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Growth of Multiple Metal/Semiconductor Nanoheterostructures through Point and Line Contact Reactions

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ABSTRACT Forming functional circuit components in future nanotechnology requires systematic studies of solid-state chemical reactions in the nanoscale. Here, we report efficient and unique methods, point and line contact reactions on Si nanowires, fabricating high quality and quantity of multiple nanoheterostructures of NiSi/Si and investigation of NiSi formation in nanoscale. By using the point contact reaction between several Ni nanodots and a Si nanowire carried out in situ in an ultrahigh vacuum transmission electron microscopy, multiple sections of single-crystal NiSi and Si with very sharp interfaces were produced in a Si nanowire. Owing to the supply limited point contact reaction, we propose that the nucleation and growth of the sugar cane-type NiSi grains start at the middle of the point contacts between two Ni nanodots and a Si nanowire. The reaction happens by the dissolution of Ni into the Si nanowire at the point contacts and by interstitial diffusion of Ni atoms within a Si nanowire. The growth of NiSi stops as the amount of Ni in the Ni nanodots is consumed. Additionally, without lithography, utilizing the line contact reaction between PS nanosphere-mediated Ni nanopatterns and a nanowire of Si, we have fabricated periodic multi-NiSi/Si/NiSi heterostructure nanonowires that may enhance the development of circuit elements in nanoscale electronic devices. Unlike the point contact reaction, silicide growth starts at the contact area in the line contact reaction; the different silicide formation modes resulting from point and line contact reactions are compared and analyzed. A mechanism on the basis of flux divergence is proposed for controlling the growth of the nano-multiheterostructures.

KEYWORDS Silicide nanowires, point contact reactions, in situ TEM, multiple nanoheterostructures, nanodots, nanopatterns

The development of nanoscale transistors based on Si nanowires has been widely investigated for applications in electronics and life sciences since the end of the very large scale integration of Si-based field effect transistors is approaching according to the semiconductor technology roadmap.[1−3] To explore the potential of Si nanowires, the formation of silicide[4−6] and, more importantly, silicide/Si heterostructure in nanowires has been studied.[7−11] The single-crystal NiSi nanowire has one of the lowest resistivity among all silicides, and it also has the remarkably high failure current densities and no degradation in electrical conductivity when being scaled to ultrasmall dimension. Therefore, the nanowire heterosturctures of NiSi/Si/NiSi are of interest and were created by Wu et al.[7] On the basis of those heterostructures, field effect transistors were fabricated, the source and drain contacts of which were defined by the metallic NiSi nanowire regions.[7] Schottky barrier field effect transistors were fabricated by Weber et al. based on similar heterostructures.[8] Additionally, nanowires of different Ni silicide phases have been synthesized, exhibiting various remarkable properties and receiving extensive attention.[5,12−14] Well-defined nanoscale building blocks such as ohmic contacts and gates on Si nanowires must be developed for being assembled into functional circuit components in future nanotechnology. To form these circuit components, it requires systematic studies of solid-state chemical reactions in the nanoscale, which, however, are not well understood. In this work, through an in situ ultrahigh vacuum transmission electron microscopy, we investigated the point contact reaction between Ni nanodots and a Si nanowire and the line contact reaction between PS sphere-mediated Ni nanopatterns and a Si nanowire, based on which multiple heterostructures of NiSi/Si in nanowires were fabricated with three important features. First, the very sharp interfaces of NiSi/Si are expected to significantly improve interface resistivity between NiSi and Si and enhance the performance of electronic devices.[15] The flatness of the interfaces may enhance the potential applications such as single electron transistor.[16] Second, the small nanogaps of Si is another contribution to better performance of

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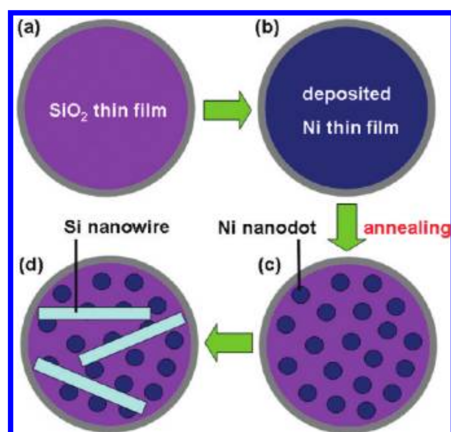

FIGURE 1. Top view of the preparation of point contact samples between Ni nanodots and Si nanowires. (a) Cu grid covered with a SiO_2 thin film, (b) deposition of a Ni thin film of 10 nm in thickness, (c) annealing at 650 °C to form Ni nanodots on the SiO_2 thin film, and (d) spreading of Si nanowires on the sample.

field effect transistors and biosensing due to the corresponding shorter channel length.[17] Third, the multinanogap structure may lead to fabrication of multiple electrode contacts for complex integrated circuits of nanoscale electronic devices.[18] In addition, in situ transmission electron microscopy (TEM)[19−29] was utilized to study the kinetics of reaction and the growth mechanism of the multinanoheterostructures of single crystal NiSi/Si in a Si nanowire is proposed. Furthermore, how to fabricate and control periodic nanostructures remains one of the biggest challenges in today's nanotechnology; thus, using a distinctive method we have achieved periodic nanowire heterostructures without lithography.

Figure 1 is the schematic illustration of how the multi-NiSi/Si-nanowire-heterostructures were produced. To prepare the sample, we deposited a Ni film of 10 nm in thickness using an ultrahigh vacuum electron beam evaporator on a Cu grid covered with a 50 nm thick Si oxide film (window). Following the deposition, the sample was annealed at 650 °C in an in situ TEM. After about half an hour of annealing, the Ni film became Ni nanodots dispersed on the Si oxide window due to agglomeration and reduction of surface energy. After that, we took the sample out and dripped droplets of the Si-nanowire-solution on it. The sample was dried under light bulbs and then it was annealed again in the in situ TEM at 650 °C. Now we have point contact reactions between Si nanowires and Ni nanodots because the contact area between them is a point region. The Si nanowires were fabricated on a p-type Si wafer by the vapor−liquid−solid method using Au nanodots as nucleation sites for single-crystal Si nanowires with [111] growth direction.[30,31] These nanowires with lengths of a few micrometers were ranged in diameter from 20 to 40 nm and stored in ethanol. Also, they have a thin surface oxide about 1−5 nm thick. All the in situ annealing was conducted in a JEOL 2000 V ultrahigh vacuum TEM with a base pressure better than 3×10^{-10} Torr.

Figure 2a−c shows in situ TEM images of a set of different sections of the multi-nanoheterostructures of NiSi/Si in a Si nanowire formed by in situ annealing of the samples prepared with the method described in Figure 1. Neighboring the nanoheterostructures are Ni nanodots of about 10−30 nm in diameter. On the basis of selected area diffraction patterns, the silicides have been verified to be single crystal NiSi. In the Si nanowire, the darker regions are NiSi, while the lighter regions are Si. Another feature that can be noticed is that the interfaces between NiSi and Si appear as sharp as the atomically flat interfaces previously reported through point contact reaction between Si nanowires and Ni nanowires.[25,26] This is because the specific axial epitaxial relationship between NiSi and Si occurs again when we used the same single crystal [111] Si nanowires with surface oxide to react with Ni dots through point contact reaction.

In forming the multiple heterostructures of NiSi in Si nanowire, it seems that the NiSi might have nucleated right below the point contact area. However, we propose that the nucleation occurs within the Si nanowire between two Ni nanodots. Figure 2d is a schematic diagram depicting the nucleation and growth of the multinano-heterostructures of NiSi/Si. After annealing at 650 °C, Ni atoms dissolve into the Si nanowire through point contacts between the Ni nanodots and the wire. Since Ni atoms diffuse interstitially in Si,[32] the interstitial Ni atoms diffuse away quickly from the point contact and lead to nucleation and growth of NiSi at about the middle of two adjacent contact points, where a higher concentration and supersaturation of Ni atoms is achieved due to the fluxes of Ni atoms coming from both sides. Subsequently, as more Ni atoms are supplied from the Ni nanodots by dissolving into the Si, diffusing from the contact points to the NiSi/Si interfaces, the growth of the NiSi occurs. Owing to the limited contact area and the oxide, the flux dissolving into the Si is small. Then the fast diffusion of Ni away from the contact point will not lead to supersaturation of Ni under the point of contact, so the nucleation and growth of NiSi does not start at the point of contact. Another reason is that it is more difficult for Ni atoms to diffuse through silicide than through Si since the latter occurs by interstitial diffusion. We reported before that in the point contact reaction between Ni and Si nanowires, the growth of NiSi starts from both ends of Si nanowires.[25,26] As for the present case of the reaction between Ni nanodots and a Si nanowire, the growth from the both ends of a Si nanowire is possible too; however, the nucleation at the middle of two adjacent point contacts requires a shorter distance of diffusion of Ni atoms as compared with that at both ends.

Since the amount of Ni atoms in a Ni nanodot is very limited, the length of the sugar cane-type NiSi grain cannot grow very long, and the growth of NiSi grains stops when the Ni in the Ni nanodot is completely consumed so that multisections of nanoheterostructures can be formed. To reconfirm that the growth is limited by the supply of Ni atoms or not, we further annealed the sample shown in

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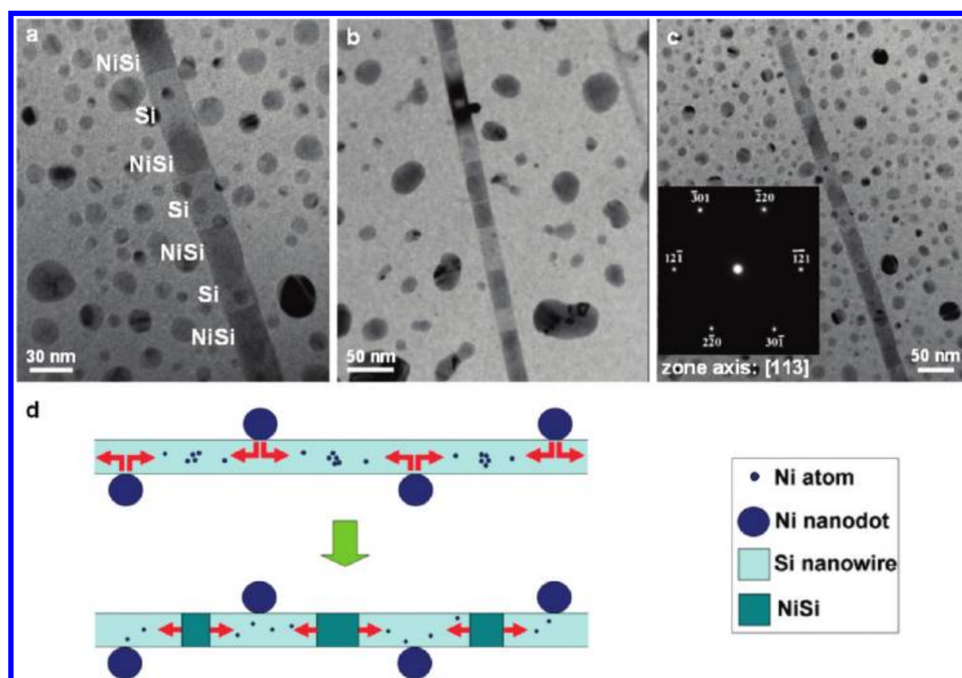

FIGURE 2. (a−c) In-situ TEM images showing the formation of multinanowire-heterostructures of NiSi/Si within a Si nanowire. The inset in (c) is the corresponding diffraction pattern with a [113] zone axis of a NiSi grain. (d) A schematic illustration of the growth of multinanowire-heterostructures of NiSi/Si within a Si nanowire.

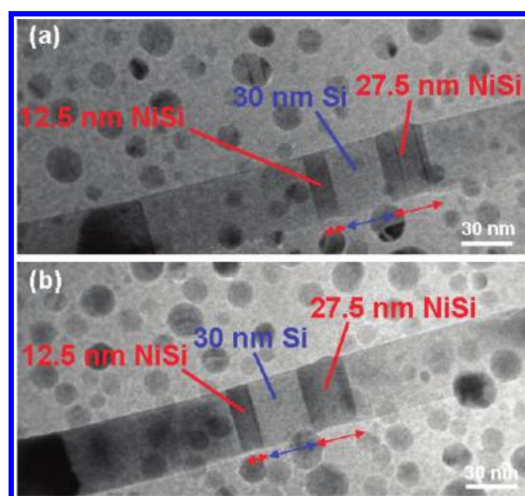

FIGURE 3. In situ TEM images of the multinanoheterostructures of NiSi/Si within the Si nanowire. (a) Before and (b) after further annealing of over two hours at 650 °C showing the high stability of the heterostructures.

Figure 2 for over two hours. Figure 3 is the resultant in situ TEM images, in which it can be seen that before and after the annealing, there is little change on the shape, size, and distance between the sugar cane-type silicide grains. In addition to the several grains of NiSi shown in Figure 3, we checked other grains of silicide in the sample; it turns out that almost no change was observed on all of them. The NiSi is stable at the annealing temperature; it does not grow, nor transforms to $NiSi_2$.

In the images, some Ni nanodots seem to have made contact with the Si nanowire without reaction. This is because the contrast is only due to overlapping in vision rather than in real contact between them for two reasons. First, during the annealing process, some Ni nanodots were embedded in the SiO_2 film as they formed. Second, the diameters of the Ni nanodots vary, instead of being equal. The growth stops due to the full consumption of Ni from the Ni nanodots, and we proposed that the formation of the multi-nanoheterostructures of NiSi/Si in a Si nanowire is through the point contact reaction between Si nanowires and Ni nanodots.

The above phenomenon proves that the NiSi growth cannot occur by surface diffusion. If so, it should have been able to support a nonstop growth. In addition, surface diffusion of Ni on the SiO_2 surface of the Si nanowire is much slower than the interstitial diffusion of Ni within Si.[33,34] Otherwise, we expect to find ripening among the Ni nanodots.

To confirm whether there was ripening during this experiment, we annealed the same sample at 800 °C for over 2 h, focusing on the change among the Ni nanodots. Figure 4 shows the in situ TEM images of the Ni nanodots before and after the annealing. It turns out that no obvious ripening was observed; neither the sizes nor the relative positions of the Ni nanodots had changed apparently. Since the gradient of Gibbs−Thomson potential between nanosize Ni dots is very large, the driving force of ripening should be large. Thus, no ripening suggests that the surface diffusion of Ni on the Si oxide surface is very slow, and so is the surface diffusion of Ni on the SiO_2 surface of a Si nanowire. It can be inferred that all the silicide formation in this study is

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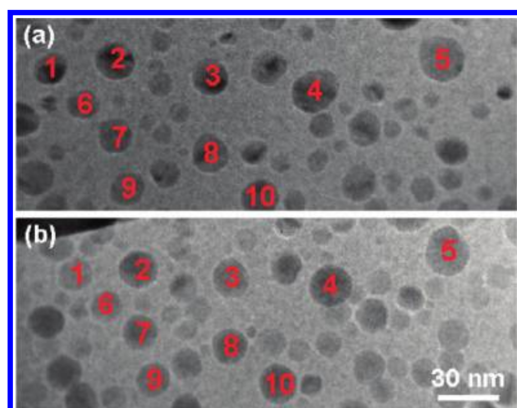

FIGURE 4. In situ TEM images of the stability investigation on the Ni nanodots at the SiO_2 thin film. (a) Before and (b) after annealing of over 2 h at 800 °C.

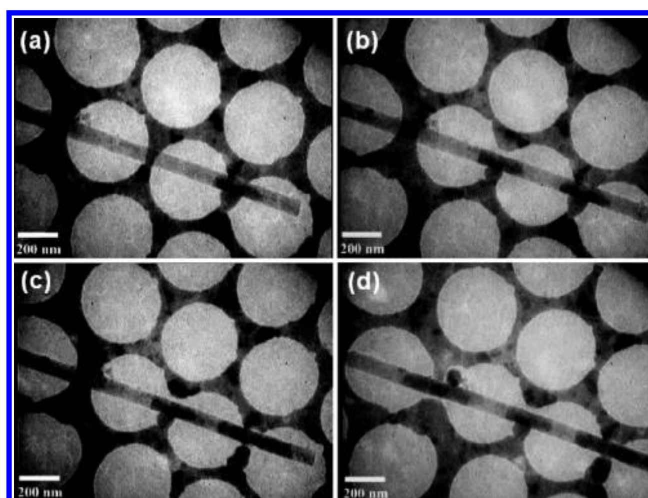

FIGURE 6. In situ TEM image sequence of fabrication of multiple NiSi/Si/NiSi nanowire heterostructures on a regular Ni nanopattern.

attributed to interstitial diffusion of Ni atoms inside a Si nanowire instead of surface diffusion of Ni atoms on a Si nanowire. While the point contact reaction between Ni and Si nanowires is a supply limited reaction due to the very small dissolution rate of Ni into Si at the point contact,[25] we propose that the point contact reaction between Ni nanodots and a Si nanowire is also supply limited.

If we can prepare a regular area array of nano-Ni particles of the same size on a surface, we can form a periodic NiSi/Si structure in Si nanowires using the method described above. The conduction behavior of the structure in terms of size, dopant, and strain is of interest.

To compare with the previously discussed point contact reaction and fabricate periodic multiple nanowire heterostructures, we designed and investigated the line contact reaction between a regular Ni nanopattern and a Si nanowire, where an essential property of nanoscale chemical reactions is that the contact between the nanopattern and the nanowire is a line contact. Additionally, with a unique PS nanosphere-mediated method as shown in Figure 5, the fabrication of the regular Ni nanopattern requires no lithography. Having the special pattern reacted with a Si nanowire enables the fabrication of periodic multiple NiSi/Si/NiSi nanowire heterostructures, the method and results of which are described and shown in Figure 5 and Figure 6, respectively. In the nanowire of Figure 6, the bright area is Si and

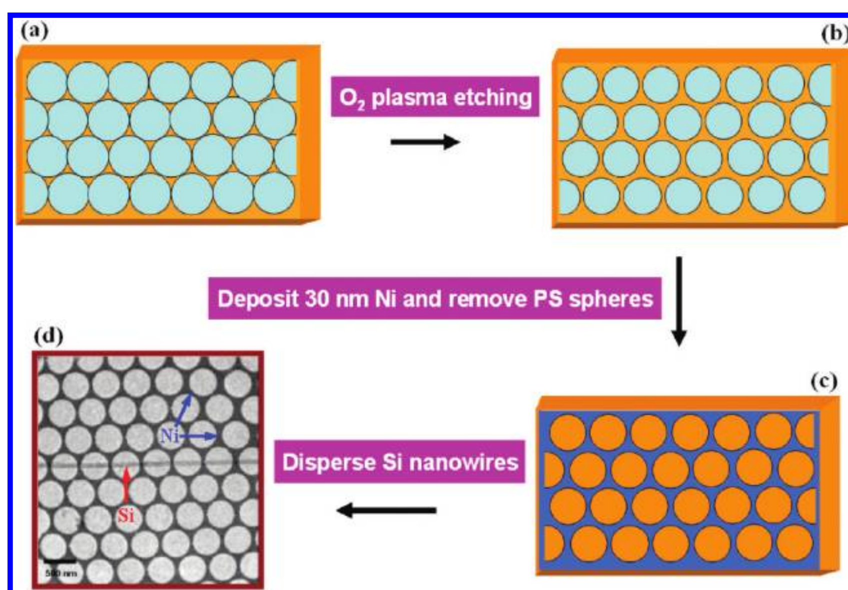

FIGURE 5. Fabrication of periodic multi-NiSi/Si/NiSi nanowire heterostructures. (a) On a Si substrate covered with SiO_2, nanospheres were arranged to be closely packed in a monolayer. (b) The diameter of PS nanospheres was reduced by reactive ion etch with oxygen as the etching gas at a flow rate of 40 sccm, a 4 Pa pressure, and a 30 W RF power. (c) After 150 s of plasma etching, 30 nm thick Ni was deposited on the patterned substrate by electron beam evaporation in a vacuum better than 1×10^{-6} Torr. Then the PS nanospheres were removed in an ultrasonic bath. (d) TEM image shows Si nanowires were dispersed on the Ni pore-array structure, forming contacts of equal spacing between Si nanowires and the Ni pattern.

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the dark area is NiSi. In contrast to the point contact reaction, through the system of the line contact reaction here, the contact of equal spacing between Si nanowires and the Ni pattern, and the larger contact area facilitate supersaturation, nucleation and growth; thereby, the silicide formation starts at the contact points, contributing to the periodic silicide structure (see Figure S1 in Supporting Information for other examples).

Notably, the greatest advantage of this structure is that after annealing, contact areas disappear due to fast Ni diffusion into Si nanowires in large amount as shown in Figure 6; this causes NiSi to stop growing and the supply limited Ni makes the length of NiSi controllable, which is beneficial for multi-NiSi/Si heterostructures more coherent in length. The corresponding in situ TEM video was shown in Movie 1 in Supporting Information.

Why do the contact areas disappear and cause the NiSi to stop growing so that we can control the growth of the periodic heterostructure? We shall use the mechanism of atomic flux divergence in void formation to explain it. The contact area disappears because the Ni atoms have diffused away and have been replaced by vacancies. This is because Ni was deposited on an oxidized surface and the thickness of Ni is thin. We have already shown in the above that the diffusivity of Ni on the oxide surface is very slow. As Ni in the contact area is being depleted by the contact reaction, the replenishment of Ni requires diffusion of Ni on the oxide surface. It results in flux divergence in which the out-going flux is larger than the in-coming flux, so vacancies will accumulate to form a void, hence we found the contact breaks and the growth of NiSi stops. Thus, we can use this mechanism to control the growth of the nano heterostructure by controlling the size of the PS spheres and the thickness of Ni thin film.

In conclusion, we report efficient and unique methods, point and line contact reactions on Si nanowires, fabricating a number of high quality multiple nanoheterostructures of axial epitaxial single crystal NiSi in Si nanowires and investigation of nano-NiSi. The growth mechanism of the point contact reaction between Ni nanodots and a Si nanowire has been proposed in which nucleation and growth of NiSi start at the middle of the point contacts. The growth of the nano-NiSi grains in a Si nanowire was found to be supply limited due to finite provision of Ni atoms in a Ni nanodot. Moreover, for long time annealing at a very high temperature, the length of the nanosilicide grains does not change and no obvious ripening among the Ni nanodots was observed. Therefore, we can conclude that surface diffusion of Ni on SiO_2 surface is negligibly small. As a result, the reaction between Ni nanodots and a Si nanowire occurs by the dissolution of Ni into Si at the point contact and by interstitial diffusion of Ni atoms within a Si nanowire, rather than by surface diffusion. Additionally, without lithography we have successfully fabricated periodic multinanowire-heterostructures of NiSi/Si using the line contact reaction between regular Ni nanopatterns, which is PS sphere-mediated, and Si nanowires. Our study here has demonstrated that the nanochemical reactions with different contact modes lead to different growth behaviors of silicide formation. The distinctive methods of fabrication of multinanoheterostructures may enhance the development of circuit elements needed in nanoscale electronic devices. A mechanism of controlling the period nanoheterostructure formation on the basis of flux divergence is proposed.

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Supporting Information Available. This manuscript includes EM images and an in situ TEM video. The former shows fabrication of the multinanoheterostructures of NiSi/Si with various patterns; the latter presents dynamic observation of the multiple NiSi/Si nanoheterostructure formation and illustrate our study of the growth kinetics. This material is available free of charge via the Internet at http://pubs.acs.org.

REFERENCES AND NOTES

(1) Cui, Y.; Lieber, C. M. *Science* **2001**, *291*, 851–853.
(2) Xia, Y.; Yang, P.; Sun, Y.; Wu, Y.; Mayers, B.; Gates, B.; Yin, Y.; Kim, F.; Yan, H. *Adv. Mater.* **2003**, *15*, 353–388.
(3) Patolsky, F.; Timko, B. P.; Zheng, G.; Lieber, C. M. *MRS Bull.* **2007**, *32*, 142–149.
(4) Schmitt, A. L.; Jin, S. *Nano Lett.* **2008**, *8*, 810–815.
(5) Song, Y.; Schmitt, A. L.; Jin, S. *Nano Lett.* **2007**, *7*, 965–969.
(6) Schmitt, A. L.; Higgins, J. M.; Szczech, J. R.; Jin, S. *J. Mater. Chem.* **2010**, *20*, 223–235.
(7) Wu, Y.; Xiang, J.; Yang, C.; Lu, W.; Lieber, C. M. *Nature* **2004**, *430*, 61–65.
(8) Weber, W. M.; Geelhaar, L.; Graham, A. P.; Unger, E.; Duesberg, G. S.; Liebau, M.; Pamler, W.; Cheze, C.; Riechert, H.; Lugli, P.; Kreupl, F. *Nano Lett.* **2006**, *6*, 2660–2666.
(9) Björk, B. T.; Ohlsson, B. J.; Sass, T.; Persson, A. I.; Thelander, C.; Magnusson, M. H.; Deppert, K.; Wallenberg, L. R.; Samuelson, L. *Appl. Phys. Lett.* **2002**, *80*, 1058–1060.
(10) Xiang, J.; Vidan, A.; Tinkham, M.; Westervelt, R. M.; Lieber, C. M. *Nat. Nanotechnol.* **2006**, *1*, 208–213.
(11) Lin, Y. C.; Lu, K. C.; Wu, W. W.; Bai, J. W.; Chen, L. J.; Tu, K. N.; Huang, Y. *Nano Lett.* **2008**, *8*, 913–918.
(12) Song, Y.; Jin, S. *Appl. Phys. Lett.* **2007**, *90*, 173122-1–3.
(13) Lee, C. Y.; Lu, M. P.; Liao, K. F.; Wu, W. W.; Chen, L. J. *Appl. Phys. Lett.* **2008**, *93*, 113109-1–3.
(14) Lee, C. Y.; Lu, M. P.; Liao, K. F.; Lee, W. F.; Huang, C. T.; Chen, S. Y.; Chen, L. J. *J. Phys. Chem. C* **2009**, *113*, 2286–2289.
(15) Poate, J. M.; Tu, K. N.; Mayer, J. W. *Thin Films: Interdiffusion and Reactions*; Wiley-Interscience Publishing: New York, 1978.
(16) Hu, S. F.; Sung, C. L.; Huang, K. D.; Wan, Y. M. *Appl. Phys. Lett.* **2004**, *85*, 3893–3895.
(17) Sze, S. M. *Semiconductor Devices: Physics and Technology*, 2nd ed.; Wiley Publishing: New York, 2001.
(18) Johnston, D. E.; Strachan, D. R.; Johnson, A. T. C. *Nano Lett.* **2007**, *7*, 2774–2777.
(19) Wang, Z. L.; Ponchara, P.; de Heer, W. A. *Pure Appl. Chem.* **2000**, *72*, 209–219.
(20) Stach, E. A.; Pauzauskie, P. J.; Kuykendall, T.; Goldberger, J.; He, R.; Yang, P. *Nano Lett.* **2003**, *3*, 867–869.

© 2010 American Chemical Society

(21) Golberg, D.; Li, Y. B.; Mitome, M.; Bando, Y. *Chem. Phys. Lett.* **2005**, *409*, 75–80.
(22) Lang, C.; Kodambaka, S.; Ross, F. M.; Cockayne, D. J. H. *Phys. Rev. Lett.* **2006**, *97*, 226104-1–4.
(23) Liu, C. H.; Wu, W. W.; Chen, L. J. *Appl. Phys. Lett.* **2006**, *88*, 133112-1–3.
(24) Hsu, H. C.; Wu, W. W.; Hsu, H. F.; Chen, L. J. *Nano Lett.* **2007**, *7*, 885–889.
(25) Lu, K. C.; Tu, K. N.; Wu, W. W.; Chen, L. J.; Yoo, B. Y.; Myung, N. V. *Appl. Phys. Lett.* **2007**, *90*, 253111-1–3.
(26) Lu, K. C.; Wu, W. W.; Wu, H. W.; Tanner, C. M.; Chang, J. P.; Chen, L. J.; Tu, K. N. *Nano Lett.* **2007**, *7*, 2389–2394.
(27) Chen, K. C.; Wu, W. W.; Liao, C. N.; Chen, L. J.; Tu, K. N. *Science* **2008**, *321*, 1066–1069.
(28) Chou, Y. C.; Wu, W. W.; Cheng, S. L.; Yoo, B. Y.; Myung, N. V.; Chen, L. J.; Tu, K. N. *Nano Lett.* **2008**, *8*, 2194–2199.
(29) Chou, Y. C.; Wu, W. W.; Chen, L. J.; Tu, K. N. *Nano Lett.* **2009**, *9*, 2337–2342.
(30) Wagner, R. S.; Ellis, W. C. *Appl. Phys. Lett.* **1964**, *4*, 89–90.
(31) Hannon, J. B.; Kodambaka, S.; Ross, F. M.; Tromp, R. M. *Nature* **2006**, *440*, 69–71.
(32) Spit, F. H. M.; Gupta, D.; Tu, K. N. *Phys. Rev. B* **1989**, *39*, 1255–1260.
(33) Thompson, R. D.; Gupta, D.; Tu, K. N. *Phys. Rev. B* **1985**, *33*, 2636–2641.
(34) Tu, K. N.; Mayer, J. W.; Feldman, L. C. *Electronic Thin Film Science*; Macmillian Publishing: New York, 1992.

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