# Epitaxial growth on 4H-SiC by TCS as a silicon precursor*

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**Abstract:** Epitaxial growth on n-type 4H-SiC 8° off-oriented substrates with a size of $10 \times 10$ mm$^2$ at different temperatures with various gas flow rates has been performed in a horizontal hot wall CVD reactor, using trichlorosilane (TCS) as a silicon precursor source together with ethylene as a carbon precursor source. The growth rate reached 23 $\mu$m/h and the optimal epilayer was obtained at 1600 °C with a TCS flow rate of 12 sccm in C/Si of 0.42, which has a good surface morphology with a low RMS of 0.64 nm in an area of $10 \times 10$ $\mu$m$^2$. The homoepitaxial layer was obtained at 1500 °C with low growth rate ($< 5$ $\mu$m/h) and the 3C-SiC epilayers were obtained at 1650 °C with a growth rate of 60–70 $\mu$m/h. It is estimated that the structural properties of the epilayers have a relationship with the growth temperature and growth rate. Silicon droplets with different sizes are observed on the surface of the homoepitaxial layer in a low C/Si ratio of 0.32.

**Key words:** 4H-SiC; TCS; epitaxial growth; growth rate

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## 1. Introduction

As a third-generation semiconductor material, silicon carbide (SiC) is a promising material in the fields of high temperature, high power and high frequency devices, due to the wide band gap, high critical breakdown field and high thermal conductivity. In particular, high power devices based on 4H-SiC are very attractive for the economization of energy in the domain of electric power. Currently, chloride-based homoepitaxial growth of 4H-SiC has attracted much interest since the addition of chlorinated species to the gas mixture completely changes the reactivity in the reactor. This prevents silicon nucleation in the gas-phase, thus allowing higher input flow rates of the precursors which results in much higher growth rate than that of standard 4H-SiC epitaxial growth[1–5]. Therefore, 4H-SiC devices including power DMOSFETs, implanted VJFETs, PiN diodes and Schottky diodes, containing a thick intrinsic drift layer with a thickness of 80–100 $\mu$m to sustain a breakdown voltage of about 10 kV, obtain great benefits from chlorine-added epitaxial growth[6–8].

In this paper, epitaxial growth on n-type 4H-SiC 8° off-oriented substrates with a size of $10 \times 10$ mm$^2$ at different temperatures with various gas flow rates was performed using trichlorosilane (TCS) as a silicon precursor source together with ethylene as a carbon precursor source. Cross-section scanning electron microscopy (SEM), Raman scattering spectroscopy (RSS) and atomic force microscopy (AFM) were used to determine the thickness, structural properties and surface morphology, respectively; silicon droplets on the homoepilayer were also observed by SEM. It is found that the growth temperature and growth rate influence the polytype of the epilayers. By analyzing the behaviors of the C–Si bilayer on the growth surface, explanations of the results are given in this study.

## 2. Experimental details

Epitaxial layers were grown at different temperatures with various gas flow rates in a horizontal hot wall CVD reactor using n-type 4H-SiC 8° off-oriented Si-face substrates with a size of $10 \times 10$ mm$^2$. The pressure for all runs was 40 Torr. The $H_2$ carrier gas flow rate was 3 slm. No intentional dopants were added during growth. Before epitaxial growth every substrate was etched in $H_2$ at 1350 °C for 30 min, and then the experiments were carried out for 60 min. In this work, the epitaxial layers were grown using trichlorosilane (TCS) as a silicon precursor source together with ethylene as a carbon precursor source. Table 1 shows the growth parameters used in this work. The epilayers were analyzed by cross-section SEM for thickness determination, AFM for surface roughness analysis and RSS for the structural properties.

Table 1. Growth parameters used in this study.

| Sample No. | Temperature (°C) | $C_2H_4$ (sccm) | TCS (sccm) | C/Si |
|---|---|---|---|---|
| 1 | 1500 | 7.5 | 15 | 1 |
| 2 | 1500 | 0.8 | 5 | 0.32 |
| 3 | 1600 | 2.5 | 6 | 0.83 |
| 4 | 1600 | 2.5 | 12 | 0.42 |
| 5 | 1650 | 5 | 12 | 0.83 |
| 6 | 1650 | 5 | 20 | 0.5 |

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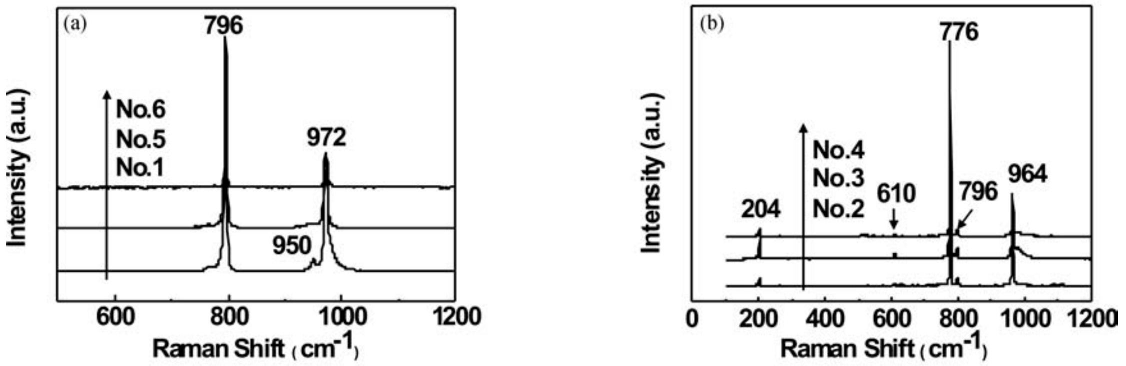


Fig. 1. Raman spectra of (a) No.1, No.5, No.6 epitaxial layers and (b) No.2, No.3, No.4 epitaxial layers.

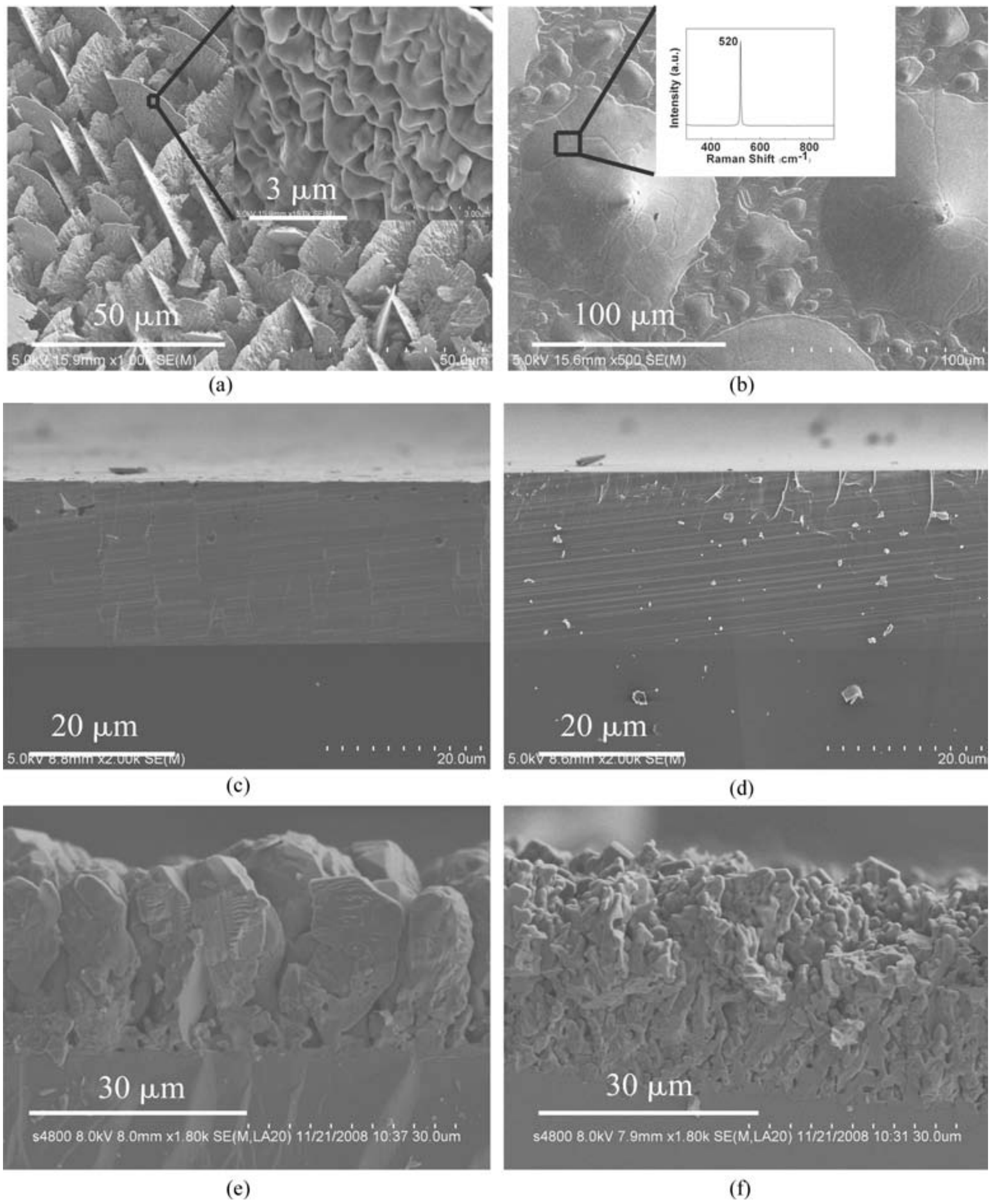
## 3. Results and discussion

The initial motivation of the experiments is to obtain the optimal growth parameters with high growth rate in a homogeneous 4H polytype. However, after a series of experiments it was found that the polytype of the epilayers is not only related to the most important parameter growth temperature but also to the growth rate.

Figure 1 shows the Raman spectra of the epitaxial layers; the plots have been offset for clarity. As seen in Fig. 1(a), the spectra of samples No.1, No.5 and No.6 all show two peaks at 796 and 972 $cm^{-1}$ corresponding to the characteristic peaks of the 3C polytype. The peak at 950 $cm^{-1}$ in the spectra of No.6 has not been found in the familiar polytype of SiC[9]; its existence needs further research. Figure 1(b) shows the Raman spectra of samples No.2, No.3 and No.4 displaying peaks at 204, 610, 776, 796 and 964 $cm^{-1}$, which are all the characteristic peaks of the 4H polytype. It should be pointed out that the peak at 796 $cm^{-1}$ corresponds to the transversal (TO) phonon modes of both 3C-SiC and 4H-SiC. In the curves of Fig. 1(a), the Raman peak at 796 $cm^{-1}$ does not correspond to that of the 4H polytype, since the peak at 776 $cm^{-1}$ is absent, while the peak at 972 $cm^{-1}$, which is the longitudinal (LO) phonon mode of 3C-SiC, is present. As seen in the curves of Fig. 1(b), the peak at 796 $cm^{-1}$ is present with that of the TO phonon mode at 776 $cm^{-1}$ and the LO phonon mode at 964 $cm^{-1}$ of 4H-SiC[9]. Therefore, it can be concluded that the polytype of No.1, No.5 and No.6 is 3C, while the polytype of No.2, No.3 and No.4 is 4H.

Figure 2(a) shows the surface image of the epilayer grown at 1500 °C with a TCS flow rate of 15 sccm in C/Si of 1. Flake bulge arrays in several specific orientations are observed on the surface. As seen in the inset, on the flake bulge surface there are many humps which are the crystal grains. It is estimated that the existence of the flake bulges is concerned with the very high growth rate ($> 100$ $\mu$m/h) resulting in priority growth along specific orientations. Figure 2(b) shows the surface image of the epilayer grown at 1500 °C with a TCS flow rate of 5 sccm in C/Si of 0.32. Apparently, there are many different-sized droplets on the wafer. The inset shows the micro Raman spectra of the droplets displaying a peak at 520 $cm^{-1}$ corresponding to the characteristic peak of silicon. The existence of the silicon droplets is due to the low C/Si ratio resulting in an overly residual silicon source after exhausting the carbon source, although the silicon species involved in the reaction changes from Si to $SiCl_2$ as the most important silicon resultant[1]. Therefore, the appropriate C/Si ratio preventing the formation of silicon droplets should be above 0.32 when grown by TCS as the precursor. Figures 2(c) and 2(d) show the cross-section images of the epilayers grown at 1600 °C with a $C_2H_4$ flow rate of 2.5 sccm in C/Si of 0.83 and 0.42, respectively. As seen in these images, both epilayers are compact and the interfaces between the substrates and epilayers are distinct. In particular, it needs to be emphasized that in the epilayers many cross grains are clearly observed, which is thought to be related to the strictly step-controlled growth mode[10]. Thus under these growth conditions high quality homogeneous epitaxial layers of 4H-SiC can be obtained by using TCS as the silicon precursor. The last two cross-section SEM images in Fig. 2 show the epilayers grown at 1650 °C with a $C_2H_4$ flow rate of 5 sccm in C/Si of 0.83 and 0.5, respectively. It is clearly observed that the epilayers are made of many grains grown in the manner of 3D nucleation of 3C-SiC. However, the grain size of the No.5 epilayer is larger than that of the No.6 epilayer; the reason for this is that the high growth rate gives rise to insufficient time for the grains to grow before new nucleation.

As seen in Table 2, the polytype of the epilayers is influenced by the growth temperature and growth rate, which represent the thermodynamic and kinetic factors controlling the growth process[11, 12]. When grown at 1500 °C, homogeneous epilayer growth on 4H-SiC is hampered by the thermodynamic factor. However, when the growth rate is very low as in the No.2 epilayer, although the surface mobility of the precursor adatoms is insufficient, the C–Si bilayer deposited on the surface still has adequate time to move to the edge of the steps that grow as the polytype of the substrate. By increasing the growth temperature to 1650 °C, the thermodynamic factor is favorable for achieving homogeneous epitaxial growth of 4H-SiC, but the polytype of these two epilayers are both 3C polytype. The origin of the 3C nucleation is the high growth rate, which results in insufficient time to allow the C–Si bilayer move to the edge of the steps, and simultaneously new nucleation has been proceeding around the old ones. Thus the



(a) (b) (c) (d) (e) (f)

Fig. 2. SEM images of (a) No.1 epilayer, (b) No.2 epilayer, (c) No.3 epilayer, (d) No.4 epilayer, (e) No.5 epilayer and (f) No.6 epilayer. The inset in Fig. 2(a) shows the SEM image of the quadrate part and the inset in Fig. 2(b) shows the micro Raman spectra of the quadrate part.

Table 2. Growth temperature, growth rate (calculated from the thickness) and polytype of each epilayer. The existence of the growth rate range is generated by non-uniform growth.

| Sample No. | Temperature (°C) | Growth rate ($\mu$m/h) | Polytype |
|---|---|---|---|
| 1 | 1500 | > 100 | 3C |
| 2 | 1500 | < 5 | 4H |
| 3 | 1600 | 10~23 | 4H |
| 4 | 1600 | 5~20 | 4H |
| 5 | 1650 | 40~50 | 3C |
| 6 | 1650 | 60~75 | 3C |

grains begin to grow in 3D mode which impedes the formation of the homogeneous epilayer of 4H-SiC. Furthermore, the higher growth rate results in smaller grain size of the heterogeneous epilayer. By kinetics, the higher growth rate results in less time available in which to grow, so before new nucleation a crystal nucleus with lower growth rate like the No.5 epilayer has time to grow to form the large grains penetrating the epilayer as seen in Fig. 2(e). In contrast, a crystal nucleus with higher growth rate like the No.1 and No.6 epilayers does not have time to grow before new nucleation, and so the pre-grains are covered with the new crystal nucleus. Thus the epilayers are made of many small grains. Ideal results such as for the No.3 and No.4 epilayers for homogeneous epitaxial growth on 4H-SiC can be obtained with appropriate growth temperature

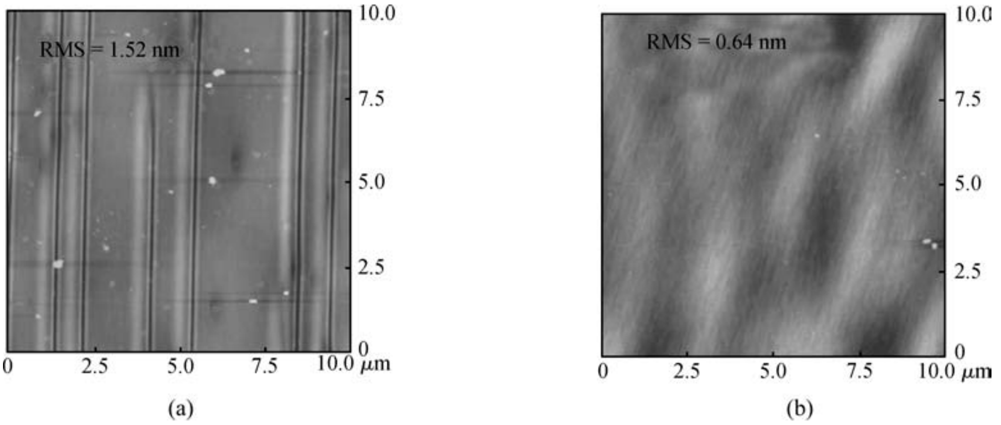


Fig. 3. AFM images of (a) No.3 and (b) No.4.

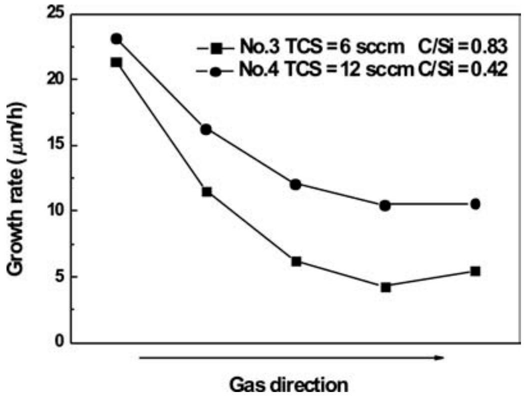


Fig. 4. Growth rates for the No.3 and No.4 epitaxial layers against gas direction. The positions were noted once at a distance of 2 mm along the gas direction.

and growth rate; this needs further investigation. From the above, it can be concluded that consideration of the growth temperature and growth rate is important for epitaxial growth on a 4H-SiC substrate using TCS as the silicon precursor.

Figure 3 shows the AFM images of the epilayers grown at 1600 °C with a TCS flow rate of 6 sccm in C/Si of 0.83 and TCS flow rate of 12 sccm in C/Si of 0.42. The RMS in an area of $10 \times 10\ \mu\text{m}^2$ is 1.52 nm and 0.64 nm, respectively. As seen in Fig. 3(a) there are several straight trenches on the surface, which cause the roughness of the No.3 epilayer to be higher than that of the No.4 epilayer. It is estimated that the existence of these trenches is related to step bunching. Figure 3(b) shows a very smooth surface without the straight trenches, which can be used to fabricate devices.

As seen from the two curves in Fig. 4 along the gas direction the growth rate of the No.4 epilayer ranges from 10.6 to 23.2 μm/h, and that of the No.3 epilayer ranges from 4.3 to 21.4 μm/h, which indicates that the growth rate of the epilayer grown with the TCS flow rate of 12 sccm in a C/Si of 0.42 is higher than that grown with the TCS flow rate of 6 sccm in C/Si of 0.83. Additionally, the uniformity of the No.4 epilayer is better than that of the No.3 epilayer. This is due to the Cl atoms in TCS ($SiHCl_3$) bonded with Si atoms, which reduces the quantity of Si atoms bonded to C atoms during growth. In Si-rich (low C/Si ratio) conditions, there are abundant Si atoms bonded to C atoms after passing through the inlet where many Si atoms are bonded to Cl atoms. In contrast, in C-rich (high C/Si ratio) conditions, the quantity of Si atoms mostly bonded to Cl atoms around the inlet does not correspond to the quantity of C atoms. Around the outlet the growth rate reduces greatly and the uniformity of the epitaxial layer is not good. It is concluded that a low C/Si ratio is an advantage in improving the uniformity of the epitaxial layer and obtaining a high quality surface morphology.

## 4. Summary

3C-SiC and 4H-SiC epilayers were obtained on n-type 4H-SiC 8° off-oriented substrates with a size of $10 \times 10\ \text{mm}^2$ at different temperatures with various gas flow rates in a horizontal hot wall CVD reactor using TCS as a silicon precursor source. The structural properties, growth rate, thickness uniformity and surface morphology of the epilayers were investigated. Both the growth temperature and growth rate influence the polytype of the epilayer grown by TCS as the precursor; in this work, a good 4H-SiC crystalline structure was obtained at 1600 °C with a growth rate of 10–23 μm/h, which has a good surface morphology with a low RMS of 0.64 nm in an area of $10 \times 10\ \mu\text{m}^2$. A low C/Si ratio is favorable for improving the uniformity and surface morphology of the 4H-SiC epilayer. When the 3C-SiC epilayer was obtained, the grain size of the epilayer decreased with increasing growth rate. In addition, it is concluded that the appropriate C/Si ratio for preventing the formation of silicon droplets should be above 0.32 when grown by TCS as the precursor. Further investigation is needed to control the epilayer polytype with accurate data on the growth temperature and growth rate.

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