

Suppressing the Memory Effect in Al Doped 3C-SiC Grown Using Chlorinated Chemistry

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Abstract. The memory effect of Al doping in 3C-SiC prevents sharp interfaces between layers of different doping levels and can lead to unintentional doping of subsequent epilayers and even growth runs. Introducing HCl into the growth phase of 3C-SiC reduces the Al incorporation but has a significant impact on Al dopant decay rates and background levels within the chamber, resulting in far sharper doping profiles. The impact of relatively high flow rates of HCl is low within a chlorine-based growth system giving fine control over its influence on the growth process and memory effect.

Introduction

The heteroepitaxial growth of cubic silicon carbide (3C-SiC) on silicon (Si) substrates offers many benefits such as a low-cost, large diameter and high quality starting substrate, lower temperature epitaxial growth as well as various properties of 3C-SiC that make it ideal for applications in power electronics, MEMS and as buffers for other semiconductor materials [1]. Aluminum (Al) is the most common p-type dopant in silicon carbide (SiC) and plays a crucial role in the formation of complex device structures. Often, ion-implantation is utilized to form doped layers in SiC, however, this damages the crystal structure, roughens the surface, offers limited distribution and requires high temperature annealing, often with poor levels of dopant activation [2,3]. High temperature activation annealing is limited further by the presence of the underlying Si substrate which limits the upper annealing temperature to ~1400°C which is insufficient to fully recrystallize the epilayer crystal structure.

In-situ doping during epitaxial growth can overcome these issues and generally offers more precise control over dopant profiles. The incorporation of Al into the 3C-SiC lattice has been found to have minimal impact on the crystallinity and defectiveness of the epilayers, making it a far more efficient doping mechanism [4]. One key issue with in-situ doping of Al is the memory effect whereby residual Al within the growth system will continue to dope subsequent SiC during the growth run, or even impact the growth of future runs. For this reason, many suppliers for SiC materials avoid in-situ doping of p-type layers and instead, device manufacturers rely on ion implantation. A method to overcome this memory effect is to flow HCl gas during and/or after doping to etch out the Al and can result in sharper dopant profiles, thus reducing the impact of the memory effect [5,6]. In the case of 3C-SiC growth using non-chlorinated precursors such as silane and propane, the introduction of small amounts of HCl suppresses the Al memory effect but can have a significant impact on the Al incorporation rate, often reducing doping levels by orders of magnitude with only low sccm flow rates of HCl. This work investigates the impact of HCl on the Al doping profiles of cubic silicon carbide (3C-SiC), grown using a chlorine-based Si precursor. The presence of chlorine in the growth system from the silicon precursor may already be suppressing the memory effect and the impact of additional HCl is assessed.

Experimental Details

Epilayers of 3C-SiC were grown within an LPE ACIS M8 RP-CVD on 100mm diameter Si(001) substrates with a 4° off-cut, using trichlorosilane (TCS) and ethylene (C₂H₄) precursors. Epilayers were doped using varying effective flows of trimethylaluminum (TMA) separated by undoped 3C-SiC spacers within the stack, see Fig. 1. The Si substrate was first carbonized at a temperature range of 900-1140°C using a high flow rate of C₂H₄ followed by the epitaxial growth of the 3C-SiC using both precursors at a temperature of 1325°C. A growth rate of approximately 6μm/hr was obtained using a TCS flow rate of 30 sccm. Epi wafers were grown with varying incorporation rates of HCl as shown in Table 1.

Table 1 HCl co-doping rates in the 3C-SiC multilayers and a description of the HCl profile within the growth process.

Sample	HCl Flow Rate (sccm)	HCl Profile
A	0	NA
B	100	All epilayers
C	300	All epilayers
D	500	All epilayers
E	500	Spacers only

i:3C-SiC	500nm	} 5.5μm
Al:3C-SiC $\sim 1 \times 10^{20} \text{cm}^{-3}$	500nm	
i:3C-SiC	500nm	
Al:3C-SiC $\sim 5 \times 10^{19} \text{cm}^{-3}$	500nm	
i:3C-SiC	500nm	
Al:3C-SiC $\sim 1 \times 10^{18} \text{cm}^{-3}$	500nm	
i:3C-SiC	500nm	
Al:3C-SiC $\sim 1 \times 10^{17} \text{cm}^{-3}$	500nm	
i:3C-SiC	1.5μm	}
Si(001) 4° off-axis n-type	525μm	

Fig. 1 Cross sectional schematic of Al doped 3C-SiC multilayers.

The doping profiles of the Al impurity levels were measured as a function of depth for the 3C-SiC samples by secondary ion mass spectroscopy (SIMS), carried out by Eurofins EAG Laboratories.

Results and Discussions

Continuous HCl Co-Doping. The addition of HCl into the growth of the Al doped multilayer structure is found to slightly reduce the growth rate with increasing HCl flow rate. At the growth temperature used, HCl will slowly etch SiC and as such the simultaneous etching and growth will slow the deposition of 3C-SiC [7].

SIMS profiles of Al impurity incorporation for samples with HCl flow rates of 0, 100 and 300 sccm are shown in Fig. 3. The addition of HCl reduces the incorporation of Al for all doping levels within the multilayer structure, dropping the highest doping level by over an order of magnitude at HCl flow of 300 sccm, see Fig. 4. This effect appears to be more pronounced with higher doping levels as rather than a systematic shift in the doping level at all flow rates, i.e. the gradient of the Al incorporation as a function of TMA flow decreases.

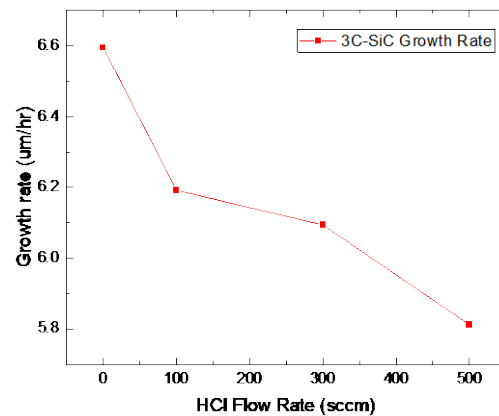


Fig. 2 Impact of HCl incorporation on the growth rate of 3C-SiC epilayers.

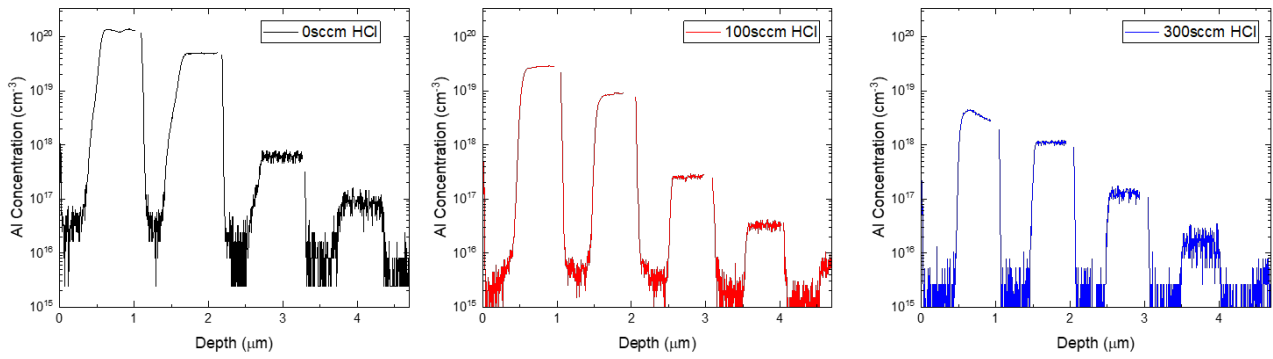


Fig. 3 SIMS profiles showing Al concentration for samples with constant HCl flow. Samples A (left).

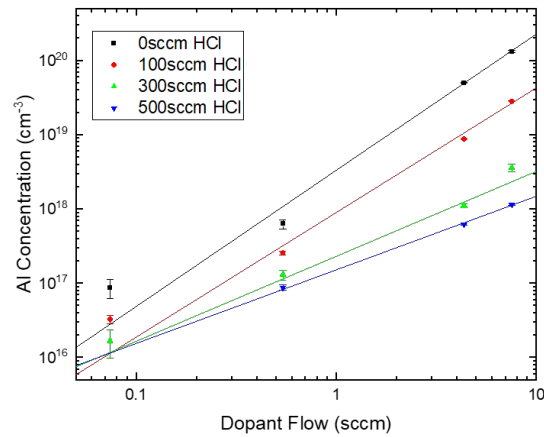


Fig. 4 Impact of HCl flow rate on dopant incorporation.

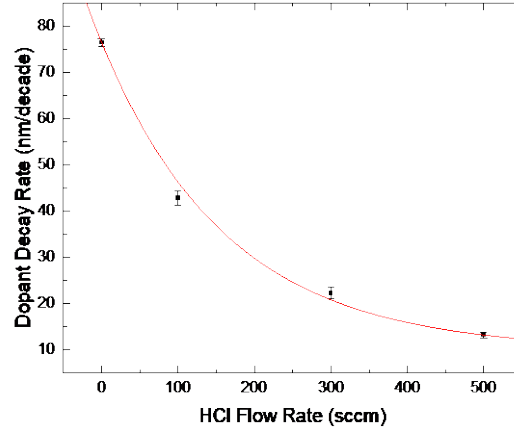


Fig. 5 Impact on HCl flow rate on Al dopant decay rate in undoped 3C-SiC.

The doping profiles of the Al multilayers are significantly sharper as HCl is added to the growth phase. This is shown by the increase in the dopant decay rate from the highest doped layer to the subsequent undoped 3C-SiC, see Fig. 5. The units are given as nm of undoped 3C-SiC required to drop the Al concentration by one order of magnitude. The addition of HCl also enables a lower base level of undoped 3C-SiC in the final epilayer dropping from $3 \times 10^{16} \text{ cm}^{-3}$ for 0 sccm HCl to $(1-2) \times 10^{15} \text{ cm}^{-3}$ for growths which included HCl. This concentration of Al impurities is at the SIMS detection limit and may in fact be lower.

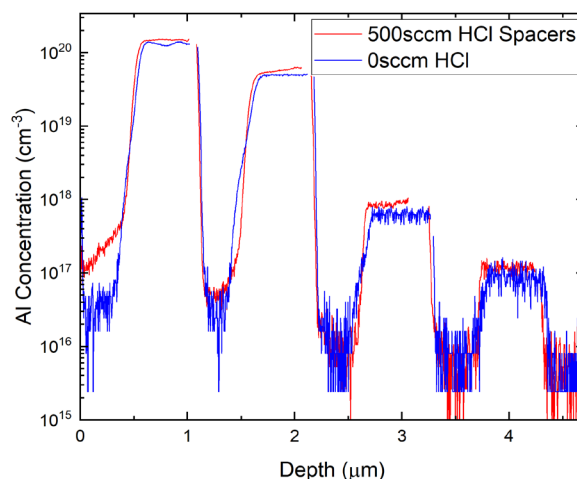


Fig. 6 SIMS profile showing Al concentration with 500sccm HCl flow in spacers only compared to Sample A without HCl.

Spacer HCl Co-Doping. The profile of Al impurity concentration in sample E is shown in Fig. 6 and compared to the profile of sample A without HCl co-doping. As expected, adding HCl only into the spacers has no impact on the doping levels achieved in each doped 3C-SiC epilayer, however, it also has minimal effect on the memory effect. The unintentional Al incorporation in the undoped spacers is unchanged from sample A without HCl and the decay rate is only slightly improved. As a consequence, the memory effect cannot be suppressed using this method and instead, HCl must be included throughout the growth of the doped epilayers to have an impact.

Summary

The addition of HCl during epitaxial growth of Al doped layers of 3C-SiC results in sharper doping profiles and reduced memory effect within the same growth run. In a chlorine-based growth system, such as the one utilized here with TCS as silicon source precursor, the impact of HCl is lower and a high level must be included to suppress the memory effect. The partial pressure of TCS during 3C-SiC epitaxy was 0.3 mBar while the addition of HCl up to 5 mBar only resulted in a minimal reduction in growth rate and dropped the Al incorporation by up to 2 orders. This offers an advantage for HCl incorporation in 3C-SiC growth by offering a far wider range of useable flow rates and is well within the range of standard mass flow controllers (MFCs) used on CVD systems without the need for dilution. The impact of HCl was also observed to reduce with lower doping levels of Al suggesting the probability that Al atoms will react with HCl rather than be incorporated as an impurity is dependent on both HCl flow rate and Al doping level.

The addition of HCl only within the undoped spacers of the multilayer stack was found to provide minimal to no benefit to the memory effect. Without HCl during the doping phases, Al is able to adsorb onto the surfaces within the CVD such as the chamber walls and graphite susceptor and “out-gas” during the epitaxial growth of subsequent layers. In fact, the presence of HCl only in the spacers may have a negative effect of etching the highly doped layers on the chamber surface. This produces an additional source of Al which incorporates during growth of the spacers, resulting in the slightly higher background doping observed in this sample. Only by including HCl during the epitaxial growth of doped layers can the memory effect be suppressed, as this would reduce the buildup of Al doped SiC layers on the chamber walls. The use of this technique in Al doped 3C-SiC would also be applicable to the growth of 4H-SiC epilayers and could offer an alternative to ion implantation in SiC based device structures.

Acknowledgments

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