Nucleation and Atomic Layer Reaction in Nickel Silicide for Defect-Engineered Si Nanochannels

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Supporting Information

ABSTRACT: At the nanoscale, defects can significantly impact phase transformation processes and change materials properties. The material nickel silicide has been the industry standard electrical contact of silicon microelectronics for decades and is a rich platform for scientific innovation at the conjunction of materials and electronics. Its formation in nanoscale silicon devices that employ high levels of strain, intentional, and unintentional twins or grain boundaries can be dramatically different from the commonly conceived bulk processes. Here, using in situ high-resolution transmission electron microscopy (HRTEM), we capture single events during heterogeneous nucleation and atomic layer reaction of nickel silicide at various crystalline boundaries in Si nanochannels for the first time. We show through systematic experiments and analytical modeling that unlike other typical face-centered cubic materials such as copper or silicon the twin defects in NiSi2 have high interfacial energies. We observe that these twin defects dramatically change the behavior of new phase nucleation and can have direct implications for ultrascaled devices that are prone to defects or may utilize them to improve device performance.

KEYWORDS: Nickel silicide, silicon nanowire, defects, twin boundary, heterogeneous nucleation, in situ TEM

Certain novel crystal growth phenomena are often attributed to nanocrystalline boundaries. These boundaries were found to significantly alter the electronic structure of semiconductor materials. An atomic level understanding of the silicidation process in the vicinity of such nanocrystallite boundaries can shed light on novel solid-state reactions at nanoscale and can bring their material electronic property interactions to new frontiers. In crystalline Si nanochannels (e.g., nanowires), nickel silicide grows by atomic layer reaction with repeating two-dimensional (2D) homogeneous nucleation and layer-by-layer growth. Heterogeneous nucleation is suppressed in this case because the only available heterogeneous site, the Si/native oxide interface is unfavorable owing to the need of creating a higher energy silicide-oxide interface. Therefore, the concentration of Ni atoms in the Si nanowire (NW) continues to grow until it reaches a level that is sufficient to initiate 2D homogeneous nucleation at the center of the Si/silicide interface in the Si NW. In nanostructures, this process can be dramatically different in the presence of crystallites and crystalline defects that introduce additional interfaces for nucleation, and such processes have not been studied before. Here, twin boundaries (TBs) and grain boundaries (GBs) (often found in advanced semiconductor devices) are intentionally built into our Si NWs to specifically study the impact of these defects on nickel silicide nucleation and step flow in Si. By using in situ high-resolution transmission electron microscopy (HRTEM), the atomic layer silicidation reaction was monitored dynamically in real time to validate and examine the nature of nucleation and step flow at TB and surface GB heterogeneous nucleation sites. Our observation of different nucleation events near TBs and GBs are repeatable on more than five nanowire samples and is consistent with the data presented and analyzed below.

Our platform for the in situ TEM heating experiment was fabricated on a 50 nm thick electron-beam transparent silicon nitride TEM membrane where Ni metal contact formation to Si NWs predeposited onto such membranes has been described in detail elsewhere.

To examine the influence of defects on silicide nucleation and growth, we first discuss the case of a Si NW with a twin...
a bicrystal consisting of two portions of Si sharing a \{111\} plane, forming a coherent \(3 \{111\}\) twin boundary with NW axis along the\{112\} orientation.\(^{15}\) We find that the silicide growth front moves asynchronously in each of the bicrystals. We hereby refer to the fast growing interface as the leading interface and to the slower one as the lagging interface (Figure 1b). Figure 1c–f shows a series of in situ TEM snapshots providing direct evidence that a new NiSi\(_2\) \{111\} plane nucleates at the TB (Figure 1c,d) and propagates on Si\{111\} plane at the leading interface and toward the edge surface of the NW (Figure 1e,f) in a layer-by-layer manner (see also Video 1 available in Supporting Information). Significantly, the new layer cannot directly propagate across the TB but rather remains in the same half of the twinned-bicrystal at which a nucleus was initially formed, and the new silicide nucleus does not form across the TB either. The formation of an individual nucleus on one side of the TB is energetically preferred as we will discuss below. As a consequence, the growth front of two halves of the bicrystal move asynchronously, and there is a chance to develop steps with heights of a few NiSi\(_2\) \{111\} planes between the two interfaces. These observations show that step nucleation and flow on NiSi\(_2\) in the presence of a twin boundary is dramatically different from that in a single crystal,\(^{9}\) where each new nickel silicide layer nucleates at the center of the nanowire in the reacting front.

Growth of NiSi\(_2\) \{111\} plane at the lagging interface also proceeds in a layer-by-layer manner (Supporting Information Video 1). A new NiSi\(_2\) \{111\} plane nucleates at the “corner” (marked in Figure 1g) and then propagates to the edge surface of the NW (Figure 1g−j). The nucleation at the lagging interface is expected to be more energetically favorable when compared to the leading interface because it annihilates part of the high energy NiSi\(_2\)/Si interface. These distinct observations on the formation of a new phase nucleus and step flow are the first to be captured in real time at crystalline boundaries and confirm unambiguously the location of the nucleus at the TB.

In addition to TBs, Si grains can also form in the processing of nanoscale semiconductor devices.\(^{12,13}\) It is therefore interesting to investigate the influence of grain boundaries at the nanowire surface on silicide nucleation. We find that heterogeneous nucleation is further facilitated at surface grain boundaries. Figure 2a shows a twinned Si NW with surface grains, and Figure 2b highlights several surface grains with different crystallographic orientations with respect to the stem of the NW. In situ TEM snapshots in Figure 2c−f show at the leading interface a single NiSi\(_2\) layer first nucleates at the surface GB and propagates toward the center of the NW (see also...
Video 2 in Supporting Information). Here, the surface grain partially overlaps with the NW along the viewing direction (marked by light blue dashed enclosure). The NiSi$_2$ (111) step flow is opposite in direction to the case where no surface GBs are present on the NW (e.g., Figure 1c−f). We note that this is due to a much higher GB energy than TB energy and quantitative analysis of this effect will be shown next. In the presence of a GB at the nanowire surface, the NiSi$_2$ growth also proceeds into the surface GB.

In contrast to the situation in Figure 1g−j, at the lagging interface of a Si NW with both TBs and GBs (Figure 2g−j) we see that the presence of the surface GB can pin the nucleation site at the surface GB instead of the corner region at the center of the TB. Figure 2g−j shows one example in which the new NiSi$_2$ (111) plane nucleates from surface GB and then propagates toward the center of the NW (see also Video 3 in Supporting Information). It is tempting to infer that a NiSi$_2$ twin has a low energy, because NiSi$_2$ has a face-centered cubic (fcc) structure, which is similar to Cu and Si, and the latter two have a much lower TB energy than the GB energy or heterointerface energy.$^{16,17}$ The formation of a coherent TB of Cu or Si only involves alternation of the stacking sequence and the nearest neighbor coordination of interfacial atoms is not disturbed. If the NiSi$_2$ twin does have a low energy, nucleation at the “corner” should be very fast. However, a close look at the structure of the TB in a NiSi$_2$ crystal reveals that the nearest neighbor configurations of the interfacial atoms are in fact disturbed (Supporting Information Figure S1) and are no longer the same as those in the bulk, so the TB energy in NiSi$_2$ is not negligible, as calculated in the Supporting Information. This also explains why NiSi$_2$ (111) planes do not nucleate or propagate across the TB as was demonstrated in Figure 1c−f, since nucleation at the “corner” would not be favored because of the need to create a high-energy NiSi$_2$ TB.

To quantitatively assess the layer-by-layer growth of NiSi$_2$ in the presence of crystalline defects, we tracked over an extended period of time the NiSi$_2$ (111) plane nucleation and step migration. The in situ experiment provides for the precise measurement of growth rate behavior of NiSi$_2$ in Si NWs. We observe a distinctive behavior in nucleation and step migration when assisted by TB alone (Figure 3a) versus GB when the TB/GB coexist in the same NW (Figure 3b). In Figure 3a, the growth (in both halves of Si bicrystal) is almost linear over a time period exceeding 20 min featuring a steady growth rate. Note that the growth was monitored when the silicide segment length (silicide−silicon interface in each half of the bicrystal, that is, leading and lagging interfaces) represents independent random events. However, the lagging interface can catch up with the leading interface because the corner is a more preferable heteronucleation site, so on the average ASH does not grow significantly, given that Ni supply is equally available for both halves of the bicrystal. On the other hand, when surface GBs are further introduced onto the NW, the growth rate fluctuates and can change by a factor of 3.8 (from 0.08 plane/s to 0.3 plane/s) over a similar NiSi$_2$ growth time.

The irregular growth behavior in the presence of surface GBs originates from the fact that the nucleation barrier of each new NiSi$_2$ (111) plane depends on the energy of surface GBs, which is a function of relative orientation of the surface grain with respect to the NW as well as the details of the atom arrangements at the GB. On the segment of the NW with high energy surface GBs, heterogeneous nucleation is more favored and the NiSi$_2$ grows faster. We note that in the time period between 600 and 630 s in Figure 3b the leading interface (black curve, left portion in the bicrystal) grows rapidly, while the growth of the lagging interface (red curve, right portion in the bicrystal) ceases, and a huge ASH (with a maximum height of 33 NiSi$_2$ (111) atomic layers) develops as a result between these two interfaces. Rapid growth of the leading interface implies high GB energy at the surface, which promptly assists nucleation of NiSi$_2$ and consume incoming Ni atoms to complete the layer-by-layer growth. Therefore, the NiSi$_2$ nuclei preferably formed at the leading interface GB act as Ni sinks and keep the Ni concentration at the lagging interface lower than that required to nucleate a new NiSi$_2$ plane. In this extreme case, NiSi$_2$ growth is completely dominated by nucleation at extrinsic surface GBs and shadows other intrinsic nucleation sites like the corner so that the lagging interface does not grow for an extended period of time. This result suggests that the defects can play a prominent role in the nickel silicide formation process. To use silicide as S/D extensions in
nanoscale Si-based devices, controlled growth of nickel silicide into 3D Si channels is extremely important and since device-to-device variation is undesirable such surface defects must be avoided.

Our experimental observations can be validated by an intuitive quantitative model based on classical nucleation theory by considering different types of defects. We consider the following heterogeneous sites: (1) Si TB, (2) Si GB, and (3) the TB corner, as depicted in Figure 4a, and discuss the corresponding interface energy parameters separately. For a silicide nucleus (Figure 4b) and assuming the 2D silicide partial disk nucleates at a certain interface in the system, the total change in the system free energy, \( \Delta G_{\text{hetero}} \), is given by

\[
\Delta G_{\text{hetero}} = -\Delta g \left[ \pi R^2 \left( \frac{1 - \theta}{\pi} \right) + R^2 \sin(\theta)\cos(\theta) \right] h + 2(\pi - \theta)Rh\bar{\gamma} + 2Rh \sin(\theta)(\gamma_{\text{new}} - \gamma_{\text{defect}})
\]

where \( \Delta g \) is the silicide formation energy, \( R \) is the radius of the disk, \( h \) is the height of one atomic step, \( \theta \) is the contact angle, \( \bar{\gamma} \) is the average interface energy between NiSi\(_2\) and Si over different orientations, \( \gamma_{\text{defect}} \) is the original defect energy, \( \gamma_{\text{new}} \) is the energy of the interface subject to nucleation with NiSi\(_2\) at the original defect boundary. Both \( \gamma_{\text{defect}} \) and \( \gamma_{\text{new}} \) assumes different values for different defects which will become clear as we discuss specific defect types below.

The critical radius, \( R^* \), can be solved by letting \( \partial \Delta G / \partial R_{\text{GB-R}} = 0 \), and invoking the Young’s equation (\( \bar{\gamma} \cos(\theta) + \gamma_{\text{defect}} = \gamma_{\text{new}} \)) to result in the heterogeneous nucleation energy barrier

\[
\Delta G_{\text{hetero}}^* = \frac{\bar{\gamma}^2h}{\Delta g} [(\pi - \theta) + \sin(\theta)\cos(\theta)]
\]

(2)

For the special case of \( \theta = 0 \), eq 2 gives the homogeneous nucleation barrier \( \Delta G_{\text{hetero}}^* = (\pi^2 h^2)/(\Delta g) \). To determine the impact of defects on reducing the nucleation energy barrier, we calculate the ratio

\[
\frac{\Delta G_{\text{hetero}}^*}{\Delta G_{\text{homo}}^*} = \frac{(\pi - \theta) + \sin(\theta)\cos(\theta)}{\pi}
\]

(3)

The exact choice of interface energy parameters is discussed in detail in the Supporting Information. Table 1 provides a summary of the interfacial energetic parameter values. The TB energy in NiSi\(_2\), \( \gamma_{\text{NiSi}_2}^{\text{TB}} \), is not known from the literature. We developed a stochastic mathematical model to depict the asynchronous silicide growth process in a twinned Si NW as a biased 1D random walk in the ASH space. We derive the statistical average ASH from the model and relate it to the experimental measured value (average of blue curves in Figure 3a) to extract \( \gamma_{\text{NiSi}_2}^{\text{TB}} = 1.13 \text{ J/m}^2 \). Details of the model are

Table 1. Summary of Interfacial Energy Parameters Used in the Nucleation Model for All Three Cases Considered in Figure 4

<table>
<thead>
<tr>
<th>nucleation boundary type</th>
<th>( \gamma_{\text{defect}} )</th>
<th>( \gamma_{\text{new}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>TB</td>
<td>( \gamma_{\text{NiSi}_2}^{\text{TB}} ) (0.05 J/m(^2))</td>
<td>( \gamma_{\text{NiSi}_2}^{\text{TB}} ) (0.6 J/m(^2))</td>
</tr>
<tr>
<td>GB</td>
<td>( \gamma_{\text{NiSi}_2}^{\text{GB}} ) (0.4 J/m(^2))</td>
<td>( \gamma_{\text{NiSi}_2}^{\text{GB}} ) (0.8 J/m(^2))</td>
</tr>
<tr>
<td>NiSi(_2)/Si twinned interface</td>
<td>( \gamma_{\text{NiSi}_2}^{\text{NiSi}_2/Si} ) (0.6 J/m(^2))</td>
<td>( \gamma_{\text{NiSi}_2}^{\text{NiSi}_2/Si} ) (1.13 J/m(^2))</td>
</tr>
</tbody>
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described in the Supporting Information. This result demonstrates that unlike typical fcc materials (e.g., Si, Cu, etc.) with typical energies 20–50 mJ/m²,16,17 the TB defect in NiSi₂ has a high interfacial energy, which is determined by the detailed atomic arrangement in its unit cell.

Figure 4c shows the effectiveness of nucleation barrier energy reduction ΔG_{hetero}/ΔG_{homo} by nucleation at various types of defects or heterogeneous sites. The ratio γ/γ_{NiSi₂} accounts for the uncertainty of γ (γ_{Si/NiSi₂} or the energy of epitaxial Si/NiSi₂ interface, provides a reference) and is assumed over a certain range as shown in Figure 4c. As a conservative estimate, we choose ΔG_{hetero}/ΔG_{homo} values to be 0.934, 0.924, and 0.835, for the nucleation at TBs, corners, and the GBs, respectively. In addition, we have computed ΔG_{hetero}/ΔG_{homo} * for a range of γ_{new} (see Figure S4 of the Supporting Information), and the results corroborate with those presented in Figure 4. Note that the nucleation rate is proportional to exp(−ΔG*/kT), so a slight change in the nucleation energy barrier can change the nucleation rate dramatically. The analysis here shows that defects can indeed change the nucleation behavior of the new silicide layer and various defects can be further differentiated by the amount of interfacial energy reduction after silicide nucleation.

There are two contributions to the heterogeneous nucleation energy barrier reduction, (i) formation of a low energy Si/NiSi₂ interface at the defect plane and (ii) annihilation of the defect itself. For heterogeneous nucleation at the TB, NiSi₂ nucleus can form a low energy epitaxial interface with Si, which facilitates heterogeneous nucleation. For nucleation at a Si GB, the reduction in nucleation energy is mainly provided by annihilation of the Si GB. Thus contribution (ii) plays an important role here and the nucleation energy barrier is even lower than the nucleation at Si TB. A general criterion for heterogeneous nucleation is that γ_{new} − γ_{defect} < γ, which captures both contributions.

Although our studies focus on the Ni silicidation reaction in a NW system, they have general implications to the kinetics of contact formation and device reliability in very large scale integration (VLSI) technologies. In a CMOS fabrication process, the S/D region of MOSFETs needs to be heavily doped to achieve low contact resistances. This is typically accomplished by dopant implantation and subsequent S/D activation thermal anneal to recrystallize the damaged S/D area where defects may form during the annealing step. Yamaguchi et al.11 found that Si(111) stacking faults form at the trench edge after S/D activation annealing, and that NiSi₂ whiskers form and elongate from such trench edges and pierce into the channel. The origin of this observation can be explained by the current study on enhanced heterogeneous nucleation of the NiSi₂ phase at stacking fault defects. While these stacking faults were unintentionally formed, as previously discussed, some are intentionally introduced in the S/D region to engineer tensile strain in n-type transistor channels and enhance electron mobilities through the strain memorization technology.9,10 Our studies imply that the presence of defects in the S/D region may change the contact silicidation process and undesired silicide encroachment into the channel may occur when silicide formation is guided by such defects. Our in situ TEM studies provide new insights into how nickel silicide formation interacts with various defect types in Si and can further guide defect engineering strategies to beneficially impact contact formation in VLSI device technologies.

Experimental Methods. Si NWs were grown by LPCVD as detailed before.20 Post growth, the Si NWs were released from the substrate into isopropanol solution by ultrasound agitation in a water bath and were randomly dispersed on the silicon nitride membrane. Chess board patterns with alternative contact pad openings were defined by photolithography. The native oxide on the Si NW at the contact areas was completely removed by dipping in diluted buffered oxide etch (BOE) solution (6 parts 40% NH₄F and 1 part 49% HF) for 20 s. Deposition of a Ni film of 100 nm by electron-beam evaporation followed.

We use an in situ TEM heating stage (Gatan single tilt heating stage 628) to anneal the specimen in a TEM (FEI Tecnai 300 keV) chamber at a vacuum level of 10⁻⁸ Torr. The temperature is controlled by an external current source, and it allows isothermal heat treatment of the sample after the initial temperature transient (about 2 min). All samples discussed in this Letter were annealed at 300 °C. High-resolution (HR) TEM images are continuously updated by the CCD scan system, and frames were captured and compiled into videos to reveal the dynamic process of the silicide growth.

ASSOCIATED CONTENT

Supporting Information
Details on structure analysis of possible NiSi₂ twin structure, interface energy parameter selection, and stochastic 1D biased random walk model. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

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