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Abstract. Silicon nanowires obtained by a top-down approach have been carburized at high temperature and atmospheric pressure with two different gaseous precursors: CH_4 and C_3H_8. These processes reveal core Si / shell 3C-SiC nanowires. After being characterized by SEM, FIB-SEM and TEM microscopies, the 3C-SiC layer has been used as seed layer for the growth of epitaxial 3C-SiC on the nanowires. Preferential growth of 3C-SiC on the sidewalls of nanowires has been observed. Thanks to the biocompatibility of SiC compared to Si, this layer could act as a protective shell for biosensors based on Si nanowires transistor.

Introduction

3C-SiC is an important material for the fabrication of electronic devices because of its high physical properties: it has a high thermal conductivity, a high mechanical strength, a high breakdown electric field, and a high electronic mobility [1]. Therefore it can operate at high power, high temperature and in harsh conditions. In the meantime, the reduction of the size of devices, and particularly one-dimensional (1D) nano-objects, has an increase interest for industrial manufacture and academic research [2]. In the case of 3C-SiC, several groups have successfully synthesized SiC nanostructures such as SiC nanowires (NWs) [3], core SiC / shell C NWs [4], SiC nanotubes (NTs) [5, 6]. However, there are still some challenges before the elaboration of SiC nanostructures suitable for making good components [7]. Indeed all the above methods lead to the same result: 3C-SiC is mainly crystalline and has a high density of twins and stacking faults.

In this study, core Si / shell 3C-SiC NWs have been elaborated by carburization of Si NWs. These as-obtained core Si / shell SiC NWs have been used to grow by epitaxy a thick layer of 3C-SiC. Each step of the synthesis has been characterized either by SEM or by TEM.

Experimental details

For this study, Si NWs are obtained by a SF_6/O_2 plasma etching of a (100) Si substrate. They are 3.4 µm long with a diameter of 200 nm. Fig. 1 shows SEM image of etched Si NWs before carburization. It can be noticed that the sidewalls display a non-negligible roughness, compared to Si NWs obtained by VLS method, due to the etching process itself. However, these etched Si NWs present major advantages such as high reproducibility of the fabrication process, single crystallinity and absence of catalyst.

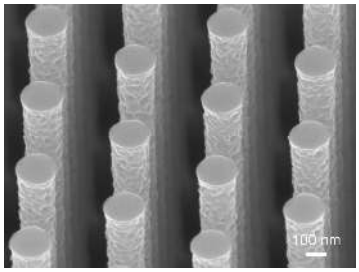

Fig. 1: SEM image of Si NWs obtained by a $SF_6/0_2$ plasma etching of Si(100).

The carburization is performed in a CVD furnace at 1100°C and atmospheric pressure [5, 8]. The main flow is composed of H_2 or H_2-diluted-in-Ar. The H_2 gas leads to a reductive atmosphere useful to remove native oxide at high temperature. CH_4 or C_3H_8 highly diluted in the main flow can be used as carbon precursors and are sent at 800°C. This high dilution allows limiting the carbon deposit in favor of the carburization of Si. After a plateau which lasts from 1 to 60 minutes, the precursor gas flow is switched off and the system is naturally cooled down.

For the 3C-SiC epitaxial growth step, C_3H_8 and SiH_4 are introduced into the reactor and the system is heated up to 1300°C. After 2 min of growth, precursors are removed and the system is naturally cooled down under H_2 until ambient temperature [8].

The obtained NWs are morphologically and structurally characterized with SEM (Zeiss Ultra Plus) and TEM (FEI Tecnaï). A dual focused ion beam – scanning electron microscope (FIB-SEM, FEI Helios 450S) is used to prepare the thin lamella for TEM characterizations of the as-grown SiC layer on carburized Si NWs.

Results and discussions

Carburized Si NWs have the same roughness than before carburization (Fig. 2a), and the overall morphology is kept, such as length and diameter.

The thickness of the 3C-SiC layer, measured by TEM, is about $\varepsilon \approx 3$ nm and the 3C-SiC layer seals entirely the surface (Fig. 2b). This thickness is in accordance with the thickness measured on Si (100) surface. Si core / SiC shell NWs have been elaborated.

Then, the role of the carburization time is studied on the thickness ε of the 3C-SiC layer. In Fig. 2c, the thickness of the 3C-SiC layer as a function of the squared root of the carburization time is reported. It appears a linear relationship between the thickness and the square root time which is typical of a limited-diffusion process. In the case of the carburization of Si, it has been shown that Si is the diffusing specie through the SiC layer. In a previous study, this phenomenon has been used to produce SiC nanotubes from carburization of Si NWs [5].

According to the second Fick's law, and the Einstein-Smoluchowski's relation, the depth ε of the Si surface affected by the carburization is given by Eq. 1:

$$\varepsilon^2 = 2 \cdot D_{Si} \cdot t \qquad (1)$$

Where t is the time and D_{Si} is the apparent diffusion coefficient of Si through the SiC layer. Applying 1, the calculation of the diffusion coefficient of Si into SiC at 1100°C under CH_4 is $D_{Si} = 1.15\times10^{-17}$ cm².sec^{-1}.This value is in accordance with previous studies conducted in similar experimental conditions [9, 10].

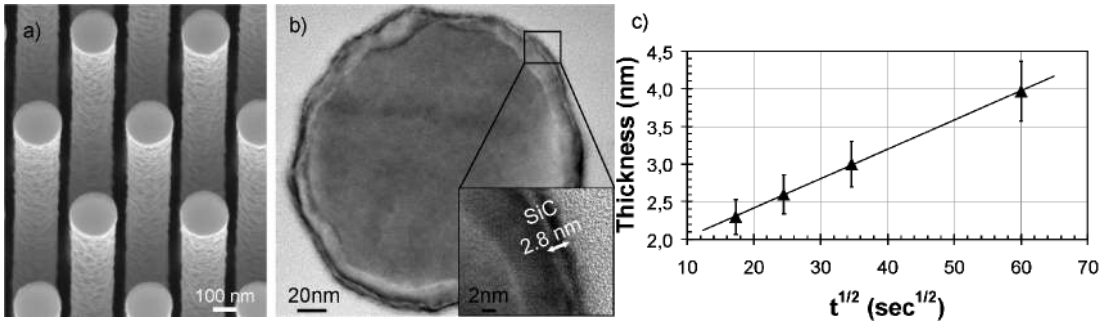

Fig. 2: a) SEM image of Si NWs carburized at 1100°C under CH_4 at atmospheric pressure. b) TEM image of the cross-section of a carburized Si NW. The SiC layer is ~ 3 nm thick, as shown in insert. A thicker layer of about 20 nm appears on the image which is only due to the original roughness of the Si NWs. c) 3C-SiC thickness as a function of the squared root of the carburization time.

Interestingly, it has to be noticed that with an important gas flow of H_2 during the rise of temperature, smoothing of sidewalls is observed, accompanied by a slight diameter reduction (~ 11 nm). A closer inspection shows that these desoxidized Si NWs display facetted sidewalls with {220} and {400} planes with an irregular octagonal section (see Fig. 3a). This is probably due to the minimization of surface energies.

After carburizing these smooth NWs, no morphological change is visible (Fig. 3a). In order to check if any SiC material was formed and to study the structure of carburized Si NWs after carburization, a thin NWs cross-section lamella was prepared thanks to the FIB-SEM. The result is shown in Fig. 3b. As mentioned earlier, the octagonal shape of the section is clearly visible. Dotted lines represent the {220} planes and the continuous lines represent the {400} planes of Si. Interestingly, the {220} planes are smaller than {400} planes. A high magnification image of the periphery is shown Fig. 3c. One can see that the carburization step leads to a single crystalline, ~ 2 nm thick 3C-SiC layer which covers perfectly the Si NWs. The diffraction pattern inserted on Fig. 3c points out the cubic polytype of the buffer layer in epitaxial relationship with the Si NW.

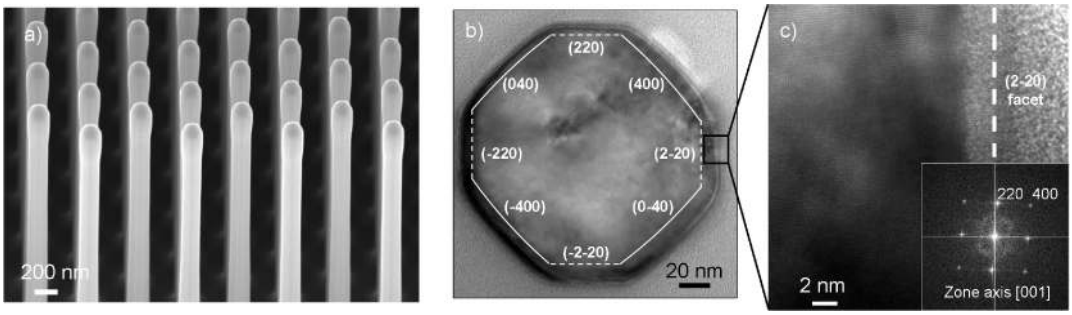

Fig. 3: a) SEM image of Si NWs carburized under C_3H_8 with an important flow of H_2. Sidewalls are smoothed and NWs exhibit an octagonal irregular cross section. b) TEM cross-section of a carburized Si NW with the octagonal shape. {220} planes (dotted lines) and {400} planes (continuous lines) are highlighted. c) Higher magnification on the edge of the NW showing the 3C-SiC carburization layer, diffraction pattern in insert.

These carburized smooth nanostructures have been then used as template for the epitaxial growth of 3C-SiC. As it can be seen on Fig. 4a, this step leads to rough sidewalls of NWs but it also enhances the faceting of the NWs leading apparently to a square section. The occurrence of this faceting suggests that the deposit is crystalline and in epitaxial relationship with the NWs. Moreover, this deposit covers completely the NWs, from the top to the bottom. A FIB-cut of the head of a NW after SiC epitaxy confirms the square shape after growth (Fig. 4b). On this image is

reported the {220} planes and the {400} planes, according to those identified after the carburization step done on smoothed NWs thanks to the difference of length between {400} and {220} planes. The anisotropic growth of 3C-SiC on carburized Si NWs is therefore favored towards {400} directions at the expense of the {220} ones. The thickness of the 3C-SiC layer is around 60 nm on the {400} planes and 10 nm on the {220} planes.

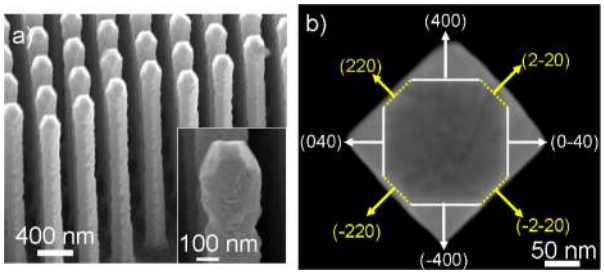

Fig. 4a) SEM image after the epitaxial growth of 3C-SiC on the smoothed and carburized Si NWs. Sidewalls are rough and the epitaxial layer is homogeneous down to the NWs feet. b) SEM image of the square section of one NW after a FIB-cut. The 3C-SiC epitaxial layer has grown preferentially on the <400> directions (continuous lines) at the expense of <220> ones (dotted lines).

Conclusion

Core Si / shell SiC NWs have been successfully elaborated from etched Si NWs. Firstly etched Si NWs are carburized under either CH_4 or C_3H_8, both diluted in H_2, at atmospheric pressure. Monitoring the H_2 flow allows us to smooth the surface of Si NWs before the carburization step but also to highlight the {400} and {220} planes because of reduction of surface energies. The as-grown 3C-SiC layer obtained by carburization is single crystalline, ~3 nm thick and covers entirely the surface. This layer is then used as seed for the epitaxial growth of 3C-SiC. This growth occurs preferentially on the {400} planes. Thanks to the biocompatibility of the SiC shell associated with a Si core in which electronic transport is excellent, this structure has high potential for bio-sensors.

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