Nucleation and growth of Ti$_3$SiC$_2$ on SiC by interfacial reaction

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Abstract. In this study, we investigated the nucleation and growth of Ti$_3$SiC$_2$ by an interfacial reaction between a SiC substrate and a Ti/Al bilayered film at various temperatures. The specimens were prepared by depositing Ti/Al on a 4H-SiC substrate and subsequently annealing the substrate in a vacuum. The interfacial structures were analyzed by X-ray diffraction analysis and transmission electron microscopy. Ti$_3$SiC$_2$ nucleated even when annealed at a low temperature of 973 K. The Ti$_3$SiC$_2$ grains formed at 973 K were isolated and nonepitaxial with respect to the SiC substrate. By increasing the annealing temperature to 1273 K, the Ti$_3$SiC$_2$ grains became epitaxial with the SiC substrate, spreading preferentially on it, and coalesced with each other, forming a layer without grain boundaries.

1. Introduction
Silicon carbide (SiC) is a semiconductor compound that is suitable for next-generation power electronic devices [1]. However, to fully exploit the potential of SiC, it is essential that the ohmic contacts used are of low resistance [2, 3]. The Schottky barrier at the SiC/metal interface has to be lowered and/or thinned to achieve ohmic contacts. However, the deep valence band edge of SiC, which is approximately 6.5 eV under vacuum [4, 5], makes it difficult to form ohmic contacts on p-type SiC. When using pure metals, the formation of high Schottky barriers at the interfaces with p-type SiC cannot be prevented. One solution to this problem is to form a thin and uniform layer of Ti$_3$SiC$_2$ at the interface [6-8].

Ti$_3$SiC$_2$ is commonly formed by an interfacial reaction between SiC and Al/Ti, starting from the multilayered structure of SiC/Ti/Al [6-8]. It is important to form Ti$_3$SiC$_2$ as a thin and uniform layer for manufacturing reliable SiC devices. The interfacial structure reported in the literature suggests that the Ti$_3$SiC$_2$ phase shows a distinct epitaxial relation with SiC [8] and grows predominantly perpendicular to its [0001] axis. Owing to this behavior, the growth tip of Ti$_3$SiC$_2$ grains can be separated from the SiC substrate, because the SiC surface is generally tilted with respect to the exact (0001) plane for polytype control [9]. On the other hand, the formation of Ti$_3$SiC$_2$ involves processing at the high temperature of 1273 K, which is not compatible with the manufacturing of electronic devices. A few studies have reported techniques of lowering the annealing temperature [10]. However, the nucleation and growth behaviors of Ti$_3$SiC$_2$ are not well understood. In particular, the behavior in the early stage, that is, while the individual grains of Ti$_3$SiC$_2$ are growing and forming a continuous layer on the SiC substrate, is important. This is because the crystallographic relation between Ti$_3$SiC$_2$...
and SiC, whether it is epitaxial or not, is defined at this stage. Understanding the behaviors at this stage is indispensable for controlling the interfacial reaction between Ti$_3$SiC$_2$ and SiC, as well as the structure of the resulting layer.

In the present study, the growth behavior of Ti$_3$SiC$_2$ was investigated, with the emphasis being on the temperature dependence of the crystallographic relation between Ti$_3$SiC$_2$ and SiC.

2. Experimental procedure
A single-crystal wafer of p-type 4H-SiC, which was tilted by 8° toward the [1120] direction from the (0001) plane, was cut into 4-mm squares to be used as substrates. The thickness and specific sheet resistance of these SiC substrates were 370 µm and 1.368 Ω cm, respectively. Only the Si-terminated surface was used. The surfaces of the substrates were cleaned ultrasonically using acetone. A Ti (50 nm)/Al (600 nm) bilayer film was deposited on the substrates by radio frequency magnetron sputtering using high-purity targets of Ti and Al. Ar ion sputtering was performed before depositing the films. The specimens were annealed at a pressure of 1.3 × 10$^{-3}$ Pa, while the temperature was varied between 973 and 1273 K using a resistance-heating vacuum furnace.

The interfacial structures of the specimens were analyzed by X-ray diffraction (XRD) analysis and transmission electron microscopy (TEM).

3. Results and discussion
Figure 1 shows the XRD patterns of the specimens annealed at 973, 1073, 1173, and 1273 K for 600 s. Figure 1(a) is the pattern of the specimen annealed at 973 K. Peaks attributable to Ti$_3$SiC$_2$ do not appear in the pattern, while these peaks appear in the patterns of the specimens annealed at temperatures of 1073 K and higher. Figure 1(b) is the pattern of the specimen annealed at 1073 K. Three peaks, at 39.44°, 40.52°, and 41.48°, which correspond to the (4110), (0008), and (5110) planes of Ti$_3$SiC$_2$, respectively, can be seen; the peaks have similar intensities. The appearance of these peaks indicates that Ti$_3$SiC$_2$ is formed by annealing at 1073 K for 600 s and that it has grown to an amount detectable by XRD analysis. However, the Ti$_3$SiC$_2$ layer formed at this temperature has a polycrystalline structure consisting of randomly oriented grains, that is, the epitaxial relation between Ti$_3$SiC$_2$ and SiC is not known. This is in contrast to the results reported by Tsukimoto et al. [8]. By increasing the annealing temperature to 1173 K, the relative intensities of the peaks corresponding to the (1014) and (1015) planes of Ti$_3$SiC$_2$ decrease, whereas the intensity of the peak attributable to

![Figure 1. XRD patterns of the specimens annealed at various temperatures for 600 s. (a) 973 K, (b) 1073 K, (c) 1173 K, and (d) 1273 K.](image-url)
the (0008) plane remains unchanged, as shown in Figure 1(c). Furthermore, only the peak of the (0008) plane is seen in the pattern of the specimen annealed at 1273 K, as can be confirmed from Figure 1(d). The differences in the changes in the relative intensities of the peaks indicate that Ti$_3$SiC$_2$ grains that have their (0001) plane parallel to the (0001) plane of SiC grow preferentially during annealing at temperatures of 1173 K and higher. This crystallographic relation corresponds to an epitaxial Ti$_3$SiC$_2$/SiC interface [8]. Therefore, there is a threshold temperature above which Ti$_3$SiC$_2$ grains that are epitaxial with the SiC substrate grow preferentially.

Figure 2 shows the interfacial structure of the specimen annealed at 973 K for 600 s. In the bright-field image (BFI) of the interface shown in Figure 2(a), a clear-faceted grain can be seen adjacent to the SiC substrate. The electron diffraction pattern (EDP) corresponding to the image, shown in Figure 2(b), suggests the existence of Ti$_3$SiC$_2$. The pattern also indicates that the (0001) plane of Ti$_3$SiC$_2$ is tilted to 2.2° with respect to that of SiC. An epitaxial relation between Ti$_3$SiC$_2$ and SiC was not observed for the specimens annealed at 973 K. The dark-field image (DFI) obtained using the Ti$_3$SiC$_2$ 0004 diffraction shown in Figure 2(c) confirms that the grain observed in Figure 2(a) is of Ti$_3$SiC$_2$. It must be noted that peaks related to Ti$_3$SiC$_2$ do not appear in the XRD pattern of the specimen annealed under the same conditions (Figure 1(a)). This may be due to the small size and low number of Ti$_3$SiC$_2$ grains existing at the interface. It was difficult to investigate Ti$_3$SiC$_2$ grain growth in the sample annealed at 973 K, but the I-V (current-voltage) properties improved with an
increase in the annealing time, $t$, with the characteristics becoming ohmic in nature at $t = 3600s$. It was revealed that Ti$_3$SiC$_2$ nuclei could grow to a small degree at 973 K or the interface between Ti$_3$SiC$_2$ grains and SiC might be changed to improve the $I-V$ properties. It was, however, found that Ti$_3$SiC$_2$ seeds nucleated even at 973K, as shown in Figure 2.

The Ti$_3$SiC$_2$ grain in Figure 2(a) appears isolated. Some parts of the SiC surface are not covered by Ti$_3$SiC$_2$ grains. These facts indicate that the nucleation frequency of Ti$_3$SiC$_2$ is low. Furthermore, the position of the Ti$_3$SiC$_2$/SiC interface appears to be the same as the edge of the SiC substrate in the other parts that are not covered by Ti$_3$SiC$_2$ grains. Although the formation of Ti$_3$SiC$_2$ consumes Si and C from SiC and Ti from Al$_3$Ti, Ti$_3$SiC$_2$ grains are formed without penetrating the SiC substrate. On the basis of this fact, the Si and C for the nucleation of Ti$_3$SiC$_2$ are probably not supplied directly by the SiC substrate, but are obtained by diffusion through Al$_3$Ti.

Figure 3 shows the interfacial structure after annealing at 1273 K for 600 s. It can be seen from Figure 3(a) that the Ti$_3$SiC$_2$ grains have grown larger. No grain boundary is observed in the layer, that is, the layer consists of a single crystal. The grains are coalesced with each other, forming a continuous layer [8]. This is probably because the difference in the crystal orientations of the Ti$_3$SiC$_2$ grains is small. The Ti$_3$SiC$_2$ layer contains a number of stacking faults. On the other hand, the Ti$_3$SiC$_2$/SiC interface becomes rough, being different from that shown in Figure 2(a). The roughened interface implies that the Si and C for the growth of the Ti$_3$SiC$_2$ grains were supplied directly by the SiC substrate. It is assumed that the roughening occurs owing to the local strain field in the vicinity of the defects and/or dopant atoms in the SiC substrate. The electron diffraction pattern corresponding to this area, which is shown in Figure 3(b), indicates that the interface between Ti$_3$SiC$_2$ and SiC exhibits an epitaxial relation when annealing is performed at 1273 K.

These results suggest that the Ti$_3$SiC$_2$ grains easily establish an epitaxial relation with SiC when annealed at 1273 K, whereas they fail to be epitaxial when it is performed at 973 K. However, it is still unclear whether only the Ti$_3$SiC$_2$ grains epitaxial with SiC nucleate at 1273 K or whether nonepitaxial Ti$_3$SiC$_2$ grains are eliminated during the growth stage once they are formed. If the former mechanism holds true, then the temperature during the major part of the annealing process can be lowered by separating the Ti$_3$SiC$_2$ grain growth process from the Ti$_3$SiC$_2$ nucleation step.

To investigate further the nucleation behavior of Ti$_3$SiC$_2$ at 1273 K, another heat treatment was implemented. First, the specimens were heated to 1273 K. Immediately after this temperature had been reached, the specimens were cooled and held at 973 K for 600 s. Figure 4 shows the XRD pattern of

![Figure 4](image-url)
one specimen after annealing. Two weak peaks related to Ti$_3$SiC$_2$ appear in the pattern. In addition, when the specimens were annealed at 1073K for 0 s, clear peaks similar to the ones seen in Figure 1 (b) were observed; however, when the samples were annealed at 1273 K for 0 s, only weak peaks appeared. The reason for this phenomenon is not known. Both of these weak peaks were related to Ti$_3$SiC$_2$ that was nonepitaxial with SiC. It is suggested that randomly oriented (i.e., both epitaxial and nonepitaxial) Ti$_3$SiC$_2$ nuclei are formed even at 1273 K. However, only the epitaxial nuclei survive owing to the preferential growth at 1273 K.

The Ti$_3$SiC$_2$/SiC interface fails to be epitaxial when the specimens are annealed at 973 K. It is likely that the interfacial energy is not low at the low temperature, because of the $\alpha$-axis lattice mismatch between SiC and Ti$_3$SiC$_2$. This lattice mismatch has to be compensated for by the elastic straining of the lattices of Ti$_3$SiC$_2$ and SiC, in order for an epitaxial interface to form. If the interfacial energy of the interface becomes higher than that of a randomly oriented interface because of the elastic straining, the interface will not be epitaxial. The lattice mismatch ($\Delta a$) can be expressed as

$$\Delta a = a_{\text{SiC}}(1 + \alpha_{\text{SiC}}\Delta T) - a_{\text{Ti}_3\text{SiC}_2}(1 + \alpha_{\text{Ti}_3\text{SiC}_2}\Delta T), \tag{1}$$

where $a_{\alpha}$, $\alpha_i$, and $\Delta T$ are the length of the hexagonal $\alpha$-axis of the substance $i$ ($i = \text{SiC}$ or Ti$_3$SiC$_2$), the coefficient of linear thermal expansion of the substance $i$, and the temperature change from 293 K, respectively. The values of $a_\alpha$ and $\alpha_i$ are listed in Table 1. Although the actual coefficients of linear thermal expansion are anisotropic and temperature dependent, they are assumed to be constant in the temperature range considered in the present study. When the annealing temperature is increased, the lattice mismatch decreases and becomes zero at 1856 K. At 1173 K and 1273 K, the values of $\Delta a$ are 8.3×10$^{-4}$ and 7.1×10$^{-4}$ nm, respectively. In addition, the elastic constants of SiC and Ti$_3$SiC$_2$ become lower at higher temperatures [14, 15]. Thus, the interfacial energy, which increases because of the lattice mismatch, decreased at higher temperatures. The present study revealed that the temperature for transitioning from a nonepitaxial interface to an epitaxial one lies between 973 and 1173 K.

4. Conclusions

The early stage of Ti$_3$SiC$_2$ formation at the interface between a SiC substrate and a Ti/Al bilayer film during annealing at temperatures ranging from 973 to 1273 K was analyzed through XRD analysis and TEM. The main conclusions of the study were the following.

1. At every annealing temperature investigated in the present study, Ti$_3$SiC$_2$ nucleates adjacent to SiC. The Ti$_3$SiC$_2$ nuclei appear dispersed and isolated, indicating that the nucleation frequency is low. The orientation of each Ti$_3$SiC$_2$ nucleus is random.

2. During annealing at temperatures of 1173 K and higher, randomly oriented Ti$_3$SiC$_2$ nuclei grow individually and form a polycrystalline layer. On the other hand, the nuclei epitaxial with the SiC substrate grow preferentially at temperatures higher than 1173 K. These epitaxial grains coalesce with each other and form a single-crystal layer.

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