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PAPER

Superior long term stability of SiC nanowires over Si nanowires under physiological conditions

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Abstract

Semiconducting nanowires (NWs) are raising a growing interest in nanoelectronic devices. While silicon is the most widely used material in this field, it lacks long-term stability in aqueous solution. The usage of Si must hence be reconsidered for specific applications such as devices operating in biological media with high ionic strength. Silicon carbide is a wide bandgap semiconductor that can efficiently replace Si for applications in harsh environments or high temperature thanks to its high chemical stability and thermal conductivity. Here, we compare the long term stability of Si and SiC NWs under mimicked physiological conditions. The degradation kinetics of both types of NWs was studied from accurate monitoring of their cross-sectional geometry by transmission electron microscopy (TEM) over a period of 4 weeks. Results show a linear dissolution of Si NWs whereas SiC NWs exhibit much slower degradation kinetics confirming the superior chemical stability of SiC nanostructures over Si. After 32 days, NWs with an initial diameter of 20 nm are expected to dissolve completely in the case of Si NWs while SiC NWs would shrink by only 16%.

1. Introduction

The fabrication of NW-based sensing devices usually requires chemical linking of receptor groups to the surface of the nanostructures, enabling them to bind to target molecules in a given sample. It is important for numerous applications, such as *in vitro* and *a fortiori in vivo* sensing, that functionalized surfaces and underlying nanostructures exhibit long-term stability in ionic solutions. Specifically, biosensors require high chemical stability in order to withstand physiological conditions and thus prevent any drift in the measurement signal or even complete failure due to the degradation of nanostructured materials. Si NWs have been widely studied as transducers in biosensors based on nanowire field-effect transistors (NWFETs) [1–8], resulting in very high sensitivities and detection limits up to the femtomolar range. However, it was recently demonstrated that Si NWs suffer from a lack of long-term stability in physiological environments at nanometer scale, which is characterized by a decrease in NW diameter along with a decrease in electrical conductivity [9–11].

For future development of sensors based on semiconducting NWs, it is essential to address the issue of Si NW stability by studying alternative materials and innovative nanostructures. Two options are generally possible. The first one is to passivate the Si NWs surface by adding a thin layer of metal oxide such as Al₂O₃ [10] or other high- κ dielectrics. The second option is to replace Si NWs entirely with a chemically inert semiconductor such as SiC NWs. SiC is a wide-bandgap semiconductor (2.3–3.3 eV) with very high breakdown field, high thermal conductivity, and CMOS compatibility. Recently, our group fabricated SiC NWFETs with the highest carrier mobility reported in the literature [12]. SiC also exhibits a high hardness and very high resistance in most acid and alkaline solutions due to its chemical inertness [13], and it was recently demonstrated to be bio- and hemo-compatible [14]. By taking advantage of the aforementioned properties, SiC could be an excellent candidate as an alternative material to Si NWs or as a coating material to form core/shell Si/SiC NWs for devices operating in harsh environments [15], e.g. biosensors with repeated exposure to samples of blood or other body fluids. Our group previously reported DNA functionalization on various SiC nanostructured surfaces [16],

leading to the first successful label-free electrical detection of DNA hybridization using 4H-SiC NW-based sensors [17, 18]. However, to our knowledge, the long-term behavior of bare SiC NWs or core/shell Si/SiC nanostructures in physiological conditions has never been studied up to now. In this letter, we compare the degradation kinetics of Si NWs and SiC NWs under mimicked physiological conditions using high-resolution TEM analysis and we demonstrate the superior chemical stability of SiC NWs over Si NWs. The results presented here are of key importance in order to optimize the reliability and performance of sensing devices based on NW transducers and operating in ionic solutions.

2. Experimental

2.1. Deposition of NWs on patterned TEM grids

Si single crystal NWs were grown in the $\langle 111 \rangle$ direction by the Vapor-Liquid-Solid (VLS) method [19] with Au catalyst. SiC NWs were synthesized by thermal chemical vapor deposition (CVD) at 1100 °C using Fe catalyst, resulting in a crystalline structure with cubic symmetry (3C-SiC) [20]. NWs were detached from their respective growth substrate by sonication in ethanol, and then dispersed on TEM gold grids as depicted in figure 1(a). The TEM grids feature reference patterns, allowing NWs to be accurately located and individually monitored throughout the experiment, and a holey carbon film providing support to the NWs along with ideal observation sites in the regions of the holes (see figure 1(b)). These regions offer an increased image contrast compared to regions of film where the inelastic scattering of electrons contributes to the background noise. After sonication, the length of both Si and SiC nanowires ranged from 2 to 10 μm. The surface density of NWs was adjusted to obtain a coverage rate of 5 to 10% in order to provide a sufficient number of observable NWs with minimal overlap.

2.2. Immersion and observation cycles

The TEM grids holding the NWs were immersed in a PBS 1x solution (Phosphate Buffer Saline, pH 7.4) at 37 °C for a set period, rinsed with deionized water, imaged with HR-TEM in order to study NW morphology, and immersed again in PBS for a new cycle under the same mimicked physiological conditions. The number of observable NWs was limited by experimental constraints related to TEM operation such as localization, orientation and observation time of the objects. TEM observations were carried out at 200 kV with a JEOL 2010 LaB₆ microscope (resolution: 0.19 nm).

3. Results and discussion

Several NWs of each material were imaged using HR-TEM. Figures 2(a) and (b) show HR-TEM images of Si and SiC NWs respectively, in their initial state. Typically, the Si and SiC NWs comprise a crystalline core covered by a thin amorphous layer. Regarding Si NW crystalline core, Si (111) planes cannot be seen on most micrographs (figure 2(a)) because Si NWs were not systematically oriented in zone axis throughout the experiment. Regarding SiC NW crystalline core, micrographs show occurrence of stacking faults along (111) planes (figure 2(b)). The $\langle 111 \rangle$ direction is angled by about 26° with the growth axis, but the electron diffraction image confirms that the polytype is 3C-SiC (see inset).

The 2–3 nm thick amorphous layer on the surface of Si and SiC cores is attributed to the native SiO_2 surface layer formed by oxidation in air. This outer shell exhibits a variable roughness along the NW surface. It also may be superposed or include fragments from the carbon film, which is difficult to distinguish from the oxide layer. For these reasons, only the inner diameter corresponding to the crystalline core of Si or SiC NWs was extracted from these micrographs for better experiment accuracy, as illustrated in figure 2(a).

The average initial core diameter of the nanowires is 30.9 ± 10.6 nm and 16.2 ± 3.8 nm for Si and SiC respectively. The standard deviation values show a greater dispersion in the case of Si compared to SiC. Their inner diameter was accurately monitored at discrete times: in their initial state, after 3, 9, and 28 days in PBS solution. Figure 3 shows micrographs of typical SiC (a–d) and Si (e–h) NWs over these time intervals. All NWs exhibit a decrease in diameter over time with no preferential reaction sites.

The variation in diameter as a function of immersion time is plotted in figures 4(a) and (b) for Si and SiC NWs respectively. It was observed that after 28 days, all of SiC NWs still remained on the TEM grid whereas only half of Si NWs were present. Indeed Si NWs with an initial diameter smaller than 30 nm were absent from the grid by the end of the experiment. As a consequence, it was difficult to determine whether they degraded completely or reached a critical size that allowed them to detach from the grid. Based on the experimental data displayed on figure 4(a), the diameter of Si NWs decreases continuously over time and the data can be fitted with a linear law independently of the initial diameter. The extracted rates range from 0.6 to 0.8 nm per day. In contrast, the diameter of all SiC NWs decreases non-linearly as a function of time at a much slower rate.

The weight loss per unit surface is calculated from the diameter diminution using the following relation, and is averaged over all NWs of each material. The weight loss is proportional to the diameter diminution of the NW following the relationship:

$$\Delta m = \rho(R - r) \quad (1)$$

where ρ is the density of Si or SiC (2.33 and 3.21 g.cm^{-3}), R the initial radius of the NW and r its radius at a given time t . Results of weight loss versus immersion time are reported in figure 5(a). There is a clear difference in weight loss between Si and SiC NWs as early as 3 days after immersion. The experimental data are fitted with the following empirical kinetic laws describing reaction controlled and diffusion controlled processes, respectively:

$$\Delta m = k_R t \quad (2)$$

$$\Delta m = k_D \sqrt{t} \quad (3)$$

where k_R and k_D are reaction constants.

Figure 3. HR-TEM images of (a)–(d) SiC and (e)–(h) Si nanowires immersed in PBS 1x at 37 °C within 28 days, each individually monitored. The same location was imaged on each NW, and the differences in background are due to the occasional displacement of NWs upon handling of the samples.

Figure 4. Diameter of (a) Si and (b) SiC nanowires immersed in PBS at 37 °C, individually monitored using HR-TEM analysis. Each data set corresponds to a single NW.

In the case of Si, corrosion of the NWs follows a linear time dependence (equation (2), $R^2 = 0.99$) which indicates that the process is controlled by the interfacial reaction. On the other hand, data from SiC NWs can be fitted with the parabolic rate law (equation (3), $R^2 = 0.98$), indicating a diffusion controlled corrosion. For Si NWs, the linear rate constant calculated from the least square fit is $k_R = 0.072 \mu\text{g} \cdot \text{cm}^{-2} \cdot \text{day}^{-1}$ and for SiC NWs the parabolic rate constant is $k_D = 0.083 \mu\text{g} \cdot \text{cm}^{-2} \cdot \text{day}^{-0.5}$.

The observed difference in corrosion kinetics between Si and SiC NWs is attributed to the formation of surface layers with different behaviours. The oxidation of Si NWs leads to the formation of a non-protective oxide layer, whereas in the case of SiC the oxide layer acts as a stronger diffusion barrier. Although it is stable in its dry state, the native SiO_2 surface layer on Si or SiC can dissolve by hydrolysis in aqueous solutions [21]. The hydrolytic dissolution of SiO_2 , and of Si surfaces through the dissolution of the native oxide layer, generally occurs as a cycle following the reactions:

The oxidation of SiC substrates is about one order of magnitude slower than that of Si in the same conditions [22], which could significantly slow down the corrosion process in the case of SiC NWs. Additionally, the shorter lattice constant of 4.36 Å for 3C-SiC versus 5.43 Å for Si could result in a denser oxide layer with lower

Figure 5. (a) Average weight loss per unit surface of Si and SiC nanowires over 28 days in PBS at 37 °C, calculated from diameter reduction, with standard deviation. (b) Model of Si and SiC nanowire diameter versus immersion time showing the projected depth of corrosion, using $r \propto t$ (reaction-controlled) and $r \propto t^{1/2}$ (diffusion-controlled) respectively with experimentally extracted parameters.

diffusivity. The reaction kinetics could also be affected by the higher bond energy of 4.47 eV for Si–C versus 1.81 eV for Si–Si.

The predicted corrosion kinetics for Si and SiC NWs based on our calculations is plotted on figure 5(b). The projection starts with an arbitrary diameter of 20 nm, which is common to both populations. This model shows that Si NWs with a diameter of 20 nm are expected to dissolve entirely after approximately 32 days of immersion in PBS at 37 °C, whereas SiC NWs of the same diameter would shrink by only 16% in diameter in the same period of time. In these conditions, SiC NWs would last nearly 25 times longer with an expected total degradation time of about 770 days. This clearly illustrates the superior long-term chemical stability of SiC over Si NWs in physiological conditions.

It should be stressed that in this study 3C–SiC NWs exhibiting high density of stacking faults were considered (figure 2(b)). These microstructures have a significant impact on properties of SiC NWs such as mechanical properties [23]. Further investigation should emphasize their influence on the dissolution behavior of SiC NWs by considering SiC NWs with various density of stacking faults as compared to single crystal 3C–SiC NWs.

4. Conclusions

To summarize, the results of this comparative study emphasize the superior chemical stability of SiC NWs over Si NWs under mimicked physiological conditions in a commonly used biological buffer. Further investigation is required to fully understand the kinetics behind SiC corrosion, using longer observation times and varying parameters influencing the rate of reaction, such as temperature, pH and ionic strength. Their superior chemical stability makes SiC NWs a potential substitute for Si NWs in nanoelectronic devices for sensing of biological molecules in liquid media. As mentioned previously, core-shell nanostructures also constitute excellent candidates for harsh environment applications, because such structures have been reported to exhibit higher long-term chemical stability than bare material [10]. In this regard, core/shell Si/SiC nanowires stand among the most promising structures for the development of nano-electronic devices with high reliability in physiological environments. These nano-structures should indeed benefit from a good electronic transport in the Si core along with the superior chemical resistance of the SiC shell, based on the results of this study.

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