Electrical transport in polymer covered Si nanowires

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It is well known that the large surface to volume ratio in nanowires (NWs) results in electrical transport highly sensitive to the surface condition of the wire. This feature can impede the expected transport or can be exploited in applications. In this work we investigate the influence of polymer coverage of the NWs on the transport processes. The aim is to change the conductivity of the Si NWs via the workfunction difference between polymer and Si, similar to modulation doping in heterojunctions. However, using spinon polymers removes the need for complicated and expensive heterojunction growth of shell-core NW configurations.

NWs are fabricated using metal-induced excessive local oxidation and dissolution of a Si wafer using electroless plating in HF/AgNO₃ followed by an etch in an aqueous HF/Fe(NO₃)₃ solution [1]. In this way NWs with a mean diameter of 200nm and length 30 to 100 µm can be fabricated. The NWs are harvested via ultrasonic vibrations in IPA and then a drop of NW in IPA is dispersed on a pre-processed SiO₂ covered Si wafer. The pre-processed wafer contains a suitable geometry for 4-point probe measurements [2] - 4 thin Au lines (2 um width) to large probe-able contacts (each 100×100 um²) – essential for the extraction of the resistivity of the Si NW without the influence of the contact resistances. An SEM picture of a Si NW on the four lines of the 4-point probe geometry is given in fig. 1. In the 4-point probe measurement a current is driven through the outer contacts and the voltage drop is measure with a high impedance voltmeter between the inner two contacts. It was found that the Au contacts to the NW were rectifying in both bias directions in the thus assembled structure and that, due to the simple NW dispersion technique on the pre-processed sample, multiple wires can potentially contact two or more of the Au lines. Focused ion beam (FIB) was used to 1) locally deposit W on the cross points between the NW and the Au lines and 2) ion mill all other wires that could potentially short the Au contact lines. The contacts were then annealed for 90 s in an Ar ambient at 500°C in an RTA. The annealing resulted in ohmic contacts. Although the contact resistance should not be important in a 4-point probe measurement, the annealing of the contacts avoids the rectification character of the contacts that impacts on the accuracy of the measurements at low current levels.

Four different polymers were spin coated on top of the Si NW: a thermoplastic plastic poly(methyl methacrylate) (PMMA) film formed from a solution of 5%wt PMMA in toluene, another thermoplastic plastic polythene (PE) film formed from a solution of 5% wt PE in decalin, a conducting polymer poly(3.4ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) with a conductivity at least 10x smaller than the Si NW and polyaniline (PAni) another conducting polymer. The first two polymers are insulators, the latter two are conducting but with a conductivity smaller than the Si NWs. The insulation polymers have a high work function of approximately 5eV. The work function of PEDOT:PSS lies in the range of 4.7 to 5.1 eV and of PAni between 4.5 and 4.7 eV. All polymer work functions are larger than the work function of moderately doped Si at ~4.3 eV. As a consequence, we expect the conductivity of the Si NW to decrease with polymer coverage as electron transfer will occur from the Si NW to the polymer upon contact.

The results of the 4-point probe measurements using the insulating polymers confirm the electron transfer from Si NW to polymer as the resistivity of the polymer covered NW has increased. A larger resistivity increase is seen for PMMA (fig. 2) than PE (fig. 3) confirming the smaller work function for the latter. Coverage of the Si NW with PEDOT:PSS gives some interesting results, given in fig. 4. Fig. 4 shows the current-voltage characteristics of the bare NW, the freshly PEDOT:PSS covered Si NWs and the same system measured after 4 days. The conductivity has seemingly increased due to the parallel current flow in PEDOT: PSS and NW in a non-linear way. After aging a current offset occurs probably due to charge detrapping in the polymer layer. The shape of the curve in the high voltage region also changes due to an increased resistivity of the PEDOT:PSS layer after aging. A reduction of the PEDOT:PSS covered area via lithography will increase the resistivity of the PEDOT film and allow a clearer picture of its effect on the conductivity of the wire. The aging effect needs to be further investigated, but is possibly due to ionexchange processes between the polymer film and Si in air.

[1] K. Peng, et al., Advanced Functional Materials, 16, 387–394 (2006).

[2] D.K. Schroder, Semiconductor material and device characterization, John Wiley & Sons Inc (1998).

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NW on top of 4 Au metal lines in a 4-point probe when covered with PMMA. set-up for resistivity measurements.

Figure 1. SEM picture of a 200 nm diameter Si Figure 2. Increase of the resistivity of the Si NW





Figure 3. Increase of the resistivity of the Si NW when covered with PE.

Figure 4. Current-voltage characteristic of a fresh and "aged" PEDOT:PSS covered Si NW compared to the uncovered Si NW.