Influence of ambient on conductivity and 1/f noise in Si nanowire arrays

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Abstract — **The conductivity and low frequency noise of n- and p-type Si nanowire arrays are measured in humid and dry environments. It was found that the conductivity increases for both n- and p-type arrays in a humid environment. The low frequency noise characteristics indicate a change in the carrier transport process from noise governed by trapping processes at the interface in a humid environment to noise governed by inhomogeneity in the Schottky barrier contacts in a dry environment.**

Keywords—Si nanowire; conductivity; low frequency noise.

I. INTRODUCTION

Due to the large surface-to-volume ratio of nanowires (NWs), surface effects play an important role in the NW conduction. This feature can be exploited for different sensing applications [1] but can be detrimental in other applications, such as in FETs [2] or thermo-electrics [3], where surface depletion or inversion can hinder the expected device operation. It has been widely reported that air humidity influences the current-voltage characteristics of Si NW arrays (NWAs) [4] and thin Si on SOI layers [5-6]. The mechanisms involved in this process are still not clear. Jie et al. [4] studied NW-based p-type FETs with Au source and drain contacts and observed an increase in current for measurements in air compared to vacuum. They associated the increased conductivity in air – a humid environment – to surface band bending and surface carrier scattering resulting from the adsorption of H_2O vapor. The adsorbed H_2O molecules trap electrons from the Si NWs, forming OH^- (silanol) ions. These negatively charged molecular groups cause an upward energy band bending at the surface and, therefore, accumulation of holes. On the other hand, Dubey et al. [5,6] studied the adsorption of H_2O molecules on thin body SOI. This structure is representative of a planar 2D structure. The Si layer was n-doped and contacts were made using InGa. The conductivity of the n-layer increased upon H_2O adsorption. The authors concluded that the increased conductivity was a consequence of a downward band-bending at the surface, leading to accumulation of electrons. The authors postulated that the band bending can be attributed to two possible, indistinguishable mechanisms, a charge transfer or the influence of the H_2O dipole moment. Humidity also changes the properties of a graphene layer, which represents an ultimate 2D surface [7] and of porphirin nanotubes, which has a very large surface-to-volume ratio as well [8].

Thus the conductivity of a thin Si conduction layer is increasing in a humid environment for both n- and p-type Si. What is contradictory is the reason for this increase which is, in both papers, related to the majority carrier accumulation at the surface.

In this work, we investigate the electrical conductivity and the low frequency noise in both p- and n-type NWAs with two different metal contacts. The NWAs consist of ~10^7/cm^2 vertically upstanding NWs attached to bulk Si. NWAs were chosen because of their easy fabrication and the availability of a large number of NWs within the array that deliver averaged results. Two types of metal contact were chosen to investigate the possible influence of the metal-semiconductor interface on the response of the devices. Since low frequency noise measurements are very sensitive to the availability and changes in trap density around the SiO_2 oxide layer that surrounds the NWs, they can give an insight into the influence of traps on the transport processes. Choosing both p- and n-type material allows evaluating surface enhancement and depletion processes that should be opposite for the p and n doping.

II. MATERIAL PREPARATION

The NWAs have been etched in both n- and p-type Si of resistivity $\rho \approx 0.01\ \Omega$ cm, using metal assisted electroless etching (MACE) [9-10]. For the etching process, two wafers are attached to each other using poly methyl methacrylate (PMMA) to protect one sample surface from NW etching. The two outer surfaces of the wafers are etched simultaneously during the subsequent MACE process. This gives two nearly identical samples. After cleaning the samples in isopropanol and deionized water, they were immersed in a solution of 0.03 M $AgNO_3$ and 5.6 M HF. An oxidizing agent was added to increase the etch rate. This process creates vertically aligned crystalline Si-NWAs wrapped with thin SiO_2 layers. Following NWA etching, the residual Ag particles were removed using a concentrated (5 M) solution of HNO_3. The length of the etched wires in the NWAs is determined by the etch time and temperature and was approximately 15 μm in our experiment, as confirmed by SEM (see Fig.1). TEM shows that the wires are crystalline. The diameter of the wires varied between 50 nm < d < 250 nm. The wires with a wider diameter show more surface roughness than the thinner wires.

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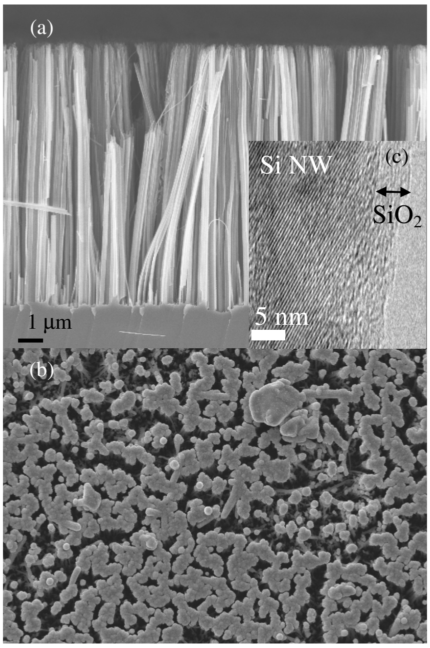

Fig.1 (a) SEM image of the cross section of an array of Si nanowires. (b) SEM of the top of a metallised NWA. (c) TEM image of a crystalline nanowire wrapped with SiO$_2$.

Two NWA samples (one n-type and one p-type) were metallized by sputtering 5 nm of Cr followed by 200 nm of Au on both sides of the samples. Contacts were left un-annealed to prevent diffusion of Au into the Si NWs. In addition, another set of n-type and p-type NWA samples were evaporated at both sides with a 200 nm Al contact. These were also left un-annealed. The consequence of non-annealed contacts is their non-Ohmic behavior, as the work function difference between Si and metal will result in a Schottky contact. Fig.1(a) gives an SEM picture of a Si NWA attached to bulk. The inset gives an indication of the thickness of the SiO$_2$ layer that wraps the NWs and shows the crystalline character of the NWs. Fig. 1(b) shows that the metallization does not completely cover the surface of the NWA and thus allows for gasses to pass to the NW surface areas. SEM characterization shows that the sputtered Cr/Au contacts lie mainly on top of the NWs, penetrating approximately 1 µm into the array. Further down, the sides of the NWs in the array are metal free. A few small metal particles are observed near the bottom of the NWs. In contrast, the evaporated Al does cover a larger part of the sides of the NWs in the array. This coverage however, is not continuous and few Al particles can be found near the bottom of the wires, preventing electrical shorts as confirmed by the current-voltage measurements.

Contacts to the NWAs for current-voltage and noise measurements were made in a specially prepared closed cylindrical container with a volume of $V \approx 1.6$ cm^3 that clamps the sample under constant load between a spring-loaded, 3 mm diameter Au probe tip and a Cu back plate. Dry air can be supplied via a tube connected to a 5 mm diameter hole in the chamber. Recovering of the characteristics to air ambient was done by removing the dry air supply without changing the contacts on the sample.

Current-voltage measurements were carried out at room temperature using a semiconductor parameter analyzer. Low-frequency noise was measured using a SR770 FFT Spectrum Analyzer. The NWAs were biased using a battery powered circuit with a variable resistor. Noise data were obtained in a frequency range from 1 Hz to 10 kHz at 300 K for the NWA under constant bias. Background noise was measured using the zero-biased sample and subtracted from the total device noise. The spectral noise density of the short circuit current fluctuations, S_I, is calculated from the parallel connection of the device and the load resistor using the expression:

$$S_I = S_V\left[(R^*_L + R_d)/(R^*_L\, R_d)\right]^2,$$

where R_d is the NWA's differential resistance determined by $R_d = \frac{dV_d}{dI_d}$ at the chosen bias point and R^*_L is the effective load resistance.

III. MEASUREMENTS

A. *Current-voltage measurements*

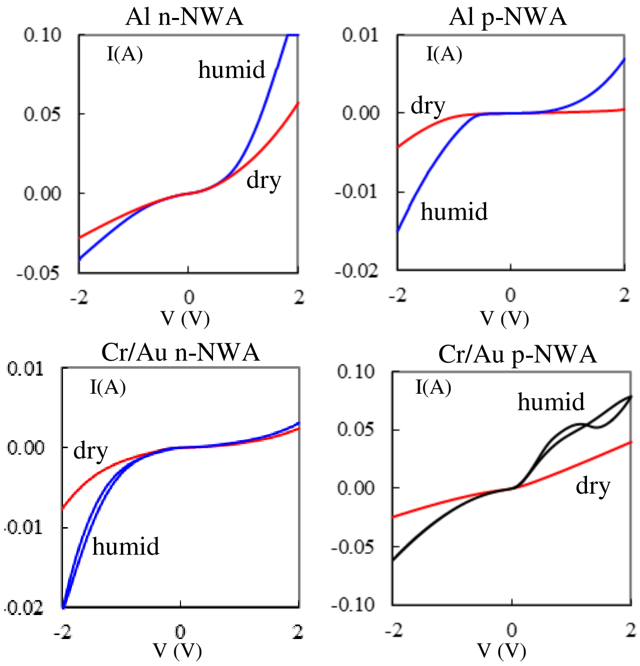

Fig.2 Current voltage characteristics. Top row: Al contacts, bottom row: Cr/Au contacts. Left column: n-type NWA, right column: p-type NWA.

Current-voltage and low frequency noise measurements were carried out under "wet" – atmospheric and "dry" condition. The relative humidity in both conditions is RH "wet" ≈ 70%, RH "dry" ≈ 15%. All 4 samples show higher currents in the humid atmosphere with respect to the dry atmosphere. This confirms that conductivity increases as a consequence of adsorption of H_20 vapor. This behavior is reversible, indicative of an adsorption characteristic rather than of chemical reactions. Any hysteresis present in the current-voltage characteristics in a humid environment disappears when dried. This relates the hysteresis to the adsorbed H_2O

molecules. Similar behavior has been observed in carbon nanotubes and Si or Ge NWs and has been attributed to the generation of charge traps by water molecules adsorbed on the surface [11]. Hysteresis was also observed in grapheme due to the polar gating effect or charge transfer due to H_2O adsorption [12].

Fig. 2 gives the current-voltage characteristics for all samples measured with the semiconductor parameter analyzer. Since both n- and p-type NWAs show increased conductivity with humidity and the doping concentration in the wires is of the order of 5×10^{18} cm^{-3}, an explanation based on energy band bending that causes majority carrier accumulation or inversion at the surface of the wires seems unacceptable. A possible explanation for the increased current in a humid environment is conduction of carriers at the surface of the SiO_2 layer as described by Voorthuyzen et al. [13] and Ho et al. [14]. These papers show that mobile charges present on an oxide-air interface move as a result of an applied lateral electric field. Mobile surface charges are associated to polar gas adsorption, such as H_2O molecules. Therefore we suggest that the increased current through the NWAs in a humid environment is a result of parallel conduction via H_2O related surface charges on the oxide interface.

B. *Low frequency noise characteristics*

All low frequency noise measurements show a $1/f^{\gamma}$ characteristic with γ close to 1. The normalized S_I/I^2 characteristics (Fig. 3) show that the normalized noise level is of the same order of magnitude for all samples. With exception of the n-type Al contacted NWA, all other NWAs show a higher value for S_I/I^2 under humid conditions than in a dry environment. In independent measurements, a higher normalized noise level in a dry environment was also observed for another n-type Al contacted NWAs. Similarly, for a Cr/Au contacted p-type NWA the normalized short circuit current noise spectrum in a humid environment was found to be higher than in a dry environment [15]. This indicates some consistency and repeatability in the measurements.

The cases in which S_I/I^2 is higher for a humid environment are consistent with the picture that adsorbed polar H_2O molecules generate charge traps on the surface of the nanowires [11]. In order to get a better insight into the transport processes in these nanowire systems, we have also compared S_I, S_I/I and S_I/I^2 in each environment for different applied voltages. We found that, with exception of the n-type Al contacted NWA, in all other cases S_I is proportional to I^2 in a wet environment while S_I is proportional to I in a dry environment. These results are indicative for a change in the carrier transport mechanism between humid and dry conditions. Conventionally, S_I is expected to be proportional to I^2 due to a variation in the noise level via variations in mobility or carrier concentration as a result of the presence to traps. Since the surface-to-volume ratio of the NWs in the arrays is large, one can expect a large trap density at the surface of the wires, which can generate generation-recombination noise. A behavior where S_I is proportional to I rather than I^2 has also been found in Schottky barrier diodes. This behavior is explained in terms of local barrier height variations [16]. S_I/I^{β} characteristics, with $1 < \beta < 2$, were observed in PtSi silicided Schottky contacts on Si. The noise characteristics are claimed to be due to spatial variations of the barrier height. In the structures the silicide forms a polycrystalline layer which features grain boundaries normally characterized by a large density of traps. These interface states cause random walk of electrons, which modulates the barrier height [17]. There is a clear analogy between the polycrystalline grain boundaries and the metallized tops in the NWAs (see Fig. 1). The metallization of the NWA covers each individual NW but does not necessarily connect all these metal dots together, forming islands on metals on top of NWs and forming multiple metal-semiconductor boundaries with different characteristics. Contact area is different because wire diameters differ and metal thickness along the wires will not all be the same. Based on these observations, we postulate that under humid conditions the adsorbed H_2O molecules increase the trap density at the surface of the wires such that these traps overwhelm the noise generated by the metal-semiconductor contact interface in-homogeneity. Removing the H_2O vapor in a dry environment removes the NWs' surface traps such that the noise due to the Schottky barrier height variation becomes dominant.

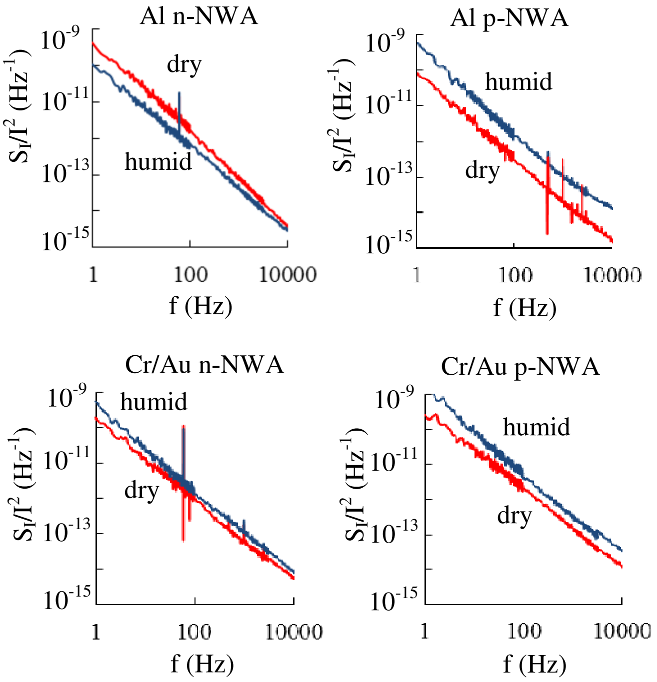

Fig.3 Normalised short circuit current noise characteristics. Top row: Al contacts, bottom row: Cr/Au contacts. Left column: n-type and righ columnt: p-type NWAs. Red: dry and blue: humid environment.

The case for the n-type Al NWA remains largely un-resolved. S_I is nor proportional to I, nor to I^2. A possible explanation is that the side coverage in those wires by Al is more extensive than in the other cases and therefore a mixed S_I^{β} characteristic occurs.

IV. CONCLUSION

Conductivity and low frequency noise measurements have been carried out on n- and p-type NWAs in humid and dry environment. Each NWA type was connected by two different metals, Al and Cr/Au. Since the conductivity and normalized short circuit current noise is higher in a humid compared to a dry environment in all devices (excl. S_I/I^2 in Al contact n-NWA), the increased current is associated to parallel conduction on the surface of the H_2O covered wires. This is also confirmed by the proportionality of the short circuit noise to I^2 in a wet environment but to I in a dry environment.

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