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Use of chlorinated carbon and silicon precursors for epitaxial growth of 4H-SiC at very high growth rates

Siva Kotamraju, Bharat Krishnan, and Yaroslav Koshka[*]

Department of Electrical and Computer Engineering, Mississippi State University, Mississippi State, MS 39762, USA

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[*] Corresponding author: e-mail ykoshka@ece.msstate.edu

A possibility to apply the advantages of chlorinated carbon precursors, which had been previously used in low-temperature epitaxial growth of 4H-SiC, to achieve very high growth rates at higher growth temperatures was investigated. Silicon tetrachloride was used as the silicon precursor to suppress gas-phase homogeneous nucleation. The temperature increase from 1300 °C (which is the temperature of the previously reported low-temperature halo-carbon epitaxial growth) to 1600 °C enabled an increase of the precursor flow rates and consequently of the growth rate from 5 to more than 100 µm/h without morphology degradation. High quality of the epilayers was confirmed by low-temperature photoluminescence spectroscopy and time-resolved luminescence. No evidences of homogeneous nucleation were detected, however, liquid Si droplet formation on the epilayer surface seems to remain a bottleneck at very high growth rate.

Demanding high-voltage applications require very thick SiC epitaxial layers (>100 µm) having low values of doping. Therefore cost efficient production of SiC high-voltage devices calls for growth rates as high as 100 µm/h. Recent developments in chloride-based epitaxial techniques to address this goal occurred in two main directions: (1) adding HCl during the epitaxial growth to induce dissociation of the gas-phase Si clusters [1, 2], and (2) use of chlorinated silicon precursors [3–5]. Use of the single chlorinated precursor methyltrichlorosilane showed the most promising results so far, though optimisation of the growth rate and doping homogeneity is yet to be demonstrated [6, 7].

In our previous work, the chloro-carbon precursor chloromethane (CH_3Cl) allowed achieving good-quality epitaxial layers at 1300 °C [8, 9]. Also, by replacing SiH_4 with $SiCl_4$, the problem of homogeneous nucleation was entirely eliminated in the low-temperature growth [10], while preserving the apparent advantages of CH_3Cl for the surface reactions as compared to the traditional hydrocarbon precursors. However, it remained unknown if the chloro-carbon precursor would provide favourable growth mechanisms at more traditional higher growth temperatures. In this work, the $CH_3Cl/SiCl_4$ precursor system was investigated at temperatures up to 1600 °C for the first time to drastically increase the growth rate compared to the growth at 1300 °C [10].

Commercial 8° off-axis 4H-SiC wafers were used as substrates for epitaxial growth. Growth experiments were performed in a horizontal hot wall CVD reactor at 140 Torr, with H_2 as the carrier gas, CH_3Cl as the carbon source and silicon tetrachloride ($SiCl_4$) as the silicon source. The thickness of the epilayers was measured by reflective Fourier Transform Infrared Spectroscopy (FTIR). The surface morphology was examined by Nomarski optical microscopy and scanning electron microcopy (SEM). The low-temperature photoluminescence (LTPL) measurements were conducted at ~15 K using an Ar^+ laser line of 301 nm wavelength as the PL excitation source, and a SPEX 500M grating spectrometer coupled with a Jobin Yvon Symphony 2048 × 512 CCD detector. Photoluminescence decay at the wavelength of the bandgap emission at room temperature was measured using the 337 nm line of a pulsed nitrogen laser (4 ns pulse width) and a Hamamatsu R928 multi-alkali photo-multiplier tube (PMT) operating in the photon counting mode.

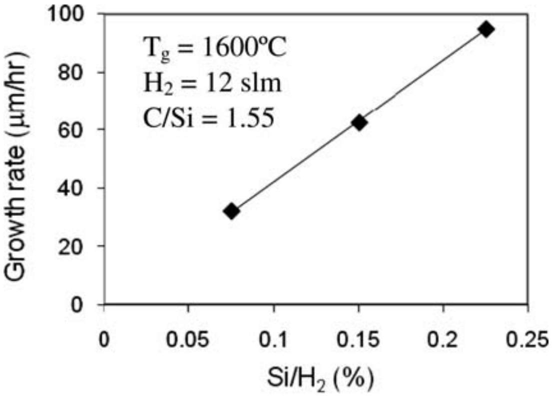

Figure 1 Growth rate of 4H-SiC epitaxial layer during CH_3Cl/$SiCl_4$ growth at 1600 °C at various flows of $SiCl_4$, with other conditions kept unchanged. Higher $SiCl_4$ flow to achieve yet higher R_g is yet to be attempted.

A growth rate (R_g) close to 100 μm/h was achieved at T_g = 1600 °C with almost featureless epilayer morphology. No vapor cloud of Si gas-phase clusters could be observed at the highest $SiCl_4$ flow attempted. The R_g dependence on $SiCl_4$ flow (Fig. 1) was linear in the entire range investigated, which also confirms that the homogeneous nucleation of Si-related species is essentially eliminated.

It was confirmed that the maximum R_g without morphology degradation strongly depends on the growth temperature T_g (Fig. 2). After measuring the curve (a) in Fig. 2, the growth was repeated at 1500 °C at exactly the same growth conditions (not shown). An only modest increase of R_g was observed. The study of the activation energy of this process is beyond the scope of this paper. However, the increase of T_g from 1300 °C to 1500 °C made it possible to increase the $SiCl_4$ flow rate by almost an order of magnitude, which resulted in about an order of magnitude increase in R_g (Fig. 2, curve (b)).

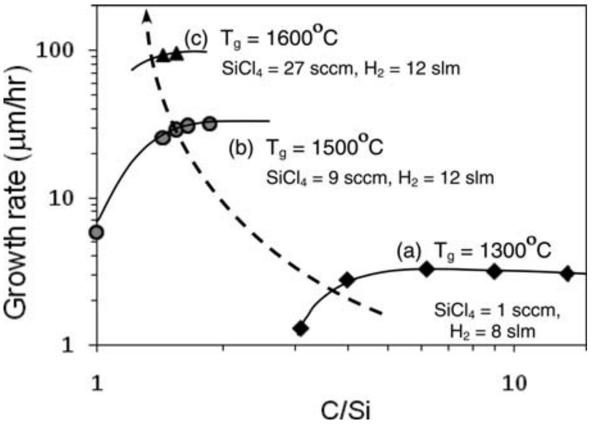

Figure 2 Growth rate versus C/Si ratio at (a) 1300 °C [10], (b) 1500 °C, and (c) 1600 °C. The $SiCl_4$ flows used in (a), (b), and (c) correspond to roughly the highest growth rate before morphology degradation. The H_2 flow was also adjusted with temperature to preserve good R_g homogeneity from upstream to downstream.

It should be noted that with increasing T_g, the R_g homogeneity deteriorated from upstream to downstream (i.e., R_g is higher at the leading edge of the wafer and drops downstream). The H_2 flow rate had to be increased by ~50% to restore the R_g homogeneity.

Comparison of the R_g dependence on the C/Si ratio at 1300 and 1500 °C (Fig. 2, curves (a) and (b)) showed a drastic change in the knee point separating the Si- and C-supply limited modes (approximately delineated with the dotted line in Fig. 2). Lower values of the C/Si ratio are required at higher T_g to enter the Si-supply limited mode. This sheds additional light on the relative kinetics of volumetric reactions involving $SiCl_4$ and CH_3Cl precursors, indicating that at 1300 °C the supply of C species to the epitaxial surface lags behind that of Si species, which requires higher values of the input C/Si ratio to provide the optimal value of the effective C/Si ratio at the growth surface. At higher T_g, the chemical reactions (possibly both volumetric and surface reactions) operate close to equilibrium bringing the knee-point value of the input C/Si ratio closer to 1.

Further increase of T_g to 1600 °C allowed an additional, at least three-times increase in $SiCl_4$ flow without morphology degradation, and consequently a proportional increase in R_g up to >90 μm/h (Fig. 2 curve(c)).

The morphology dependence on the value of the C/Si ratio at 1300 °C (corresponding to Fig. 2 curve (a)) is reported elsewhere [10]. However, the morphology limiting mechanisms for CH_3Cl/$SiCl_4$ growth at higher T_g were expected to be different. Nomarski optical micrographs of epilayers grown at 1500 °C at two extreme values of the C/Si ratio of 1 and 1.86 showed distinct patterns of morphology degradation (Fig. 3). At higher CH_3Cl flow rates, line defects appeared predominantly oriented along the off-cut direction of the 8° off-axis substrate (Fig. 3b). At yet higher values of the C/Si ratio, this pattern developed into severe step-bunching (not shown).

At lower flows of CH_3Cl (i.e., C/Si = 1), the excess of Si over C at the growth surface resulted in the formation of Si droplets (Fig. 3a). At slightly higher values of the C/Si ratio (up to ~1.4), rare pits of evaporated Si droplets were observed at the epilayer surface. Apparently, the droplets

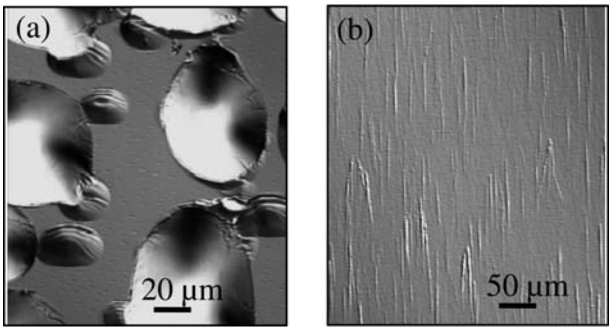

Figure 3 Nomarski optical micrographs of epitaxial layers grown with high R_g at 1500 °C at two extreme values of C/Si ratio: (a) C/Si = 1 and (b) C/Si = 1.86. Mirror-like epilayer morphology was observed at intermediate values of the C/Si ratio.

are not a result of Si raining on the epilayer surface following the homogeneous nucleation during the Si precursor dissociation, since this mechanism was shown to be largely suppressed by using the $SiCl_4$ precursor. Instead, surface reactions involving the products of CH_3Cl and $SiCl_4$ decomposition favor relatively high silicon partial pressure at the growth surface.

A nearly featureless morphology was obtained at conditions corresponding to the data points of curve (c) in Fig. 2. However, rare pits of evaporated droplets were observed at some location on the wafer. The R_g and morphology dependence on the C/Si ratio at 1600 °C is yet to be investigated.

LTPL confirmed the high quality of the 50 µm thick epitaxial layer grown with $R_g = 90$ µm/h. Strong low-temperature photoluminescence with sharp excitonic lines was observed (Fig. 4). Due to the insufficiently baked susceptor that was previously used for trimethylaluminum (TMA) doping, a significant emission of aluminum and nitrogen bound excitons was observed (e.g., the Al-BE, Q_0 and P_{76} lines). However, the intensity of the free exciton emission (e.g., I_{76} line) was also relatively strong. The epilayers were closely compensated, with the net free dopants concentration below 5×10^{14} cm^{-3}, as measured by the capacitance–voltage technique. The intrinsic defect D_I line and the titanium line Ti are very weak.

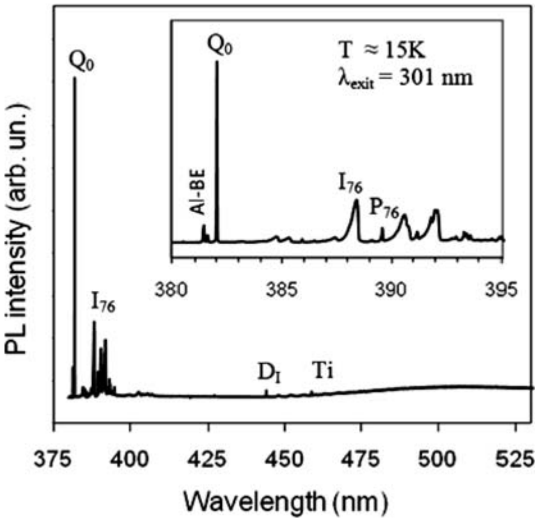

Figure 4 PL spectrum of a 50 µm thick epitaxial layer grown at 1600 °C. The inset shows the near-bandgap portion of the spectrum dominated by nitrogen bound excitons (e.g., the Q_0 and P_{76} lines), free excitons (the I_{76} line), and the aluminum bound exciton (Al-BE). The intrinsic defect D_I line and the titanium line Ti are very weak.

Two values of the PL decay time constants – 150 and 780 ns – were extracted. Besides a possible contribution from the surface recombination, the value of the minority carrier lifetime is expected to be reduced due to a significant concentration of nitrogen and aluminium dopants (Fig. 4). The standard efforts to achieve high purity thick epitaxial layers will be undertaken in subsequent work.

In summary, the very first attempt of applying the CH_3Cl precursor to the higher temperature growth was successful and revealed a possibility of increasing the growth rate beyond 100 µm/h. Use of $SiCl_4$ as the silicon precursor along with CH_3Cl is essential in suppressing the homogeneous nucleation in the gas phase. However, the relative importance of the two chlorinated precursors for achieving high crystalline quality at high growth rate remains to be investigated. The lower values of the C/Si ratio will be essential for avoiding the step bunching; however, other growth condition dependencies should be investigated to eliminate the problem of Si droplets. Further increase of the growth rate and longer growth time in order to achieve very thick epitaxial layers is the subject of future work.

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