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Qiang Tang, Xian Liu, Theodore I. Kamins, Glenn S. Solomon, and James S. Harris

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Twinning in TiSi₂-island catalyzed Si nanowires grown by gas-source molecular-beam epitaxy

Qiang Tang^{a)} and Xian Liu Stanford University, Stanford, California 94305

Theodore I. Kamins Hewlett-Packard Laboratories, Palo Alto, California 94304

Glenn S. Solomon and James S. Harris Stanford University, Stanford, California 94305

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Using TiSi2 islands as a catalyst, we have grown Si nanowires by gas-source molecular-beam epitaxy using Si_2H_6 as the gas source. The dominant $TiSi_2$ islands are C49 phase with the orientation: Si[110]//C49-TiSi₂[100] and Si(001)//C49-TiSi₂(010). Twinning in the grown Si nanowires is observed by reflection high-energy electron diffraction and transmission electron microscopy. The twining also causes kinking, i.e., an abrupt change of growth direction of the Si nanowires. Lattice mismatch stress between the TiSi2 islands and the Si nanowires possibly leads to twinning and kinking of the Si nanowires. © 2002 American Institute of Physics. [DOI: 10.1063/1.1509096]

As devices in modern integrated circuits become smaller and smaller, the fabrication process becomes increasingly expensive, and sub-100 nm feature sizes become difficult to produce, primarily due to the hurdles of deep ultraviolet optics and materials. Therefore, new nanoscale self-assembling technology, such as catalyzed silicon nanowire growth,¹⁻³ and quantum dot growth may benefit integrated-circuit production by eliminating critical lithography steps. In these self-assembled systems, small feature sizes are defined using chemical reactions and/or crystal growth with limited or coarse lithography.

Silicon nanowires have been grown using Au,²⁻⁵ Fe,^{6,7} Zn,⁵ Ni,⁶ Co,⁶ and Ti (Ref. 1) islands as catalysts. Although all these transition metals form deep levels in silicon, which are detrimental to device functionality, the diffusivity and solubility of Ti in silicon are at least two orders of magnitude lower than that of Au, Fe, Zn, Ni, and Co.⁸ Furthermore, Ti has been widely used in integrated-circuit processing to form low-resistance contacts to silicon and polysilicon. Therefore, the Ti-catalyzed silicon nanowire system is more compatible with integrated-circuit components and applications.

Ti-catalyzed silicon nanowires were initially grown by chemical vapor deposition (CVD).¹ This letter reports Ticatalyzed silicon nanowires grown by gas-source molecularbeam epitaxy (MBE) and an investigation of their properties by in situ reflection high-energy electron diffraction (RHEED) and by *ex situ* transmission electron microscopy (TEM). Both MBE and CVD grown Ti-catalyzed silicon nanowires have TiSi₂ islands at the nanowire tips, because incoming Si atoms transport to and grow at the TiSi2-Si interface.

The Ti-catalyzed nanowires were grown in a Varian Gen-II MBE system using Si₂H₆ as the Si source and a resistively heated Ti filament as the Ti source. A VG Scientific

LEG110 RHEED system was used to characterize the surface in situ. The RHEED electron beam has an energy of 14 keV (λ = 0.01 nm) and an incidence angle of ~1°. The base pressure of the MBE system is 4×10^{-11} Torr and the chamber pressure during nanowire growth is 3×10^{-7} Torr.

To form the catalyzing islands, of the order of one monolayer of Ti was first deposited on Si(001) wafers at 500 °C, annealed at 820 °C for 10 min to form TiSi2 islands, then cooled to 500 °C, after which silicon nanowires were grown using a Si₂H₆ gas flow of 2.5 sccm. The resulted TiSi₂ islands have the diameters of 20 nm to 40 nm and cover about 20% of the wafer surface area. At the growth temperature of 500 °C, the growth rate on the noncatalyzed Si surface is very low, typically approximately 0.15 nm/min.9 The average growth rate of the Si nanowires in our experiment is about 3 nm/min.

RHEED pattern for the sample after Ti deposition and before annealing is shown in Fig. 1(a), where we see the streaks of the silicon (2×1) surface reconstruction, Kikuchi lines, and a strong background [compared with Fig. 1(b)] which is caused by the surface Ti or TiSi_x layer. While 500 °C is high enough for Ti atoms to migrate and intermix with Si atoms, RHEED indicates that no single-crystalline phase is dominant in the surface Ti or TiSi_x layer, otherwise there would be at least Laue rings in the RHEED pattern, in addition to the observed silicon surface reconstruction stripes. The presence of well-orientated C49-TiSi2 can be seen in the RHEED pattern [shown in Fig. 2(a)] observed near the beginning of the nanowire growth (after the first 30 s of the 60 min typical nanowire growth time). In Fig. 2(a), we see the C49 TiSi₂ (0,6,0), (2,6.0), (0,12,0), and (2,12,0)diffraction spots clearly. This shows that the surface Ti has been fully alloyed with silicon, forming the final Si-rich phase C49-TiSi₂ after annealing at 820 °C for 10 min. One orientation of the TiSi2 islands dominates, namely

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^{a)}Electronic mail: qtang@snow.stanford.edu



FIG. 1. RHEED patterns for (a) the substrate surface with approximately one monolayer of Ti deposited at 550 °C, and (b) the reconstructed clean Si surface before Ti deposition, with substrate [110] as electron-beam-incidence direction. L_0 is the zero-order Laue zone.

and

$$Si(001)//C49-TiSi_2(010).$$
 (1)

This is consistent with the observations of Briggs *et al.*¹⁰ Because (1) only approximately one monolayer of Ti was deposited, and (2) the TiSi₂ islands cover only $\sim 20\%$ of the wafer surface, the clearly observable extra TiSi₂ diffraction spots in the RHEED pattern indicates that most of the TiSi₂ islands have this orientation. In Fig. 2(a), we can also see Si (0, 0, 4), (1, -1, 3), (1, -1, 5), (2, -2, 4), and other diffraction spots that do not belong to the Si substrate. The additional diffraction spots come from the Si twins in the Si nanowires, which can be seen in Fig. 3. The configuration of the Si pattern and the Si twin pattern has been confirmed through simulation.¹¹

Figure 2(b) shows the RHEED pattern after nanowire growth for 60 min; we see the Si spots from the epitaxially oriented nanowires and the spots from the twinned regions, as in Fig. 2(a). The twin spots here are brighter than in Fig. 2(a). In addition, we do not see the C49 diffraction spots



FIG. 2. RHEED patterns for (a) the beginning of silicon nanowire growth article is (30 s), and (b) after silicon nanowire growth (60 min), with substrate [110] as electron-beam-incidence direction.



FIG. 3. Transmission electron micrograph of a Si nanowire containing twin crystals. The insets are the enlarged Si lattice image at positions 1, 2, and 3. The white lines represent Si(111) planes orientation. Si lattice at position 1 is twin relative to that at position 2, which is twin relative to that at position 3.

observed in Fig. 2(a), but we do see a diffuse Laue ring corresponding to C49-TiSi₂ {060}. Other C49 Laue rings are too weak to be clearly observed. For the wafer surface corresponding to Fig. 2(b), the incident RHEED electron beam is mainly diffracted by Si nanowires, and only a small portion of incident electrons are diffracted by the TiSi₂ islands at the tip of nanowires, which are almost randomly oriented due to growth direction change of nanowires and possible change of TiSi₂–Si relative orientation during growth. This is the reason why only strong Si spots and a weak C49-TiSi₂ {060} ring appear in Fig. 2(b).

Si and C49-TiSi₂ are not lattice matched because Si has a diamond structure with lattice parameter of 0.5431 nm and C49-TiSi₂ has an orthorhombic structure with lattice parameters of 0.362, 1.376, and 0.360 nm. Moreover, in our growth process, the TiSi₂ islands remain in the solid state, which is different from vapor–liquid–solid growth¹² situation where¹³ the catalyzing islands are in the liquid state, reducing the stress at the island–Si interface. For the orientation of Si[110]//C49-TiSi₂[100] and Si(001)//C49-TiSi₂(010), the lattice mismatch between Si[110] and C49-TiSi₂[100] is approximately 6%. So in Ti-catalyzed Si nanowire growth, the strain between C49-TiSi₂ islands and Si lattice is possibly responsible for the kinking shown in Fig. 3.

Figure 4(b) shows a Si nanowire growing toward the right-hand side, in which a twin is starting to develop at its lower edge and a highly defected Si crystal containing stacking faults is being formed at the upper edge. The possible understanding for Fig. 4(b) is that the stress at the interface between C49-TiSi₂ islands and Si causes the Shockley partial dislocation to glide through silicon crystal along {111} planes, possibly starting from the edge of TiSi₂ islands, where the stress is highest and the starting of dislocation is between the Shockley partial dislocation programmer and the starting of dislocation is between the stress is highest and the starting of dislocation is between the Shockley partial dislocation glides through ev-



FIG. 4. Transmission electron micrographs of the grown Si nanowires. (a) Upper part of a nanowire. (b) A short nanowire. There is a thin layer of native oxide ($\sim 2 \text{ nm}$) surrounding the nanowires and the C49-TiSi₂ islands, but the amorphous coating layer also comes from the wax we used for preparing the TEM samples, especially where close to the substrate. In (b), no lattice fringe is observed in the C49-TiSi₂ crystal because the imaging electron beam was not aligned for it. In (b), the dark part in the upper portion of the image is the substrate.

ery parallel {111} plane, a twin crystal forms; otherwise, a highly defective crystal full of stacking faults forms.

After the twin is formed, it grows along with the nanowire, as shown at position 1 in Fig. 3. When the twin is large enough to dominate the growth, the wire changes to the new growth direction dominated by the twin crystal, resulting in a kink. The twinning process can happen several times during the nanowire growth. Therefore, the nanowire can change growth direction several times, leaving large amounts of twinned regions in the nanowires. These twinned regions cause the twin diffraction spots in the RHEED pattern after growth [Fig. 2(b)] to be brighter than in the RHEED pattern observed early in the growth process [Fig. 2(a)].

For TiSi₂-catalyzed nanowires, twinning does not occur in every nanowire, with Fig. 4(a) as an example. Notice that the (021) planes in the C49-TiSi₂ tip are parallel to and matching the (111) planes in the Si nanowire very well. This orientation relationship between C49-TiSi₂ tip and Si nanowire is different form the one observed in RHEED. The calculated interplanar distance of C49-TiSi₂ (021) is 0.3190 nm, which is 1.7% larger than the calculated Si (111) interplanar distance of 0.3136 nm. Since in Fig. 4(a) no twinning is observed, the 1.7% lattice mismatch between C49-TiSi₂ tip and Si nanowire is probably not big enough to form twin or highly defected crystal in the Si nanowire given that fact that the Si nanowire is only about 25 nm wide and both the tip and the nanowire are not confined laterally.

In summary, we have grown Si nanowires using selfassembled TiSi₂ as catalyzing nanoparticles and Si₂H₆ as the gas source in MBE. The dominant TiSi₂ islands are C49-TiSi₂ with the orientation of Si[110]//C49-TiSi₂[100] and Si(001)//C49-TiSi₂[010]. The nanowires change their growth direction by twinning, which is possibly caused by lattice mismatch between C49-TiSi₂ tip and Si nanowire.

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