NANO LETTERS

2007
Vol. 7, No. 4
885−889

Growth of High-Density Titanium Silicide Nanowires in a Single Direction on a Silicon Surface

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Received October 19, 2006; Revised Manuscript Received February 13, 2007

ABSTRACT

Understanding the growth mechanisms of nanowires is essential for their successful implementation in advanced devices applications. In situ ultrahigh-vacuum transmission electron microscopy has been applied to elucidate the interaction mechanisms of titanium disilicide nanowires ($TiSi_2$ NWs) on Si(111) substrate. Two phenomena were observed: merging of the two NWs in the same direction, and collapse of one NW on a competing NW in a different direction when they meet at the ends. On the other hand, as one NW encounters the midsection of the other NW in a different direction, it recedes in favor of bulging of the other NW at the midsection. Since crystallographically the nanowires are favored to grow on Si(110) only in the [1 –1 0] direction, this crucial information has been fruitfully exploited to focus on the growth of a high density of long and high-aspect-ratio Ti silicide NWs parallel to the surface on Si(110) in a single direction. The achievement in growth of high-density NWs in a single direction represents a significant advance in realizing the vast potential for applications of silicide NWs in nanoelectronics devices.

Thin-film science has been well established in the past half-century, in parallel with the advancement of electronic and optical devices for the consumer electronics, computer, and communications industries. It has laid foundation for highly successful development in a vast spectrum of modern technology. The key to the fruitful applications of thin films is having a good understanding of their growth mechanisms.[1]

Recently, nanowire-based materials have been demonstrated as building blocks for nanocircuits and nanosystems.[2,3] To realize the immense potential for applications in advanced devices, unprecedented efforts have been made toward the controlled growth of nanowires (NWs). Following the same scenario for thin-film applications, understanding the formation mechanisms is a crucial step toward the successful implementation of nanowires for practical employment. In situ ultrahigh-vacuum transmission electron microscopy (UHV-TEM) is an extremely valuable method for clarifying the growth mechanism of nanowires since it can monitor, at the nanoscale, the dynamical process as it occurs. In contrast, postprocess investigations often lead to confusing hypotheses owing to the complexity of the process. Nanowires have been synthesized from a wide range of materials, including metals, semiconductors, and metal oxides.[4−9]

In the past three decades, transition metal/Si systems have attracted great scientific and technological interest. Applications of these silicides include electrical contacts, gates, and local interconnects. For the sub-100 nm devices, $TiSi_2$, $CoSi_2$, and NiSi are three competing contact silicides, mainly because they are the silicides with the lowest resistivty.[10] Wu et al. found that single-crystal and defect-free NiSi NWs have ideal resistivities and remarkably high failure current densities.[11] A large number of epitaxial silicide NWs have been investigated due to their low resistivity, small dimension, and excellent compatibility with silicon device processing.[11−17] They exhibit novel physical and electrical properties, making them promising candidates for future nanoscale devices. However, very little is known about the growth mechanisms of silicide NWs.

Among transition metal silicides, C54-$TiSi_2$ has been widely used in the microelectronics industry, primarily because it forms metallurgically stable contacts to silicon and has low resistivity.[10,18] For titanium silicide NWs, a low-energy electron microscopy (LEEM) study[19] has found that the NWs advance at both ends at a constant rate. In addition, NWs that intersect during growth will separate instead of fusing together. On the other hand, the interaction mechanisms have not been elucidated since the resolution of LEEM is relatively poor. In this work, in situ observations of the growth of titanium silicide NWs in the Ti/Si(111) system were carried out in an ultrahigh-vacuum transmission electron

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10.1021/nl062465e CCC: $37.00

microscope. The focus of the investigation has been on the dynamic observations to gain a fundamental understanding of the interactions and agglomeration between different NWs. The crucial information obtained was fruitfully exploited to focus on the growth of a high density of long and high-aspect-ratio titanium silicide NWs on Si(110) in a single direction, since crystallographically the nanowires are favored to grow on Si(110) only in the [1 −1 0] direction.

The TEM specimens were prepared from n-type Si(111) or Si(110) substrates with miscut orientation of 0.1°. The Si substrate with a small miscut angle was specially selected so that the Si surface is very flat, to minimize the complications of surface steps in the growth of nanowires. The central areas of TEM specimens were thinned by chemical etching from the unpolished side with an acid solution ($HF:CH_3COOH:HNO_3 = 1:1:2$). The samples were then loaded into a direct heating double-tilt stage in a 200 keV UHV-TEM (JEM-2000V) with a base pressure of 3×10^{-10} Torr. The Si(111)-7×7 reconstructed surface was achieved by direct current heating at ~600 °C for several hours, followed by flashing several times at 1200 °C, for a total of 1 min below 2×10^{-9} Torr in the preparation chamber. Ti (99.99% purity) evaporation was performed with a well-outgassed electron-beam evaporator attached to the UHV-TEM column on the Si surface, heated at 600−800 °C. Unless otherwise mentioned, the deposition rate was calibrated to be 0.07 nm/min by cross-section TEM. The temperatures of the sample were determined using an optical pyrometer with an accuracy of ±10 °C. Both Ti deposition and in situ observation with a TV camera were conducted in the main column. The STM experiments were carried out in an ultrahigh-vacuum scanning tunneling microscope (Omicron STM1) with a base pressure below 5×10^{-11} Torr. The procedures to obtain the Si(111)-7×7 reconstructed surface and Ti deposition were the same as those used for UHV-TEM. All STM images were taken at room temperature in the constant current mode, with a tunneling current of ~0.2 nA. Atomic force microscopy (AFM) images were obtained in tapping mode (DI 3100).

Figure 1a shows the AFM image of a sample with Ti deposition on Si(111) at 700 °C. Rectangular clusters and NWs were observed and oriented along three equivalent Si⟨1 −1 0⟩ directions. Similar results in a Ti/Si(111) system have been reported in previous STM investigations.[20] The rectangular clusters are several tens of nanometers in both width and length, but NWs are a few nanometers in width and several hundreds of nanometers in length. For comparison, in samples deposited at 600 °C, the NWs formed were of smaller sizes than those in samples formed at 700 °C. The average length of NWs increases with substrate temperature at 600−700 °C. For samples deposited at 800 °C, most of the Ti silicides were clusters along a few nanorods. In samples deposited at 700 °C, the NWs are 3−8 nm in width with high aspect ratio. A NW 3.3 nm in width and 1650 nm in length and having an aspect ratio as high as 500 is shown in Figure 1b, obtained with 90 min Ti deposition. This is in contrast with the epitaxial silicide NWs formed that were several tens of nanometers in width and had low aspect ratios in several previous studies.[12−15] The NWs with small width and high aspect ratio are potentially significant for applications in future nanoscale devices.

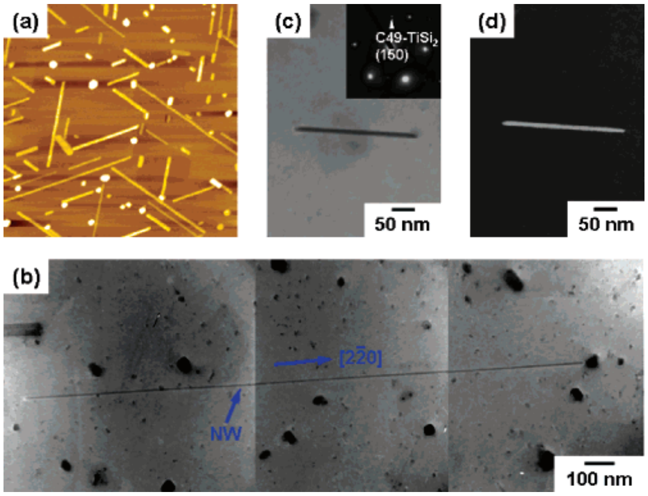

Figure 1. Images of titanium silicide NWs on Si(111). (a) AFM image (1 μm × 1 μm) of titanium silicide NWs oriented along three equivalent Si⟨1 −1 0⟩ directions. (b) Composite TEM image of a titanium silicide NW with high aspect ratio. (c) Bright-field image and (d) C49-$TiSi_2$ [150] dark-field image of a titanium silicide NW on Si(111).

Figure 1c,d shows the bright-field and dark-field images of a Ti silicide NW. From the analysis of corresponding electron diffraction pattern in the inset of Figure 1c, the NW was identified to be of single-crystal C49-$TiSi_2$ phase. Furthermore, the NW was found to orient along the Si[2 −2 0] direction, with C49-$TiSi_2$[2 0 0]//Si[2 −2 0].

The growth of Ti silicide NWs on Si(111) surface occurs in three symmetrically equivalent directions, as can be seen in Figure 1a. During the continuous deposition of Ti atoms on Si(111), interactions of NWs in the same or different directions were observed. A sequence of images clipped from the video are shown in Figure 2a−d, displaying the growth kinetics of two NWs in the same direction. (The video is shown in Supporting Information S1.) In the process of continuous Ti deposition, the length of Ti silicide NWs increases slowly, as visualized by the increase in the number of moiré fringes at both ends of the NWs, while the width does not change appreciably at the same time. When these two NWs are in touch with each other, they eventually combine into one NW, as shown in Figure 2d. During the growth process, the two NWs, marked “A” and “B” in Figure 2a, have different growth rates, 1.99×10^{-2} and 6.33×10^{-3} nm/s, respectively. Furthermore, the right end of NW “A” has a faster growth rate than the left end. In a previous study, it was found that Si atoms at step edges preferentially reacted with Ti atoms to form silicide, as observed from STM and AFM images.[20] In addition, Hwang et al. have observed that Si(111) steps fluctuate at elevated temperatures through detachment and attachment of Si clusters.[21] It is therefore inferred that the distance of Ti silicide NWs from step edges significantly influences the growth rate of these NWs. It is anticipated that NWs closer to the step edges grow faster than those farther away from the step edges. On the other hand, LEEM dynamic observations showed that the rate-

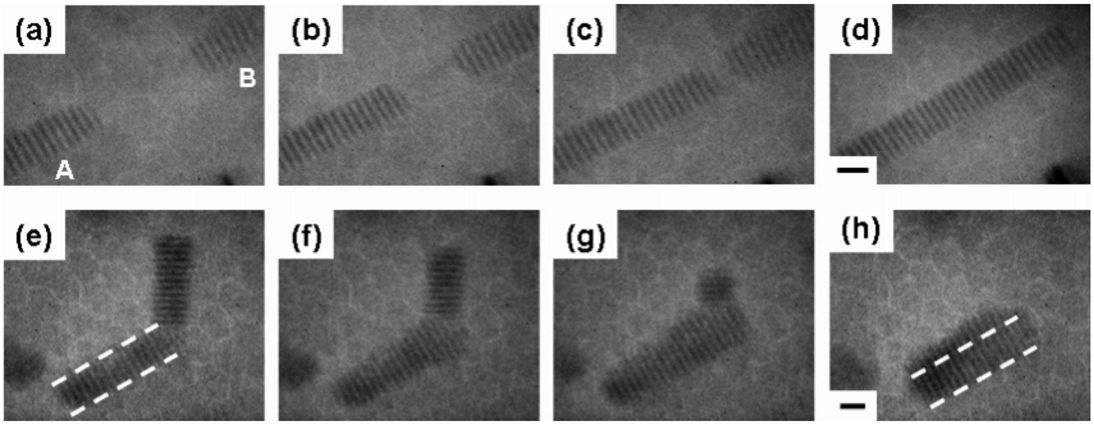

Figure 2. In situ TEM images of the interactions of titanium silicide NWs at 700 °C. The images of NWs in the same direction were obtained at elapsed times of (a) 0, (b) 9, (c) 18, and (d) 19 min. The images of NWs in different directions were obtained at elapsed times of (e) 0, (f) 25, (g) 49, and (h) 80 s. The scale bars correspond to 6 nm in (d) and 4 nm in (h).

limiting kinetic step during both growth and shrinking of the NWs is the Ti silicide reaction at the island ends, albeit at a much higher temperature (∼850 °C).[19] Therefore, the precise mechanism is likely to depend on the temperature, deposition rate, and other factors affecting the surface diffusion.

The interaction of NWs in inclined directions is different from that of two NWs in the same direction. Figure 2e−h shows two NWs colliding with each other. One of the NWs appears to collapse into the other along the side of the NW and was eventually absorbed by the other NW. (The corresponding video is shown in Supporting Information S2.) From the dotted line plotted in Figure 2e,h, a significant increment in the volume of the surviving NW was observed. However, the total surface area of the two NWs is diminished by their fusing together. The merging of the two NWs in different crystalline directions occurred as a result of minimizing the total surface energy. It is worth mentioning that the TEM images show the projections of nanowires in the viewing direction. Although the minimization of the total surface energy is a plausible explanation, the statement that "the total surface area is diminished" was made assuming that the thicknesses of the nanowires did not change.

During Ti deposition, as a Ti silicide NW continued to grow and encounter the midsection of an inclined NW, the NW tended to recede rapidly. From the successive images shown in Figure 3a−d, the NW "B", as marked in Figure 3a, collided with the midsection of NW "A", and then the NW "B" shrank immediately. On the other hand, the midsection of NW "A" is bulged, as marked in Figure 3b by the dotted line, indicating that the silicide atoms migrated from NW "B" to "A". (The corresponding video images are shown in Supporting Information S3.) According to the Gibbs−Thomson equation (G-T equation),[1] the equilibrium concentration C_r of clusters of radius r is

$$C_r = C_0 \exp(2\gamma\Omega/rkT)$$

where C_0 is the equilibrium concentration for the planar surface (i.e., $r \rightarrow \infty$), γ is the surface energy per unit area,

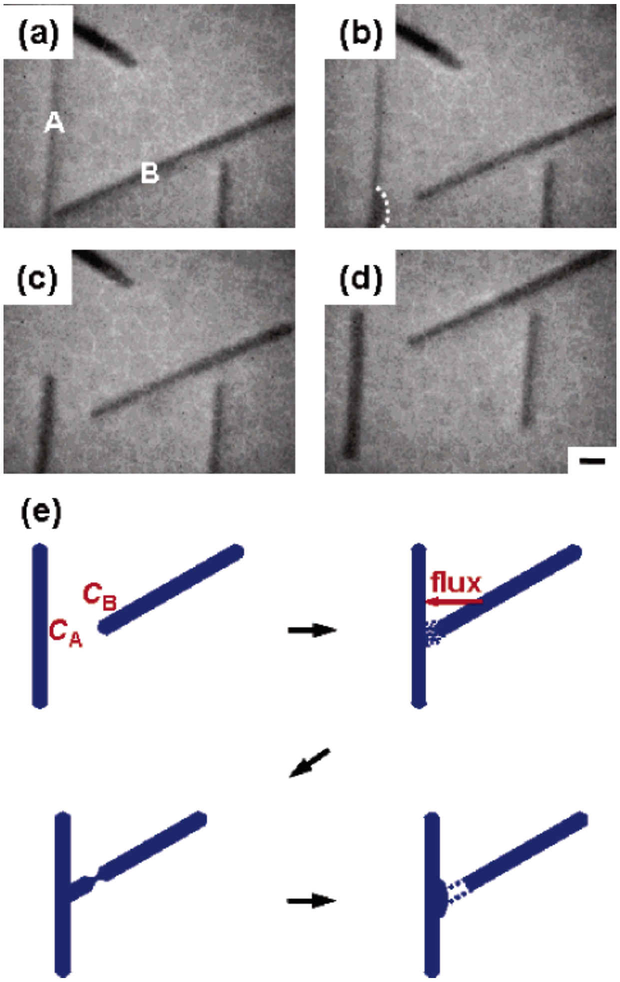

Figure 3. In situ TEM images showing the interaction of one titanium silicide NW with another at its midsection at 700 °C. The images were obtained at elapsed times of (a) 0, (b) 16, (c) 56, and (d) 81 s. The scale bar corresponds to 30 nm. (e) Schematic diagrams showing the interactions of the two NWs marked "A" and "B" in (a).

and Ω is the volume per atom. From the G-T equation, the concentration is strongly related to the curvature along the NW ends. As a result, the concentrations of constituent atoms (Ti and Si) at the curved end of NW "B" are higher than

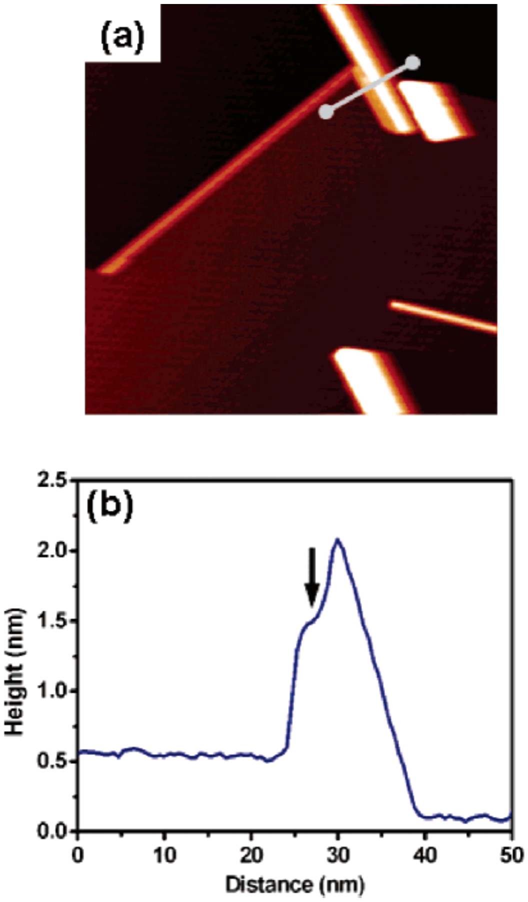

Figure 4. STM image of titanium silicide NWs on Si(111). (a) STM image (125 nm × 125 nm) of Ti deposited on Si(111) at 700 °C. (b) Line profile of the marked line seen in (a).

those at the flat side of NW “A”, resulting in the diffusion of Ti and Si atoms from NW “B” to “A”. Owing to the supply of silicide for the NW “B” taking a relatively long time to arrive from the far end to the contact area, receding of the NW was observed. With the decrease in the flux of constituent Ti and Si atoms from the front end of the receding NW toward the flat side of the other NW, it may reach a point that the lost flux is compensated by the flux of newly arriving Ti and Si atoms from the deposition and the steps of the substrates, respectively. As a result, the receding of the NW stopped. Schematic diagrams illustrating the interaction are shown in Figure 3e. As can be seen in Figure 3d, although there is a supply of Ti and Si atoms from NW “A”, the shortening of NW “B” is attributed to the interaction with a NW at its top side. On the other hand, the relative stability of the NW below NW “B” is yet to be clarified since its environment was not adequately surveyed during the in situ investigation.

The interpretation of the TEM results has been corroborated by STM observation, as shown in Figure 4. In the STM image taken at room temperature, as two NWs in different directions collided with each other, interdiffusion of silicide occurred between the NWs and a new silicide region was formed along the side of one NW at the midsection. From the line profile in Figure 4b, the height of the new silicide region was lower than the original NW, as

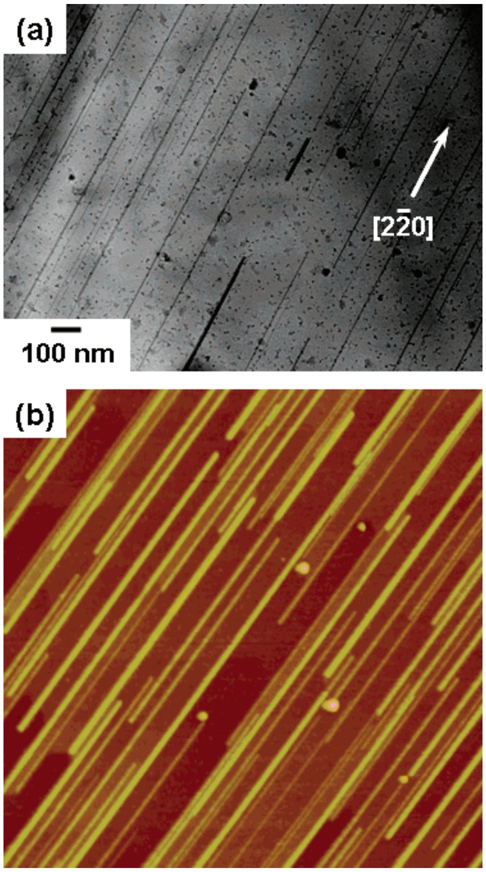

Figure 5. (a) TEM and (b) AFM (1.5 μm × 1.5 μm) images of titanium silicide NWs grown on Si(110) along one [1 −1 0] direction.

marked by an arrow, indicating that the region grew at a later stage. The NWs have flat surfaces in the long direction but are sloped near the edges in the short direction.

The three modes of interaction for the NWs on Si(111) indicate that if two neighboring nanowires grow in the same direction, they would merge to form a single nanowire with the combined length of the two NWs. On the other hand, for two neighboring NWs grown in the directions inclined with respect to each other, either one NW collapses on the other, or one NW would recede against the other. Therefore, in order to grow a high density of long and high-aspect-ratio NWs, it is highly desirable to grow NWs along a single direction. This important insight has been fruitfully exploited to focus on the growth of Ti silicide NWs on Si(110), since crystallographically the NWs are favored to grow only in the [1 −1 0] direction. Figure 5 shows TEM and AFM images of Ti silicide NWs grown on Si(110). A comparison between Ti silicide NWs grown on Si(111) and Si(110) with Ti deposition for 10 min is presented in Table 1. The NWs grown on Si(110) are about 6 times longer and 4 times higher in aspect ratio than those grown on Si(111). The growth of TiSi$_2$ NWs on Si(110) was found to be significantly affected by the Ti deposition rate and growth time. In Supporting Information S4, Figure S1 shows AFM images of TiSi$_2$ NWs grown on Si(110) with different deposition rates and growth times. At 1.5 times the normal deposition rate (0.07 nm/min), the NWs grow with time up to 45 min (top row). For

Table 1. Comparison between Titanium Silicide NWs Grown on Si(111) and Si(110)[a]

substrate	length	average length	width	average width	average aspect ratio
Si(111)	150−400	246	6−12	9.8	26
Si(110)	1000−2500	1445	6−30	15.3	109

[a] Deposition time, 10 min; units, nm.

60 min growth, the interference of neighboring NWs with each other became very severe (not shown) and the growth of NWs was impeded. For one-half the growth rate (bottom left), the NWs are of low density accompanied by a high density of clusters.

The results demonstrate the power of the in situ UHV-TEM observation. The changes in nanostructures involve nucleation, growth, and agglomeration. The dominant mechanisms for the evolution of nanostructures are often obscured if only the end products are observed. In the present study, the interaction modes of NWs were unambiguously determined by in situ UHV-TEM. This crucial information is in turn used to grow the NWs with desired length and aspect ratio.

Three interaction modes of Ti silicide NWs on Si(111) at 700 °C have been identified by in situ UHV-TEM. The spontaneously grown TiSi$_2$ NWs are oriented in three equivalent Si⟨2 −2 0⟩ directions with C49-TiSi$_2$(2 0 0)//Si-(2 −2 0). Two NWs grown in the same direction, and eventually colliding with each other, merged into one NW with the combined length of the two. On the other hand, for two neighboring NWs grown in directions inclined with respect to each other, either one NW collapses on the other, or one NW recedes against the other. This crucial information has been fruitfully exploited to focus on the growth of long and high-aspect-ratio Ti silicide NWs on Si(110) in a single direction. The results demonstrate the power of the in situ UHV-TEM observation. Most importantly, the achievement in focusing on the growth of high-density NWs parallel to the surface in a single direction represents a significant advance in realizing the vast potential for applications of silicide NWs in nanodevices.

Acknowledgment. The research was supported by the Republic of China National Science Council (grant no. NSC 94-2215-E-007-003) and Ministry of Education (grant no. 94-E-FA04-1-4).

Supporting Information Available: In situ video images of the interactions of two titanium silicide NWs in the same direction at 700 °C, of two inclined titanium silicide NWs with one collapsing into the other, and of one titanium silicide NW with another at its midsection at 700 °C (AVI; files are compressed with XviD MPEG-4 codec). AFM images showing the TiSi$_2$ NWs grown on Si(110) with different deposition rate and growth time (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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NL062465E