

Ti<sub>5</sub>Si<sub>3</sub> Nanowire and Its Field Emission Property

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Because of their distinct properties, one-dimensional (1D) nanostructures have attracted a tremendous amount of attention for technological applications, such as sensors,<sup>1</sup> laser devices,<sup>2</sup> and electrical systems.<sup>3</sup> An increasing effort has been devoted to fabricating nanomaterials for new field emitters, such as CNTs (carbon nanotubes),<sup>4</sup> nanodiamond coated Si nanowires (NWs),<sup>5</sup> SiC NWs and nanotubes,<sup>6</sup> metal oxides,<sup>7</sup> and metal silicides.<sup>8</sup> Many studies about the fabrication of free-standing silicide NWs of Ti, Cr, Fe, Co, Ni and Ta have been reported because of their superior properties and compatibility with Si based integrated circuit devices.<sup>8–14</sup> Among them, titanium

Table 1. Summary of Samples

sample	growth conditions	morphologies and phases	$E_0^a$ (V/ $\mu\text{m}$ )	$\beta^b$
I	973 K, 6h	Ti <sub>5</sub> Si <sub>3</sub> NWs/C54-TiSi <sub>2</sub> film	5.4	816
II	773 K, 6h	$\alpha$ -Ti <sub>3</sub> Si <sub>2</sub> NWs/C54-TiSi <sub>2</sub> film	7.6	<sup>c</sup>
III	973K, 1h	C54-TiSi <sub>2</sub> film	10.4	343

<sup>a</sup> Turn-on field. <sup>b</sup> Field enhancement factor. <sup>c</sup> Cannot be obtained due to the lack of work function of amorphous Ti<sub>3</sub>Si<sub>2</sub>.

silicides are potential candidates for field emission devices due to their relative low resistivity (10–28  $\mu\Omega$  cm), high thermal stability, and low work function.<sup>15–17</sup> Research on the fabrication of TiSi and TiSi<sub>2</sub> NWs and arrays through various processing techniques, including chemical vapor deposition (CVD) and physical vapor deposition (PVD), have been demonstrated recently.<sup>9,18–20</sup> On the other hand, fabrication of nanostructures of metal-rich titanium silicide Ti<sub>5</sub>Si<sub>3</sub>, which is a suitable refractory material with a melting point 2403 K, has not been reported. In this work, we report the first growth of Ti<sub>5</sub>Si<sub>3</sub> NWs via a unique CVD process.<sup>21</sup> Microstructures and field emission properties of the NWs will be discussed in detail.

All reactions were performed in a low pressure horizontal hot-wall quartz tube reactor heated by a three-zone tube furnace. TiCl<sub>4</sub>, the precursor, was vaporized into the reaction chamber at a controlled partial pressure. Close to the precursor inlet, Ti powders were placed at the heating zone at 1173 K. Si(100) wafers were placed at the center heating zone at 773–973 K. After 1–6 h, deposition of a gray layer on the substrates was observed. A summary of the representative samples prepared in this study is listed in Table 1. Figure 1 shows the morphology and the chemical composition of sample **I** grown at 973 K on Si for 6 h. Figure 1a is a top-view scanning electron microscopic (SEM) image of **I**. It displays that on top of a deposited thin film, there are a considerable amount of thread-like NWs a few micrometers long. A representative high-magnification SEM image in Figure 1b shows that the 1D nanostructures have diameters 20–50 nm. In addition, the image does not show evidence for the presence of metal particles, which may act as catalysts, on the tips of the wires. An energy-dispersive X-ray (EDX) spectrum of **I** in Figure 1c indicates that the sample contains Ti and Si only. A side view SEM image in Figure 1d reveals that numerous NWs of a few micrometers in length extend randomly from the top of a deposited film with a thickness of approximately 6  $\mu\text{m}$  on Si. X-ray diffraction

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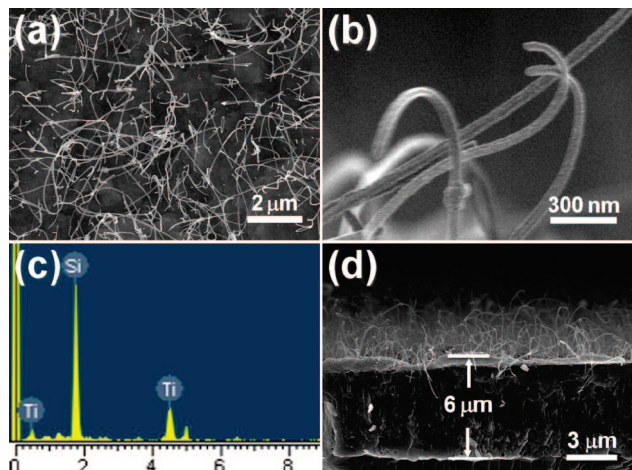
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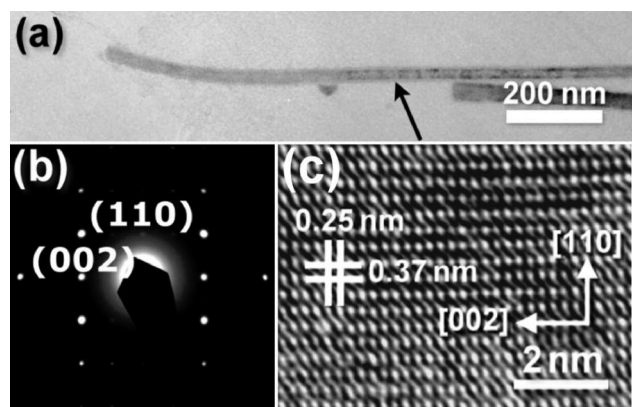
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- (1) Cui, Y.; Wei, Q.; Park, H.; Lieber, C. M. *Science* **2003**, *293*, 1289.
- (2) Huang, M. H.; Mao, S.; Yan, H.; Wu, Y.-Y.; Kind, H.; Weber, E.; Russo, R.; Yang, P.-D. *Science* **2001**, *292*, 1897.
- (3) Huang, Y.; Duan, X.; Wei, Q.; Lieber, C. M. *Science* **2001**, *291*, 630.
- (4) Heer, W. A.; Chatelain, A.; Ugarte, D. *Science* **1995**, *270*, 1179.
- (5) Tzeng, Y.-F.; Lee, Y.-C.; Lee, C.-Y.; Lin, I.-N.; Chiu, H.-T. *Appl. Phys. Lett.* **2007**, *91*, 063117.
- (6) (a) Zhou, X.-T.; Lai, H.-.; Peng, H.-Y.; Au, F. C.-K.; Liao, L.-S.; Wang, N.; Bello, I.; Lee, C.-S.; Lee, S.-T. *Chem. Phys. Lett.* **2000**, *318*, 58. (b) Wang, C.-H.; Lin, H.-K.; Ke, T.-Y.; Palathinkal, T. J.; Tai, N.-H.; Lin, I.-N.; Lee, C.-Y.; Chiu, H.-T. *Chem. Mater.* **2007**, *19*, 3956.
- (7) Tseng, Y.-K.; Huang, C.-J.; Cheng, H.-M.; Lin, I.-N.; Liu, K.-S.; Chen, I.-C. *Adv. Funct. Mater.* **2003**, *13*, 811.
- (8) Chueh, Y.-L.; Ko, M.-T.; Chou, L.-J.; Chen, L.-J.; Wu, C.-S.; Chen, C.-D. *Nano Lett.* **2006**, *6*, 1637.
- (9) (a) Xiang, B.; Wang, Q.-X.; Wang, Z.; Zhang, X.-Z.; Liu, L.-Q.; Xu, J.; Yu, D.-P. *Appl. Phys. Lett.* **2005**, *86*, 243103. (b) Du, J.; Du, P.-Y.; Hao, P.; Huang, Y.-F.; Ren, Z.-D.; Han, G.-R.; Weng, W.-J.; Zhao, G.-L. *J. Phys. Chem. C* **2007**, *111*, 10814.
- (10) (a) Seo, K.; Varadwaj, K. S. K.; Cha, D.; In, J.; Kim, J.; Park, J.; Kim, B. *J. Phys. Chem. C* **2007**, *111*, 9072. (b) Szczech, J. R.; Schmitt, A. L.; Bierman, M. J.; Jin, S. *Chem. Mater.* **2007**, *19*, 3238.
- (11) (a) Quyang, L.; Thrall, E. S.; Deshmukh, M. M.; Park, H. *Adv. Mater.* **2006**, *18*, 1437. (b) Schmitt, A. L.; Bierman, M. J.; Schmeisser, Dieter.; Himpel, F. J.; Jin, S. *Nano Lett.* **2006**, *6*, 1617. (c) Varadwaj, K. S. K.; Seo, K.; In, J.; Mohanty, P.; Park, J.; Kim, B. *J. Am. Chem. Soc.* **2007**, *129*, 8594.
- (12) (a) Schmitt, A. L.; Zhu, L.; Schmeiber, D.; Himpel, F. J.; Jin, S. *J. Phys. Chem. B* **2006**, *110*, 18142. (b) Seo, K.; Varadwaj, K. S. K.; Mohanty, P.; Lee, S.; Jo, Y.; Jung, M.-H.; Kim, J.; Kim, B. *Nano Lett.* **2007**, *7*, 1240.
- (13) (a) Song, Y.; Jin, S. *Appl. Phys. Lett.* **2007**, *90*, 173122. (b) Song, Y.; Schmitt, A. L.; Jin, S. *Nano Lett.* **2007**, *7*, 965.
- (14) Chen, L.-J. *Silicide Technology for Integrated Circuits*; IEE: London, 2004.

- (15) Bucher, E.; Schultz, S.; Lux-Steiner, M. C.; Munz, P.; Gubler, U.; Greuter, F. *Appl. Phys. A: Mater. Sci. Process.* **1986**, *40*, 71.
- (16) Maex, K.; Rossum, M. V. *Properties of Metal Silicides*; IEE: London, 1995.
- (17) Murarka, S. P.; Fraser, D. B. *J. Appl. Phys.* **1980**, *51*, 350.
- (18) Bennett, P. A.; Ashcroft, B.; He, Z.; Tromp, R. M. *J. Vac. Sci. Technol. B* **2002**, *20*, 2500.
- (19) Hsu, H.-C.; Wu, W.-W.; Hsu, H.-F.; Chen, L.-J. *Nano Lett.* **2007**, *7*, 885.
- (20) Choi, S.-S.; Jung, M.-Y.; Joo, M.-S.; Kim, D.-W.; Park, M.-J.; Kim, S.-B.; Jeon, H.-T. *Surf. Interface Anal.* **2004**, *36*, 435.
- (21) Lee, C.-Y. *Chem. Vap. Deposition* **1999**, *5*, 69.



**Figure 1.** SEM images of sample **I** grown on Si. (a) Top view, (b) high magnification image, (c) EDX, and (d) side view image.

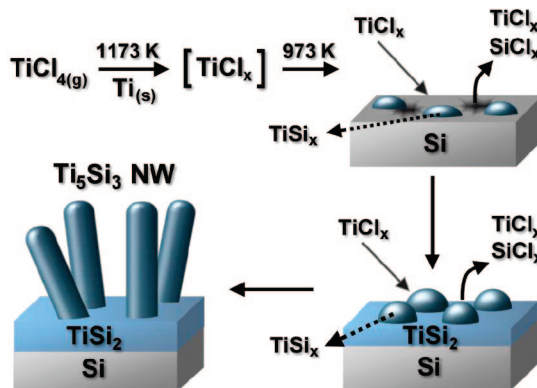


**Figure 2.** TEM studies of a NW isolated from **I**. (a) Low magnification image, (b) SAED pattern of the sample in part a showing a  $[1\bar{1}0]$  zone axis, and (c) high-resolution image from the selected section in part a.

(XRD) of **I** suggested that the film was composed mainly of orthorhombic C54-TiSi<sub>2</sub> phase (JCPDS 35-0785). However, transmission electron microscopic (TEM) studies of the NWs showed that the 1D material had a different titanium silicide phase. The presence of Ti metal powders at the heating zone at 1173 K was important for the successful NW growth. Without it, a TiSi<sub>2</sub> film with uneven surface was deposited on the Si substrate.

A typical TEM image of NWs isolated from **I** is shown in Figure 2a. It reveals a long NW with a diameter of approximately 30 nm. The image also confirms that on the tip of the wire, there is no evidence for the existence of any metal particles. A selected-area electron diffraction (SAED) image in Figure 2b, taken from the point indicated in Figure 2a, displays a dot pattern. This could be assigned to (002) and (110) planes of single crystalline hexagonal Ti<sub>5</sub>Si<sub>3</sub> with a  $[1\bar{1}0]$  zone axis. Figure 2c is the high-resolution TEM (HRTEM) image taken at the same place. From the image, two sets of fringes spaced at 0.25 and 0.37 nm apart could be assigned to the lattice spacing of (002) and (110) planes of the Ti<sub>5</sub>Si<sub>3</sub> phase, respectively. The wire growth direction is determined to be along the [002] axis of Ti<sub>5</sub>Si<sub>3</sub>. Thus, sample **I** is designated as Ti<sub>5</sub>Si<sub>3</sub> NWs/TiSi<sub>2</sub>. An Auger depth profile of **I** also confirmed that the sample contained a high

**Scheme 1.** Proposed Growth Steps of Ti<sub>5</sub>Si<sub>3</sub> NWs



quantity of Ti on the surface while the Si content was rich inside the deposited layer.

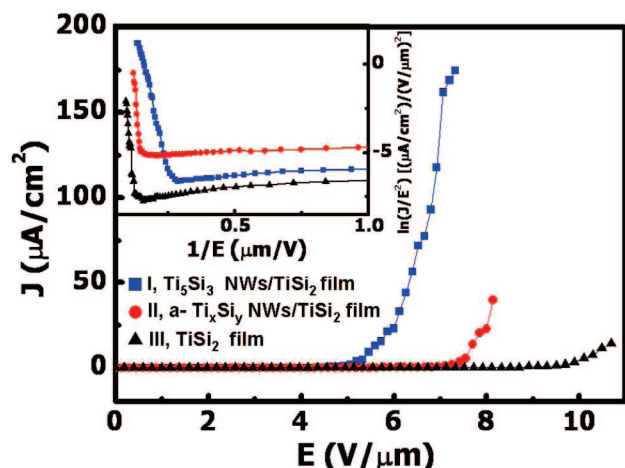
Both reaction temperature and time were essential factors in the synthesis of the single crystalline Ti<sub>5</sub>Si<sub>3</sub> NWs. When the reaction temperature was decreased to 773 K, sample **II** containing abundant amorphous Ti<sub>x</sub>Si<sub>y</sub> NWs on a C54-TiSi<sub>2</sub> thin film (designated as *a*-Ti<sub>x</sub>Si<sub>y</sub> NWs/TiSi<sub>2</sub>) was produced in 6 h. As the reaction time was reduced to 1 h, sample **III**, which showed sparse and short NWs on a layer of C54-TiSi<sub>2</sub> thin film, was obtained. Consequently, we conclude that the titanium silicide 1D nanostructures could be fabricated only with sufficient reaction time. Furthermore, the crystal structures of the NWs depend highly on the reaction temperature.

Vapor–liquid–solid (VLS) growth is employed most frequently to account for the growth of many NWs. However, according to the observations discussed above, the VLS model can be ruled out easily, owing to the absence of metal particles on the tip of the NWs.<sup>22</sup> On the basis of the experimental observations, a plausible reaction pathway is proposed in Scheme 1 to rationalize the Ti<sub>5</sub>Si<sub>3</sub> NW growth. It suggests that titanium subchlorides TiCl<sub>x</sub> ( $x = 2, 3$ ), generated by the reaction between TiCl<sub>4</sub>(g) and Ti metal in the high temperature zone at 1173 K initially, could serve as the Ti source in two ways.<sup>23</sup> One is their disproportionation into TiCl<sub>4</sub> molecules and Ti atoms in the low temperature zones below 973 K. The deposited Ti atoms could react with the Si surface atoms to form TiSi<sub>x</sub> clusters for further nucleation and growth. The second one is that TiCl<sub>x</sub> could react directly with the Si substrate to form Si-rich TiSi<sub>x</sub> clusters and gaseous SiCl<sub>x</sub> byproducts, which might serve as another Si source in the formation of TiSi<sub>x</sub>.<sup>24</sup> As the reaction proceeds further, a TiSi<sub>2</sub> thin film is grown on the substrate. In the mean time, the disproportionation of the incoming TiCl<sub>x</sub> to deposit Ti atoms remains. But the supply of Si atoms either from the substrate or from the SiCl<sub>x</sub> byproducts could be hampered by the relative inertness of the as-formed TiSi<sub>2</sub> layer. In addition, the diffusion length of Si atoms from the substrate through the TiSi<sub>2</sub> layer

(22) Wagner, R. S.; Ellis, W. C. *Appl. Phys. Lett.* **1964**, *4*, 89.

(23) Ameen, M. S.; Leusink, G.; Hillman, J. T. U.S. Patent No. 5926737, 1999.

(24) (a) Reynolds, G. J.; Cooper, C. B.; Faczli, P. J. *J. Appl. Phys.* **1989**, *65*, 3212. (b) Southwell, R. P.; Seebauer, E. G. *J. Vac. Sci. Technol. A* **1995**, *13*, 221.



**Figure 3.** EFE current density as a function of applied electric field of samples **I–III**. The inset shows their corresponding F–N plots.

becomes extended.<sup>25</sup> All these reasons caused the Si concentration on the surface to decrease at this stage. As a consequence, the  $\text{TiSi}_x$  clusters nucleated are Ti-rich. Because  $\text{Ti}_5\text{Si}_3$  has the highest melting point and the lowest standard heat of formation among all of the titanium silicide phases, we suggest that  $\text{Ti}_5\text{Si}_3$  should be the first silicide phase solidified.<sup>26</sup> Further migration and coalescence of small titanium silicide clusters to these nucleation sites elongates them into the observed  $\text{Ti}_5\text{Si}_3$  NWs.

Electron field emission (EFE) properties and the corresponding Fowler–Nordheim (F–N) plots of the samples are illustrated in Figure 3.<sup>27</sup> Important EFE parameters extracted from the J–E curves, including the turn-on field  $E_0$ , which is defined as the electric field required to produce a current density of  $10 \mu\text{A cm}^{-2}$ , and the field enhancement factor  $\beta$ , calculated from the equation  $\beta = \phi^{3/2}/\phi_e$ ,<sup>27</sup> where  $\phi$  is the work-function of the studied material and  $\phi_e$  is the effective work-function derived from the slope of the F–N plot, are listed in Table 1. Among the samples studied, **I**, which is  $\text{Ti}_5\text{Si}_3$  NWs on  $\text{TiSi}_2$ , shows a markedly superior EFE property compared to the others. The solid squares in Figure

3 illustrate that  $E_0$  of **I** is only  $5.4 \text{ V}/\mu\text{m}$ . Sample **II**, which is composed of  $a\text{-Ti}_x\text{Si}_y$  NWs on  $\text{TiSi}_2$ , displays a higher  $E_0$  of  $7.6 \text{ V}/\mu\text{m}$  while sample **III**, which is the C54- $\text{TiSi}_2$  thin film, shows the highest  $E_0$  of  $10.4 \text{ V}/\mu\text{m}$ . We assume that the work functions  $\phi$  of the  $\text{TiSi}_2$  thin film and the  $\text{Ti}_5\text{Si}_3$  NWs are the same as their bulk materials, that is,  $\phi_{\text{TiSi}_2} = 4.53 \text{ eV}$  and  $\phi_{\text{Ti}_5\text{Si}_3} = 3.71 \text{ eV}$ .<sup>15</sup> Then, we can calculate  $\beta$  from  $\phi$  and  $\phi_e$ .  $\phi_e$  values are proportional to the slopes of the F–N plots shown in Figure 3. For sample **I**,  $\text{Ti}_5\text{Si}_3$  NWs/ $\text{TiSi}_2$ , we suppose that most electrons were emitted from the  $\text{Ti}_5\text{Si}_3$  NWs because they were closer to the anode and were under higher electric field than the  $\text{TiSi}_2$  film below. Thus, the  $\beta$  value of **I**, estimated using  $\phi_{\text{Ti}_5\text{Si}_3}$  and the  $\phi_e$  value of **I**, is 816. This result can be regarded as  $\beta_{\text{Ti}_5\text{Si}_3\text{NWs}}$ , the  $\beta$  value of  $\text{Ti}_5\text{Si}_3$  NWs. It is higher than the reported  $\beta$ -value of  $\text{TiSi}_2$  NWs, which is 500.<sup>9a</sup> The  $\beta$ -value of sample **III** is estimated to be 343. The value is high for a thin film. This may be the result from the surface roughness of **III**. Since there is no  $\phi$  value available for  $a\text{-Ti}_x\text{Si}_y$ , it is not possible to estimate the  $\beta$ -value of **II**. Even though the SEM images demonstrated that **II** and **I** had similar entangled morphology, it appears that **II** could not perform better than **I** did. The amorphous NWs on **II** may not emit electrons as efficiently as the ones on **I**. By assuming that the  $\phi$  value of  $a\text{-Ti}_x\text{Si}_y$  is close to those of various silicides, we can expect that the  $\beta$ -value of  $a\text{-Ti}_x\text{Si}_y$  NWs is between the values found for samples **I** and **III**.

In conclusion, this study is the first growth of  $\text{Ti}_5\text{Si}_3$  NWs on C54- $\text{TiSi}_2$  thin films through a unique CVD process without additional catalyst. The diameters of the NWs are about 20–50 nm and the lengths are several micrometers. The  $\text{Ti}_5\text{Si}_3$  NWs show excellent field emission properties, a low turn-on field  $E_0$  of  $5.4 \text{ V}/\mu\text{m}$ , and a high field enhancement factor  $\beta$  of 816. These notable results suggest that  $\text{Ti}_5\text{Si}_3$  NWs could serve as a promising candidate for future field emission devices.

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**Supporting Information Available:** Experimental section, Auger depth profile, SEM, TEM, ED, EDX, and XRD (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(25) Southwell, R. P.; Seebauer, E. G. *J. Electrochem. Soc.* **1997**, *144*, 2122.

(26) Wang, M. H.; Chen, L. J. *J. Appl. Phys.* **1992**, *71*, 5918.

(27) Fowler, R. H.; Nordheim, L. W. *Proc. R. Soc. London, Ser. A* **1928**, *119*, 173.