
Volume 201, Numbers 22–23, 25 September, 2007
ISSN 0257-8972
ELSEVIER
SURFACE & COATINGS TECHNOLOGY
Proceedings of the 16th European Conference in Chemical Vapor Deposition (EUROCVD-16)
The Hague, The Netherlands, September 16–21, 2007
Editors
A. Matthews
Y. Pauleau
W.D. Sproul
Proceedings Editor
C.R. Kleijn
Available online at
ScienceDirect
www.sciencedirect.com
http://www.elsevier.com/locate/surfcoat

Available online at www.sciencedirect.com
ScienceDirect
Surface & Coatings Technology 201 (2007) 8931–8934
SURFACE & COATINGS TECHNOLOGY
www.elsevier.com/locate/surfcoat

Very high epitaxial growth rate of SiC using MTS as chloride-based precursor

H. Pedersen [a,*], S. Leone [a,b], A. Henry [a], V. Darakchieva [a], E. Janzén [a]

[a] Department of Physics, Chemistry and Biology, Linköping University, SE-581 83 Linköping, Sweden
[b] Caracal Inc., 611 Eljer Way, Ford City, PA 16226, USA

Available online 4 April 2007

Abstract

We present results on chloride-based homoepitaxial growth of 4H-SiC in a hot wall CVD reactor. 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 SiC epitaxial growth using only silane, SiH_4, and ethylene, C_2H_4, as precursors. We have achieved growth rates higher than 100 μm/h, as compared to 5 μm/h for the standard case. The chlorinated precursor used is methyltrichlorosilane (MTS), CH_3SiCl_3, but since MTS contains both silicon and carbon, with the C/Si ratio 1, we have also added silane or ethylene to optimise the C/Si ratio in order to improve the morphology of the epitaxial layers. We present studies on how the growth rate depends on both the flow of MTS and C/Si ratio. The morphology of the grown epitaxial layer has been investigated using Nomarski microscope and atomic force microscope showing extremely smooth surface and low epi-defect density. The net doping has been determined using capacitance-voltage measurements. Low temperature photoluminescence and high-resolution X-ray diffraction confirm the high quality of the grown epilayers.

Keywords: Silicon cabide; Chemical vapour deposition

1. Introduction

Silicon carbide (SiC) is a promising material for high power and high frequency devices due to its wide band gap. 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 formations of aggregates in the gas phase; for SiC CVD these aggregates are mainly silicon droplets. 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 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, 597, 400, 330, 234 kJ mol^{-1}, 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, CH_3SiCl_3, (MTS) 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 1. 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],

* Corresponding author. Tel.: +46 13 28 24 76; fax: +46 13 14 23 37.
E-mail address: henke@ifm.liu.se (H. Pedersen).

0257-8972/$ - see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.surfcoat.2007.03.052

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. used MTS to grow 6H-SiC [18] but without focusing on growth rates. Lu et al. grew 4H- and 6H-SiC in a small cold wall CVD reactor using MTS [19] 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

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 $[11\bar{2}0]$ 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 and etch away small scratches on the substrate. The susceptor is then further heated to 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 a 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(220) configuration and a channel cut analyzer with 12 arc sec acceptance in triple axis setup, and by (2) low temperature photo luminescence (LTPL) in a bath cryostat with the temperature kept at 2 K; the 244 nm Ar^+ laser line was used as excitation. The luminescence was dispersed by a single monochromator on which a UV sensitive CCD camera was mounted to rapidly detect the LTPL spectrum.

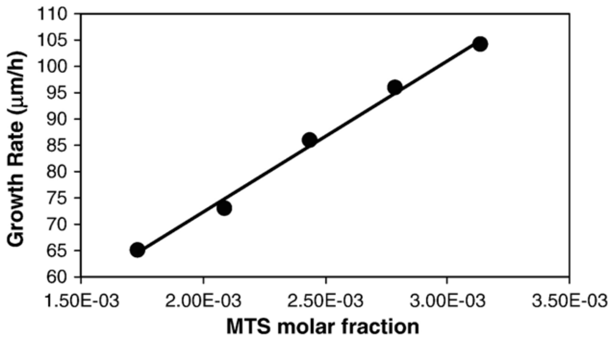

Fig. 1. Growth rate of 4H-SiC epitaxial layers for various flows of MTS. All layers are grown at 1600 °C using only MTS as precursor; only the flow of MTS into the reactor is changed between the runs.

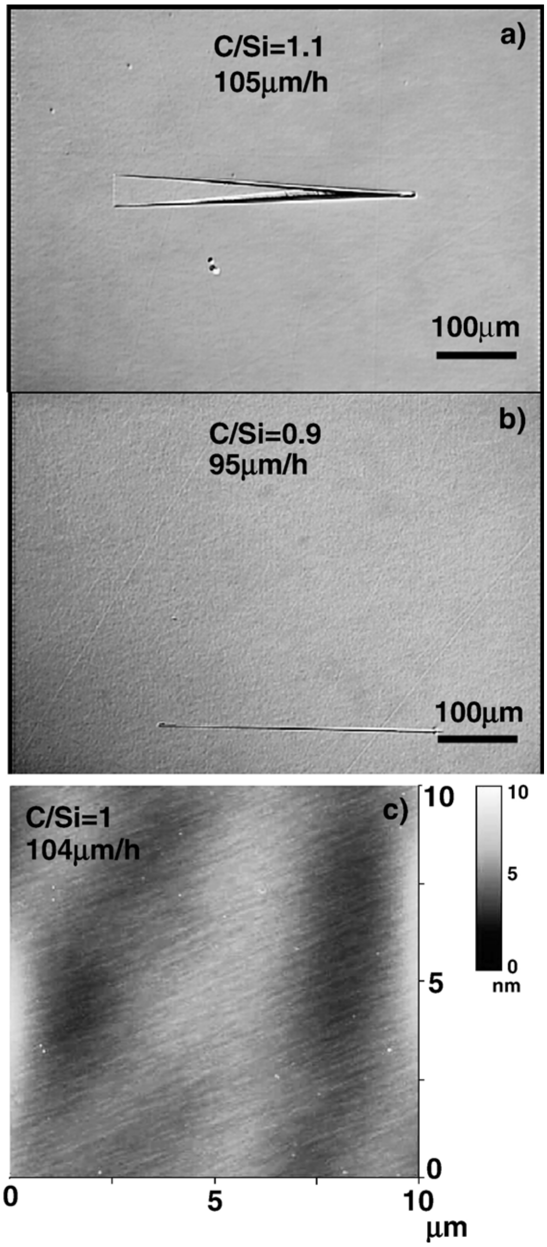

Fig. 2. The morphology of the epitaxial layers illustrated by Nomarski microscope images showing the morphology and epi-defect shape of a) a 52 μm thick epilayer grown with C/Si = 1.1 and b) a 48 μm thick epilayer grown with C/Si = 0.9, in c) a 10 × 10 $μm^2$ AFM image of a 52 μm thick epilayer grown with C/Si = 1; the RMS value is 7 Å.

3. Results and discussion

3.1. Growth rate and morphology

The growth rate dependence of the MTS flow is given in Fig. 1. The highest growth rate achieved was 104 μm/h. Only the flow of MTS was varied between the different growth runs presented in Fig. 1.

The grown epilayers have very smooth morphology, for all growth rates investigated, as shown in the Nomarski microscope images in Fig. 2a) and b). The images also show how the shape of the typical epilayer defect observed varies with the 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. AFM measurements of the surface roughness of the epilayers give an RMS value of 7 Å for a 52 μm epilayer grown at 104 μm/h (on the $10\times10\ \mu m^2$ area shown in Fig. 2c). This is comparable with the value previously reported for a 42 μm epilayer grown using the standard $SiH_4+C_3H_8$ process at 5 μm/h [21].

3.2. Quality of the grown material

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 shows a FWHM of 17 arc sec, which is similar to what has previously been reported by Lu et al. [19]. The beam size used was $0.2\times0.2\ mm^2$.

To further investigate the impurity levels and also the crystal quality of the grown epilayers LTPL was used. The LTPL spectra recorded from the samples grown with high growth rate exhibit typical 4H-SiC luminescence as shown in Fig. 3. The spectra are dominated by the near-band gap emission with free exciton (FE) related lines 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 b) in the insert) which confirm the results obtained by CV with p-type conductivity and very low net doping. As stated earlier, the nitrogen comes from contamination of the MTS bubbler, aluminium is believed to come from the graphite susceptor. Nitrogen and aluminium incorporation into SiC can be controlled by adjusting the C/Si ratio within the site competition theory described in detail elsewhere [12]. It is believed that nitrogen replaces carbon while aluminium replaces silicon in the SiC lattice. Other luminescence features such as the D_I center or the Ti related lines were only weakly observed. The D_I center is believed to 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.

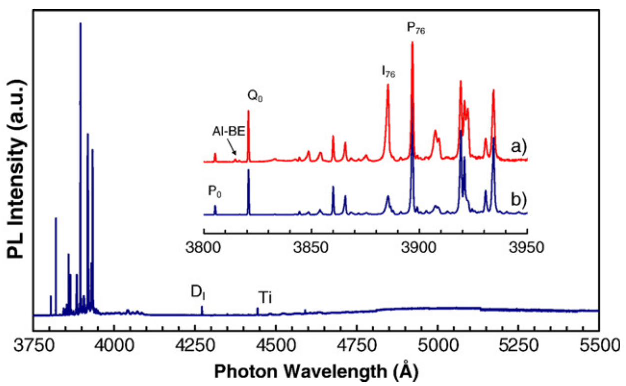

Fig. 3. LTPL spectra recorded from a sample grown with C/Si = 0.9 and a growth rate of 95 μm/h. The inset shows the near-band gap emission for a) the same sample and b) a sample with C/Si = 1.2 grown at 105 μm/h.

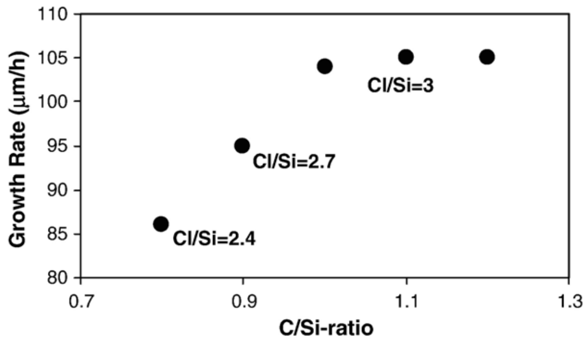

Fig. 4. Growth rate of 4H-SiC epitaxial layers for various C/Si ratios. The total amount of Si into the reactor is constant for all the runs, the changing Cl/Si ratio is indicated in the plot.

3.3. Effect of C/Si ratio

The C/Si ratio is an important parameter in epitaxial growth of SiC since it influences the incorporation of dopants and impurities. To study how different C/Si ratios affect the growth rate 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

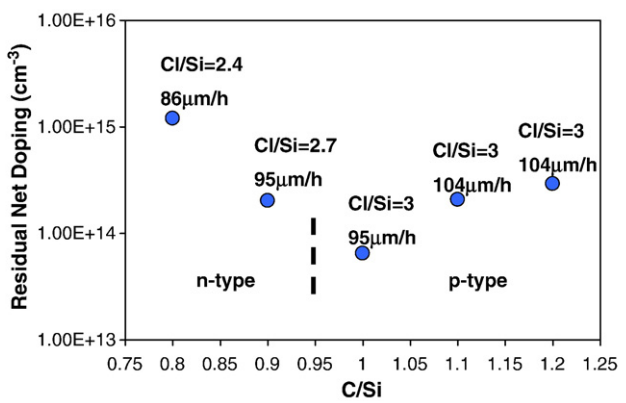

Fig. 5. The residual net doping for various C/Si ratios. Note that the growth rate and Cl/Si ratio are not the same for all runs, as indicated by the inserts in the plot. The dashed vertical line in the plot shows which epilayers are n- and p-type.

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 Cl/Si ratio is a process parameter in the chloride-based growth of SiC of which the importance is not yet fully investigated.

In Fig. 4, the growth rate for various C/Si ratios is given. 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 Cl/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.

For unintentionally doped layers, the net doping dependence of the C/Si is plotted in Fig. 5. It can be seen that the lowest net doping is achieved for C/Si = 1. At lower C/Si ratio the epilayers are more n-type doped, while a higher C/Si ratio gives more p-type doped layers. According to the LTPL measurements, the n-type doping is caused by nitrogen and the p-type dopant by aluminium. From Fig. 5, it can be seen that more nitrogen is incorporated when the C/Si and Cl/Si ratios are decreased. If also the growth rate is decreased, even more nitrogen is incorporated. This is in line with previous results for the standard process [23]. For the p-type layers, the aluminium incorporation increases with increasing growth rate and also with higher C/Si ratio, also this in line with previous results for the standard 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.

Surface morphology was also 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. 2. Also the density of these defects increased at higher C/Si ratio.

4. Conclusions

This study shows that the chloride containing precursor MTS can be used to grow 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.

Acknowledgement

The Swedish Foundation for Strategic Research (SSF) is gratefully acknowledged for financial support.

References

[1] R.L. Meyers, Y. Shishkin, O. Kordina, S.E. Saddow, J. Cryst. Growth 285 (2005) 486.
[2] J. Zhang, J. Mazzola, C. Hoff, Y. Koshka, J. Casady, Mater. Sci. Forum 483–485 (2005) 77.
[3] T. Kimoto, H. Matsunami, European Conference on Silicon Carbide and Related Materials 2006, to be published in Mater. Sci. Forum 2007.
[4] G. Aylward, T. Findlay, SI Chemical Data, 4th ed., John Wiley & Sons Australia, Milton, 1998, p. 115.
[5] D. Crippa, G.L. Valente, A. Ruggiero, L. Neri, R. Reitano, L. Calcagno, G. Foti, M. Mauceri, S. Leone, G. Pistone, G. Abbondanza, G. Abbagnale, A. Veneroni, F. Omarini, L. Zamolo, M. Masi, F. Roccaforte, F. Giannazzo, S. Di Franco, F. La Via, Mater. Sci. Forum 483–485 (2005) 67.
[6] R. Myers, O. Kordina, Z. Shishkin, S. Rao, R. Everly, S.E. Saddow, Mater. Sci. Forum 483–485 (2005) 73.
[7] F. La Via, G. Galvagno, G. Foti, M. Mauceri, S. Leone, G. Pistone, G. Abbondanza, A. Veneroni, M. Masi, G.L. Valente, D. Crippa, Chem. Vap. Depos. 12 (2006) 509.
[8] S. Leone, M. Mauceri, G. Pistone, G. Abbondanza, F. Portuese, G. Abagnale, G.L. Valente, D. Crippa, M. Barbera, R. Reitano, G. Foti, F. La Via, Mater. Sci. Forum 527–529 (2006) 179.
[9] M.F. MacMillian, M.J. Loboda, G. Chung, E. Carlson, J. Wan, Mater. Sci. Forum 527–529 (2006) 175.
[10] G. Dhanaraj, M. Dudley, Y. Chen, B. Ragothamachar, B. Wu, H. Zhang, J. Cryst. Growth 287 (2006) 344.
[11] Y. Koshka, H.-D. Lin, G. Melnychuk, C. Wood, J. Cryst. Growth 294 (2006) 260.
[12] D.J. Larkin, Phys. Status Solidi B 202 (1997) 305.
[13] Th. Kunstmann, S. Veprek, Appl. Phys. Lett. 67 (21) (1995) 3126.
[14] M.T. Schulberg, M.D. Allendorf, D.A. Outka, Surf. Sci. 341 (1995) 262.
[15] A.J. Steckl, J. Devrajan, S. Tlali, H.E. Jackson, C. Tran, S.N. Gorin, L.M. Ivanova, Appl. Phys. Lett. 69 (25) (1996) 3824.
[16] S.N. Gorin, L.M. Ivanova, Phys. Status Solidi, B Basic Res. 202 (1997) 221.
[17] J. Hofmann, S. Veprek, Thin Solid Films 318 (1998) 18.
[18] V.V. Zelenin, V.G. Solov'ev, S.M. Starobinets, S.G. Konnikov, V.E. Chelnokov, Semiconductors 29 (6) (1995) 581.
[19] P. Lu, J.H. Edgar, O.J. Glembocki, P.B. Klein, E.R. Glaser, J. Perrin, J. Chaudhuri, J. Cryst. Growth 285 (2005) 506.
[20] A. Henry, J. Hassan, J.P. Bergman, C. Hallin, E. Janzén, Chem. Vap. Depos. 12 (2006) 475.
[21] H. Pedersen, A. Henry, J. Hassan, J.P. Bergman, E. Janzén, European Conference on Silicon Carbide and Related Materials 2006, to be published in Mater. Sci. Forum 2007.
[22] T. Kimoto, H. Nishino, W.S. Yoo, H. Matsunami, J. Appl. Phys. 73 (2) (1993) 726.
[23] U. Forsberg, Ö. Danielsson, A. Henry, M.K. Linnarsson, E. Janzén, J. Cryst. Growth 236 (2002) 101.
[24] U. Forsberg, Ö. Danielsson, A. Henry, M.K. Linnarsson, E. Janzén, J. Cryst. Growth 253 (2003) 340.