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Silicidation of Silicon Nanowires by Platinum

Bangzhi Liu,*,† Yanfeng Wang,‡ Sarah Dilts,† Theresa S. Mayer,‡,§ and Suzanne E. Mohney*,†,§

Department of Materials Science and Engineering, Department of Electrical Engineering, and Materials Research Institute, The Pennsylvania State University, University Park, Pennsylvania 16802

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ABSTRACT

The solid-state reaction between platinum and silicon nanowires grown by the vapor−liquid−solid technique was studied. The reaction product PtSi is an attractive candidate for contacts to p-type silicon nanowires due to the low barrier height of PtSi contacts to p-type Si in the planar geometry, and the formation of PtSi was the motivation for our study. Silicidation was carried out by annealing Pt on Si nanowires from 250 to 700 °C, and the reaction products were characterized by transmission electron microscopy. Strikingly different morphologies of the reacted nanowires were observed depending on the annealing temperature, platinum film thickness, silicon nanowire diameter, and level of unintentional oxygen contamination in the annealing furnace. Conversion to PtSi was successfully realized by annealing above 400 °C in purified N_2 gas. A uniform morphology was achieved for nanowires with an appropriate combination of Si nanowire diameter and Pt film thickness to form PtSi without excess Pt or Si. Similar to the planar silicidation process, oxygen affects the nanowire silicidation process greatly.

Silicon nanowires (SiNWs) have been successfully used in prototype devices such as field effect transistors[1,2] and biosensors.[3−5] Low-resistance contacts to the nanowires are important for efficient operation of many of these devices. Either Ti/Au or Ni contacts (which form NiSi upon annealing) were used for the above-mentioned devices. The NiSi contacts were reported to form ohmic contacts to p-type SiNWs in one study,[6] but they introduced an unwanted Schottky barrier in vertical p-type SiNW field effect transistors in another study.[7]

Generally speaking, there are two ways to make ohmic contacts to semiconductors in the conventional or planar geometry. One way is to heavily dope the semiconductor so that the Schottky barrier at the metal/semiconductor interface narrows and allows carriers to tunnel through. The other is to reduce the barrier height so that carriers can go over it easily by thermionic emission. The former is what has been used extensively in planar silicon processes and can be realized in SiNWs if the NW diameters are not too small. However, selectively doping the ends of nanowires to improve ohmic contacts requires extra processing steps or growth of NWs in a reactor with in situ doping capabilities. Another route to making ohmic contacts to a nanowire device is to use a contact metallization that provides a very low Schottky barrier height.

It has been reported that platinum monosilicide (PtSi) has a barrier height as low as 0.21 eV on p-type Si,[8] and it has found application in infrared detectors.[9] Additionally, it forms at fairly low temperatures (∼180−600 °C).[10−14] These properties make PtSi an attractive candidate for ohmic contacts to p-type SiNWs. Platinum silicides have been formed through reaction of Pt with SiNWs. A recent report showed that $PtSi_x$ NW segments form when reacting Pt with SiNWs fabricated by sidewall transfer lithography, and the resistivity of the silicide segments were measured.[15] Platinum NWs in membranes have also been silicided using $SiCl_4$ at 1093 K, which it is reported converts them into Pt_6Si_5. In some cases, Si segments also grow attached to the silicide segments.[16] However, a study of the solid-state reaction between Pt- and VLS-grown SiNWs is still missing. Therefore, the solid-state reaction between Pt and vapor−liquid−solid (VLS) SiNWs was examined in this work. The silicidation results are compared to the results for silicidation of planar Si wafers, including the effect of oxygen on the SiNW silicidation process.

The SiNWs used in this study were grown by the vapor−liquid−solid (VLS) technique[17] on oxidized Si wafers.[18] The nanowire diameters were widely distributed between 20 and 100 nm because the VLS growth was catalyzed by a thin Au film deposited on the oxidized wafer prior to VLS growth. To prepare the nanowire for Pt deposition, as-grown

* Corresponding authors. E-mail: bul2@psu.edu (B.L.) and mohney@ems.psu.edu. (S.E.M.).
† Department of Materials Science and Engineering.
‡ Department of Electrical Engineering.
§ Materials Research Institute.

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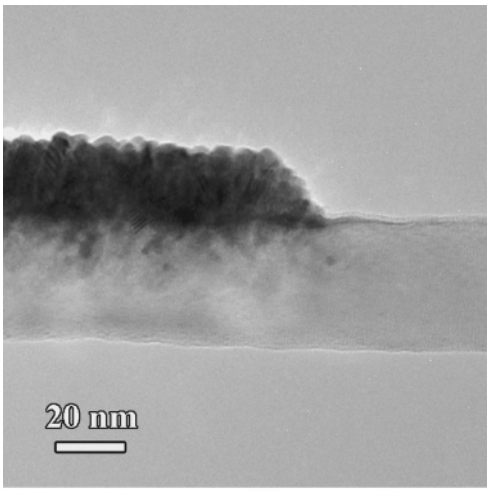
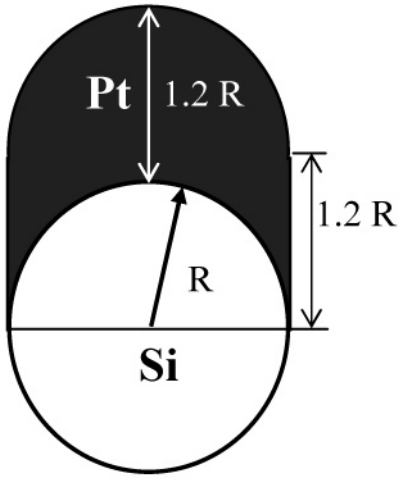


(a)



(b)

Figure 1. (a) TEM image of the side view of 20 nm Pt deposited on a SiNW and (b) schematic of the end view of Pt on a SiNW.

samples were treated in buffered oxide etch (BOE) for 1−2 min to remove the native oxide, then rinsed in DI water, blown dry with N_2, and loaded promptly into an electron-beam evaporation chamber. Platinum films of 20 and 50 nm thicknesses were evaporated at a base pressure of 10^{-7} Torr. After deposition, samples were annealed under UHP N_2 in a tube furnace at temperatures between 250 and 700 °C for 5−60 min. The flow rate of UHP N_2 was 100 sccm, and the gas passed through a Supelco high-capacity gas purifier to further remove O_2. Then the NWs were released from the wafer on which they were grown by sonication and put on lacey carbon films for observation by transmission electron microscopy (TEM). Samples were investigated with a JEOL 2010F transmission electron microscope operating at 200 kV.

The as-grown SiNW surface has negligible native oxide on its surface, similar to the nanowires reported by Wu et al.[19] The deposited Pt film, polycrystalline in nature, covers only one side of the NW due to the geometry of the deposition method, as shown Figure 1a. By assuming that the Pt film thickness is constant around the top portion of the NW, as shown in Figure 1b, the cross-sectional area of the Pt film would be $2Rt$, where R is the radius of the wire,

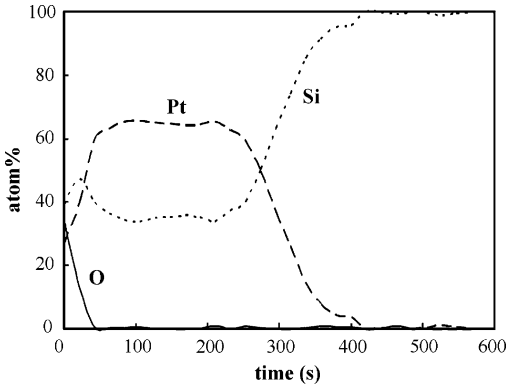


Figure 2. Auger depth profile a 50 nm Pt film on a Si wafer sample annealed at 550 °C for 5 min.

and t the thickness of Pt. Therefore, a thickness of $1.2R$ would be needed for Pt to form PtSi if ideal Pt density is assumed.

Oxygen in the annealing environment is reported to greatly affect the silicidation of planar Si wafers.[20−23] We see that the SiNW silicidation process is affected as well. First, the silicidation of SiNWs under clean conditions is described in this letter, followed by silicidation under oxygen-contaminated conditions. Auger depth profiling was used to monitor the oxygen contamination in planar control samples that were prepared along with the NW samples. Under clean conditions, the Auger depth profiles showed no oxygen in the films before and after annealing. The latter is shown in Figure 2. This profile demonstrates that our film deposition and furnace annealing was relatively clean. Allowing for the base pressure (10^{-7} Torr) during deposition and the detection limit of Auger electron spectroscopy, however, the term "clean conditions" does not mean that there is no oxygen in the system; rather, the trace oxygen in the annealing gas does not appear to affect the silicidation process greatly. Next, a series of SiNW samples with 50 nm Pt were annealed at 250, 350, and 550 °C, followed by TEM investigation. The morphology did not change significantly compared to the as-deposited sample after 1 h of annealing at 250 °C, as shown in Figure 3a. This micrograph indicates that most of the Pt film remained unreacted, making the interfacial reaction difficult to view through the unreacted Pt. It has been reported that aqua regia (4 H_2O/3 HNO_3/1 HCl) can selectively etch Pt and Pt_2Si but leave PtSi unattacked.[13] Therefore, etching with aqua regia was performed at 70 °C for 30 min. Moiré fringes were observed on top of the SiNW surface, as shown in Figure 3b. The most commonly observed reaction products between Pt films and Si wafers are PtSi and Pt_2Si,[11,14] and these were the only products observed in our samples annealed at higher temperature. Therefore, it is likely that these Moiré fringes resulted from the interference between PtSi grains and the underlying Si. Although we cannot rule out the possibility of the formation of Pt_6Si_5, which was observed in a previous study of platinum silicide nanowires formed by a different technique,[16] the processing temperatures used for Pt_6Si_5 formation were far greater than those used in our work or those used for the processing of platinum silicide contacts

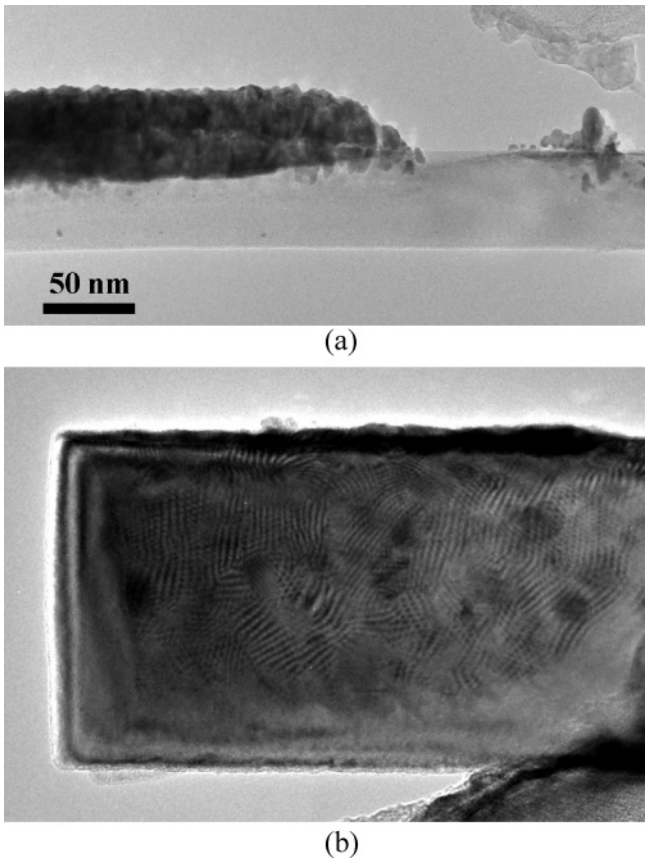


Figure 3. TEM images showing morphologies of SiNWs with 50 nm Pt on them after annealing at 250 °C for 1 h (a) before and (b) after aqua regia etching.

in the planar geometry, for which only Pt_2Si and PtSi are commonly observed.

When samples were annealed at 350 °C for 1 h, greater reaction was observed between Pt and the underlying silicon, as shown in Figure 4a. Polycrystalline grains (again presumably PtSi) were observed after etching in aqua regia, as shown in Figure 4b and c. As indicated by the dimensions of regions of Moiré fringes in the same direction, however, the grain size is much larger after annealing at this temperature than at 250 °C. For both annealing temperatures, most of the silicon remained unreacted.

When 50 nm Pt was deposited on the SiNWs and annealed at 550 °C for 45 min, more significant reaction occurred, as shown in Figure 5. However, the morphology of the reacted nanowire was rough and curved. Electron diffraction patterns showed that Pt_2Si was the dominant phase formed along with PtSi. Unreacted Pt was also observed, indicating that Pt was present in excess compared to the amount of Si available to form PtSi. This high Pt/Si ratio is linked to the poor morphology shown in Figure 5, as explained later in this work. We reduced the Pt film thickness to 20 nm in our next experiments.

The samples with 20 nm Pt were annealed only above 350 °C, as only slight interfacial reaction was observed in the samples with 50 nm annealed below this temperature. Full consumption of Pt was observed when the samples were annealed over a temperature range of 400−700 °C for 30 min. The uniformity was improved above 450 °C. A large number of SiNWs were converted into PtSi NWs with diameters between 35 and 45 nm. A typical morphology is shown in Figure 6a. Figure 6b is a high-magnification image of the boxed area in Figure 6a, showing that the converted NWs are well crystallized. The diffraction pattern shown in the inset of Figure 6b confirms that the phase formed is PtSi. The resulting NWs are polycrystalline, similar to the $PtSi_x$ NWs observed in ref 14. A single grain constitutes a segment of the wire, as determined from the contrast difference resulting from the varying crystallographic orientation of each grain. On average, PtSi grains grow bigger with higher annealing temperature. Besides PtSi, occasionally Pt_2Si was found in some sections of the NWs.

If the SiNW diameter is large, only part of it can be consumed by 20 nm Pt, as shown in Figure 7a. The original diameter of this SiNW is 77 nm, as measured from the unreacted part. The top side is believed to be the Pt-covered side before annealing, judging from the morphology. Interestingly, the Pt silicide is covered by an amorphous layer that was found to be silicon oxide by energy dispersive X-ray spectroscopy (EDS). It also had some small unidentified particles embedded in it. The high-magnification image (Figure 7b) shows missing silicon underneath the PtSi, indicating some silicon movement during reaction. This amorphous layer was also observed covering one side of the PtSi grains, as shown in Figure 6.

A significant difference was observed in the silicidation process under contaminated conditions, where oxygen was introduced into the annealing furnace unintentionally. The presence of oxygen was confirmed by Auger depth profiling of a planar control sample, as shown in Figure 8, where a considerable amount of oxygen was found through the whole reaction layer in the sample annealed at 350 °C for 1 h. However, the reaction between Pt and Si was not prevented because Pt and Si still fully reacted with each other. The phase formed was PtSi, as determined by X-ray diffraction (XRD).

A series of experiments was conducted under these conditions. Similar to the findings when oxygen contamination was negligible, a slight interfacial reaction was observed in the sample that was annealed at 250 °C for 4 h following etching with aqua regia. No more significant reaction was observed for annealing temperatures up to 400 °C. Increasing the annealing duration did not promote further reaction. For example, one sample was annealed at 350 °C for 14 h without changes in the morphology. When samples were annealed at 450 and 550 °C, the morphology started to change, indicating greater reaction. A typical morphology is shown in Figure 9 for a sample annealed at 550 °C for 45 min, where unreacted Pt was removed by aqua regia. Grains of varying sizes and shape can be observed. It is quite possible that most of the grains, if not all, are actually growing out of the SiNW surface, as evidenced by the protruding grains on the sides of the NW. Some grains have an elongated shape. One such grain is shown on top of the wire in Figure 9, and the electron diffraction pattern from the elongated grain (shown in the inset) matches PtSi.

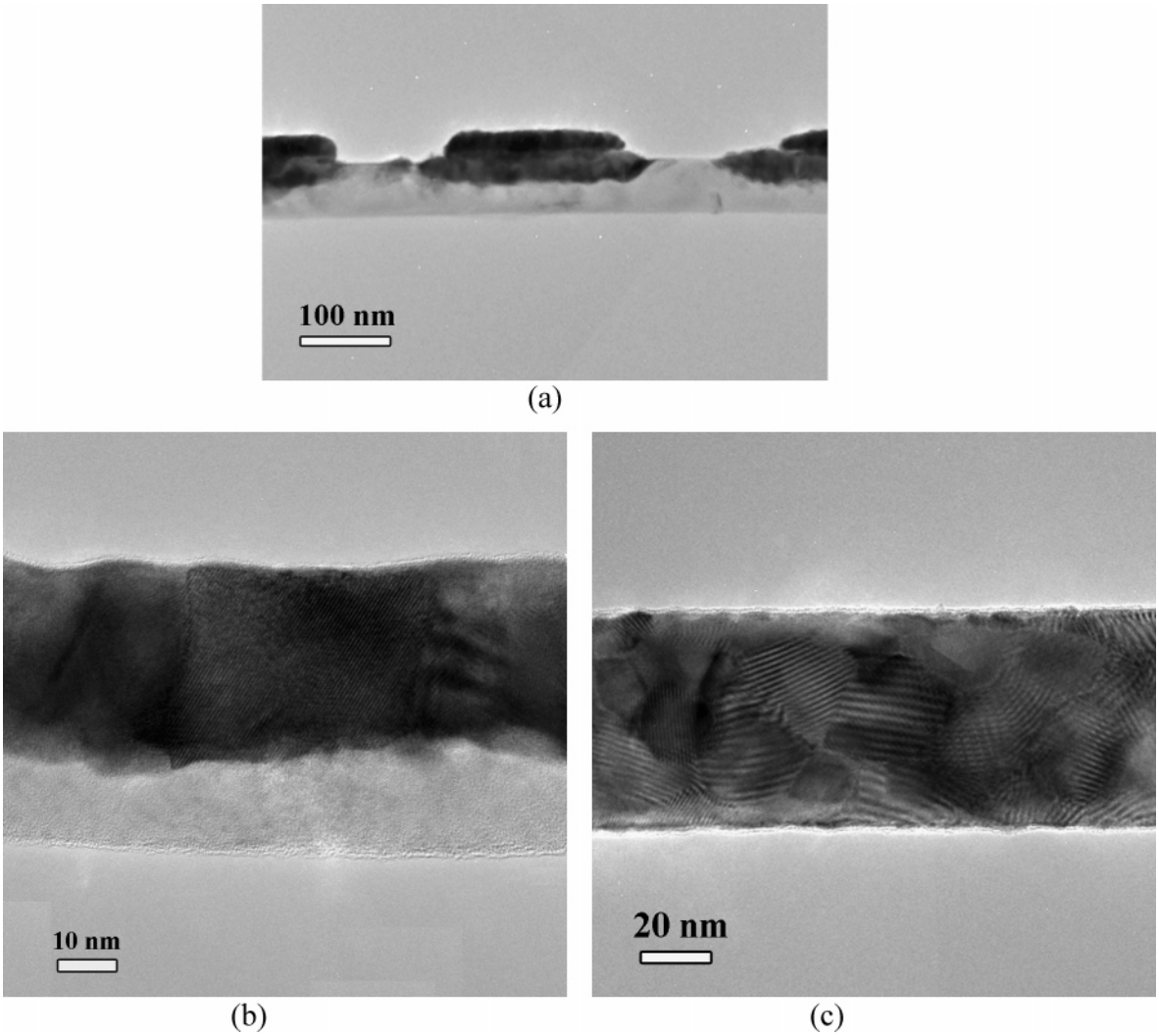


Figure 4. (a) TEM image showing morphology of SiNWs with 50 nm Pt on them annealed at 350 °C for 1 h. (b) Side view and (c) top view of the reacted region after aqua regia etching.

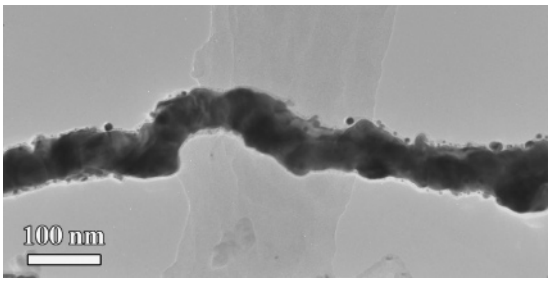


Figure 5. TEM image showing morphology of 50 nm Pt deposited on a SiNW and annealed at 550 °C for 45 min.

Overall, three types of morphologies were observed when the samples were annealed above 400 °C under clean conditions: fully silicided SiNWs with uniform morphology, fully silicided NWs with curvy and irregular shapes, and partially silicided SiNWs. The type of morphology depends on the starting SiNW diameters and the amount of metal deposited, or alternatively, the atomic ratio between Pt and Si. Because of the diameter distribution of the as-grown SiNWs, the amount of silicon available for reaction with a given thickness of Pt varied, again leading to three different cases: Si in excess, Pt in excess, and Pt/Si in an approximately 1:1 atomic ratio. At the end of the reaction, PtSi and unreacted Si are the only phases found when Si is in excess. The uniformity of the silicided NWs was strongly correlated to the final phases formed for both thicknesses of Pt studied. The phase PtSi was dominant in the uniformly converted NWs, but Pt_2Si was dominant in the rough, curved NWs. The difference in the final phase formed and morphological uniformity may be due to the varying atomic ratio of Pt/Si and the volume change of Pt_2Si and PtSi compared to the original volume of the SiNWs.

PtSi has an orthorhombic structure ($a = 0.5932$ nm, $b = 0.5595$ nm, $c = 0.3603$ nm). After silicidation, the volume change of PtSi is about 50% more than the original silicon volume, and the resultant PtSi diameter is about 1.22 times the SiNW diameter if uniform conversion is assumed. Following the profile of the Pt film shown in Figure 1b, 20 nm Pt will react with a SiNW of 33 nm and form a PtSi NW 40 nm in diameter. This explains why the observed PtSi NWs have diameters around 40 nm, and also tells us that the thickness of the Pt film is critical for converting SiNWs to PtSi NWs uniformly. For 50 nm Pt, however, an 83 nm

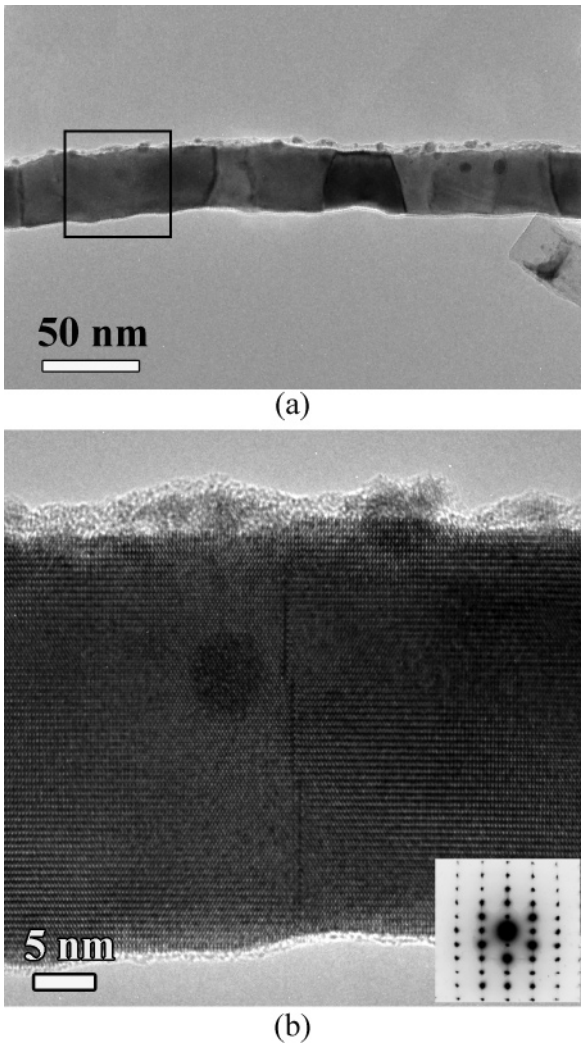


Figure 6. (a) TEM image showing 20 nm Pt on a SiNW annealed at 550 °C for 30 min. (b) High-resolution image of the boxed area in (a). Inset in (b) is the PtSi [011] zone pattern from the boxed area.

SiNW in diameter is needed for full conversion into PtSi. As a result, Pt is in excess in most of the cases because most of the SiNWs have smaller diameters, leading to the formation of Pt_2Si (tetragonal structure: $a = 0.3933$ nm, $c = 0.591$ nm). Its volume is about 2.29 times the initial silicon volume, resulting in the development of large strain during silicidation, forcing the silicided NWs to bend, as observed in Figure 5. This curved morphology has also been observed in ref 14, where the reason was ascribed to photolithography. However, we observe the same morphology with no photolithography. Therefore, another explanation for the observation in ref 14 could be the bending induced when Pt_2Si forms. The formation of Pt_2Si is possible in those experiments, although a decisive determination of the phase(s) formed was not performed. Interestingly, a modest relative volume change between the silicide and Si occurs along with the smooth morphology of NiSi NWs formed when Ni reacts with Si.[6] The volume of the NiSi is only 10% more than that of the consumed silicon, hence only 5% change in diameter is expected after silicidation by Ni.

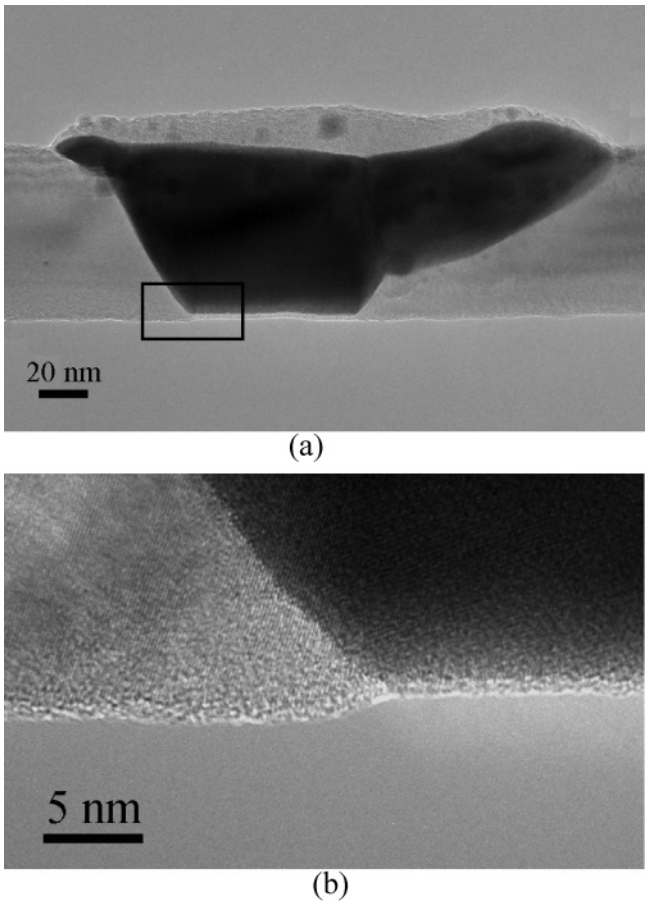


Figure 7. (a) Morphology of 20 nm Pt on a SiNW of 77 nm diameter annealed at 700 °C for 30 min, and (b) a high-magnification image of the boxed area in (a).

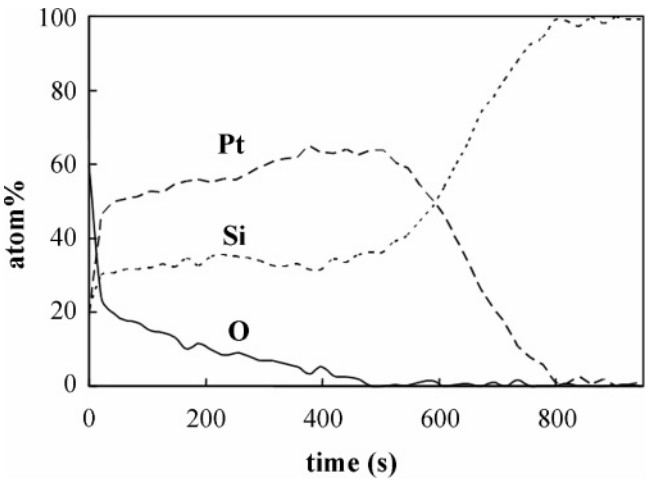


Figure 8. Auger depth profile showing elemental distribution of an 80 nm Pt on a Si wafer annealed at 350 °C for 1 h.

The morphology of the nanowires after silicidation by Pt is also sensitive to the oxygen content in the annealing furnace, especially at temperatures of 450 and 550 °C. Under oxygen-contaminated conditions, the morphology of the silicided NWs becomes fairly rough, with the protrusion of PtSi grains, as shown in Figure 9. This case is opposite to silicidation by Pt under clean conditions, in which uniform morphology is achieved for the proper Pt/Si ratio. This

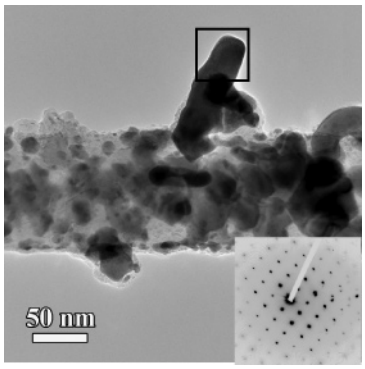


Figure 9. TEM image showing morphology of 80 nm Pt/SiNW annealed at 550 °C for 45 min followed by aqua regia etching. Inset shows the diffraction pattern for the [$\bar{1}$11] zone axis of PtSi for the protruding grain marked by the box.

phenomenon may be explained by the relative atomic movement of Pt and Si.

It has been reported that the solid-state reaction between Pt and Si follows a special sequence on Si wafers when oxygen contamination in the annealing gas is low. First Pt_2Si forms, followed by PtSi.[20,21] Platinum is the dominant diffusion species (DDS) during Pt_2Si formation, but Si is the DDS during PtSi formation.[24] Our experiments do not reveal if the sequential reaction is followed in the nanowire silicidation process, but it is quite possible because Pt_2Si and PtSi were the only phases observed. If this is the case, Pt will be consumed by diffusing through Pt_2Si and reacting with Si at the interface. After the consumption of Pt, Si starts to diffuse and PtSi results. Then two possibilities may occur, depending on the availability of Si. If the Si source is exhausted, Pt_2Si cannot be fully converted into PtSi, resulting in the coexistence of both phases. We observed this case frequently when we had 50 nm Pt on our SiNWs. If Si is present in excess, then Si will continue to move after the transformation of Pt_2Si into PtSi is complete, ending up over the top of the PtSi and being oxidized, even when the background contamination of oxygen is modest. This oxidation of Si is catalyzed by Pt.[25] Consequently, a layer of amorphous oxide results where the surface of the Pt film was originally, as observed over PtSi in Figures 6 and 7a. The movement of Si is also confirmed by the loss of Si on the bottom of the wire, as shown in Figure 7b. Similarly, the formation of a SiO_2 capping layer on PtSi has been reported in the planar silicidation processes.[14]

The scenario changes if oxygen is present. As reported in the literature, oxygen segregates at the Pt_2Si/Si interface upon annealing, preventing the transport of Pt. As a result, the silicidation process is either slowed down or stopped completely if the oxygen concentration is high enough.[20,23] This explains the limited interfacial reaction we observed at 250 °C annealing under clean conditions and up to 400 °C annealing under oxygen-contaminated conditions. The difference in the annealing temperature where the reaction temperature is limited is due to differences in the purity of the annealing gas, which in turns governs the concentration of oxygen at the silicide growth front. However, Si movement is not prohibited by the interfacial oxygen accumulation, and the migration of Si into Pt has been reported.[22,25] This is quite possibly what happens at 450 and 550 °C when annealing under contaminated conditions. The out-diffused Si reacts with Pt, leading to the formation of protruding PtSi grains.

With all the results obtained in this study, it would be meaningful to give a comparison between Pt silicidation processes in the nanowire geometry and in the planar thin film/wafer geometry. First of all, in the conventional planar geometry, the Si source is generally in excess for thin film silicidation, and as a result, PtSi is the final phase formed. For the nanowire silicidation, however, the Si source may or may not be in excess, depending on the nanowire diameter and the Pt film thickness. Nevertheless, similarities exist between the two processes. Platinum starts to react with SiNWs at a temperature as low as 250 °C, which is the lowest temperature we used and is comparable to the low starting temperature (~200 °C) reported for the reaction in the thin film case.[10,14] The reaction in the nanowire case may follow the same sequential phase transformation as the thin film case. Oxygen affects both processes in a similar way in terms of elemental movement. However, oxygen affects the nanowire silicidation more profoundly. As shown in Figure 8, the oxygen under the contaminated conditions did not greatly retard the thin film reaction, but it prevented Pt from reacting extensively with the SiNWs. Again, in Figure 8, annealing for 1 h at 350 °C was sufficient for 80 nm of Pt to react fully with a Si wafer. Even under the clean conditions, however, this annealing condition did not cause 50 nm of Pt to fully react with the SiNWs, as shown in Figure 4a. The difference could be due to the geometry of the nanowire samples. Different from the continuous film on a planar wafer, Pt only covers half of the surface of the NW. Oxygen can enter the metal film more easily from the sides and reach the interface more quickly, slowing down the reaction between Pt and Si to a greater extent.

In summary, the silicidation of SiNWs by Pt was studied under clean and oxygen-contaminated conditions. Similar to the thin film silicidation process, the reaction between Pt and SiNWs starts at low temperature (250 °C) and is sensitive to the oxygen contained in the annealing ambient. Under clean conditions, the reaction is limited only at the interface at low temperature (250 °C). Conversion of SiNWs into PtSi NWs can be realized upon annealing above 400 °C. The atomic ratio between Pt and Si, determined by the Pt film thickness and SiNW diameter, is critical to the uniformity of the silicided NWs. Ideally, it is desirable to achieve a 1:1 ratio between the Pt and Si to obtain uniformly converted PtSi NWs. If Pt is in excess, nanowire bending induced by the formation of Pt_2Si can occur. Compared to the reaction of Pt films on Si wafers, oxygen has a larger effect on the SiNW silicidation process, more severely preventing or slowing down the reaction at low temperatures (less than 400 °C) and making the morphology rough after silicidation at high temperatures (above 450 °C).

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References

(1) Cui, Y.; Zhong, Z.; Wang, D.; Wang, W. U.; Lieber, C. M. *Nano Lett*. **2003**, *3*, 149.
(2) Wang, Y.; Lew, K.-K.; Ho, T.; Pan, L.; Novak, S. W.; Dickey, E. C.; Redwing, J. M.; Mayer, T. S. *Nano Lett*. **2005**, *5*, 2139.
(3) Zheng, G. F.; Patolsky, F.; Cui, Y.; Wang, W. U.; Lieber, C. M. *Nat. Biotechnol.* **2005**, *23*, 1294.
(4) Cui, Y.; Wei, Q. Q.; Park, H. K.; Lieber, C. M. *Science* **2001**, *293*, 1289.
(5) Hahm, J.; Lieber, C. M. *Nano Lett*. **2004**, *4*, 51.
(6) Wu, Y.; Xiang, J.; Yang, C.; Lu, W.; Lieber, C. M. *Nature* **2004**, *430*, 61.
(7) Goldberger, J.; Hochbaum, A. I.; Fan, R.; Yang, P. D. *Nano Lett*. **2006**, *6*, 973.
(8) Bucher, E.; Schulz, S.; Lux-Steiner, M. C.; Munz, P.; Gubler, U.; Greuter, F. *Appl. Phys. A* **1986**, *40*, 71.
(9) Rogalski, A. *Prog. Quantum Electron.* **2003**, *27*, 59.
(10) Tsui, B. Y.; Chen, M. C. *J. Appl. Phys*. **1990**, *68*, 6246.
(11) Pant, A. K.; Murarka, S. P.; Shepard, C.; Lanford, W. *J. Appl. Phys*. **1992**, *72*, 1833.
(12) Wang, P.; Yin, J.; Sheng, W.; Zheng, Y.; Zhao, L.; Xu, D. *J. Vac. Sci. Technol., B* **2000**, *18*, 2406.
(13) Jin, S.; Bender, H.; Donation, R. A.; Maex, K. *J. Mater. Res*. **1999**, *14*, 2577.
(14) Larrieu, G.; Dubois, E.; Wallart, X.; Baie, X.; Katcki, J. *J. Appl. Phys*. **2003**, *94*, 7801.
(15) Zhang, Z.; Hellstrom, P. E.; Ostling, M.; Zhang, S. L.; Lu, J. *Appl. Phys. Lett.* **2006**, *88*, 043104.
(16) Luo, J.; Zhang, L.; Zhu, J. *Adv. Mater*. **2003**, *15*, 579.
(17) Lew, K. K.; Redwing, J. M. *J. Cryst. Growth* **2003**, *254*, 14.
(18) Cui, Y.; Lauhon, L. J.; Gudiksen, M. S.; Wang, J. F.; Lieber, C. M. *Appl. Phys. Lett*. **2001**, *78*, 2214.
(19) Wu, Y.; Cui, Y.; Huynh, L.; Barrelet, C. J.; Bell, D. C.; Lieber, C. M. *Nano Lett*. **2004**, *4*, 433.
(20) Crider, C. A.; Poate, J. M.; Rowe, J. E.; Sheng, T. T. *J. Appl. Phys*. **1981**, *52*, 2860.
(21) Naem, A. A. *J. Appl. Phys*. **1988**, *64*, 4161.
(22) Hiraki, A.; Nicolet, M. A.; Mayer, J. W. *Appl. Phys. Lett*. **1971**, *18*, 178.
(23) Nava, F.; Valeri, S.; Majni, G.; Cembali, A.; Pignatel, G.; Queirolo, G. *J. Appl. Phys*. **1981**, *52*, 6641.
(24) McLeod, J. E.; Wandt, M. A. E.; Pretorius, R.; Comrie, C. M. *J. Appl. Phys*. **1992**, *72*, 2232.
(25) Kobayashi, H.; Yuasa, T.; Yamanaka, K.; Yoneda, K.; Todokoro, Y. *J. Chemi. Phys*. **1998**, *109*, 4997.

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