phys. stat. sol. (RRL) **2**, No. 4, 188–190 (2008) / **DOI** 10.1002/pssr.200802081

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Very high crystalline quality of thick 4H-SiC epilayers grown from methyltrichlorosilane (MTS)

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Received 30 April 2008, accepted 9 May 2008
Published online 15 May 2008

PACS 61.05.cp, 68.55.ag, 78.55.Hx, 81.05 Hd, 81.10.Bk, 81.15.Gh

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200 µm thick 4H-SiC epilayers have been grown by chloride-based chemical-vapor deposition using methyltrichlorosilane (MTS) as single precursor. The very high crystalline quality of the grown epilayer is demonstrated by high resolution X-Ray Diffraction rocking curve with a full-width-half-maximum value of only 9 arcsec. The high quality of the epilayer is further shown by low temperature photoluminescence showing strong free exciton and nitrogen bound exciton lines. The very high crystalline quality achieved for the thick epilayer grown in just two hours at 1600 °C suggests that MTS is a suitable precursor molecule for SiC bulk growth.

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 very high voltage SiC devices thick (>100 µm) low-doped epilayers are needed. In order to grow such thick epilayers in a reasonable time, a chloride-based CVD technique has been developed [1–6], where chlorine is added to the gas mixture either as HCl or by use of some chlorinated silicon- or carbon precursor, allowing growth rates higher than 100 µm/h, as compared to about 5 µm/h for the standard growth process (with silane and hydrocarbon precursors). Also a bulk CVD process, called halide CVD (HCVD), using the chlorinated silicon precursor $SiCl_4$ at temperatures in the 2000–2200 °C range, has been developed [7–9] and growth rates as high as 300 µm/h and 300 µm thick boules have been demonstrated. In this study, we have used methyltrichlorosilane (MTS), CH_3SiCl_3, as SiC precursor, providing carbon, silicon and chlorine to the gas mixture. We have recently showed that MTS can be used to grow 4H-SiC epilayers with growth rates up to 170 µm/h [10], and in this letter we now show that it is possible to grow epilayers as thick as 200 µm, a thickness sufficient for 25 kV blocking SiC devices, in a very short time.

The epilayers were homoepitaxially grown in a horizontal hot wall CVD reactor [11] using n-type 4H-SiC (0001) wafers as substrates, which were Si-face and off-cut 8° towards the $[11\bar{2}0]$ direction. The epilayers were grown for two hours with a MTS-molar fraction corresponding to a growth rate of 100 µm/h [5]. No intentional dopant was added to the gas mixture during the growth. The growth process has previously been described in detail [5].

The epilayer thickness was measured by Fourier transform infrared (FTIR) reflectance and by studying the cross section of the epilayer by optical microscopy. The net doping was studied with capacitance–voltage measurements (CV) using a mercury probe. The crystalline quality of the grown material was investigated by (i) high-resolution X-ray diffraction (HRXRD), using a triple axis diffractometer equipped with a four-crystal monochromator in Ge(220) configuration and a channel cut analyzer with 12 arcsec acceptance in triple axis setup, and by (ii) low temperature photoluminescence (LTPL) in a bath cryostat with the temperature kept at 2 K; the 351 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).

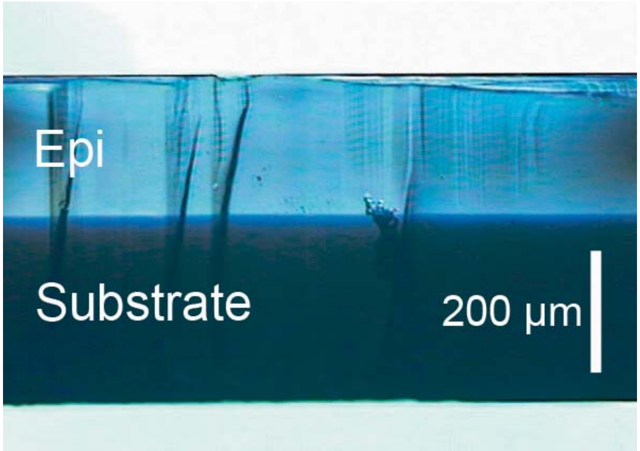

Figure 1 (online colour at: www.pss-rapid.com) Cross sectional view in an optical microscope of the 200 µm thick epilayer grown in two hours time at 100 µm/h using MTS as single precursor. Some damages (vertical and horizontal features) related to the cleaving of the sample are seen.

A cross sectional view of the grown epilayer is shown in Fig. 1; the epilayer is slightly thicker than 200 µm and there is no visual evidence of degradation of the crystalline quality due to the thickness of the layer or the high growth rate.

The residual net doping in the epilayer was determined to be n-type 4.0×10^{14} cm^{-3} as measured both by CV and PL [12]. The PL measurements also suggest that the n-type dopant is nitrogen, most likely emanating from contaminations in the MTS bubbler. In our previous investigation using similar growth conditions we achieved p-type background doping in the low 10^{14} cm^{-3} range but then a different MTS bubbler was used [5].

The LTPL spectra recorded from the 200 µm thick sample exhibit typical 4H-SiC luminescence as shown in Fig. 2.

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}) and is very similar to spectra obtained from high quality samples grown using the standard, low growth rate process. Other luminescence features such as the D_I center or the Ti related lines are only very 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.

Possible chlorine incorporation in the epilayer was investigated by secondary ion mass spectrometry (SIMS), which showed that the chlorine content in the epilayer was 1×10^{14} cm^{-3}, a value close to the SIMS detection limit for Cl. There have been no other reports on chlorine content in SiC grown by chloride-based CVD as far as we are aware of.

HRXRD ω-scan rocking curve measurements were performed on the epilayer and the rocking curve from the (0004) plane is shown in Fig. 3. The full width at half maximum (FWHM) of the ω-scan rocking curve peak, measured with a 10×10 mm^2 footprint, is only 9 arcsec showing that the epilayer is of very high crystalline quality. The width of the $2\theta/\omega$ scan peak (1×1 mm^2 footprint) is only 18 arcsec showing very low strain in the material.

From the HRXRD measurements it is clear that the crystalline quality is high and well in line and even better than what has been published for 6H-SiC bulk material grown by halide CVD, where FWHM of about 30 arcsec for ω-scans and 19 arcsec for $2\theta/\omega$ scan measured on a 200 µm thick layer have been reported [8]. Here it should also be noted that the HCVD grown material has been grown in a vertical bulk reactor at significantly higher temperature, while we have used a horizontal epi reactor. The FWHM of the rocking curve is substantially smaller

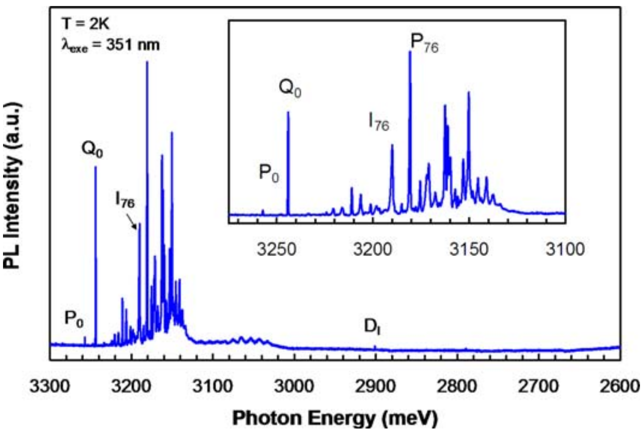

Figure 2 (online colour at: www.pss-rapid.com) Low temperature photoluminescence spectrum of the 200 µm thick epilayer. The insert shows the near band gap emission.

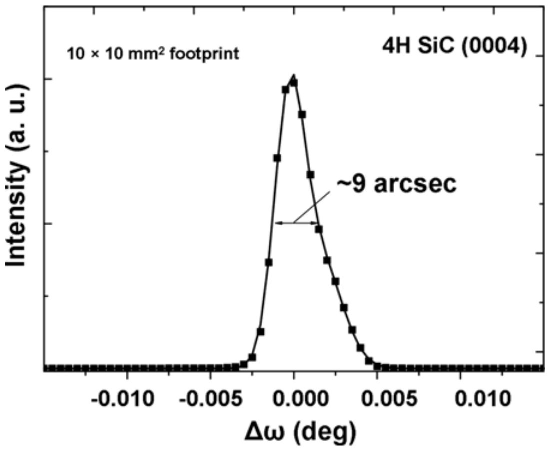

Figure 3 High resolution rocking curve of the 0004 peak for the 200 µm thick 4H-SiC epilayer. The FWHM of the peak is 9 arcsec.

than that we have previously reported for thinner epilayers of SiC grown from MTS [5]. This can be explained by the model previously suggested for improved crystalline quality in thick sublimation grown epilayers [13]. In this model, domains from the substrate at the substrate edge opposite to $[11\bar{2}0]$ grow larger in the step-flow direction during step-flow growth, and in the ideal case an epilayer should then consist of just one domain if it is thick enough.

EPR and FT-IR measurements indicate that the grown material is very pure; in EPR only one very weak peak could be observed to rise above the noise and is attributed to SI-1 [14, 15]. The only detected peaks in the FT-IR spectrum are attributed to V, Cr and UD-1 [16], all of them with very low intensities.

This study shows that the chloride containing precursor MTS can be used as single molecule SiC precursor for growth of very thick low-doped, high crystalline quality SiC epilayers at high growth rates (>100 µm/h). The fact that SiC growth from MTS gives 200 µm single crystal epilayers with good crystalline quality indicates that MTS could be a good precursor molecule also for SiC bulk growth.

Acknowledgements The Swedish Foundation for Strategic Research (SSF) and the Swedish Research Council (VR) are gratefully acknowledged for financial support.

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