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Influence of chemical modification on the electrical properties of Si nanowire arrays

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Abstract. The influence of the chemical modification on the electrical property of Si nanowire array was studied. It is found that H-terminated Si nanowire has a better electrical conductivity while OH-passivation could increase their resistance. It is believed that the introducing of OH group on the surface nanowire increases the interface traps and it is confirmed by our 1/f noise measurement.

Introduction

Si nanowires (NWs), with a large surface to volume aspect ratio, promise to have excellent potential in nanoelectronics [1-5] and sensors [6-9]. The large surface area of the NWs makes them ultra sensitive to the termination of the Si atoms at this surface. On one side this means that they represents excellent opportunities for sensing of compounds which are adsorbed on the Si surface but on the other hand represents a challenge concerning the controllability of the response of the devices. Controllably adjusting the electronic characteristics of Si NWs through the attachment of functional molecular groups to their surfaces is a compelling goal [10]. It has been shown that the chemical modification can change their properties such as band gap, Fermi level, work function and electrical conductivity [10-19]. Moreover, properly chemically modified surfaces can also slow the cooling [20, 21] of photo-generated carrier and improve the efficiency of solar cells. Most of the research carried out on this topic focuses on single NWs and only little work has been done on the NW arrays. Nanowire arrays are promising devices in a multitude of nanoelectronics based applications. In this paper, we study the influence of the chemical modification of the surface of NWs on the conductivity of an array of NWs. The array of NWs is fabricated via metal-assisted electroless chemical etching of a Si substrate.

Experiment

P-type Si (100) wafers with resistivity of 1-10 Ω·cm were used in our experiment. The back side of the wafer was protected by sputtered Cr/Au and can be subsequently used as back electrode. After cleaning with acetone, isopropanol and deionized water, the samples were immersed in a solution of 0.03 M silver nitrate and 5.6 M HF for Si NW etching. After NW etching, the residual Ag particles were removed using a high concentrating of HNO_3 (5M) solution. Metal-assisted electroless chemical etching offers a simple and cheap way to prepare large-area NWs arrays. The NWs used in this experiment have a diameter of 30-300 nm (Fig. 1).

Contact metals were deposited on the top of NW array by sputtering to form the top electrode. Rapid thermal annealing treatment was applied to improve the contact characteristics. Chemical treatment was performed to modify the surface of NWs after the metal contact was deposited on the top of the NW array. In order to enable comparison between the different treatments a large area NW array was cleaved into different pieces. This ensured that the base material is the same for all measurements. An untreated “as-grown” sample will be used for reference.

Results and discussion

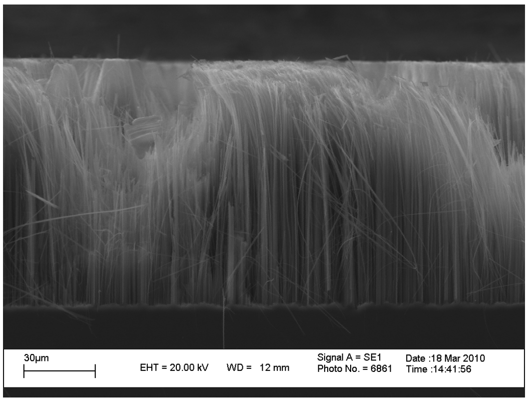

Fig.1 SEM image of a Si NW array.

In the first type of experiments the NW arrays were treated by dipping in HF or H_2O_2 for 2 min to passivate their surface. No rinse was performed of dip treatment. This leaves the Si NWs in the array terminated by -H or -OH group respectively. The samples were then loaded in the vacuum deposition machine for Cr/Au contact evaporation. The IV measurements on the different Si NW arrays are given in Fig.2a. It is clear that a Schottky barrier is formed before annealing for all samples. For the NWs terminated with H atoms, a good rectification characteristic can be seen with a low on-voltage. The current limit is set at 0.1A to protect the NWs in the array. After annealing of the NW arrays at 370 ^{o}C in Ar gas a Cr silicide is formed that gives in all cases a good ohmic contact with a resistivity of 0.34 Ω cm^2 [22] (Fig.2b). However, for the other samples, due to the influence of SiO_2 on the surface of Si NWs, the IV curves are not linear even after annealing at 370 ^{o}C. Compared with the as grown sample, the thicker SiO_2 layer caused by the dip in H_2O_2 induces a higher resistance.

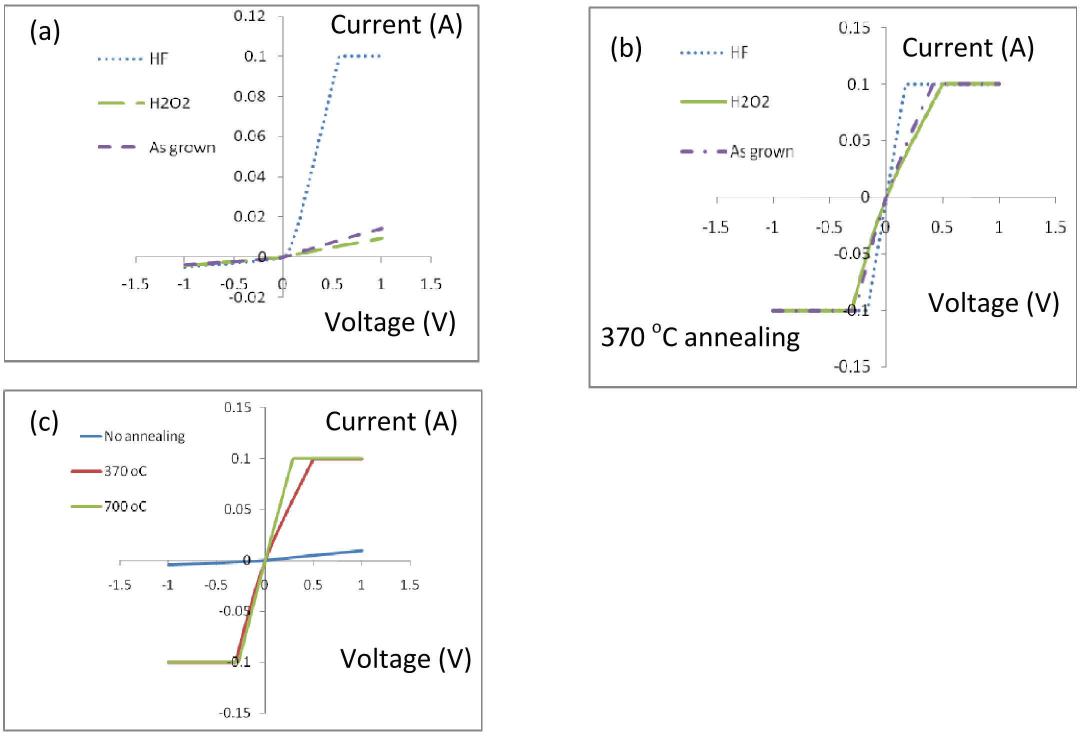

Fig. 2 Current-voltage characteristics of Si NW arrays before (a) and after annealing (b). (c) further annealing of the H_2O_2 passivated NW array to improve the ohmic contact formation. The surface termination was obtained by dipping the NW arrays in HF or H_2O_2 for 2 minutes before contact formation.

In order to obtain an ohmic contact for the samples terminated with OH groups, annealing at higher temperatures was performed. Experimental results are given in Fig. 2c and indicate that Cr can penetrate through the SiO_2 layer and form a Cr-silicide at 700 °C. A good ohmic contact with a resistivity of 1.38 Ω cm^2 was obtained. Similarly for the as-grown samples the contact becomes ohmic at higher annealing temperatures.

In the second type of experiments, further HF treatments were done after contact formation and annealing at 700 °C. This subsequent HF treatment removes the SiO_2 layer and improves the conductivity of the Si NW array as shown in Fig. 3a. The resistivity decreased from 1.38 Ω cm^2 down to 0.47 Ω cm^2 [22]. It is believed that the HF treatment greatly reduces the charge carrier trapping due to the formation of a fresh H-terminated surface. The stability of this H termination was investigated by leaving the sample in air at room temperature. It was found that after 2 days, the resistance increased again as a result of the native oxide growth and reintroduction of defects on the NW surface (Fig.3b). A similar experiment was done with the non-polar solvent cyclohexane, C_6H_{12} which does not contain OH groups. After HF passivation the sample was dipped in C_6H_{12} and the current-voltage characteristics were measured. The measurements were repeated after two days. The results shown in Fig. 3b, illustrate that C_6H_{12} can effectively passivate the Si NW surface and maintain the lower resistance value of the NW array for up to 2 days of exposure in air at room temperature. Further measurements indicate that the C_6H_{12} passivation disappears after 5 days of air exposure.

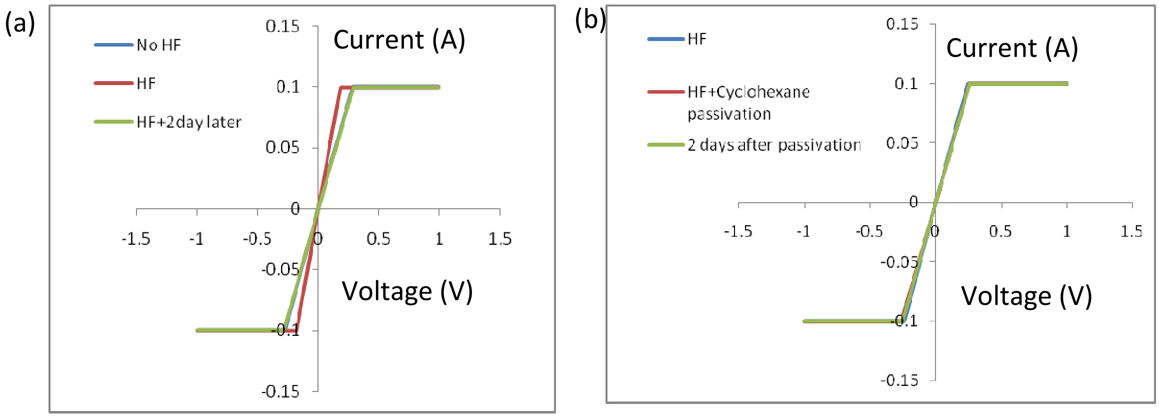

Fig. 3 Current-voltage characteristics of Si NW arrays immediately after surface treatment and after 2 days of aging in air at room temperature (a) HF treatment and (b) cyclohexance passivation.

Due to the sensitivity of the electrical characteristics of the Si NW array it might be used as a gas sensor. The difference between the method applied for the passivation of the Si NW array and the gas sensing experiment is that the 1st technique is done in liquid while the 2nd is based on gases. The density of molecules in a gas is much lower than that of a liquid and thus one expects that the influence will be smaller. Indeed, flowing a gas, such as from evaporating solvents, across the NW array does not cause immediate current-voltage changes. However it was found that changes could be observed in the low frequency (1/f) noise characteristics of the Si NW array in the presence of solvent vapours. It is well known that the 1/f noise characteristics are sensitive to the trap density of oxide-semiconductor interfaces and it is expected that this trap density will be influenced by the adsorption of molecules in the gas. We have done some preliminary experiments on the gas evaporating from isopropanol (IPA), an alcohol with available –OH groups, and hexane, a hydrocarbon with high vapour pressure and without–OH groups. The results of the measurements are given in Fig.4.

No influence of solvent vapour can be observed in the bulk Si samples because no Si area is available for vapour adsorption. However, in the case of the Si NW arrays the 1/f noise characteristics change upon the release of solvent vapours. Interestingly the noise power density is increasing upon contact with IPA and decreases upon contact with hexane vapours. This observation can be interpreted as an increase in surface trap density by IPA vapours and a decrease in trap density when exposed to hexane vapours. This result is consistent with the hypothesis that the conductivity changes of the Si NW arrays in the liquid passivation experiments are due to surface traps. We found that when the NWs are passivated with H_2O_2 the conductivity is decreasing, postulated to be as a consequence of an increased trap density. This is consistent with the IPA vapour experiment that makes –OH groups available at the surface and increases the noise spectral density which is indicative of an increase in the number of interface traps. For the liquid cyclohexane, C_6H_{12} and hexane vapour, C_6H_{14} experiments the same is happening. It was postulated that the conductivity increases due to a reduction of the trap density for a dip in cyclohexane and this is confirmed by the 1/f spectrum of hexane vapours where the noise spectral density is decreasing, indicative of a decreasing trap density.

Summary

We investigated the electrical property of Si NW arrays by chemical modifying their surfaces. It is found that the electrical conductivity of NW devices is sensitive to chemical agent. H-terminated Si NW devices always show a low resistance while OH-passivations decrease their conductivity. We believe that the introducing of OH group on the surface NWs increases the interface traps and our 1/f noise measurement confirmed this explanation.

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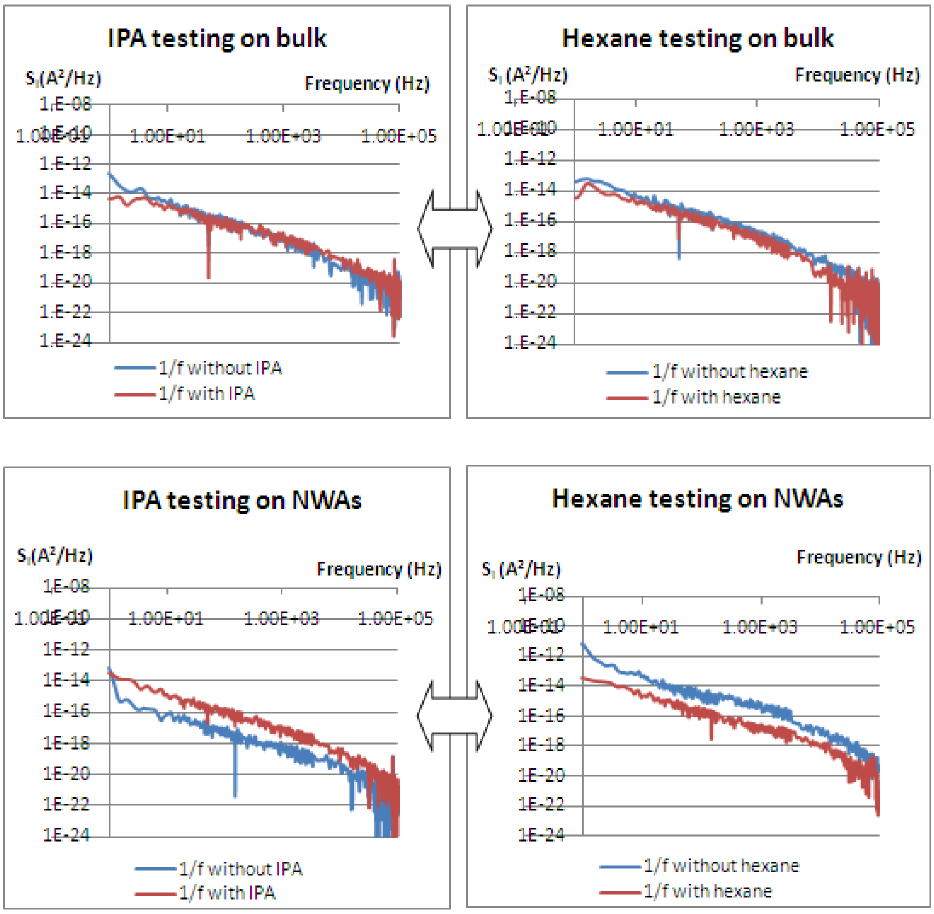

Fig. 4: Low frequency power spectral density of Si bulk (top) and Si NW arrays (bottom) under the influence of IPA (left) and hexane (right) vapours.

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