High-resolution analytical electron microscopy of silicon nanostructures

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We report on both the fabrication of hexagonally ordered, vertically aligned silicon nanowires (SiNW) and their characterization by means of analytical transmission electron microscopy. Combining colloidal lithography, plasma etching, and catalytic wet etching, SiNW with well defined diameter, length, and density can be obtained. For this purpose hexagonally closed packed monolayers of monodisperse polystyrene particles are transferred into non-closed packed particle arrays. These arrays are used as a mask for silver deposition by thermal evaporation. After the lift-off of the spheres, the silver layer serves as a catalyst for the wet-etching process in an H_2O_2/HF solution. In this way, arrays of SiNW of sub-50 nm diameter with an aspect ratio of up to 10 could be fabricated. Scanning electron microscopy as well as scanning transmission electron microscopy have been applied in order to investigate the morphology, the internal structure and the composition of the catalytically etched SiNW. The analysis yielded a single crystalline, porous structure composed of crystalline silicon and SiO_x with $x \leq 2$.

1 Introduction Silicon nanowires (SiNW) are potential candidates for applications in electronics, photonics and thermoelectrics. Compared with bulk silicon, a change in several characteristic features is expected due to their dimension. Therefore, the possibility to control these features by varying the size, the morphology or the surface structure is indispensable. On the basis of the well-known vapor-liquid-solid process [1] fabrication methods like chemical vapor deposition, molecular beam epitaxy and solution growth have been developed in order to grow SiNW following the "bottom-up" approach.

In contrast, also "top-down" approaches have been developed successfully in order to improve the regularity of the SiNW.

Here we report on the combination of colloidal lithography, plasma etching and chemical wet etching in order to produce SiNW with well defined length, diameter, density and arrangement.

The working principle is based on a metal-induced local oxidation and dissolution of silicon in a solution containing fluorine ions whereas the metal acts as a catalyst

[2,3]. In this galvanic exchange process the metal (e.g. Ag, Au or Pt) layer represents the local cathode and the silicon substrate serves as an anode. The etching solution consists of HF and H_2O_2, whereas the H_2O_2 oxidizes the silicon substrate under the generation of SiF_4, which is removed by HF subsequently. This process can be specified by the following reactions [4]:

Cathode reaction at the metal:

$$H_2O_2 + 2H^+ \rightarrow 2H_2O + 2H^+ \qquad (1)$$

Anode reaction at the silicon:

$$Si + 4H^+ + 4HF \rightarrow SiF_4 + 4H^+ \qquad (2)$$

$$SiF_4 + 2HF \rightarrow H_2SiF_6 \qquad (3)$$

Overall reaction:

$$Si + H_2O_2 + 6HF \rightarrow 2H_2O + H_2SiF_6 + H_2 \qquad (4)$$
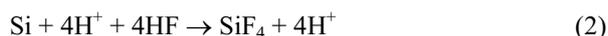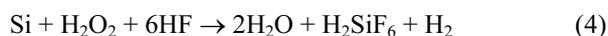
The oxidation process generates pores in the silicon substrate where the silver layer sinks in so that a stable re-

action is formed. The areas that are not covered with silver stay non-etched.

2 Fabrication of well ordered SiNW arrays Mirror-polished arsenic doped n-type Si(111)-wafers with a resistivity between 0.001 Ωcm and 0.006 Ωcm were used for our experiments. The substrate was cut into 10×10 mm^2 pieces, which were treated afterwards for 15 min at 75 °C in an RCA solution, containing H_2O_2 (30 wt.%), NH_4OH (25 wt.%) and H_2O at a volume ratio of 1:1:5, in order to remove organics. Subsequently, the substrate was immersed in deionized water.

The strategy to fabricate well ordered SiNW arrays consists of three main steps, which combine the methods of colloidal lithography [5] and chemical wet-etching. A short overview of this process is given in Fig. 1.
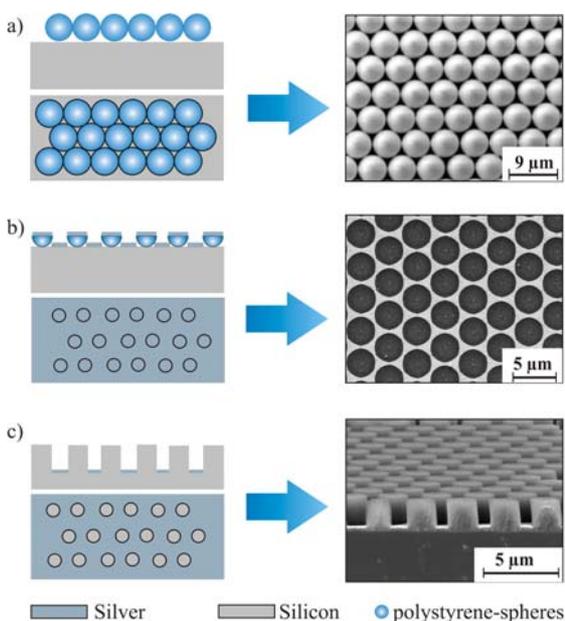
Figure 1 The main steps of the formation process of SiNW via catalytic etching are shown as a scheme and the corresponding scanning electron microscope image: a) Deposition of a monolayer of polystyrene spheres on a silicon substrate by colloidal lithography; b) modification of the sphere diameter by oxygen plasma etching, followed by silver evaporation and removal of the mask; c) catalytic etching with HF/H_2O_2 and removal of the silver layer.

In a first step, monolayers of polystyrene spheres with diameters of 200 nm, 780 nm or 2.55 μm respectively, received from microparticles GmbH (Germany) as a 10 wt.% water solution, were deposited on the cleaned silicon substrate via colloidal lithography (Fig. 1a).

The generation of theses monolayers was based on the self-assembling of the polystyrene spheres at a water-air interface. For this purpose, the particle solution was mixed with an equal amount of ethanol. In order to dissolve agglomerates, the mixture was immersed into an ultrasonic

bath for 15 min. Afterwards the polystyrene particle solution was pipetted onto a clean glass substrate which was immersed in a glass vessel filled with 100 ml of Milli-Pore Q-water. A bordering of the particles was achieved by changing the water tension when adding 2% dodecylsodiumsulfate. Thus, an ordered close-packed monolayer of the polystyrene spheres was formed which has been transferred from the water surface onto the silicon substrate subsequently.

Oxygen plasma at a flow rate of 400 sccm/min and a pressure of 0.06 mbar was applied in order to reduce the diameter of the spheres as well as transforming the close-packed monolayer masks into a non-closed packed assembly. The diameter of the spheres could be controlled by varying the etching time while the center-to-center distance among them remained constant.

In the next step, these modified masks were covered with a silver layer by thermal evaporation (HVT B30.2 system). The following removal of the polystyrene occurred in an ultrasonic bath consisting of $CHCl_3$. At the end a silver mask could be obtained (Fig. 1b).

Finally the silver structured silicon substrate was immersed in an etching mixture consisting of HF and H_2O_2 with concentrations of 4.6 M or 0.44 M respectively (at room temperature) so that SiNW were formed. In a last step the removal of the silver could be achieved by immersion in boiling aqua regia.

3 SEM investigations of SiNW We used a Philips XL30 FEG scanning electron microscope (SEM) to investigate the dependence of the formed SiNW from the process parameters as well as the regularity of the SiNW and their morphology. Especially the shape of the SiNW and their surface were of high interest. An acceleration voltage of 2 kV has been applied for the investigations of the morphology, and otherwise an acceleration voltage of 12 kV.
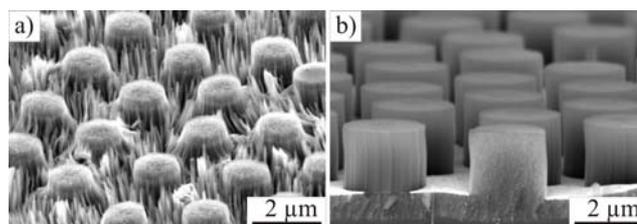
Figure 2 Etching results with silver layers of different thicknesses: a) with 10 nm a random formation of thin SiNW inbetween the positions of the polystyrene spheres is observed and b) with 15 nm well-ordered SiNW are obtained.

In many experiments it can be observed that the thickness of the silver layer is an important parameter for a controlled etching of SiNW. When the silver layer is about 10 nm thick, the silver film is not closed but contains many small holes. Then a random nanowire etching occurs as can be seen in Fig. 2a. If the silver thickness increases, the gaps are getting smaller which leads to a silver film net-

work, and well ordered nanowires are obtained (Fig. 2b). If the silver layer is thicker than 20 nm the film prevents the etching solution from getting into contact with the silicon and hence no nanowire formation is observed.

The diameter of the SiNW is determined by the diameter of the polystyrene spheres which mask the silicon substrate. It can be controlled by varying the etching time of the polystyrene spheres in the oxygen plasma. The density of the SiNW can be changed by the nominal diameter of the polystyrene spheres. Figure 3 shows two masks containing polystyrene spheres with a nominal diameter of 780 nm which were modified by plasma etching for different times. The according catalytic etched SiNW are shown on the right side. After 5 min plasma treatment, the 780 nm wide spheres have a diameter of about 530 nm (Fig. 3a), and after 20 min a diameter of nearly 220 nm (Fig. 3c). The resulting SiNW have the same diameters, as can be seen in Fig. 3b and Fig. 3d.
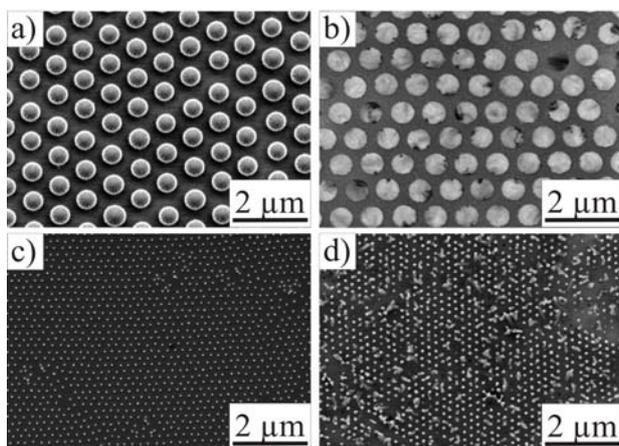
Figure 3 Different plasma etched polystyrene spheres (nominal diameter: 780 nm) and the corresponding catalytically etched SiNW: a) after 5 min plasma etching the spheres have a diameter of 530 nm, b) the SiNW of the 5 min plasma etched mask have a diameter of 530 nm, c) after 20 min plasma etching the sphere diameter is 220 nm and d) the SiNW according to c) have a diameter of 220 nm.

While the diameter of the SiNW depends on the diameter of the polystyrene spheres their length and their shape are mainly determined by the etching time. Catalytically etched SiNW are shown in Fig. 4 where the etching time was varied from 4 min to 50 min. Since the etching process is nearly linear, the length of the SiNW can be adjusted by the etching time.

Figure 4a shows the etching result after 4 min. In this case the length of the SiNW is about 0.5 µm. After 15 min wet etching the SiNW are 2.4 µm (Fig. 4b), after 25 min 4.1 µm (Fig. 4c) and after 50 min 8.2 µm (Fig. 4d) long. The diameter at the basis of the shown SiNW is about 1.4 µm and remains constant during the whole etching duration. However, the shape of the SiNW changes when applying long etching times (Fig. 4d).
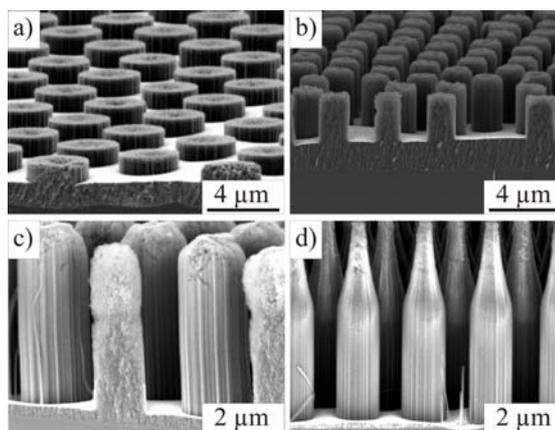
Figure 4 Length of SiNW as a function of etching time. Polystyrene spheres with a diameter of 2.55 µm have been used for masking the substrate. Afterwards they were reduced down to 1.4 µm by plasma etching. The results of catalytic etching after: a) 4 min, b) 15 min, c) 25 min, and d) 50 min are shown.
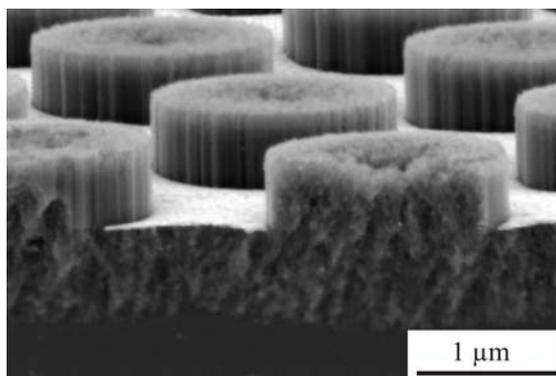
Figure 5 Magnification of Fig. 4a: Both the etched SiNW and the silicon substrate show a porous inner structure.
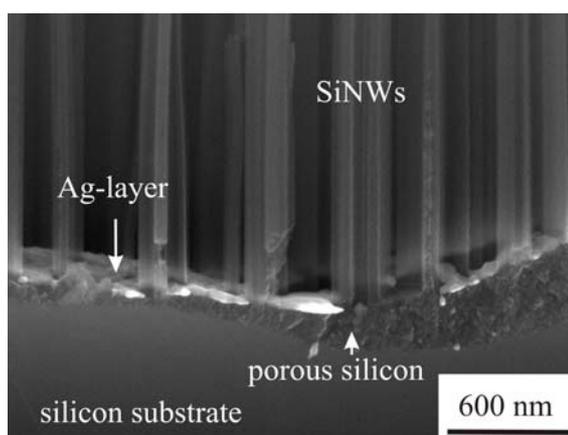
Figure 6 Cross-sectional view of an etched SiNW array with Ag-clusters at the bottom of the wires. A general porous silicon layer under the silver layer as well as beneath the SiNW is assumed.

As can be seen in Fig. 4 as well as in Fig. 5, the catalytic etching under the conditions described above causes a

porous inner structure of the SiNW. Obviously the silicon substrate beneath the wires has a porous structure, too.

In the previous considerations only fundamental results of investigations at bigger SiNW have been discussed. The results obtained have been proved at smaller nanowires with nominal diameters of about 70 nm. A SEM image of comparable SiNW is shown in Fig. 6. The silver layer is well visible at the bottom of the etched SiNW while their inner structure is not resolvable. However, the porous layer beneath the SiNW also emerges after the catalytic etching.

4 STEM investigations of SiNW In order to investigate the internal structure and the composition of the nanowires, electron-transparent cross-section samples have been prepared by applying the standard preparation of mechanical grinding, polishing, dimpling, and Ar ion milling.

Analytical transmission electron microscopy (AEM) has been applied by utilizing a VG HB 501 UX scanning transmission electron microscope (STEM) equipped with a Gatan ENFINA 1000 parallel electron energy loss spectrometer and an EUMEX energy dispersive X-ray detector. The acceleration voltage was 100 kV.

An overview of a typical sample is given in Fig. 7a. Some SiNW are curved or broken which could be induced by the cross-section preparation. The porous silicon layer and the crystalline silicon substrate are visible beneath the SiNW. They can be distinguished through the changed contrast at their border. The SiNW are separated from the porous layer by a chain of silver clusters that is equivalent to the bottom of the nanowires in Fig. 6. However there are also bigger silver clusters beneath this chain deep in the porous layer. The higher magnification of such a sample position is presented in Fig. 7b where aside from the silver clusters also the traces they left during the etching process are visible. At sample position where bigger silver particles break through the silver chain no SiNW are existent. Though, it has to be noticed that a possible influence of the sample preparation on such a behavior could not be excluded.

It is well known that by catalytic etching porous silicon is formed through the generation of holes in crystalline silicon [6]. This process does not imply a loss of crystallinity. In order to verify this assumption diffraction patterns of one single SiNW on the one hand and of both the porous layer and the silicon substrate on the other hand were recorded. Due to the fact that the diffraction pattern of the substrate and the porous layer were identical, only one of them is shown in Fig. 8b. The lower thickness of the SiNW causes the visibility of only a few diffraction spots in Fig. 8a. Nevertheless, both patterns in Fig. 8 represent the same crystalline structure.

We conclude that the SiNW as well as the porous layer consist of a single crystalline skeleton, which is surrounded by silicon oxide.
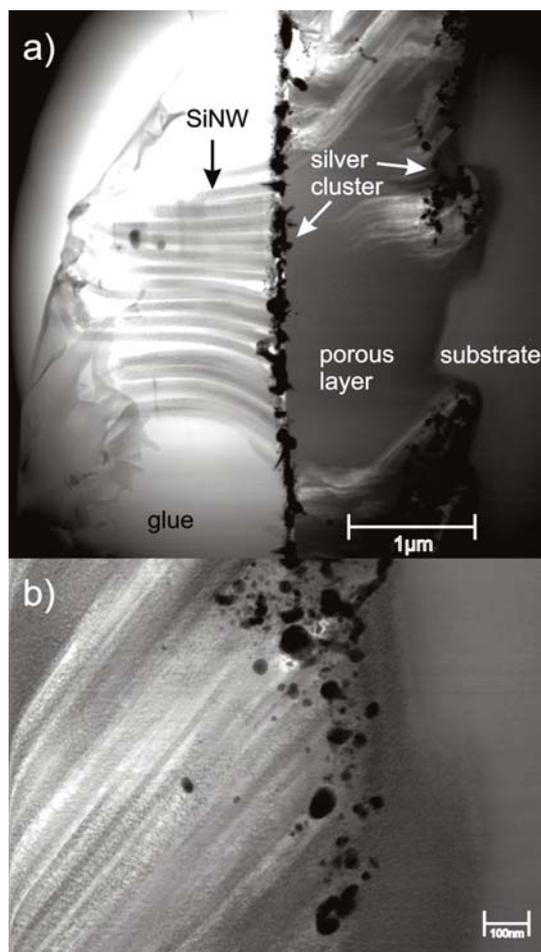
Figure 7 Bright field (BF) STEM images of a cross-section sample, a) an overview and b) an enlarged detail of the upper image.
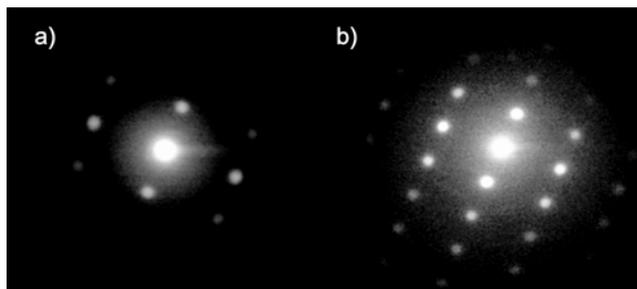
Figure 8 Diffraction patterns of a) one SiNW and b) the porous layer or the substrate respectively.

Electron energy loss spectroscopy (EELS) has been applied in order to receive further information about both the structure and the composition of the SiNW.

EEL spectra of the silicon $L_{2,3}$ edge from a SiNW as well as from bulk silicon and from reference SiO_2 have been recorded with a measuring time of 3 s per spectrum. The $L_{2,3}$ edges are shown in Fig. 9 after a background correction with a power law.
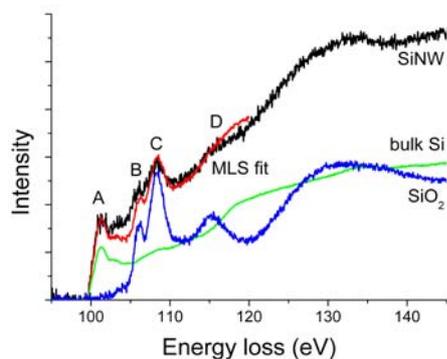
Figure 9 Silicon $L_{2,3}$ edges of a SiNW, bulk silicon and SiO_2 and the according MLS fit. The bulk silicon/SiO_2 ratio (atomic fraction) is determined to nearly 3 by the coefficients of the MLS procedure.
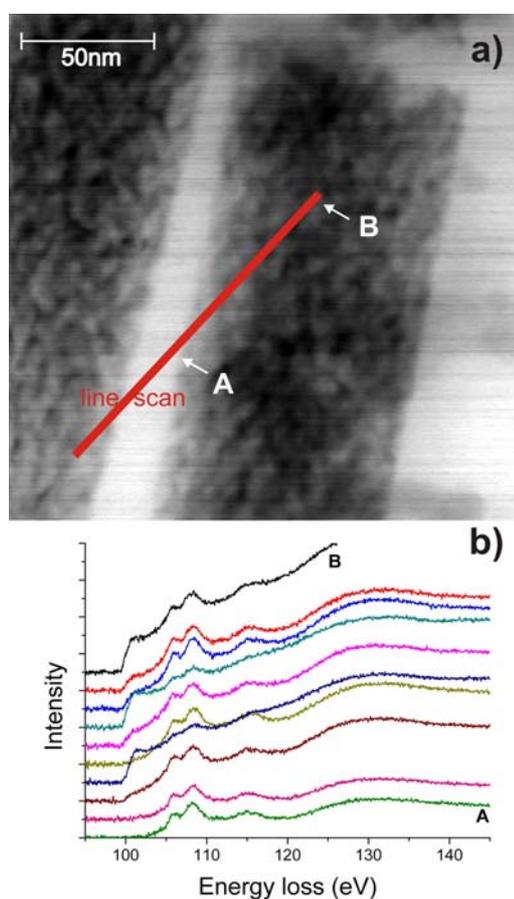
Figure 10 a) BF STEM image of a SiNW with a linescan indicated. b) EEL spectra between the marks A and B. The particular spectra are shifted in the intensity for a better visibility.

Referring to the Eqs. (1) to (4), the SiNW should only consist of bulk silicon and SiO_2. Hence, we assumed the silicon $L_{2,3}$ edge of the SiNW to be a superposition of the silicon $L_{2,3}$ edges of bulk silicon and SiO_2. At the first view

its structure exhibits four main features (labeled with A to D in Fig. 9) that could be well assigned: Peak A is characteristic for bulk silicon while the peaks B to D arise from the presence of SiO_2.

In order to quantify the ratio of bulk silicon and SiO_2 in SiNW, a multiple least squares procedures (MLS) was applied [7]. The spectra of bulk silicon and SiO_2 in Fig. 9 were used as a reference for the MLS procedure after they have been normalized to the integrated counts in the energy range between 125 eV and 145 eV. The MLS fit is also illustrated in Fig. 9: The fit worked very well at the peaks but for instance between the peaks A and B it failed. A more detailed investigation of the composition reveals that other constituents of silicon oxide or amorphous silicon have to appear inside the SiNW. This conclusion is supported by the measurement of spectra where instead of peak A only a shoulder at peak B has occurred. These spectra could not be fitted sufficiently with the two reference spectra.

Figure 10a shows the bright field (BF) image of a SiNW where the porous surface structure is clearly visible. In order to obtain spectra from the surface region as well as from the interior a line scan across the SiNW has been carried out with an average measuring time of 2.5 s per measuring point. The silicon $L_{2,3}$ edges, obtained after background correction, are given in Fig. 10b. The two lower spectra measured next to position A (surface region of the SiNW) are comparable to the spectrum of SiO_2 in Fig. 9. This fact indicates that the SiNW are surrounded by a thin SiO_2 layer. The other spectra in Fig. 10b can be interpreted as a superposition of the silicon $L_{2,3}$ edges of bulk silicon and SiO_x ($x \leq 2$) respectively. The alternating shape of the silicon $L_{2,3}$ edges along the line scan reflects the inhomogeneity inside the SiNW that is caused by the porous structure: Following the line scan from the surface region of the SiNW to its center the EEL spectra show no correlation between the position at the SiNW and its composition or structure respectively.

Since silver has acted as a catalyst during the etching process, its distribution and its content inside the SiNW was of high interest. Therefore energy dispersive X-ray spectrometry (EDX) has been applied.

A BF image of the SiNW investigated is given in Fig. 11a. EDX spectra have been acquired at the three marked position with a measurement time of 50 s at each position. The spectra are shown in Fig. 11b. A microscope aperture consisting of molybdenum was used to shield the detector from scattered radiation.

Silver clusters of different sizes have been investigated at the positions A and B in order to determine the sensitivity of the method. A clear silver signal arises in both cases. In addition, both the silicon signal and the molybdenum signal arise through excitations by fluorescent silver X-rays. The diameter of the silver cluster at position B is around 5 nm. No smaller silver clusters could be detected.

The EDX measurement at the SiNW (position C) yields only signals from silicon and oxygen whereas no silver could be detected.
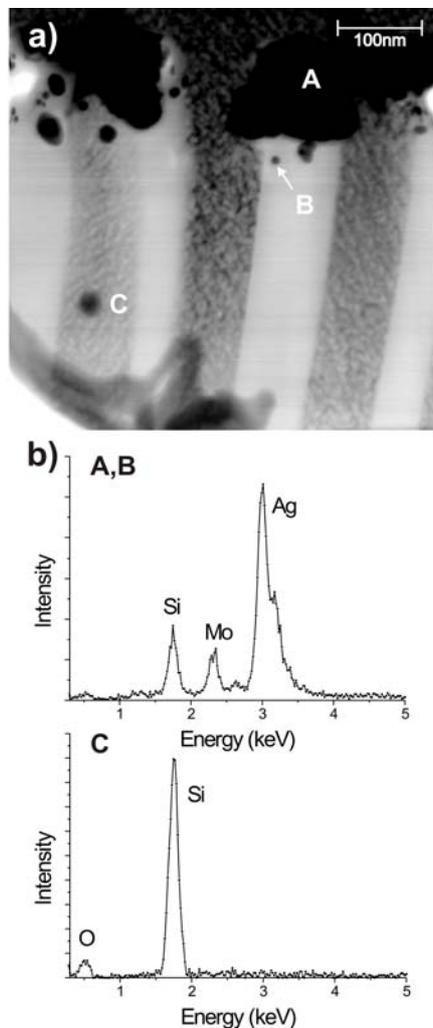
Figure 11 a) BF STEM image of a SiNW with silver clusters. b) EDX spectra at the sample positions marked. The molybdenum signal arises through the absorption of fluorescent silver X-rays at the aperture used during the measurement.

5 Conclusions We described the formation of hexagonally ordered, vertically aligned SiNW fabricated by catalytic etching. Both the internal structure and the composition of these catalytically etched SiNW were investigated by analytic electron microscopy. SEM images as well as STEM images show the porous structure of the SiNW where an additional porous silicon layer is formed beneath the SiNW.

Diffraction patterns show that the SiNW as well as the porous layer consist of a single crystalline skeleton surrounded by silicon oxide. The crystal structure is the same as the silicon substrate.

The SiNWs mainly consist of a mixture of bulk silicon and SiO_2, whereas no correlation between the varying composition and the position at the SiNW exists. Due to the differences between the recorded spectra and the corresponding MLS fits, the presence of amorphous silicon or other oxidation states of silicon oxide is assumed. A possible influence of quantum confinement effects on the EEL spectra due to the micropores has been neglected in this paper and has to be subject of further research. This also holds for a more detailed investigation of the silver distribution inside the SiNW.

References

[1] R. S. Wagner and W. C. Ellis, Appl. Phys. Lett. **4**, 89 (1964).
[2] Z. Huang, H. Fang, and J. Zhu, Adv. Mater. **19**, 744 (2007).
[3] K. Peng, J. Hu, Y. Yan, Y. Wu, H. Fang, Y. Xu, S. T. Lees, and J. Zhu, Adv. Funct. Mater. **16**, 387 (2006).
[4] X. Li and W. Bohn, Appl. Phys. Lett. **77**, 2572 (2000).
[5] U. C. Fischer and H. P. Zingsheim, J. Vac. Sci. Technol. **19**, 881 (1981).
[6] H. Föll, M. Christophersen, J. Carstensen and G. Hasse, Mater. Sci. Eng. R **39**, 93 (1981).
[7] R. Leapman, in: Transmission Electron Energy Loss Spectrometry in Materials Science and the EELS Atlas (Wiley, Weinheim, 2004), pp. 70-75.