly dependent on the low frequency data, which has the lowest signal and highest error of the spectrum. Consequently only highly dense and uniform arrays with a G_{dc} value large enough to be distinguishable from zero relative to the ac conductance at the lowest measured frequency could generate extrapolated dc conductance estimates.

The $G(f)$ spectra, measured in atmosphere at 293 K and in vacuum at several temperatures, of an array consisting of approximately 10^4 n-type SiNWs are shown in Figure 2. The high signal and excellent uniformity of this sample provided the highest accuracy in fit parameters achieved. The conductance exhibits sublinear frequency dependence under all conditions with the exponent s increasing slightly from 0.30 in atmosphere to 0.39 at 4 K in vacuum. We can estimate average SiNW parameters by naively dividing the admittance by the number of nanowires. This produces an average value for the individual contact capacitance of 0.6 fF, in reasonable agreement with a classical estimate of 0.7–3 fF.[21] The individual SiNW capacitances for all of the samples were found to be approximately equal. Similarly dividing G_{dc}

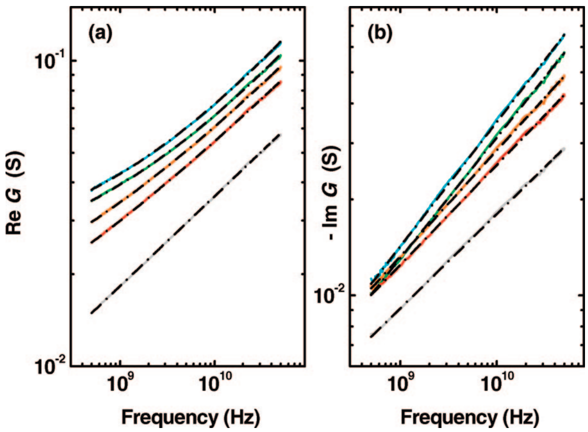

Figure 2. (a) Real and (b) negative imaginary parts of the SiNW array conductance spectrum at several temperatures for an n-type sample consisting of approximately 10^4 SiNWs. In both subfigures, the top four curves are data taken in vacuum of 10^{-5} Torr at 4 K (blue), 100 K (green), 200 K (orange), and 293 K (red) from top to bottom, respectively. The bottom curve (gray) represents data taken at 293 K in atmosphere. The dashed curves (black) were calculated by fitting SiNW array admittance data with the circuit model of Figure 1c and $G(f)$ from eq 1. Values of the exponent s obtained were 0.39 (4 K), 0.38 (100 K), 0.33 (200 K), 0.31 (293K), and 0.30 (atmosphere). The corresponding values of G_{dc} are 0.022, 0.020, 0.011, 0.0067, and 1.2×10^{-4} S and the A parameters are 3.8×10^{-6}, 4.6×10^{-6}, 1.5×10^{-5}, 2.3×10^{-5}, 2.6×10^{-5} for 4 K, 100 K, 200 K, 293 K, and atmosphere, respectively. The value found for C_C was approximately 6 pF under all conditions.

yields dc resistivity estimates of 0.018, 0.020, 0.035, 0.060, and 3.5 Ω•cm, for 4 K, 100 K, 200 K, 293 K, and ambient temperature, respectively. The room temperature vacuum value of 0.06 Ω•cm is an order of magnitude larger than that expected from four-point resistance measurements[12] of similarly grown SiNWs. This may be partially explained by the increased systematic error at lower frequencies. Additionally, it was found that the arrays formed by ACDEP contained many SiNWs of smaller diameter than those measured in ref 12. These smaller SiNWs may have higher resistivity due to increased surface effects.

For all of the n-type samples, as in Figure 2, the magnitudes of Re G and −Im G across the measured frequency range increased significantly following bake-out under vacuum and as temperature was lowered to 4 K. Alternatively, for the p-type arrays, Re G and −Im G decreased monotonically upon bake-out and cooling. The changes in conductance upon bake-out suggest that adsorbates from atmosphere alter the carrier density and/or distribution in the SiNWs, effectively enhancing p-type conduction and diminishing n-type. The temperature dependence of the n-type and p-type samples is generally consistent with dc conductivity in bulk silicon doped above and below the metal−insulator transition, respectively. However, the sublinear frequency dependence of $G(f)$ is not consistent with the conventional Drude ac conduction seen in bulk doped silicon from dc up to terahertz frequencies.[23–25]

Conductivity spectra showing sublinear frequency dependence have been reported in a wide variety of seemingly unrelated electronic systems, whose only common feature is strong microscopic disorder.[10,11] Like the SiNW arrays, these systems have conductances that satisfy the Kramers−Kronig relation and exhibit weak dependence of the exponent s on temperature. However, with the exception of silicon at cryogenic temperatures,[26] the systems are generally noncrystalline whereas the SiNWs studied were predominantly single crystal and exhibited sublinear frequency dependent conduction at all temperatures. Additionally, the exponent range found for the SiNW arrays, $0.25 < s < 0.45$, is significantly lower than the range, $0.6 < s < 1.0$, reported for the vast majority of disordered systems. In the theoretical treatment of this universal disordered conductance behavior,[11] the statistical properties of the local mobility or potential distribution determine the exponent s. Although knowledge of s does not uniquely specify the underlying statistical physics, it may help rule out classes of distributions and ultimately aid in developing models for the disorder, analogous to what has been done for $1/f$ noise.[27] The distinct material properties and range of s for the SiNW arrays suggest that they may have a distinct class of disorder mechanism compared to bulk systems.

It is therefore of interest to consider the origin of the disorder. There are two possibilities: (1) macroscopic disorder from statistical variations of electronic properties within the ensemble, such as individual nanowire resistivity and coupling capacitance, dislocations, and nanowire crossings and (2) microscopic electronic disorder in the individual SiNWs. To further investigate the origin of the disorder, a second measurement technique[21,28] was utilized which is more sensitive to arrays of fewer SiNWs but limited to smaller arrays, lower signal, and higher systematic error. As before, multiple calibration CPWs were fabricated together with test and control measurement structures. Here however, the measurement structures consisted of CPWs with a 2 μm gap interrupting the center conductor. Systematic error, again estimated from measurements of bare test (pre-ACDEP) and control (pre- and post-ACDEP) structures, ranged from approximately 1% at lower frequencies to 10% at higher frequencies due to the reflective nature of the test structures. Arrays consisting of 11 to approximately 200 n-type SiNWs were assembled by ACDEP across the 110 μm wide center conductor gap of several test structures and microwave measurements were made in atmosphere. The difference in admittance of the bare control and assembled test structure gap admittances, calculated from the measured S parameters,[21] yielded the SiNW array admittance.

Signal to systematic error was limited at lower frequencies by SiNW conductance and at higher frequencies by systematic error. For the 11 SiNW array, signal to systematic error ranged from approximately 1 to 5, while for the 200 SiNW array it ranged from approximately 10 to 100. The spectra again indicated sublinear frequency dependence not attributable to conventional Drude conduction and were fit with the conductance model of Figure 1c and eq 1. Conductance spectra for arrays of 11 to over 10^4 n-type SiNWs measured by the two techniques are plotted together in Figure 3. The exponent values obtained for these arrays also fell in the range $0.25 < s < 0.45$. Since s is essentially independent of the number of SiNWs N forming the array across greater

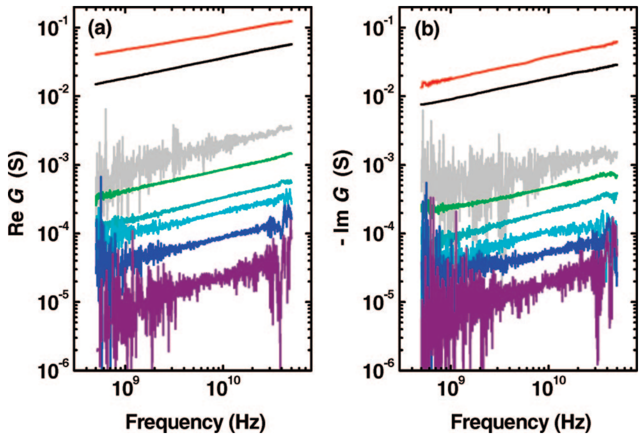

Figure 3. (a) Real and (b) negative imaginary parts of the conductance of various SiNW arrays measured in atmosphere by the two techniques discussed in the text. The arrays consisted of, from bottom to top, approximately 11 (purple), 23 (blue), 50 (light blue), 100 (blue-green), 200 (green), 500 (gray), 10000 (black), and 50000 (red) n-type SiNWs. Values of the exponent *s* obtained from data fits (not shown) were 0.44, 0.34, 0.30, 0.38, 0.32, 0.35, 0.30, and 0.31 respectively.

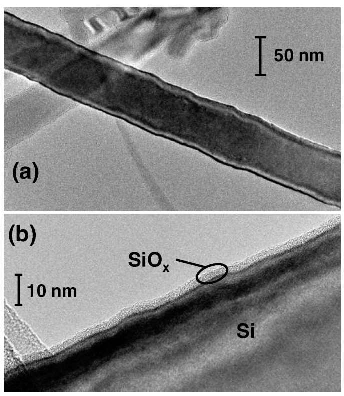

Figure 4. TEM images of typical n-type SiNWs showing (a) the overall surface roughness and (b) detail of the Si/SiO_x interface.

than 3 orders of magnitude and between two different measurement geometries, it would be surprising for *s* to be strongly dependent on N for $N < 11$. This result suggests that the sublinear conductance results from electronic disorder in the individual SiNWs rather than among the SiNWs forming an array.

While the SiNWs measured are not small enough to be one-dimensional in a quantum sense, their large surface-to-volume ratio makes them highly susceptible to surface effects, as seen in the SiNW conductance changes between atmosphere and vacuum. If the disorder is indeed microscopic in origin, a possible source is suggested by the transmission electron microscope (TEM) images in Figure 4. The images show the Si/SiO_x interfaces of typical SiNWs accompanied by considerable roughness. It has been shown that Si/SiO_x interface roughness correlates with interface state density[29] and interface states have been predicted to cause sublinear conduction in crystalline solids.[30] Additionally, the disorder involved in elastic carrier scattering from a fixed interface potential should be insensitive to temperature. This is consistent with the weak variation of the exponent *s* in the SiNW array conductance from 4 K to room temperature, in stark contrast to disordered behavior in bulk silicon.[26] These observations suggest that the SiNW conductance may be dominated by disordered interface states.

In summary, we have developed techniques to accurately measure the microwave conductance spectra of nanowire arrays at microwave frequencies and cryogenic temperatures. We have used these techniques to measure arrays consisting of 11 to $<10^4$ doped SiNWs from 0.5 to 50 GHz. The conductance spectra consistently increase sublinearly with frequency as f^s, where $0.25 < s < 0.45$, indicating that the microwave conductance is dominated by disorder. Sublinear frequency dependence has been observed in many diverse disordered systems including bulk silicon and is considered to be a universal property. However, the *s* values found for the SiNW arrays are considerably lower than the vast majority of disordered systems including bulk silicon. Changes observed in the SiNW array conductance magnitude with temperature are consistent with the behavior of doped bulk silicon. However, unlike bulk silicon which only exhibits sublinear conductivity at low temperature, the nanowire array conductance has essentially temperature invariant frequency dependence from 4 K to room temperature. These comparisons suggest that a distinct disorder mechanism associated individually or collectively with the nanowire form itself dominates the conductance. One possible cause of the disorder is macroscopic variation among the electronic properties and physical configuration of the constituent SiNWs within the array. However, because the behavior is common to arrays consisting of over 10^4 to as few as 11 SiNWs, it is likely that the disorder is microscopic in origin. Sensitivity of the conductance magnitude to atmosphere indicates a high degree of SiNW surface influence, relevant to sensing applications and suggestive of a possible disorder source. A disordered surface potential arising from Si/SiO_x interface states is proposed as the dominant disorder mechanism.

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Supporting Information Available: Notes of conventions used for electromagnetic waves and ac circuit elements and impedance calibration techniques used, calculation of CPW propagation constant and SiNW array admittance from the *S* parameters for SiNWs assembled across the gap between CPW center conductor and ground electrodes (shunt arrays), calculation of SiNW array admittance from the *S* parameters for SiNWs assembled across the gap in the interrupted CPW center signal conductor (series array), and circuit model for

Y and extraction of G from Y. This material is available free of charge via the Internet at http://pubs.acs.org.

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