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Very high growth rate of 4H-SiC epilayers using the chlorinated precursor methyltrichlorosilane (MTS)

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Abstract

The chlorinated precursor methyltrichlorosilane (MTS), CH_3SiCl_3, has been used to grow epitaxial layers of 4H-SiC in a hot wall chemical vapour deposition (CVD) reactor with growth rates higher than 100 μm/h. The addition of chlorinated species to the gas mixture prevents silicon nucleation in the gas phase, thus allowing higher input flows of the precursors resulting in much higher growth rate than that of standard silicon carbide (SiC) epitaxial growth using only silane, SiH_4, and hydrocarbons as precursors. Since MTS contains both silicon and carbon, with the C/Si ratio 1, MTS was used both as single precursor and mixed with silane or ethylene to study the effect of the C/Si and Cl/Si ratios on growth rate, morphology, and doping of the epitaxial layers. When using only MTS as precursor, the growth rate showed a linear dependence on the MTS molar fraction in the reactor. The growth rate dropped for C/Si < 1 but was constant for C/Si > 1. Further, the growth rate decreased with lower Cl/Si ratio. This study shows that MTS is a promising precursor for homoepitaxial growth of SiC within the concept of chloride-based SiC growth.

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Keywords: A3. Chemical vapour deposition processes; B. Methyltrichlorosilane; B. Silicon carbide

1. Introduction

Silicon carbide (SiC) is a promising material for high-power and high-frequency devices due to its wide band gap, high break down field and high thermal conductivity. For devices made of SiC, thick (> 100 μm) epi layers are needed in some cases. The most established technique to grow epitaxial layers of SiC is the chemical vapour deposition (CVD) at around 1550 °C using silane, SiH_4, and light hydrocarbons, e.g. propane, C_3H_8, or ethylene, C_2H_4, as precursors diluted in hydrogen. Normal growth rate is ~5 μm/h, rendering long manufacturing times for SiC-based devices. The main problem one faces when trying to achieve higher growth rate by increasing the precursor flows is formation of aggregates in the gas phase; for SiC CVD these aggregates are mainly silicon droplets and result in saturation of the growth rate. If the gas flow does not manage to transport these droplets out of the growth zone, they will eventually come in contact with the crystal surface and thereby creating very big defects on the epilayer. One approach to overcome this problem is lowering the pressure in the cell and/or increasing the carrier gas flow to give a faster gas flow capable of transporting the aggregates out of the susceptor. This has been realised by several research groups [1–3], and growth rate up to 50 μm/h has been achieved. Another approach is to use chloride-based epitaxy, which is based on the idea that the silicon droplets can be dissolved by the presence of species that bind stronger to silicon than silicon itself. An appropriate candidate is then to have some halogen-containing molecule present since the halogen atoms all bind strongly to silicon. Average bond enthalpies at 25 °C for the Si–Si, Si–F, Si–Cl, Si–Br, and Si–I bonds are 226,

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597, 400, 330, and 234 kJ/mol, respectively [4]. The best choice here is chlorine since bromine and iodine are too large atoms and have weak bonds to Si and fluorine has too strong bond to Si. Chlorine is introduced in the CVD reactor either as HCl [5–7], SiH_xCl_y [8–10], CH_xCl_y [11], or $SiC_xH_yCl_z$ molecules. Several studies have been made on chloride-based epitaxy and growth rates over 110 μm/h have been achieved [7]. In this study we have used methyltrichlorosilane (MTS), CH_3SiCl_3, as Cl-containing molecule. MTS has also the role as SiC precursor, providing both carbon and silicon to the gas mixture. However, when using only MTS as precursor, the C/Si ratio will be fixed at one. In order to adjust the C/Si ratio, which has been proved to be an important way of controlling the morphology and the amount of impurities incorporated in the material [12], we therefore adjusted the C/Si ratio in some runs by addition of C_2H_4 to get C/Si > 1 and addition of SiH_4 to get C/Si < 1. MTS has previously been used to grow cubic SiC on Si [13–17] at substantially lower temperatures than homoepitaxy of hexagonal SiC. Few reports on homoepitaxy of hexagonal SiC using MTS as precursor can be found. Zelenin et al. [18] used MTS to grow 6H-SiC but without focusing on growth rates. Lu et al. [19] grew 4H- and 6H-SiC in a small cold wall CVD reactor using MTS and achieved growth rates of 90 μm/h. We now report 4H-SiC growth from MTS in a larger scale hot wall CVD reactor.

2. Experimental procedure

Epitaxial layers of 4H-SiC were homoepitaxially grown in a horizontal hot wall CVD reactor [20]. Commercial n-type 4H-SiC (0 0 0 1) wafers were used as substrates and all epilayers were grown on the Si-face of the wafer. The wafers were off-cut 8° towards the $[1 1 \bar{2} 0]$ direction. For a typical experiment a quarter of a 35 mm wafer was placed in the optimum position in the susceptor; rotation of the sample holder was not used in the experiments. As carrier gas, Pd–Ag membrane purified hydrogen gas with a flow of 80 l/min was used. All growth runs start with a 10 min heat treatment at 1250 °C to condition the cell. The susceptor is then further heated to the growth temperature, 1600 °C, which has previously been shown to be a suitable growth temperature [19]. The precursors are introduced in the cell at roughly 40 °C below the growth temperature, starting with a low flow that is subsequently increased during first few minutes. The stainless steel bubbler with MTS was kept in a water/glycol bath to ensure a constant temperature of 20 °C and thereby a constant MTS vapour pressure. The pressure in the cell was 100 mbar and a typical growth time was 30 min. No intentional dopants were added during the growth. The net carrier concentration is thus the background doping, mainly due to nitrogen contamination in the MTS bubbler.

The thickness of the grown epilayers was measured by Fourier transform infrared (FTIR) reflectance. The surface of the grown layers was studied by Nomarski optical microscope; the surface roughness and morphology were further studied using atomic force microscopy (AFM). The net doping was studied with capacitance–voltage measurements (*CV*) using a mercury probe. The quality of the grown material was investigated by (1) high-resolution X-ray diffraction (HRXRD), performed using a triple-axis diffractometer equipped with a four-crystal monochromator in Ge (2 2 0) configuration and a channel cut analyzer with 12 arcsec acceptance in triple axis setup; (2) low temperature photoluminescence (LTPL) in a bath cryostat with the temperature kept at 2 K, the 244 nm Ar^+ laser line was used for excitation (the luminescence was dispersed by a single monochromator on which a UV sensitive CCD camera was mounted to rapidly detect the LTPL spectrum); and (3) deep level transient spectroscopy (DLTS) measurements performed in the temperature range from 85 to 680 K by applying a reversed pulse of −10 V and a pulse height of 10 V. Transients were acquired during 500 ms. The data were evaluated using boxcar technique [21]. Nickel Schottky contacts with a thickness of approximately

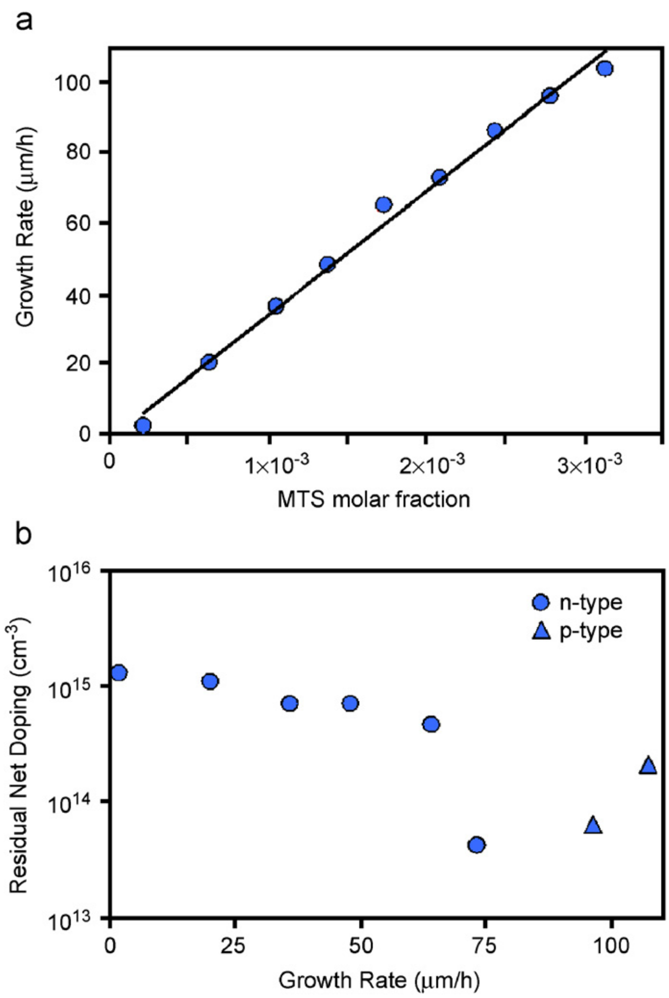

Fig. 1. (a) Growth rate of 4H-SiC epitaxial layers for various flows of MTS. All layers are grown at 1600 °C using only MTS as precursor; only the flow of MTS into the reactor is changed between the runs. The highest growth rate achieved is 104 μm/h. (b) The dependence of the residual doping of the unintentionally doped layers on the growth rate.

1000 Å were thermally evaporated on the epilayer. The large ohmic contacts were realized by conducting silver paint at the backside of the sample.

3. Results and discussion

3.1. Effect of MTS molar fraction

To investigate the growth rate of SiC epilayers using MTS as precursor, a number of experiments were done where only the flow of MTS into the reactor was varied between the different growth runs. The growth rate dependence of the MTS molar fraction is given in Fig. 1a. It is clearly seen that there is a linear dependence between growth rate and MTS molar fraction for growth rates between 2 and 100 μm/h. The highest growth rate achieved in this study was 104 μm/h. The linear trend line has successfully been used to determine the needed flow for a specific growth rate. It also gives a negative growth rate at zero MTS molar fraction, indicating that substrate etching is accounted for.

The residual doping dependence on growth rate is plotted in Fig. 1b; it can be seen that, for low growth rates, the net doping is n-type and the net doping decreases with higher growth rate for growth rates up to about 80 μm/h, when the net doping turns p-type and increases slightly with higher growth rates.

The grown epilayers have very smooth morphology, for all growth rates investigated, as shown in the Nomarski microscope images in Fig. 2. AFM measurements of the surface roughness of a 49 μm thick epilayer grown at 98 μm/h gives an RMS value of 5.7 Å as measured on a $50 \times 50\,\mu m^2$ area.

The crystal quality of the grown material was studied by high-resolution X-ray diffraction rocking curve measurements. The reflection peak from the (0 0 0 4) plane of a 52 μm thick epilayer grown with 104 μm/h is shown in Fig. 3 and it gives a FWHM of 35 arcsec, but it can be seen that the X-ray beam probed more than one domain on the sample, and the peak is thus broadened. The peak has therefore been fitted with three Gaussians; each with a FWHM of less than 10 arcsec. The beam size used was $0.2 \times 0.2\,mm^2$.

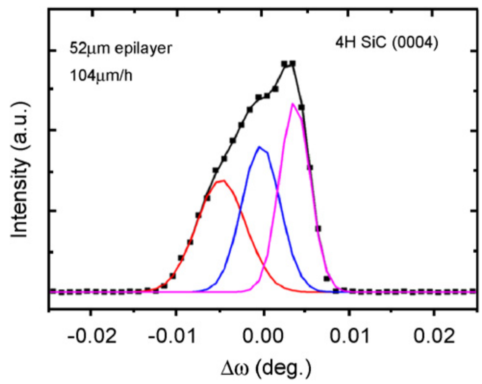

Fig. 3. High resolution XRD rocking curve showing the high crystal quality of the 52 μm thick epilayer grown with 104 μm/h using only MTS as precursor. The FWHM value for the whole peak is about 35 arcsec. However, the curve fitting shows that at least three domains are probed, each with a FWHM of about 10 arc s.

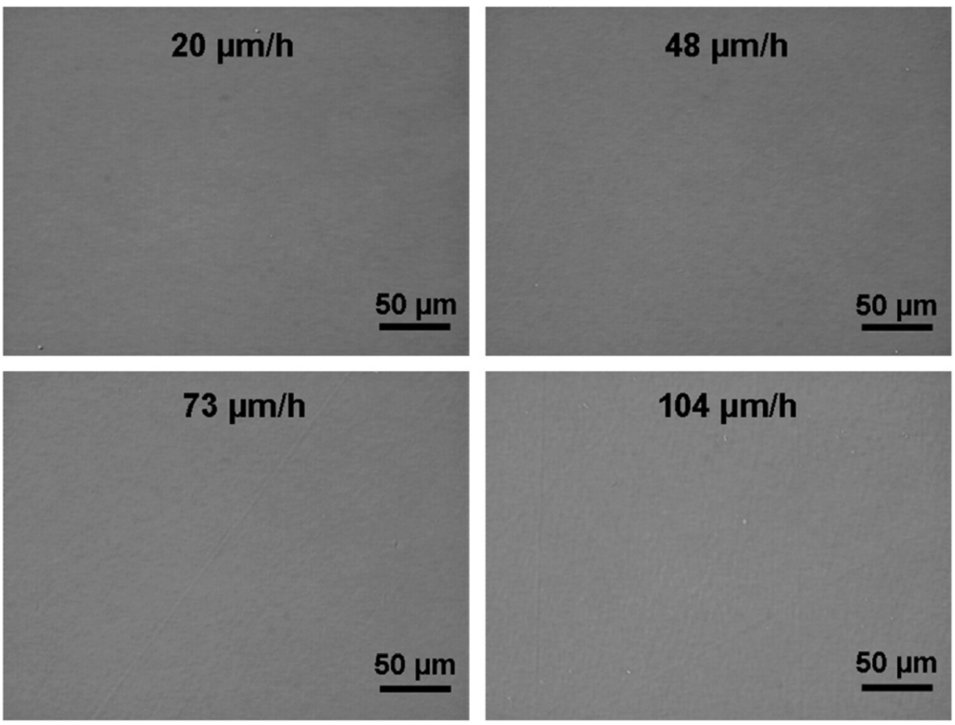

Fig. 2. The morphology of the epitaxial layers illustrated by Nomarski microscope images, showing the morphology of the epilayers grown using only MTS as precursor at various growth rates.

3.2. Effect of C/Si ratio

The C/Si ratio of the inlet gas mixture is an important process parameter in epitaxial growth of SiC since it influences the incorporation of dopants and impurities. In the "site-competition theory" presented by Larkin [12], it is believed that nitrogen replaces carbon while aluminium replaces silicon in the SiC lattice. Adjusting the growth conditions to more carbon or silicon rich can thereby affect the number of nitrogen and aluminium atoms incorporated. To study how different C/Si ratios affect the growth rate, morphology and doping of the epilayers, a series of growth runs with C/Si between 0.8 and 1.2 was done. The total amount of silicon flow is kept constant for all the runs and thus the growth rate is expected to be the same, 104 μm/h. The C/Si ratio of the inlet gas mixture was varied in the following way:

- For C/Si > 1, C_2H_4 was added to the gas mixture and the flow of MTS was kept constant.
- For C/Si < 1, the flow of MTS was decreased and SiH_4 was added.

It should be noted that when decreasing the flow of MTS and adding silane, the Cl/Si ratio is changed in the gas mixture. The growth rate dependence on Cl/Si ratio is further investigated below.

In Fig. 4a, the growth rate for various C/Si ratios is plotted. From the figure it can be seen that the growth rate is not affected by addition of C_2H_4, i.e. C/Si > 1. But for C/Si < 1, the growth rate drops. This might be explained by the lower Cl/Si ratio for these runs. The Cl/Si ratio for the run with C/Si = 0.9 is 2.7 whereas for the run with C/Si = 0.8 the C/Si ratio has dropped to 2.4; for all the other runs Cl/Si = 3. It should be noted that the growth rate obtained for lower C/Si ratios with some of the MTS replaced with silane, is roughly the same as the expected growth rate for the actual MTS flow alone. It thus seems that the addition of silane to the gas mixture does not influence the growth rate, suggesting that the critical parameter is not the total flow of silicon but rather the Cl/Si ratio. However, similar dependencies between growth rate and C/Si ratio have previously been reported [22], where the growth rate is constant above a critical C/Si value but drops below that value. This was suggested to be caused by shortage of carbon.

The surface morphology was affected by the change in C/Si ratio; the straight "carrot-like" defects at low C/Si ratio changes to a triangular shape at high C/Si ratio, as seen in Fig. 5. Also the density of these defects increased at higher C/Si ratio. These defects are observed at low density and assuming they emanate at the epi/substrate interface, their lengths allow an estimation of the thickness of the epilayer.

For unintentionally doped layers, the net doping dependence of the C/Si is plotted in Fig. 4b. It can be seen that the lowest net doping is achieved when the C/Si ratio is close to 1. The epilayers grown with C/Si < 1 are n-type doped, and the n-type doping increases with lower C/Si. The epilayers grown at a higher C/Si ratio are p-type, and the p-type doping increases slightly with higher C/Si. Similar doping dependence for high growth rate without Cl-addition has previously been reported [1].

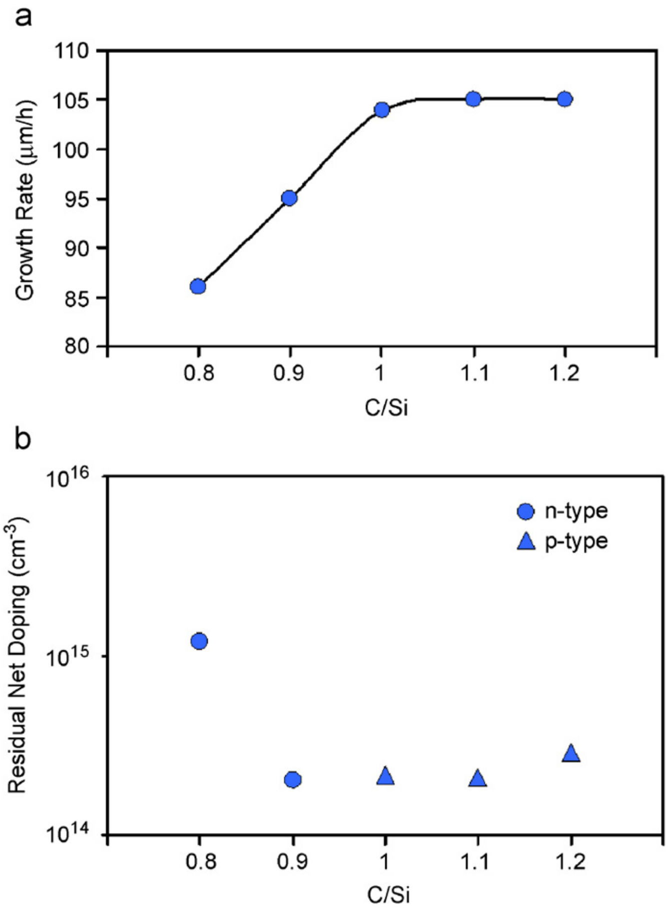

Fig. 4. (a) Growth rate of 4H-SiC epitaxial layers for various C/Si ratios. The total amount of Si into the reactor is constant for all the runs. It should be noted that the change in C/Si to a value below 1 is accompanied by a change in Cl/Si ratio. The Cl/Si ratio is 2.7 and 2.4 for the C/Si = 0.9 and 0.8, respectively. (b) The dependence of the residual doping of the unintentionally doped layers on C/Si ratio, using the same samples as in (a).

To further investigate the impurity levels and also the crystal quality of the grown epilayers, LTPL and DLTS were used. The LTPL spectra recorded from the samples grown with high growth rate exhibit typical 4H-SiC luminescence as shown in Fig. 6a. The spectra are dominated by the near band gap emission with free exciton (FE) related lines such as the I_{76} line and nitrogen bound exciton lines (N-BE: P_0 and Q_0 and their phonon replica such as P_{76}). For the highest C/Si ratio used in this study, very weak Al-related lines (Al-BE) are observed (spectrum (i) in the insert) which confirm the results obtained by *CV* with p-type conductivity and very low net doping. Other luminescence features such as the D_I centre or the Ti-related lines were only weakly observed. The D_I centre is believed to

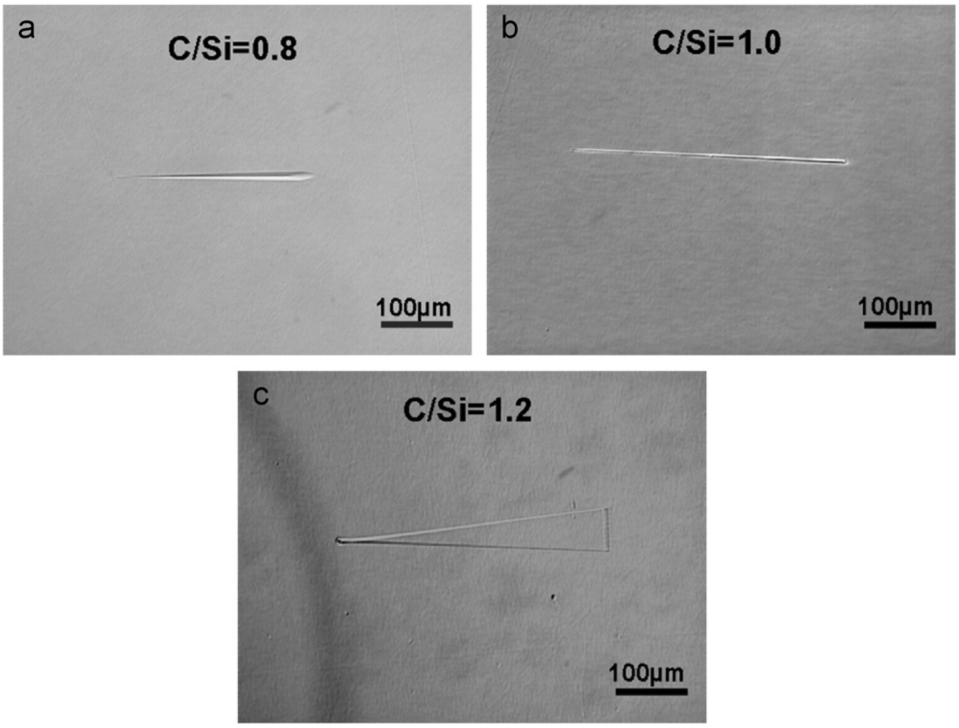

Fig. 5. Nomarski images showing the morphology of the epilayers grown at various C/Si ratios. The changing shape of the typical epidefect with different C/Si ratio is shown. (a) 43 μm thick epilayer grown with C/Si = 0.8, (b) 52 μm thick epilayer grown with C/Si = 1, (c) 53 μm thick epilayer grown with C/Si = 1.2.

be an intrinsic defect, which always appears with very high intensity after ion- or electron irradiations with subsequent annealing and more weakly in as-grown material. Ti is often observed as a contamination when the SiC coating of the susceptor degrades. According to the LTPL measurements, the n-type doping is caused by nitrogen and the p-type dopant by aluminium. From Fig. 4b, it can be seen that more nitrogen is incorporated when the C/Si ratio (and thereby also the Cl/Si ratio) is decreased. If also the growth rate is decreased, even more nitrogen is incorporated. This is also in line with previous results for the standard growth process [23]. For the p-type layers, the aluminium incorporation increases with increasing growth rate and also with higher C/Si ratio. This is also in line with previous results for the standard growth process [24]. This indicates that dopant incorporation at high growth rates using chloride-based epitaxy is similar to the standard process at low growth rates.

DLTS measurements were done on a sample grown with a lower growth rate (22 μm/h); 1 h growth time and C/Si = 0.8, such epilayer will be n-type doped according to Figs. 1 and 4. The carrier capture cross section and the energy position were deduced from the Arrhenius plot. Two peaks at 300 and 650 K dominated the DLTS spectrum shown in Fig. 6b. These peaks can be assigned to the $Z_{1/2}$ and the $EH_{6/7}$ centres; the $Z_{1/2}$ centre has an energy level of $E_c - 0.67$ eV and capture cross section of 2×10^{-14} cm^2. The trap concentration was determined to be 1.3×10^{13} cm^{-3}. The $EH_{6/7}$ centre has an energy level of $E_c - 1.52$ eV and capture cross section of 1×10^{-14} cm^2, the trap concentration was here determined to 8×10^{12} cm^{-3}. At about 90 K, a small sharp peak is obvious which can be assigned to the Ti acceptor [25,26]. The activation energy was determined to $E_c - 0.15$ eV and the capture cross section to 2×10^{-15} cm^2.

3.3. Effect of Cl/Si ratio

To study the effect that the Cl/Si ratio has on the growth rate, a series of experiments was done in which some of the MTS were replaced with silane plus ethylene. This was done in such a way that the total amount of silicon and carbon was constant for the growth runs, but the number of chlorine atoms decreased when MTS was replaced with $SiH_4 + C_2H_4$. The growth rate dependence of the Cl/Si ratio is plotted in Fig. 7, where it is clearly seen that the growth rate drops when the Cl/Si ratio is decreased. This might be explained by the change in chemistry introduced by the addition of Cl to the gas mixture. From simulations it has been shown that the main Si-containing specie when using $SiHCl_3$ as silicon precursor is the $SiCl_2$ molecule [27]. When the Cl/Si ratio is lowered from 3 to 2, the growth rate drops from 104 to 90 μm/h, possibly since the excess of Cl for the $SiCl_2$ formation is removed and less $SiCl_2$ then will be formed. It might also be argued that the $SiCl_x$ species possibly have a higher mobility on the growing surface and less Cl in the gas mixture will then lower the mobility on the surface and thereby reducing the growth rate.

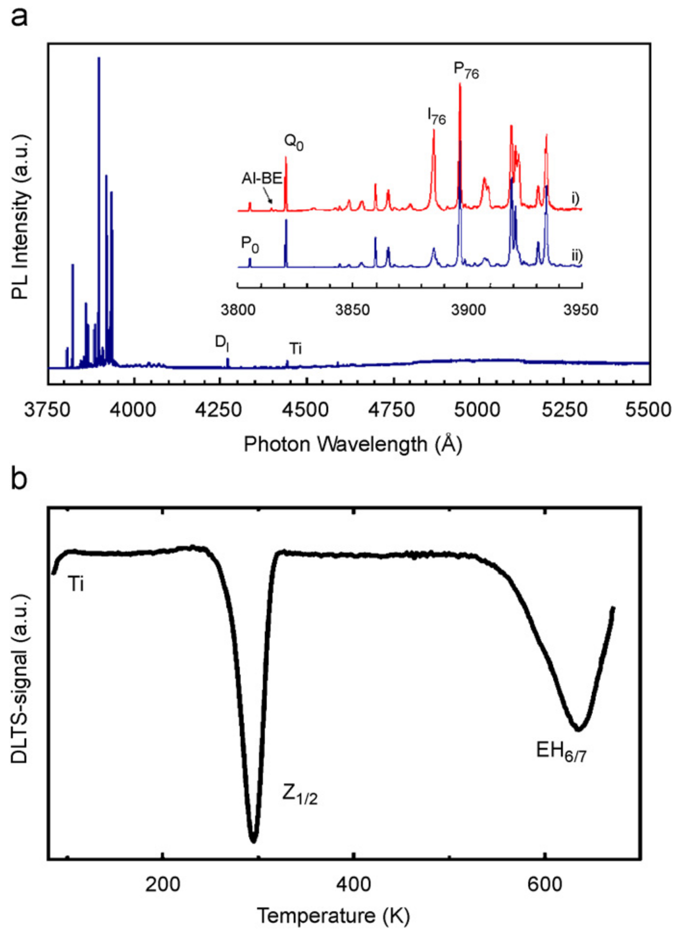

Fig. 6. (a) LTPL spectra recorded from a sample grown with C/Si = 0.9 and a growth rate of 95 μm/h. The inset shows the near-band gap emission for (i) a sample with C/Si = 1.2 grown at 105 μm/h and (ii) the sample grown with C/Si = 0.9 at 95 μm/h. (b) DLTS spectrum with a time constant of 100 ms of an 22 μm thick n-type epilayer grown with 22 μm/h and C/Si = 0.8 showing clear $Z_{1/2}$ and $EH_{6/7}$ signal, a weak Ti related peak can also be seen.

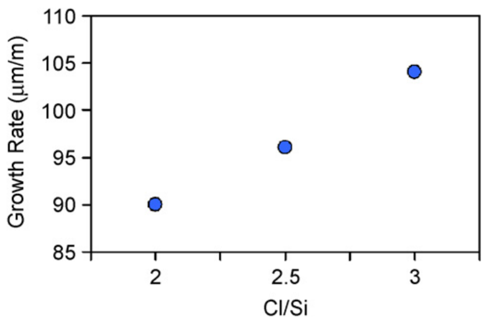

Fig. 7. Growth rate of 4H-SiC epitaxial layers for various Cl/Si ratios. The total amount of Si and C into the reactor was constant for all runs.

4. Conclusions

This study shows that the chloride-containing precursor MTS can be used to grow low-doped epitaxial SiC at high growth rates (> 100 μm/h) within the concept of chloride-based epitaxy. MTS can be used as single molecule SiC precursor with a fixed C/Si ratio of 1 and a Cl/Si ratio of 3. But it is also possible to adjust the C/Si ratio by adding SiH_4 or C_2H_4 to the gas mixture, which makes it possible to control the amount of incorporated dopants and morphology of the epitaxial layers. The incorporation of nitrogen and aluminium seems to follow the same mechanisms as for the standard process.

However, the Cl/Si ratio has proven to be a process parameter of potentially high importance. When using MTS as precursor, a change in Cl/Si by addition of silane and ethylene to the gas mixture will also be accompanied by a change in C/Si ratio. And vice versa a change in the C/Si to more Si-rich conditions will also be accompanied by a change in Cl/Si ratio.

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