Quantitative Evaluation of Cobalt Disilicide/Si Interfacial Roughness

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The formation of smooth, conformal cobalt disilicide (CoSi2) without facets or voids is critical for microelectronics device reliability owing to the ultra-shallow contact areas. Here we demonstrate the formation of smooth and conformal CoSi2 films by chemical vapor deposition (CVD) of cobalt nitride (Co,N) films on silicon (Si) or on silicon on insulator (SOI) substrates, followed by in-situ rapid thermal annealing (RTA) at 700 °C. To reveal the CoSi2/Si interfacial morphology, we report a back-to-front sample preparation method, in which mechanical polishing, anisotropic tetramethylammonium hydroxide (TMAH) wet etching, hydrofluoric acid (HF) wet etching, and isotropic xenon difluoride (XeF2) dry etching are employed to remove the SOI substrate from the back side to expose the CoSi2/Si interface. This method offers a robust and reliable procedure for quantitative assessment of the CoSi2/Si interfacial roughness, as well as analytical support for advanced fabrication process development.

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Metal silicides have been widely used as self-aligned contacts in silicon-based microelectronics devices for the past decades.1 Among various metal silicides, CoSi2 is considered as an attractive contact material because of its low resistivity (10–20 μΩ·cm), no line-width dependence in narrow lines, and its superior chemical and thermal stability.2–4 CoSi2 has been used for various electronic devices, such as memory electrode for 3D structure5 and the metallization material for nanoparticles and nanowires.6,7 As devices scale down, a thin, uniform CoSi2 layer is essential for those nano-electronic applications. Otherwise, cobalt silicide spikes will cause severe junction leakage and lead to device failure.8 However, the complicated growth mechanism of CoSi2 can result in a problematic, rough CoSi2/Si interface.9,10 The complex kinetics results from several concurrent mechanisms: nucleation, diffusion and perhaps interface reaction.11 Many efforts have been focused on the formation of a smooth CoSi2 interface with Si by optimizing the fabrication process. For example, a Ti capping layer was introduced to reduce interfacial roughness induced by ambient contamination.12 Hence, the quantitative evaluation of the CoSi2/Si interfacial roughness is crucial for optimization of fabrication processes for CoSi2.

CoSi2 is typically fabricated by annealing sputtered Co films on active source, drain and gate regions.2 However, the conventional sputtering process results in poor step coverage and induces high ion damage in the active regions, making it undesirable for complex 3D architectures in modern transistors. Chemical vapor deposition (CVD) can avoid these problems by producing conformal cobalt-containing thin films without ion-induced damage.13–15

In this paper, we evaluate quantitatively the roughness of the cobalt silicide/Si interface, in which the cobalt silicide is produced from CVD-deposited Co,N films by in-situ RTA at 700 °C. The CVD process produced smooth, uniform and highly conformal Co,N, and also resulted in a smooth and high-quality CoSi2/Si interface.11 To reveal the CoSi2/Si interface for analysis of its roughness, we adapted and modified a SIMS sample preparation technique to remove the back side of the sample. This method uses both wet-etching and dry etching to remove a SOI substrate below the CoSi2. This work provides direct quantitative assessment of cobalt silicide/Si interfacial roughness for the first time, and offers critical insights for future process optimization.

**Experimental**

Cobalt nitride films on Si and SOI substrates were prepared by CVD using bis(N-tert-butyl-N'-ethyl-propionamidobato) cobalt(II) and a mixture of 20 sccm NH3 and 40 sccm H2 at 200 °C. The details of this process have been described elsewhere.13 The Si and SOI substrates were first treated by UV-ozone and then cleaned by HF before deposition. After cleaning, the substrates were immediately placed into the reactor chamber and evacuated, to suppress oxidation of the substrates. As Co is unable to react with SiO2,12 the cobalt silicide formation might be slowed down or even blocked by any interfacial native oxide. Therefore, a clean substrate without native oxide is critical to obtain a uniform and smooth CoSi2 films.

The as-deposited Co,N films were treated by in-situ RTA at elevated temperatures from 500 °C to 700 °C for 30 sec in purified N2. Those gases used in the deposition and annealing processes were purified by gas purifiers (Entegris Gatekeeper) to reduce the impurities below 1 ppb for all contaminants including O2, CO, CO2, and H2O. This purification is needed because the CoSi2 formation process is highly sensitive to traces of oxygen-containing impurities in the annealing ambient.16–18 Extremely low levels of these impurities are essential for smooth CoSi2 formation.19 Indeed, attempts to form CoSi2 from Co,N by ex-situ RTA were unsuccessful owing to the sample contamination during the exposure to the air and the annealing ambient (our ex-situ RTA tool does not use purified gas for annealing). Those impurities resulted in discontinuous CoSi2 with many voids. A previous study also showed that impurities in the annealing atmosphere formed voids during silicidation.19 Therefore, we employed in-situ annealing inside our cobalt deposition system to produce consistent, continuous CoSi2 films.

The back side sample preparation included 5 steps to reveal the CoSi2/Si interface. First, the sample was bonded upside down to a glass slide of similar size for mechanical support. Epoxy Bond 110 (Ted Pella Inc.) is used for bonding the two. Thin epoxy glue was carefully applied in between and degassed, then cured at 125°C for 10 min to obtain a homogenous glue film with good adhesion.

Second, the bonded sample stack was mounted onto a specimen mount – a cylindrical Pyrex stub (Gatan Inc.) using a low-melting-point wax (Crystalbond 509, Ted Pella Inc.). The stub was heated on a hot plate at 130 °C~160 °C to melt a tiny granule of wax for mounting the sample stack to be ground flat. Then a metal ring (Gatan Inc.) was used to hold the stub flat on the polishing sand paper. Rough silicidation of the specimen was performed with a polisher (Allied High Tech Products Inc.) until a thickness of 100 μm or less was achieved. The thickness of the specimen was measured and monitored by the micrometer to reach the desired thickness of less than 100 μm after polishing. The Si substrate was coarsely polished sequentially by SiC
sand paper of 600 grit and 1200 grit. The polished specimen was
detached from the mounting stub by melting the wax on a hot plate
and dissolving the remaining wax in acetone.

Third, the remaining Si substrate was removed by a heated TMAH
(25 wt%) bath at 85°C. TMAH etching is highly selective toward
the thermal oxide. Thus when no more bubbles were formed in the
etching solution, it indicated the bulk Si had been completely removed,
exposing the SiO2 layer. Then the sample was immersed in 10:1
buffered HF solution until the SiO2 layer of the SOI was removed,
which is the fourth step.

In the final step, the remaining Si layer (~100 nm) from SOI
(originally 200 nm) was removed by dry etching with XeF2 gas.
This was performed in a home-built XeF2 etching tool. Exposed Si
was quickly etched by alternating exposure to XeF2 and subsequent
pumping away of gaseous reaction products. Si reacts with XeF2 to
form gaseous Xe and SiF4. XeF2 etching has been used to selectively
remove Si because it removes only silicon, but not photoresist, SiO2,
silicon nitride, Al, Cr, or TiN.18 We measured that in our system the
XeF2 etch rate of CoSi2 is 200 times slower than that of Si; thus XeF2
etching can selectively remove the thin layer of residual Si. As a result
of the excellent selectivity toward CoSi2, the XeF2 etching process is
highly robust and tolerant toward some over-etch. This final step leaves
a clean CoSi2 surface, allowing the CoSi2/Si interface to be examined
by atomic force microscopy (AFM). The interfacial roughness study
is valuable for optimizing cobalt silicide process.

Results and Discussion

As shown in Figure 1, we used X-ray diffraction (XRD, Bruker
D8) to study cobalt silicidation process by annealing CoN/Si(100)
structure in-situ at 500 °C, 600 °C and 700 °C in N2 for 30 sec. XRD
measurements were carried out by using D8 diffractometer and 2-
Dimensional detector. The as-deposited CoN showed a face-cubic-
centered (fcc) phase, as indicated by our previous study.13 Figure 1
shows that the CoN remained stable in its fcc phase after RTA at 500°C.
After RTA at 600°C, CoSi2 with (111) and (220) orientations
dominated the resulting films, while CoSi (210) and (211) orientations
occurred simultaneously. This suggests polycrystalline CoSi2 started
to appear together with CoSi after annealing at 600°C. Meanwhile,
the intensity of CoSi2 (111) peak is greater than of other CoSi and
CoSi peaks, indicating that the film is textured. The CoSi completely
transformed to CoSi2 after RTA at 700°C, forming a textured CoSi2
with a (111) preferred orientation on the Si (100) substrate. The cubic
CoSi2 and CoSi phases were formed directly from cubic CoN films
without any intermediate Co-rich phases, such as tetragonal CoSi or
orthorhombic CoSi at low temperatures. In a conventional Co
silicide process, Co-rich silicide phases such as Co3Si or CoSi gener-
ally formed at a low temperature ranging between 400°C and 500°C.1
These results indicate that because of retardation of the Co-Si reaction
by the nitrogen in the CoN film, the conversion of CoN to CoSi2
does not form any intermediate Co-rich phases. This finding agrees
with a previous study of CoSi2 formation by annealing CoN/Si(100)
structures.19 Additionally, CoSi2 grown by the reaction of CoN on
Si(100) produced polycrystalline CoSi2 films as expected. Although
CoSi2 (cubic CaF2 structure with a = 5.36 Å) and Si (cubic diamond
structure with a = 5.43 Å) have a small lattice mismatch of only
1.2% and similar crystallographic structure, it has proved challeng-
ing to form epitaxial CoSi2 on Si substrates. Bulle-Lieuwma et al.20
explained the possible reason for the polycrystalline nature of CoSi2
on Si (100). They suggested that the competition between different
epitaxial orientations with similar matching resulted in the growth of
polycrystalline CoSi2.

Figure 2 shows electron diffraction (ED) images of CoSi2 from
transmission electron microscopy (TEM; JEOL 2100 TEM system).
ED shows that the films are polycrystalline cubic cobalt disilicide.
The speckled pattern of the diffraction rings indicates that the specimen
has relatively large grain sizes. The pattern showed part of the ring
is more intense compared to the rest, indicating a textured film. This
result agreed with the XRD result.

Figure 1. The XRD spectra of the as-deposited CoN/Si (100) and the films
after in-situ annealing under 1 Torr of N2 at various temperatures (T_a
= 500 °C, 600 °C, 700 °C) for 30 s.

The resistivity of CoN and CoSi2 thin films could be obtained by
measurements of the thickness and sheet resistance. A four point probe
was applied to measure the sheet resistance. The unreacted cobalt ni-
trides (if any) on top of the formed CoSi2 were removed by a dilute
sulfuric acid solution at 50°C before the measurements. A scanning
electron microscope (SEM) was used to measure the physical thick-
nesses. An as-deposited 30 nm CoN film on a Si (100) substrate
generated around 120 nm of CoSi2 by in-situ annealing at 700 °C
(Figure 5). The formed polycrystalline CoSi2 film was composed of
grains and displayed thickness variation in the field of view as ob-
served in SEM image (Figure 5b). The interfacial roughness between
CoSi2 film and Si substrate fabricated from CVD CoN is similar to
that from PVD Co.21 The resistivity of the CoN films decreased from
140 μΩ · cm to 20 μΩ · cm due to the formation of more conductive

Figure 3. XPS depth-profile study of CoSi₂ formed by annealing Co₅N/Si (100) at 700 °C.

XPS depth-profile study of CoSi₂ formed by annealing Co₅N/Si (100) at 700 °C.

This value is close to reported resistivity of CoSi₂, i.e., 16 ∼ 20 μΩ·cm.¹

X-ray photoelectron spectroscopy (XPS) was used to measure the composition of CoSi₂ films formed by annealing Co₅N on Si (100) substrates at 700 °C, of which the results are presented in Figure 3. XPS spectra (Figure 3) taken during argon sputtering determined the composition profiles using the Co 3p, Si 2s, C 1s, O 1s and N 1s XPS peaks. The trace of nitrogen near the surface can be attributed to a small amount of unreacted Co₅N left on the surface. Carbon and oxygen remain on the surface of the film from air exposure. The Co:Si ratio is about 1:2 inside the film. This result confirmed that we obtained cobalt disilicide with the expected stoichiometry after annealing Co₅N/Si at 700 °C.

The CoSi₂/Si interfacial roughness is an important factor that affects device performance. We highlight here the back side sample preparation procedure to examine the CoSi₂/Si interfacial roughness by AFM (Asylum MFP-3D AFM). The initial back side sample preparation was first proposed for SIMS sample preparation.²² We adapted this method to remove the substrate and reveal the CoSi₂ layer of interest. The CoSi₂ sample was prepared by in-situ annealing Co₅N/SiO₂ at 700 °C. We selected SOI instead of Si (100) as the substrate owing to its built-in etch-stop layer (i.e., the buried oxide of an SOI wafer). The buried oxide in SOI allowed selective removal of most of the SOI substrate.²² We employed a combination of mechanic polishing, wet etching, and dry etching to reveal the CoSi₂/Si interface. Wet etching of Si-substrate is commonly performed using heated TMAH (tetramethylammonium hydroxide) or KOH solutions.¹⁸ The wet etching is fast and easy to perform. However, the wet etching of thick and roughly polished remaining Si inadvertently leads to the formation of <111> faceted Si-pyramids. This formation of faceted Si-pyramids is caused by the highly anisotropic etch rates, with etch rates of crystallographic orientation being 2–3 orders of magnitude lower than those of other major crystallographic orientations.¹⁸ Therefore, wet etching cannot be used as a high-precision polishing step, and an etch-stop layer is crucial for eliminating the roughness from the anisotropic wet-etching step. Alternatively, the Si dry etching using XeF₂ gas exhibits essentially isotropic etch rates regardless of crystallographic orientations.¹⁸ And XeF₂ dry etching has been proved to be highly selective toward CoSi₂. Thus the XeF₂ dry etching process was applied to remove the thin Si remaining on top of CoSi₂.

To reveal and analyze the CoSi₂/Si interfacial morphology, we adopted a modified back-to-front sample preparation method, in which mechanical polishing, anisotropic tetramethylammonium hydroxide (TMAH) wet etching, hydrofluoric acid (HF) wet etching, and isotropic xenon difluoride (XeF₂) dry etching are employed to remove the SOI substrate from the back side to expose the CoSi₂/Si interface, as schematically illustrated in Figure 4. Note that for all roughness
CoSi2 (cubic, lattice constant $a = 5.54$ Å), compared with CoSi (cubic, $a = 5.36$ Å) has a smaller lattice mismatch with Si ($c = 3.84$ Å). The resulting CoSi2 was determined to be around 10.3% (12.3 nm) of the silicide thickness (120 nm), while the interface roughness is 7.6% (9.1 nm) of the silicide thickness (120 nm). Comparing the samples annealed at 600 °C and 700 °C, the surface roughness of CoSi/Si did not change much while the CoSi/Si interfacial roughness is substantially reduced after conversion of CoSi to CoSi2 at 700 °C.

Table I. Cobalt silicide roughness of both surface and interface at different silicidation temperatures. Note: For roughness study, “interface” is defined as the interface between CoSiX and Si; “surface” is defined as the other side of CoSiX, which was analyzed before mounting the sample upside down onto the substrate by epoxy.

<table>
<thead>
<tr>
<th>Annealing Temperature (°C)</th>
<th>Silicide Thickness (nm)</th>
<th>Surface Roughness</th>
<th>Interface Roughness</th>
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<tbody>
<tr>
<td></td>
<td></td>
<td>rms (nm)</td>
<td>Percentage</td>
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<tr>
<td>600</td>
<td>110</td>
<td>10.1</td>
<td>9.2%</td>
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<tr>
<td>700</td>
<td>120</td>
<td>12.3</td>
<td>10.3%</td>
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**Conclusions**

We successfully evaluated the CoSi2/Si interfacial roughness quantitatively by a back side sample preparation procedure. We obtained stochiometric cobalt disilicide, which has low interfacial roughness because of its small lattice mismatch with Si, by in-situ rapid thermal annealing CVD-CoX:N at 700 °C in N2. The back side sample preparation utilized a combination of mechanical polishing, wet etching and dry etching to expose the CoSi2/Si interface for AFM measurements. This approach provides a robust and reliable procedure to acquire quantitative morphological information about silicon-silicide interfaces, which can serve as an important assessment method for modern silicidation and metallization processes.

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**References**