The Effect of Substrate Crystal Orientations on Surface Properties of SiC Thin Layer Grown by MBE*

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Abstract

Silicon carbide is expected to be used as a next-generation material because of its more effective mechanical and electronic properties. The hetero Molecular Beam Epitaxy process may provide a method to form thin layered mono-crystal Silicon carbide on a Silicon substrate. The present paper aims to clarify the relation between the layer’s properties and the substrate crystal orientations, especially (100) and (110), and discusses the mechanism of Silicon carbide growth under certain operating conditions through a series of tests and evaluations.

Key words: Silicon Carbide, Molecular Beam Epitaxy, Substrate Crystal Orientation, Mono-Crystal, Mirror Surface

1. Introduction

Silicon carbide (SiC) has many effective mechanical and electronic properties and is thus expected to be utilized as a material in such advanced devices as X-ray mirrors, MEMS and so on. However, it is difficult not only to form high purity mono-crystal SiC but also, due to the hardness, to finish it with a smooth surface at the atomic level by using conventional mechanical machining processes. Some attempts have been made to create a flat surface on SiC by using other processes, for example low-pressure CVD(1).

Molecular Beam Epitaxy (MBE) is one of the PVD processes for the thin layer crystal growth. It is based on autonomous alignment and crystal growth of the molecules supplied from molecular beam sources. In an attempt to achieve accuracy at the molecular level, MBE has been applied to mechanical applications utilizing high purity, mono-crystal materials. For example, the present authors experimentally investigated the relation between processing conditions and surface properties(2). We reported in previous papers(3,4) that mono-crystal thin SiC layer of up to 0.4 nm rms surface roughness over 10 µm length could be obtained through the use of the Si/carbon (C) hetero-MBE process. However, these results are limited to specific surface properties under specific conditions. It is not possible to apply this process to surfaces with complex contours. Previous investigations have been carried out involving only crystals with specific substrate orientations, though it is known that the substrate orientations affect the mechanical and electronic properties(5).

Regarding this point, the present study aims to clarify the relation between surface orientation and the properties of the generated surface. The crystal orientation of the Si
substrate is varied at (111), (100), and (110), which belongs to <110> crystal zone. This study chiefly describes the case of (100) and (110), since the case of (111) has been previously reported\(^6\).

2. MBE Process and Experimental Method

2.1 Principles of SiC Thin Layer Surface Generation Using MBE

The lower side of Fig. 1 shows how a thin layer at the molecular level can be generated by using MBE. First, the deposited material is evaporated from solid state to become independent molecules or a cluster of weakly bound molecules by a beam source under an ultra high vacuum state and are then carried on a substrate that is heated in advance. These molecules receive thermal energy from the substrate and migrate on its surface; some of these molecules are captured in high crystal bond energy position as molecular steps and/or defects and are deposited as either step flow growth or three dimensional nuclei formations, while the remained ones are left free having received a higher amount of energy\(^7\). If the process can be controlled appropriately, an ideal flat surface can be expected to be generated.

In the case in which a thin layer composed of multiple elements such as SiC is created by MBE, both Si and C molecules must be supplied simultaneously from respective beam sources as shown in upper side of Fig. 1. The factors that should be controlled are the amount of incident molecules, their ratio of composition, and the substrate temperature.

In the experiments described in the present paper, molecular Si was supplied by irradiating an Electron Beam (EB) onto a solid Si ingot and evaporating it, while C was supplied as pure acetylene (C\(_2\)H\(_2\)) gas that has the highest percentage of C involvement.

2.2 Substrate Orientation

Figure 2 shows the difference of the direction of the dangling bonds and the numbers of
surface atoms in each surface orientation of a diamond-type crystal structure, such as Si and SiC. Table 1 shows the difference in the dangling bond density of each surface orientation calculated in terms of the ideal crystal structure.

It is known that these differences cause the variations in growth type and thus the required process conditions of MBE such as substrate temperature. It is thought that Si can grow at a lower temperature than SiC because its surface energy is generally lower and the adhesion molecule can move more easily.

### Table 1 Dangling bond density of orientation

<table>
<thead>
<tr>
<th>Orientation</th>
<th>Si</th>
<th>SiC</th>
</tr>
</thead>
<tbody>
<tr>
<td>(111)</td>
<td>7.82</td>
<td>9.76</td>
</tr>
<tr>
<td>(100)</td>
<td>13.56</td>
<td>16.92</td>
</tr>
<tr>
<td>(110)</td>
<td>9.59</td>
<td>11.97</td>
</tr>
</tbody>
</table>

2.3 Experimental Method

Figure 3 shows the deposition process of a SiC layer on a mono-crystal Si substrate with 4-inch diameter. As SiC cannot be deposited directly on a Si substrate because of the difference of their lattice constants, a carbonized layer must be prepared between the Si substrate and the SiC layer in order to adjust the lattice constant toward the deposition.
direction⁸. For this purpose, acetylene gas is provided to a heated Si substrate as shown in the carbonization process illustrated in Fig. 3.

In the experiments, all of the conditions except substrate temperature (973 to 1273 K) and substrate orientation were kept constant.

3. Experimental Results and Discussions

Figure 4 shows RHEED images of the carbonization process for different substrate orientations. It is judged that according to the heating process, that is, temperature increase, a clean mono-crystal Si surface first appears on the Si substrate, next, mono-crystal SiC appears coexisting with the Si of the substrate, and finally, the entire substrate is covered with a mono-crystal SiC carbonisation layer in each orientation. It is shown that the generation of the carbonisation layer varies according to substrate temperature. That is, the transition temperature was 1173 K, 1073 K, and 1273 K on (111), (100), and (110), respectively. This indicates means that (100) is the most easily carbonised. Though the transition is influenced by substrate orientation, there was little correlation with surface energy. This phenomenon is currently being investigated, and it can be said that the proper transition temperature has been determined for each substrate orientation.

In the SiC growth process after carbonisation, the crystallinity of the SiC growth layer was better than that of the carbonisation layer in each substrate orientation. The crystallinity of the (110) SiC layer was better than the (100) one under this experimental condition. In the case of (110), a higher temperature is needed because the transition temperature is
higher than those of other orientations. Therefore, it is thought that the substrate temperature under this experimental condition was not high enough in the case of (110), and crystallinity worsened.

Figure 5 shows the variation of the thickness of the carbonized layer in the carbonization process in the cases of (100) and (110). It can be observed that thickness is proportional to duration, with saturation ultimately being reached in each orientation. We consider that a critical thickness exists, and the selection of an appropriate carbonization time is crucial.

The chemical compositions of the epitaxially grown layer were analyzed by Auger electron spectroscopy and argon ion etching toward the depth direction of the substrate. Observations were made each time etching was performed, and were carried out post process. Thus, contamination layer may have been generated on the surface of the layer, and this effect may be included in the observations. Fig. 6 shows an example of analysis results. The composition ratio of silicon to carbon is uniformly about 50-50 in the grown layer. This layer contains no impurities. It is confirmed that a stable silicon carbide layer was generated by this process under these conditions.

Figure 7 shows AFM 1 µm x 1 µm images of the carbonization process and the SiC growth process for different substrate orientations. Fig. 7 (a) shows the carbonization process and (b) the SiC process. Figures 8 and 9 show AFM 100 µm x 100 µm images of the carbonization process and the SiC growth process for (100) and (110) substrate orientations, respectively.

In the case of the (100) carbonization process, the island of about 10 nm in height
appeared at 1073 K and became smoother at 1173 K, and three dimensional nuclei were created at 1273 K. Moreover, many triangular pits were observed at 1173 K. The pits grew as the temperature increased to 1273 K, and the shape became clear. However, the pits were not observed after 30 min at 1273 K, and the smoothing carbonization layer was observed (Fig. 10). Therefore, it is thought that the pits were buried in this process.

In the case of (110), a similar process was observed at higher temperatures than in the case of (100). The pits were not observed in (110) during any step. It can be considered that a carbonization layer without pits could be produced in each substrate orientation under these experimental conditions.

In the case of the (100) SiC growth process, three dimensional nuclei which have ridges in the {110} direction were created. The height of the nuclei did not change as the process progressed. This means that the nuclei grew in a direction horizontal to the substrate.

On the other hand, in the case of the (110) SiC growth process, three dimensional nuclei which have ridges in random directions were created. The height of those nuclei increased as the process progressed. This indicates that the nuclei grew in {110} direction horizontal to the substrate. Therefore, it can be considered that the growth of the nuclei can be promoted in a direction similar to that of the crystal orientations, namely, {110} in any substrate orientation. This indicates that {110} is the minimum potential energy orientation, that is, one which is stable.

It was observed that island of approximately 5 µm in diameter was created in all substrate orientations of the SiC growth process. This island was not observed on the carbonization layer. Moreover, the growth of the island was promoted to the surrounding area. It is thought that the incident molecules were selectively absorbed in an area.
surrounding a part of the created island and growth was promoted there.

![Diagram of nuclei origination](image)

**Fig. 7(b)** Chronologically observed AFM images of SiC growth process (1 μm x 1 μm)

![Carbonization images](image)

**Fig. 8** Chronologically observed AFM images of carbonization and SiC growth process of (100) (100 μm x 100 μm)
In addition, SiC growth was observed under conditions in which the pits were easily created in each substrate orientation, verifying the influence of the substrate orientation on the SiC growth process. Figure 11 shows a comparison of the shape of the pits in each orientation. It is observed that the shape of the pits depends on substrate orientation; triangular, square, and rectangular pits were created on (111), (100), and (110), respectively.
All these ridges are in the direction of \{110\}. This shows that \{110\} is the minimum potential energy orientation, that is, a stable one as in the case of the nuclei mentioned above.

From the above, it is thought that substrate orientation influences the generation of shape geometry in both the carbonization and SiC growth processes. However, the growth mechanism is the same in each orientation. A shape having a specific orientation can be easily generated by minimizing the potential energy of each substrate orientation. Therefore, it is thought that the geometry of a generated shape is determined according to the surface orientations appearing on the original surface.

4. Conclusion

This study investigated SiC growth on (111), (100), and (110) Si substrate orientations by using hetero MBE processes. This study clarified the relation between surface orientation and the generated surface properties. More detailed observation is necessary to verify the influence of substrate orientation; however, it is clear that there is no difference in the growth mechanism in each orientation.

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References