The microstructure of a Cr buffer layer between a stainless steel (SS) layer, which is a catalytic layer for carbon nanotube growth, and a Si (100) substrate was investigated by high-resolution transmission electron microscopy. The SS film is polycrystalline, and the thickness is not uniform. It was partly covered by a surface Cr$_2$O$_3$ layer. The Cr buffer layer reacted with the Si substrate to form CrSi$_2$. Definite orientation relationships (ORs) between CrSi$_2$ and Si were observed: $\{2\bar{1}0\}\langle0001\rangle_{\text{CrSi}_2}/(200)\langle011\rangle_{\text{Si}}$ (OR D) and $\langle0001\rangle_{\text{CrSi}_2}/(1\bar{1}1)\langle011\rangle_{\text{Si}}$ (OR A). OR D is a new OR found in the CrSi$_2$/Si system. We also found several other new ORs which are similar to OR A and are denoted OR E, OR F, OR G, and OR H. For OR E and OR F, the CrSi$_2$ crystals are rotated, respectively, about 18° and 34° counterclockwise around the $\langle10\bar{1}0\rangle$ zone axis with respect to OR A. For OR G and OR H, the CrSi$_2$ crystals are rotated, respectively, about 35° and 107° clockwise around the $\langle10\bar{1}0\rangle$ zone axis with respect to OR A. These findings not only enrich the crystallography of the CrSi$_2$/Si epitaxial system, but also provide new insight into the role of the Cr buffer layer in the growth of carbon nanotubes.

1. Introduction

Carbon nanotubes (CNTs) are considered to be the best electron emitters for future flat panel displays. For such applications, it is necessary to grow CNTs on a substrate such as Si. In order to increase the adhesion of CNTs to the substrate and to improve the quality of the CNTs, a metal buffer layer is deposited prior to the deposition of metal catalysts on the Si. The buffer layer is critical to the growth of the desired CNTs [1]. It was reported that even when sputter deposition of the catalytic metal layers and the hot filament chemical vapour deposition of the carbon films were carried out under identical conditions, different buffer layers resulted in substantially

*Corresponding authors. Email: huangje@bc.edu, renzh@bc.edu
different carbon film growth. Namely, carbon-nanoparticle films were deposited with either Cr or W buffer layers, whereas carbon-nanotube films were deposited with either Ti or Ta buffer layers. The different results were attributed to the different interface reactions between the buffer layer and the substrate, and between the buffer layer and the carbon source. It was proposed that Cr and W reacted with carbon more readily than with the Si substrate to form \( \text{Cr}_3\text{C}_2 \) and WC, respectively, thus depleting the carbon source and hindering CNT formation. Ti and Ta were proposed to react with the Si substrate more readily than with the carbon source, thus retaining the carbon source and enabling CNT growth. These conclusions were based on X-ray diffraction (XRD) and scanning electron microscopy (SEM) observations. However, the microstructure of buffer layers and the interface reactions have not been widely studied.

We report here cross-sectional high-resolution transmission electron microscopy (HRTEM) investigations of the interface reactions between Cr and Si. We found that Cr reacted with Si to form \( \text{CrSi}_2 \), and definite orientation relationships (ORs), including several new distinct ones, were found between \( \text{CrSi}_2 \) and Si.

2. Experimental

A Cr film of thickness from 100 to 200 nm was deposited on a Si substrate by rf magnetron sputtering. A 60 nm thick stainless steel (SS) film was deposited as the catalyst for CNT growth on top of the Cr buffer layer. Prior to deposition of the SS film, the chamber was evacuated to a pressure of \( 3 \times 10^{-6} \) Torr. The pressure was maintained at 4–6 mTorr by introducing 4–10 sccm Ar gas, and the substrate temperature was maintained at 300°C during sputtering.

CNT growth was carried out in a tube furnace (quartz tube 80 cm length and 5 cm OD). The catalyst layer was first reduced at 660°C in 50 Torr of a flowing mixture of H\(_2\) (10 sccm, 99.999% purity) and N\(_2\) (100 sccm, 99.998% purity) for 2 h to obtain the required catalyst particles and enhance the catalytic activity.

Cross-sectional HRTEM samples were prepared using the following procedure. The as-grown CNTs were first penetrated with M-Bond 610, and then cut into thin slices of thickness about 100 \( \mu \)m. The samples were further mechanically polished to 40 \( \mu \)m before being ion milled to become electron transparent.

HRTEM observations were carried out using a JEOL 2010F field emission gun electron microscope with an ultra-high resolution polepiece (\( C_s = 0.5 \) mm) operating at 200 kV. It has a point-to-point resolution of about 0.19 nm. Composition analysis was performed using an Oxford Instrument energy dispersive X-ray spectroscopy (EDS) system attached to the microscope.

3. Experimental results

3.1. SEM observations

SEM images of the as-grown CNTs are shown in figure 1. The density of the CNTs is relatively low, and they do not cover the whole surface of the Si wafer, as seen in figure 1a. From figure 1b, it can be seen that the particle size of the catalyst, which appears as white spheres, is close to the diameter of the CNTs, which is about 40 nm.
3.2. Film morphology

The thicknesses of the Cr and SS films are not uniform, for example the thickness of the Cr film shown in figure 2a is about 200 nm, while that shown in figure 2b is about 120 nm. In figure 2b, a SS layer and a Cr$_2$O$_3$ layer can be seen on top of the Cr film.
whereas in figure 2a these layers are missing, clearly indicating that deposition is not uniform. The thickness of the SS and Cr$_2$O$_3$ layers shown in figure 2b is about 12 nm and 40–90 nm, respectively. The microstructure of these layers was determined by a combination of selected electron diffraction pattern (EDP), EDS, and HRTEM. Both images in figure 2 show the presence of a SiO$_2$ layer and a reaction layer beneath it. This is seen more clearly in the higher-magnification image of figure 3a. The thickness of the SiO$_2$ layer and the reaction layer beneath it is about 1 and 40 nm, respectively. The reaction layer consists of a number of strained and faceted individual grains of size around 50 nm. The presence of a SiO$_2$ layer above the Si surface and beneath the Cr film is clearly demonstrated in the HRTEM image depicted in figure 3b. The Cr film, SS film, and the Cr$_2$O$_3$ layer are all polycrystalline, and there are no definite ORs between these layers, nor does any texture exist. The grains in these films are randomly orientated, and in many cases they are elongated along the interfaces. An HRTEM image of these layers is shown in figure 4. The SS grain shown in figure 4 is heavily strained and orientated close to the $[110]$ zone axis, as determined from the two-dimensional lattice image. The Cr and Cr$_2$O$_3$ layers in figure 4 only show one-dimensional lattice fringes. The interfaces between these different layers are not flat, but curved and heavily strained, possibly caused by the large lattice mismatch of the randomly orientated grains.

3.3. Orientation relationships between CrSi$_2$ and Si

Special attention was focused on the reaction layer between Cr and Si. EDP, EDS and HRTEM analyses indicated that this layer consists of CrSi$_2$. Several typical ORs, hereafter referred to as ORs A, D, E, F, G, and H, were found between CrSi$_2$ and Si.

HRTEM images and the EDP of OR D are shown in figure 5. OR D can be summarized as

$$[0001]_{\text{CrSi}_2} \parallel [011]_{\text{Si}} \quad \text{and} \quad (\overline{2}2\overline{0})_{\text{CrSi}_2} \parallel (200)_{\text{Si}}.$$

Figure 3. (a) Low-magnification view of the reaction layer and the SiO$_2$ layer. (b) HRTEM image of the SiO$_2$ layer between the Cr and the Si layers.
Figure 4. HRTEM image of the Cr$_2$O$_3$, stainless steel, and Cr layers.

Figure 5. HRTEM images (a, b) and an EDP (c) showing OR D: (T2T0)[0001]$_{\text{CrSi}_2}$//(200) [011]$_{\text{Si}}$. The EDP in (c) is obtained by FFT of the image shown in (a). The circles and hexagons in (c) mark the EDPs from Si and CrSi$_2$, respectively.
The CrSi$_2$ crystal is almost rectangular in shape with a length of about 25 nm and a thickness of 10 nm, as shown in figure 5a. From both figures 5a and (b), it can be seen that the interface planes are parallel to either $(\overline{1}2\overline{1}0)_{\text{CrSi}_2}//(200)_\text{Si}$ or $(10\overline{1}0)_{\text{CrSi}_2}//(0\overline{2}2)_\text{Si}$. The interface plane parallel to $(\overline{1}2\overline{1}0)_{\text{CrSi}_2}//(200)_\text{Si}$ is flat, while that parallel to $(10\overline{1}0)_{\text{CrSi}_2}//(0\overline{2}2)_\text{Si}$ is curved. The corners of the CrSi$_2$ crystal are round. The interface planes are strained because of the lattice mismatch. OR D is confirmed from the EDP (figure 5c) obtained from a fast Fourier transformation (FFT) of the HRTEM image shown in figure 5a.

Some of the CrSi$_2$ crystals follow a second OR (OR A) with the substrate, and an example is shown in figure 6. OR A can be summarized as

$$[10\overline{1}0]_{\text{CrSi}_2}//[01\overline{1}]_\text{Si} \quad \text{and} \quad (0001)_{\text{CrSi}_2}//(1\overline{1}1)_\text{Si}.$$  

The crystal shown in figure 6a is faceted on $(0001)_{\text{CrSi}_2}//(1\overline{1}1)_\text{Si}$, $(1\overline{2}12)_{\text{CrSi}_2}//(200)_\text{Si}$, and $(\overline{1}2\overline{1}1)_{\text{CrSi}_2}//(\overline{1}1\overline{1})_\text{Si}$; its shape is close to a ‘V’ shape with the bottom of the ‘V’ being flattened on the $(1\overline{2}12)_{\text{CrSi}_2}//(200)_\text{Si}$ planes. The HRTEM image shown in figure 6b indicates that the interface is flat on the atomic scale. OR A is confirmed by EDP, as shown in figure 6c.

![HRTEM images and EDP](image)

**Figure 6.** HRTEM images (a, b) and an EDP (c) showing OR A: $(0001)[10\overline{1}0]_{\text{CrSi}_2}//(1\overline{1}1)[01\overline{1}]_\text{Si}$. The EDP in (c) is obtained by FFT of the image shown in (a). The circles and hexagons in (c) mark the EDPs from Si and CrSi$_2$, respectively.
ORs close to OR A were observed frequently. For convenience when describing these ORs, we use the Si substrate as the reference ordination. All ORs reported in this paper are referred to this coordination, which is fixed as shown in figure 6. All the other ORs, similar to OR A, can be derived by keeping the zone axis of the CrSi$_2$ crystal [10$ar{1}$0] unchanged while rotating it along this zone axis. If we consider the rotation of the CrSi$_2$ crystal in OR A as 0°, i.e. (0001)$_{\text{CrSi}_2}$ is rotated 0° with respect to (1$ar{1}$1)$_{\text{Si}}$, the rotation angles between (0001)$_{\text{CrSi}_2}$ and (1$ar{1}$1)$_{\text{Si}}$ in the other ORs are 18° counterclockwise (CCW, figure 7, OR E), 34° CCW (figure 8, OR F), and 35° (OR G) and 107° clockwise (CW, figure 9, OR H).

The CrSi$_2$ crystal in figure 7a is irregular in shape, elongated along the CrSi$_2$/Si interface plane, and faceted on (3$ar{1}$1)$_{\text{Si}}$ and (200)$_{\text{Si}}$. The HRTEM image shown in figure 7b indicates that the (0001)$_{\text{CrSi}_2}$ plane is rotated 18° CCW with respect to the (1$ar{1}$1)$_{\text{Si}}$ plane, which is also confirmed by the corresponding EDP, as show in figure 7c.

Figure 7. HRTEM images (a, b) and an EDP (c) showing OR E, which is similar to OR A (figure 6), but with the CrSi$_2$ crystal rotated 18° CCW about the [10$ar{1}$0] zone axis. The EDP in (c) is obtained by FFT of the image shown in (a). The rotation angle is indicated in (b). The white-edged black lines and the white lines in (c) outline the unit cells for the EDPs from Si and CrSi$_2$, respectively.
The CrSi₂ crystal shown in figure 8a is about 50 nm in size and almost round in shape. The interface is smoothly curved without obvious facets. From both figures 8b and c, it can be seen that the (0001) plane is rotated 34° CCW with respect to the (111)Si plane.

Figure 9a shows two CrSi₂ grains denoted 'I' and 'II' formed on Si. The two crystals have a twinning relationship with each other with the twinning plane being (1211). The (0001) planes in crystals I and II are rotated, respectively, 35° and 107° CW with respect to (111)Si. In order to see these ORs more clearly, the EDP obtained from the FFT of the image in figure 9a is shown in figures 9b and c.
4. Discussion

The epitaxial growth of CrSi$_2$ on Si has been studied extensively [2–7]. One of the reasons for this may be due to the fact that CrSi$_2$ is a refractory metal silicide with a narrow bandgap (0.35 eV) and high thermal electric power [7]. Therefore, it is attractive for both high-temperature thermo-electric applications and integrated circuits [6]. Although many ORs have been reported in the CrSi$_2$/Si system, a careful crystallographic analysis found that, actually, only three distinct ORs exist, which are referred to as types A, B, and C and are summarized in table 1. We found that the three ORs reported by Shiau et al. [2] are actually crystallographically equivalent. A detailed stereographic projection analysis was carried out and is shown in figure 10. This figure shows a stereographic projection under the conditions of OR A (II) in table 1, i.e. $(\overline{1}122)[1\overline{1}00]_{\text{CrSi}_2}/(001)[1\overline{1}0]_{\text{Si}}$. It can clearly be seen that, under OR A (II) conditions, ORs A (I) and A (III) in table 1 are also satisfied, indicating that they are actually the same OR, but viewed along different directions.

Figure 9. (a) HRTEM image showing OR G and OR H, which are similar to OR A, but with the two CrSi$_2$ crystals (denoted ‘I’ and ‘II’) rotated 35° CW and 107° CW, respectively, relative to that in OR A (figure 6), about the [10\(\overline{1}\)0] zone axis. Note that crystals I and II have a twinning relationship. (b) EDP obtained by FFT of the image shown in (a). (c) The same EDP as shown in (b), but with noise filtered. The white-edged black lines, the white lines, and the dotted white lines indicate the unit cells for the EDP from Si, crystal II, and crystal I shown in (a).
Table 1. Orientation relationships in the CrSi$_2$/Si system.

<table>
<thead>
<tr>
<th>Authors</th>
<th>OR</th>
<th>Designated type</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fathauer et al. [4]</td>
<td>CrSi$_2$(0001)[1010]/Si(011)[01T]</td>
<td>A</td>
</tr>
<tr>
<td></td>
<td>CrSi$_2$(0001)[1120]/Si(111)[10T]</td>
<td>B</td>
</tr>
<tr>
<td>Shiau et al. [2]</td>
<td>CrSi$_2$(0001)[1010]/Si(111)[10T]</td>
<td>A (I)</td>
</tr>
<tr>
<td></td>
<td>CrSi$_2$(TT22)[1100]/Si(001)[1T0]</td>
<td>A (II)</td>
</tr>
<tr>
<td></td>
<td>CrSi$_2$(2114)[01T0]/Si(011)[01T]</td>
<td>A (III)</td>
</tr>
<tr>
<td>Rocher et al. [5]</td>
<td>CrSi$_2$(0001)[1120]/Si(111)[112]</td>
<td>A</td>
</tr>
<tr>
<td></td>
<td>CrSi$_2$(0001)[1120]/Si(111)[10T]</td>
<td>B</td>
</tr>
<tr>
<td>Heck et al. [6]</td>
<td>CrSi$_2$(0001)[1120]/Si(001)[1T0]</td>
<td>C</td>
</tr>
<tr>
<td>Filonenko et al. [7]</td>
<td>CrSi$_2$(1122)[1100]/Si(001)[110]</td>
<td>A</td>
</tr>
<tr>
<td></td>
<td>CrSi$_2$(0001)[2T0]/Si(001)[110]</td>
<td>C</td>
</tr>
<tr>
<td>Huang et al. (present study)</td>
<td>CrSi$_2$(T2T0)[0001]/Si(200)[011]</td>
<td>D</td>
</tr>
<tr>
<td></td>
<td>CrSi$_2$(0001)[1010]/Si(1T1)[011]</td>
<td>A</td>
</tr>
<tr>
<td></td>
<td>CrSi$_2$(01T0)/Si[011]</td>
<td>E</td>
</tr>
<tr>
<td></td>
<td>CrSi$_2$(0001) rotated 18° CCW with respect to Si(1T1)</td>
<td>F</td>
</tr>
<tr>
<td></td>
<td>CrSi$_2$(01T0)/Si[011]</td>
<td>F</td>
</tr>
<tr>
<td></td>
<td>CrSi$_2$(0001) rotated 34° CCW with respect to Si(1T1)</td>
<td>G (D)</td>
</tr>
<tr>
<td></td>
<td>CrSi$_2$(0001)[1010]/Si(022)[011]</td>
<td>G (D)</td>
</tr>
<tr>
<td></td>
<td>CrSi$_2$(0001) rotated 35° CW with respect to Si(1T1)</td>
<td>G (D)</td>
</tr>
<tr>
<td></td>
<td>CrSi$_2$(10T0)/Si[011]</td>
<td>H</td>
</tr>
<tr>
<td></td>
<td>CrSi$_2$(0001) rotated 107° CW with respect to Si(1T1)</td>
<td>H</td>
</tr>
</tbody>
</table>

Figure 10. (1T00)CrSi$_2$/1(1T0)Si stereographic projection showing that the three ORs reported by Shiau et al. [2] are crystallographically equivalent.
OR A was also observed in our investigation. In addition, we also observed several new ORs, which are similar to OR A: namely, the zone axes of each CrSi$_2$ crystal remain unchanged, but the (0001)$_{\text{CrSi}_2}$ plane is rotated 18° CCW (OR E), 34° CCW (OR F), 35° CW (OR G), and 107° CW (OR H) with respect to (111)$_{\text{Si}}$. These ORs can also be considered to be the result of maintaining the Si orientation unchanged, but rotating the CrSi$_2$ crystal about its [10$ar{1}$0] zone axis. Because of the rotation of the CrSi$_2$ crystals, the interface planes change dramatically. In several cases, the mismatch between the two lattices is quite large, indicating that lattice match is not a prerequisite for definite ORs between two phases.

OR D observed in this study has never been observed previously, and is therefore a new OR in the CrSi$_2$/Si system. Also, it was actually the least commonly observed OR in this investigation. These results imply that this is an unfavourable OR in the CrSi$_2$/Si system. This can be understood from the fact that the lattice mismatch in this OR is very large, for example the mismatch between (T2T0)$_{\text{CrSi}_2}$ and (200)$_{\text{Si}}$ (figure 5) is about 20%. The lattice spacing of (10$ar{1}$0)$_{\text{CrSi}_2}$ is 0.383 nm, which is about twice the lattice spacing of (0$ar{2}$2)$_{\text{Si}}$ of 0.192 nm (figure 5), implying that a mismatch dislocation should appear in every two (0$ar{2}$2)$_{\text{Si}}$. Because of such a large lattice mismatch, the interface is entirely incoherent, as seen in figure 5.

It should be noted that OR G is crystallographically equivalent to OR D, as seen from the stereographic projection shown in figure 11, which clearly shows that OR G can be derived from OR D, indicating that they are the same OR, but viewed from different directions.

Figure 11. (0001)CrSi$_2$//(011)Si stereographic projection showing that OR D and G are crystallographically equivalent.
It is interesting to note that even after the interface reaction, the SiO$_2$ layer remains unchanged (figures 3, 5a and 6a), suggesting that the Cr atoms can penetrate this thin layer to react with Si. We also found that diffusion occurred preferentially on the (T1)$_{Si}$ or (1T1)$_{Si}$ planes, as seen from figure 12, which shows the early stage of formation of CrSi$_2$ along the (1T1) and (T1T) planes in Si. The surfaces of the two crystals are exactly parallel to the (1T1) and (T1T) planes in Si, indicating that diffusion occurred along the two {111} planes. This explains why the CrSi$_2$ crystals are usually faceted on the two sets of {111} planes (figure 6a).

We also found that the reaction can initiate from the Si interior, as shown in figure 13. It can be seen from this figure that a CrSi$_2$ crystal forms less than 5 nm below the Si surface. It is unclear why and how the solid-state reaction starts from the interior of the Si.

The formation of the Cr$_2$O$_3$ layer above the SS layer is possibly caused by the non-uniform deposition of the SS layer above the Cr layer, which leads to the direct exposure of part of the Cr layer to the reaction gas. No CNT growth is expected on those areas covered by a Cr$_2$O$_3$ layer, which possibly explains why the CNT did not cover the whole Si surface.

Our results are quite different from those reported by Lee et al. [1]. These authors deposited a Cr buffer layer of about 100 nm thickness between a Ni–Fe alloy catalytic layer of about 60 nm and the Si substrate, and found that Cr reacted preferentially with the carbon source to form Cr$_3$C$_2$, which exhausted the carbon source and hindered CNT formation. The experimental conditions, such as the deposition temperature and the catalytic and buffer layers thicknesses, of our experiment are quite similar to those of Lee et al. However, we found that Cr reacted preferentially with Si to form CrSi$_2$ rather than with carbon to form Cr$_3$C$_2$. Because of this different interface reaction, we could grow CNTs using Cr as a buffer layer, although the density of the CNT is quite low. In Lee et al.’s experiment, no CNT growth was observed using Cr as a buffer layer. The reason for this difference is unclear.
5. Conclusions

(1) CrSi$_2$ was formed as a result of interfacial reactions between the Cr buffer layer and Si. Several new orientation relationships, i.e. OR D ($T2T0$)[0001]$_{CrSi_2}$//(200)[011]$_{Si}$, and ORs similar to OR A, i.e. (0001) $[10\overline{1}0]_{CrSi_2}$//(11$\overline{1}$)[011]$_{Si}$, were found. The new ORs, deviating from OR A, can be considered as having the zone axis of the CrSi$_2$ the same as that in OR A, but with the CrSi$_2$ crystals rotated about the [1010] zone axis at various angles, which are about $18^\circ$ CCW and $34^\circ$ CCW in OR E and OR F, and $35^\circ$ CW and $107^\circ$ CW in OR G and OR H, respectively.

(2) The SS film is polycrystalline and the thickness is not uniform, and was partly covered by a surface Cr$_2$O$_3$ layer, which results in the partial growth of CNTs on the sample surface.

References