

# Precise Control of Al Incorporation during CVD Growth of SiC Epilayers by Using Hydrogen Chloride

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**Abstract.** Experimental results presented in this contribution demonstrate that adding HCl to the SiC CVD process is not only an efficient way to suppress the Aluminum memory effect but may also be considered as a powerful tool for fine tuning of intentional Al incorporation in 3C-SiC and 4H-SiC thin films. The approach is easy to implement and seems more reliable than changing TMA bubbling/dilution parameters during the growth. An *ad-hoc* phenomenological model is proposed to explain the correlation between the HCl supply and Al incorporation.

## Introduction

Aluminum is a principal p-type dopant in silicon carbide epitaxy. Precise and reproducible control of epilayer doping is of major concern in fabrication of epitaxial stacks for electronic devices. It requires a detailed understanding of the influence that the growth conditions may have on dopant incorporation (see [1] and references therein).

The precursor used in CVD growth of Al-doped SiC epilayers is liquid Tri-Methyl-Aluminum (TMA). The TMA bubbler has to be kept under stabilized pressure / temperature and connected to an H<sub>2</sub> dilution line to allow fine tuning of precursor supply. Consequently, modifications of the TMA supply during the growth process are more complex to achieve than for gas precursors (like Nitrogen as n-type dopant), due to longer stabilization times.

Another issue in SiC:Al deposition is related to the Al memory effect [2] which prevents obtaining sharp doping interface after growing heavily Al-doped layer and maintains high residual incorporation of Aluminum in subsequent runs. Several solutions limiting the influence of this uncontrolled Al contamination were proposed: reactor baking between runs, site-competition growth with high Si/C ratio or adding hydrogen chloride (HCl) gas to the process. The latter solution, proposed by Ji et al, was particularly efficient to reduce Al residual and achieve abrupt p+/NID interface [3], however the mechanism was not explained.

To better understand the interplay between the presence of HCl during the growth process and the reduction of Al incorporation in the epilayer we performed a series of growth experiments involving simultaneous introduction of TMA and HCl in the reactor chamber. The growth trials included heteroepitaxial 3C-SiC/Si and homoepitaxial 4H-SiC growth. We used SIMS, C-V and contactless sheet resistance measurements to evaluate the variations of doping between samples. The results led us to propose a phenomenological model that explains Al doping variations observed experimentally.

## Experimental Details

**CVD setup.** SiC thin films were deposited in previously described horizontal, low pressure, resistively heated hot wall CVD system with rotating sample holder [4]. Standard chemistry was used with purified hydrogen (H<sub>2</sub>) as carrier gas, high purity (5N) silane (SiH<sub>4</sub>) and propane (C<sub>3</sub>H<sub>8</sub>) as

principal precursors, Tri-Methyl-Aluminum (TMA) as Al source and hydrogen chloride (HCl) diluted in H<sub>2</sub>. The bubbler containing liquid TMA under stabilized pressure / temperature was connected to H<sub>2</sub> dilution line, allowing the control of TMA supply in the range  $1 \times 10^{-4}$  – 2 sccm. The supply of pure HCl could be controlled in the range 1-100 sccm.

**Table 1:** Characteristics of sample series analyzed in present study.

Series	Polytype	T <sub>EPI</sub> (°C)	Growth Rate (μm/h)	TMA (sccm)	HCl (sccm)
(A)	3C-SiC	1400	2	$4.0 \times 10^{-3} - 1.1 \times 10^0$	0
(B)				$2.3 \times 10^{-1} - 9.1 \times 10^{-1}$	0
(C)				$9.1 \times 10^{-1}$	0 – 40
(D)				$5.6 \times 10^{-2}$	0 – 21
(E)				$1.7 \times 10^{-1}$	0 – 42
(F)	4H-SiC	1750	15	$1.1 \times 10^0$	0 – 42
(H)				$1.1 \times 10^{-1}$	0 – 100

**Sample growth.** The deposition of 3C-SiC films on Si(100) on-axis substrates was performed using broadly described 3-step process (annealing / carbonization / CVD) with CVD step at relatively high temperature (~1400°C) and low growth rate (2 μm/h) in order to attain the best possible structural quality of 3C-SiC epilayer. Typical 3C-SiC film characteristics are given in Ref. [5]. Additionally, homoepitaxial 4H-SiC films were deposited on the Si-face of 4H-SiC 4° off substrates. Growth was carried out at 1750°C with deposition rate of 15 μm/h under different TMA and HCl flow rates.

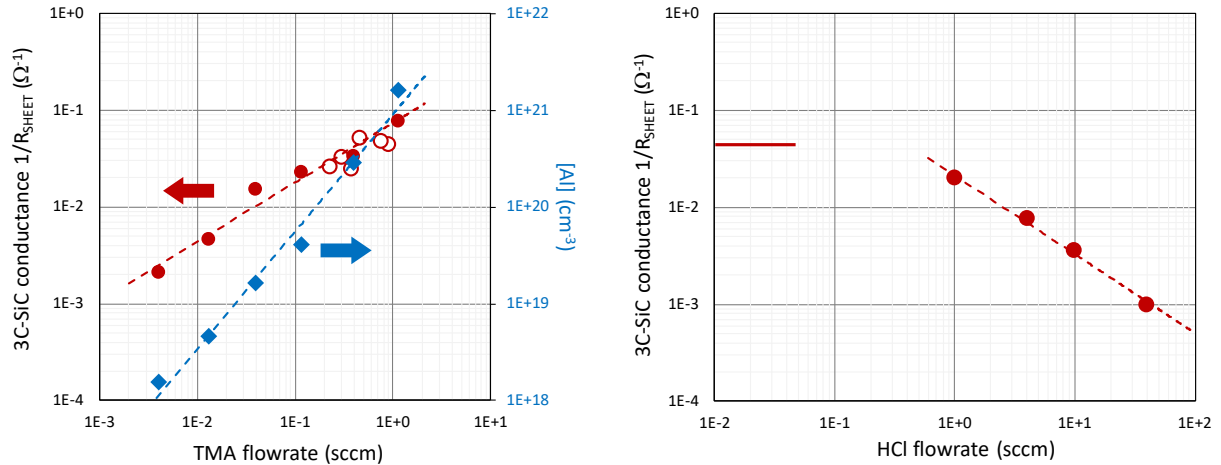
**Samples.** Three series of ~1 μm thick 3C-SiC(100) epilayers were prepared. Series (A) and (B) were grown without HCl, with different TMA flow rates ( $\Phi_{\text{TMA}}$ ). For series (C), the TMA was fixed and various HCl flow rates were applied. Furthermore, 3C-SiC multilayer stacks (D-F), for SIMS analyses of Al incorporation [Al], were deposited by varying TMA and HCl flow rates. For each SIMS sample deposition started with NID SiC grown without HCl (step 1), then HCl was added (step 2). TMA with constant flow rate was introduced into reactor during step 3 and HCl flow rate was progressively reduced to zero (steps 3-10). The process finished with NID layer (step 11) grown under same HCl flow as in step 2. The experiments were performed for three different TMA flow rates.

For 4H-SiC we show in this paper the results for a representative series of samples grown with TMA supply 0.11 sccm, under HCl flow rates covering all the available range 0-100 sccm. The results will be referred to as series (H). The principal characteristics of sample series are shown in Table 1.

**Characterizations.** Secondary ion mass spectrometry (SIMS) measurements of [Al] depth profiles were carried out on a Cameca IMS 6f machine using a  $^{16}\text{O}_2^+$  primary beam and positive secondary ions ( $^{27}\text{Al}^+$  for Al and  $^{30}\text{Si}_2^+$  as reference signal). Usual detection limit (DL) for Al was  $\sim 10^{15}$  at/cm<sup>3</sup>. For 3C-SiC/Si samples, the sheet resistance  $R_{\text{SHEET}}$  and conductance ( $1/R_{\text{SHEET}}$ ) of 3C-SiC film was systematically estimated from contactless, eddy current measurements of the wafer before / after the growth. For 4H-SiC samples Al incorporation was estimated from C-V measurements with an Hg-probe.

## Experimental Results

Figure 1a shows the evolution of 3C-SiC conductance ( $1/R_{\text{SHEET}}$ ) with  $\Phi_{\text{TMA}}$  for sample series (A) and (B). [Al] is also reported. As expected, stronger conductance was measured for samples with high [Al]. The observed conductance variation (less than 2 decades) is smaller than that of [Al] (3 decades) due to concomitant evolution of carrier mobility [6].



**Figure 1:** (a) Conductance of 3C-SiC epilayers as a function of Al supply for sample series (A-B), full & open circles. [Al] values for series (A) are also reported (full diamonds). (b) Conductance of 3C-SiC epilayers (series (C)) as a function of HCl supply.

In Figure 1b the evolution of conductance with HCl flow rate ( $\Phi_{\text{HCl}}$ ) for sample series (C) shows clearly decreasing trend. We conjecture that observed tendency reflects the reduction of Al incorporation under HCl flow. This supposition is confirmed by SIMS analyses of multilayer samples (D-F). Figure 2a shows the [Al] profile for the sample (D). It reflects the doping sequence described in previous section. The [Al] peak at the interface is related to the presence of residual impurities in the reactor. Introduction of HCl in step 2 leads to the reduction of [Al] down to SIMS detection limit, validating the previous observations of Ji et al [5]. After the introduction of TMA, [Al] increases with decreasing HCl flow rate ( $\Phi_{\text{HCl}}$ ), following well defined levels for every growth step 3-10. During the last NID step (11), with HCl, [Al] is reduced to a level as low as in the step 2. The 3 decades' [Al] transition between steps 10 and 11 is extremely abrupt.

The aluminum concentrations obtained in samples (D-F) are presented in Figure 2b as a function of  $\Phi_{\text{HCl}}$ , using log-log scale. The incorporation without HCl is also reported (solid, horizontal lines on the left part of the plot). For each dataset, the points follow a line with constant slope close to -1, suggesting inversely proportional dependence of [Al] *versus*  $\Phi_{\text{HCl}}$ . Interesting point is that even for low value  $\Phi_{\text{HCl}}=3\text{sccm}$ , almost tenfold reduction of [Al] is observed with respect to incorporation without HCl. On the same Figure 2 we reported also the results of series (H) obtained for 4H-SiC. As for 3C-SiC samples, a reduction of [Al] is observed with increasing  $\Phi_{\text{HCl}}$ . However, for low HCl flow rates, slower variation is observed. The tenfold reduction of [Al] is achieved for  $\Phi_{\text{HCl}}\sim 20\text{sccm}$ .

## Discussion

As illustrated in Figure 2b, [Al] values seem inversely proportional to  $\Phi_{\text{HCl}}$ . On the other hand, for very low HCl supply, [Al] should not increase infinitely but ought to be limited by the total amount of available Al species. This leads us to propose quantitative, phenomenological model for Al – HCl interaction during the growth.

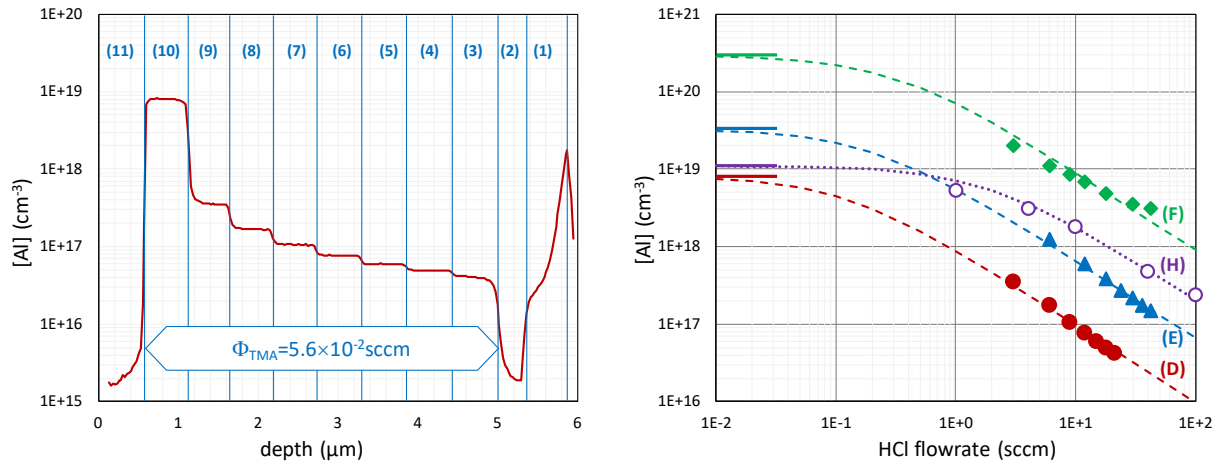
Introduction of HCl in the reactor opens an additional reaction path for Aluminum atoms: they can be either introduced as impurity in SiC layer or react with chlorine to form other species that won't participate in SiC film growth and will be extracted from reactor chamber as a reaction byproduct. The probability for Al atoms to react with chlorine  $p_{\text{Al-Cl}}$  is increasing with HCl supply, from 0 (without HCl) to 1 at high HCl flow rate. We propose to introduce dimensionless quantity  $c = \Phi_{\text{HCl}}/\Phi_0$ , directly proportional to HCl flow rate, and to quantify  $p_{\text{Al-Cl}}$  in the following way:

$$p_{\text{Al-Cl}} = c/(1 + c) \quad (1)$$

The probability  $p_{Al-SiC}$  for Al atom to incorporate the SiC layer is  $p_{Al-SiC} = 1 - p_{Al-Cl}$ . Consequently, the Aluminum concentration, proportional to  $p_{Al-SiC}$ , should follow the relation:

$$[Al] = [Al]_0 / (1 + c) \quad (2)$$

where  $[Al]_0$  denotes the aluminum incorporation in absence of HCl.  $\Phi_0$  is considered as fitting parameter. Power function evolution  $[Al]_0 \propto (\Phi_{TMA})^k$  is generally reported [2], with the exponent  $k$  between 1 and 2, depending on the experimental conditions and geometry of CVD reactor (see also the result on Fig. 1a).



**Figure 2:** (a) [Al] depth profile in sample (D) with indicated sub-layers. (b) Evolution of [Al] with  $\Phi_{HCl}$  for samples (D-F) and (H). Dashed lines correspond to the best fit using proposed model.

The datasets (D-F) and (H) shown in Figure 2b were fitted using the above described approach.  $[Al]_0$  value for each dataset was taken directly from the experiments with  $\Phi_{HCl} = 0$ .  $\Phi_0$  values adjusted for datasets (D-F) increase progressively (0.12, 0.20, 0.31 sccm) with increasing  $\Phi_{TMA}$  applied during the process. For dataset (H), considerably higher value  $\Phi_0 = 1.9 \text{ sccm}$  was found. We may associate this effect either to different growth rate and growth temperature settings, or link it with difference of polytype / lattice orientation.

## Conclusion

We observed and clarified the variation of intentional Al incorporation, inversely proportional to the flow rate of HCl added during CVD process of SiC. For 3C-SiC samples, tenfold [Al] reduction was obtained for HCl flow rates as low as 2 sccm. For higher HCl supply, the reduction exceeded 2 decades without degradation of surface morphology or structural quality of 3C-SiC film. For 4H-SiC, tenfold reduction was achieved for  $\Phi_{HCl} = 20 \text{ sccm}$ . Proposed phenomenological model describes well the tendencies observed in 3C-SiC and 4H-SiC. In parallel, we could verify that in 4H-SiC, the nitrogen incorporation was not affected by HCl presence in the process.

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