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Low-temperature formation of an interfacial buffer layer using monomethylsilane for 3C–SiC/Si(100) heteroepitaxy

Hideki Nakazawa[a] and Maki Suemitsu
Research Institute of Electrical Communication, Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai 980-8577, Japan

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By using monomethylsilane (MMS:H_3Si-CH_3), we have formed a $Si_{1-x}C_x$ interfacial buffer layer for 3C–SiC/Si(100) heteroepitaxy at substrate temperature T_f of as low as 450–650 °C, which is compared to the conventional carbonization temperature of 900 °C or higher. The buffer layer allows the subsequent growth of high-quality single-crystalline 3C–SiC films at 900 °C without formation of voids in the Si substrate at the interface. The grown 3C–SiC films degrade for $T_f<450$ or >650 °C. The low processing temperature as well as the suppressed Si outdiffusion can be related to the inclusion of both Si–H and Si–C bonds within the MMS molecule. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1390476]

The heteroepitaxy of SiC on Si(SiC/Si) has been an important issue in SiC epitaxy since it potentially provides a solution to the problem of micropipes that exist even in state-of-the-art SiC wafers. To achieve qualified SiC/Si heteroepitaxy, insertion of an appropriate interfacial buffer layer is strongly required, which bridges the lattice mismatch (~20%) at the interface and impedes the Si outdiffusion from the substrate. The surface of the buffer layer is especially crucial. Surface degradation may initiate defects such as stacking faults in the growing film, which, once formed, are very difficult to remove.

The carbonization method, which utilizes reactions between hydrocarbon molecules and the Si substrate, has been a common tool in forming a 3C–SiC buffer layer having the same crystal orientation as the Si substrate.[1–3] Recent investigations[4] are revealing that the role of carbonization is more on forming a diffusion barrier against Si atoms than on relaxing the lattice mismatch. Problems with carbonization, however, are: (1) the high temperatures ($T\geqslant900$ °C) required to decompose the hydrocarbon molecules and to form the SiC lattice structure, and (2) Si outdiffusion from the Si substrate caused by the high-temperature process. The high process temperature causes surface roughening as well. The Si outdiffusion causes degradation of the SiC buffer layer, which includes Si voids within the Si substrate at the interface.

We here notice that the greater bonding energy of the Si–C bond (13.09 eV) (Ref. 5) than that of the Si–Si (7.45 eV) (Ref. 5) or C–H (12.55 eV) (Ref. 5) bonds can be the most responsible for driving the Si outdiffusion. This consideration, as well as the problematic high processing temperature, suggests two logical strategies to overcome the problems with carbonization: lowering of the formation temperature[6,7] and simultaneous supply of Si atoms in addition to C atoms. In this study, we have utilized monomethylsilane (H_3Si-CH_3; MMS) and have formed $Si_{1-x}C_x$/Si(100) interfacial buffer layers at temperatures as low as T_f=450–650 °C. The function of the buffer layer, which we term the organosilane (OS) buffer layer, has been evaluated by forming a 3C–SiC film on it with MMS gas-source molecular-beam epitaxy (GSMBE) at T_g=900 °C.[8,9]

Figure 1 presents reflection high-energy electron-diffraction (RHEED) patterns from (a) the interfacial buffer layer prepared at T_f=650 °C, $P_{MMS}=5.0\times10^{-5}$ Torr for 5 min and (b) the SiC film grown onto the buffer layer at T_g=900 °C, $P_{MMS}=5.0\times10^{-5}$ Torr for 60 min. Choice of this growth temperature is based on our previous growth experiments using MMS.[8,9] Figure 1(a) shows only 3C–SiC spots, indicating the formation of a uniform, single-crystalline SiC buffer layer that fully covers the Si substrate. The formation temperature T_f=650 °C can be compared to the conventional carbonization temperatures of ~900 °C or higher. The pattern from the film grown onto the buffer layer [Fig. 1(b)] indicates that it is from a 3C–SiC single crystal. Although some three-dimensional (3D) features are evident, the appearance of streaks indicates that a relatively flat, qualified single-crystalline 3C–SiC is grown onto the OS-buffer layer using MMS GSMBE at T_g=900 °C.

The formation temperature T_f has a strong effect on the surface structure of the buffer layer. The RHEED pattern from the buffer layer formed at T_f=300 °C showed a 2×1 reconstructed Si(100) surface structure with Kikuchi lines. This suggests that the MMS molecules are dissociatively adsorbing at the two dangling bonds of a Si dimer at this low temperature. With increasing T_f up to 400–450 °C, the intensity of the half-order spots are gradually weakened, indicating that the Si–Si dimerbonds begin to break up due to interactions between the surface Si atoms and the MMS molecules. At 500–600 °C, the RHEED pattern became that of Si(100)1×1 with a highly intensified background. This indicates the occurrence of the entire breaking of the surface Si–Si dimerbonds and preservation of the atomically flat surface as well. Further increase of T_f up to 700–800 °C initiated continuous SiC growth, but with very poor quality, including poly-SiC crystals.

The formation temperature of the buffer layer also has a strong effect on the quality of the 3C–SiC film grown on it. RHEED patterns from the SiC films grown onto the buffer

[a]Electronic mail: nakazawa@bunshi.riec.tohoku.ac.jp

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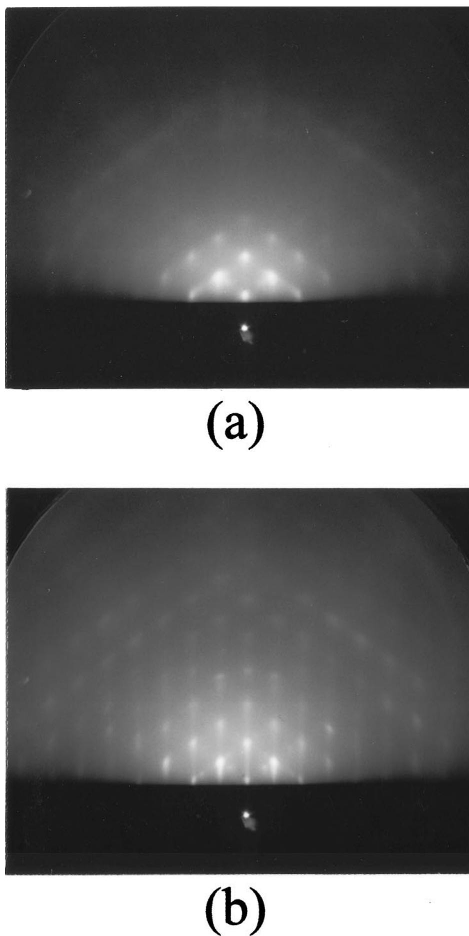

FIG. 1. Reflection high-energy electron-diffraction (RHEED) patterns for (a) the interfacial buffer layer formed at T_f=650 °C for 5 min onto a clean Si(100) surface and (b) the SiC film grown at T_g=900 °C for 60 min onto the buffer layer.

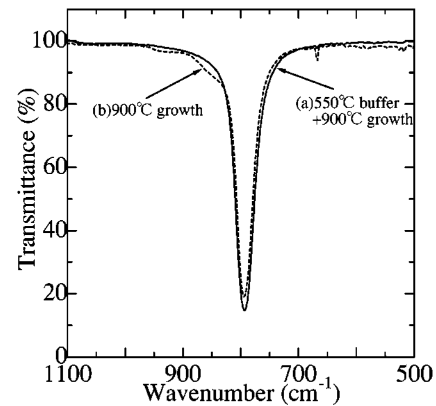

FIG. 2. Fourier-transform infrared-spectroscopy (FTIR) spectra obtained from SiC films grown (a) with and (b) without T_f=550 °C buffer layer formation.

layer formed at T_f=450–650 °C presented a clear 3C–SiC 1×1 pattern with streaks, indicating the formation of a qualified SiC film on these buffer layers. For buffer layers formed at $T_f \leqslant 400$ °C or $700 \leqslant T_f \leqslant 800$ °C, however, extra spots and ring patterns, in addition to the 3C–SiC 1×1 spots, were observed on the grown films, indicating the formation of polycrystals. At T_f=700 °C, in particular, the grown film became purely polycrystalline. Namely, there is a process window in T_f as for the formation of a qualified buffer layer in the present OS-buffer method.

The epitaxial nature of the 3C–SiC films grown onto the optimized buffer layer (T_f=450–650 °C) can also be confirmed by x-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR), and cross-sectional transmission electron microscopy (XTEM) observations. The XRD, conducted using a Cu $K\alpha$ line, exhibited a sharp 3C–SiC(200) peak at 41.37° and a 3C–SiC(400) peak at 90.10°, in addition to the major Si(400) reflection peak from the substrate. The absence of extra peaks is consistent with the epitaxial nature of the 3C–SiC film. In fact, the results from RHEED, XRD, and XTEM (Fig. 3) altogether indicate that the film is of single-crystalline 3C–SiC without any other orientations or polytypes. The full width at half maximum (FWHM) value of the 3C–SiC(200) peak was ~0.68° for a ~350-Å-thick sample. For T_f=700 °C, on the other hand, SiC(111) and (220) peaks were also observed. Figure 2 shows the FTIR spectra obtained from the SiC films grown (a) with and (b) without the T_f=550 °C buffer layer. The spectrum (a) from the film grown onto the buffer layer presents a sharp 3C–SiC transverse-optical (TO) -phonon absorption peak at 795 cm^{-1} with a FWHM of ~38 cm^{-1}. This peak position is identical with that from ideal bulk 3C–SiC.[10] The peak becomes asymmetrical and blueshifted for the film grown directly onto the Si substrate [(b)]. These results indicate that a fully relaxed, high-quality SiC crystal is obtained by employing the optimized OS-buffer layer. Extra components observed at 850–950 cm^{-1} in (b) are also observed for films grown onto buffer layers formed at T_f=300 °C or $T_f \geqslant 700$ °C. XTEM observations indicate the presence of voids with surrounding (111) facets for these samples. We thus relate the extra components in the FTIR spectrum to degradation at the SiC/Si interface in the film, such as stacking faults. Figure 3 shows the XTEM image of the SiC film grown onto the OS-buffer layer formed at 650 °C. A high-quality 3C–SiC film is seen to be successfully grown on Si(100), with an atomically flat interface without Si voids in the Si substrate. Low-resolution XTEM observation clarified that the distribution of stacking faults in the film is not uniform but there are some regions with 80–100 nm in diameter that contain no stacking faults.

The surface morphology of the grown films was investigated using atomic-force microscopy (AFM). The surface morphology of the film formed onto the buffer layer at $450 \leqslant T_f \leqslant 650$ °C presented rectangular-shaped steps with each

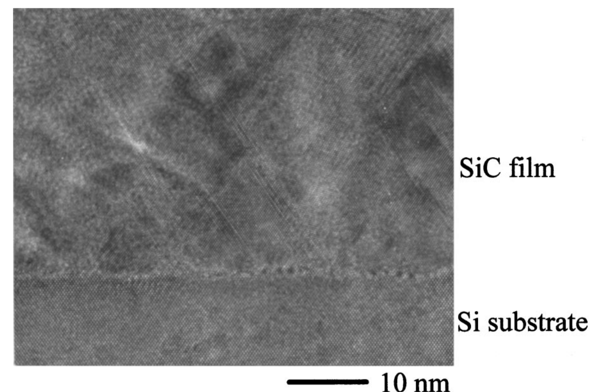

FIG. 3. Cross-sectional transmission electron microscopy image of a SiC film grown onto a buffer layer formed at 650 °C.

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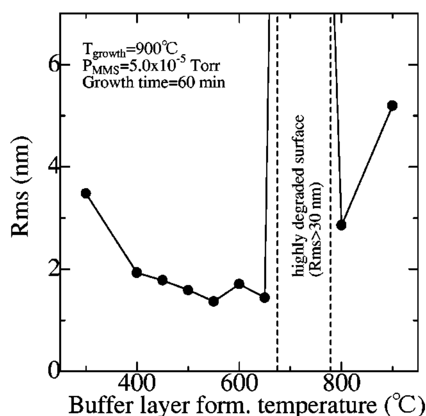

FIG. 4. Root-mean-square (rms) roughness of the SiC film surface obtained with atomic-force microscopy (AFM) as a function of the formation temperature of the buffer layer.

side parallel to the [011] direction. This indicates that the grown SiC film is epitaxially aligned along the Si substrate orientation. Voids or pits were not observed on the film surfaces. Contrary to this, the surface morphology of the films grown onto the buffer layers formed at $T_f \leqslant 400\,°C$ or $T_f \geqslant 800\,°C$, or directly onto the Si substrate was smeared. In particular, pits with depth of >30 nm were observed for films grown onto the buffer layer formed at $T_f \leqslant 400\,°C$ or directly onto the Si substrate. These deep pits suggest the occurrence of Si outdiffusion from the Si substrate to the film surface during growth. The root-mean-square (RMS) roughness of the grown films is plotted in Fig. 4 as a function of the formation temperature T_f of the buffer layer. Figure 4 clearly indicates the presence of a minimum at temperatures $450 \leqslant T_f \leqslant 650\,°C$. For $\sim 700 \leqslant T < 800\,°C$, a high degradation (rms>30 nm) occurs. This result completely coincides with the process window found by RHEED observations (Fig. 1).

The present success of the OS-buffer method: lowered formation temperature, suppressed Si outdiffusion, and realization of an atomically flat SiC/Si interface, can all be ascribed to the presence of a Si–C bond within the MMS molecule. In our previous study using temperature-programed desorption (TPD),[11] we have clarified that no Si–C bond cleavage occurs within MMS molecules during their adsorption on the Si(100) surface. Also, the sticking coefficient of the MMS molecules (~0.07) was as high as that of the Si_2H_6 molecule (~0.1). These results indicate that cleavage of the Si–H bonds is the most predominant pathway for the initial MMS adsorption. Energetically, the cleavage of the weaker Si–H bond (10.01 eV) (Ref. 5) and the preservation of the stronger Si–C bonds (13.09 eV) (Ref. 5) in the MMS molecule account for this mechanism. This finding implies that MMS gas adsorption not only incorporates C atoms into the buffer layer but also provides molecular SiC units even at low temperatures. This explains why a qualified SiC lattice structure can be formed at temperatures as low as 650 °C using MMS. Hydrocarbon gas molecules, on the other hand, cannot be fully decomposed at low temperatures, and cannot thereby provide sufficient Si–C bonds to form qualified SiC. Another equally important finding in Ref. 11 is that atomic exchange between the surface C and the substrate Si atoms hardly occurs on MMS/Si(100) even after annealing up to ~650 °C, which is contrasted to acetylene/Si(100). This can also be understood in terms of the strong Si–C bonds already present in the MMS molecule. When hydrocarbon molecules are used instead of MMS, intermixing of Si and C atoms at the SiC/Si interface occurs to form stable Si–C bonds,[11] which leads to degradation of the surface and formation of Si voids.[3]

In summary, we have formed a buffer layer for 3C–SiC/Si(100) heteroepitaxy by using MMS at T_f=450–650 °C. The ability of the buffer layer has been demonstrated by the quality of the SiC film grown onto the buffer layer, which is comparable with the bulk 3C–SiC. The interface is shown to be atomically flat without Si voids in the Si substrate. The authors would like to acknowledge Futami Satoh and Professor Michiyoshi Tanaka at the Research Institute for Scientific Measurements, Tohoku University for their great support in the XTEM observations. This work was supported in part by a Grant-in-aid for Scientific Research (No. 12650025) from the Ministry of Education, Culture, Sports, Science, and Technology, Japan.

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